Neutron diffraction of crystalline materials

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Animations made with Blender 2.62

Scope of the lecture

- Diffraction techniques (X-ray, neutron) are used to study thin films , engineering materials, liquids, polymers, crystalline solids.

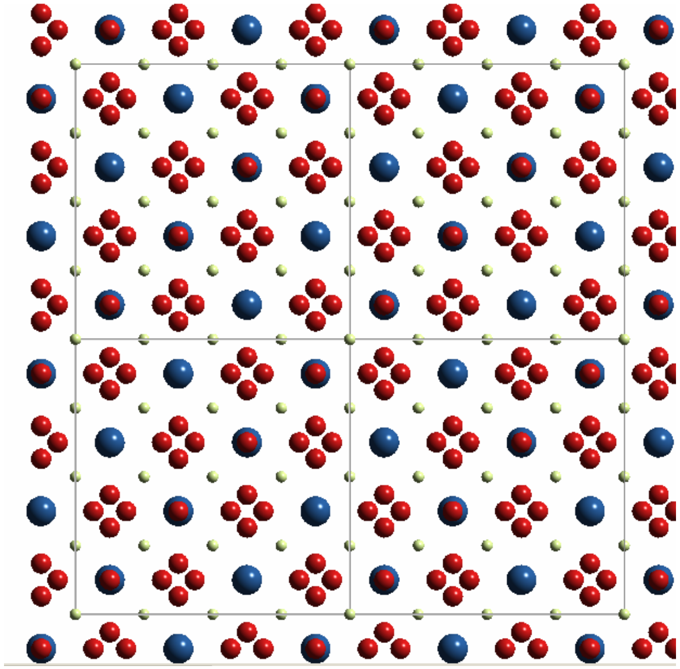
- Whatever the technique used (Small Angle Scattering, Reflectometry, Strain-Scanning, conventional powder or single crystal Diffraction), all of these refer to the coherent elastic scattering of a beam of neutrons or X-rays.

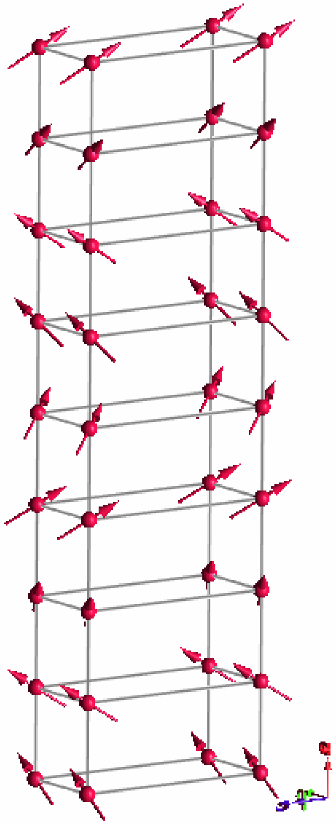
- The keyword here is “elastic”, which means no energy is transferred between the beam and the sample, which in virtue of the conservation of energy means that the incident and scattered wave have the same wavelength.

- Of course, momentum is also a conserved quantity.

Scope of the lecture

- This lecture will focus on Crystallography, i.e. the study of crystalline solids.
- This form of matter is characterized by infinite translational symmetry (infinite periodic)
- We will study the periodic arrangement of atoms and magnetic moments (*magnetism :lecture from Prof. A. Wildes*)

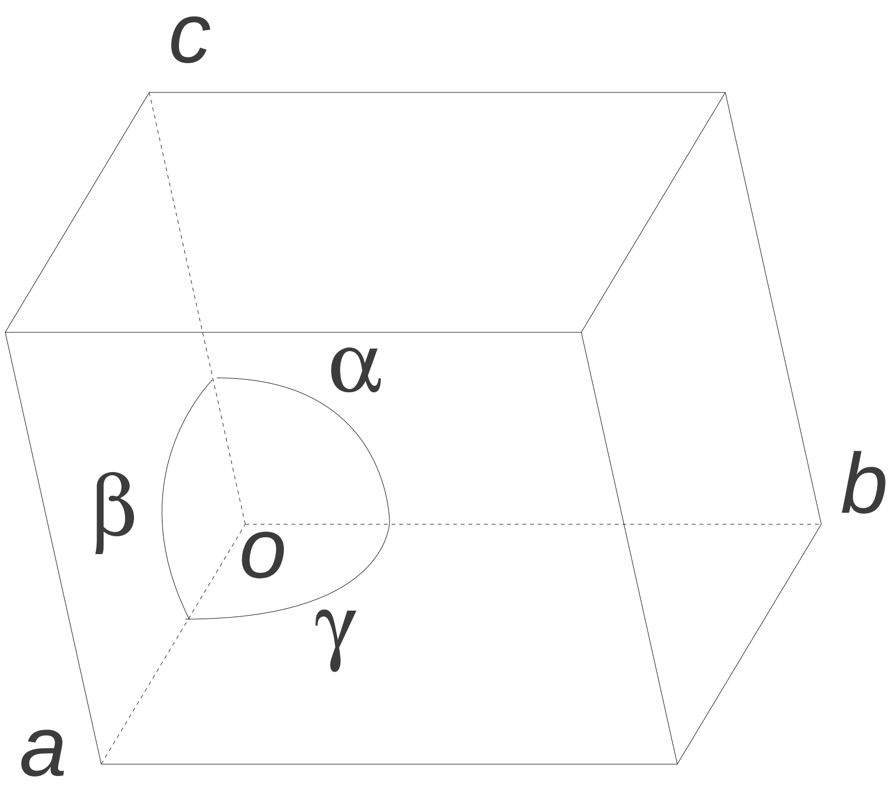




Outline

- Direct lattices, symmetry
- Reciprocal system of axes and reciprocal lattice
- Fourier transform of a *Dirac comb*
- Nuclear scattering from crystalline materials.
- Unit-cell structure factors
- Ewald construction and different type of diffractometers
- Basics of Rietveld refinement

Periodic solids: Crystal systems



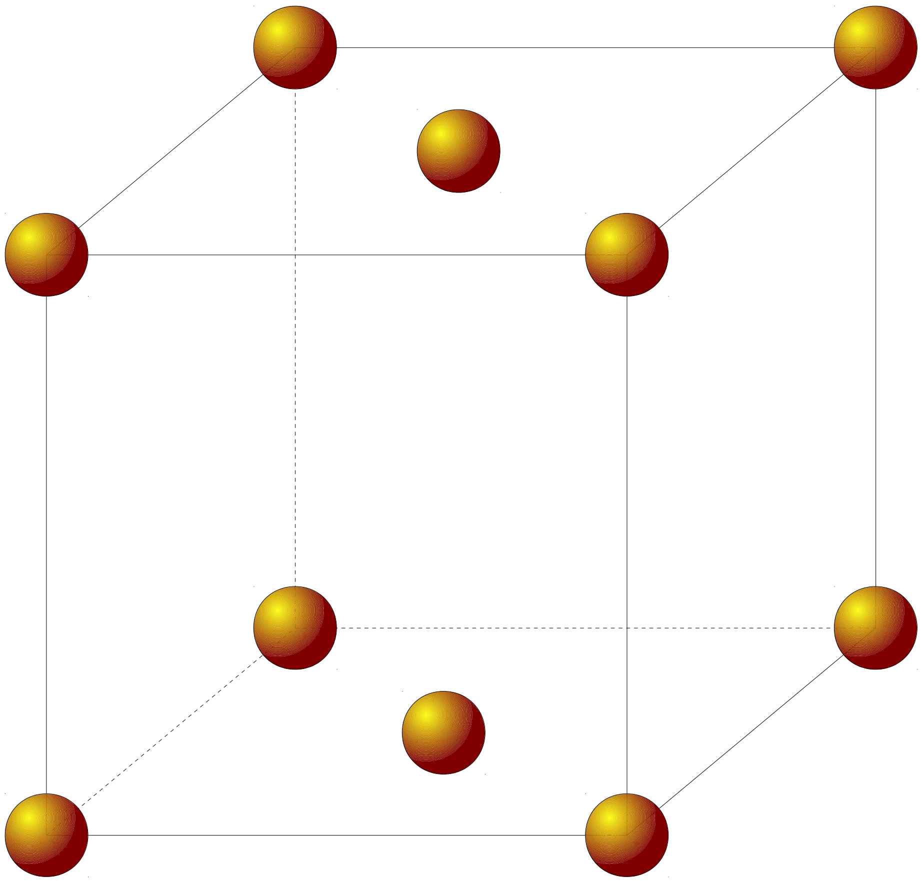
7 crystal systems :

Crystal system	Type of axes
Triclinic	a≠b≠c, α≠β≠γ
Monoclinic	a≠b≠c, α=γ=90°, β≠90°
Orthorhombic	a≠b≠c, α=β=γ=90°
Tetragonal	a=b≠c, α=β=γ=90°
Trigonal	a=b=c, α=β=γ≠90°
Hexagonal	a=b≠c, α=β=90°,γ=120°
Cubic	a=b=c, α=β=γ=90°

Periodic solids: Centring translations

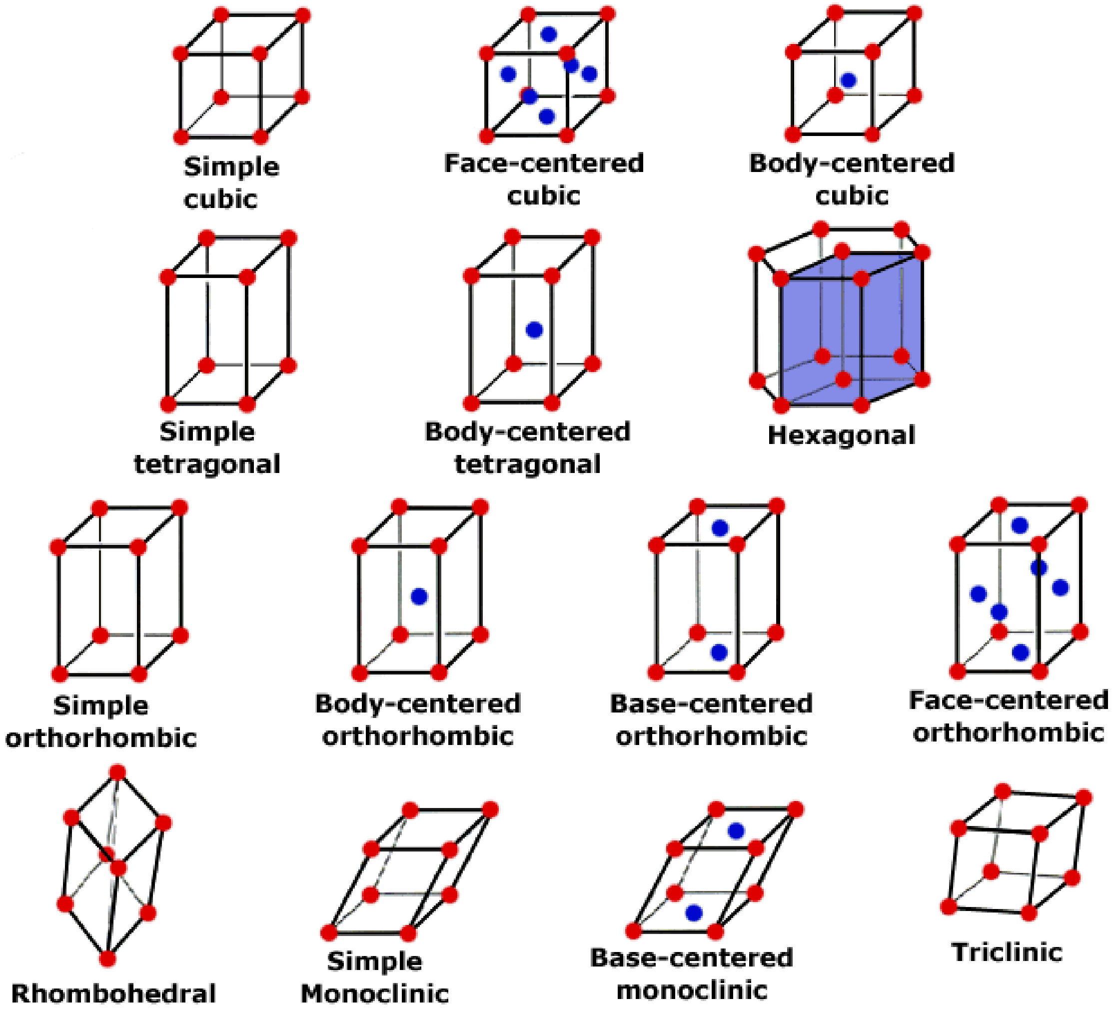
It is often inconvenient to work with primitive lattices, and one uses centered lattices:

Centring type	Symbol	Translations
Primitive	P	
(One face centred) A-centred B-centred C-centred	 A B C	 x,y+1/2,z+1/2 x+1/2,y,z+1/2 x+1/2,y+1/2,z
Body centred	I	x+1/2,y+1/2,z+1/2
Face centred	F	x+1/2,y+1/2,z x,y+1/2,z+1/2 x+1/2,y,z+1/2
Rhombohedrally centred	R	x+2/3,y+1/3,z+1/3 x+1/3,y+2/3,z+2/3



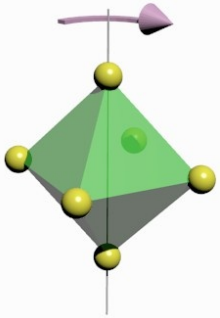
Bravais lattice

- Crystal classes + centring translations → 14 Bravais lattices

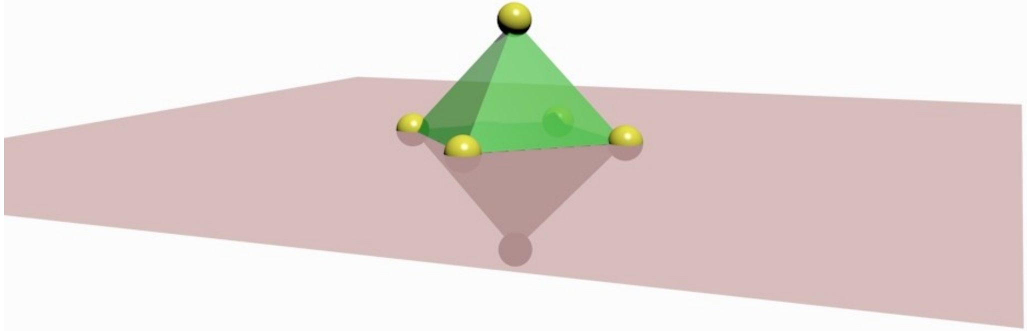


Symmetry operations

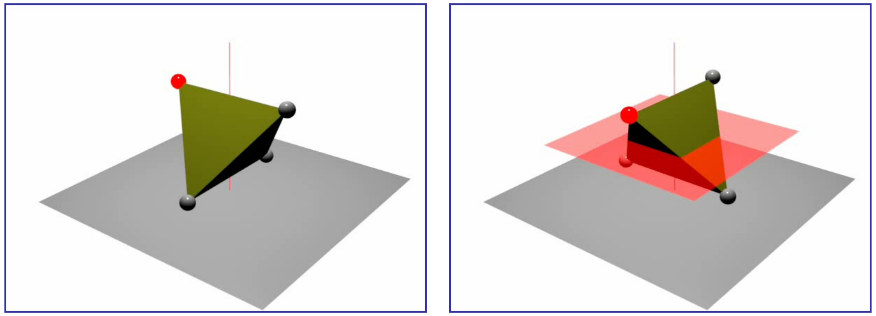
Rotations (order n : 2π/n)



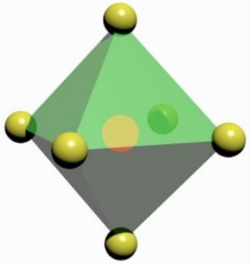
Mirror planes (m)



Roto-inversion ($\overline{n}$)



Inversion point ($\overline{1}$)



Symmetry operations

Screw axis (n_m) is a compound operation of:

- rotation of order n
- translation of 1/m

Example: screw axis 2_1 along a

Glide plane is a compound operation of:

- mirror symmetry
- translation

Example: *c* glide plane $\perp$ *a*

Symmetry operations

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

► Determinant +1 (proper) -1 (improper)

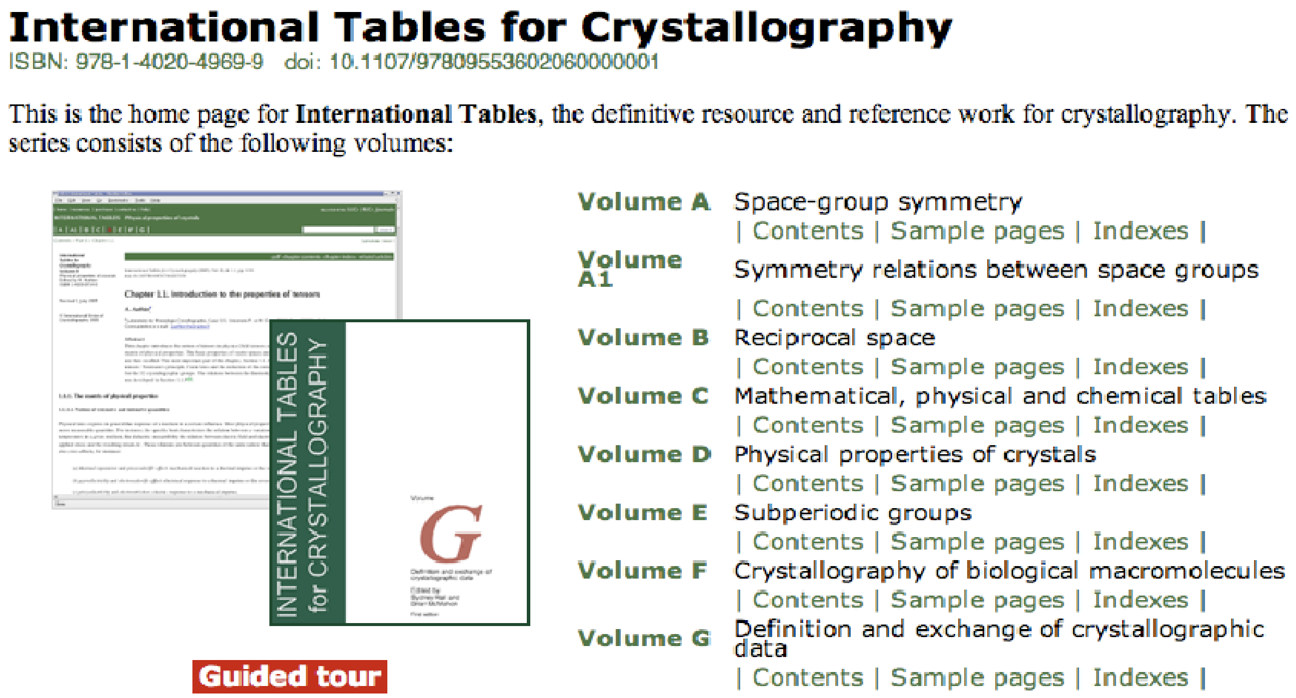
- Seitz notation: **(R|t)**

- Symmetry contained in the coordinate triplet: for example 2_1 screw axis along *b:* -x,y+1/2,-z

Space groups : International Tables

Combining the 14 Bravais lattices and all symmetry operations, leads to the 230 space groups.

- http://it.iucr.org/



International Tables for Crystallography

ISBN: 978-1-4020-4969-9 doi: 10.1107/97809553602060000001

This is the home page for **International Tables**, the definitive resource and reference work for crystallography. The series consists of the following volumes:

Volume A Space-group symmetry
| Contents | Sample pages | Indexes |

Volume A1 Symmetry relations between space groups
| Contents | Sample pages | Indexes |

Volume B Reciprocal space
| Contents | Sample pages | Indexes |

Volume C Mathematical, physical and chemical tables
| Contents | Sample pages | Indexes |

Volume D Physical properties of crystals
| Contents | Sample pages | Indexes |

Volume E Subperiodic groups
| Contents | Sample pages | Indexes |

Volume F Crystallography of biological macromolecules
| Contents | Sample pages | Indexes |

Volume G Definition and exchange of crystallographic data
| Contents | Sample pages | Indexes |

Space groups : Example

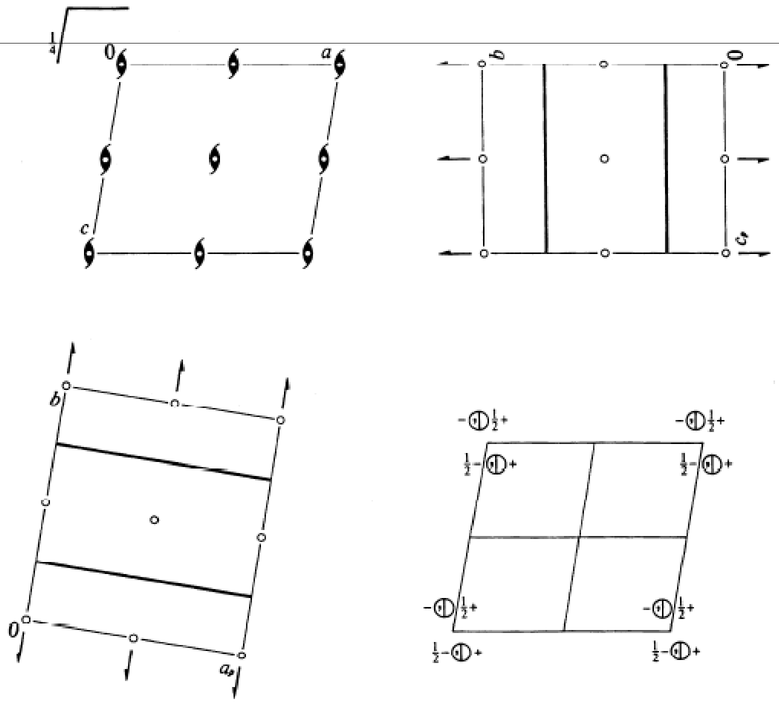
$P2_1/m$ C_{2h}^2 $2/m$ Monoclinic

Crystal class

No. 11 $P\,1\,2_1/m\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b

Space group symbol



Origin at $\bar{1}$ on 2_1

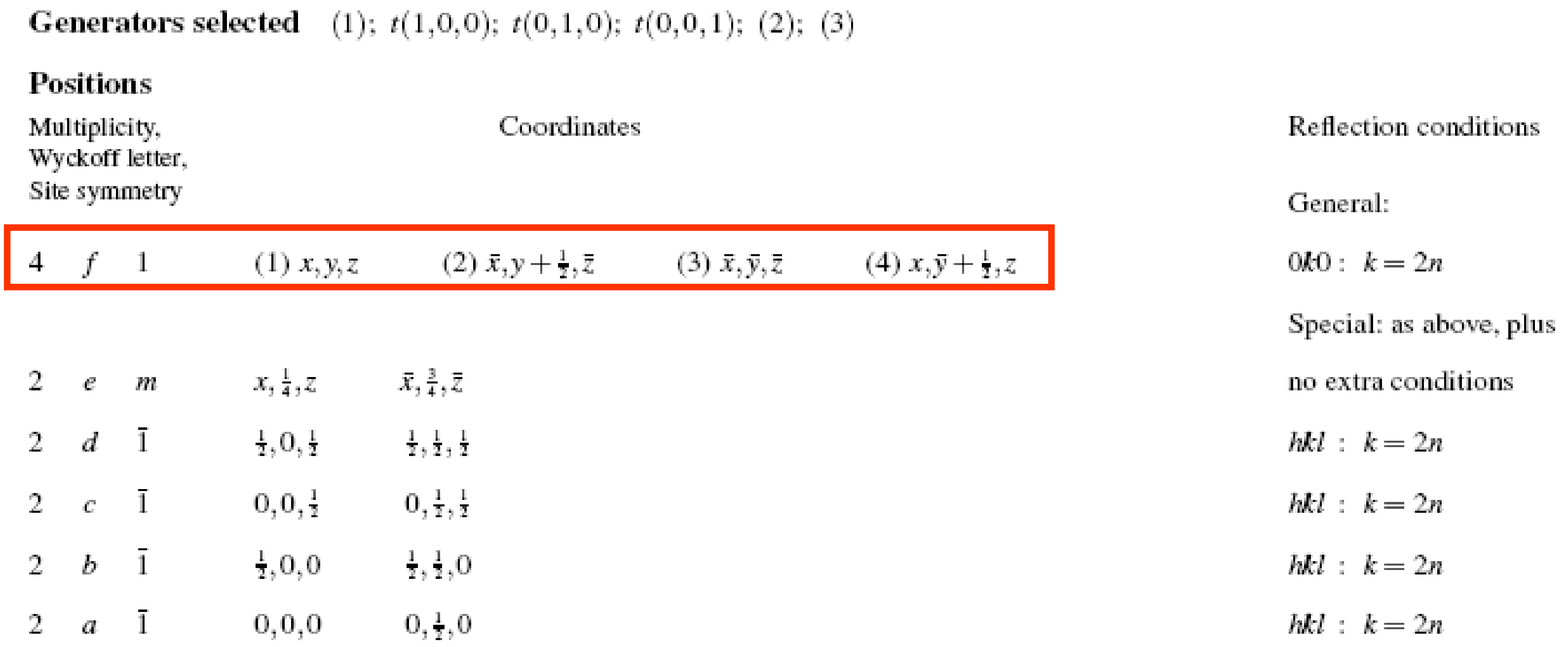
Asymmetric unit $0 \le x \le 1;\ \ 0 \le y \le \frac{1}{4};\ \ 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)$ $0,y,0$ (3) $\bar{1}$ $0,0,0$ (4) m $x,\frac{1}{4},z$

Symmetry operations

Space groups : Example



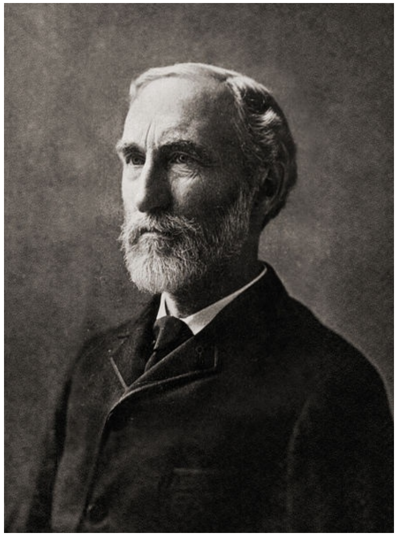
Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	f	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z$	$0k0$: $k=2n$
							Special: as above, plus
2	e	m	$x,\frac{1}{4},z$	$\bar{x},\frac{3}{4},\bar{z}$			no extra conditions
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},0$			hkl : $k=2n$

High symmetry points

Reciprocal system

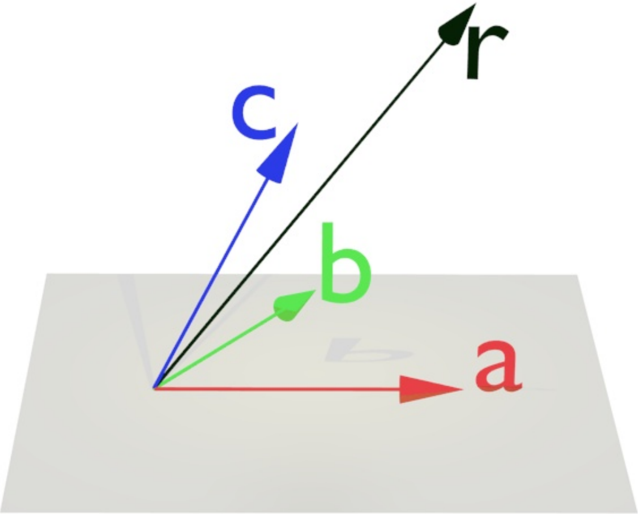


[Wikipedia]

- First introduced by Gibbs :
  Vector analysis: A textbook for the use of students of mathematics and Physics by E. Wilson, New Haven Yale University Press, 1901

How to express a vector in terms of three non-coplanar vectors ?

$$\vec{r} = \alpha\,\vec{a} + \beta\,\vec{b} + \gamma\,\vec{c}$$



Reciprocal system

$$\vec{r}\cdot[\vec{b}\times\vec{c}]=\alpha\,\vec{a}\cdot[\vec{b}\times\vec{c}]+\beta\,\underbrace{\vec{b}\cdot[\vec{b}\times\vec{c}]}_{=0}+\gamma\,\underbrace{\vec{c}\cdot[\vec{b}\times\vec{c}]}_{=0}$$

$$\alpha=\vec{r}\cdot\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$$

Equally, $\beta=\vec{r}\cdot\dfrac{\vec{c}\times\vec{a}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$ and $\gamma=\vec{r}\cdot\dfrac{\vec{a}\times\vec{b}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$

$$\alpha=\vec{r}\cdot\overrightarrow{a^*}\qquad\beta=\vec{r}\cdot\overrightarrow{b^*}\qquad\gamma=\vec{r}\cdot\overrightarrow{c^*}$$

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Reciprocal system

$$\vec{a}^* = \frac{\vec{b}\times\vec{c}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$$

$$\vec{b}^* = \frac{\vec{c}\times\vec{a}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$$

$$\vec{c}^* = \frac{\vec{a}\times\vec{b}}{\vec{a}\cdot[\vec{b}\times\vec{c}]}$$

$$\vec{a}_i\cdot\overrightarrow{a_j{}^*}=\delta_{ij}$$

- For each system of three non-coplanar vectors, one can construct a dual system of vectors, also non-coplanar, called the reciprocal system.

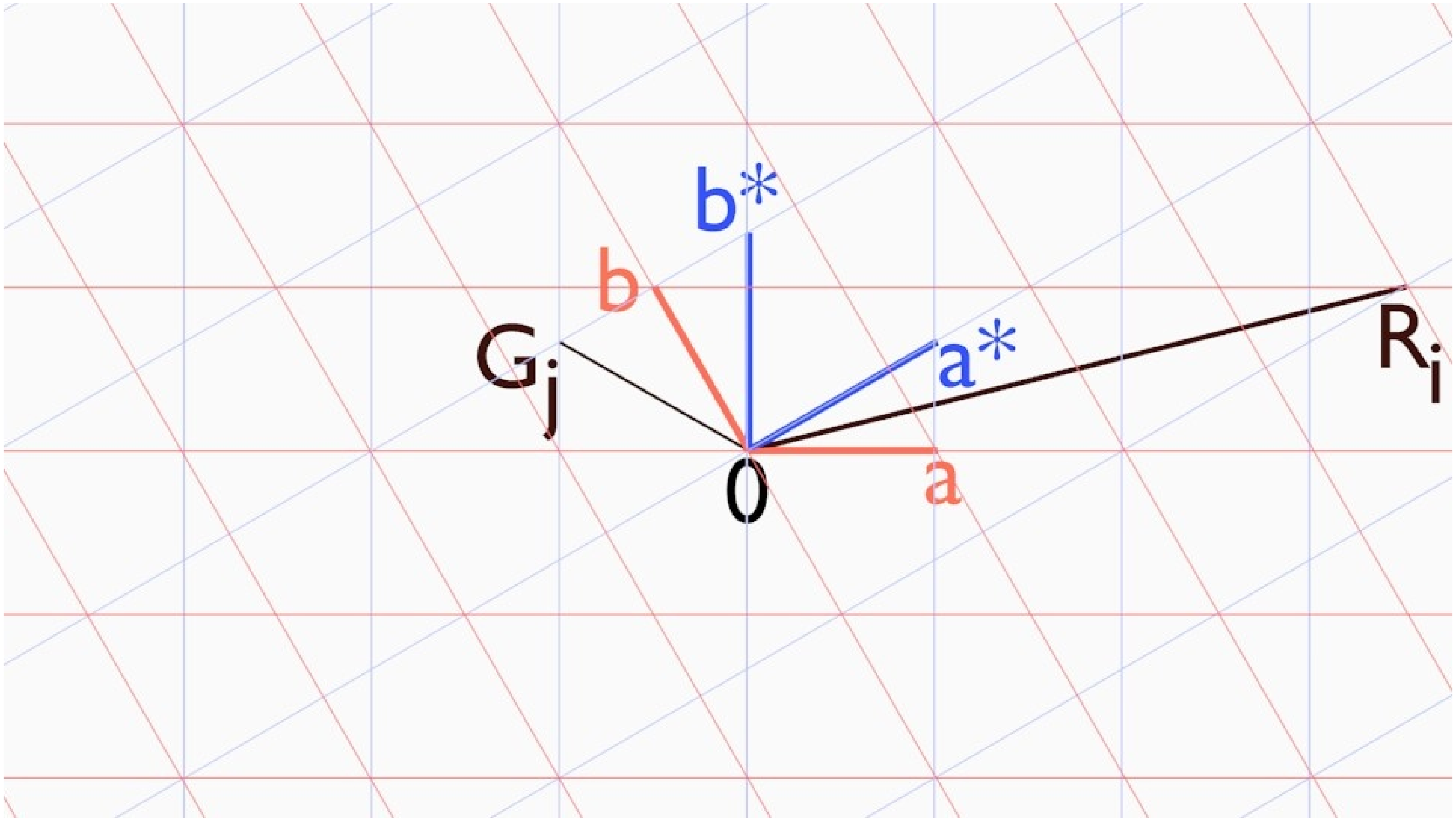
- The reciprocal of a reciprocal system is the direct axis itself.

- Reciprocal and direct systems are equal only for an orthonormal unit lattice.

- Condition (2) is necessary and sufficient for $\{a_j^*\}$ to be reciprocal system of $\{a_j\}$

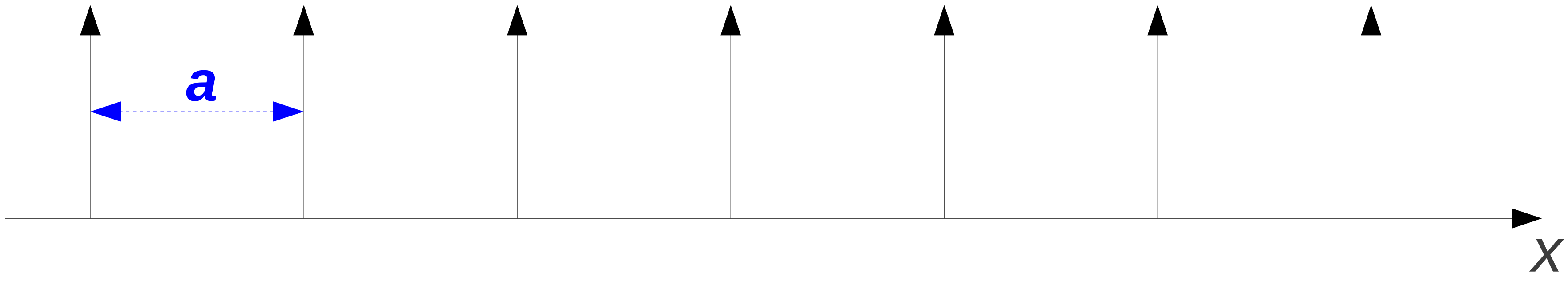
Reciprocal lattice

Let's construct a periodic lattice from the $\{a_i\}$ and $\{a_i{}^*\}$ systems of vectors called **R** and **G**



The scalar product between any vector $\mathbf{R}_i$ in **R** and any vector $\mathbf{G}_j$ in **G** is an integer!

Fourier transform of a Dirac comb

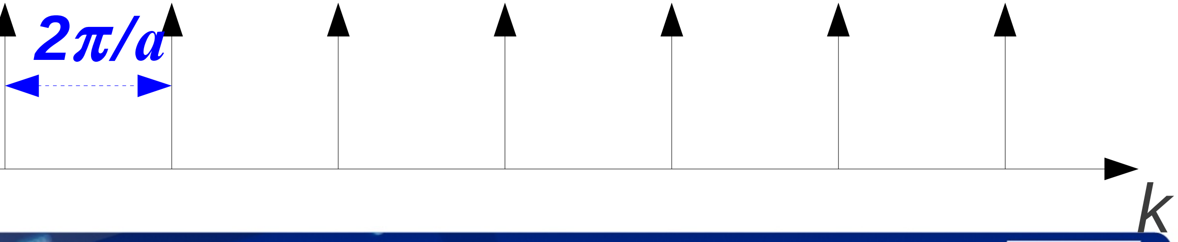


$$comb_a(x)=\sum_{n=-\infty}^{\infty}\delta(x-na)$$

Fourier transform:

$$\int\sum_{n=-\infty}^{\infty}\delta(x-na)e^{-ikx}.dx=\sum_{n=-\infty}^{\infty}\int\delta(x-na)e^{-ikx}.dx=\sum_{n=-\infty}^{\infty}e^{-ikna}$$

$$\sum_{n=-\infty}^{\infty}e^{-ikna}=\frac{2\pi}{a}\sum_{h=-\infty}^{\infty}\delta\left(k-\frac{2\pi}{a}h\right)$$



Fourier transform of Dirac comb in 3D

Let ***L*** be a direct lattice of volume ***V***. Consider a Dirac comb of this lattice (δ function at every lattice point)

$$L(\vec{r}) = comb_{\vec{abc}}(\vec{r}) = \sum_{\vec{R}_n \in R} \delta^3(\vec{r} - \vec{R}_n)$$

Fourier transform:

$$FT(L(\vec{r})) = \int \sum_{\vec{R}_n \in R} \delta^3(\vec{r} - \vec{R}_n) e^{-i\vec{k}\cdot\vec{r}} d\vec{r} = \sum_{-\vec{R}_n \in R} e^{-i\vec{k}\cdot\vec{R}_n}$$

What is the set of ***k*** vectors that ensure that this sum is non-zero ?

$$\sum_{\vec{R}_n \in R} e^{-i\vec{k}\cdot\vec{R}_n} = \frac{(2\pi)^3}{V} \sum_{\vec{G}_j \in \vec{G}} \delta^3(\vec{k} - 2\pi\vec{G}_j)$$

Fourier transform of a Bravais lattice of Dirac functions is a lattice of Dirac functions centred at the reciprocal lattice points!

Reciprocal lattice

From now on, we shall use the alternate definition:

$$\vec{a^*} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot [\vec{b} \times \vec{c}]}$$

$$\vec{b^*} = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot [\vec{b} \times \vec{c}]}$$

$$\vec{c^*} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot [\vec{b} \times \vec{c}]}$$

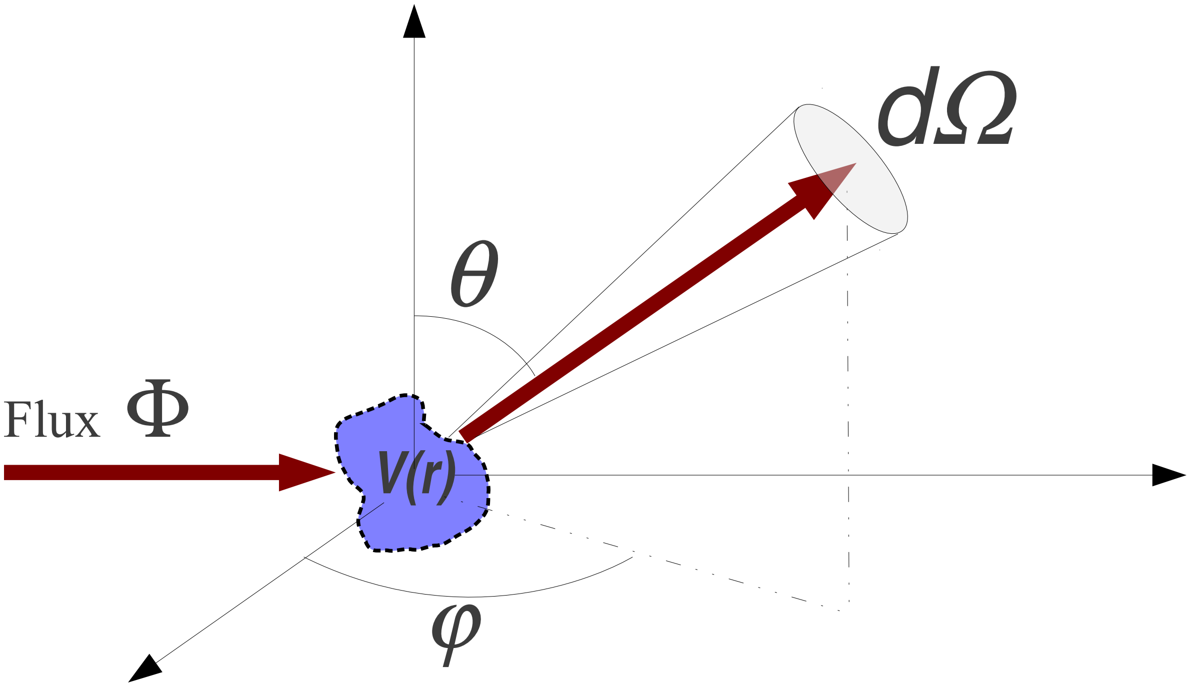
$$\vec{a}_i \cdot \overrightarrow{a_j^*} = 2\pi \delta_{ij}$$

A vector of the reciprocal lattice ***G*** will usually be written as:

$$\vec{G} = h \cdot \vec{a^*} + k \cdot \vec{b^*} + l \cdot \vec{c^*}$$

h,k,l are named the Miller indices.

Scattering by a potential *V(r)*

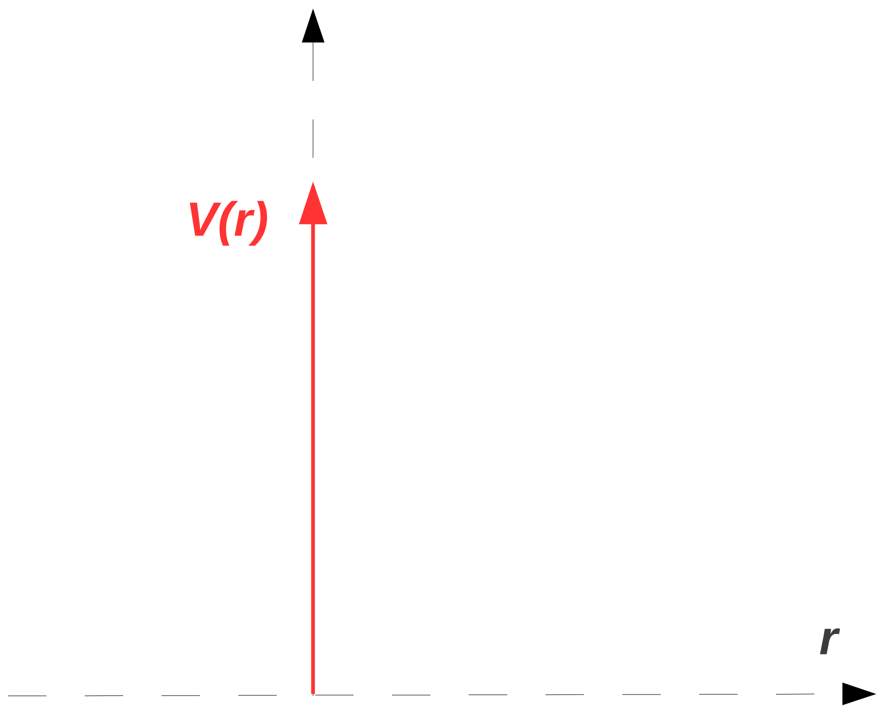


$$\overbrace{dn}^{n.s^{-1}} = \overbrace{\Phi}^{n.cm^{-2}.s^{-1}} \overbrace{d\Omega}^{n.u} \sigma(\theta,\phi)$$

- σ has the dimension of a surface
- Usually in barns=10^{-24} cm^2

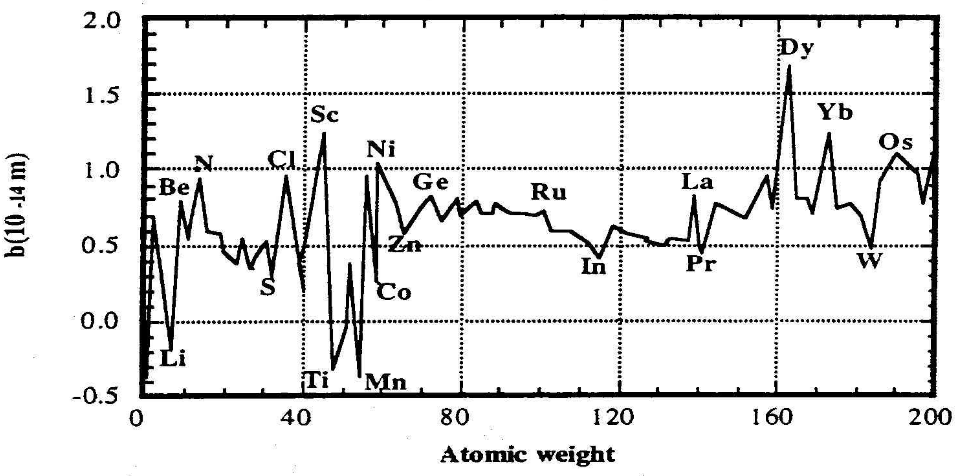
Nuclear scattering

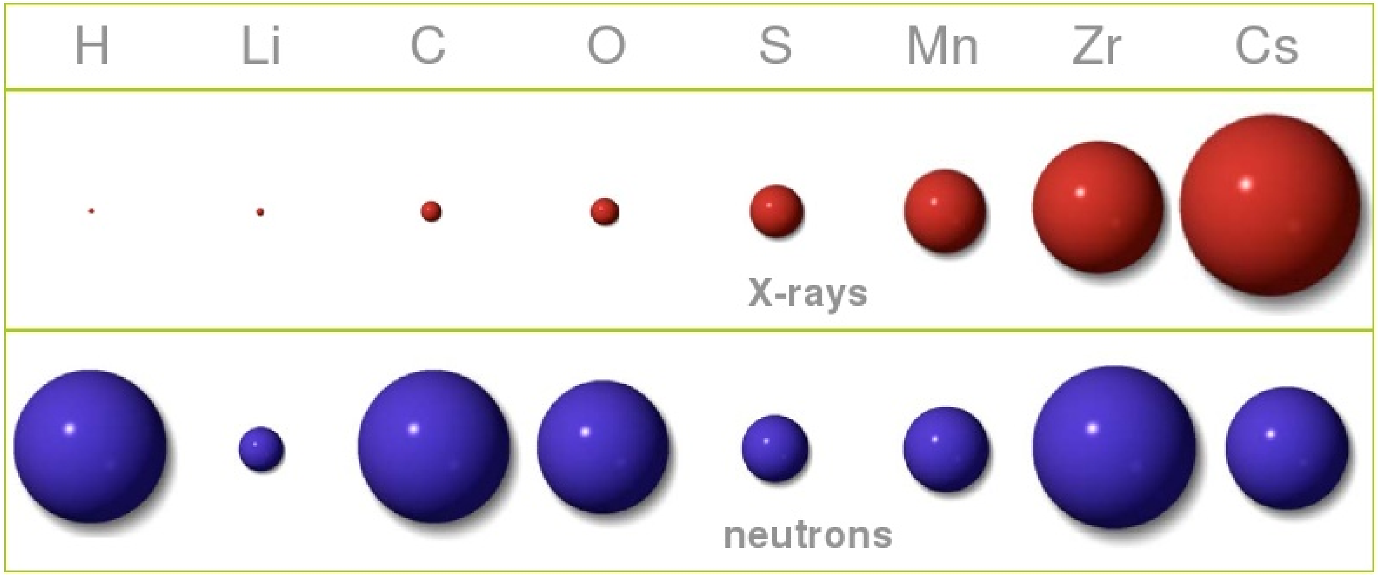
- Nuclear scattering mediated by the strong force, extremely short range (fm=1.10^{-15}m).
- Neutron wavelength much larger (Å=1.10^{-10}m), can not probe internal nuclear structure: scattering is isotropic.
- The interaction between the neutron and the atomic nucleus is represented by the Fermi pseudo-potential, a **scalar field** that is zero except very close to the nucleus (δ function).



$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_r} a\,\delta^3(\vec{r})$$

Scattering lengths

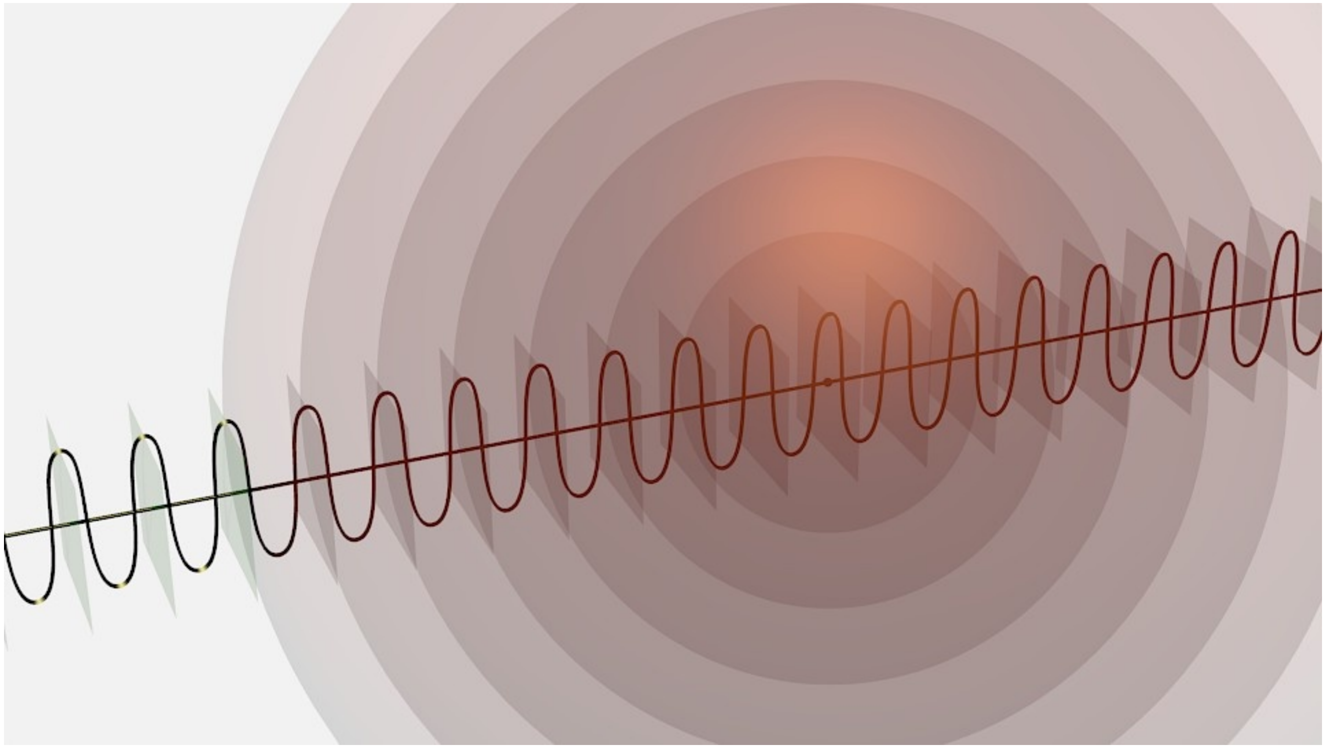




Scattering by a potential *V(r)*

The wavefunction at a spatial position ***r*** = ***sum of transmitted and scattered spherical wavefunction:***

$$\psi = e^{i\vec{k}\cdot\vec{r}} + f_k(\theta,\varphi)\frac{e^{ik\cdot r}}{r}$$



Reminder Born approximation

- In the quantum mechanical treatment of scattering by a central potential, the stationary states φ(r) verify:

$$[\Delta+k^2]\varphi(\mathbf{r})=\frac{2\mu}{\hbar^2}V(\mathbf{r})\varphi(\mathbf{r})$$

- In the integral equation of scattering, the stationary wave-function is written :

$$v_k^{scat}(\mathbf{r})=e^{i\mathbf{k}_i.\mathbf{r}}+\frac{2\mu}{\hbar^2}\int G_+(\mathbf{r}-\mathbf{r}')V(\mathbf{r}')v_k^{scat}(\mathbf{r}')d^3r'$$

- One can expend iteratively this expression (Born expansion).
If the potential is weak, one can limit the expansion to the first term, this is the first Born approximation.
In this case the scattering amplitude is related to the Fourier transform of the potential function:

$$\boxed{f_k(\theta,\phi)\propto-\int V(\mathbf{r})e^{-i\mathbf{Q}\mathbf{r}}d^3r}$$

$$I=|f_k(\theta,\phi)|^2=|V(\vec{Q})|^2$$

Quantum Mechanics,
Claude Cohen-Tannoudji et al., Vol 2, Chapt 8

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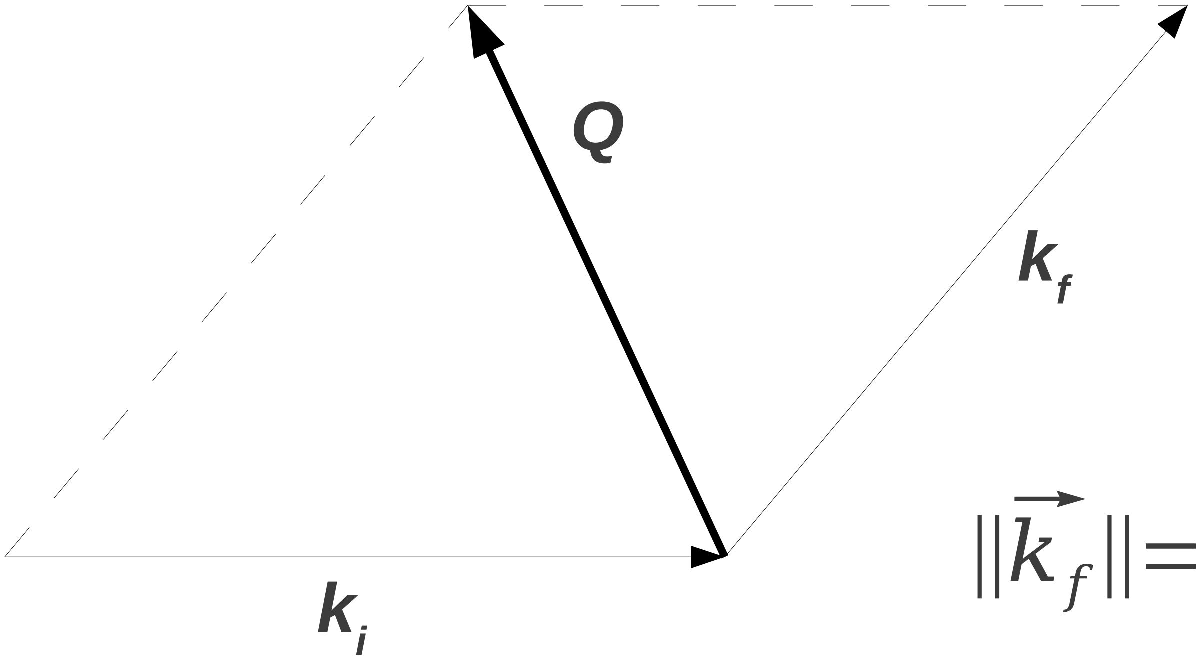
Conventions for this lecture

$$f_k(\theta,\phi) \propto -\int V(\mathbf{r}) e^{-i\mathbf{Q}\mathbf{r}} d^3r$$

V(r) is positive for a repulsive potential

$\vec{Q} = \vec{k}_f - \vec{k}_i$ **= momentum transferred from the crystal to the neutron**

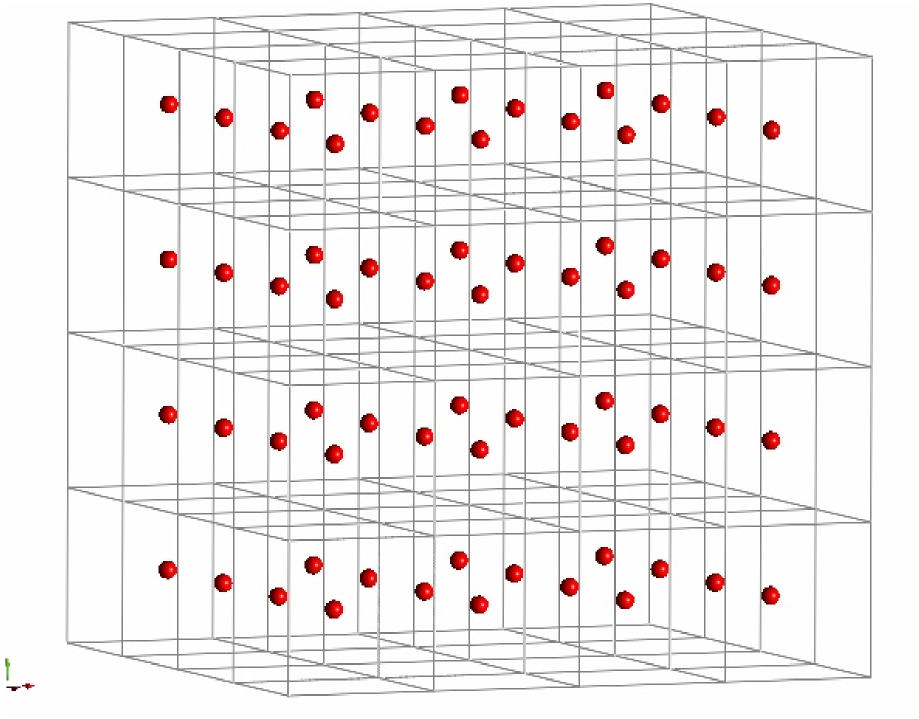


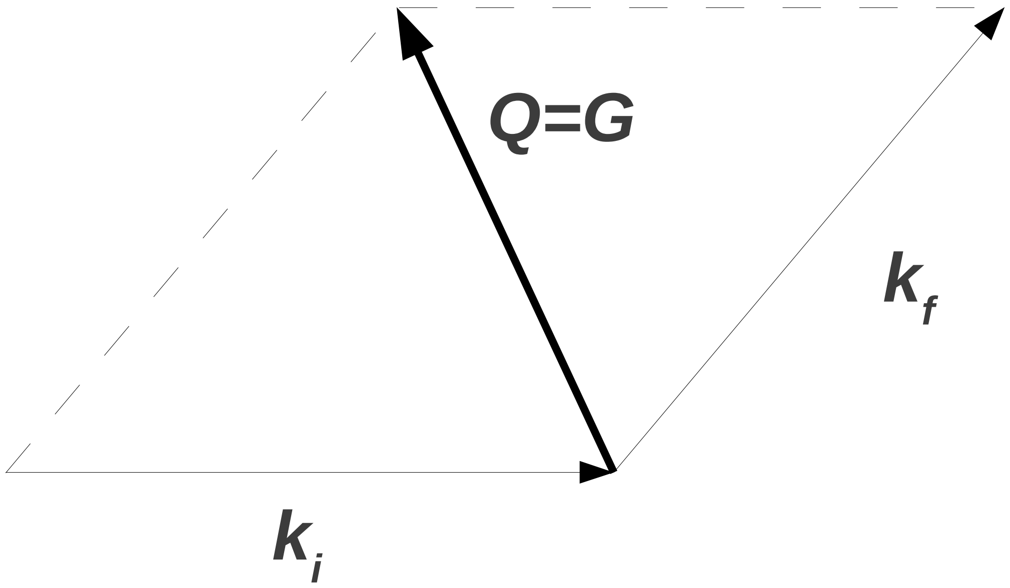
$\|\vec{k}_f\| = \|\vec{k}_i\|$ **(elastic scattering)**

Nuclear scattering

Imagine a crystal with only one atom per unit-cell. ***For which Q, is the intensity non zero?***

V(r) is a 3D Dirac comb!

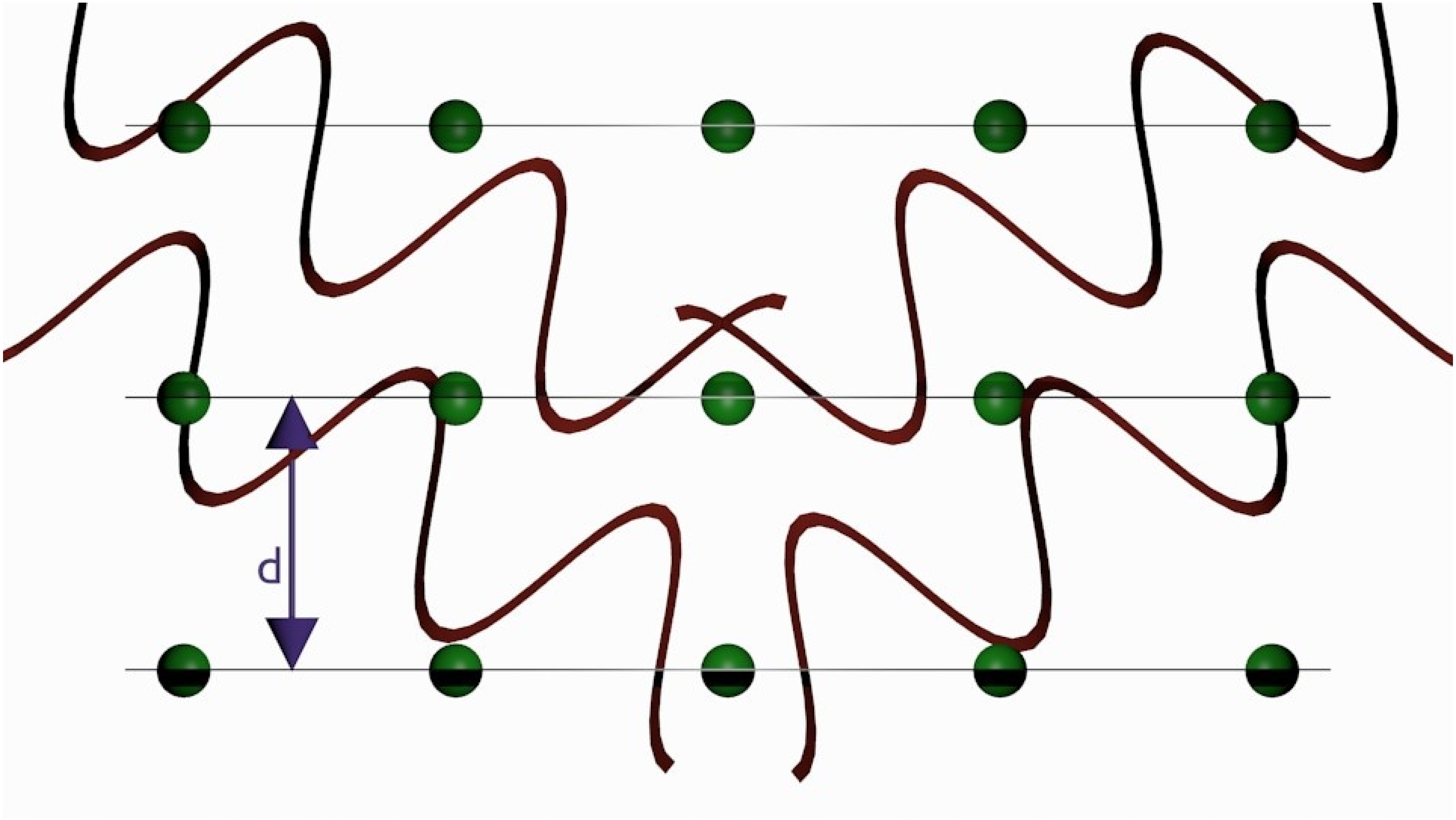




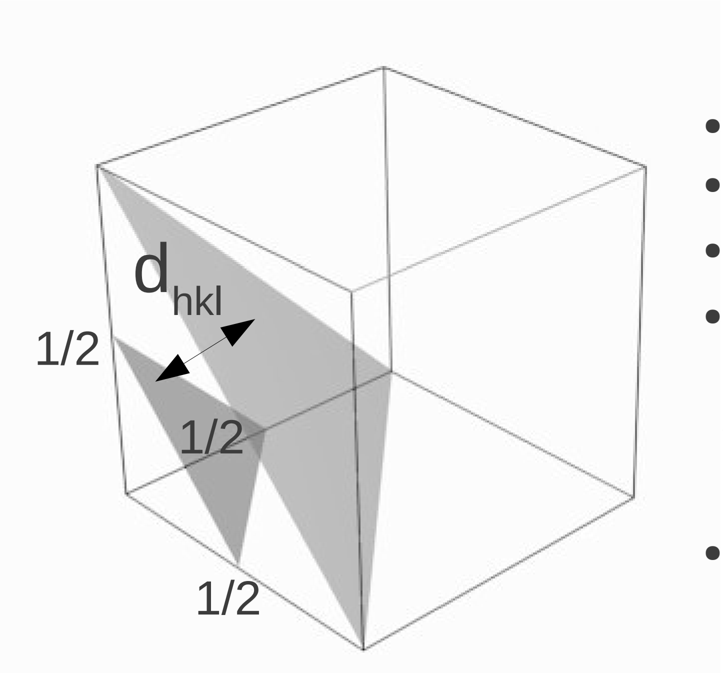
During a diffraction experiment, a crystalline material can only provide discrete momentum kicks !

Diffraction condition in real and reciprocal space

$$2\,d\sin(\theta)=n\,\lambda$$

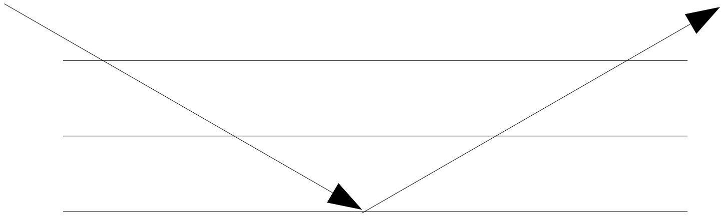


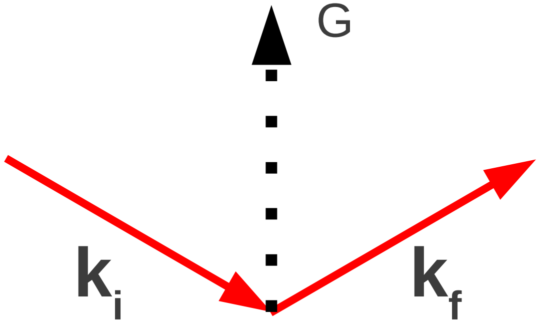
Diffraction condition in real and reciprocal space



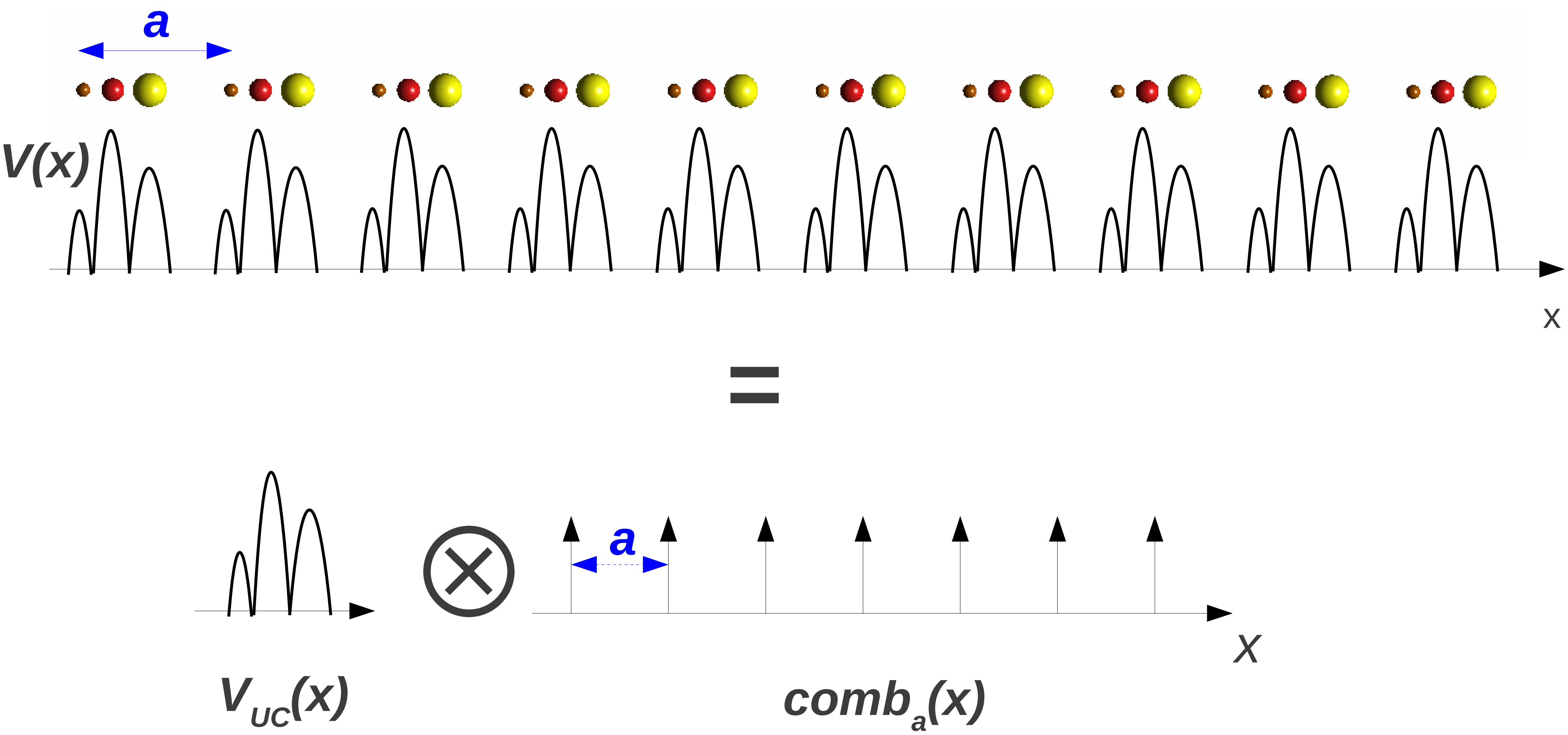
- Lattice planes (Miller planes) are indexed by the indices h,k,l.
- A (h,k,l) plane intercept the real crystal axes at a/h, b/k, l/c
- d_{hkl} is the distance to the origin.
- Diffraction can be considered as the coherent superposition of scattered waves from these the set of planes parallel to the (h,k,l) plane and equidistant.

- The reciprocal lattice vector G=ha*+kb*+lc* is :
  - Perpendicular to the lattice plane (h,k,l)
  - Of length: $2\pi/d_{hkl}$





More than one atom/unit cell (1D example)



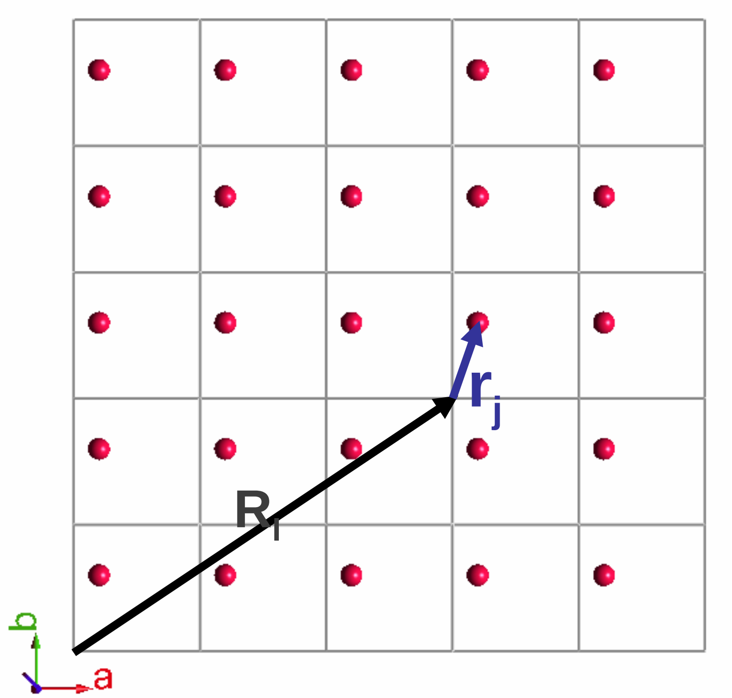
Unit cell structure factor (approximation: no atomic displacement)

From the convolution theorem, the Fourier transform of a convolution is the product of the individual Fourier transforms:

$$V(\vec{Q}) = FT(V(\vec{r})) = FT(V_{UC}(\vec{r}) \otimes comb_{\overrightarrow{abc}}(\vec{r}))$$

$$= FT(V_{UC}(\vec{r})) \times FT\underbrace{(comb_{\overrightarrow{abc}}(\vec{r}))}$$

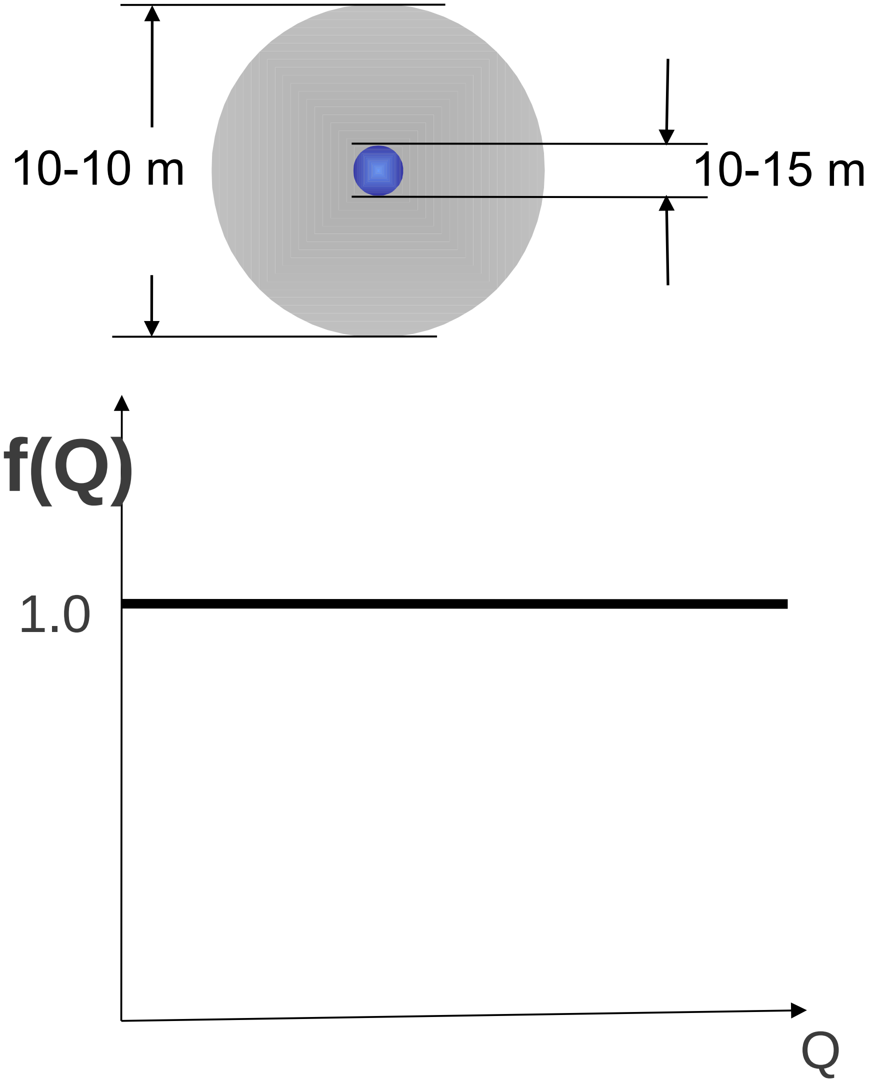
=0 unless Q is
a reciprocal lattice vector



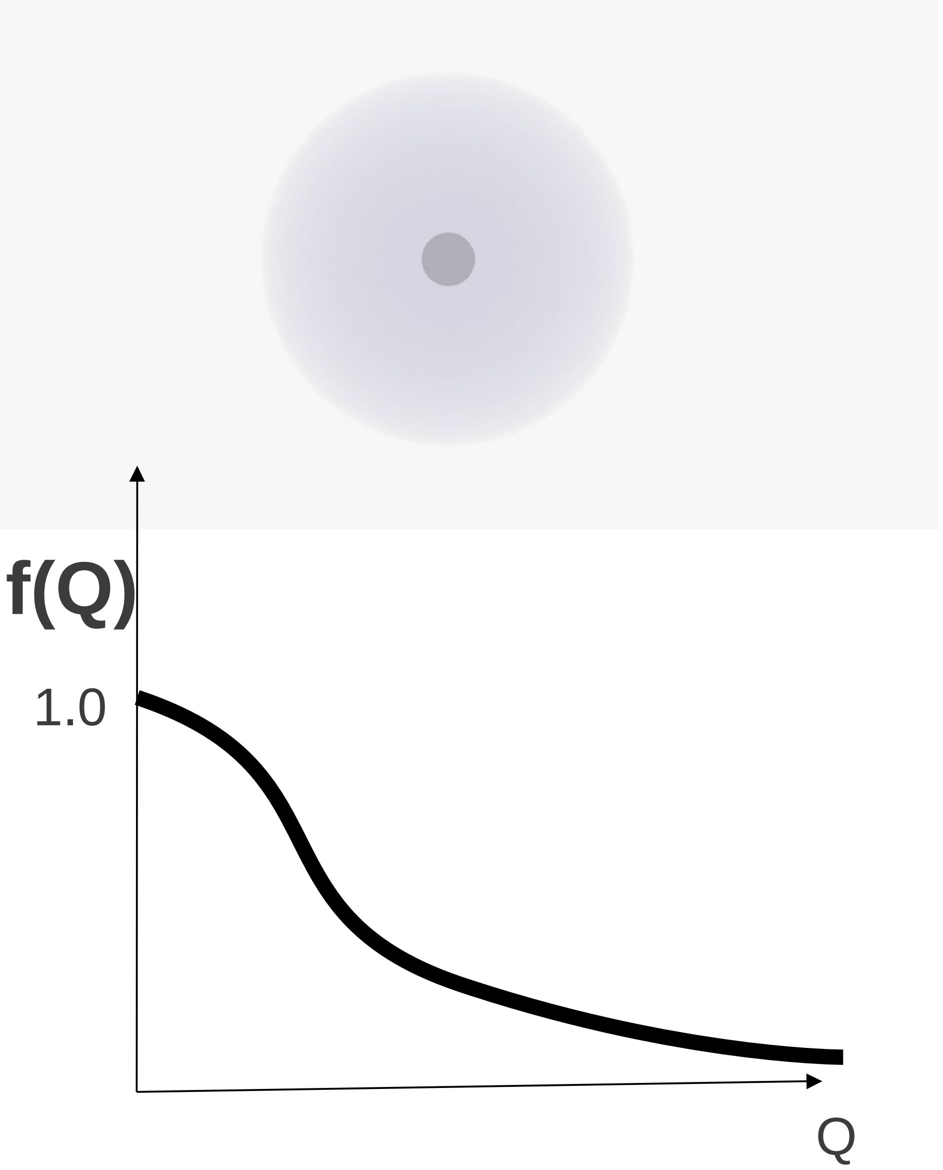
$$\boxed{\sum_{atom\ j \in UC} b_j e^{-i\vec{Q}\cdot\vec{r}_j}}$$

Nuclear from factor (X-ray comparison)

Neutrons

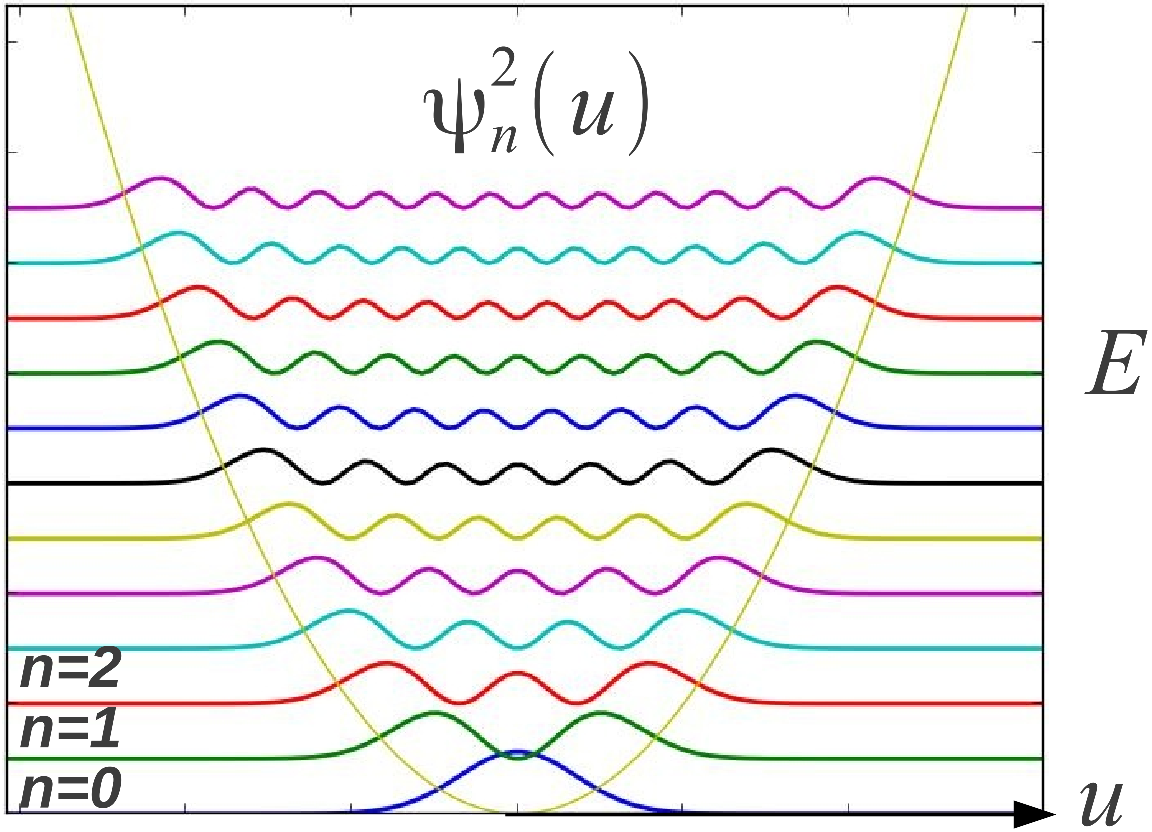


X-ray



Unit cell structure factor (including Atomic Displacement)

- There is one approximation in the previous slide: We haven't taken into account the effect of thermal motion, i.e. the fact that the atoms are not a fixed position but undergo very large displacements with respect to the Fermi length.
- Needs to consider a *Quantum Harmonic Oscillator*



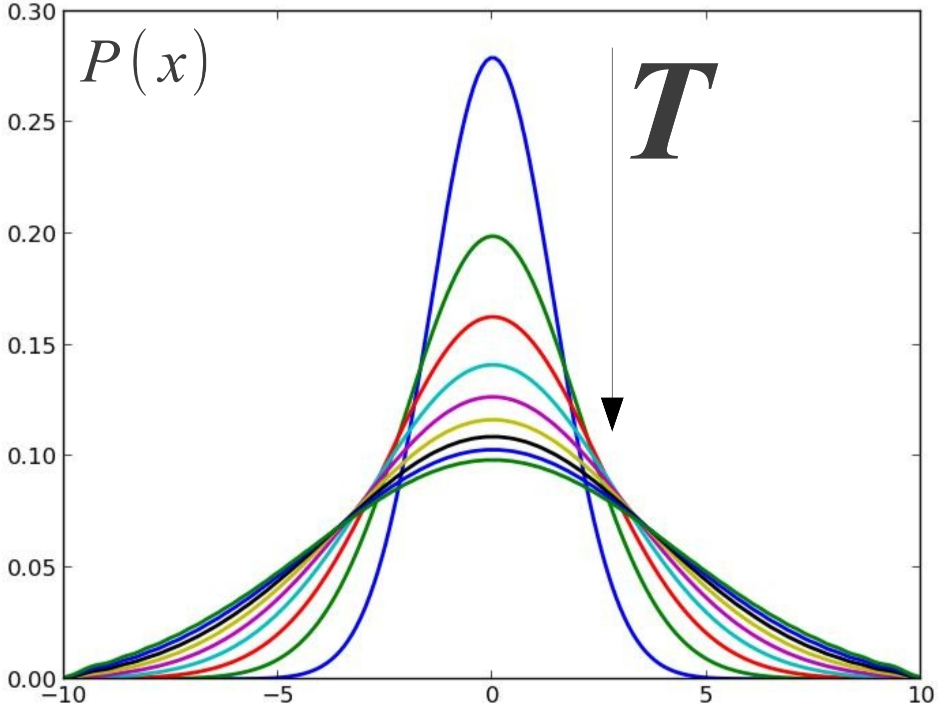
$$E_n = \hbar\,\omega\left(n + \frac{1}{2}\right)$$

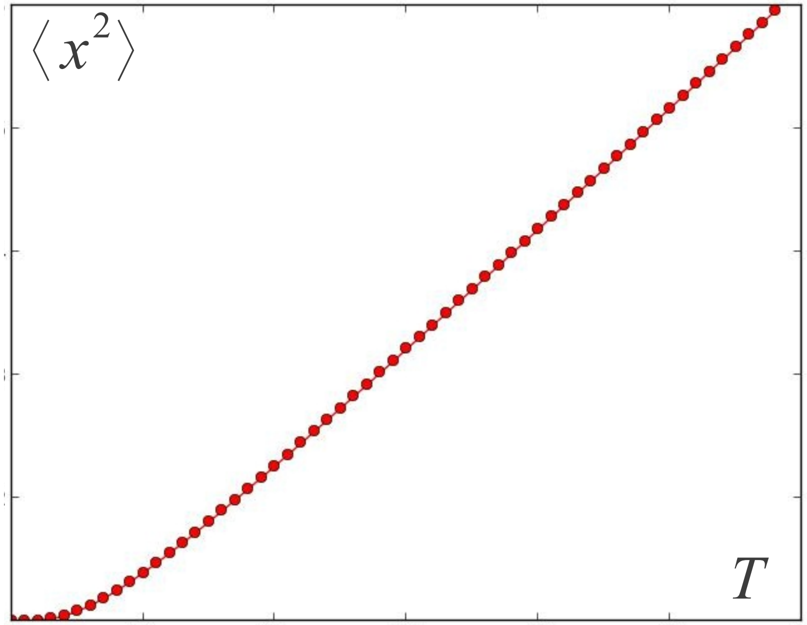
Unit cell structure factor (including Atomic Displacement)

- Probability to find the atom displaces by u is related to the Boltzmann distribution:

$$P(u)=\frac{\sum_n \psi_n^2(u)\cdot e^{\frac{-E_n}{k.T}}}{\sum e^{\frac{-E_n}{k.T}}}=\frac{1}{\sqrt{2\pi\langle u^2\rangle}}e^{\frac{-u^2}{2\langle u^2\rangle}}$$

….a Gaussian distribution





Unit cell structure factor (Isotropic ADP)

- Fourier transform of a Gaussian is also a Gaussian

$$P(u)=\frac{1}{\sqrt{2\pi\langle u^2\rangle}}\,e^{\frac{-u^2}{2\langle u^2\rangle}} \xrightarrow[FT]{} e^{\frac{-1}{2}u^2Q^2}=e^{-8\pi^2\langle u^2\rangle\frac{\sin^2(\theta)}{\lambda^2}}$$

- If the motion is isotropic, the **A**tomic **D**isplacement **P**arameter for atom j is:

$$\boxed{B_j=8\pi^2\langle u_j^2\rangle}$$

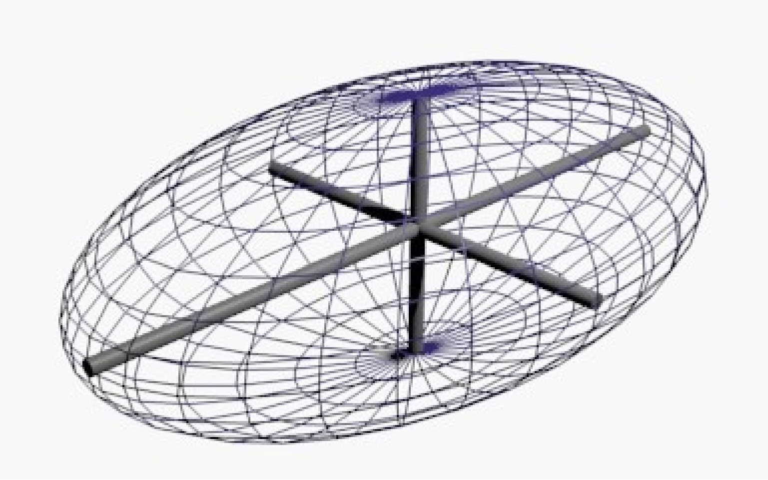
Unit-cell structure factor:

$$F(\vec{Q})=\sum_{atom\ j\in UC} b_j e^{-i\vec{Q}\cdot\vec{r}_j}\cdot e^{-B_j\frac{\sin(\theta)^2}{\lambda^2}}$$

$$F(h,k,l)=\sum_{atom\ j\in UC} b_j e^{-i2\pi(h\cdot x_j+k\cdot y_j+l\cdot z_j)}\cdot e^{-B_j\frac{\sin(\theta)^2}{\lambda^2}}$$

For full nomenclature on ADP from IUCR: see Acta Cryst. (1996). A52, 770-781

Unit cell structure factor (Anisotropic ADP)



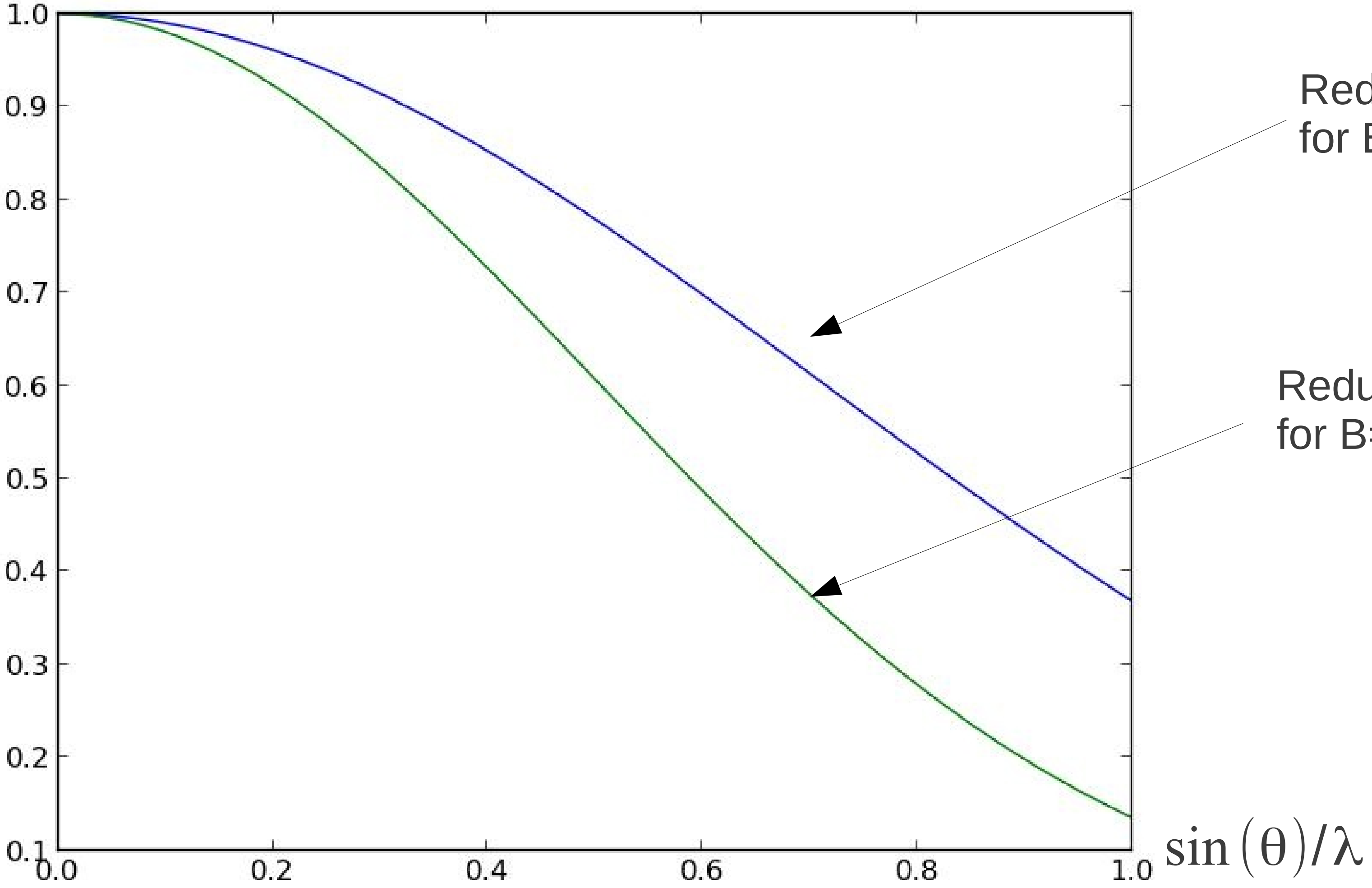
- The Atomic Displacement parameter can be anisotropic, in which case a trivariate Gaussian is assumed.
- In the most general case (no constraint from point symmetry of the site), there are 6 independent u_{ij} displacement parameter (second rank tensor).

$$\begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{pmatrix}$$

$$F(\vec{h})=F(h,k,l)=\sum_{atom\ j\in UC} b_j e^{-i2\pi(h\cdot x_j+k\cdot y_j+l\cdot z_j)}\cdot e^{-2\pi^2\langle(\vec{u}\cdot\vec{h})^2\rangle}$$

Effect of ADP on intensities

- Scattering function is damped at high momentum transfer



Reduction of F(h,k,l)
for B=1Å^2

Reduction of |F(h,k,l)|^2
for B=1Å^2

Reminder: the phase problem

Now that you know how to write structure factors:

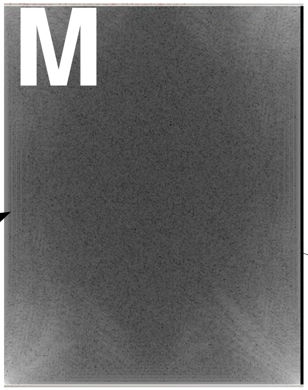
-Reminder: We measure F^2 !

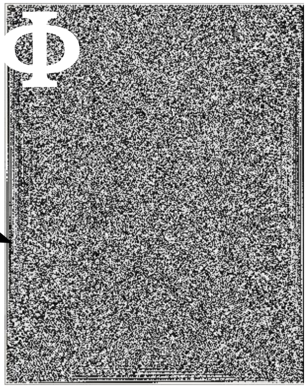
$$F(u,v)=M(u,v)e^{(i\Phi)}$$

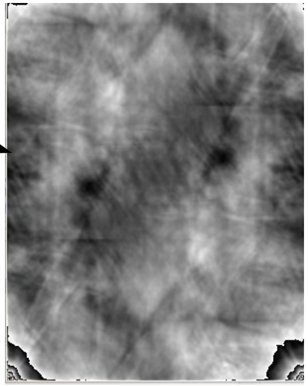
$$F(u,v)=\frac{1}{N_x N_y}\sum_x\sum_y f(x,y)e^{(-2\pi i(\frac{xu}{N_x}+\frac{yv}{N_y}))}$$

$$f'(x,y)=\frac{1}{N_u N_v}\sum_u\sum_v M(u,v)e^{(2\pi i(\frac{xu}{N}+\frac{yv}{N}))}$$

James Chadwick







Loss of information in a physical measurement :

The phase information is crucial to reconstruct the image

One can not determine V(r) without model

Symmetry in reciprocal space(Friedel's law)

Friedel's law, relates the scattering intensity of inverse Q points and stems from the property of Fourier transforms of real functions:

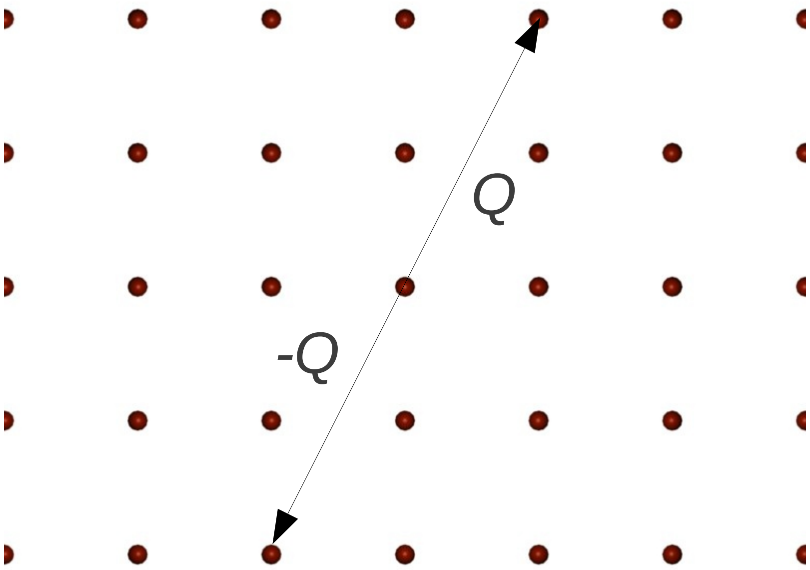
$$F(\vec{Q})=\sum_j f_j \cdot e^{i\vec{Q}\cdot\vec{R}_j}$$

If f_j is real then :

$$F(-\vec{Q})=\sum_j f_j \cdot e^{-i\vec{Q}\cdot\vec{R}_j}=F^*(\vec{Q})$$

Since the scattered intensity is proportional to FF^*:

$$I(\vec{Q})=F(\vec{Q})F^*(\vec{Q})=F^*(-\vec{Q})F(-\vec{Q})=I(-\vec{Q})$$



Even if the lattice lacks inversion symmetry, in the case when f_j are reals, the scattered intensity of Friedel pairs are equal.

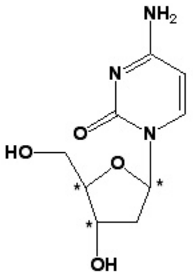
Symmetry in reciprocal space(Friedel's law)

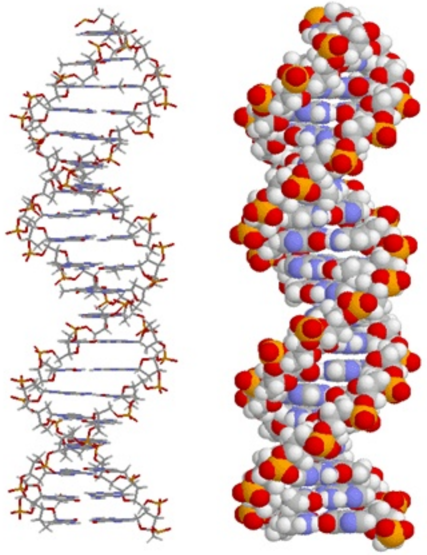
- Friedel's law is violated if we are close to a resonance, in which case one needs to consider the anomalous part of the scattering length: $b=b'-ib''$.

- In such case, and in the absence of inversion symmetry in the crystal:

$$F(-\vec{Q})=\sum_j f_j\cdot e^{-i\vec{Q}\cdot\vec{R}_j}\neq F^*(\vec{Q})$$

- This property can be used to determine the absolute handedness of chiral crystals for example. (most commonly X-ray anomalous scattering is used)





Symmetry in reciprocal space

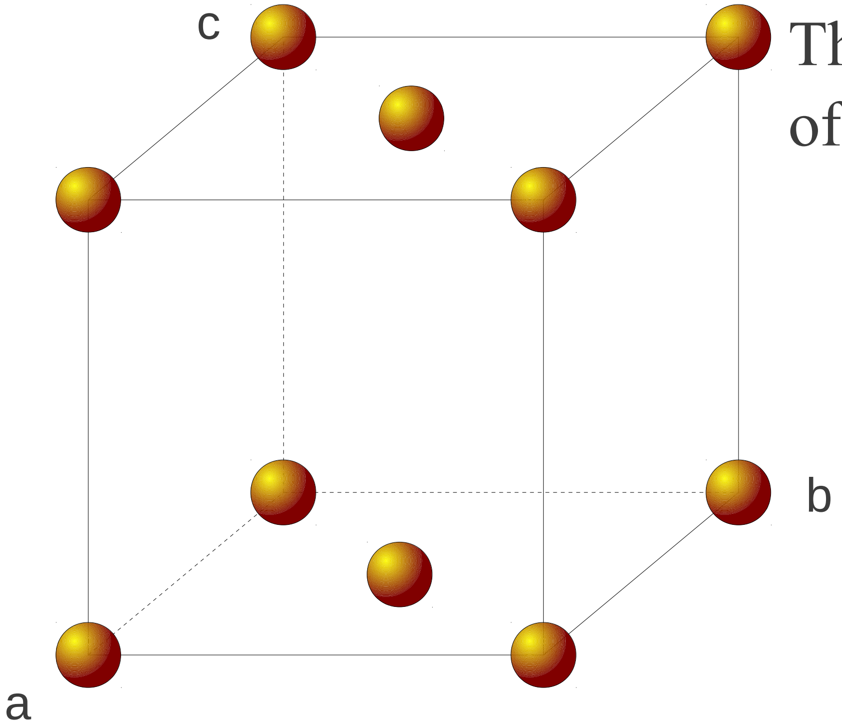
- Friedel's law holds most of the time (especially in neutron scattering unless very high incident energies are employed)
- The symmetries that we have listed in real space, are also valid symmetries in reciprocal space once their translational part has been taken away.
- Combining the two → 11 Laue groups

Crystal system	Laue Class
Triclinic	-1
Monoclinic	2/m
Orthorhombic	mmm
Tetragonal	4/m ; 4/mmm
Trigonal	-3 ; -3/m
Hexagonal	6/m; 6/mmm
Cubic	m3 ; m3m;

Systematic absences

Systematic absences referred to the systematic lack of intensity (for some crystal symmetries) for certain lines or planes in reciprocal space and are due to:

- Lattice centering
- Symmetry operations with translations (screw axes and glide planes)



This is a direct consequence of exact cancellation of structure factors. Example: C-centering

$$F(h,k,l)=b\left(e^{2\pi i(hx+ky+lz)}+e^{2\pi i(h(x+1/2)+k(y+1/2)+lz)}\right)$$

$$F(h,k,l)=b\,e^{2\pi i(hx+ky+lz)}\left(1+e^{\pi i(h+k)}\right)$$

$$\downarrow$$

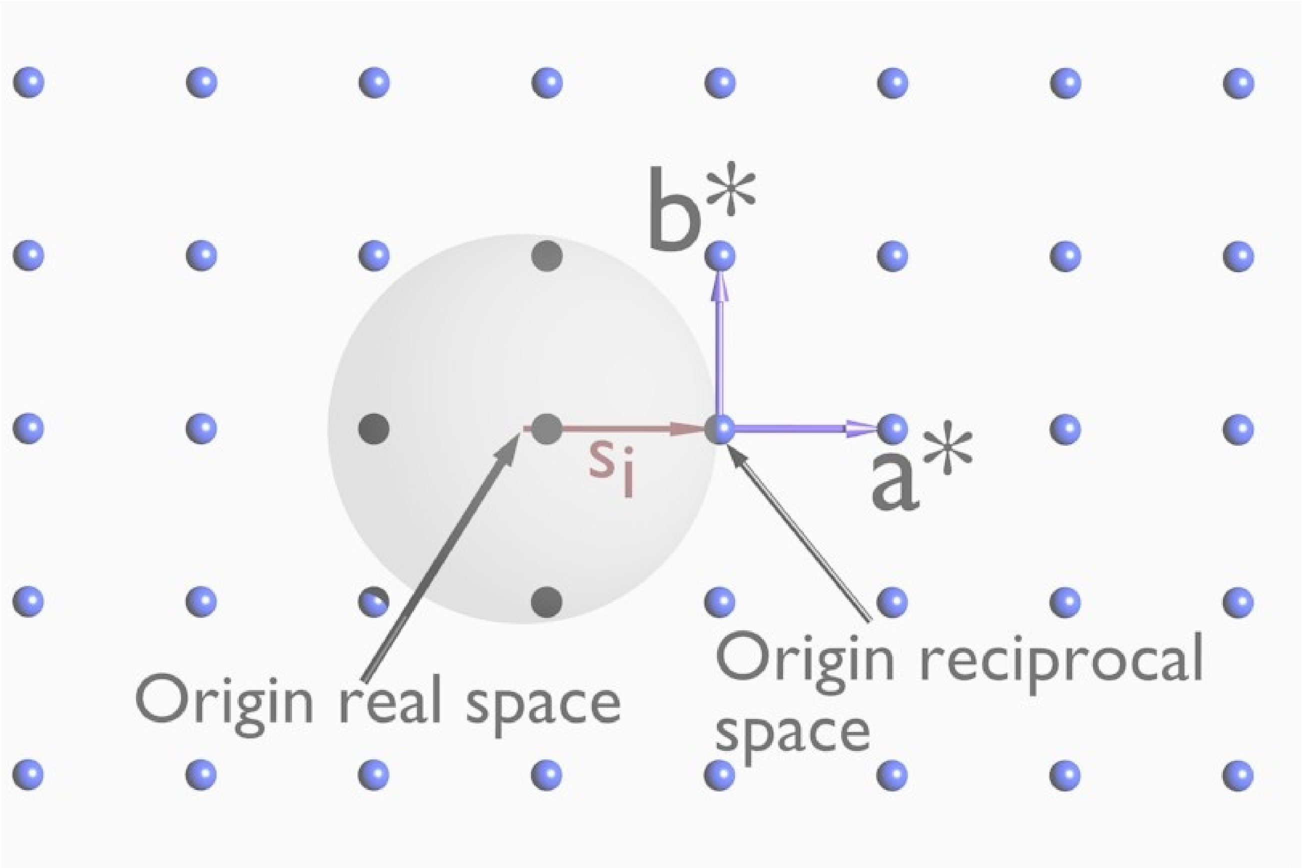
$$h+k=2\mathrm{n}$$

Ewald construction (monochromatic source)

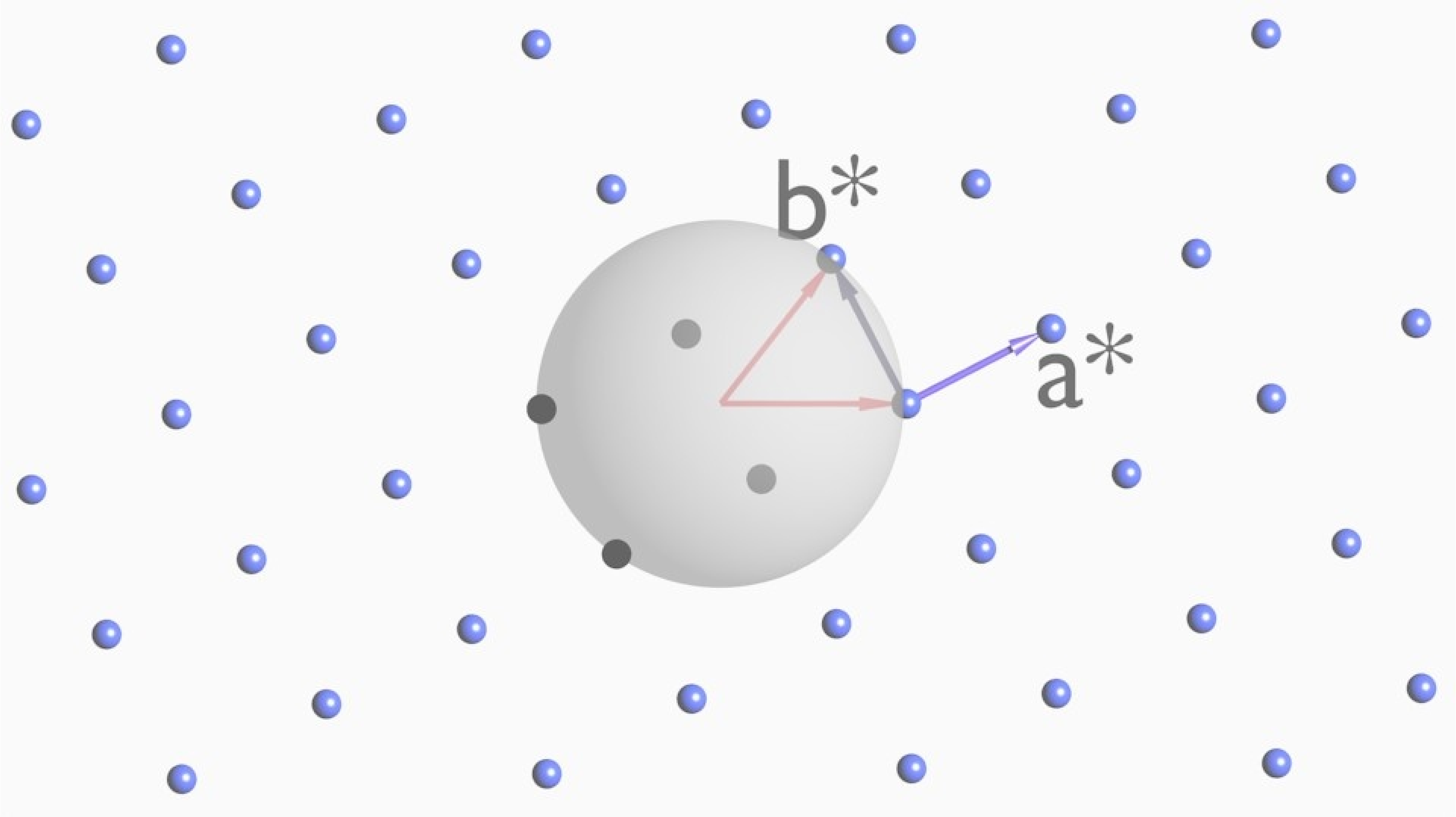
- The idea of P. P. Ewald is to decouple real and reciprocal spaces.
- The crystal is drawn at the center of the figure.
- Use incident wavenumber

  $s_i = k_i / 2\pi$
- Draw a sphere of radius $s = 1/\lambda$
- Origin of reciprocal space

  is at the extreme point of s_i

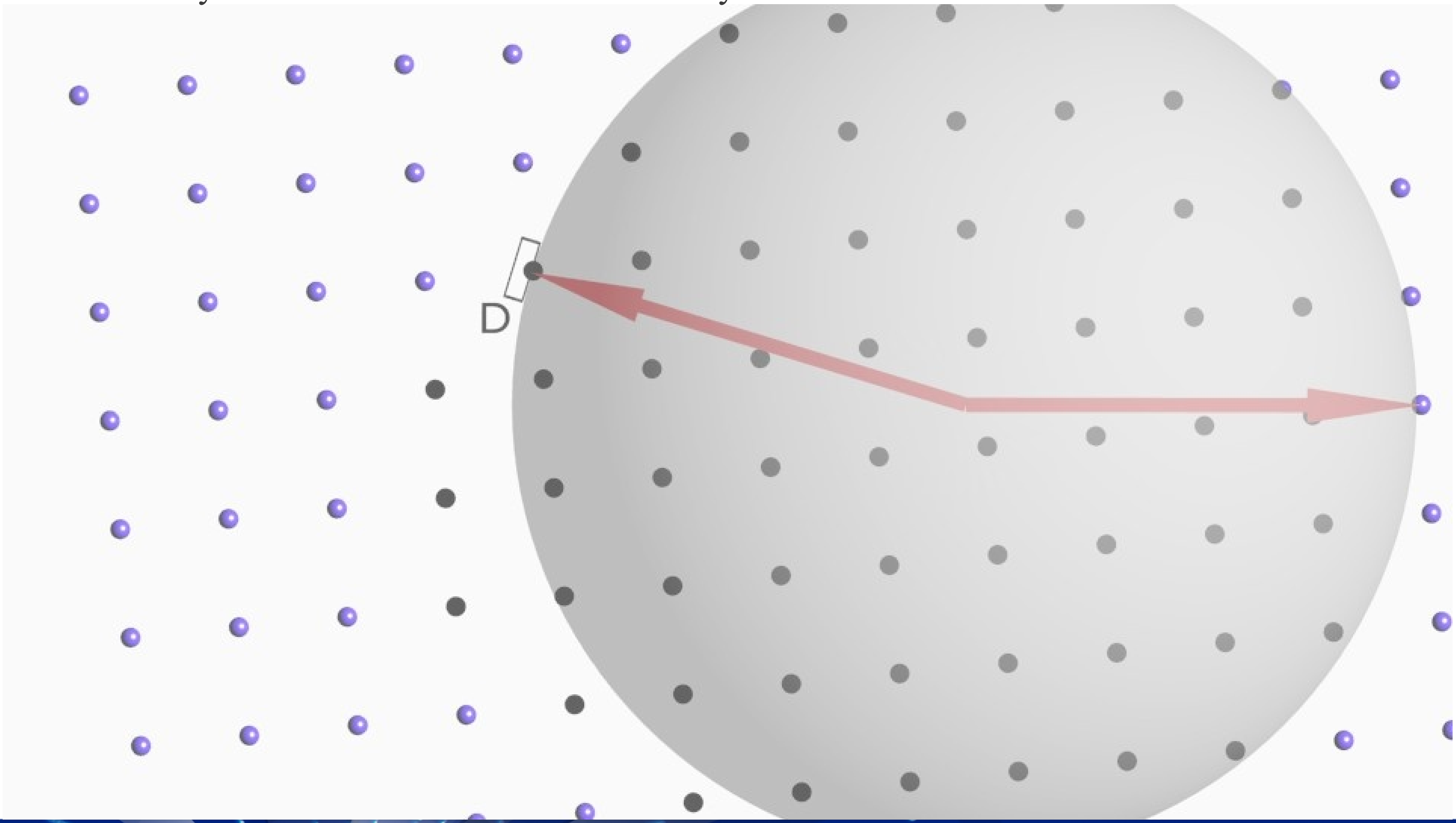


Ewald construction (ω-scan)



Ewald construction (ω-2θ scan)

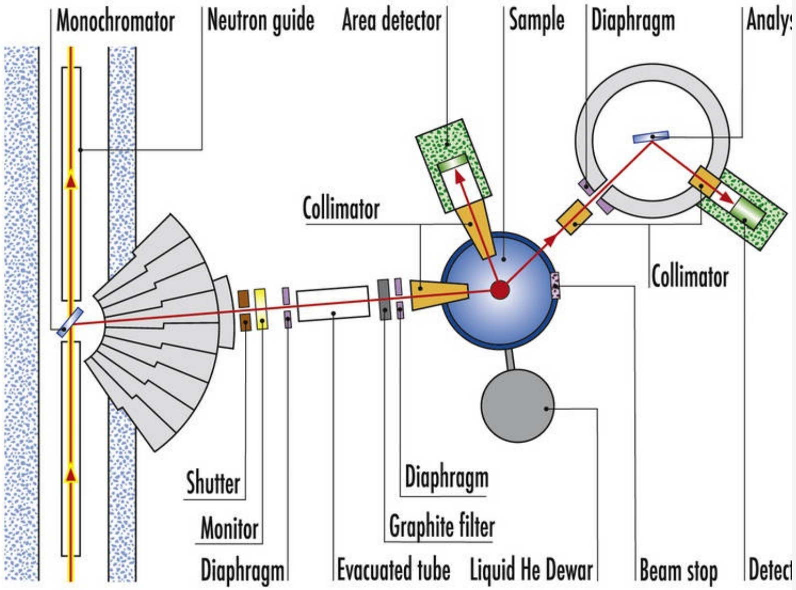
Rotate the crystal and the detector simultaneously

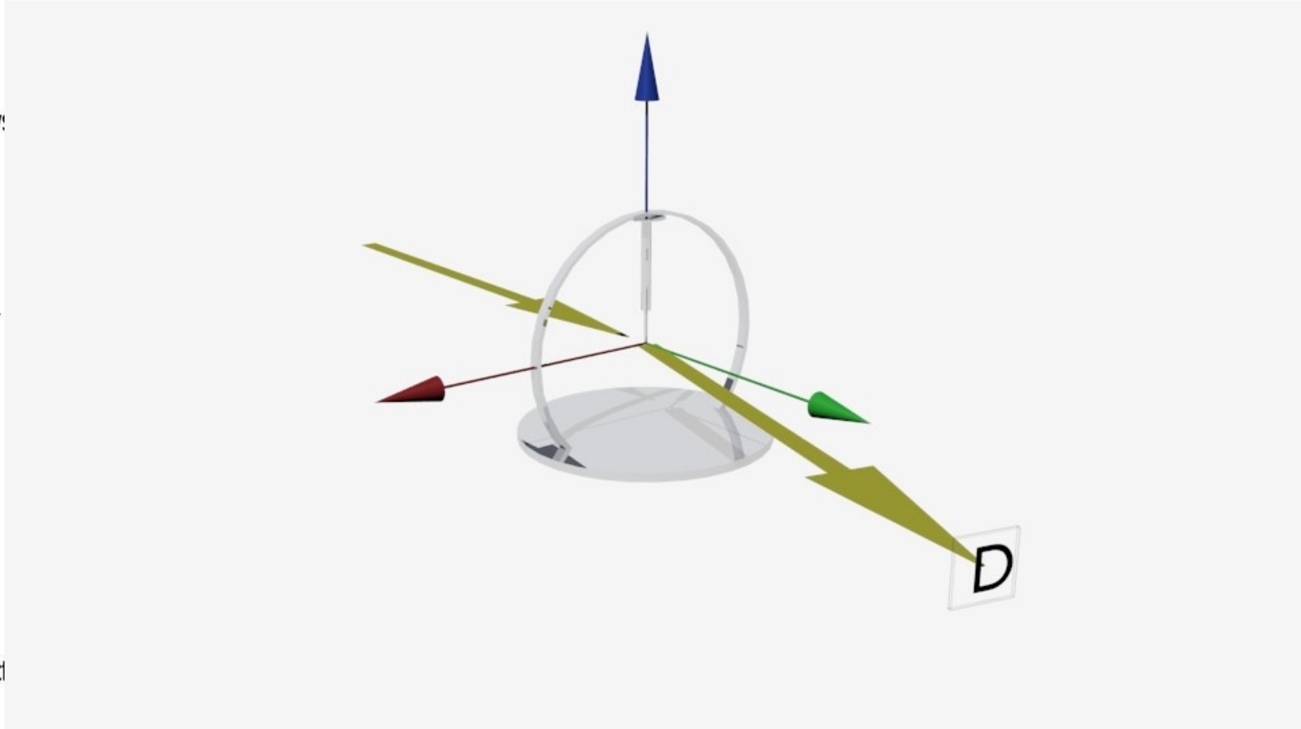


4-circle diffractometer

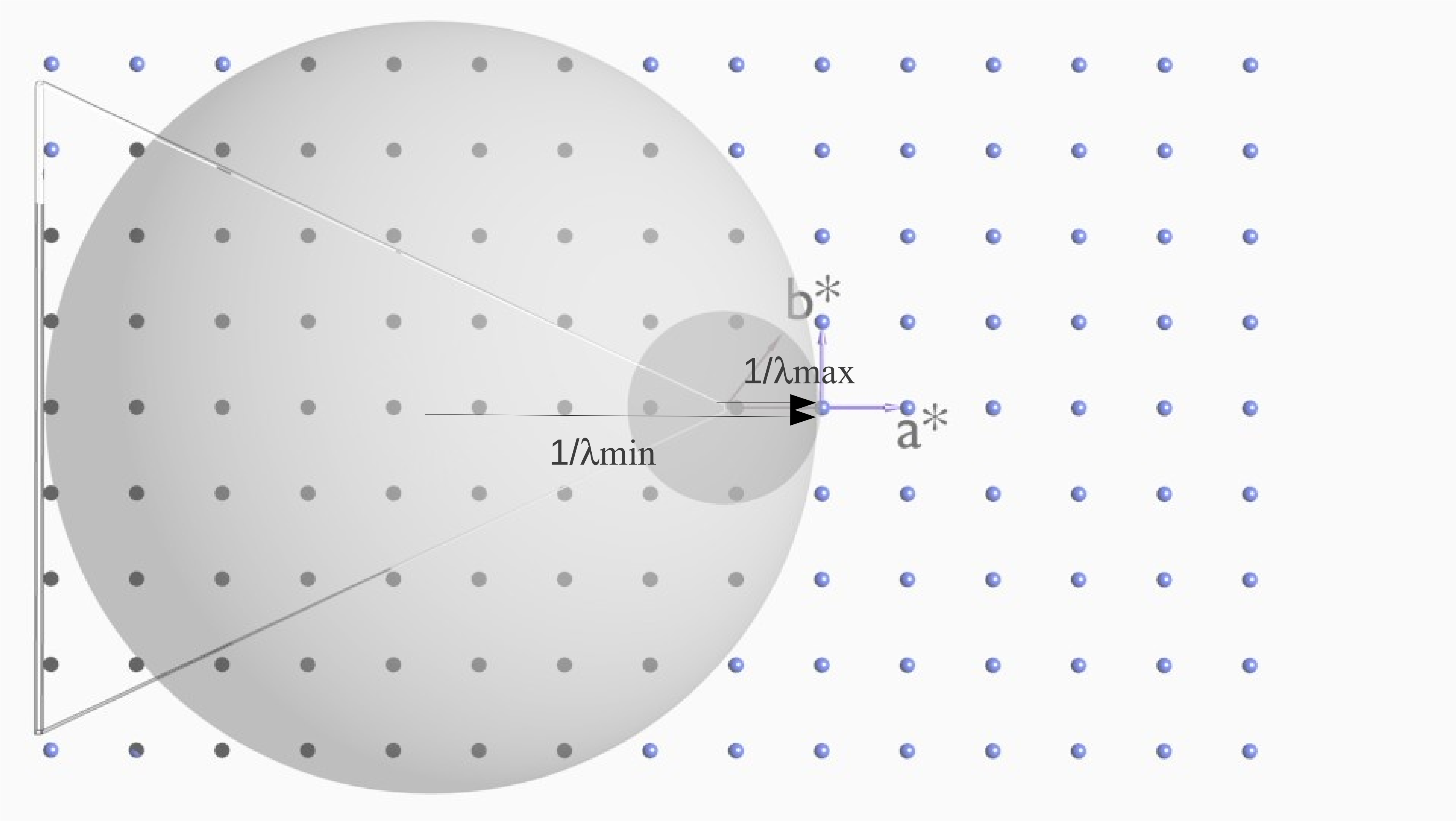
- Detector in place in the horizontal scattering plane.
- Crystal is rotated through a 3-axis goniometer (Like Euler rotations ZYZ)
- Access a large number of Bragg peaks by rotating the crystal

D10 @ ILL





Ewald construction (Laue method)



Laue method

***“During my first stay in Gottingen I had made a half-hearted attempt to attend a mineralogy course but had given up very soon. From books I then learned the rudiments of crystallography,that is to say, crystal classes, that was all*.”**

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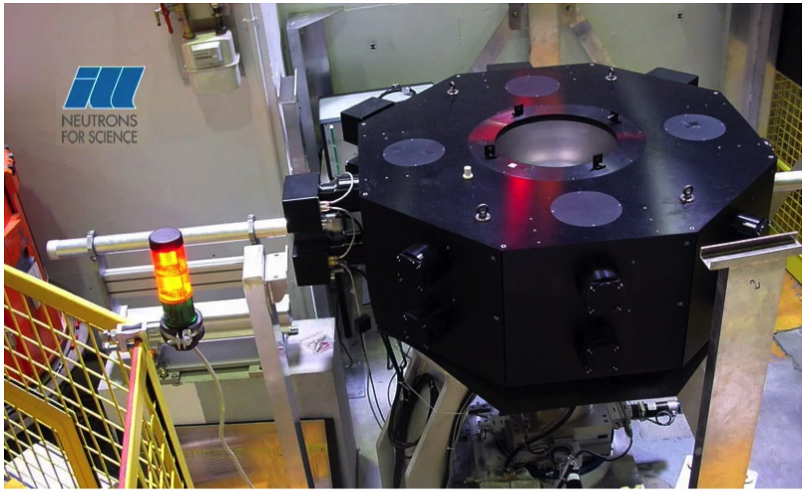
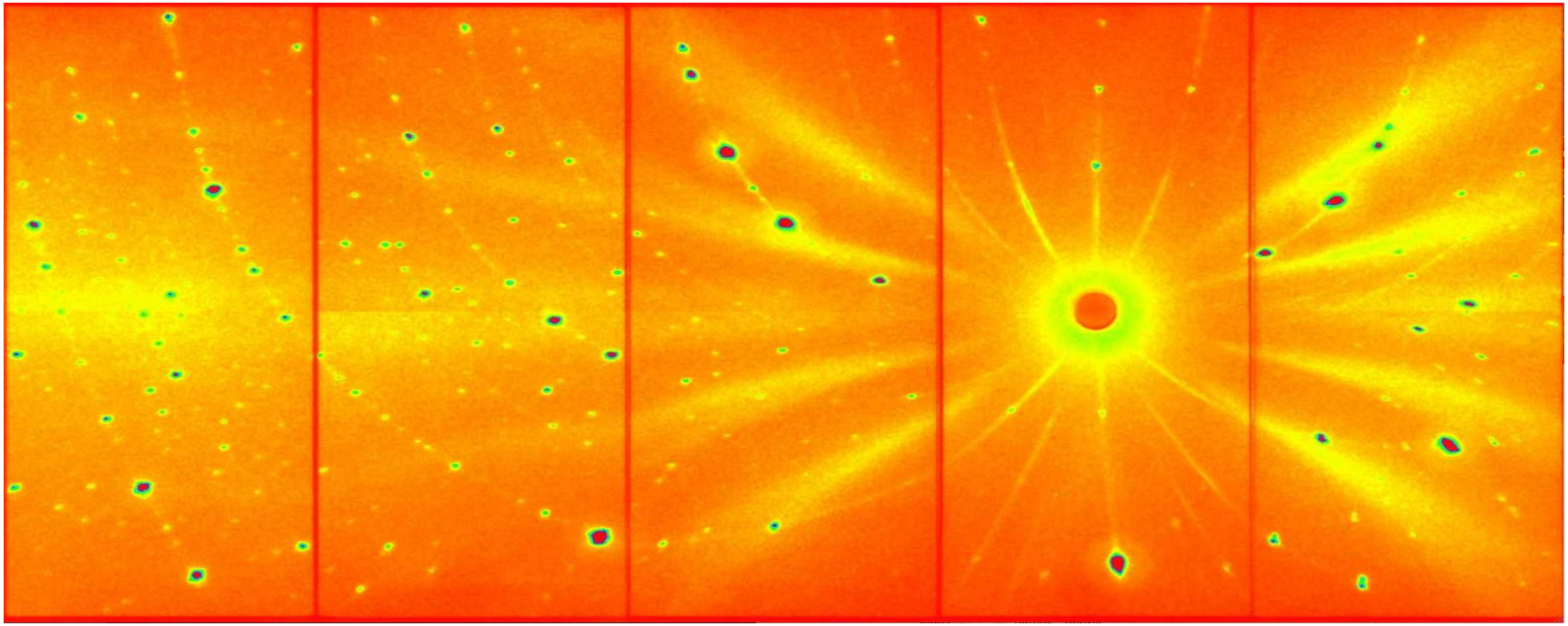
M. Von. Laue Nobel Lecture

Laue method

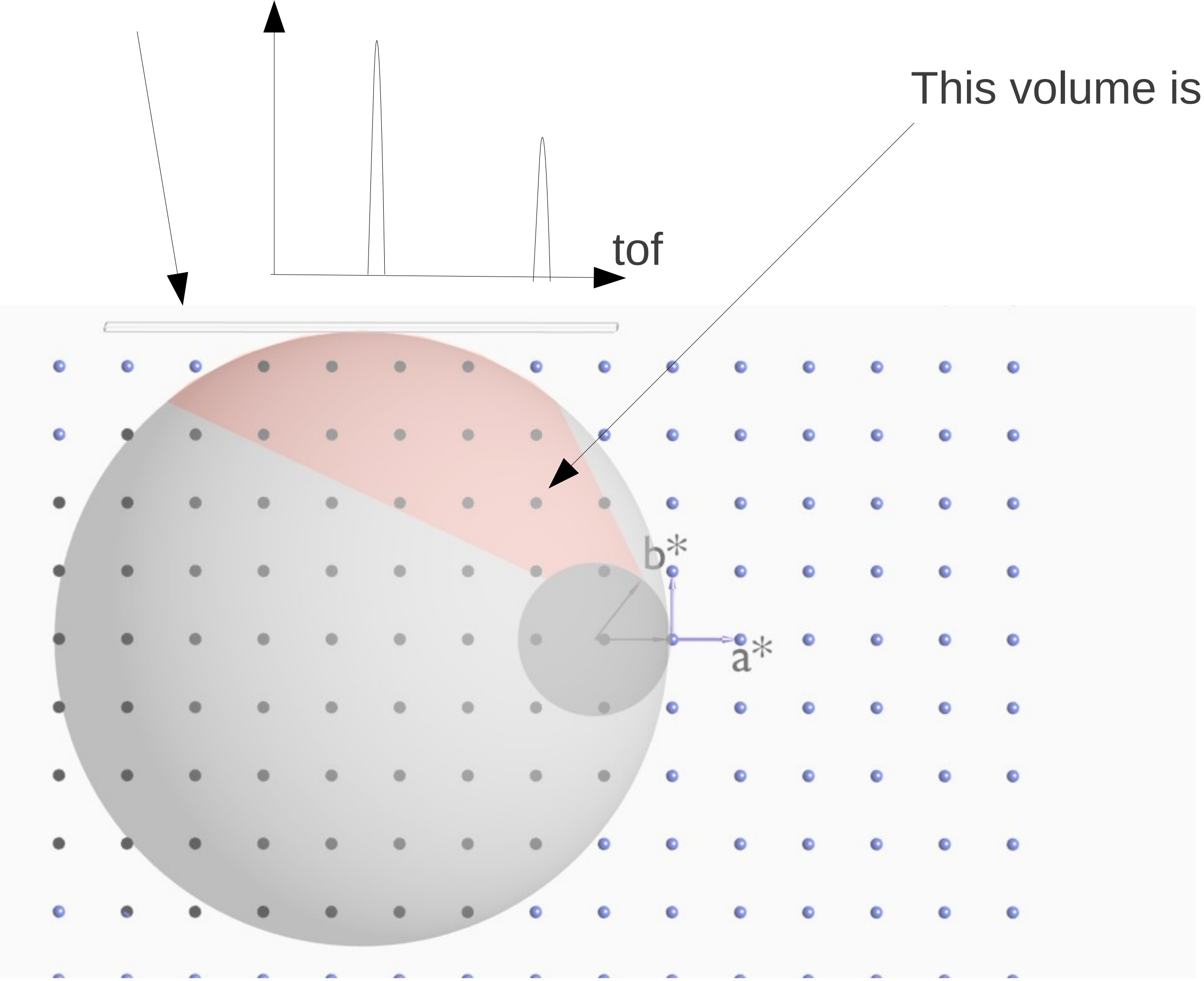


Neutron Laue Cyclops @ILL

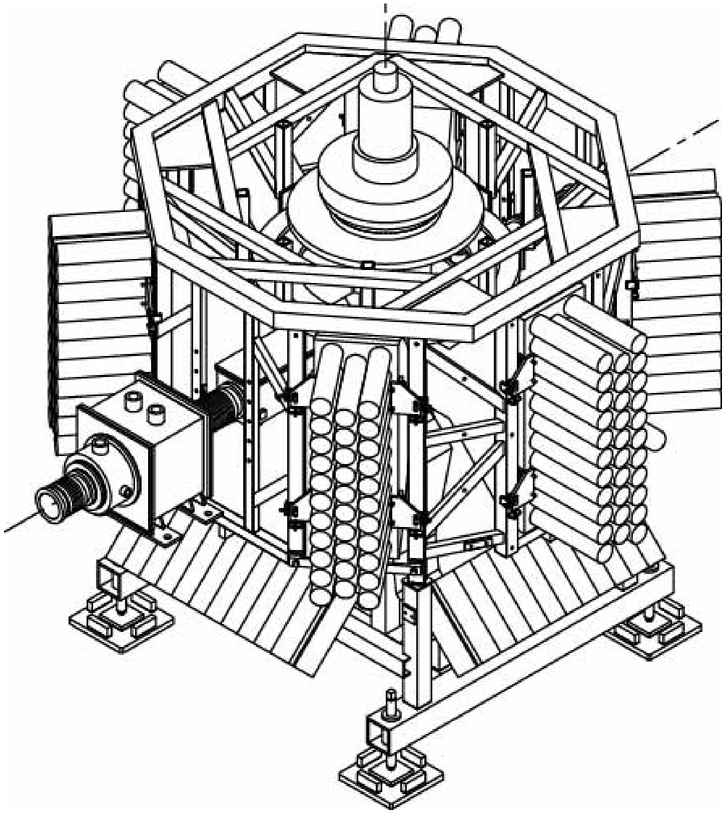


T.O.F Single Crystal

For each pixel on the Detector:



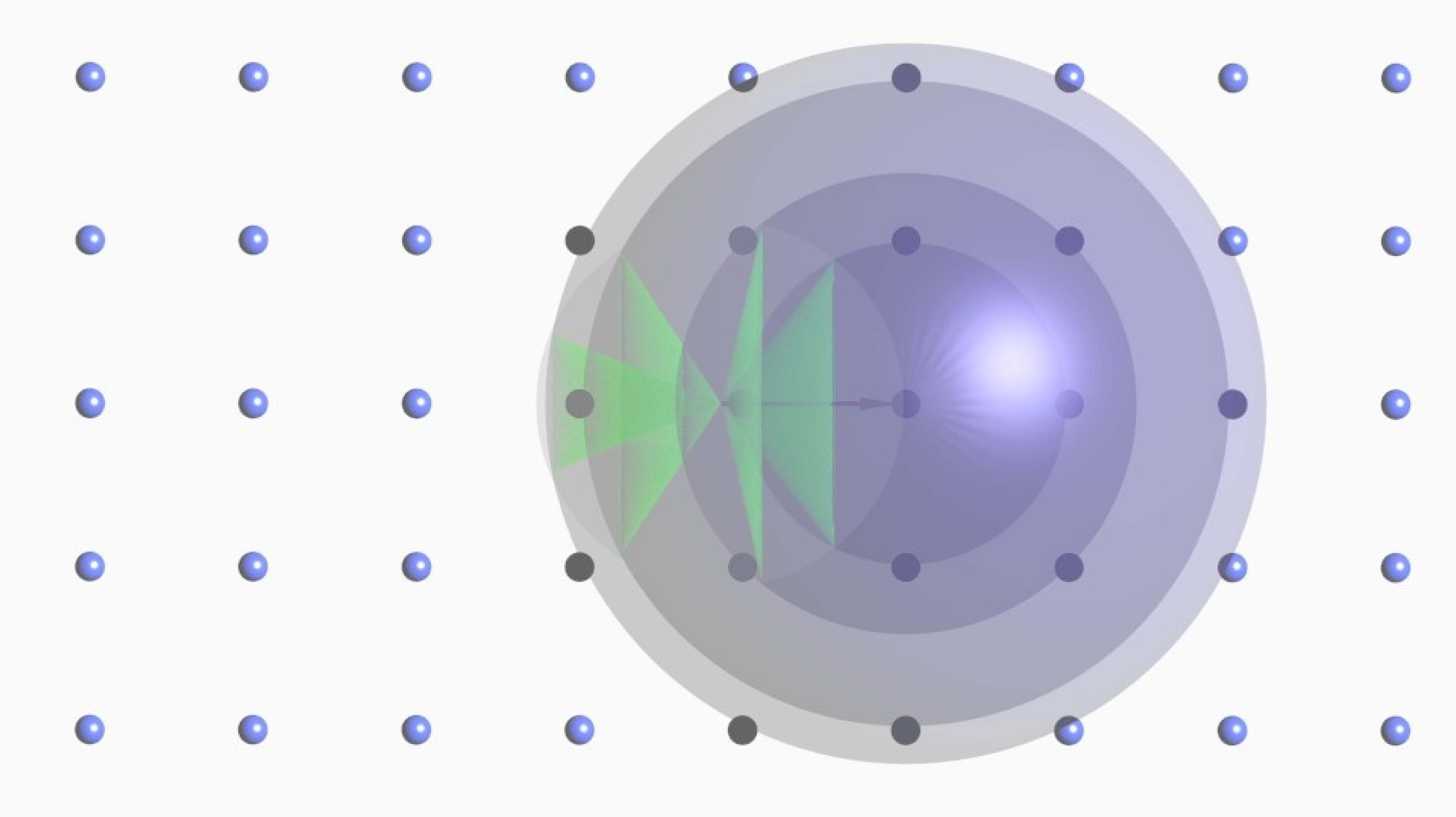
This volume is available in a single shot



TOF Laue SXD @ ISIS

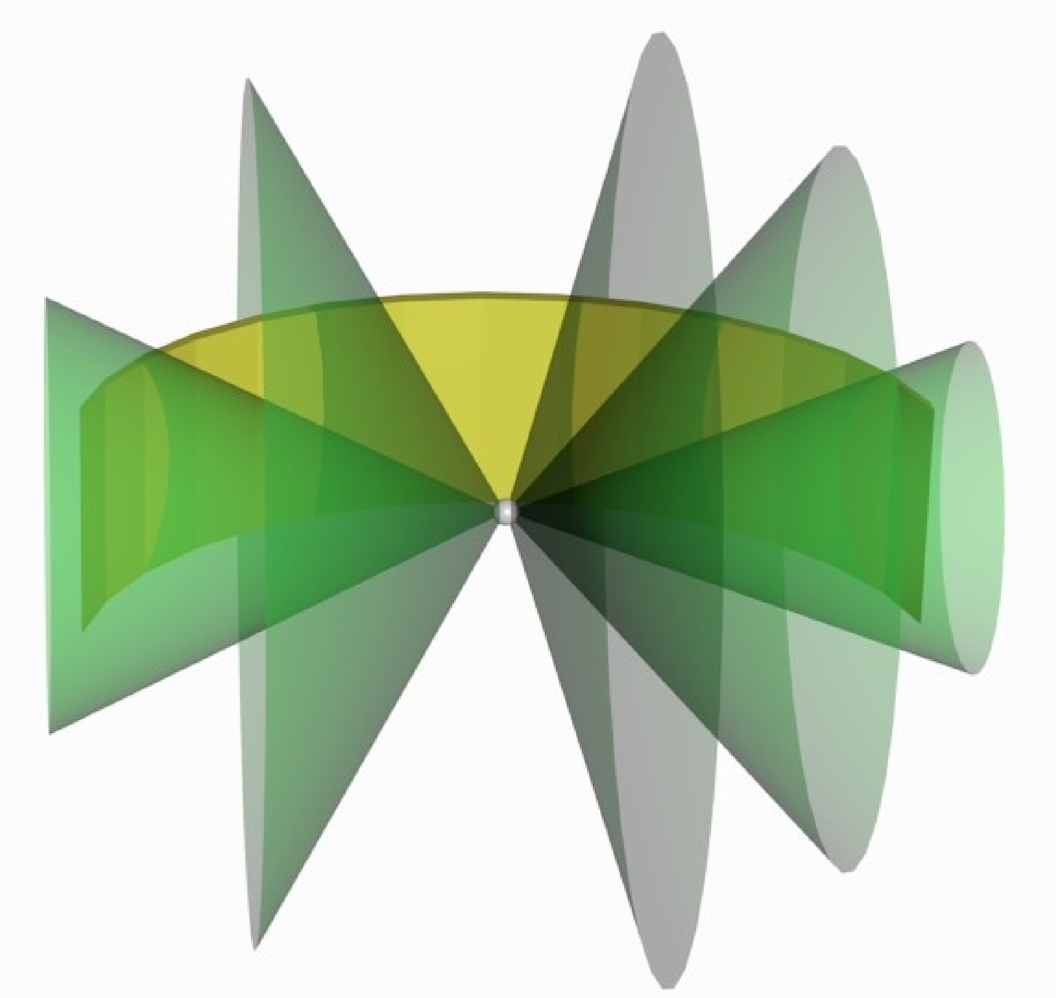
Debye-Scherrer cones (powder method)

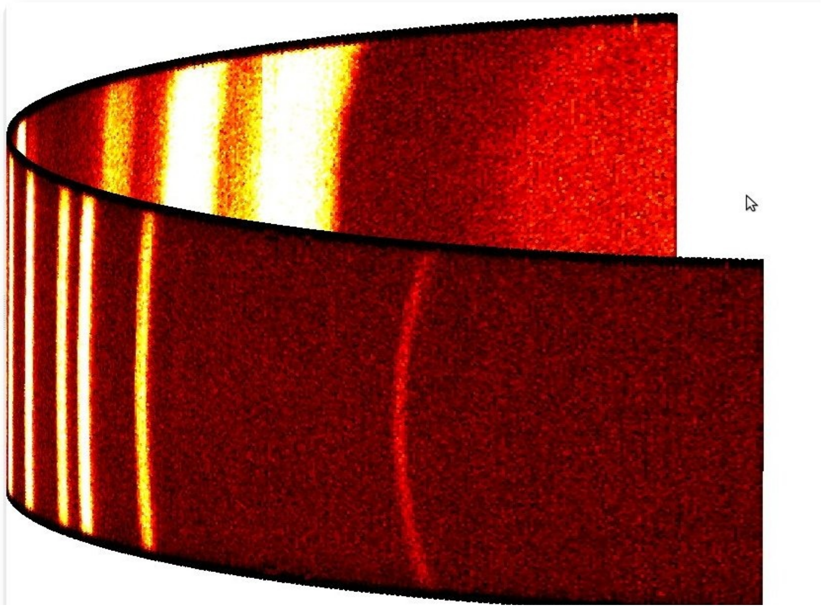
Intersection of Ewald sphere with spheres in reciprocal space.



Debye-Scherrer cones (powder method)

Intersection of scattering cones with cylindrical detector

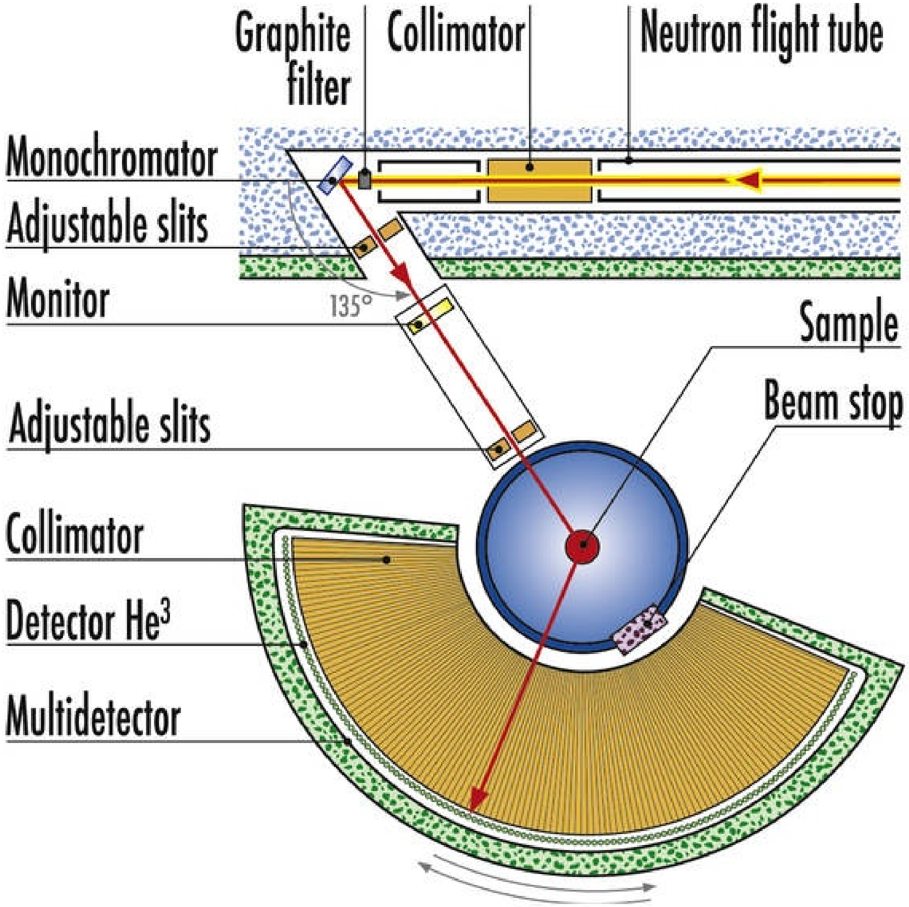




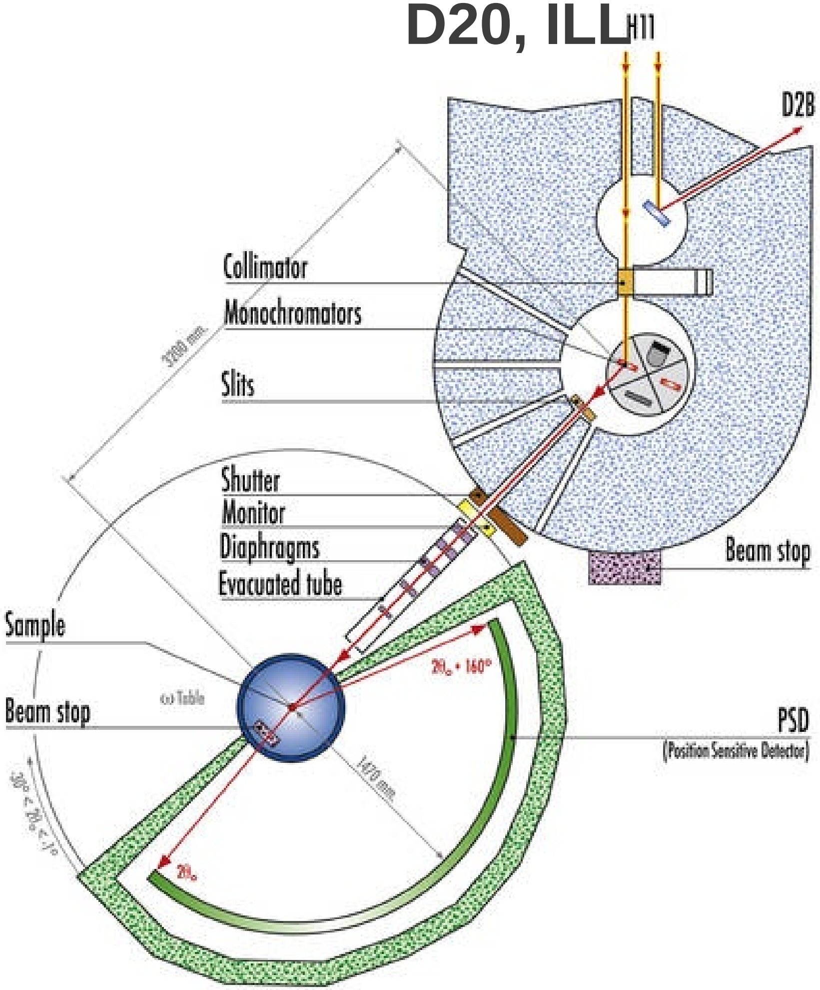
WISH@ISIS

CW powder instruments

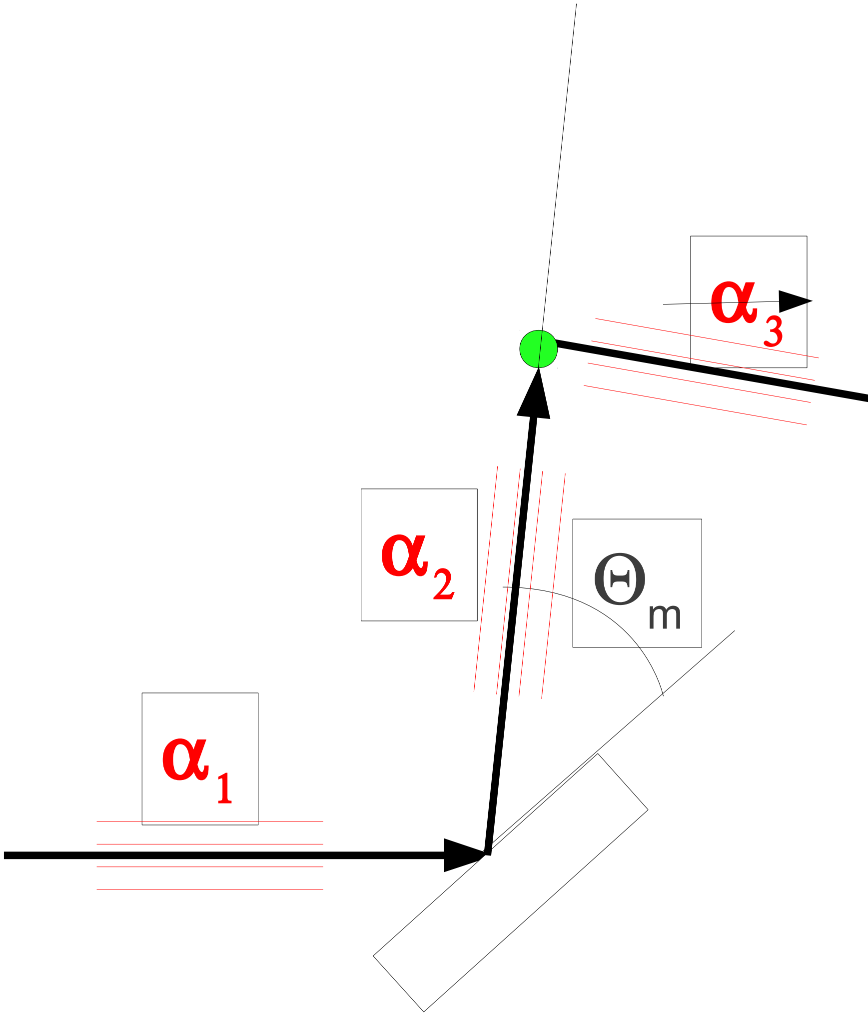
D2B, ILL



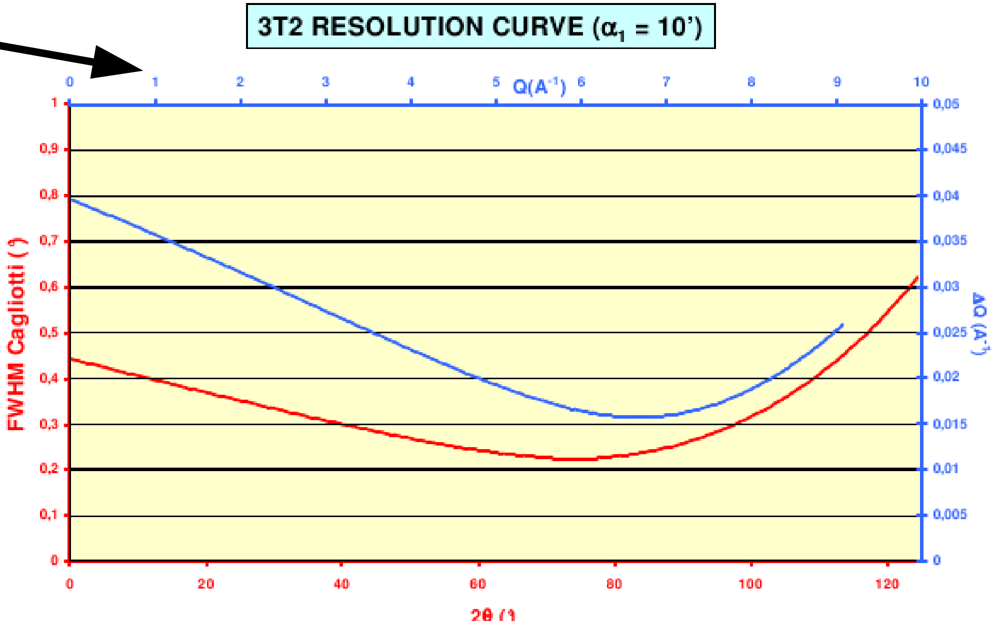
D20, ILL



CW powder instrument: Resolution function

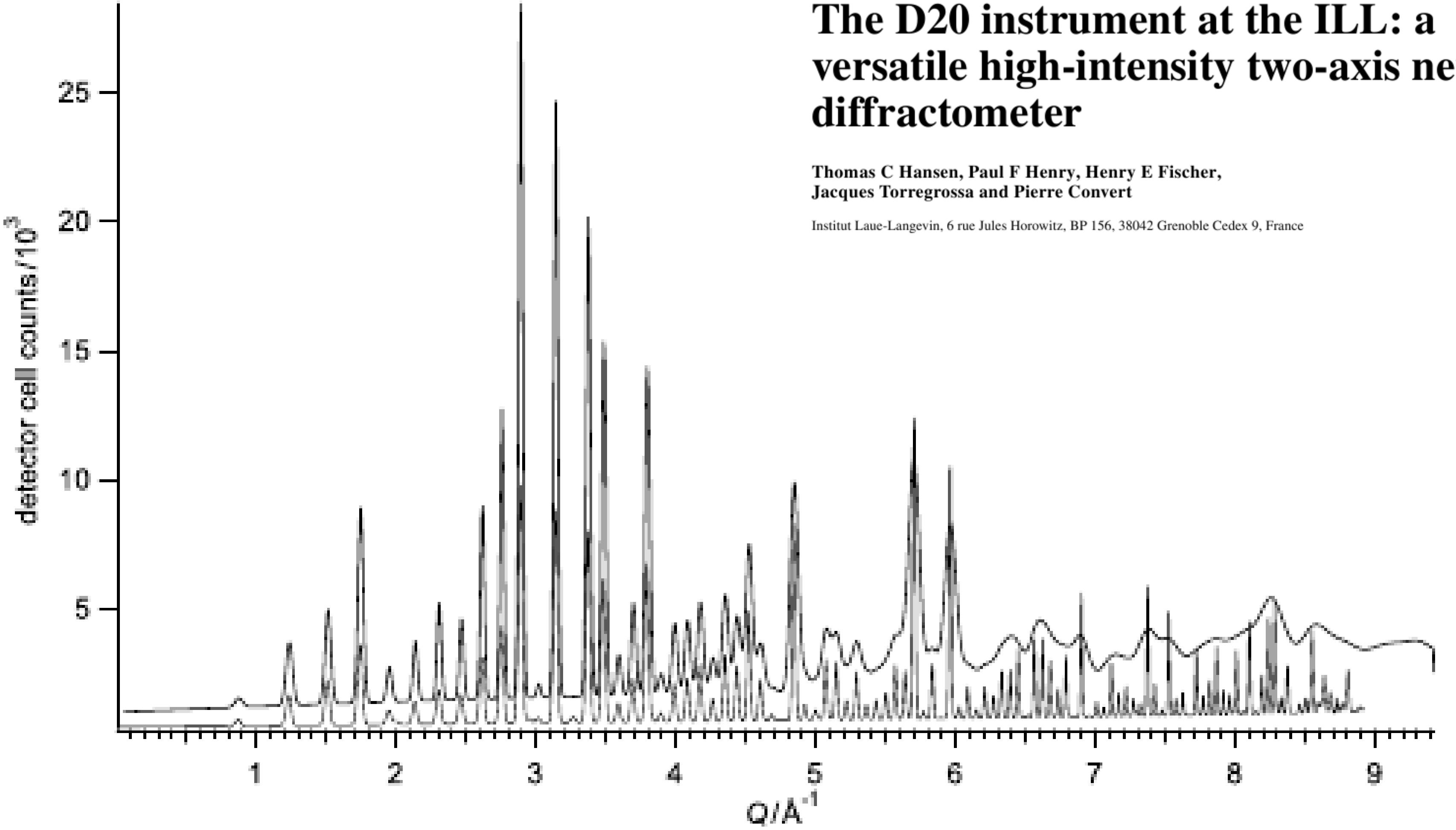


$$\frac{\Delta d}{d}=\frac{1}{2}\sqrt{U.\cot^2(\theta)+V.\cot(\theta)+W}$$



LLB, Saclay, 3T2

Trade resolution-flux



IOP PUBLISHING MEASUREMENT SCIENCE AND TECHNOLOGY

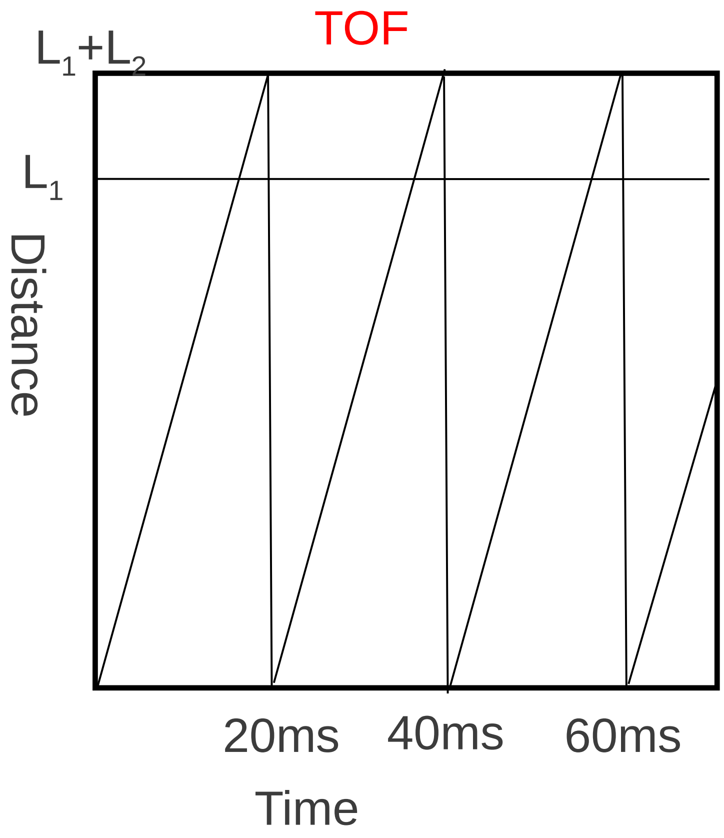
Meas. Sci. Technol. **19** (2008) 034001 (6pp) doi:10.1088/0957-0233/19/3/034001

The D20 instrument at the ILL: a versatile high-intensity two-axis neutron diffractometer

Thomas C Hansen, Paul F Henry, Henry E Fischer,
Jacques Torregrossa and Pierre Convert

Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

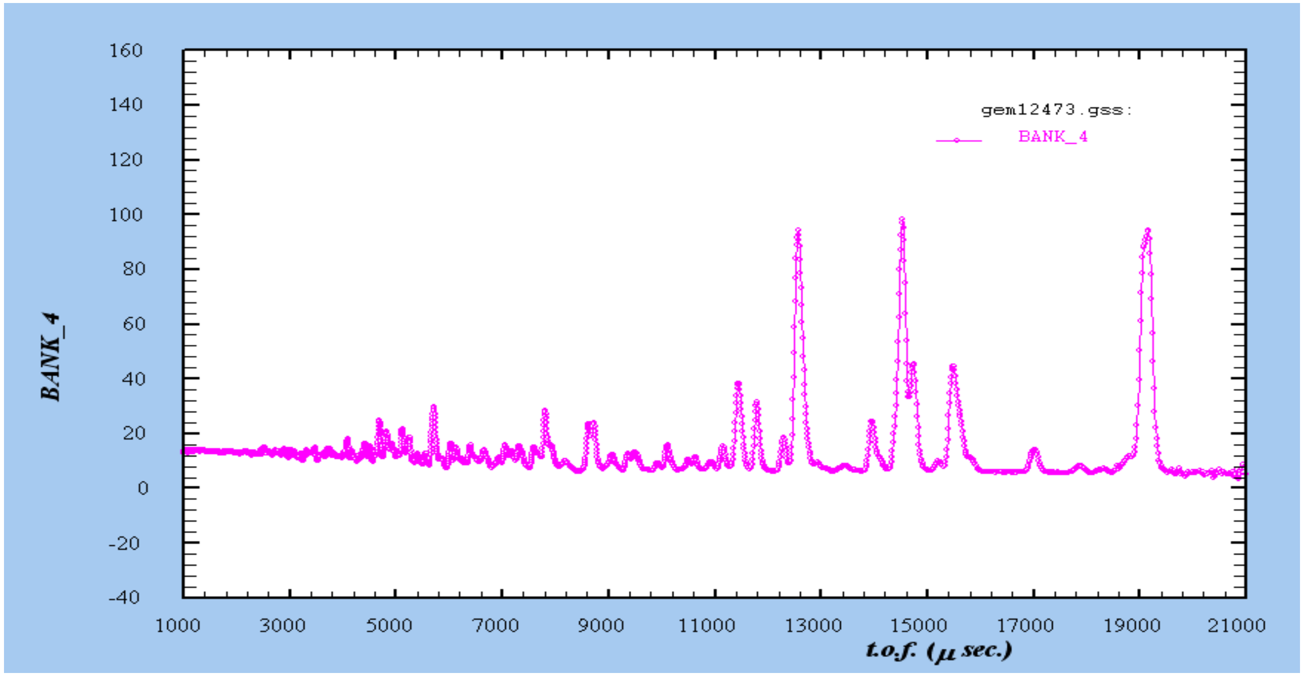
TOF- powder diffracion



$$p=\hbar k=\frac{h}{\lambda}=\frac{h}{2d\sin(\theta)}$$

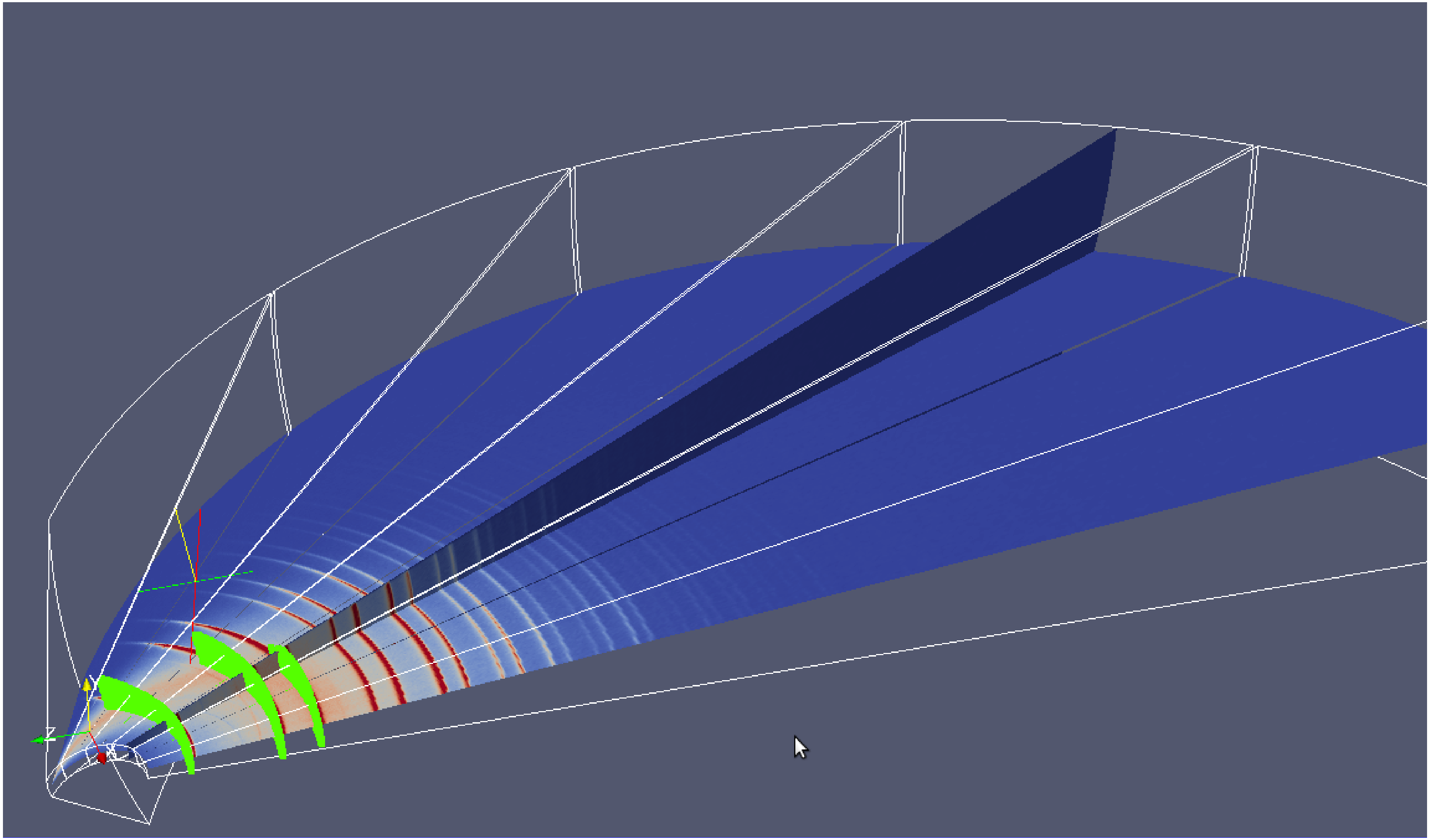
$$p=m\frac{L}{t}$$

$$d=\frac{ht}{2mL\sin(\theta)}$$

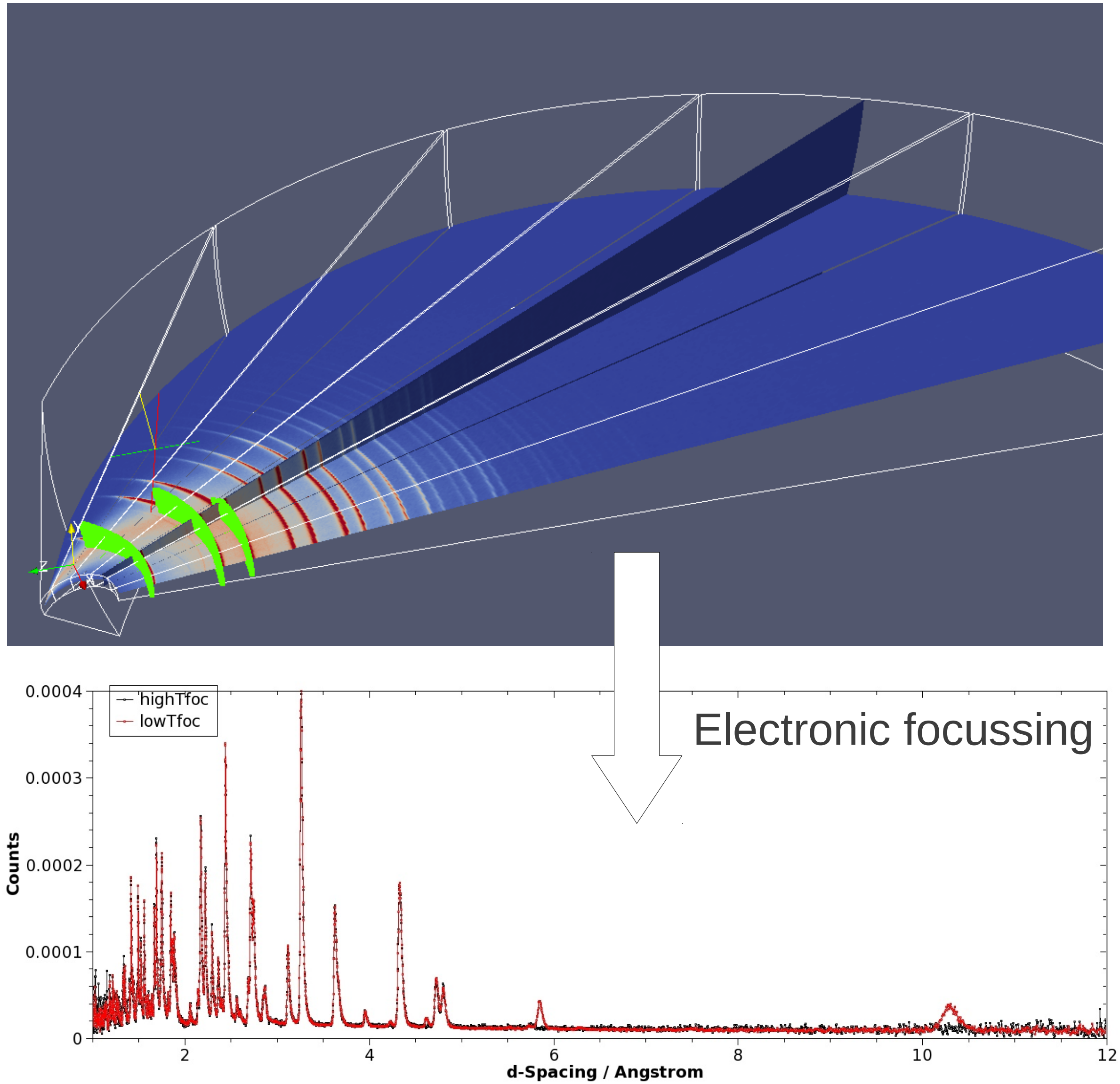


The x-axis is simply the time-of-flight usually given in microseconds

TOF powder data from WISH@ISIS



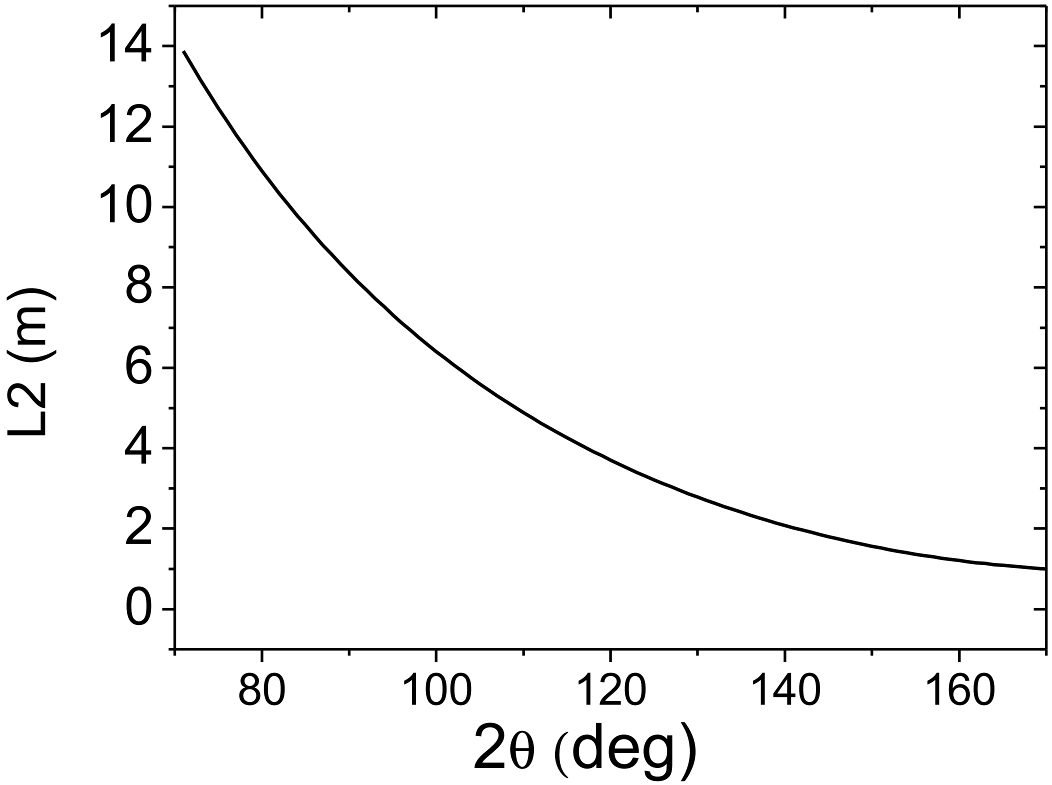
TOF powder data from WISH@ISIS



Electronic focussing

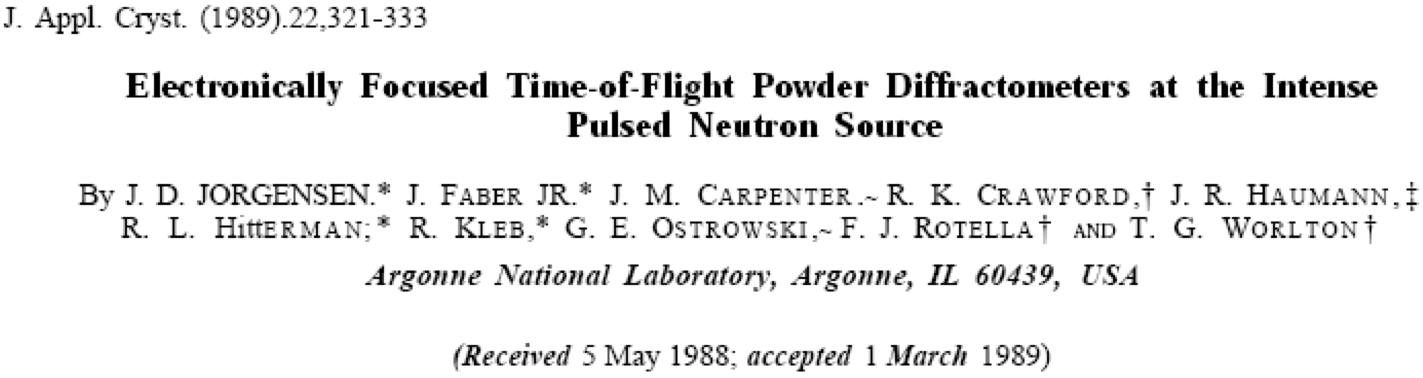
Geometric focussing

$$t = \frac{2dmL\sin\theta}{h}$$



- L.sin(θ)=const.
- L= total flight path

Electronic focussing



J. Appl. Cryst. (1989). 22, 321-333

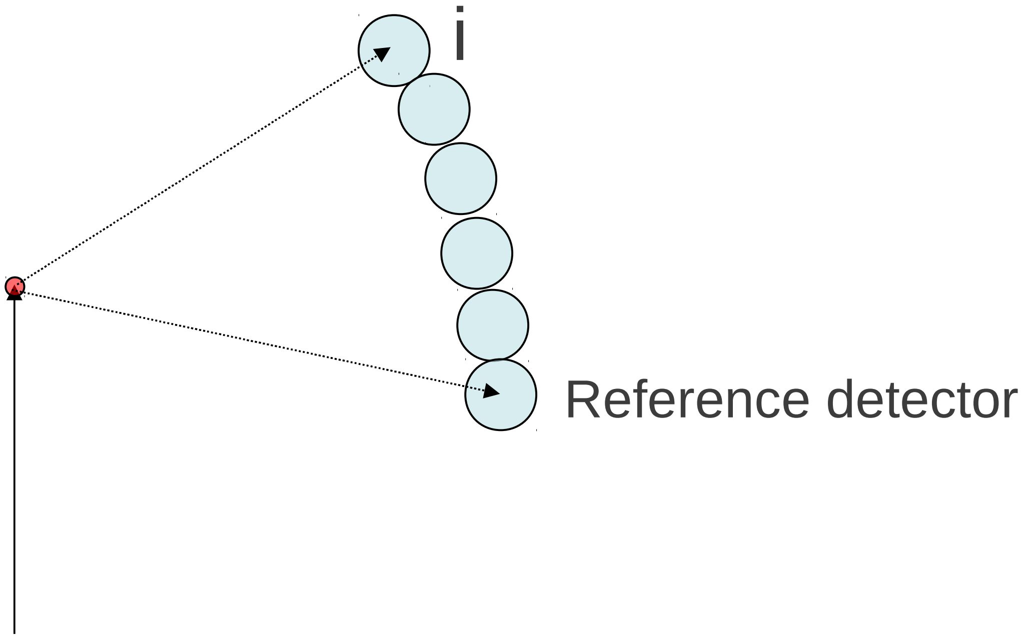
Electronically Focused Time-of-Flight Powder Diffractometers at the Intense Pulsed Neutron Source

By J. D. JORGENSEN,* J. FABER JR,* J. M. CARPENTER,~ R. K. CRAWFORD,† J. R. HAUMANN,‡ R. L. HITTERMAN,* R. KLEB,* G. E. OSTROWSKI,~ F. J. ROTELLA† AND T. G. WORLTON†

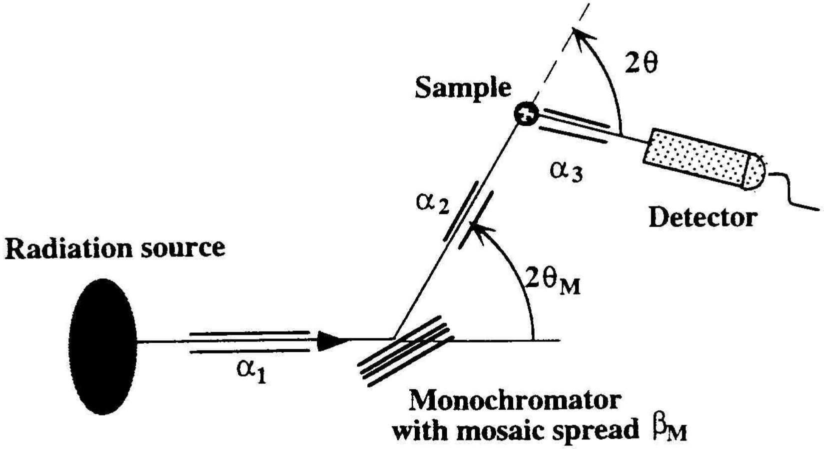
Argonne National Laboratory, Argonne, IL 60439, USA

(*Received* 5 May 1988; *accepted* 1 *March* 1989)

$$t^* = \frac{t_i(l_0 \sin\theta_0)}{(l_i \sin\theta_i)}$$



TOF resolution function

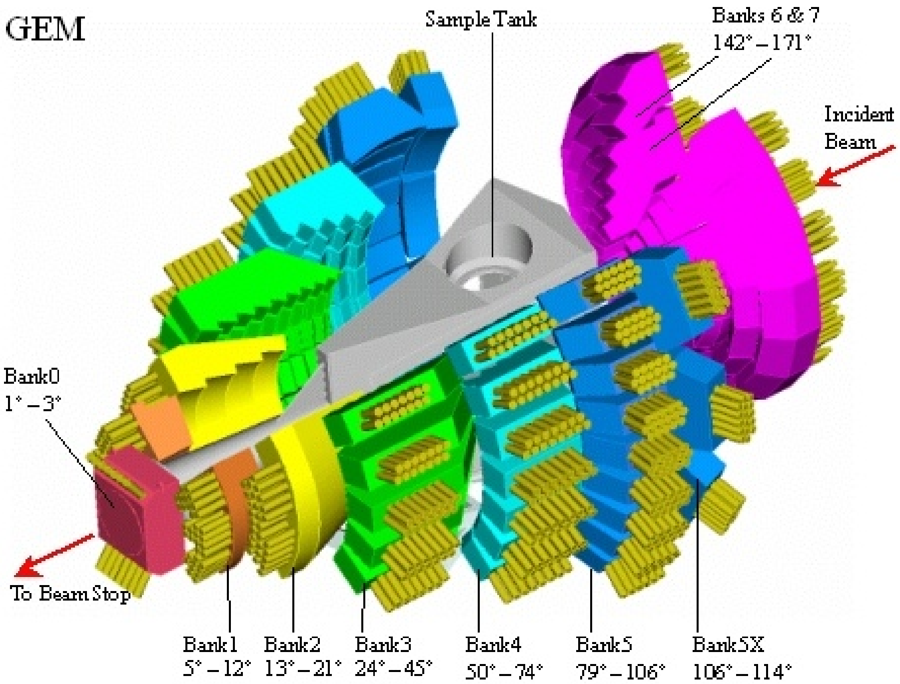


$$\frac{\Delta d}{d} = \frac{1}{2}\sqrt{W\cot^2\theta + V\cot\theta + U}$$

$$U = \frac{\alpha_1^2 + \alpha_2^2}{\tan^2\theta_M}$$

$$V = -\frac{2\alpha_2^2}{\tan\theta_M}$$

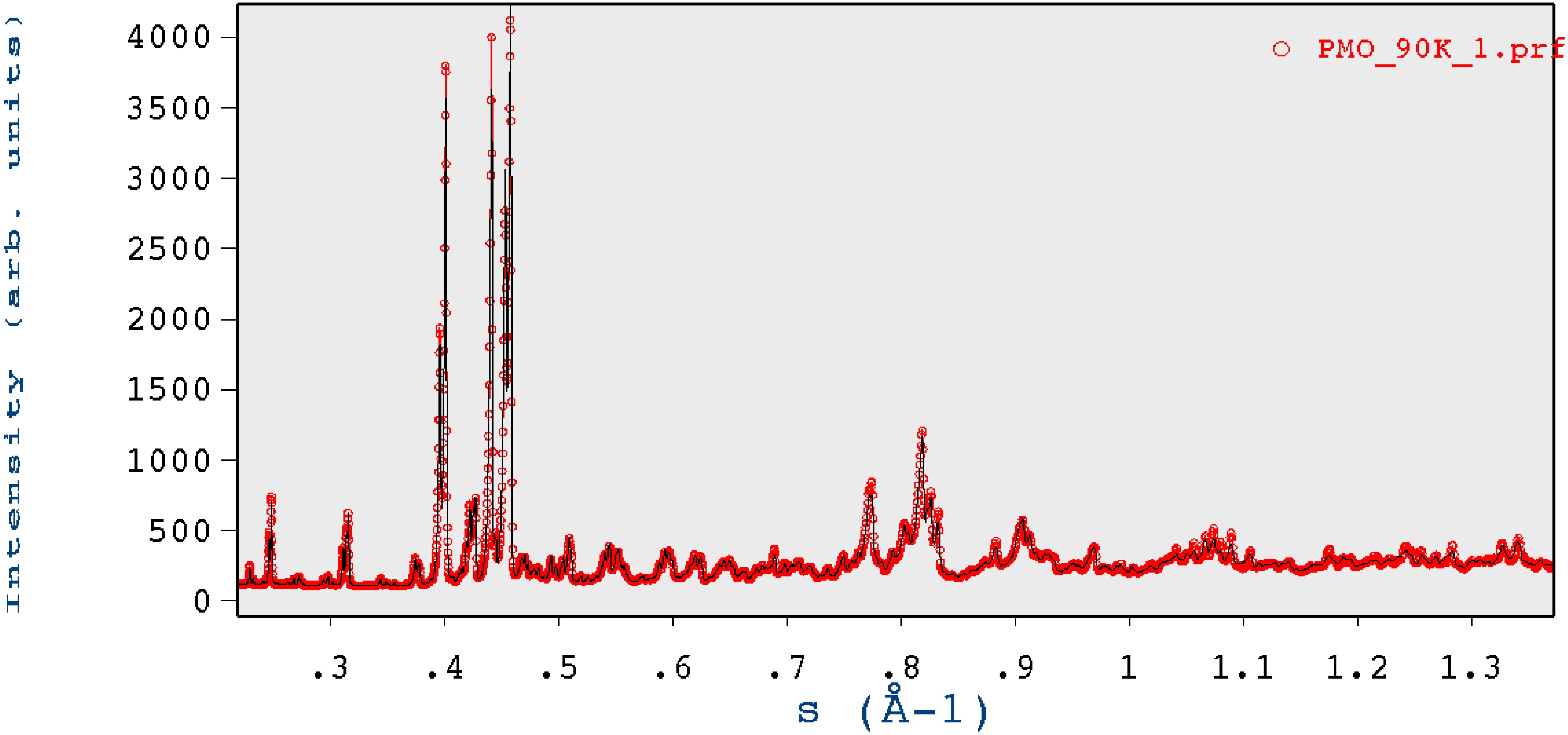
$$W = \alpha_2^2 + \alpha_3^2$$



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

Powder data: peak overlap

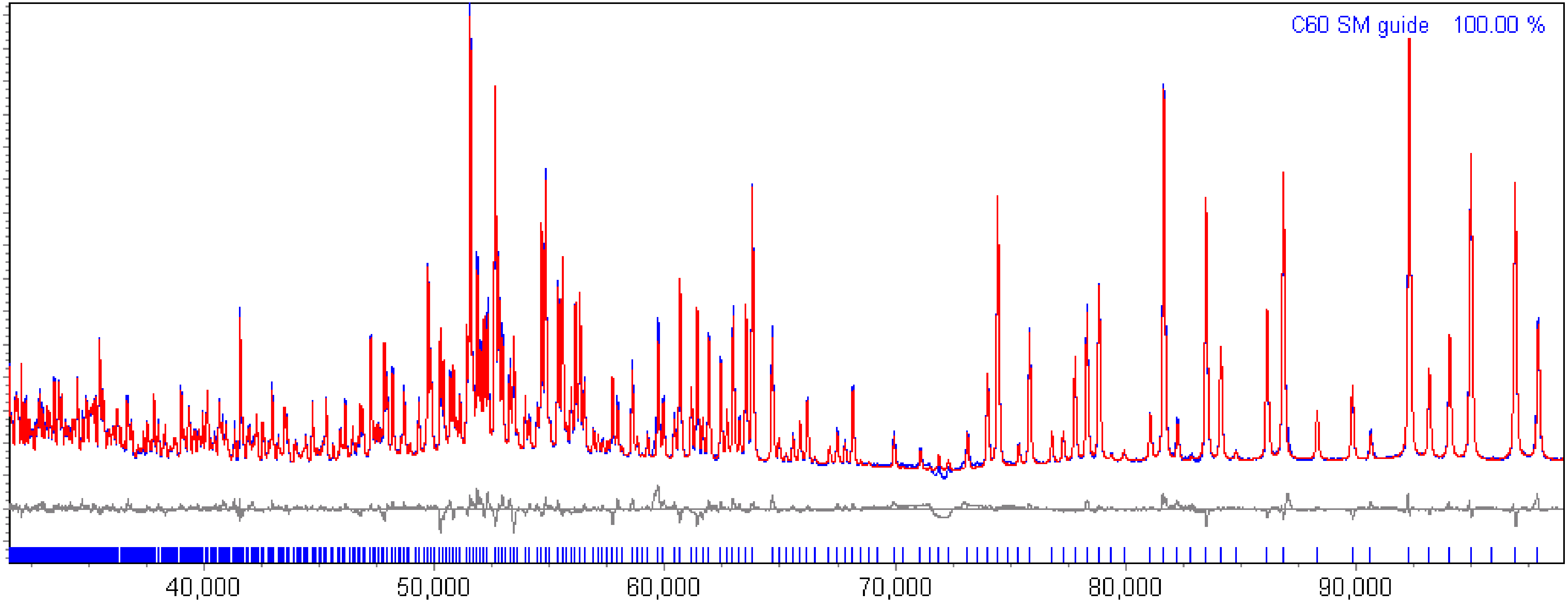
In powder data there is a substantial amount of overlap from the compression of data to 1D



High Flux Reactor of the Energy Reseach Foundation ECN in Petten, The Netherlands. (1987)

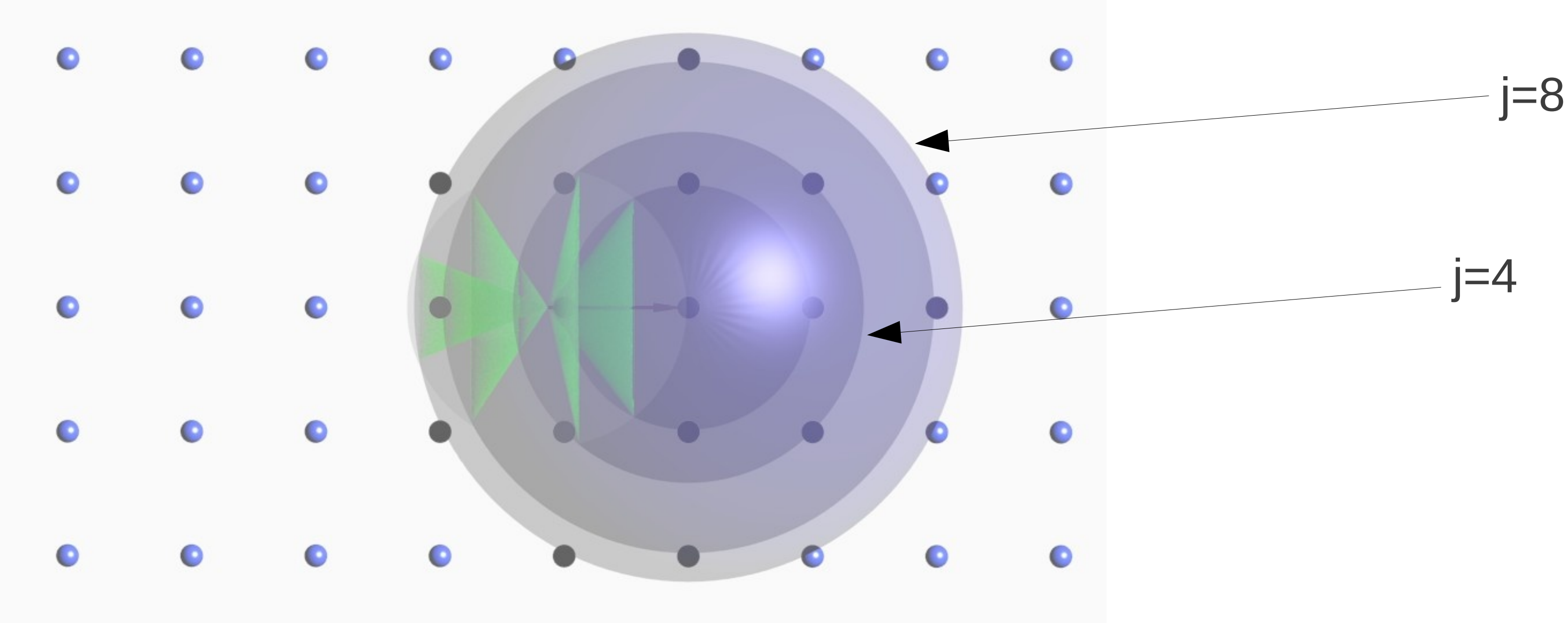
Powder diffraction: The Rietveld method

The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram." H. M. Rietveld



Powder instrument-Multiplicity

In the powder case, the data is compressed to 1 Dimension. Several equivalent Bragg peaks contribute to the intensity at the same scattering angle. To calculate the intensity, one needs to include this “multiplicity” (j)



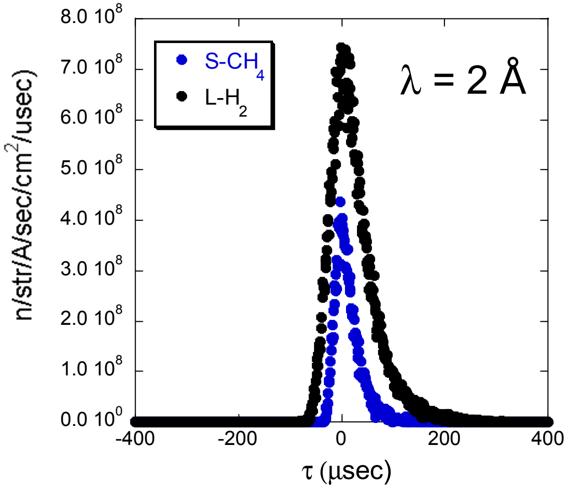
$$F(h,k,l)=\sum_{atom\ j\in UC} b_j e^{-i2\pi(h\cdot x_j+k\cdot y_j+l\cdot z_j)}\cdot e^{-B_j\frac{\sin(\theta)^2}{\lambda^2}}$$

$$I(h,k,l)\propto j|F(h,k,l)|^2$$

TOF profile function(1): Back to back exponential

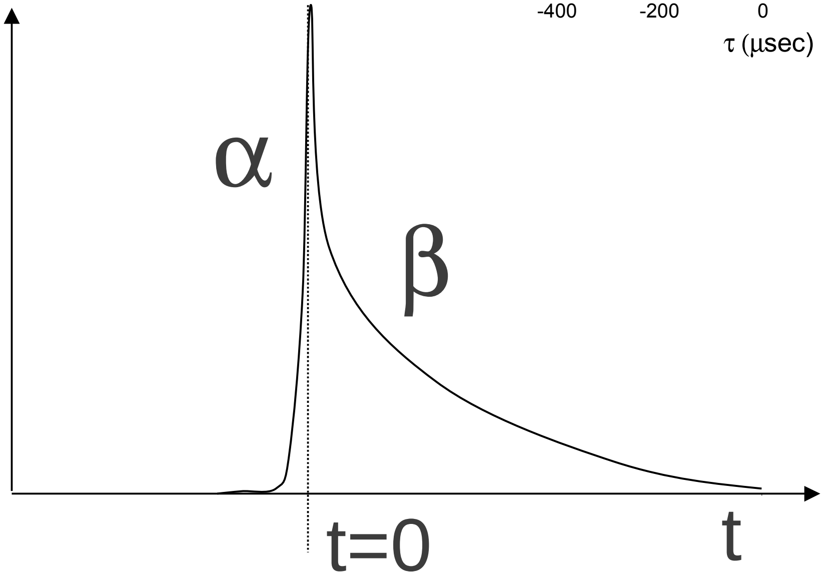
Profile functions for CW , usually Pseudo-Voigt including asymmetry

In the case of TOF, requires convolution with “pulse” function



$$\Omega(x) = pV(x) \otimes E(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt$$

$$\begin{aligned} E(t) &= 2Ne^{\alpha t} && t \le 0 \\ E(t) &= 2Ne^{-\beta t} && t > 0 \\ N &= \frac{\alpha\beta}{2(\alpha+\beta)} \end{aligned}$$



TOF profile function(2) : Ikeda-Carpenter

$$S_k(t) = \frac{\alpha^3}{2} t^2 e^{-\alpha t}$$

Slow-down spectrum

$$R_k(t) = (1 - R)\delta(t) + R\beta e^{-\beta t}$$

Mixing:
-Delta function
-Exponential decay

More complex analytic expression but often used

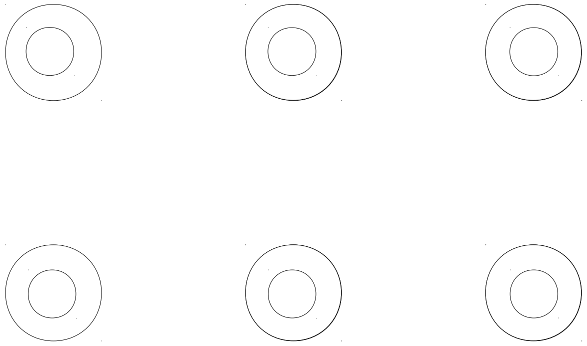
Microstructure (strain/size)

The profile function results from:

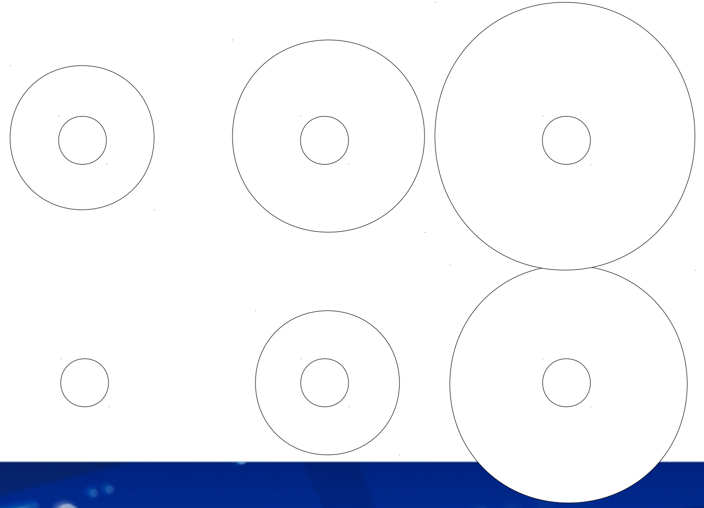
1) the specific instrumental resolution
2) broadening from microstructural effects
    - Microsize: small coherent diffracting domain (not quite crystallite size but often related)
    - Microstrain: crystal lattice distortion with a coherent domain due to dislocations

The two later effects have different Q dependences an usually can be separated.

Size effects: ΔQ=cste



Strain effects: $\Delta Q/Q$=cste

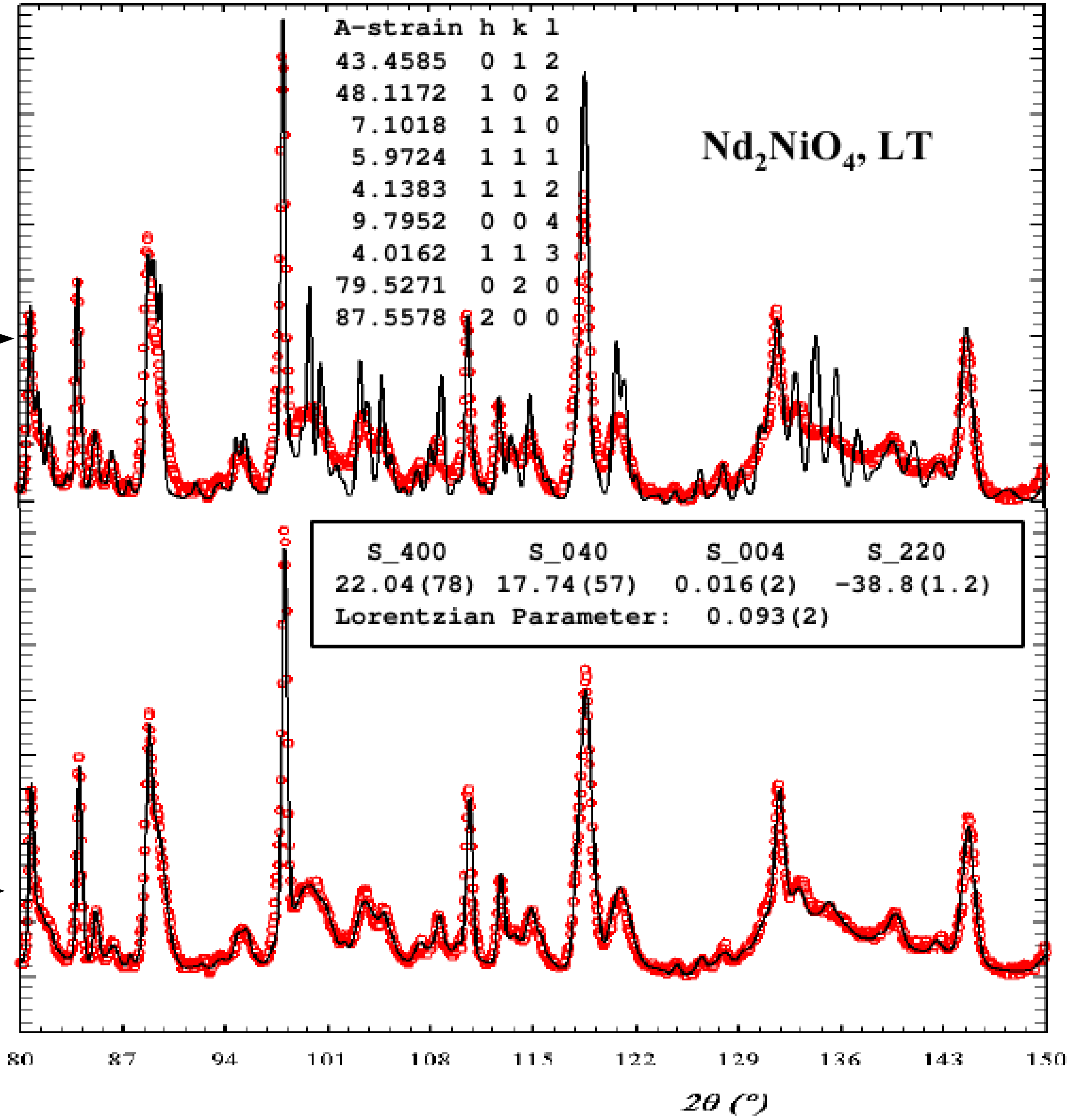


Microstructure (example)

Example of anisotropic strain (given in FullProf Manual)

Instrumental resolution function

Refinement with anisotropic strain to model the peak-shape function



A-strain	h	k	l
43.4585	0	1	2
48.1172	1	0	2
7.1018	1	1	0
5.9724	1	1	1
4.1383	1	1	2
9.7952	0	0	4
4.0162	1	1	3
79.5271	0	2	0
87.5578	2	0	0

S_400	S_040	S_004	S_220
22.04(78)	17.74(57)	0.016(2)	-38.8(1.2)

Lorentzian Parameter: 0.093(2)