# Elastic scattering from atomic aggregates Part 2

➢ Atomic aggregates
➢ Debye formula
➢ X-ray scattering from non-crystalline materials
➢ X-ray scattering from crystals
  ➢ Diffraction conditions
  ➢ Experimental methods
  ➢ The structure factor
  ➢ The phase problem
  ➢ Thermal effects
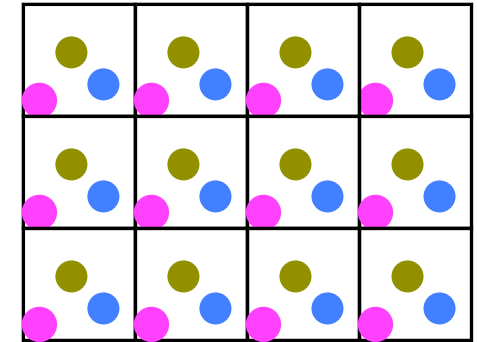➢ Synchrotron Radiation and diffraction
➢ Neutron scattering

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April 2017
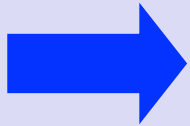
# X-ray scattering from crystals
## Diffraction conditions

# Scattering from crystals: amplitude

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$$\vec{R}_{m\alpha} = \vec{R}_m + \vec{R}_\alpha$$

$m,n$ = cell indices

$\alpha, \beta$ = atomic indices

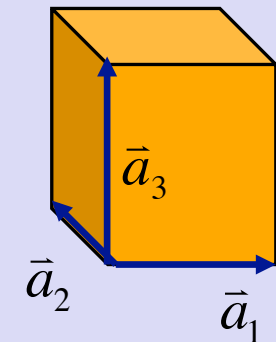$$A_{e.u.}\left(\vec{K}\right) = \sum_{m\alpha} f_\alpha \, e^{i\vec{K}\cdot\vec{R}_{m,\alpha}}$$

$$= \sum_m e^{i\vec{K}\cdot\vec{R}_m} \sum_\alpha f_\alpha \, e^{i\vec{K}\cdot\vec{R}_\alpha}$$
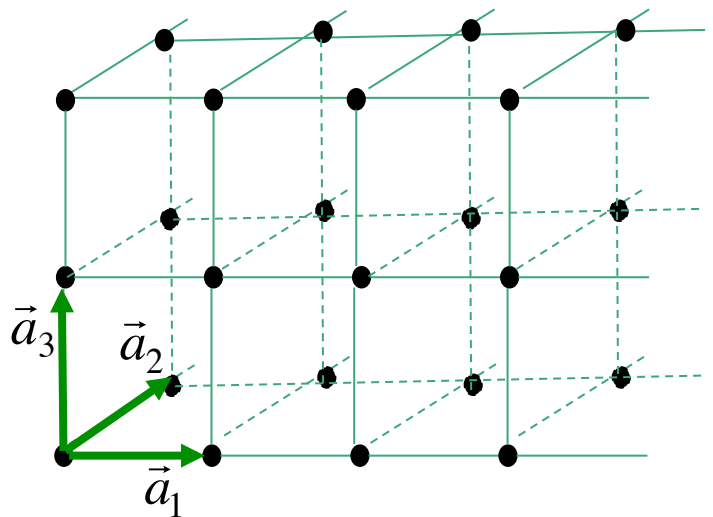
Sum over lattice points

Sum over atoms in cell

$$F\left(\vec{K}\right) = \sum_\alpha f_\alpha \, e^{i\vec{K}\cdot\vec{R}_\alpha} \quad \text{Structure factor}$$

$\vec{a}_3$

$\vec{a}_2$

$\vec{a}_1$

# Sum over lattice points

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$$\vec{R}_m = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3$$

$$\sum_m e^{i\vec{K}\cdot\vec{R}_m} = \sum_{m_1 m_2 m_3} e^{i\vec{K}\cdot\left(m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3\right)}$$

$$= \sum_{m_1=0}^{N_1-1} e^{im_1\vec{K}\cdot\vec{a}_1} \times \sum_{m_2=0}^{N_2-1} e^{im_2\vec{K}\cdot\vec{a}_2} \times \sum_{m_3=0}^{N_3-1} e^{im_3\vec{K}\cdot\vec{a}_3}$$

$$\sum_{k=0}^{n-1} a^k = a^0 + a^1 + \cdots + a^{n-1} = \frac{a^n - 1}{a - 1}$$

geometric progression

$$\frac{e^{iN_1\vec{K}\cdot\vec{a}_1} - 1}{e^{i\vec{K}\cdot\vec{a}_1} - 1}$$

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$$\left(\sum_m e^{i\vec{K}\cdot\vec{R}_m}\right)\left(\sum_n e^{-i\vec{K}\cdot\vec{R}_n}\right) = \left(\sum_{m_1=0}^{N_1-1} e^{im_1\vec{K}\cdot\vec{a}_1}\right)\left(\sum_{n_1=0}^{N_1-1} e^{-in_1\vec{K}\cdot\vec{a}_1}\right) \times \cdots \times \cdots$$

$$= \left(\frac{e^{iN_1\vec{K}\cdot\vec{a}_1}-1}{e^{i\vec{K}\cdot\vec{a}_1}-1}\right)\left(\frac{e^{-iN_1\vec{K}\cdot\vec{a}_1}-1}{e^{-i\vec{K}\cdot\vec{a}_1}-1}\right) \times \cdots \times \cdots$$

$$= \frac{\sin^2\left(N_1\vec{K}\cdot\vec{a}_1/2\right)}{\sin^2\left(\vec{K}\cdot\vec{a}_1/2\right)} \times \cdots \times \cdots$$

$$e^{ix} = \cos x + i\sin x$$
$$e^{-ix} = \cos x - i\sin x$$
$$\sin^2\frac{x}{2} = \frac{1-\cos x}{2}$$

# Laue interference function (1-dim)

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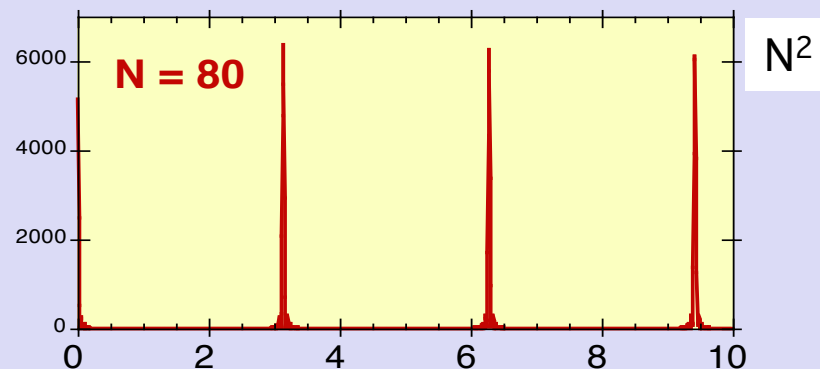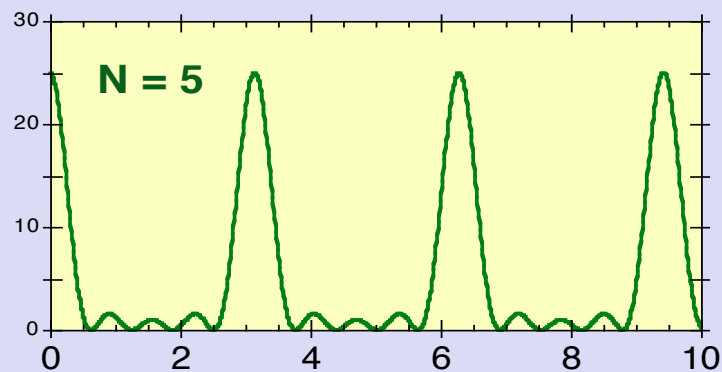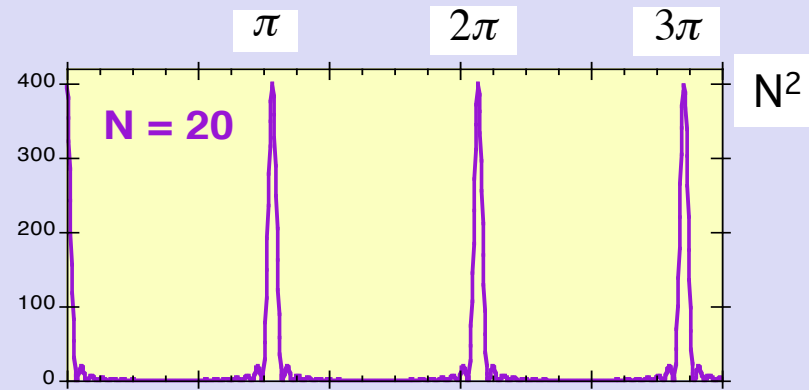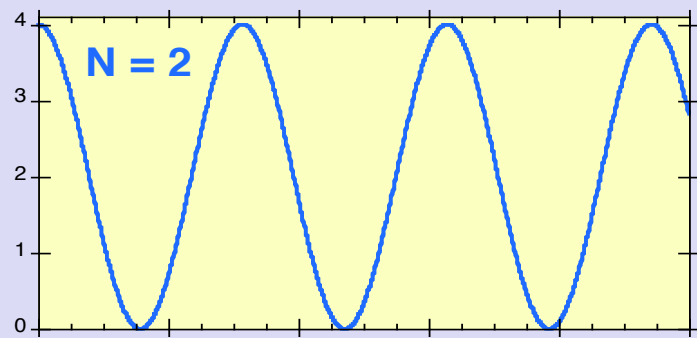Univ. Trento

$$\frac{\sin^2\left(N_1 \vec{K} \cdot \vec{a}_1 / 2\right)}{\sin^2\left(\vec{K} \cdot \vec{a}_1 / 2\right)}$$

Maxima for

$$\vec{K} \cdot \vec{a}_1 / 2 = n\pi$$

Info on $a_1$



$N = 2$

$N = 5$

$\vec{K} \cdot \vec{a}_1 / 2$

$N = 20$

$N^2$

$\pi$  $2\pi$  $3\pi$

$N = 80$

$N^2$

$\vec{K} \cdot \vec{a}_1 / 2$

$N \approx 10^{23}$

sharp peaks

# Scattering from crystals: intensity

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$$I_{e.u.}\left(\vec{K}\right) = \sum_{mn} e^{i\vec{K}\cdot\vec{R}_{mn}} \sum_{\alpha\beta} f_\alpha f_\beta \, e^{i\vec{K}\cdot\vec{R}_{\alpha\beta}}$$
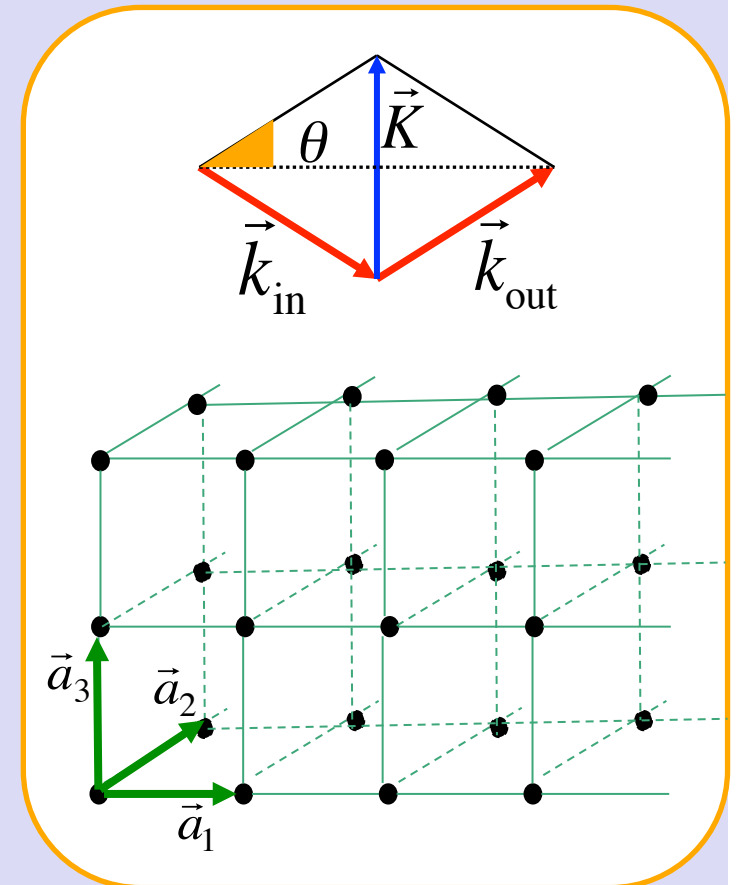
$$\vec{R}_{mn} = \vec{R}_m - \vec{R}_n$$

$$\vec{R}_{\alpha\beta} = \vec{R}_\alpha - \vec{R}_\beta$$

$$= \prod_{i=1}^{3} \frac{\sin^2\left(N_i \vec{K}\cdot\vec{a}_i/2\right)}{\sin^2\left(\vec{K}\cdot\vec{a}_i/2\right)} \qquad \left|F\left(\vec{K}\right)\right|^2$$

Laue interference function

Structure factor

# Interference conditions (3-dim)

$$I_{\text{e.u.}}\left(\vec{K}\right)=\prod_{i=1}^{3}\frac{\sin^2\left(N_i\vec{K}\cdot\vec{a}_i/2\right)}{\sin^2\left(\vec{K}\cdot\vec{a}_i/2\right)}\left|F\left(\vec{K}\right)\right|^2$$

$N^2$ if

$0$ otherwise

### Laue conditions

$$\left.\begin{cases}\vec{K}\cdot\vec{a}_1=2\pi h\\[4pt]\vec{K}\cdot\vec{a}_2=2\pi k\\[4pt]\vec{K}\cdot\vec{a}_3=2\pi l\end{cases}\right\}\quad (h,k,l \text{ integers})$$

to be simultaneously fulfilled

### Ewald condition

$$\vec{K}=\vec{G}$$

↑

Reciprocal
lattice vector

### Bragg condition

$$2d_{hkl}\sin\theta=n\lambda$$

↑

Inter-planar
spacing

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The scattered amplitude of a lattice is the FT of the lattice function

$$A_{\text{e.u.}}(\vec{K}) \;=\; \mathcal{F}[L(\vec{r})] \;=\; \sum_{\vec{T}} e^{i\vec{K}\cdot\vec{T}}$$

For an infinite crystal, the FT of the lattice function is a lattice in reciprocal space

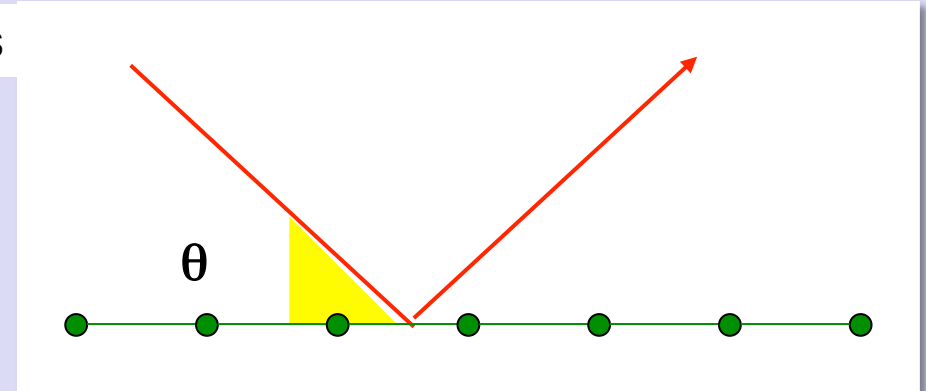$$\mathcal{F}[L(\vec{r})] \;=\; \frac{1}{V} \sum_{\vec{G}} \delta(\vec{K} - \vec{G})$$

$$\vec{K} = \vec{G}$$

$$\left.\begin{array}{rl}
\vec{K} \cdot \vec{a}_1 = & 2\pi\,h \\
\vec{K} \cdot \vec{a}_2 = & 2\pi\,k \\
\vec{K} \cdot \vec{a}_3 = & 2\pi\,\ell
\end{array}\right\} \quad (h, k, \ell \ \text{integer})$$

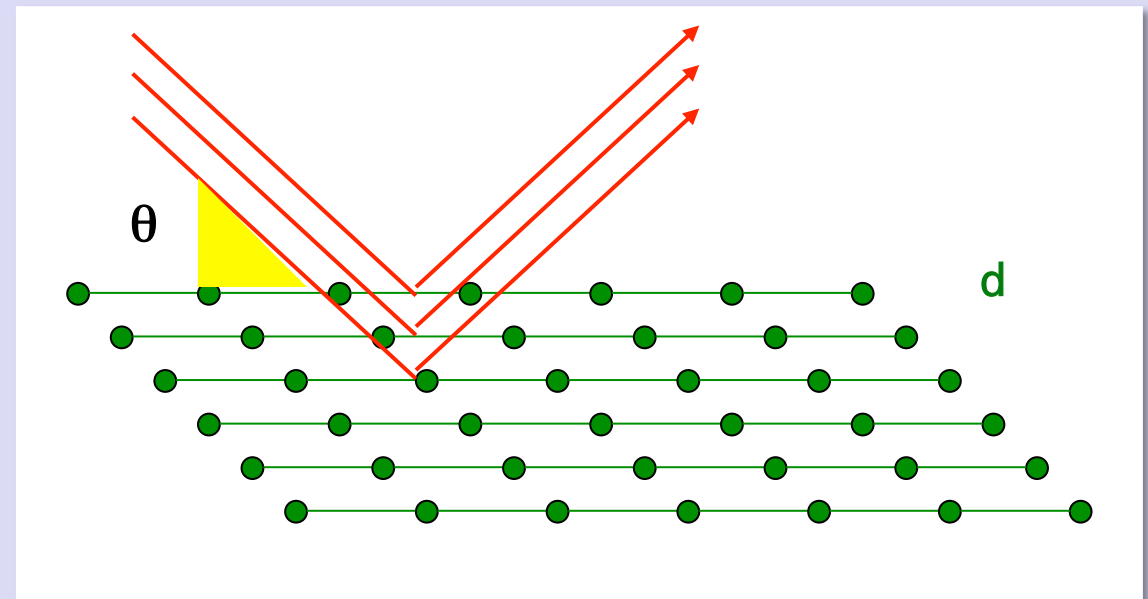"Reflection" from a plane of atoms

$\theta$

Interference between x-rays
reflected by parallel planes
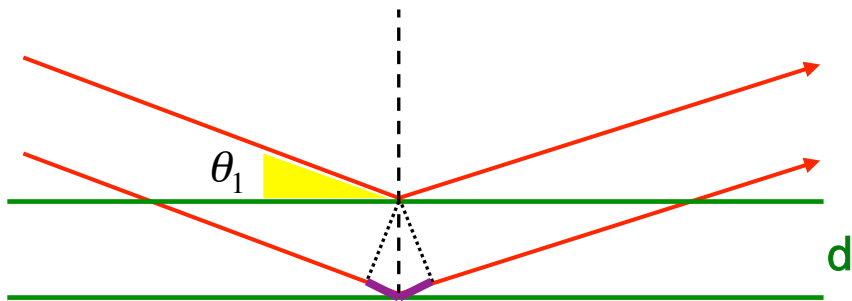
**Bragg law**

$$2\,d_{hkl}\,\sin\theta = n\,\lambda$$

Incidence angle $\Leftrightarrow$ distance $d$

$\theta$

d

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$$2\,d_{hkl}\,\sin\theta = n\,\lambda$$

fixed



$2d\sin\theta_1 = \lambda$

$n = 1$

*h k l*



$2d\sin\theta_2 = 2\lambda$

$n = 2$

*2h 2k 2l*

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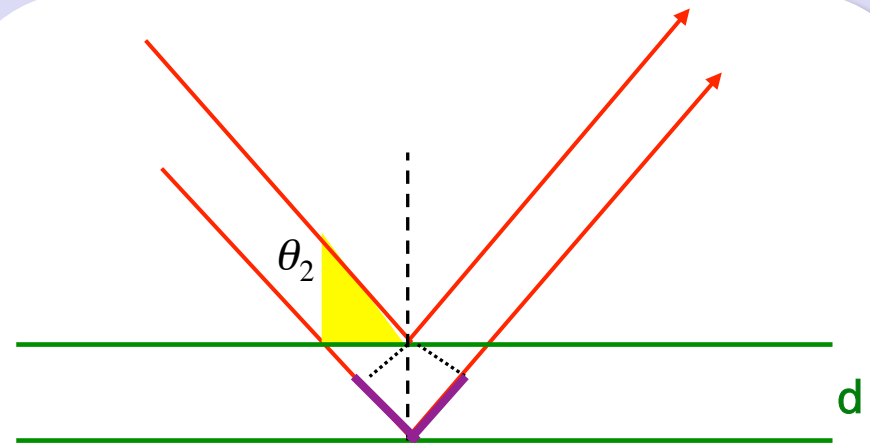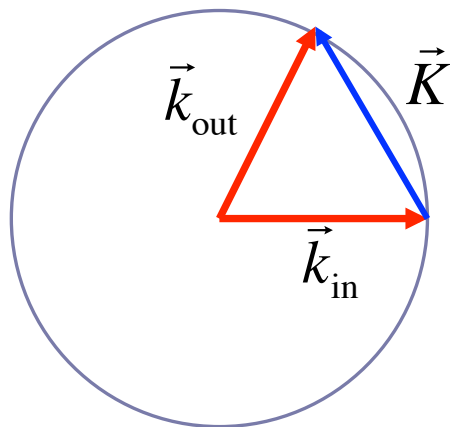
(2-dimensional projection)

Ewald sphere

Radius: $\quad k_{in} = \dfrac{2\pi}{\lambda}$

Center: origin of $\vec{k}_{in}$

+

Reciprocal lattice

$\vec{k}_{out}$ $\quad \vec{K}$

$\vec{k}_{in}$

$\vec{G}$
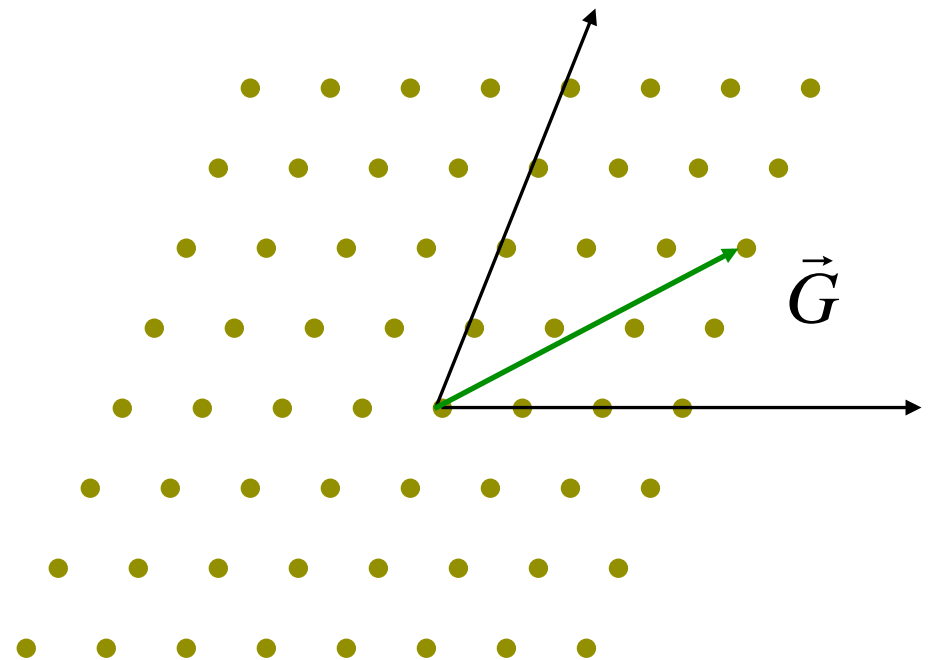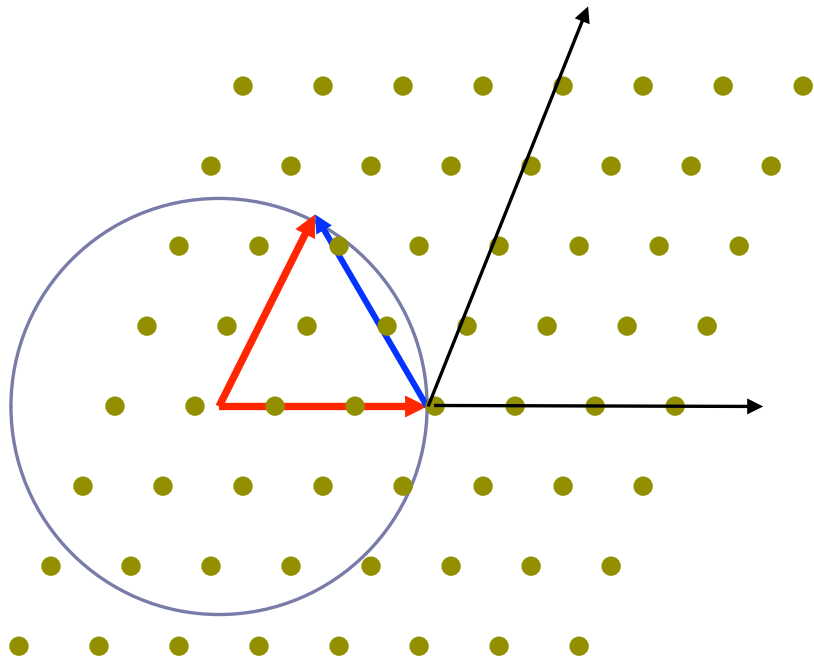
# The Ewald condition

(2-dimensional projection)



End of $k_0$ vector = origin of reciprocal space

Interference condition:

$$\vec{K} = \vec{G}$$

Scattering vector = reciprocal lattice vector

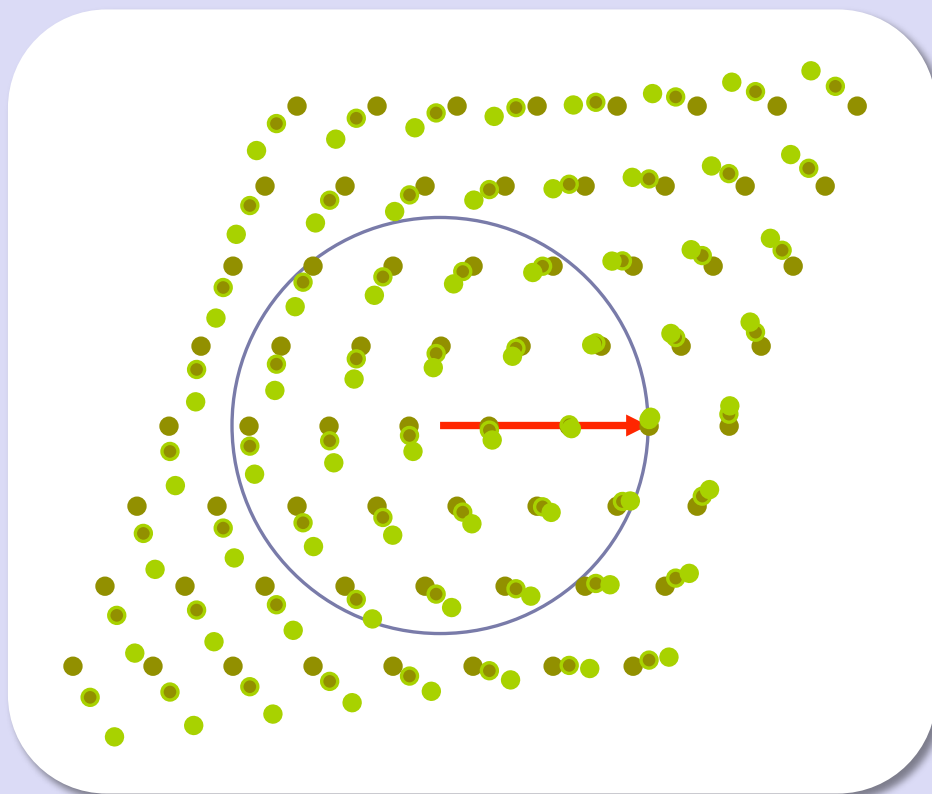The condition is very difficult to fulfill even for one reflection

while

A large number of reflections is sought for structure determination
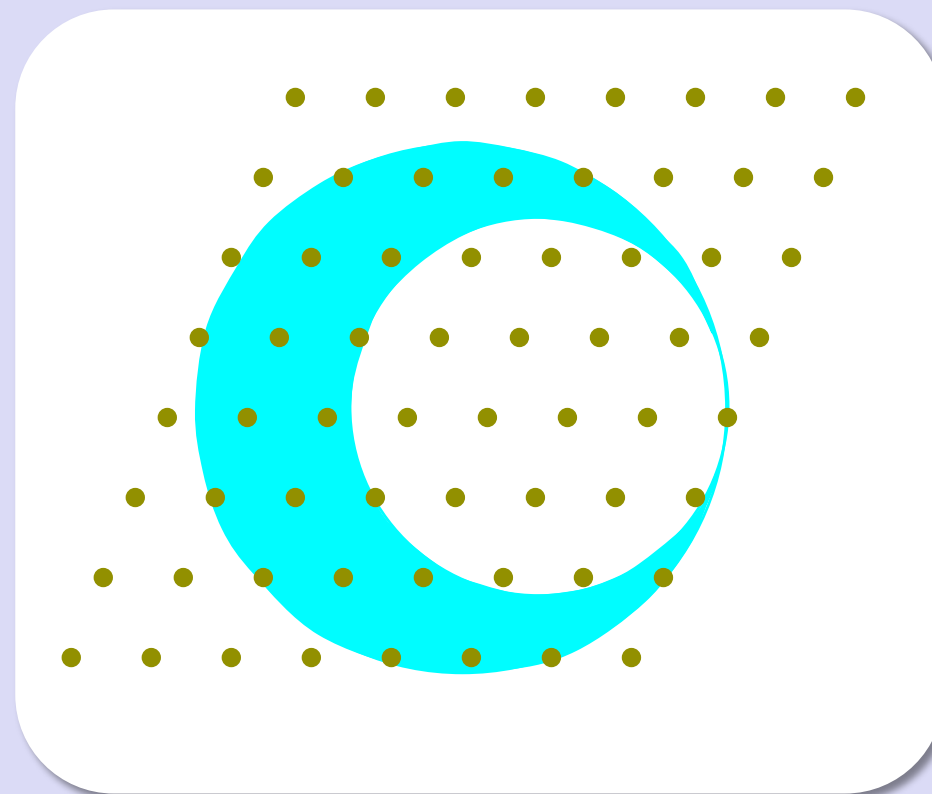
Various solutions

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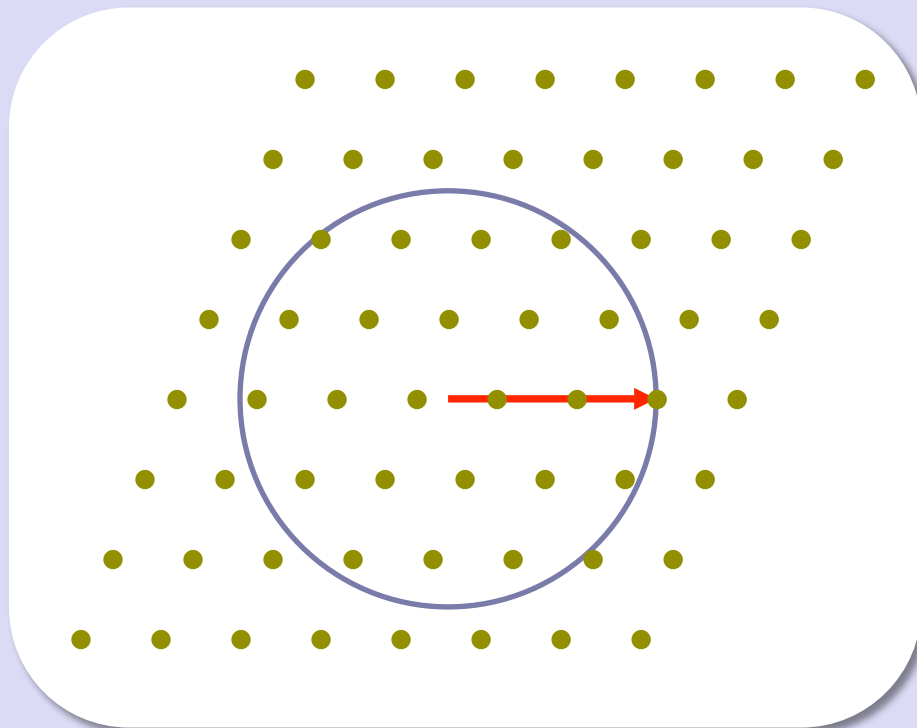
Single crystal
Monochromatic radiation

Single crystal
Polychromatic radiation



The crystal orientation is varied
4-circles diffractometer
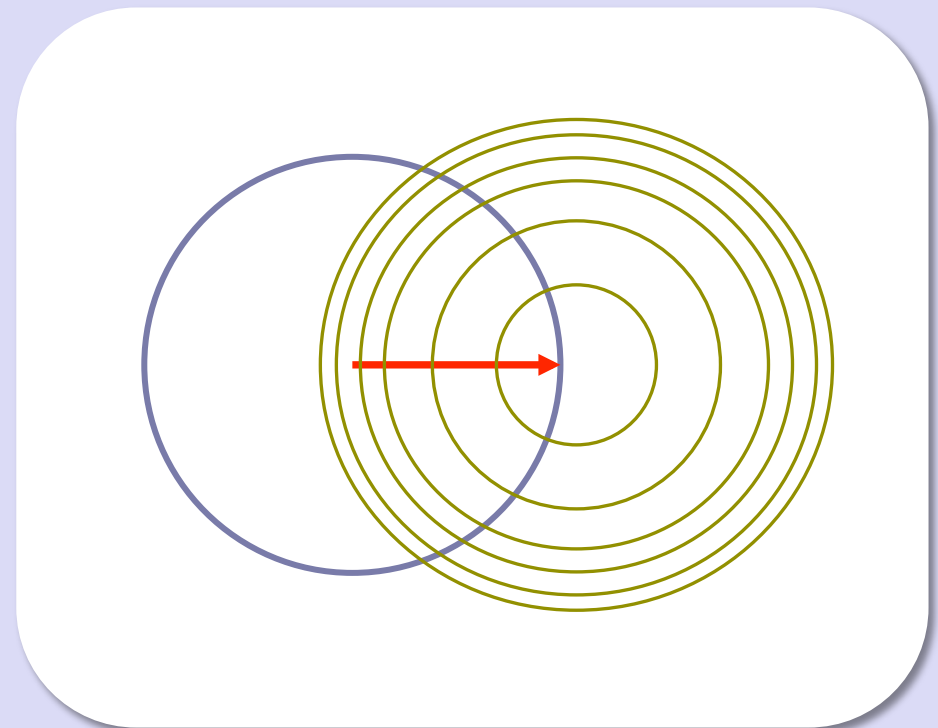
Laue set-up

Ewald: powders

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Single crystal
Monochromatic radiation

Powders
Monochromatic radiation

Many single crystals randomly oriented

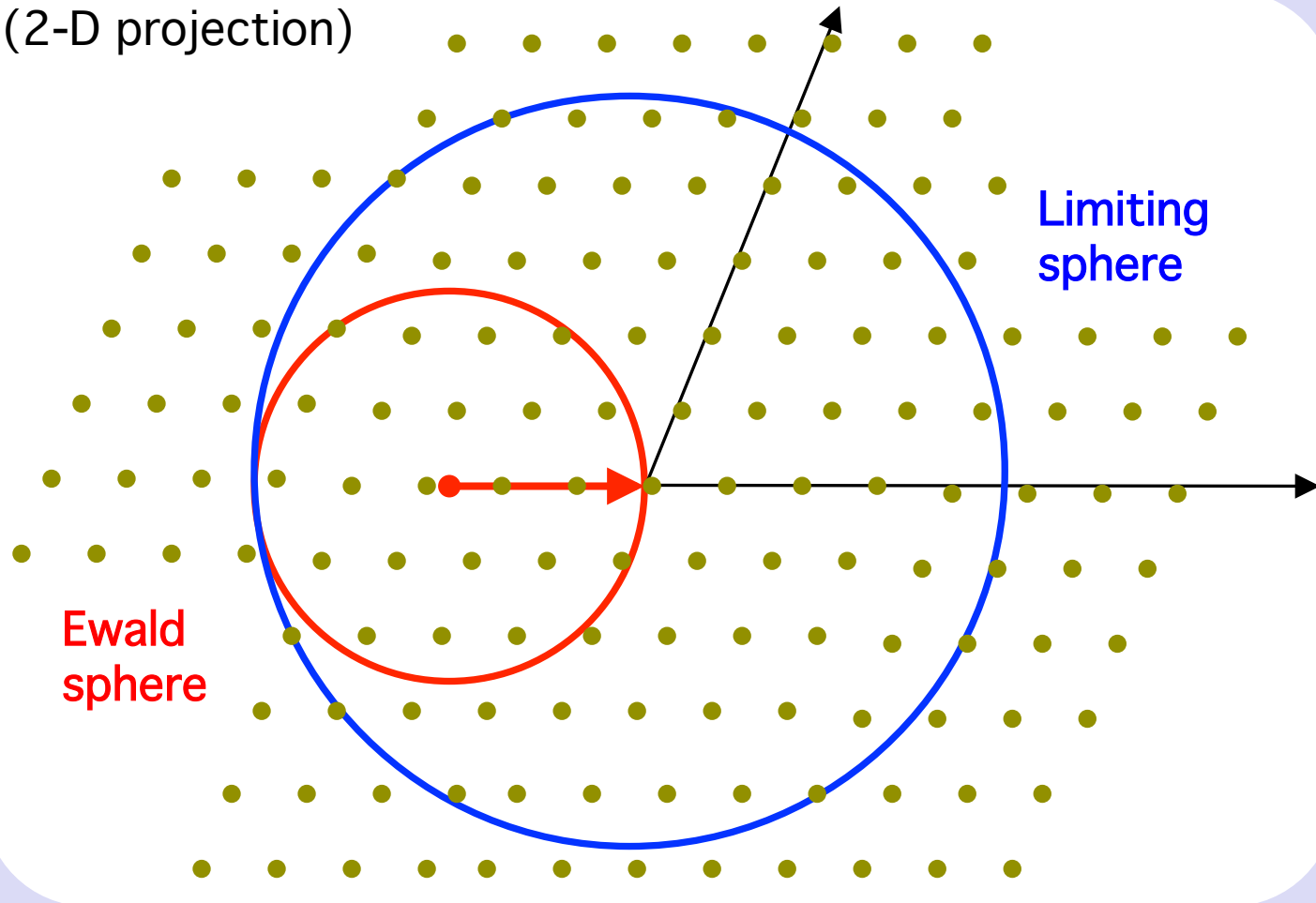# Powder diffraction rinciple

Monochromatic input beam

Randomly
oriented
powders
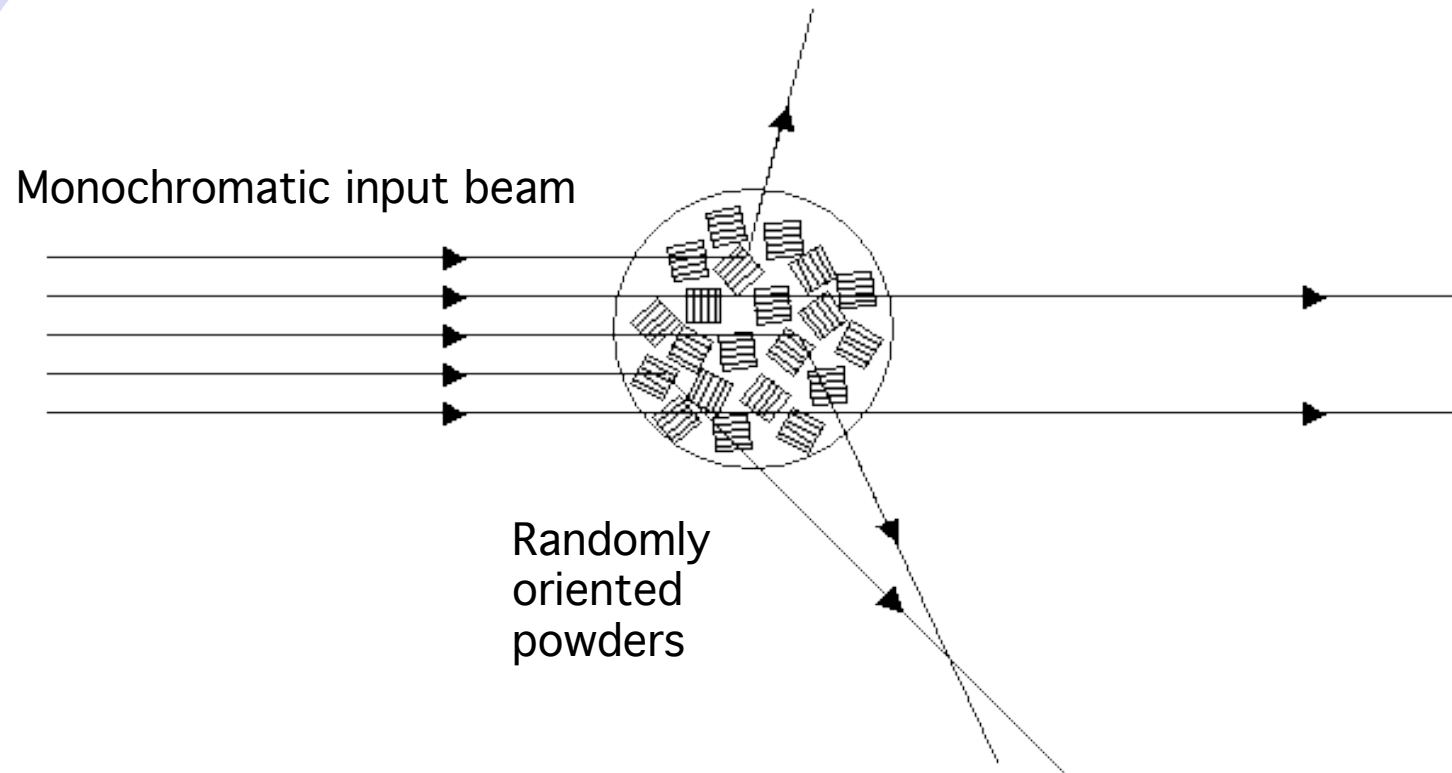
$$\lambda = 2d \sin \theta$$

# Ewald sphere and limiting sphere

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(2-D projection)



Limiting sphere

Ewald sphere

$$\vec{K} = \vec{G}$$

fulfilled only if

$$\vec{G} \in \text{ limiting sphere}$$

$$\lambda = \frac{2\pi}{k_{\text{in}}} \;\Rightarrow\; G_{\text{max}} = 2k_{\text{in}} = \frac{4\pi}{\lambda} \;\Rightarrow\; d_{\text{min}} = \frac{2\pi}{G_{\text{max}}} = \frac{\lambda}{2}$$

Further limitation:
K-dependent
atomic scattering factor

# X-ray scattering from crystals
## Experimental methods

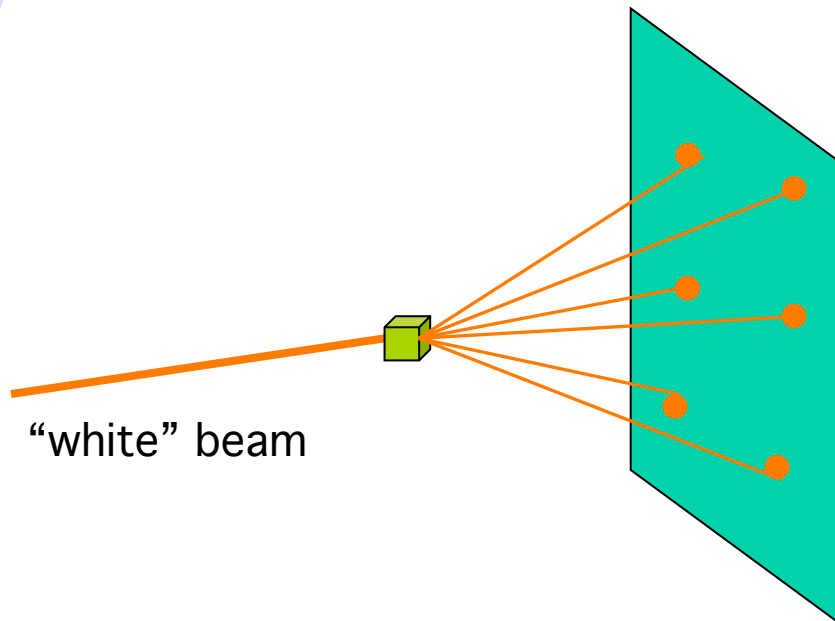## 4-circles diffractometer

The sample orientation is varied
with respect to the incident radiation
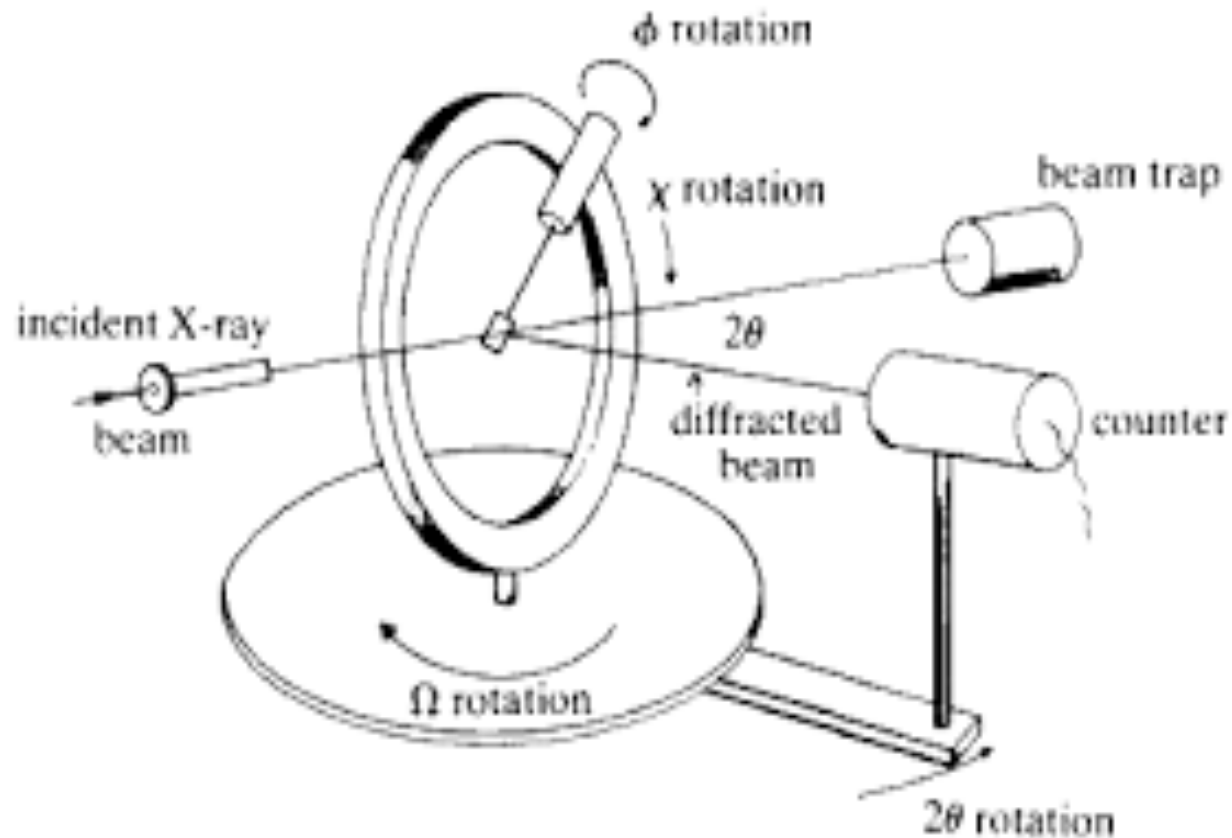
# "White-beam" single crystal diffraction



"white" beam

Forward scattering
or
backward scattering
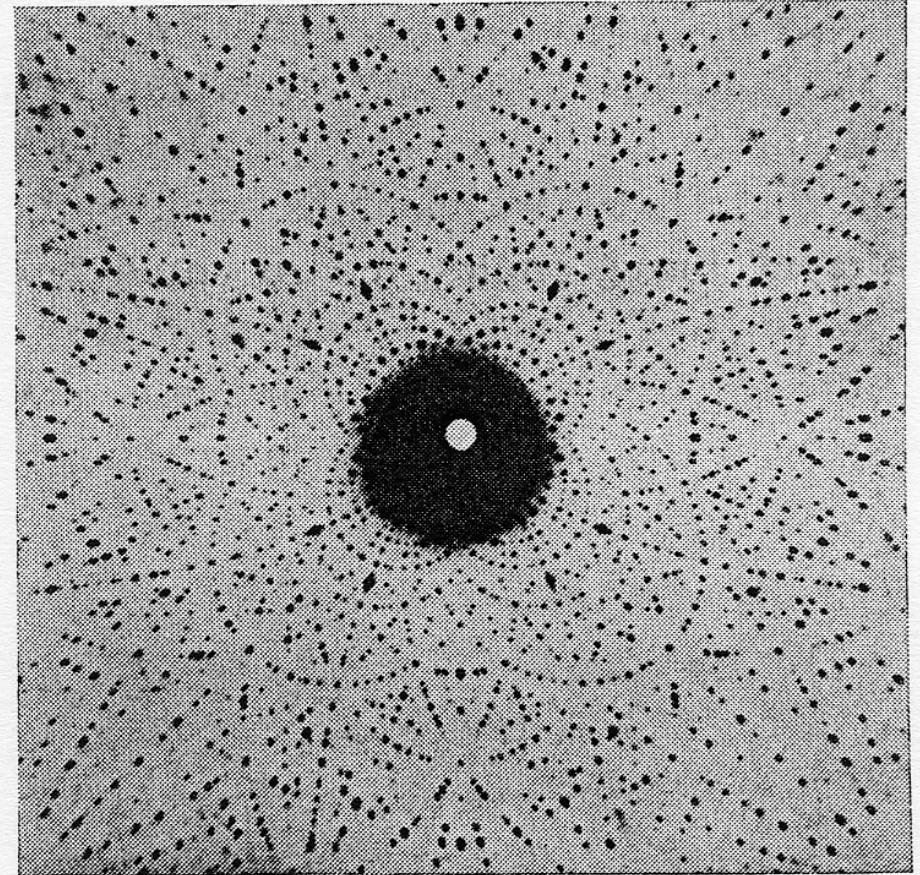
Laue photograph of a complex silicate

$\theta - \theta$

Bragg-Brentano geometry



$\theta - 2\theta$

Germanium

Intensity (arb. u.)

2θ (deg)

OK for amorphous materials too

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## Debye-Scherrer camera



Film

Powder sample





Germanium

Intensity (arb. u.)

2θ (deg)

OK for amorphous materials too

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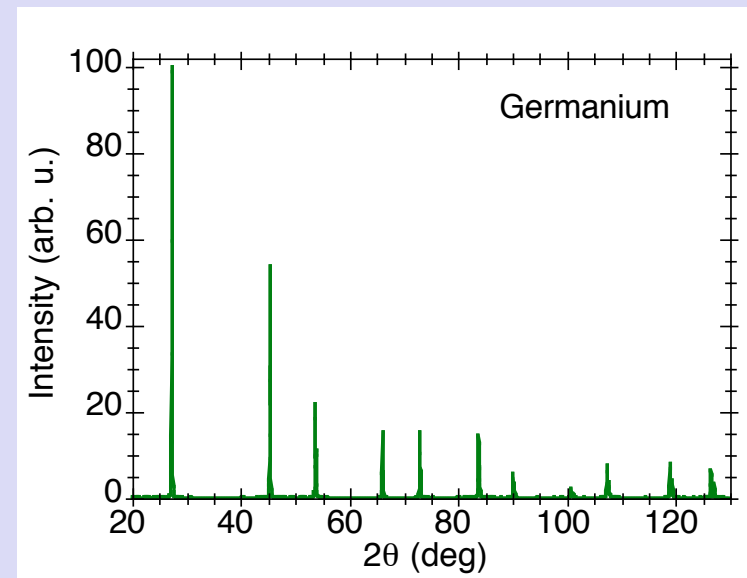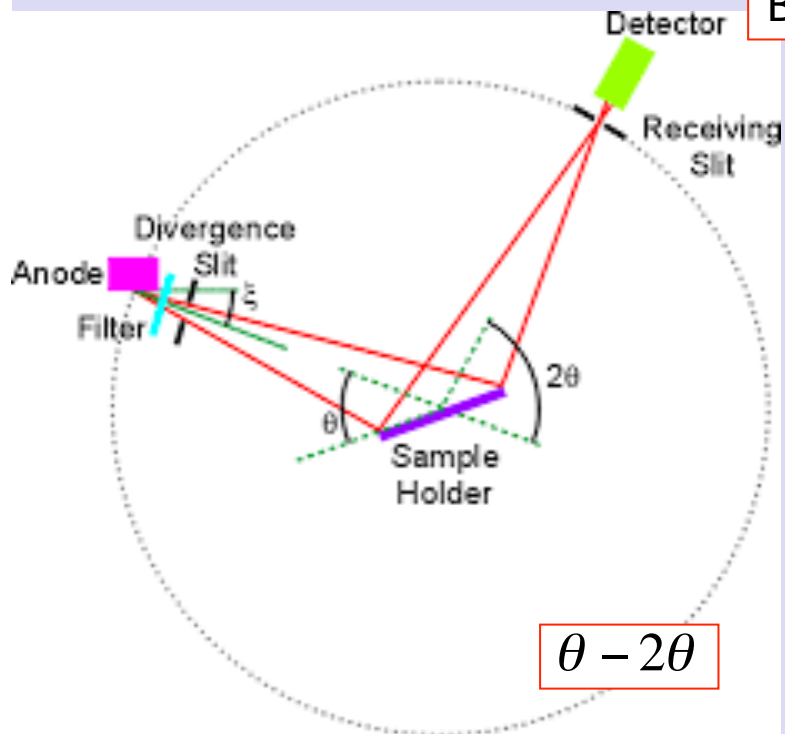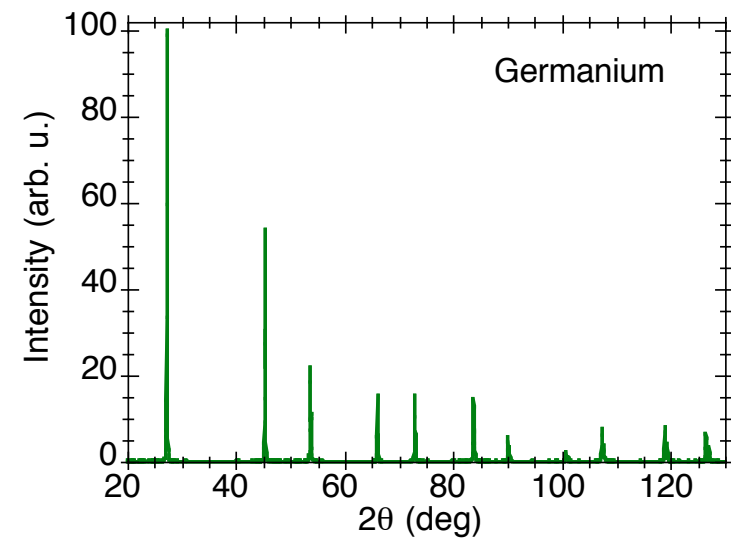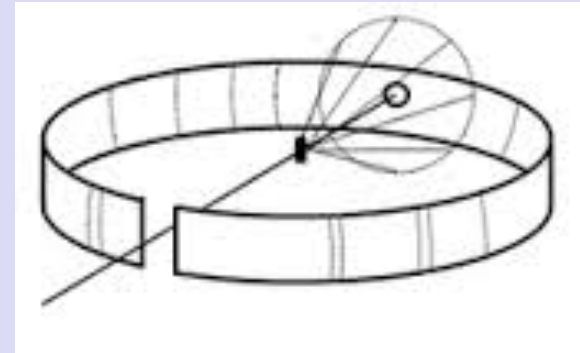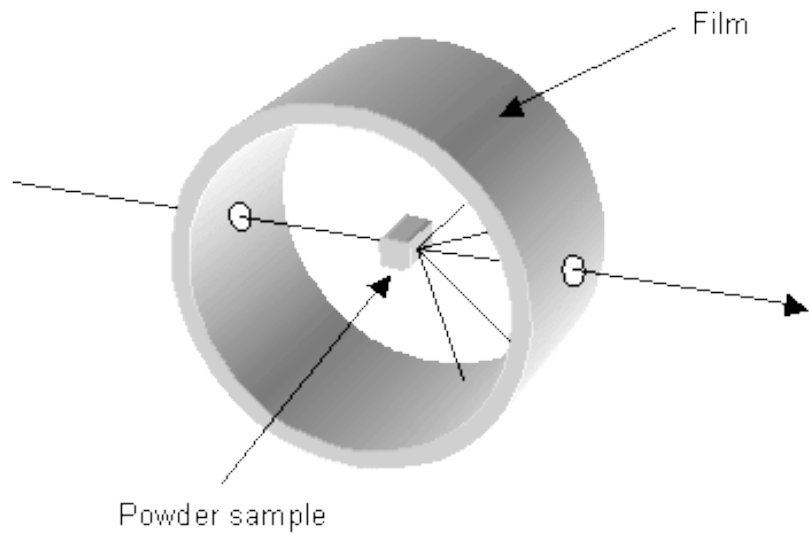


Debye-Scherrer method
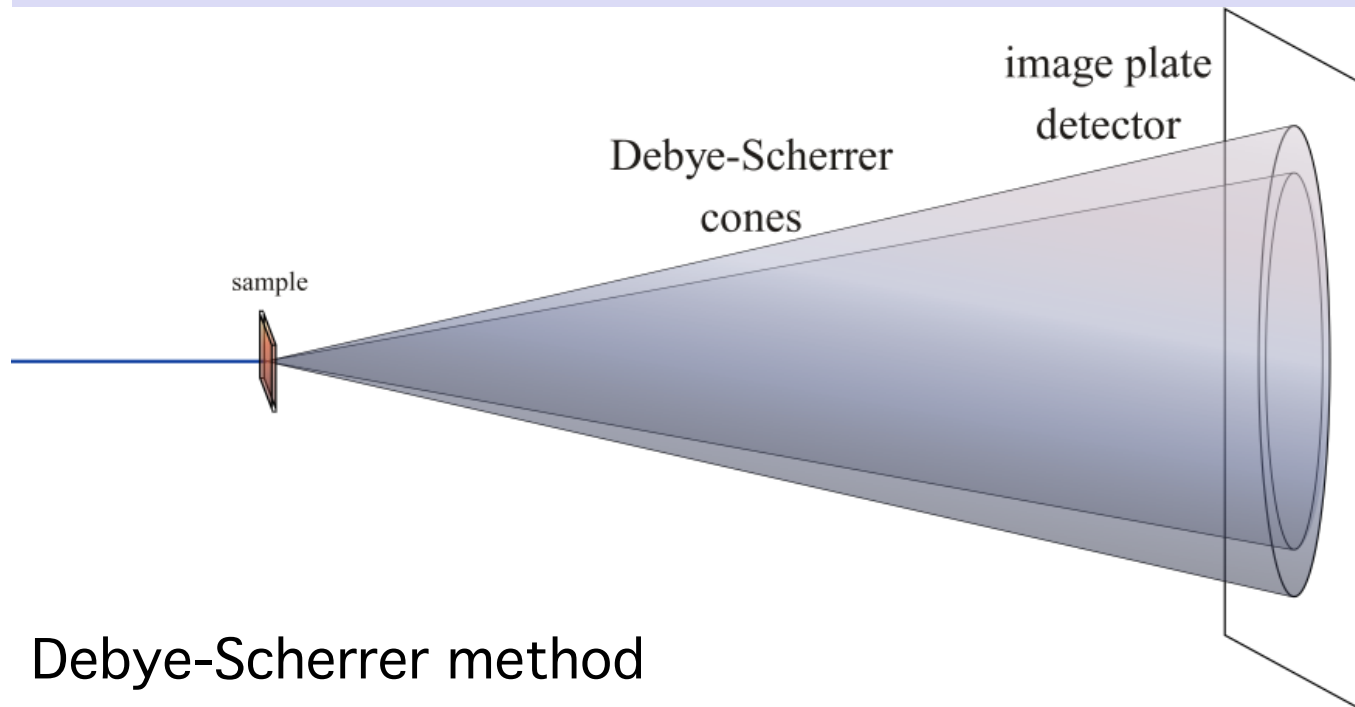
# Laboratory powder diffraction

Cu anode

$K_{\alpha 1} = K\_L_3 = 1.54056$ Å
$K_{\alpha 2} = K\text{-}L_2 = 1.54439$ Å

$K_\beta = K\text{-}M_3 = 1.3922$ Å

ln(I)
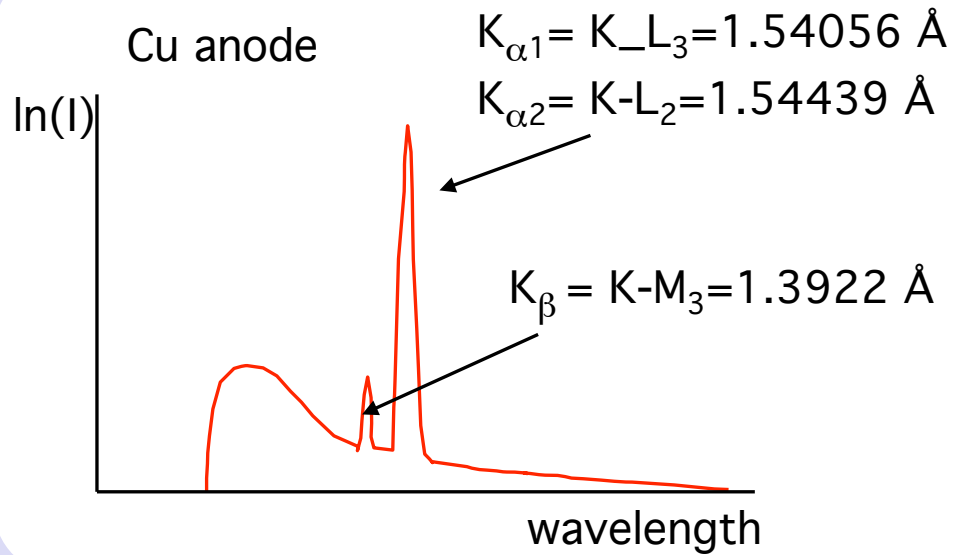
wavelength

$$\lambda_0 = 2d \sin\theta$$

$K_\beta$ filtered

$K_{\alpha 1}$ $K_{\alpha 2}$ both present

$\vartheta$ $2\vartheta$

Germanium

Intensity (arb. u.)

2θ (deg)

AlPO$_4$-40
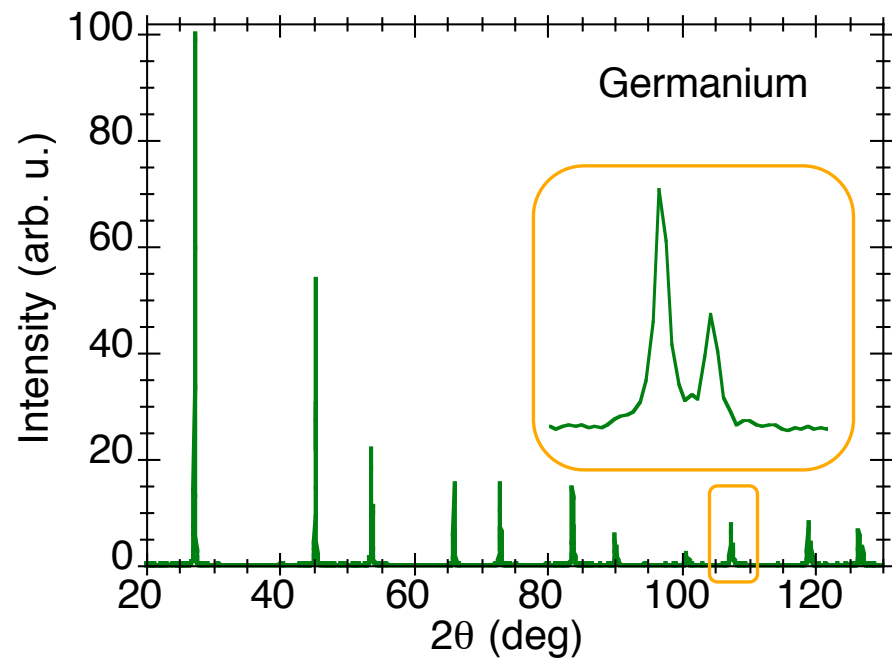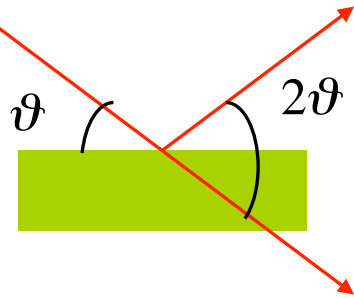
# Powder diffraction detection methods
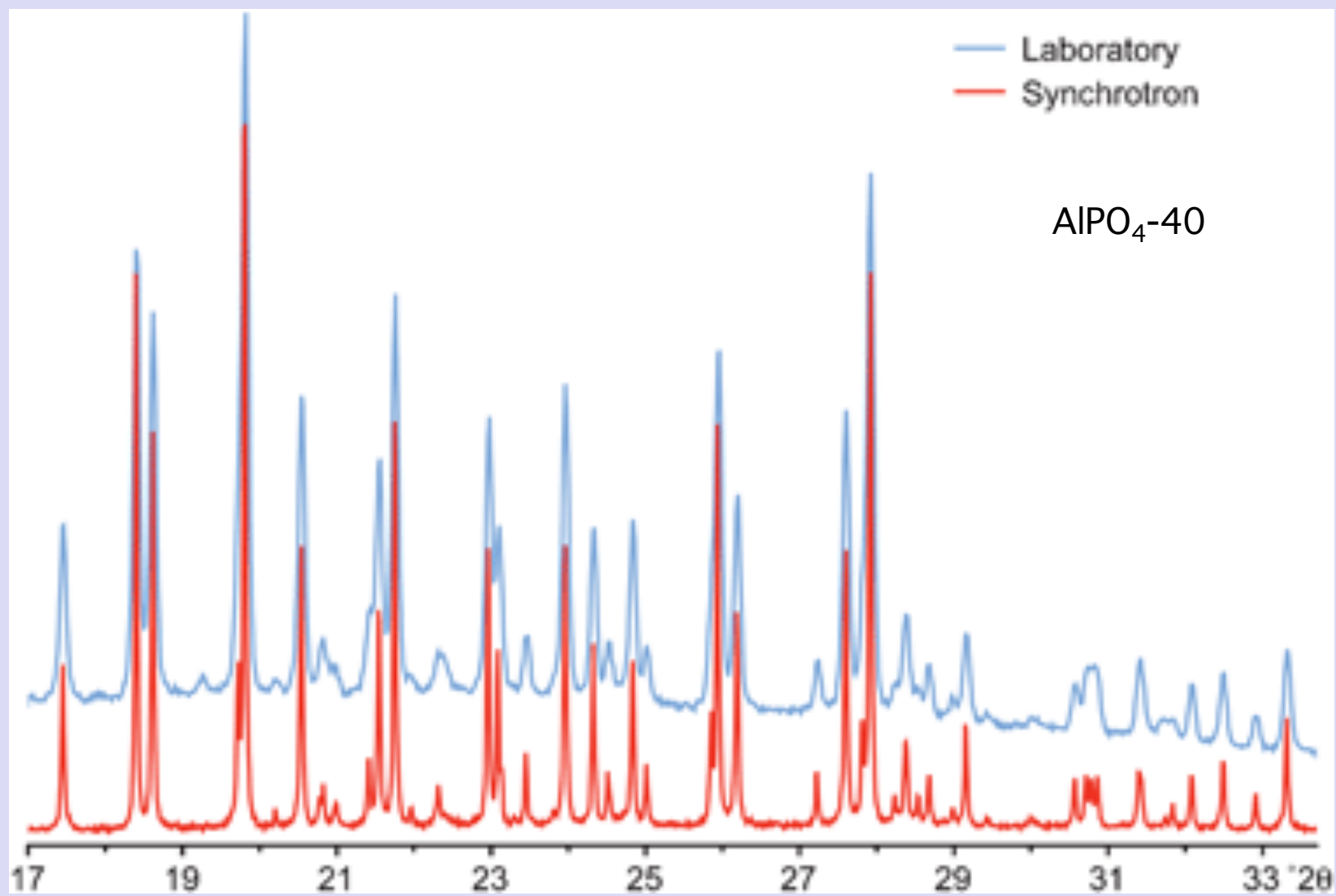
$$\lambda = 2d\sin\theta$$

**Angle dispersive**

$$\lambda_0 = 2d\sin\theta$$

fixed wavelength

**Energy dispersive**

$$\lambda = 2d\sin\theta_0$$

fixed angle

**X-rays**

EDXD

Energy-dispersive
solid-state detectors

**Pulsed neutrons**

TOF
Time of flight

$$\lambda = h/mv$$

# X-ray scattering from crystals
## The structure factor

# Structure factor

$$I_{\text{e.u.}}(\vec{K}) = \prod_{i=1}^{3} \frac{\sin^2(N_i \vec{K} \cdot \vec{a}_i / 2)}{\sin^2(\vec{K} \cdot \vec{a}_i / 2)} \qquad \left| F(\vec{K}) \right|^2$$

Laue interference function

Structure factor

conventional lattice

$$F(\vec{K}) = \sum_{\alpha} f_{\alpha} \, e^{i\vec{K} \cdot \vec{R}_{\alpha}}$$

sum within <u>conventional</u> unit cell

Interference of X-rays scattered within the cell

Selection rules >    discrimination of different lattice structures

Peak intensities >  atomic structure electronic density

# Structure factors

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## Crystalline solids

$$\frac{d\sigma}{d\Omega} = r_e^2 \prod_{i=1}^{3} \frac{\sin^2\left(N_i \vec{K} \cdot \vec{a}_i / 2\right)}{\sin^2\left(\vec{K} \cdot \vec{a}_i / 2\right)} \left|F(\vec{K})\right|^2$$

Laue interference function

Structure factor

## Non-crystalline systems

$$\frac{d\sigma}{d\Omega} = r_e^2 \left|f(K)\right|^2 S(K)$$

Structure factor

# Structure factor and selection rules

$$F\left(\vec{K}\right) = \sum_{\alpha} f_{\alpha}\, e^{i\vec{K}\cdot\vec{R}_{\alpha}}$$

$$= \sum_{\alpha} f_{\alpha}\, \exp\left[2\pi\, i\left(xh + yk + zl\right)\right]$$

$$\vec{R}_{\alpha} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3$$

$$\vec{K} = \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

Example: Orthorhombic lattice, Bragg reflections from (001) planes



Unit cell
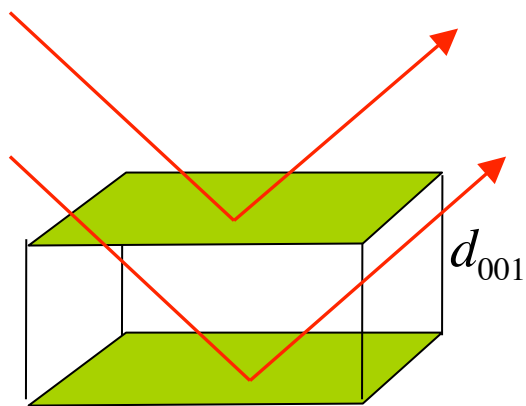
$d_{001}$

$$2d_{001}\sin\theta = \lambda$$

Base centred
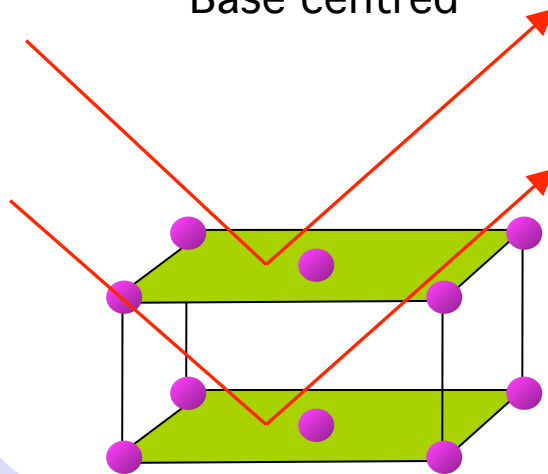
Allowed 001 reflection

Body centred
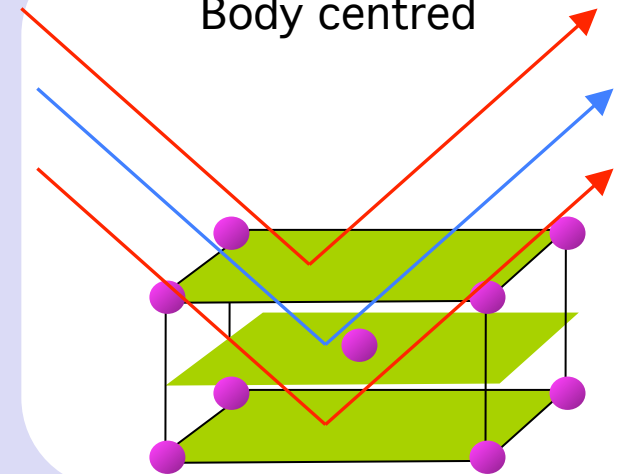
Forbidden 001 reflection

# Selection rules for fcc structure

$$F\left(\vec{K}\right) = \sum_{\alpha} f_{\alpha}\, e^{i\vec{K}\cdot\vec{R}_{\alpha}}$$

$$= \sum_{\alpha} f_{\alpha}\, \exp\left[2\pi i\left(xh + yk + zl\right)\right]$$

$$\vec{R}_{\alpha} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3$$

$$\vec{K} = \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

fcc structure

fcc Bravais lattice
+
1 atom per point

or

cubic conventional cells
+
4 atom per cell

Cu, Ag, Au ...

$$F = \begin{cases} 0 \\ 4f \end{cases} \qquad |F|^2 = \begin{cases} 0 & hkl \quad \text{mixed} \\ 16f^2 & hkl \quad \text{all even or all odd} \end{cases}$$
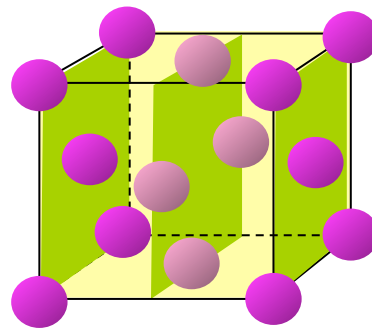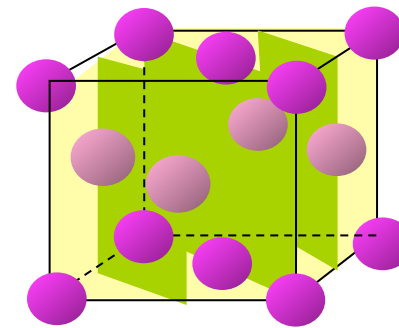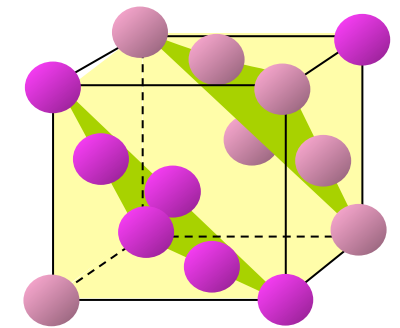


200          220          111

# Selection rules for diamond and zincblende

cubic conventional cell, 8 atoms per cell

### Diamond structure ➔ equal atoms

$$|F|^2 = \begin{cases} 0 & hkl \quad \text{mixed} \\ 32f^2 & hkl \quad \text{odd} \\ 0 & hkl \quad \text{even} \quad h+k+l \neq 4n \\ 64f^2 & hkl \quad \text{even} \quad h+k+l = 4n \end{cases}$$



$a$
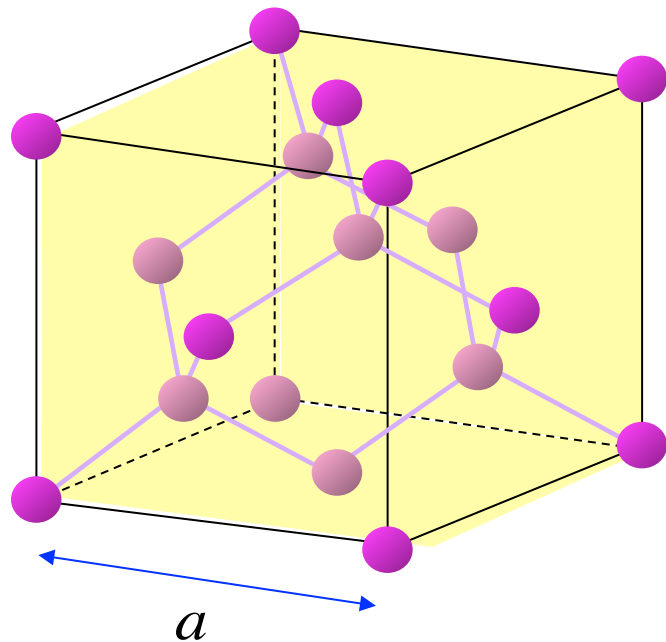
### Zincblende structure ➔ different atoms

$$|F|^2 \begin{cases} = 0 & hkl \quad \text{mixed} \\ \neq 0 & hkl \quad \text{un-mixed} \end{cases}$$



$a$
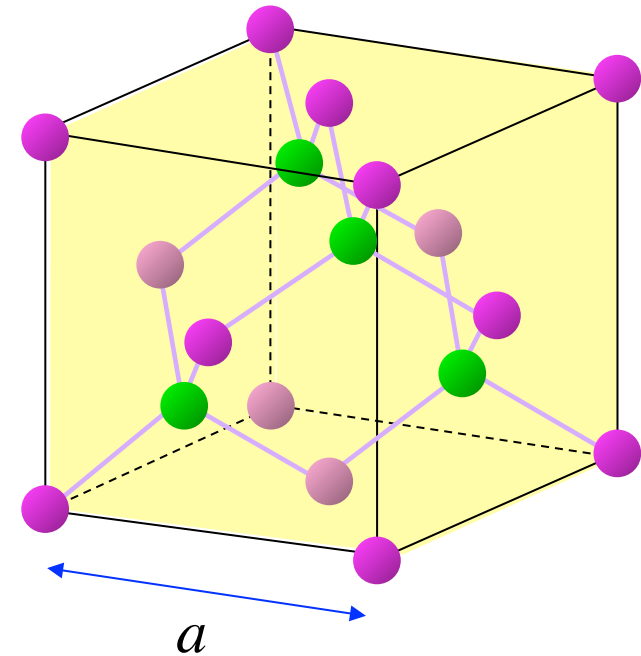
# Calculated pattern of Germanium (a)
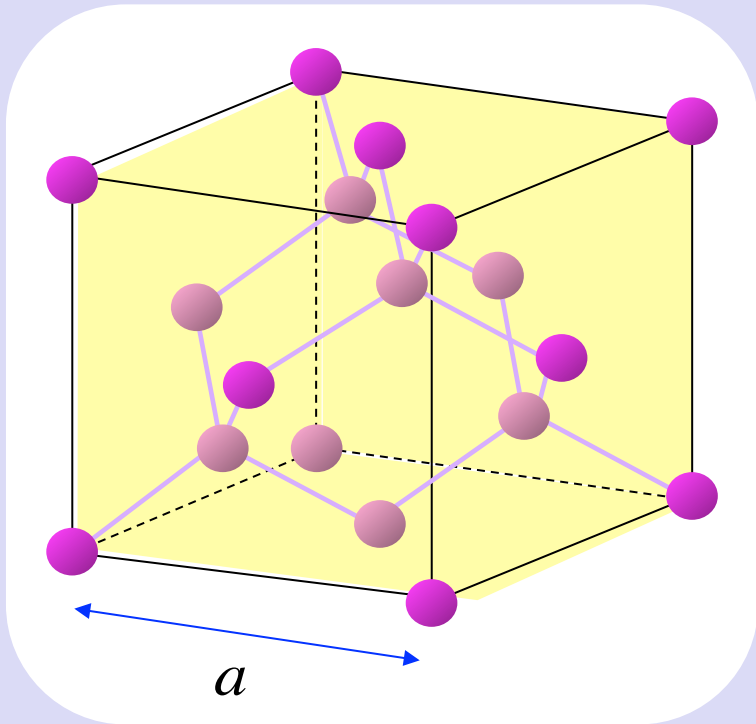


From selection rules:

$$|F|^2 = \begin{cases} 0 & hkl & \text{mixed} \\ 32f^2 & hkl & \text{odd} \\ 0 & hkl & \text{even} & h+k+l \neq 4n \\ 64f^2 & hkl & \text{even} & h+k+l = 4n \end{cases}$$



Cu Kα, λ=1.5425 Å

Squared atomic scattering factor

$|f_0|^2$

Ge

$\lambda=1.5425\ \text{Å}$

2 θ (deg)
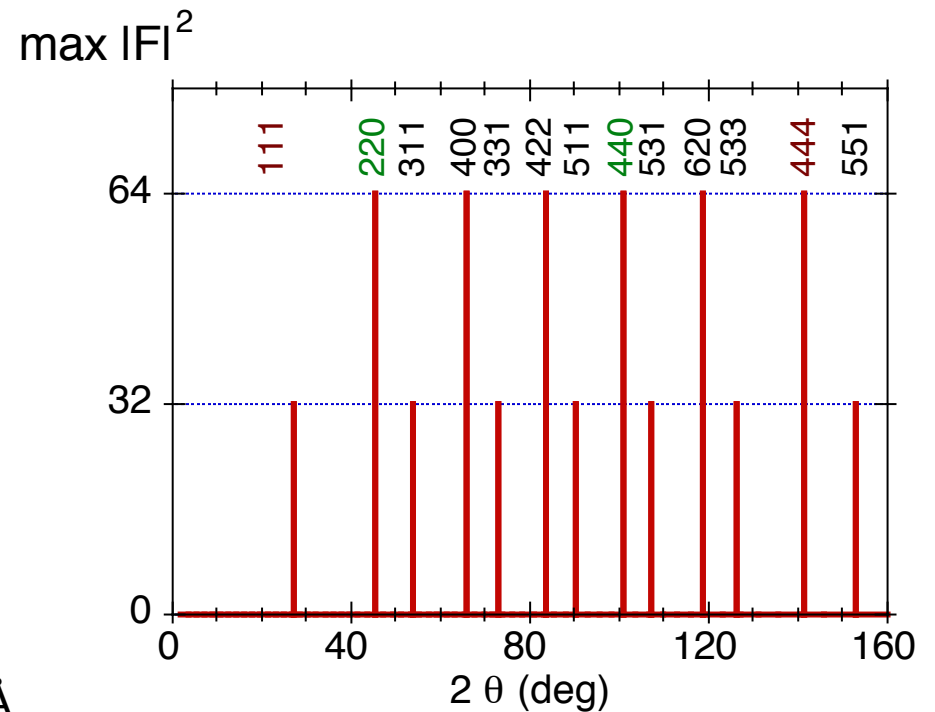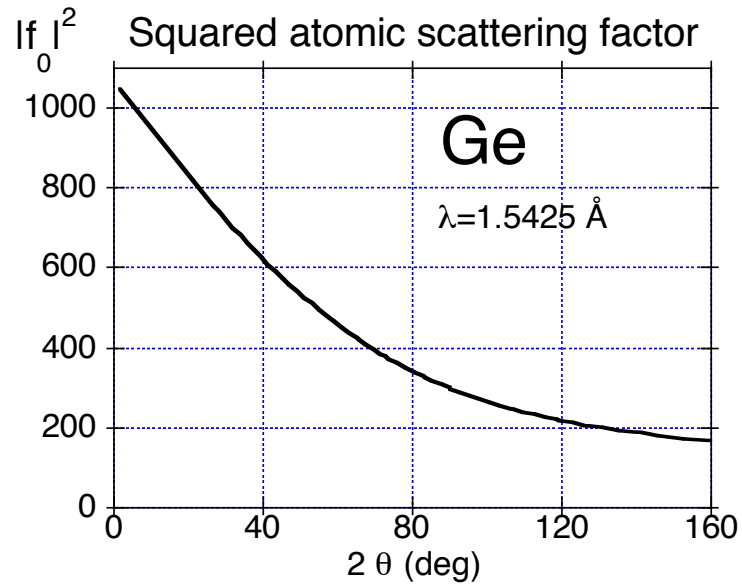
K-dependence of atomic scattering factor

$I\ (\%)$

$|F_{hkl}|^2$

2 θ (deg)

Cu Kα, λ=1.5425 Å
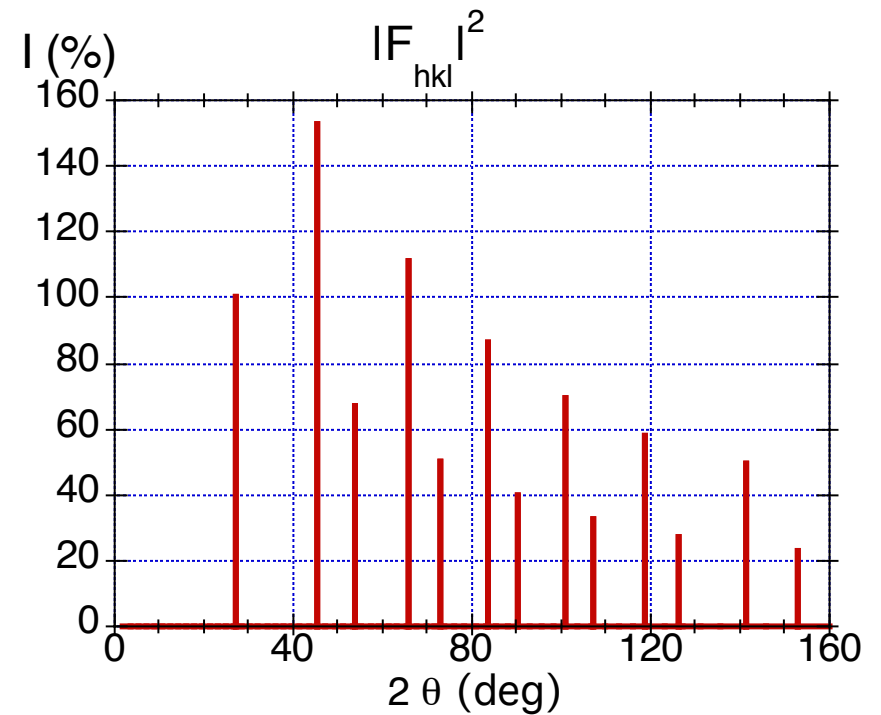
## Multiplicity of reflections

| | |
|---|---|
| *hkl* | 48 |
| *hhl* | 24 |
| *0kl* | 24 |
| *0kk* | 12 |
| *hhh* | 8 |
| *00l* | 6 |

Cu Kα, λ=1.5425 Å



Ge - multiplicity effect
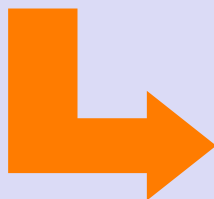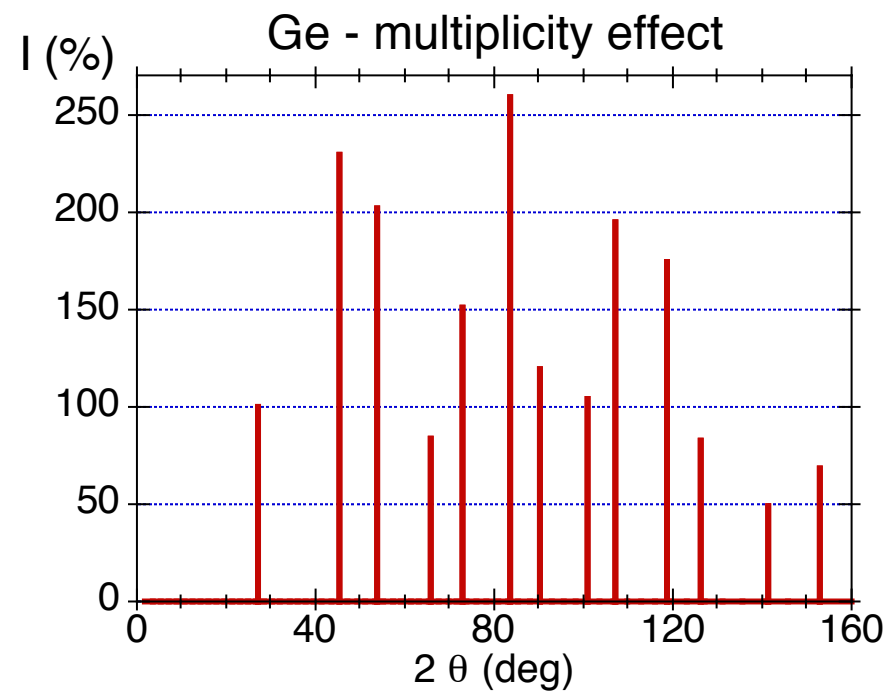
# Lorentz factor in powder diffraction

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$\vec{k}_2$

$\vec{k}_1$

$\vec{k}_{in}$

Spheres for different G values

the width is due to the finite size of crystallites
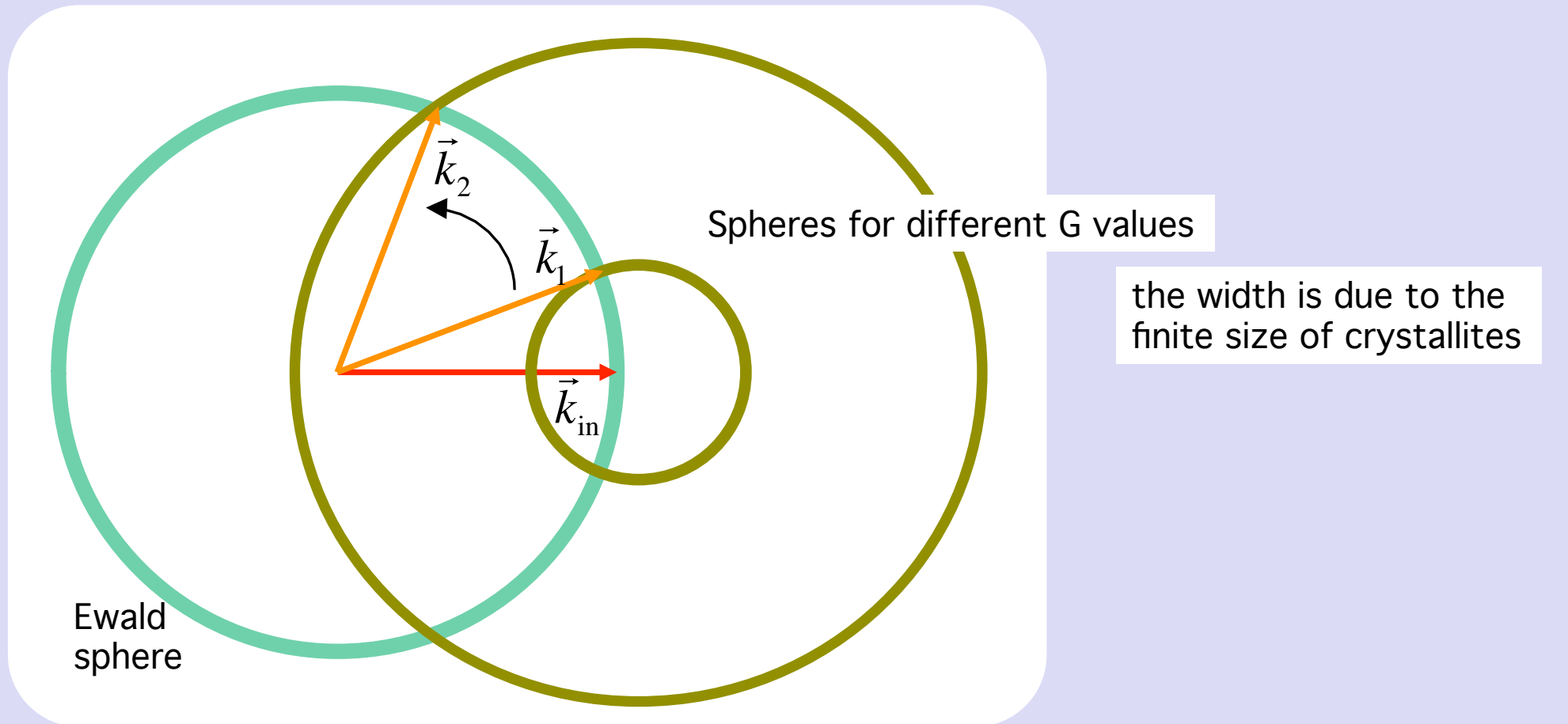
Ewald sphere

The intersections of the G spheres with the Ewald sphere are different for different G values ➡ Lorentz factor

# Calculated pattern of Germanium (d)

Lorentz-polarization factor

100
80
60
40
20
0

0    40    80    120    160

2 θ (deg)
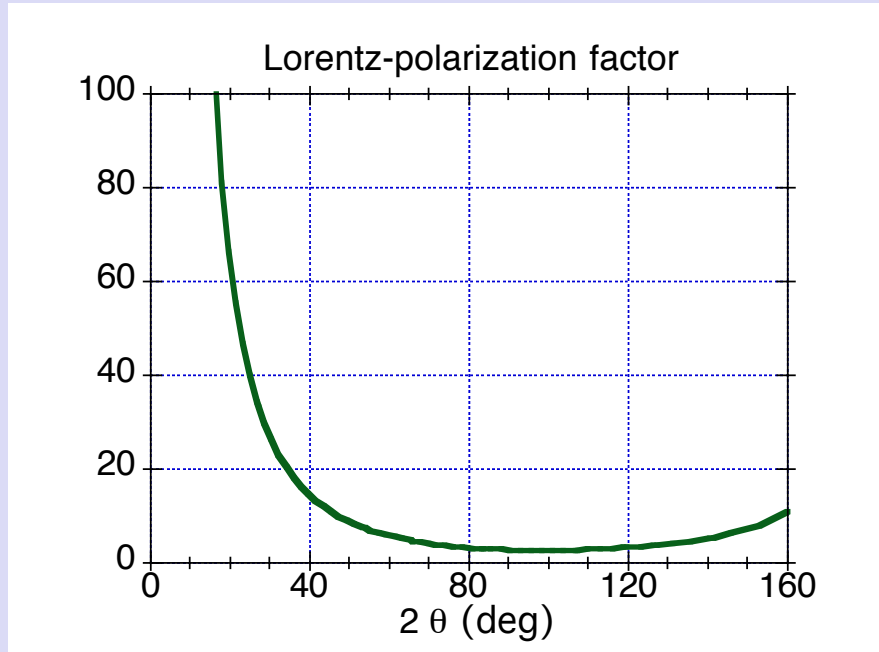
## Lorentz & polarization factor

$$\frac{1+\cos^2(2\theta_B)}{\sin^2\theta_B \,\cos\theta_B}$$

for un-polarized beam

I (%)    Ge - Lorentz-pol. effect

100
80
60
40
20
0

0    40    80    120    160

2 θ (deg)

Cu Kα, λ=1.5425 Å

Copper (Goodfellow)
99.97 %, 5$\mu$m, annealed @ 700 C
Source: Cu k$\alpha$
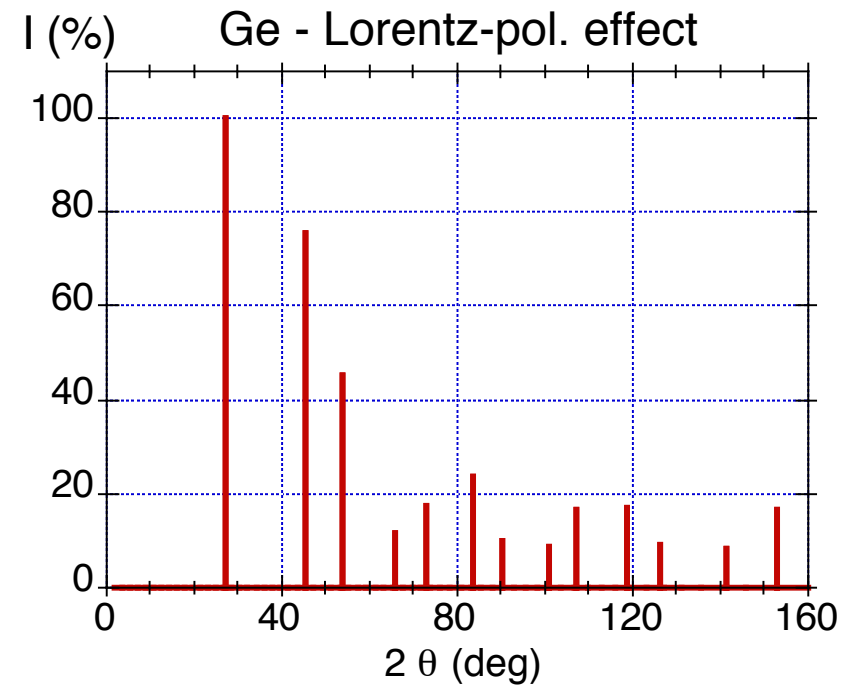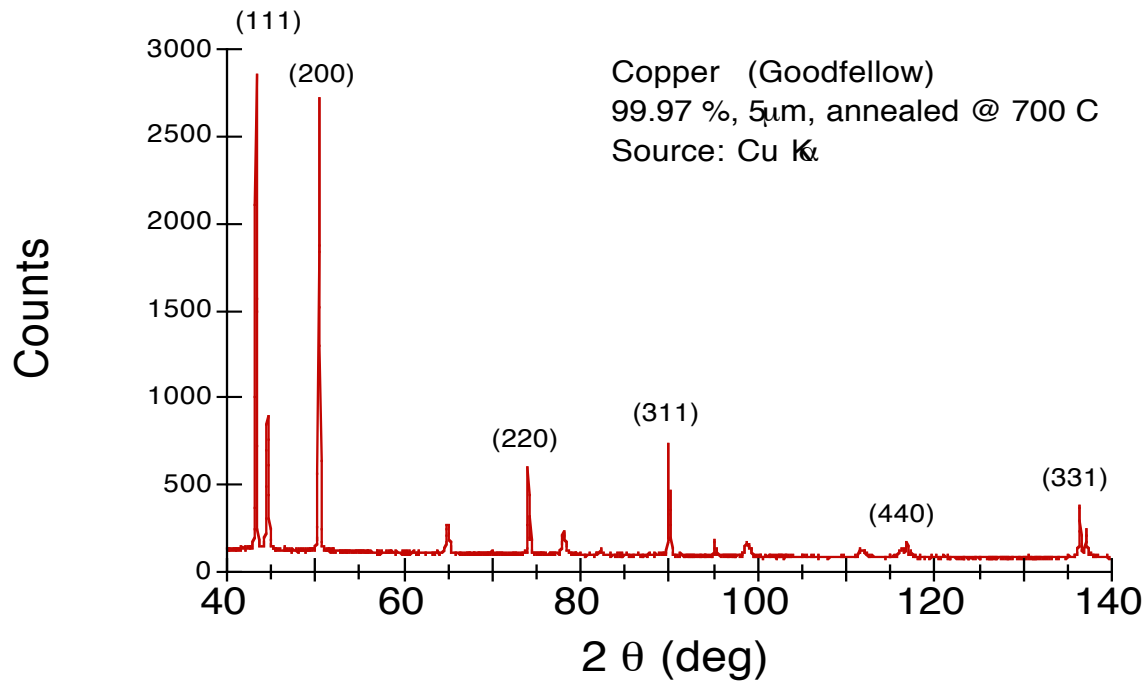
- Lattice constants
- Fingerprint (phases identification)
- Thermal expansion
- Defect structure
- Residual stresses

# Powder diffraction: info from intensities

Copper   (Goodfellow)
99.97 %, 5 μm, annealed @ 700 C
Source: Cu Kα

**Integrated intensities**

Multiplicity

Constants

Lorentz & polarisation

$$I_{\vec{K}} = S \; j_{\vec{K}} \; LP_{\vec{K}} \; \left| F_{\vec{K}} \right|^2$$
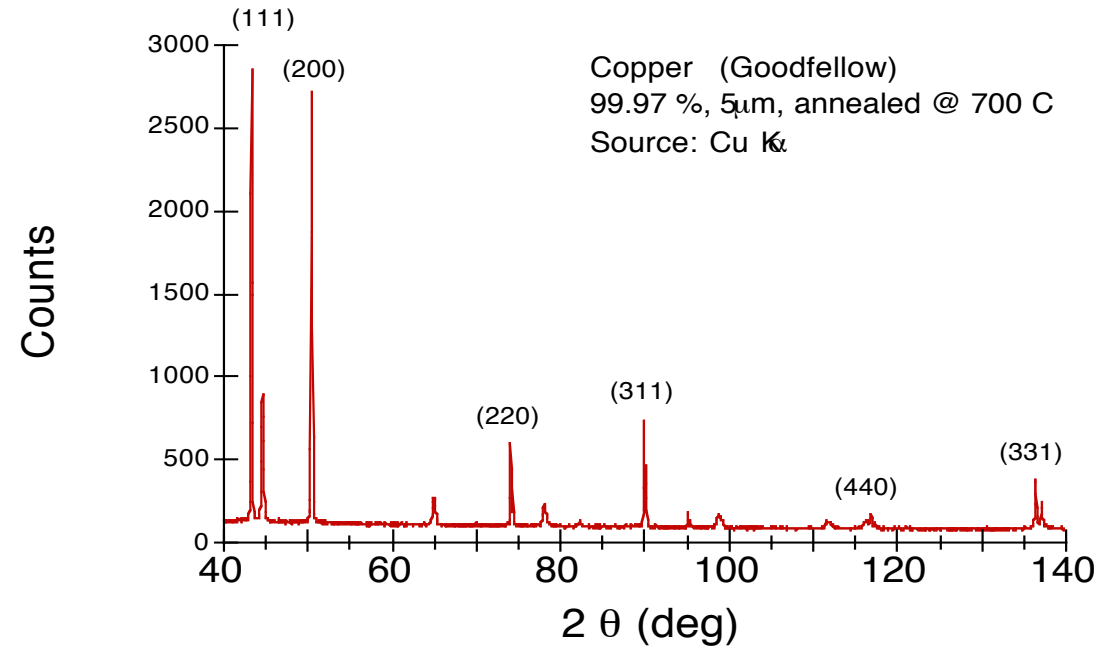
- Structure factors
- Quantitative analysis of phases
- Texture (grains orientation)
- Temperature effects

# Powder diffraction: info from profile shape



Cu

(200)

(111)

- as rolled
- anneal. 700 C

2 θ (deg)
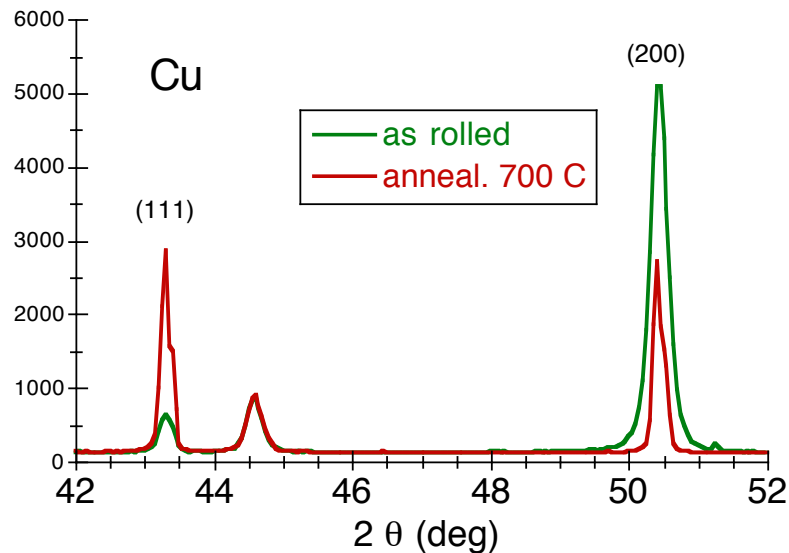
Contributions:

Spectral + $\boxed{Sample}$ + Instrumental

crystallite
size

lattice
strain

- Perfect infinite sample
- Particle size broadening
- Microstrain broadening

Dirac delta

$$\Delta(2\theta) = k\lambda/L\cos\theta \qquad L = \text{average size}, \ k = \text{constant}$$

$$\Delta(2\theta) = \eta\tan\theta \qquad \eta = \text{strain}$$

# Powder diffraction and structure refinement

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1st step:   Peaks Indexing ➔ size and symmetry of the unit cell

2nd step:   Measured intensities ➔ Structure factor

3rd step:   Structure factor ➔ Structural model guess

4th step:   Refinement of structural model
by fit to the entire powder profile
(Rietveld method)

Getting structural info from scattering
The phase problem

# Structure factor and electron density

The structure factor is the F.T. of the electron density of a cell

$$
\begin{aligned}
F(\vec{K}) &= \sum_{\alpha} f_{\alpha}(\vec{K})\, e^{i\vec{K}\cdot\vec{R}_{\alpha}} \\
&= \sum_{\alpha} \left[ \int_{\alpha} \rho_{\alpha}(\vec{r})\, e^{i\vec{K}\cdot\vec{r}}\, d\vec{r} \right] e^{i\vec{K}\cdot\vec{R}_{\alpha}} \\
&= \int_{\text{cell}} \rho(\vec{r})\, e^{i\vec{K}\cdot\vec{r}}\, d\vec{r}
\end{aligned}
$$

$$
\rho(\vec{r}) = \int F(\vec{K})\, e^{-i\vec{K}\cdot\vec{r}}\, d\vec{K}
$$

real

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

$$
\left| F(-\vec{K}) \right|^{2} = \left| F(\vec{K}) \right|^{2}
$$

Friedel law

Discrete diffraction peaks

$$
\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} F(hk\ell)\, \exp[-2\pi i(xh + yk + z\ell)]
$$

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} F(hk\ell) \exp[-2\pi i(xh + yk + z\ell)]$$

$$F(hk\ell) = |F(hk\ell)| \, e^{i\phi(hk\ell)}$$

complex

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} |F(hk\ell)| \exp\{-2\pi i[xh + yk + z\ell + \phi(hk\ell)]\}$$

modulus
measured

phase
not measured
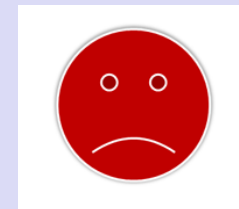
# The Patterson method

The **scattered intensity**  is the Fourier transform  of the **density-density autocorrelation function**

$$I(\vec{K}) = \left|A_{\mathrm{el}}\right|^2 \int \left\langle \rho_e(\vec{r})\rho_e(\vec{r}+\vec{r}\,') \right\rangle e^{-i\vec{K}\cdot\vec{r}\,'} dV$$

The Patterson function is the F.T. of the scattered intensity

$$P(\vec{R}) = \frac{1}{V} \sum_{h,k,\ell=-\infty}^{+\infty} I(hk\ell) \exp[-i\vec{K}\cdot\vec{R}],$$

and corresponds to the **density-density autocorrelation function**

$$P(\vec{R}) = \left\langle \rho_e(\vec{r})\rho_e(\vec{R}-\vec{r}) \right\rangle$$

The Patterson map gives peaks in correspondence of all interatomic vector distances, translated at the origin of real space (3D RDF).

# Effects of atomic vibrations

# Static crystal approximation

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### Conservation of energy

$$\hbar\left(\omega - \omega_0\right) = 0$$
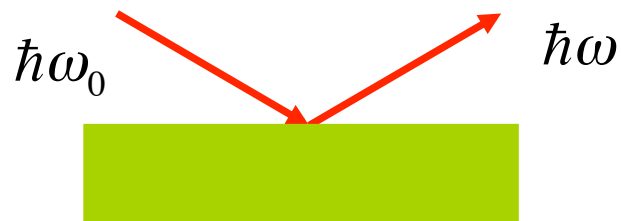


### Conservation of momentum

$$\hbar\left(\vec{k}_{\text{out}} - \vec{k}_{\text{in}}\right) = \hbar\vec{K} = \hbar\vec{G}$$
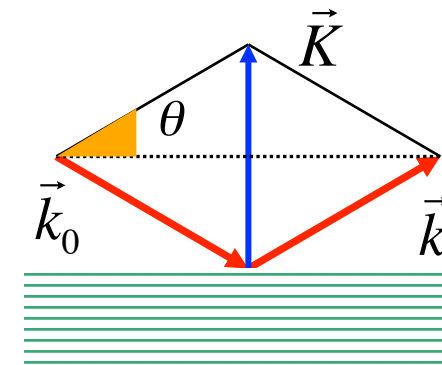


Beyond the static crystal approximation: atomic vibrations

- zero point
- thermal

# Effect of atomic vibrations (monatomic crystal)

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Still atoms
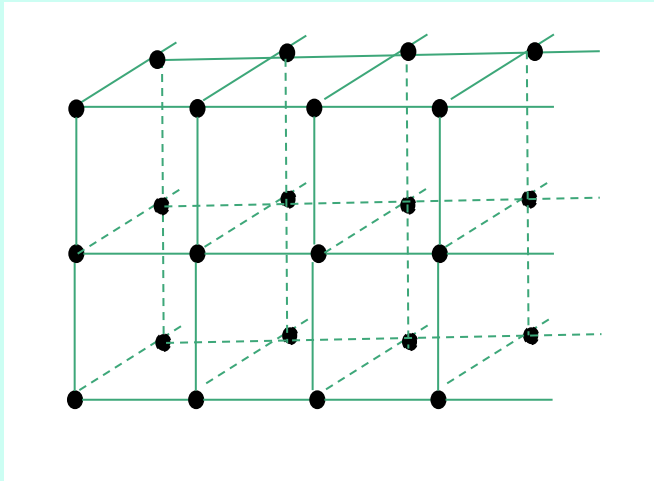
Vibrating atoms

$$\vec{r}_m$$
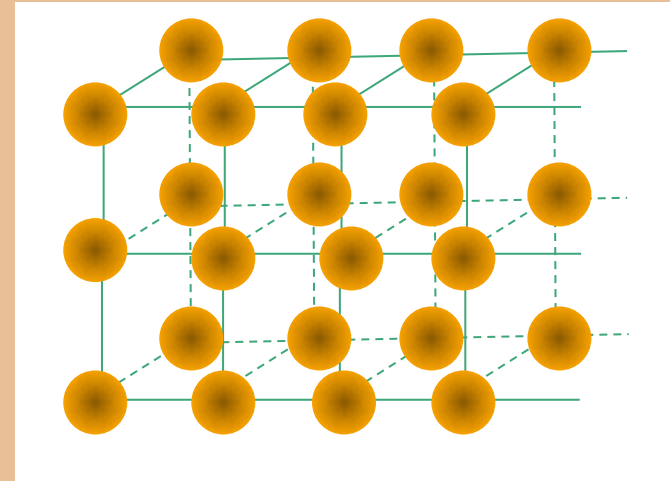
$$\vec{r}_m + \vec{u}_m(t)$$

instantaneous displacements

$$A_{\text{e.u.}}\left(\vec{K}\right) = f\left(\vec{K}\right)\sum_m e^{i\vec{K}\cdot\vec{r}_m}$$

$$A_{\text{e.u.}}\left(\vec{K}\right) = f\left(\vec{K}\right)\sum_m e^{i\vec{K}\cdot\left[\vec{r}_m+\vec{u}_m(t)\right]}$$

$$I_{\text{e.u.}}\left(\vec{K}\right) = \left|f\left(\vec{K}\right)\right|^2 \sum_{mn} e^{i\vec{K}\cdot\left(\vec{r}_m-\vec{r}_n\right)}$$

$$I_{\text{e.u.}}\left(\vec{K}\right) = \left|f\left(\vec{K}\right)\right|^2 \sum_{mn} e^{i\vec{K}\cdot\left(\vec{r}_m-\vec{r}_n\right)}\left\langle e^{i\vec{K}\cdot\left(\vec{u}_m-\vec{u}_n\right)}\right\rangle$$

# Average over instantaneous displacements

$$I_{\text{e.u.}}(\vec{K}) = \left| f(\vec{K}) \right|^2 \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)} \left\langle e^{i\vec{K}\cdot(\vec{u}_m - \vec{u}_n)} \right\rangle$$

Gaussian distrib.

$$\left\langle e^{ix} \right\rangle = e^{-\frac{1}{2}\left\langle x^2 \right\rangle}$$
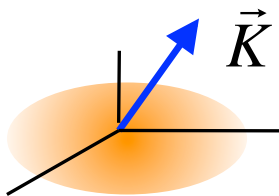


ellipsoid of atomic vibrations

$$e^{-\frac{1}{2}\left\langle \left(\vec{K}\cdot\vec{u}_m\right)^2 \right\rangle} \; e^{-\frac{1}{2}\left\langle \left(\vec{K}\cdot\vec{u}_n\right)^2 \right\rangle} \; e^{\left\langle \left(\vec{K}\cdot\vec{u}_m\right)\left(\vec{K}\cdot\vec{u}_n\right) \right\rangle}$$

$$e^{-\frac{1}{2}\left\langle \left(\vec{K}\cdot\vec{u}_m\right)^2 \right\rangle} \; e^{-\frac{1}{2}\left\langle \left(\vec{K}\cdot\vec{u}_n\right)^2 \right\rangle} \left\{ 1 + \left[ e^{\left\langle \left(\vec{K}\cdot\vec{u}_m\right)\left(\vec{K}\cdot\vec{u}_n\right) \right\rangle} - 1 \right] \right\}$$

# Debye-Waller factor (monatomic crystals)

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$\vec{K}$
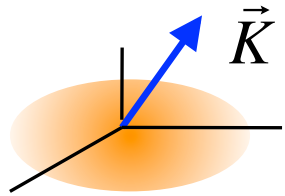
ellipsoid of atomic vibrations

$$\left\langle \left( \vec{K} \cdot \vec{u}_m \right)^2 \right\rangle$$

Increases with

increasing $K$

increasing temperature

$$e^{-\frac{1}{2}\left\langle \left( \vec{K} \cdot \vec{u}_m \right)^2 \right\rangle}$$

Decreases with

increasing $K$

increasing temperature

Isotropic vibrations ➜ Debye-Waller factor

$\vec{K}$
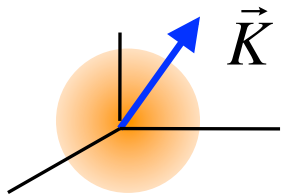
$$e^{-\frac{1}{2}\left\langle \left( \vec{K} \cdot \vec{u}_m \right)^2 \right\rangle} = e^{-W(T,K)}$$

Two equal atoms

$$e^{-\frac{1}{2}\left\langle \left( \vec{K} \cdot \vec{u}_m \right)^2 \right\rangle} e^{-\frac{1}{2}\left\langle \left( \vec{K} \cdot \vec{u}_n \right)^2 \right\rangle} = e^{-2W(T,K)}$$

# Partition of total scattering intensity

$$I_{\mathrm{e.u.}}\left(\vec{K}\right) = \left|f\left(\vec{K}\right)\right|^2 e^{-2W(K,T)} \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)}$$

← Laue scattering

$$+ \left|f\left(\vec{K}\right)\right|^2 e^{-2W(K,T)} \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)} \left[ e^{\left\langle (\vec{K}\cdot\vec{u}_m)(\vec{K}\cdot\vec{u}_n) \right\rangle} - 1 \right]$$

← Diffuse scattering

$$e^{\left\langle [\vec{K}\cdot\vec{u}_m(0)][\vec{K}\cdot\vec{u}_n(t)] \right\rangle} = 1 + \left\langle [\vec{K}\cdot\vec{u}_m(0)][\vec{K}\cdot\vec{u}_n(t)] \right\rangle + ....$$

$$I_{\mathrm{e.u.}}\left(\vec{K}\right) = \left|f\left(\vec{K}\right)\right|^2 e^{-2W(K,T)} \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)}$$

← Laue scattering

$$+ \left|f\left(\vec{K}\right)\right|^2 e^{-2W(K,T)} \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)} \left[ \left\langle (\vec{K}\cdot\vec{u}_m)(\vec{K}\cdot\vec{u}_n) \right\rangle + ..... \right]$$

← Diffuse scattering

# Laue scattering

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$$I_{\text{e.u.}}\left(\vec{K}\right) = \left|f\left(\vec{K}\right)\right|^2 e^{-2W(K,T)} \sum_{mn} e^{i\vec{K}\cdot\left(\vec{r}_m - \vec{r}_n\right)}$$

⬇

Debye_Waller factor

⬇

Reduction of Laue intensities

Decreases with
- increasing $K$
- increasing temperature
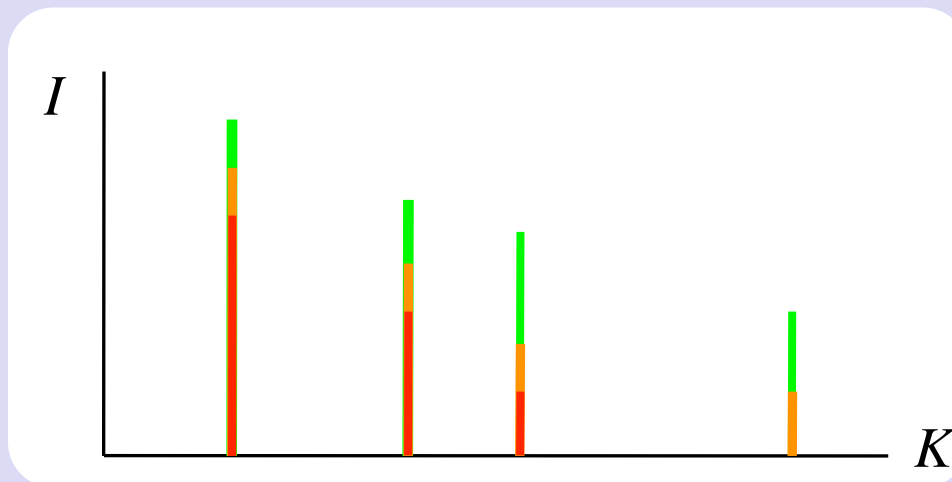


Energy lost for elastic scattering goes into diffuse scattering

# Diffuse scattering

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X-rays exchange energy with crystal normal modes

1-phonon processes     2 or more phonons

$$\left|f\left(\vec{K}\right)\right|^2 e^{-2W(\vec{K})} \sum_{mn} e^{i\vec{K}\cdot(\vec{r}_m - \vec{r}_n)}\left[\left\langle\left(\vec{K}\cdot\vec{u}_m\right)\left(\vec{K}\cdot\vec{u}_n\right)\right\rangle + .....\right]$$
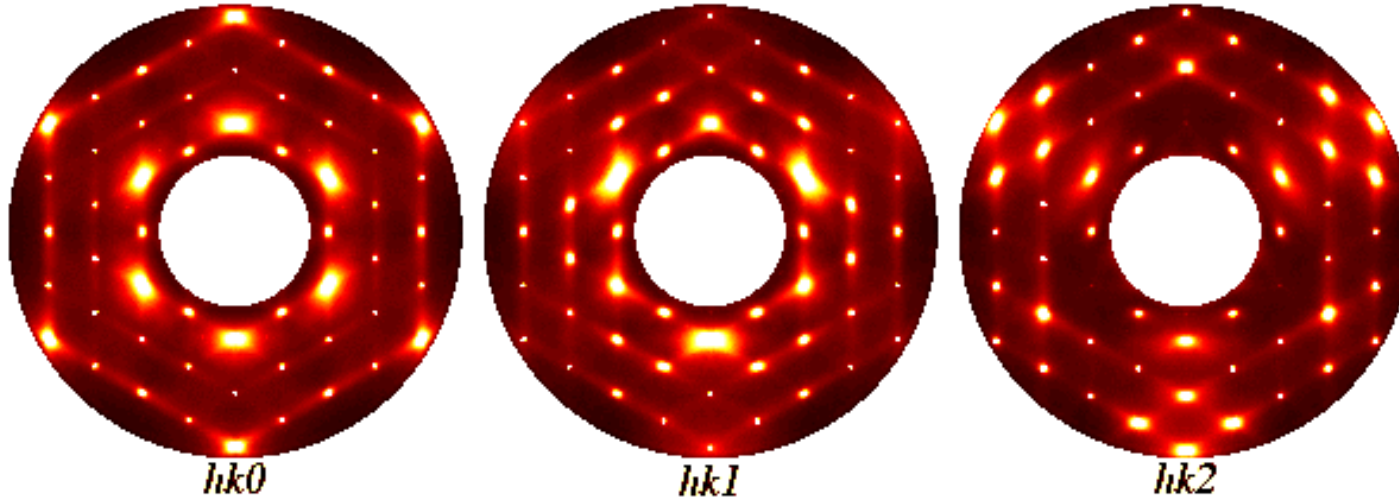
correlation significant
only for neighbouring atoms

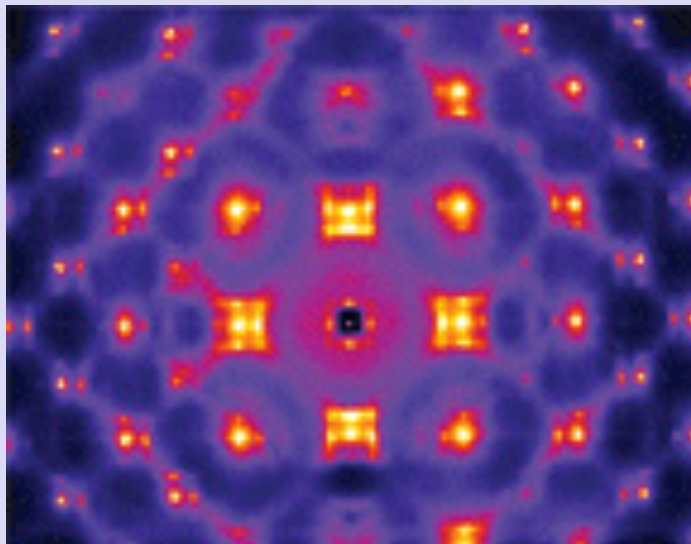sum limited to
neighbouring atoms

significant intensity for $\quad \vec{K} \neq \vec{G}$

# Diffuse scattering

Observed X-ray Diffraction patterns

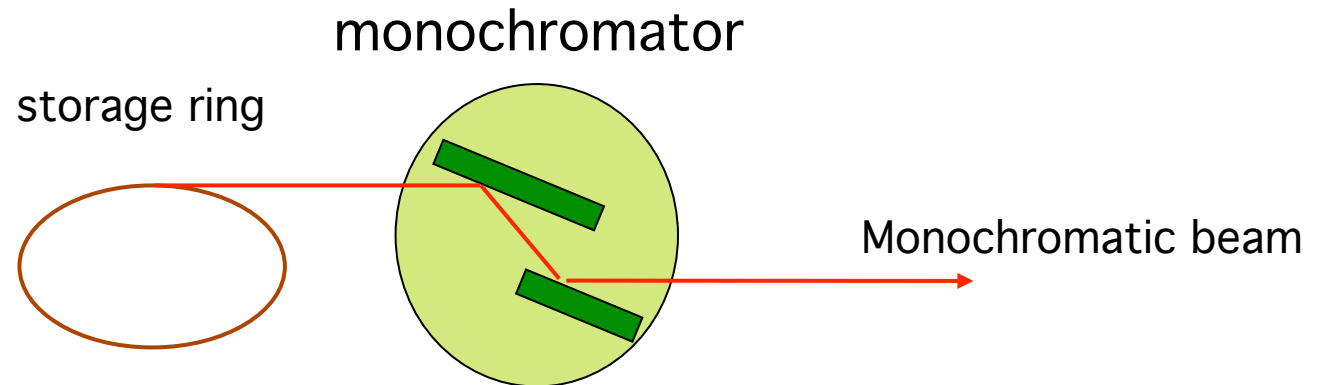hk0    hk1    hk2

Benzil, $C_{14}H_{10}O_2$



Wüstite, $Fe_{1-x}O$, viewed down [001],

Complex distribution of defect clusters (structural disorder)

# Synchrotron Radiation and diffraction

# Tunability

- •High intensity
- •Tunability
- •Collimation

monochromator

storage ring

Monochromatic beam

Bragg law
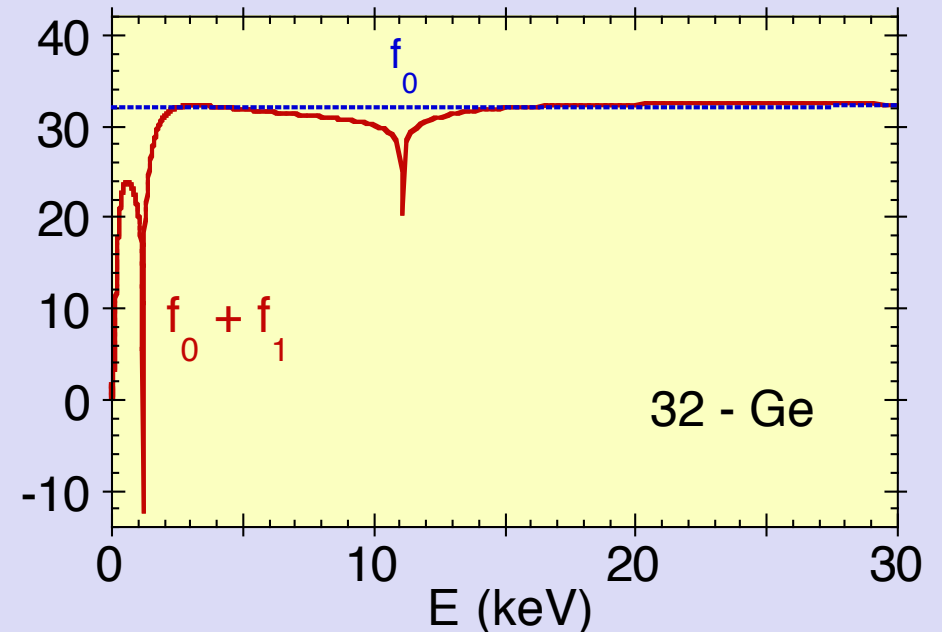
$$2 d_{hkl} \sin \theta = n \lambda$$

Incidence angle $\Leftrightarrow$ wavelength

➢ Possibility of selecting the beam energy

➢ High energy > High K > useful for amorphous systems

# Tunability and resonant scattering

- High intensity
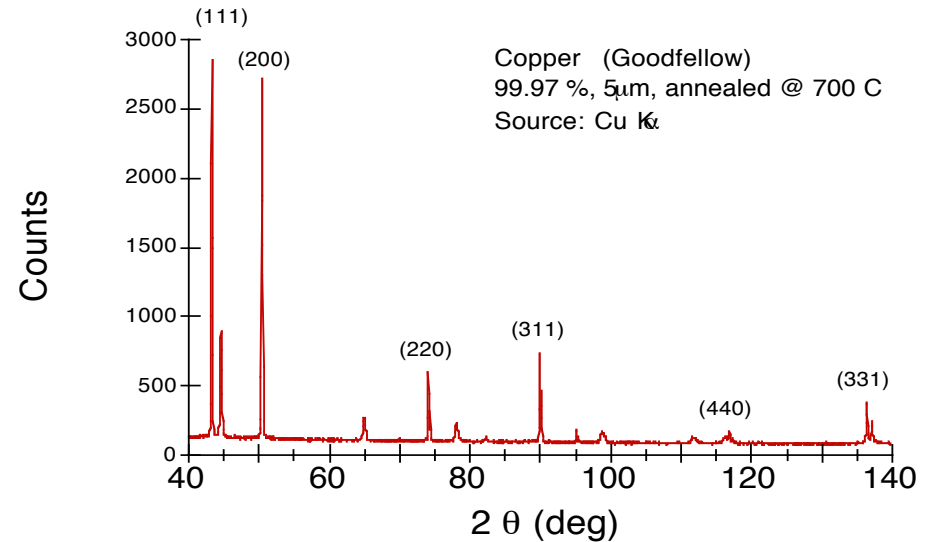- **Tunability**
- Collimation

$$f(\vec{K}) = f_0(\vec{K}) + f_1 + i\, f_2$$

MAD (Multi-wavelength Anomalous Diffraction)

➤ Possibility of distinguishing neighbouring elements (similar Z)
➤ Partial PDF in non-crystalline materials:   M(M+1)/2

# Powder diffraction

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- **High intensity**
- Tunability
- **Collimation**



Copper (Goodfellow)
99.97 %, 5μm, annealed @ 700 C
Source: Cu Kα

- ➤ Angular accuracy, better indexing of patterns
- ➤ Better extraction of intensities, structure solution
- ➤ In-situ dynamic measurements
- ➤ Grazing incidence ➔ surface structure
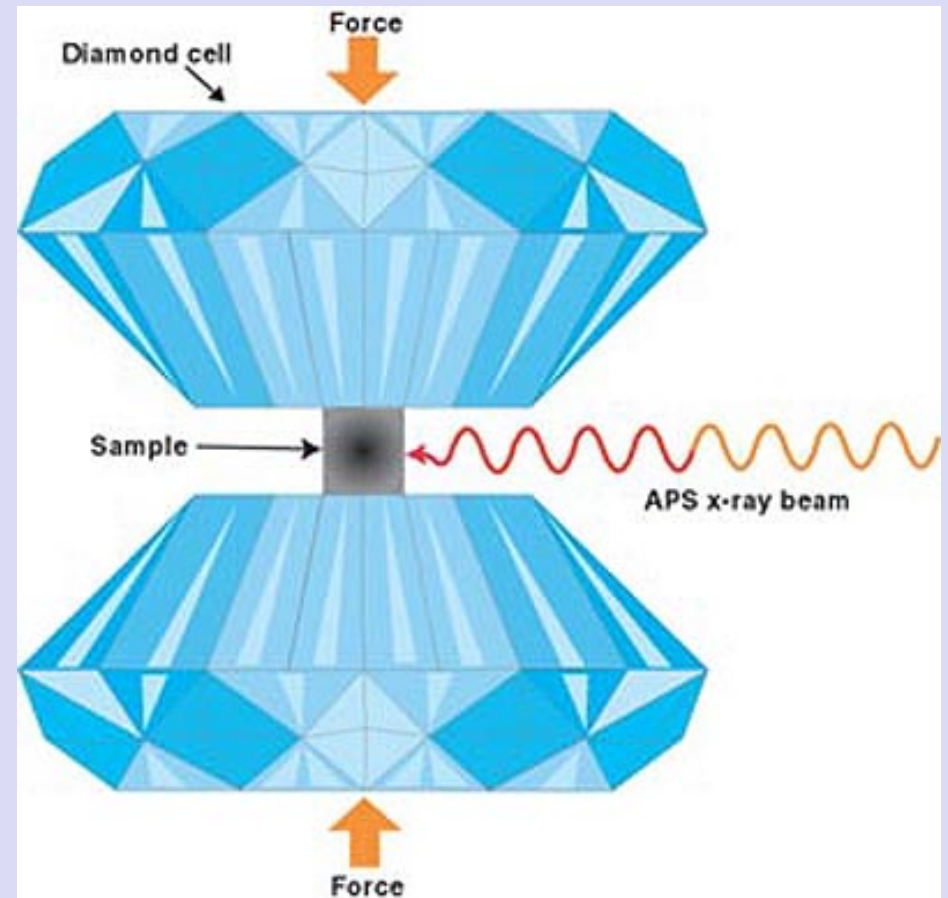- ➤ Pressure studies

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- **High intensity**
- Tunability
- **Collimation**

$$P = \frac{F}{S}$$

Diamond anvil cell

| Sample ∅ | Pressure |
|----------|----------|
| 100 μm | $10^5$ bar |
| 10 μm | $10^6$ bar |

# In-situ dynamic studies

- **High intensity**
- **Tunability**
- **Collimation**



Crystallization of BN-$N_2H_4$
@ 4.1 GPa = 41000 bar
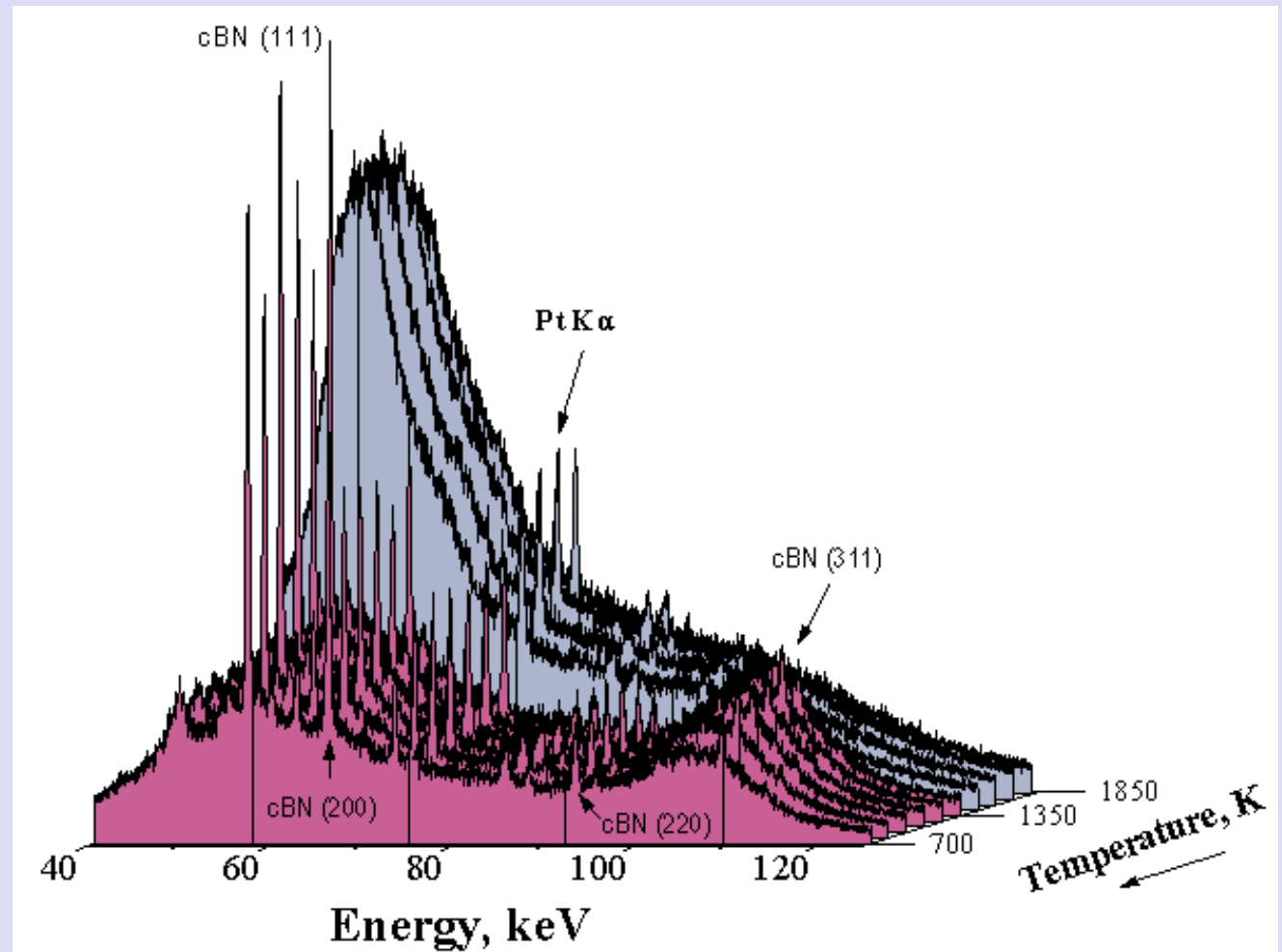
# Macromolecular crystallography (MX)

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- **High intensity**
- Tunability
- **Collimation**
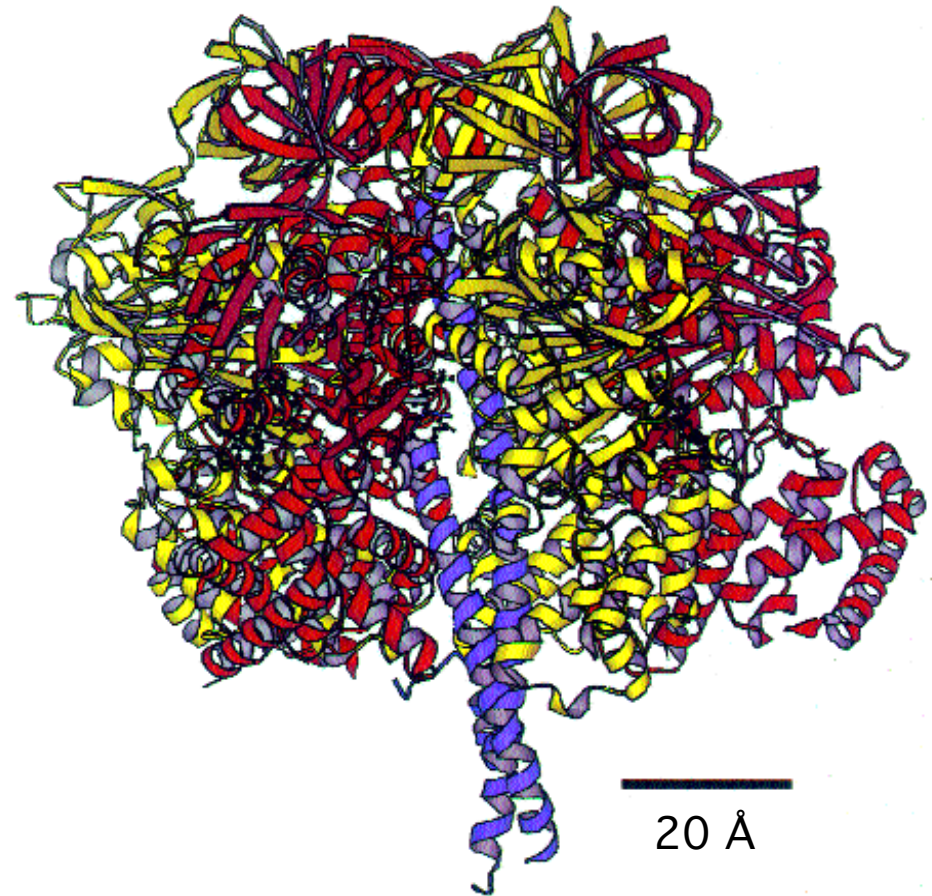


A schematic representation of the structure
of F1-ATPase,
which contains the catalytic sites
where ATP is synthesised.

20 Å

## Production of single crystals from supersaturated solution

- Trial and error empirical approaches
- High purity requirements
- Nucleation, growth, end of growth
- Growth time varying from hours to months
- Improved quality under 'microgravity' conditions (in space)

## Crystals of organic materials

- Volume < 0.1 mm$^3$, lattice parameters > 100 Å
- Linear size 10-100 $\mu$m
- Weak interaction between molecules
- Stabilisation energy < protein folding energy
- Poor mechanical stability, high solvent content
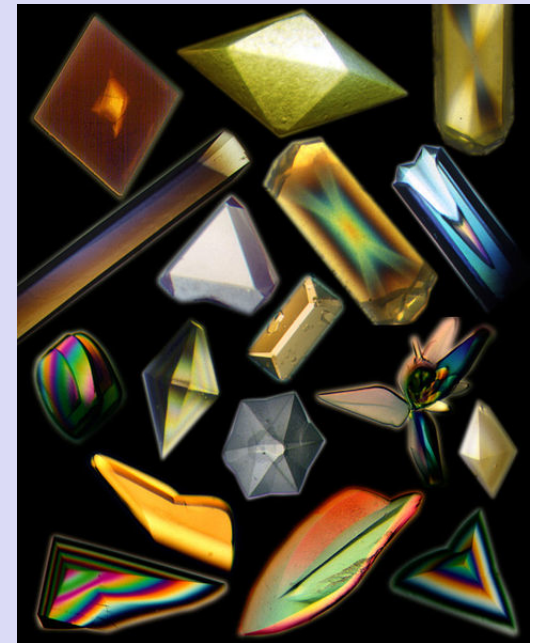


Protein and virus crystals, grown on Space Stations

# Diffraction by macromolecular crystals (1)

Paolo
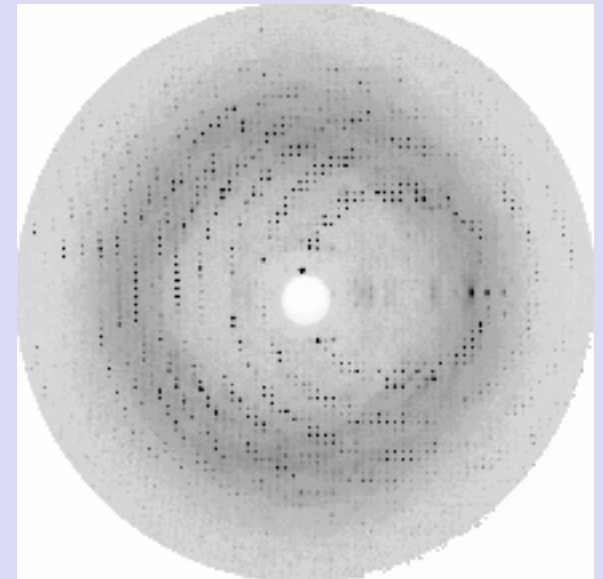Fornasini
Univ. Trento

## Sample

- Contained in thin-walled capillary, together with solvent
- Capillary mounted on goniometer head for orientation
- Cooling to LN to reduce radiation damage (fast freezing to avoid water cryst.)

## Measurement set ups

1. Monochromatic X rays > rotation of the crystal
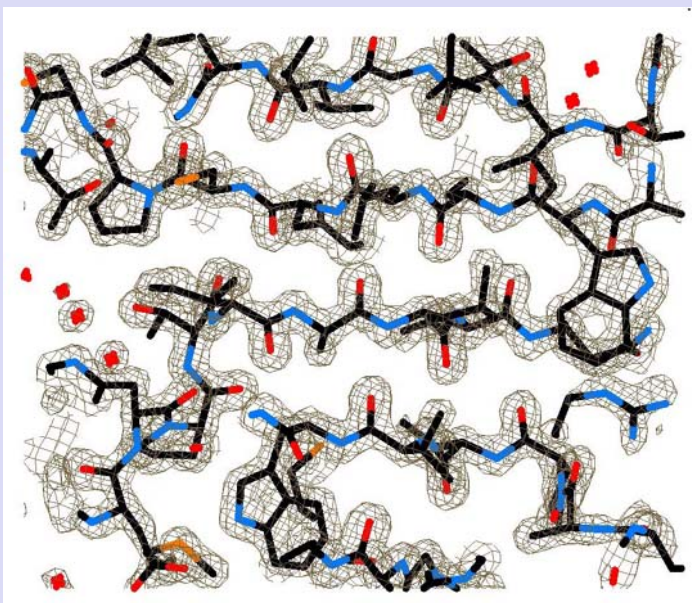2. White beam Laue technique

## Radiation damage

- Absorption of X-rays > free radicals (OH) > damage the proteins
- Lower for higher energies (reduced absorption)
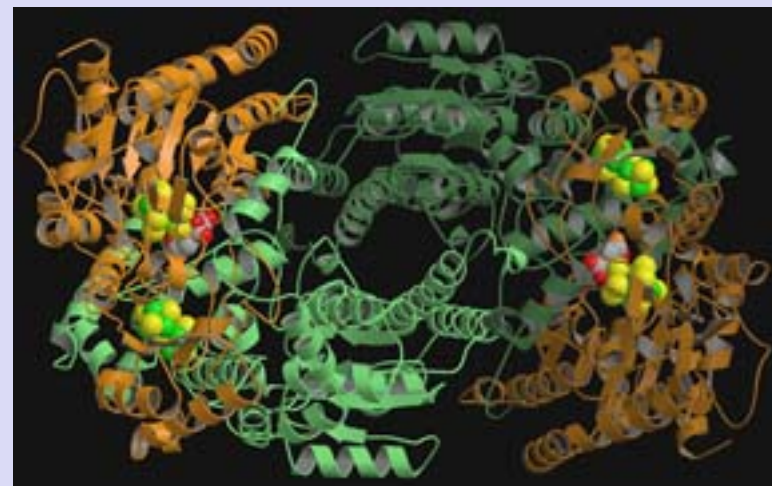- Reduced by cooling the sample

The phase problem

Various methods available > estimate of the electron density



Model building

Crystallographic refinement (least squares)

# Neutron scattering

# Elastic neutron scattering

Cross sections:

a) one atom

$$\frac{d\sigma}{d\Omega} = |b|^2$$

b) atomic aggregate

$$\frac{d\sigma}{d\Omega} = \sum_m \sum_n b_m b_n^* \, e^{i\vec{K}\cdot\vec{R}_{mn}}$$

sum over atomic positions
- neglecting thermal effects
- neglecting absorption

Atomic positions are
randomly occupied by different
- isotopes
- nuclear spins

$$\frac{d\sigma}{d\Omega} = \sum_m \sum_n \langle b_m b_n \rangle \, e^{i\vec{K}\cdot\vec{R}_{mn}}$$

For each pair of positions $m,n$ : $\langle b_m b_n \rangle$ = average over isotopes and nuclear spins

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$$\frac{d\sigma}{d\Omega} = \sum_m \sum_n \langle b_m b_n \rangle \, e^{i\vec{K}\cdot\vec{R}_{mn}}$$

$$b_m = \langle b \rangle + \Delta b_m \qquad \langle \Delta b_m \rangle = 0$$

$$b_m b_n^* = \left(\langle b \rangle + \Delta b_m\right)\left(\langle b \rangle + \Delta b_n^*\right)$$

$$= \langle b \rangle^2 + \langle b \rangle\left(\Delta b_m + \Delta b_n^*\right) + \Delta b_m \Delta b_n^*$$

$$\langle b_m b_n^* \rangle = \langle b \rangle^2 + 0 + \langle \Delta b_m \Delta b_n^* \rangle \qquad \neq 0 \text{ only for m=n}$$

$$= \langle b \rangle^2 + \langle \Delta b_m \Delta b_m \rangle$$

$$= \langle b \rangle^2 + \langle \left(b_m - \langle b \rangle\right)^2 \rangle$$

mean        variance

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{m,n} e^{i\vec{K}\cdot\vec{R}_{mn}} + N\left[\langle b^2 \rangle - \langle b \rangle^2\right]$$

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{coherent}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{incoherent}}$$

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$$\frac{d\sigma}{d\Omega} = \sum_m \sum_n \langle b_m b_n \rangle e^{i\vec{K}\cdot\vec{R}_{mn}}$$

Alternative derivation

$$\langle b_m b_n \rangle = \begin{cases} \langle b^2 \rangle & \text{if } m = n \\ \langle b_m \rangle \langle b_n \rangle = \langle b \rangle^2 & \text{if } m \neq n \end{cases}$$

$$\langle b_m b_n \rangle = \langle b \rangle^2 + \delta_{mn}\left[\langle b^2 \rangle - \langle b \rangle^2\right]$$
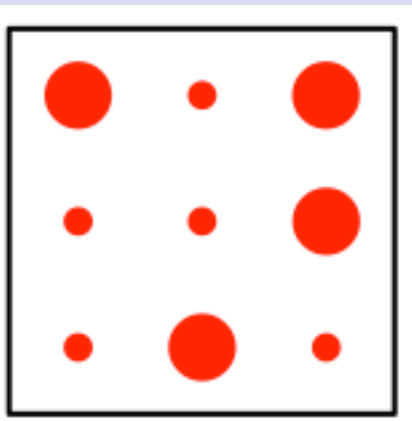
mean     variance

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{m,n} e^{i\vec{K}\cdot\vec{R}_{mn}} + N\left[\langle b^2 \rangle - \langle b \rangle^2\right]$$
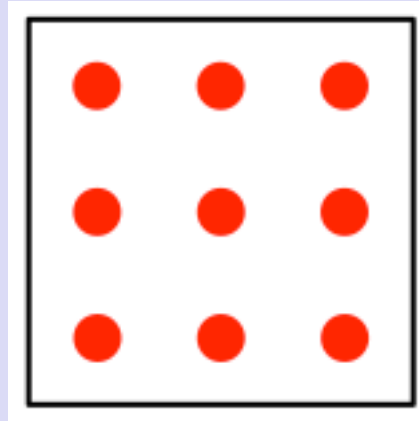
$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{coherent}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{incoherent}}$$
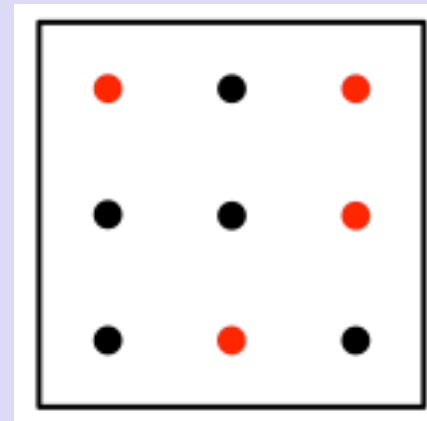
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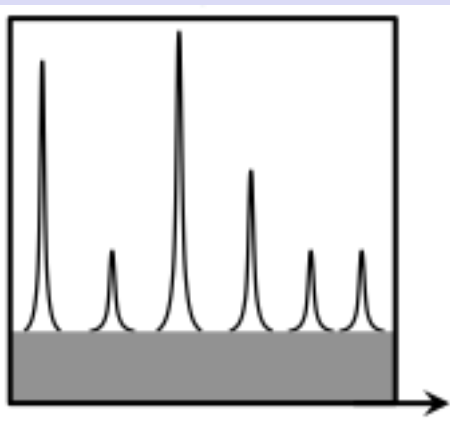
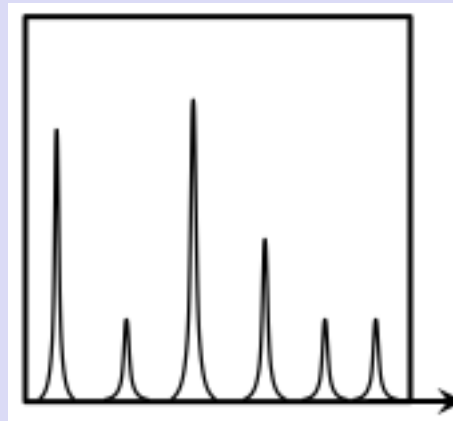Example: 2 scattering lengths randomly distributed



$$\langle b \rangle = \frac{b_1 + b_2}{2}$$

$$\Delta b_i$$

From
Peter M. Gehring,
NIST
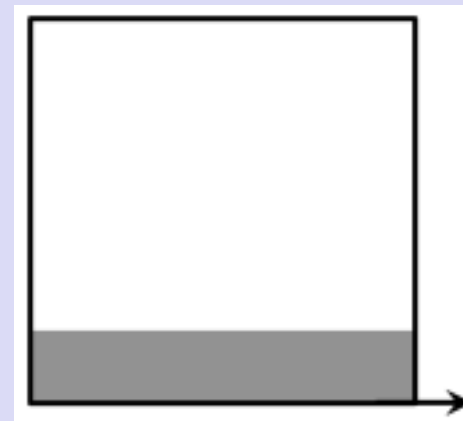
Total = Coherent + Incoherent

# An example: random spins
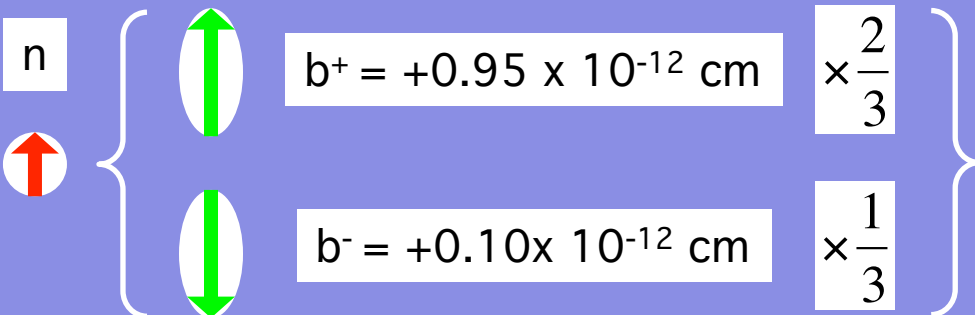
## Hydrogen

n

$b^+ = +1.04 \times 10^{-12}$ cm $\quad \times \dfrac{3}{4}$

$b^- = -4.74 \times 10^{-12}$ cm $\quad \times \dfrac{1}{4}$
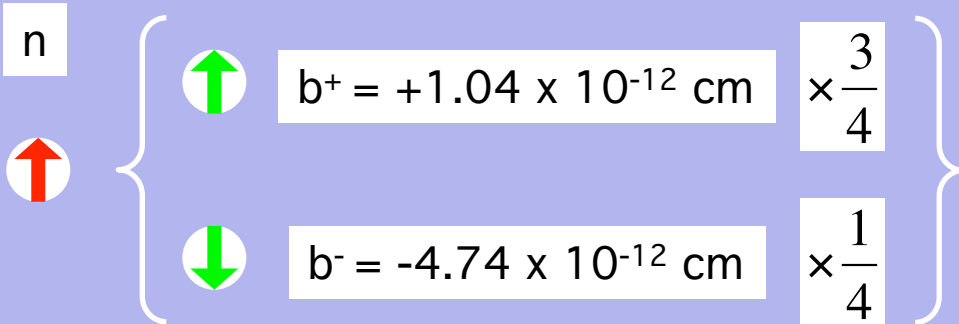
$\langle b^2 \rangle - \langle b \rangle^2 = 6.264$ barn

$\langle b \rangle^2 = 0.164$ barn

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{m,n} e^{i\vec{K}\cdot\vec{R}_{mn}} + N\left[\langle b^2 \rangle - \langle b \rangle^2\right]$$

## Deuterium

n

$b^+ = +0.95 \times 10^{-12}$ cm $\quad \times \dfrac{2}{3}$

$b^- = +0.10 \times 10^{-12}$ cm $\quad \times \dfrac{1}{3}$

$\langle b \rangle^2 = 0.444$ barn

$\langle b^2 \rangle - \langle b \rangle^2 = 0.161$ barn

$1\text{barn} = 10^{-24}\,\text{cm}^2$

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| Nuclide | $\sigma_{coh}$ | $\sigma_{inc}$ | Nuclide | $\sigma_{coh}$ | $\sigma_{inc}$ |
|---------|----------------|----------------|---------|----------------|----------------|
| $^1$H | 1.8 | 80.2 | V | 0.02 | 5.0 |
| $^2$H | 5.6 | 2.0 | Fe | 11.5 | 0.4 |
| C | 5.6 | 0.0 | Co | 1.0 | 5.2 |
| O | 4.2 | 0.0 | Cu | 7.5 | 0.5 |
| Al | 1.5 | 0.0 | $^{36}$Ar | 24.9 | 0.0 |

- Difference between hydrogen and deuterium
- Vanadium is used for containers

http://webster.ncnr.nist.gov/resources/n-lengths/

# Silica: neutrons .vs. X-rays
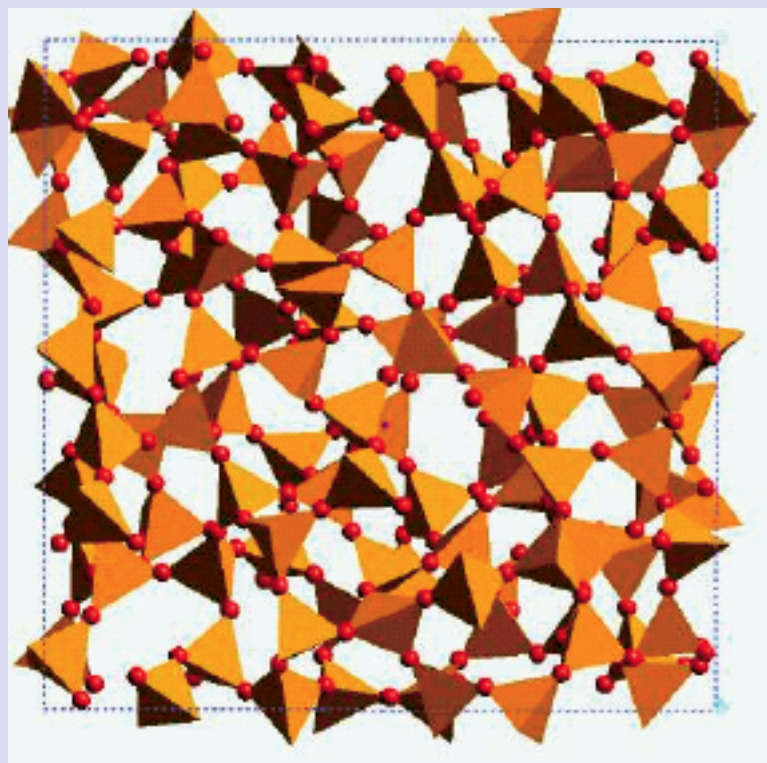


Amorphous $SiO_2$

## Total interference function

# Basic references
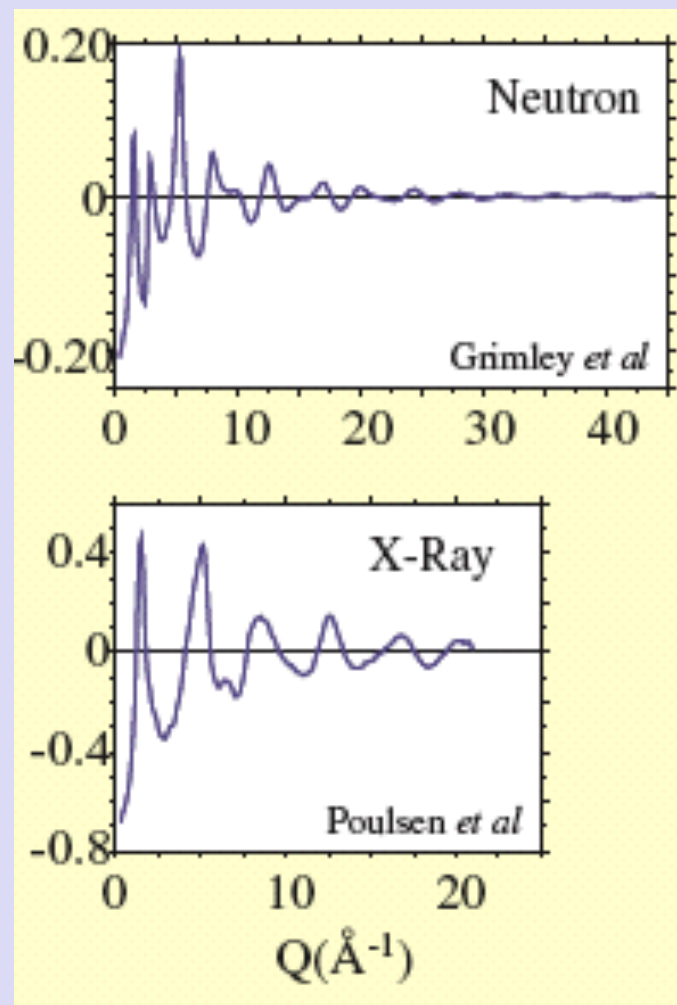
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