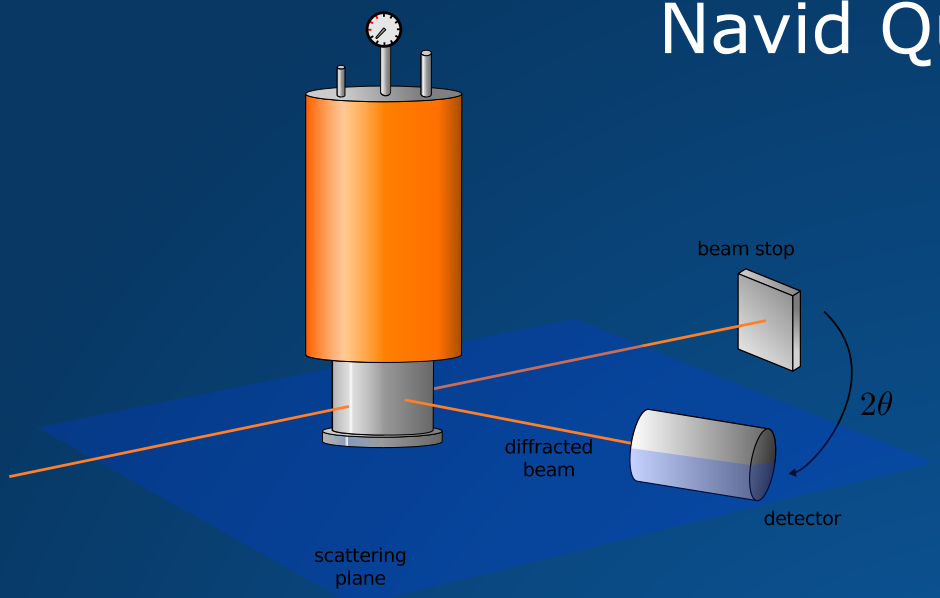
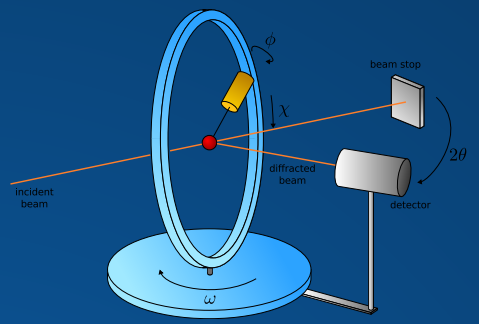
Neutron diffraction

Navid Qureshi (ILL, Grenoble)





14th Oxford School on Neutron Scattering

Scope of the lectures

- Diffraction techniques (X-rays, neutrons) are used to investigate crystalline solids, engineering materials, liquids, thin films, …

- Whatever the technique used (conventional powder or single crystal diffraction, small angle scattering, reflectometry, …) all of these refer to the coherent **elastic** scattering of a X-ray or neutron beam

- This lecture will focus on crystallography, i.e. the study of crystalline solids, which are described by infinite translational symmetry

- The scattered X-ray or neutron beams contain information which allow to reveal the 3-dimensional arrangement of atoms (and magnetic moments ⟶ Magnetism lecture by Prof. Wildes)

Outline

Today

- Crystallography

Direct lattice, symmetry operations, reciprocal lattice, Miller indices, ...

- Interaction neutron-sample

scattering by a potential, scattering length, form factor, structure factor, Debye Waller factor, …

- Diffraction condition

Bragg's law, Laue condition

Tomorrow

- Symmetry in reciprocal space

Friedel law, Laue groups, forbidden reflections, Ewald construction

- Basic diffractometer

monochromators, collimators, detectors, …

- Diffraction techniques

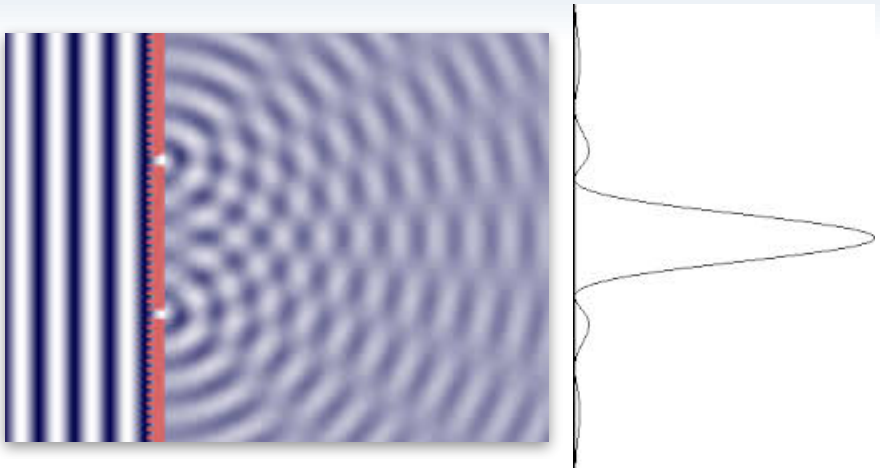
powder diffraction, single crystal diffraction, Laue diffraction, …

- Examples

Motivation

When waves (water, light, neutrons, electrons, …) pass through two slits whose distance is in the order of the wavelength, the scattered waves will interfere.

The interference scheme gives information about the distance of the slits.



Particles like neutrons can be associated with a de Broglie wavelength which is 1.8 Å for thermal neutrons.

Interatomic distances in solids are in the order of a few Ångstroms.

Neutrons are ideal to reveal the atomic arrangement in crystalline solids!

How to describe a crystalline material?

Direct lattice

An ideal crystal is an infinite sequence of identical structure units in 3D space.

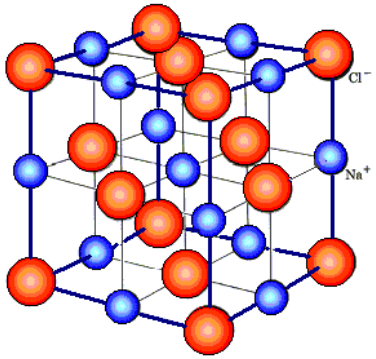
→ periodic structure

crystal = lattice + basis

infinite lattice of **equivalent** points

structure unit on each point

NaCl structure:

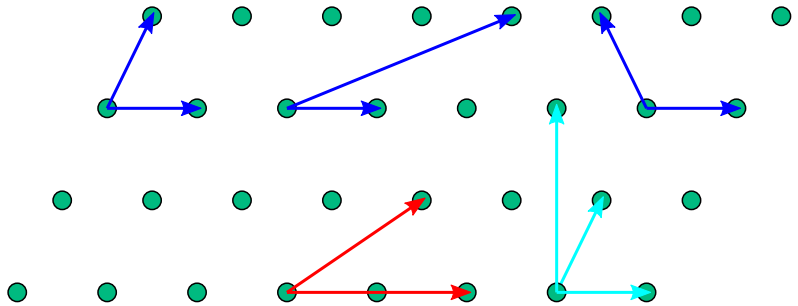


lattice vectors

OK

not OK

centered cell



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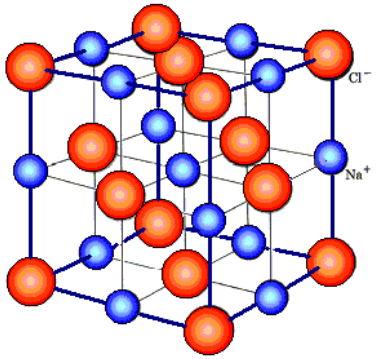
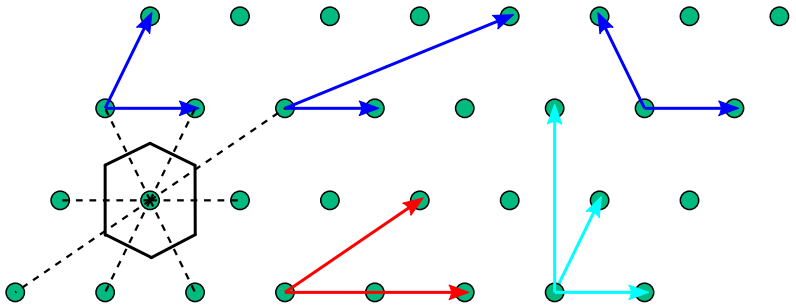
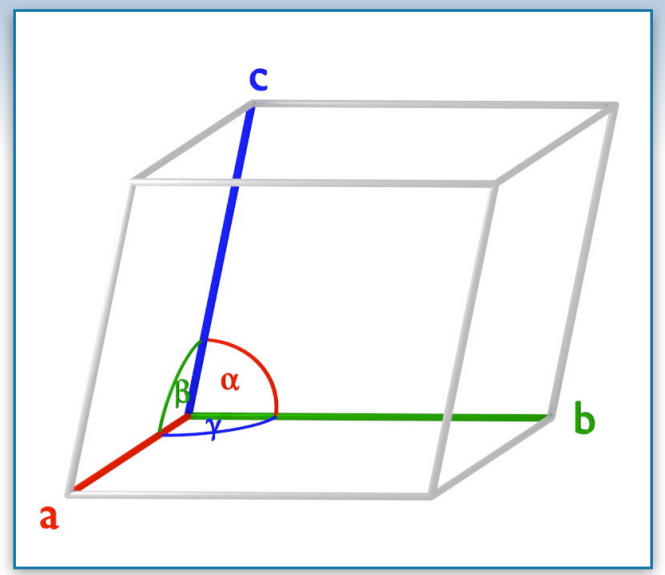




Wigner-Seitz cell

Direct lattice

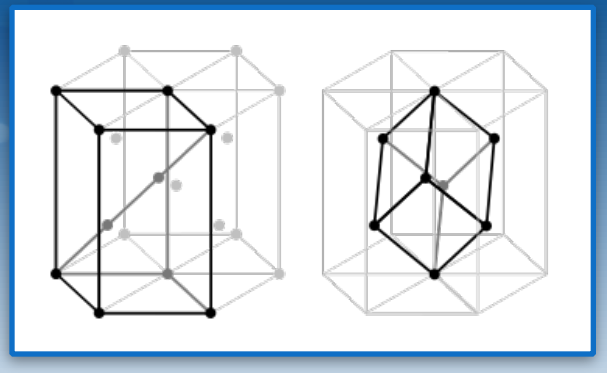
Crystal systems

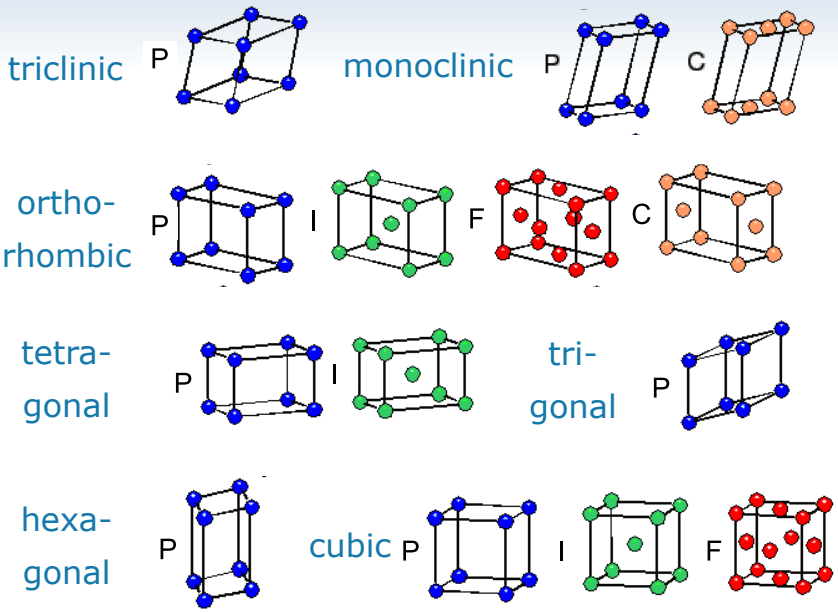


Crystal system	*Laue class*
triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$
monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$
orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$
trigonal	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$
hexagonal	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$
cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$

Direct lattice

Centering translations → 14 Bravais lattices



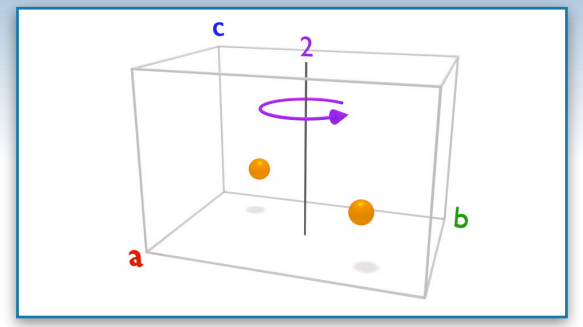


Centering type	*Symbol*	*Translations*
primitive	P	
one-face centered	A B C	*x, y+1/2, z+1/2* *x+1/2, y, z+1/2* *x+1/2, y+1/2, z*
body centered	I	*x+1/2, y+1/2, z+1/2*
face centered	F	*x, y+1/2, z+1/2* *x+1/2, y, z+1/2* *x+1/2, y+1/2, z*
rhombohedrally centered	R	*x+2/3, y+1/3, z+1/3* *x+1/3, y+2/3, z+2/3*

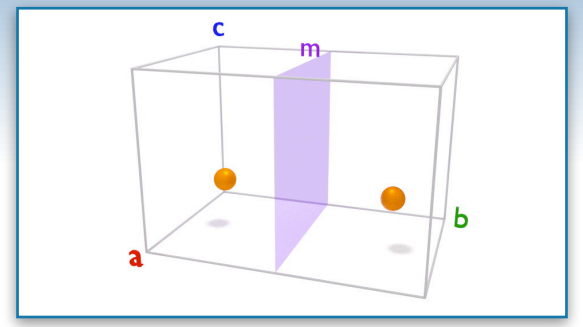
Direct lattice

Symmetry operations

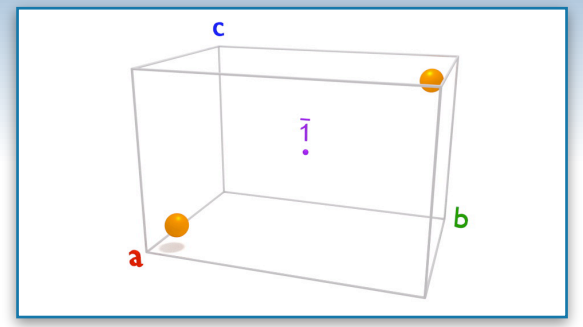
Rotations (order *n:* $2\pi/n$)



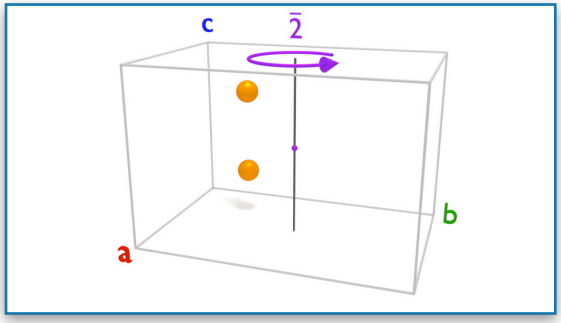
Mirror planes (m)



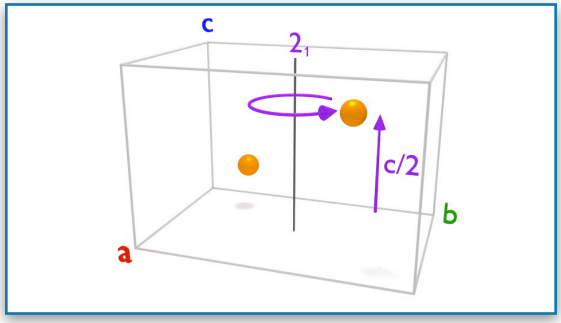
Inversion ($\bar{1}$)



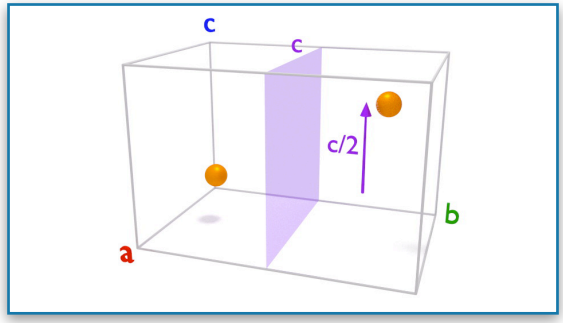
Roto-inversion ($\bar{n}$)



Screw axes (rot + trans)



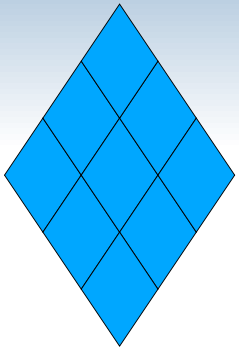
Glide planes (mirror + trans)



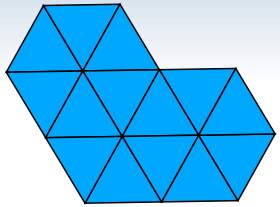
Direct lattice

Why no 5-fold rotation?

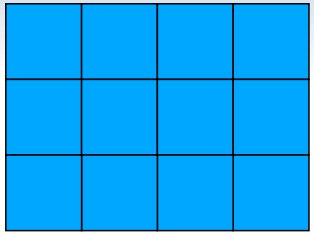
2-fold



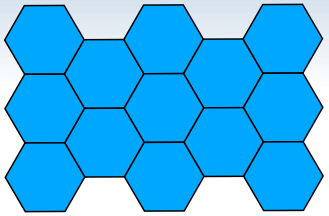
3-fold



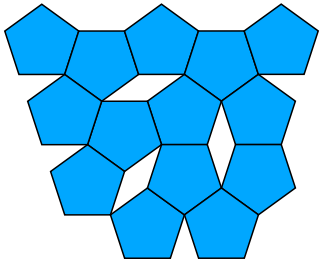
4-fold



6-fold



5-fold

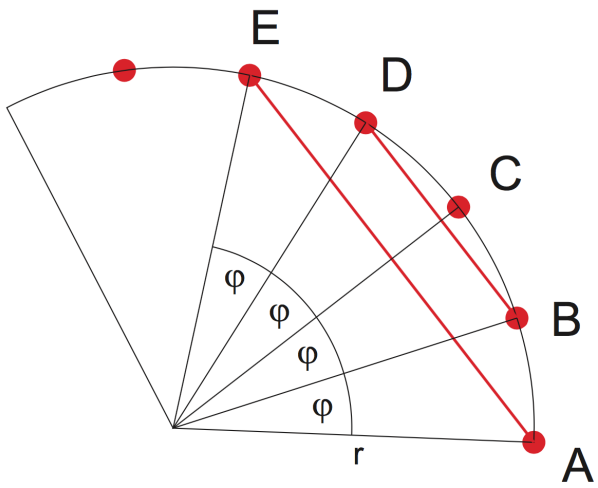


no gapless filling

Direct lattice

Why no 5-fold rotation?

5-fold rotation not compatible with translation symmetry:



Points generated by a rotation axis form a lattice plane.
Lattice plane needs to fullfil translation symmetry:

$$\overline{AE} = n \cdot \overline{BD}$$

$$\overline{AE} = 2r \cdot \sin(2\varphi) = 4r \sin\varphi \cos\varphi$$

$$\overline{BD} = 2r \sin\varphi$$

$$4r \sin\varphi \cos\varphi = n \cdot 2r \sin\varphi \Rightarrow \cos\varphi = \frac{n}{2}$$

$$n = -2, -1, 0, 1, 2 \Rightarrow \varphi = 180°, 120°, 90°, 60°, 0°$$

Only 1-, 2-, 3-, 4- and 6-fold rotation compatible with translation symmetry

Direct lattice

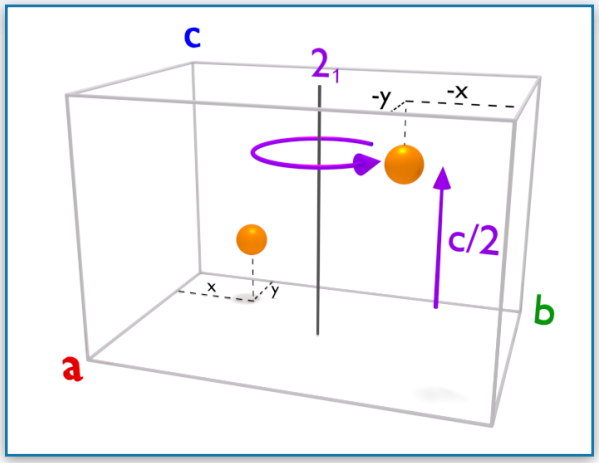
Symmetry operations

Mathematical description:

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

Seitz notation: (R|t)

Symmetry contained in the coordination triplet:
e.g. 2_1 screw axis along c: -x, -y, z+1/2



Direct lattice

Space groups

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

http://it.iucr.org/

International Tables for Crystallography

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Symmetry database

Direct lattice

Space groups

space group symbol

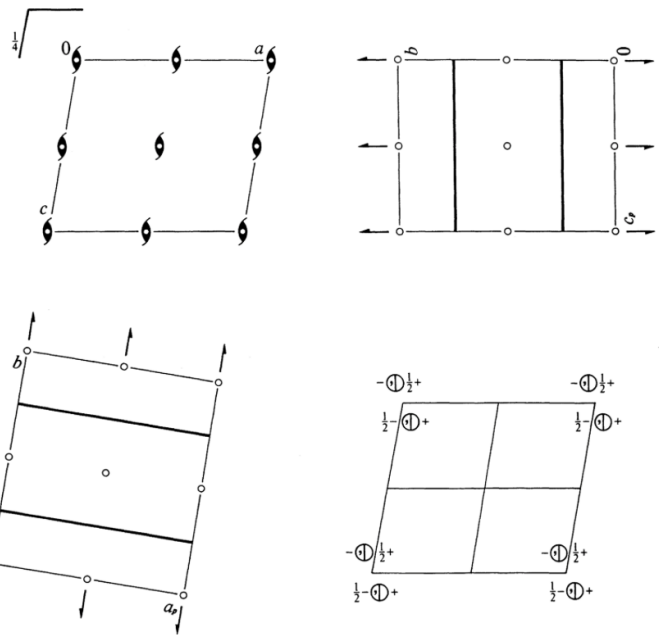
crystal class

symmetry operations

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

No. 11 $P12_1/m1$ **Patterson symmetry** $P12/m1$

UNIQUE AXIS *b*



Origin at -1 on 2_1

Asymmetric unit $0 \le x \le 1; 0 \le y \le 1/4; 0 \le z \le 1$

Symmetry operations

(1) 1 (2) 2(0, 1/2, 0) 0, y, 0 (3) -1 0, 0, 0 (4) *m* x, 1/4, z

Direct lattice

Space groups

space group symbol

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$P2_1/m$ C_{2h}^2 2/m — Monoclinic

No. 11 $P12_1/m1$ Patterson symmetry $P12/m1$

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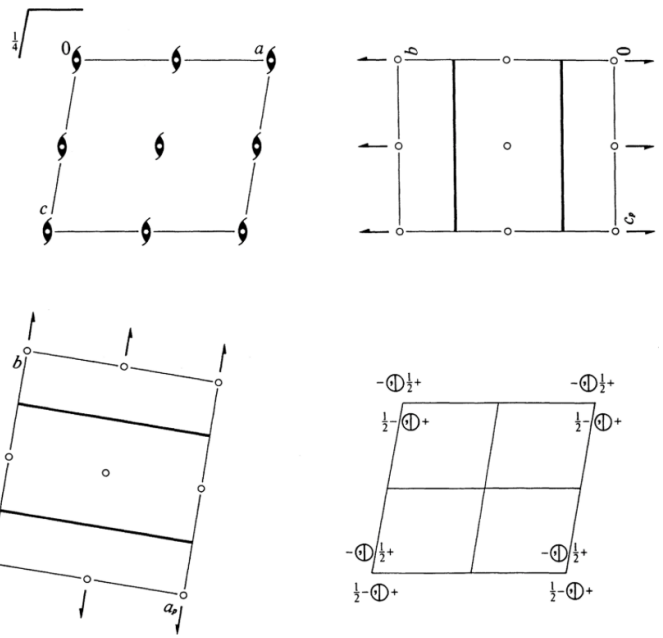

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Direct lattice

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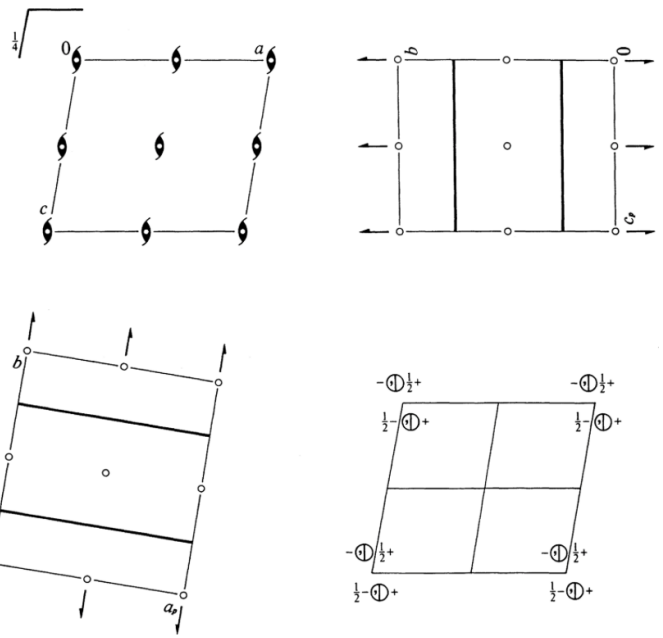

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(1) 1 (2) 2(0, 1/2, 0) 0, *y*, 0 (3) -1 0, 0, 0 (4) *m* *x*, 1/4, *z*

Direct lattice

Space groups

multiplicity

Wyckoff letter

site symmetry

extinction rules

Positions

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

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							Special: as above, plus
2	*e*	*m*	*x*, 1/4, *z*		-*x*, 3/4, -*z*		no extra conditions
2	*d*	-1	1/2, 0, 1/2		1/2, 1/2, 1/2		*hkl* : *k* = 2*n*
2	*c*	-1	0, 0, 1/2		0, 1/2, 1/2		*hkl* : *k* = 2*n*
2	*b*	-1	1/2, 0, 0		1/2, 1/2, 0		*hkl* : *k* = 2*n*
2	*a*	-1	0, 0, 0		0, 1/2, 0		*hkl* : *k* = 2*n*

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2	*d*	-1	1/2, 0, 1/2		1/2, 1/2, 1/2		*hkl* : *k* = 2*n*
2	*c*	-1	0, 0, 1/2		0, 1/2, 1/2		*hkl* : *k* = 2*n*
2	*b*	-1	1/2, 0, 0		1/2, 1/2, 0		*hkl* : *k* = 2*n*
2	*a*	-1	0, 0, 0		0, 1/2, 0		*hkl* : *k* = 2*n*

Direct lattice

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Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
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2	*e*	*m*	*x*, 1/4, *z*		-*x*, 3/4, -*z*	no extra conditions
2	*d*	-1	1/2, 0, 1/2		1/2, 1/2, 1/2	*hkl* : *k* = 2*n*
2	*c*	-1	0, 0, 1/2		0, 1/2, 1/2	*hkl* : *k* = 2*n*
2	*b*	-1	1/2, 0, 0		1/2, 1/2, 0	*hkl* : *k* = 2*n*
2	*a*	-1	0, 0, 0		0, 1/2, 0	*hkl* : *k* = 2*n*

Reciprocal lattice

Space of wave vectors

Crystal lattice is periodic → periodic functions to describe it: $\Psi(\mathbf{r}) = \exp(i\mathbf{kr})$

The reciprocal lattice of a Bravais lattice consists of all vectors **k** for which

$$\Psi(\mathbf{r}) = \exp(i\mathbf{kr}) = \Psi(\mathbf{r}+\mathbf{R}) = \exp[i\mathbf{k}(\mathbf{r}+\mathbf{R})]$$

$\mathbf{R}$ is a direct lattice vector

→ reciprocal lattice reflects the symmetry of the direct lattice

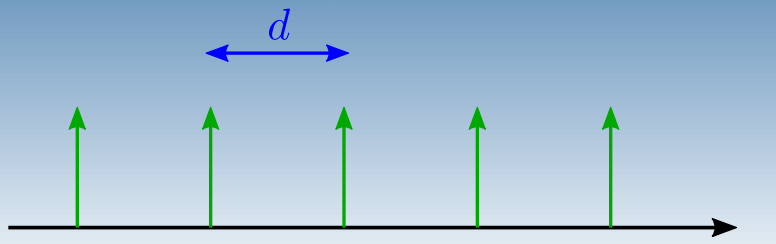
Which k-vectors build up the reciprocal space?

Reciprocal lattice

Example: 1D Dirac comb

Every periodic function $f(x) = f(x + \lambda)$
can be expressed by a Fourier series with

$$k = m \cdot 2\pi/\lambda$$



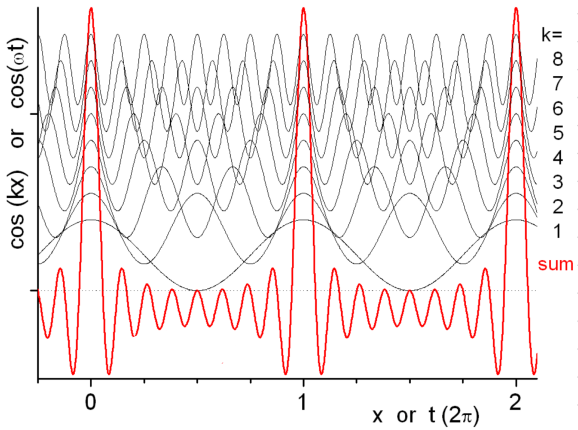
$$f(x) = \sum_n \delta(x - nd) \quad n \in \mathbb{Z}$$

Calculate Fourier coefficients by Fourier transform:

$$F(k) = \int \sum_{m=1}^{\infty} \cos(m \cdot \tfrac{2\pi}{d} \cdot x) \cdot e^{-ikx} = \sum_m \delta(k - m \cdot \tfrac{2\pi}{d})$$

with

$$FT[\cos(k_0 x)] = \delta(k - k_0) + \delta(k + k_0)$$



$$f(x) = \sum_{m=1}^{\infty} \cos(m \cdot \tfrac{2\pi}{d} \cdot x)$$

Reciprocal lattice

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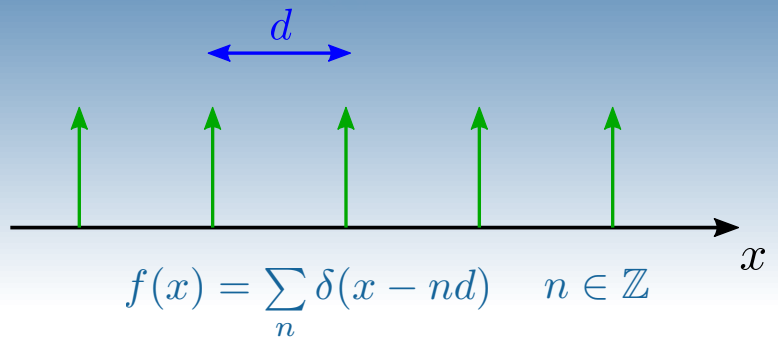
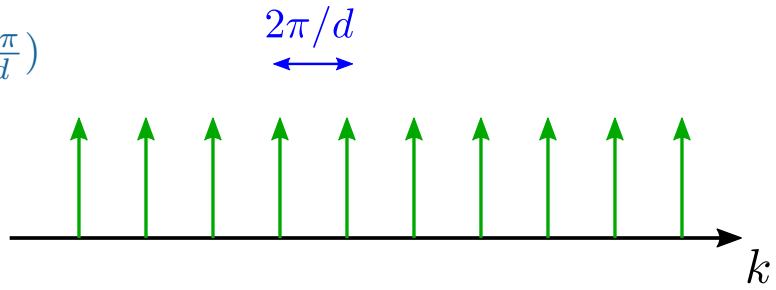


Calculate Fourier coefficients by Fourier transform:

$$F(k) = \int \sum_{m=1}^{\infty} \cos(m \cdot \tfrac{2\pi}{d} \cdot x) \cdot e^{-ikx} = \sum_m \delta(k - m \cdot \tfrac{2\pi}{d})$$

with

$$FT[\cos(k_0 x)] = \delta(k - k_0) + \delta(k + k_0)$$



→ reciprocal lattice of a Dirac comb is a Dirac comb with $2\pi/d$

Reciprocal lattice

Bravais lattice in 3D

Consider a direct lattice L with a δ function on each lattice point:

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

Set of k-vectors must correspond to reciprocal lattice vectors **G**, hence …

$$\Psi(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{R}) \Rightarrow e^{i\mathbf{G}\mathbf{r}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})} \Rightarrow e^{i\mathbf{G}\mathbf{R}} = 1 \text{ or } \mathbf{G}\mathbf{R} = n \cdot 2\pi$$

which is fulfilled for the **reciprocal lattice vectors**:

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \qquad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \qquad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$

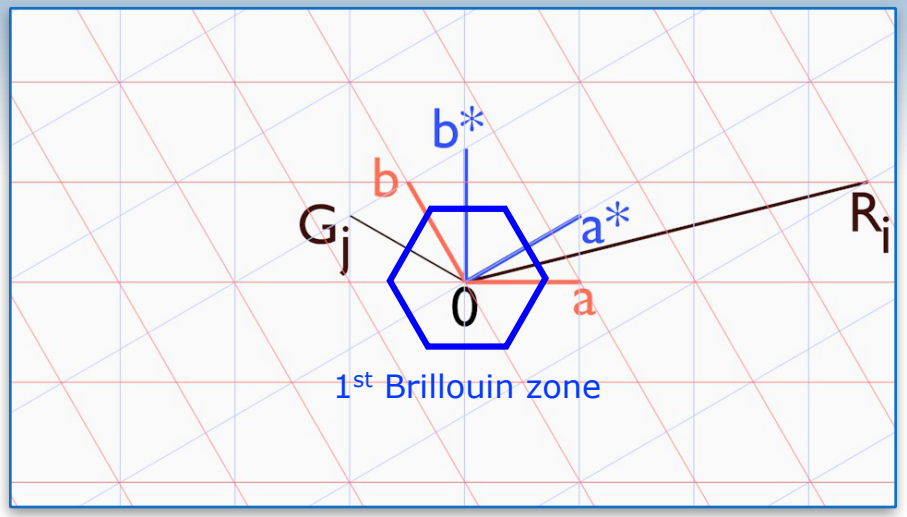
$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij}$$

Each direct lattice has a reciprocal lattice.

The reciprocal lattice of a reciprocal lattice is the direct lattice itself.

Reciprocal lattice

Construction of reciprocal lattice $\mathbf{a}_j^*$ from direct lattice $\mathbf{a}_i$



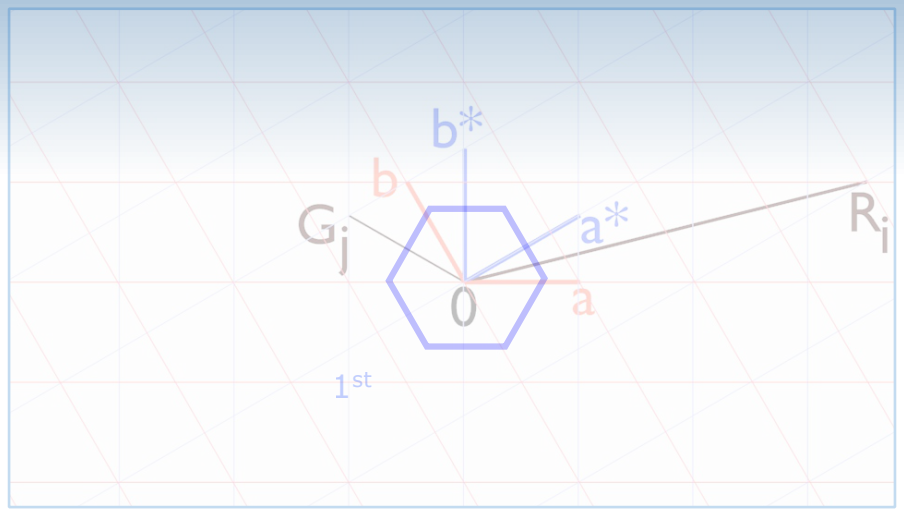
The scalar product of any direct lattice vector R_i and reciprocal lattice vector G_j is an integer (times 2π).

A reciprocal lattice vector is expressed by the Miller indices *hkl*.

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

Reciprocal lattice

Construction of reciprocal lattice $\mathbf{a}_i$ $\mathbf{a}_j^*$

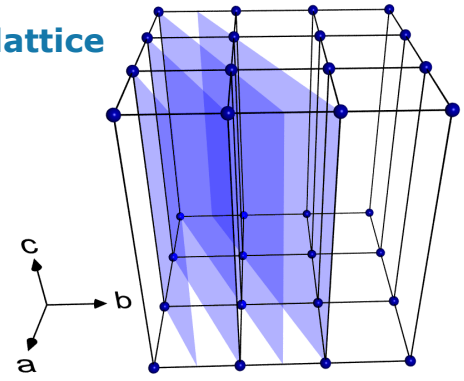


The scalar product of any direct lattice vector R
an integer (times 2

A reciprocal lattice vector is expressed by the Miller indices *hkl*.

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

Direct lattice



reciprocal integer intersections with main axes:

a: -1 b: 1/2 c: ∞ ⇒ (-1 2 0)

Every point in reciprocal space represents a set of direct lattice planes.

The reciprocal lattice vector is perpendicular to these planes.

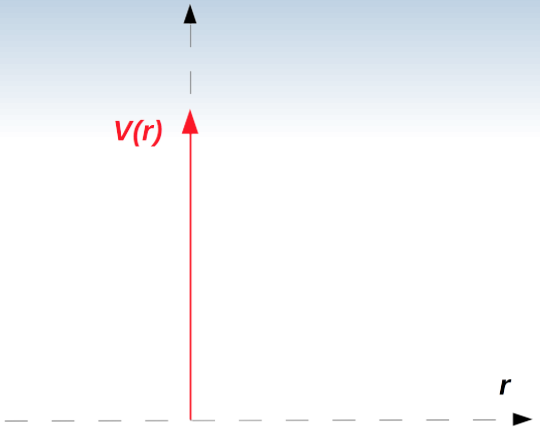
Interaction neutron-sample

Nuclear scattering

- mediated by strong force, short ranged (fm = 10^{-15} m)

- neutron wavelength much larger (10^{-10} m)
  → cannot probe internal 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 0 except very close to the nucleus



$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b\delta^3(\mathbf{r})$$

advantage: neutron senses atomic position and not the electron cloud (bonds)

Scattering by a potential

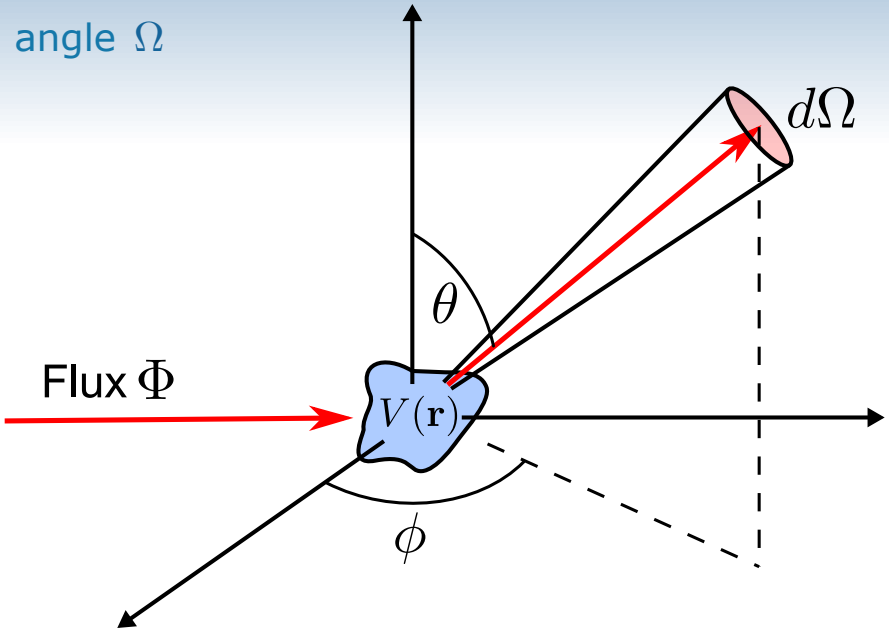
Scattering cross section

Number of neutrons *n* detected in solid angle Ω

$$\underbrace{dn}_{\mathrm{n}s^{-1}} = \underbrace{\Phi}_{\mathrm{n}cm^{-2}\mathrm{s}^{-1}} \cdot \underbrace{d\Omega}_{1} \cdot \underbrace{\sigma(\theta,\phi)}_{cm^2}$$

σ has the unit of a surface

usually in barns = 10^{-24} cm^2



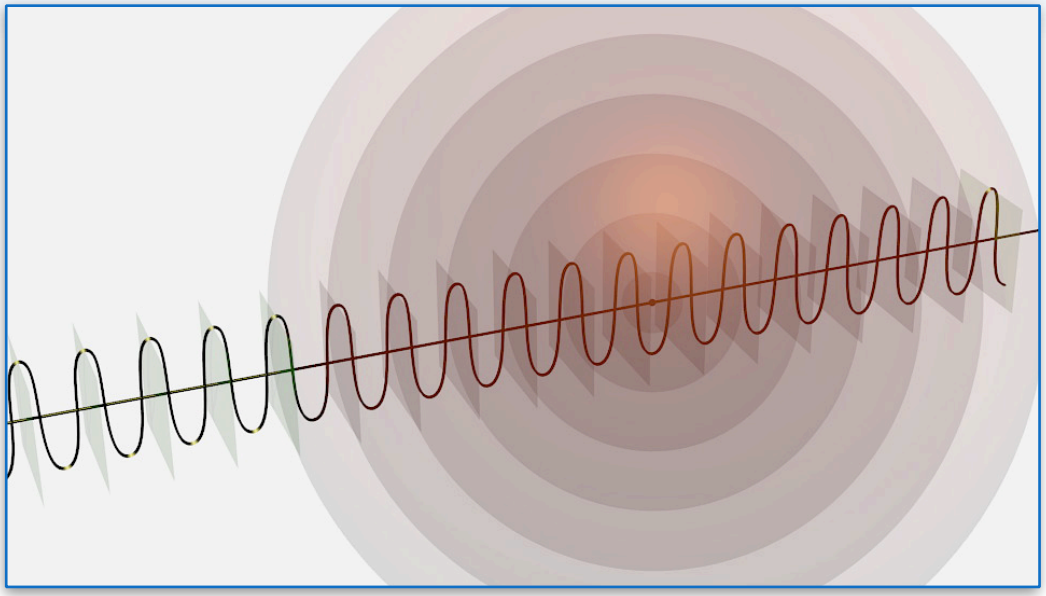
Scattering by a potential

Nuclear scattering

The wave function at a spatial position r = sum of transmitted and scattered spherical wave function

$$v_k^{scat}(\mathbf{r}) = e^{i\mathbf{kr}} + f_k(\theta,\varphi)\frac{e^{ikr}}{r}$$

Only $f_k(\theta,\varphi)$ depends on the scattering potential $V(\mathbf{r})$.



Scattering by a potential

Nuclear scattering

In the quantum mechanical treatment of scattering by a central potential, the stationary states $\varphi(\mathbf{r})$ verify:

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

(from Cohen-Tannoudji, Quantum Mechanics, Volume 2 Chapter 8)

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

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

where G_+ is the outgoing Green's function used to solve the differential equation by using:

$$(\Delta + k^2)G(\mathbf{r}) = \delta(\mathbf{r})$$

it can be shown that:

$$G_\pm(\mathbf{r}) = -\frac{1}{4\pi} \frac{e^{\pm i\mathbf{kr}}}{r}$$

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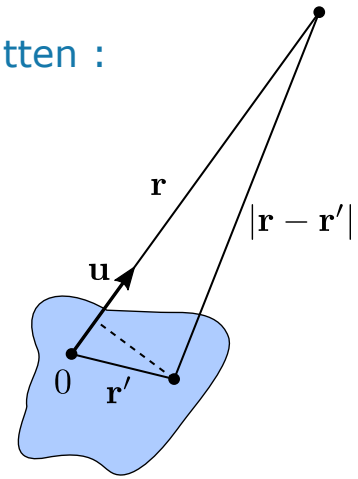

asymptotic behaviour $r \to \infty$

$$|\mathbf{r}-\mathbf{r}'| \approx r - \mathbf{ur}'$$

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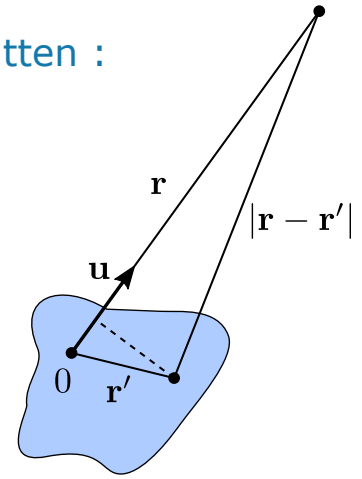
$$v_k^{scat}(\mathbf{r}) = e^{i\mathbf{kr}} + f_k(\theta,\varphi)\frac{e^{ikr}}{r} \approx e^{i\mathbf{kr}} - \frac{1}{4\pi}\frac{e^{ikr}}{r}\frac{2\mu}{\hbar^2}\int e^{-ik\mathbf{ur}'}V(\mathbf{r}')v_k^{scat}(\mathbf{r}')d^3r'$$

$$f_k(\theta,\varphi) = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int e^{-ik\mathbf{ur}'}V(\mathbf{r}')v_k^{scat}(\mathbf{r}')d^3r'$$



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Scattering by a potential

Born expansion

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

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

Simple change of notation ($r \rightarrow r'$ and $r' \rightarrow r''$) :

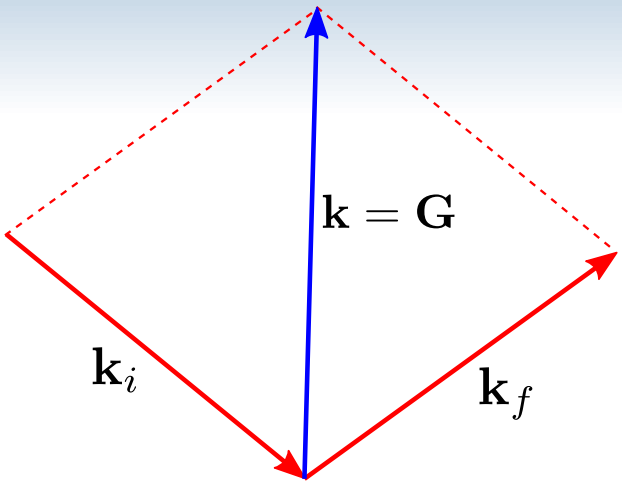
$$v_k^{scat}(\mathbf{r}') = e^{i\mathbf{kr}'} + \frac{2\mu}{\hbar^2}\int G_+(\mathbf{r}'-\mathbf{r}'')V(\mathbf{r}'')v_k^{scat}(\mathbf{r}'')d^3r''$$

Born expansion:

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

Scattering by a potential

Conventions for this lecture



$\mathbf{k}_i$: initial wavevector

$\mathbf{k}_f$: final wavevector

$\mathbf{k}$: momentum transfer, scattering vector

$\mathbf{G}$: reciprocal lattice vector

Elastic scattering: $|\mathbf{k}_i| = |\mathbf{k}_f| = k$

Scattering by a potential

Born approximation

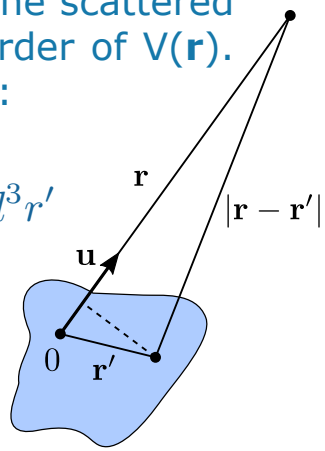
Born expansion:

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

Inserting this into the scattered amplitude would give the Born expansion of the scattered amplitude. If the potential V(**r**) is weak, we can limit ourselves to the first order of V(**r**). This is the **Born approximation**. The scattered amplitude therefore becomes:

$$f_k(\theta,\varphi) = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int e^{-ik\mathbf{u}\mathbf{r}'}V(\mathbf{r}')v_k^{scat}(\mathbf{r}')d^3r' = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int e^{-ik\mathbf{u}\mathbf{r}'}V(\mathbf{r}')e^{i\mathbf{k}_i\mathbf{r}'}d^3r'$$

$$= -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int e^{-i(\mathbf{k}_f-\mathbf{k}_i)\mathbf{r}'}V(\mathbf{r}')d^3r' = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int e^{-i\mathbf{k}\mathbf{r}'}V(\mathbf{r}')d^3r'$$



The scattering amplitude is related to the **Fourier transform of the potential function.**

Scattering by a potential

Born approximation

The scattering amplitude is related to the **Fourier transform of the potential function.**

$$f_k(\theta,\phi) = -\frac{1}{4\pi}\frac{2\mu}{\hbar^2}\int V(\mathbf{r})e^{-i\mathbf{kr}}d^3r$$

With the Fermi pseudo potential for neutron scattering from a nucleus $V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b\delta^3(\mathbf{r})$

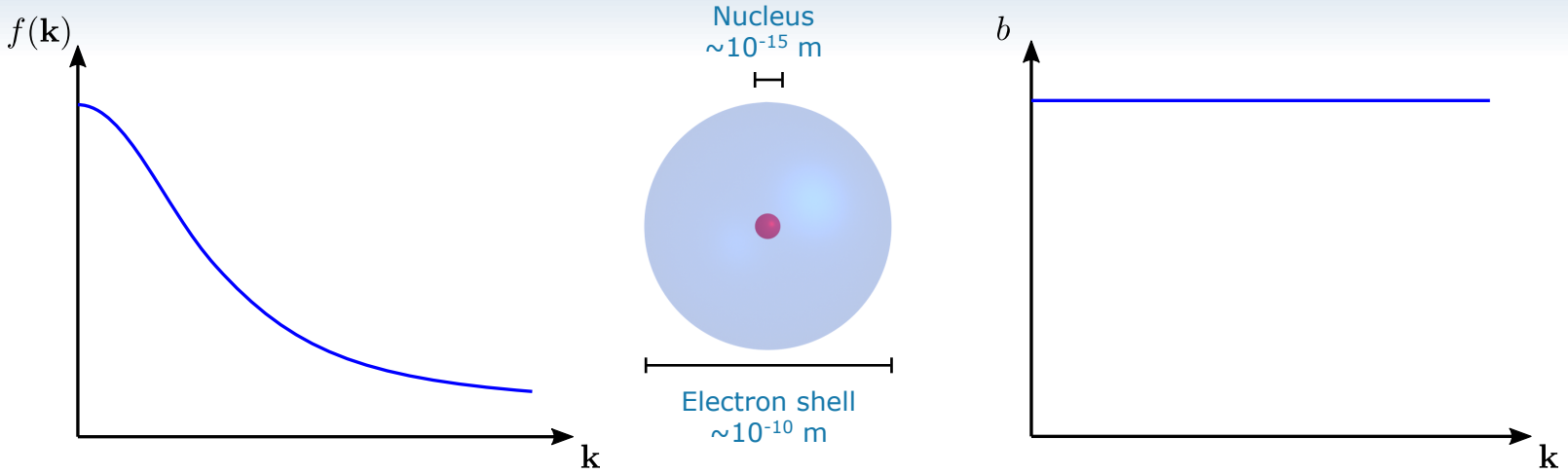
$$|f_k(\theta,\phi)| = b$$

Neutron scattering from a nucleus is isotropic!

Scattering by a potential

Atomic form factor or scattering length

The amplitude of the scattered wave (the Fourier transform of the potential function) is called the atomic **form factor** *f* (X-rays) or **scattering length** *b* (neutrons).

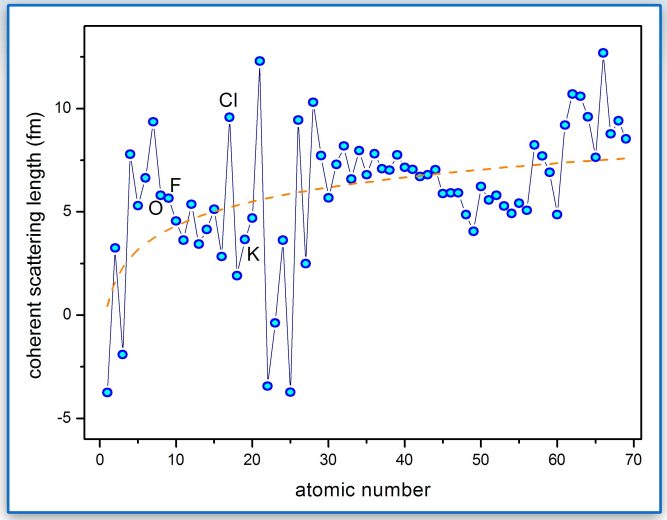


advantage with neutrons: scattered intensity does not drop with increasing scattering angle

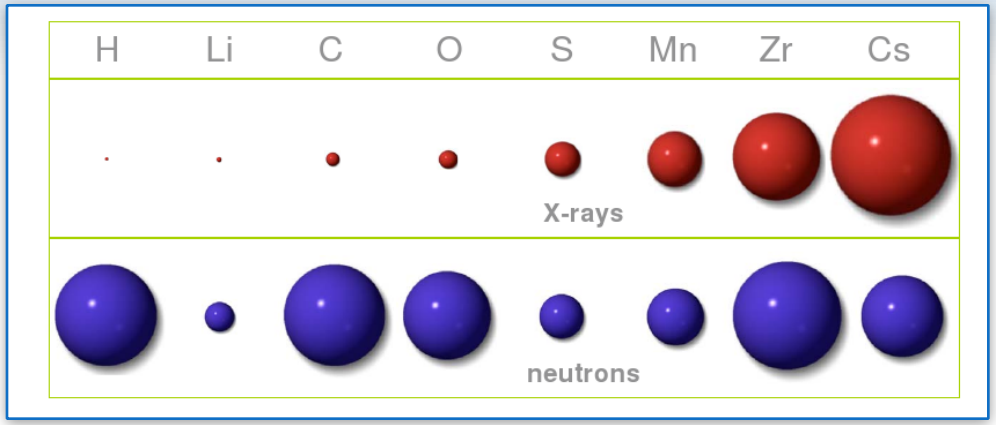
Scattering by a potential

Nuclear scattering

Scattering lengths (analog to X-ray form factor)



superposition of resonance scattering with slowly increasing potential scattering due to atomic weight

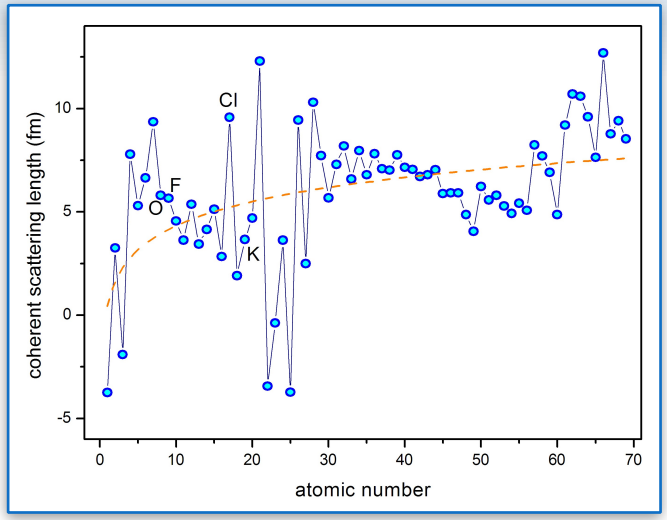


advantages: contrast between neighbouring elements
light elements can be measured easily
isotope effect (b_H=-3.7, b_D=6.8)

Scattering by a potential

Nuclear scattering

Scattering lengths (analog to X-ray form factor)

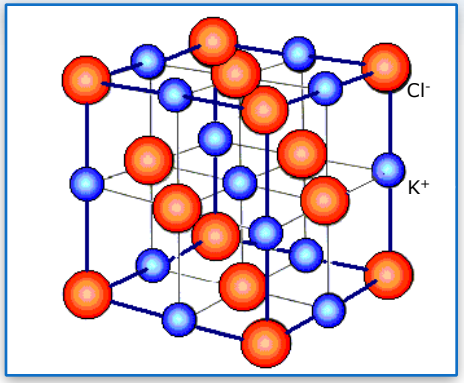


superposition of resonance scattering with slowly increasing potential scattering due to atomic weight

Example KCl:

scattering lengths of K and Cl are very different ⟶ strong contrast

X-rays would see a primitive cell with half the lattice constant



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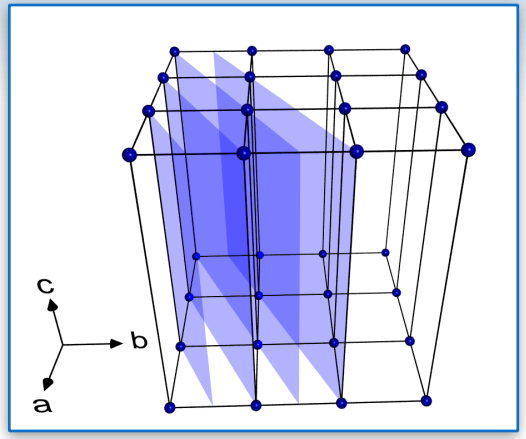
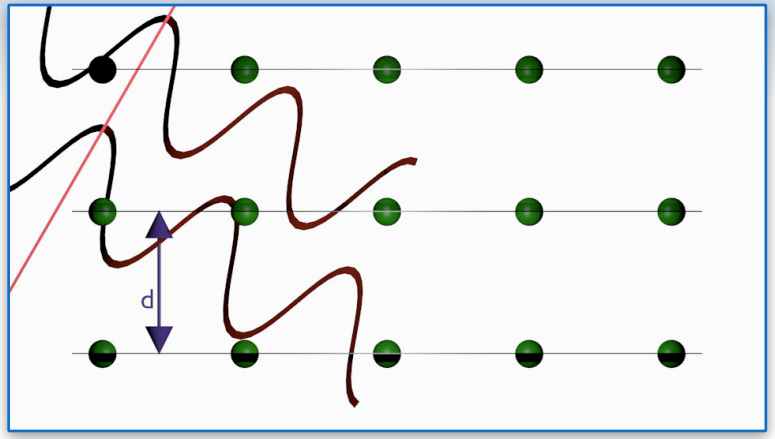
Diffraction condition

Bragg's law

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



lattice planes with Miller indices *hkl*
(hkl) intercepts real cell axes at a/h b/k c/l
d is the distance between the planes



Diffraction can be considered as the coherent superposition of scattered waves from this set of planes

Diffraction condition

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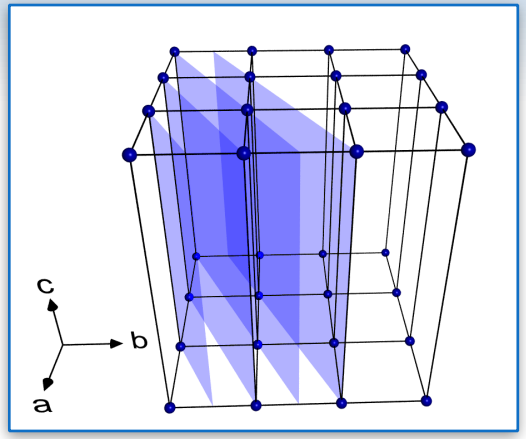

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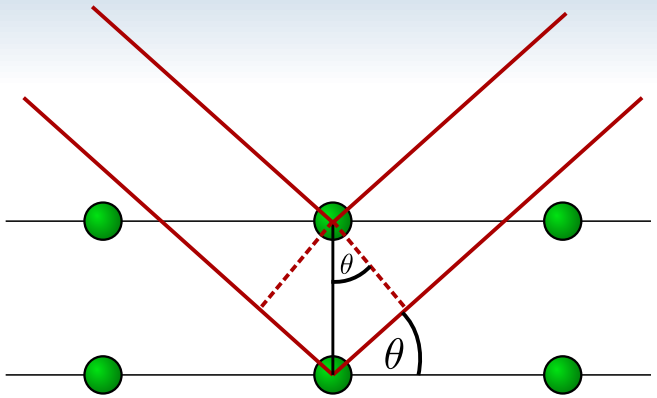


Path length difference: $2d\sin\theta$
Constructive interference: $n \cdot \lambda$
Bragg law: $n\lambda = 2d\sin\theta$

Diffraction condition

Laue condition (equivalent to Bragg's law)

Scattering of plane wave exp(i**kr**) from two lattice points at 0 and **R**

The path difference is:

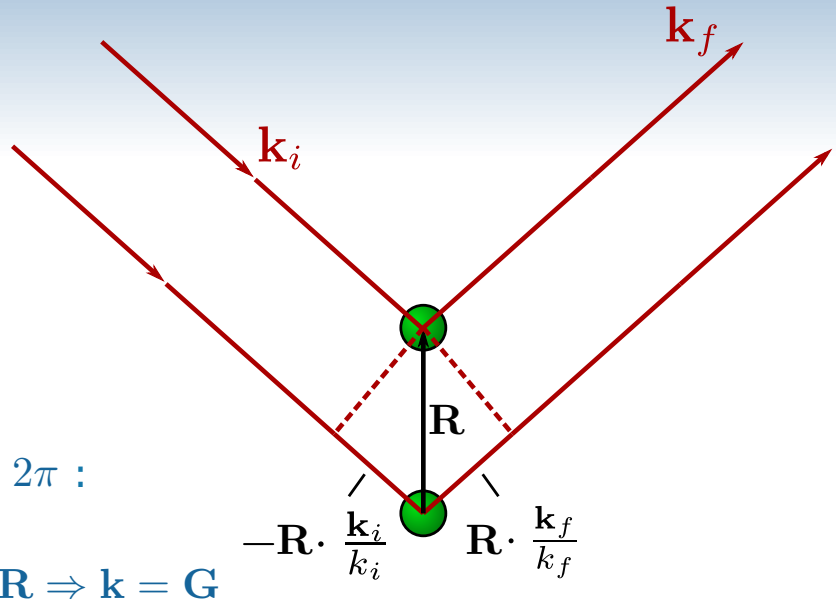
$$\Delta s(\mathbf{R}) = \mathbf{R} \cdot \frac{\mathbf{k}_f}{k_f} - \mathbf{R} \cdot \frac{\mathbf{k}_i}{k_i}$$

Constructive interference for:

$$\Delta s = n \cdot \lambda = n \cdot \frac{2\pi}{k} \qquad (k = k_i = k_f)$$

With definition of reciprocal lattice $\mathbf{G} \cdot \mathbf{R} = n \cdot 2\pi$:

$$\Delta s \cdot k = \mathbf{R} \cdot (\mathbf{k}_f - \mathbf{k}_i) = \mathbf{R} \cdot \mathbf{k} = n \cdot 2\pi = \mathbf{GR} \Rightarrow \mathbf{k} = \mathbf{G}$$



Momentum transfer equal to a lattice vector ⟶ Crystal can only provide discrete momentum kicks

Scattering from a unit cell

Structure factor (nuclear scattering)

imagine two scattering potentials (atoms), the first at 0, the second at **r**

The path difference is:

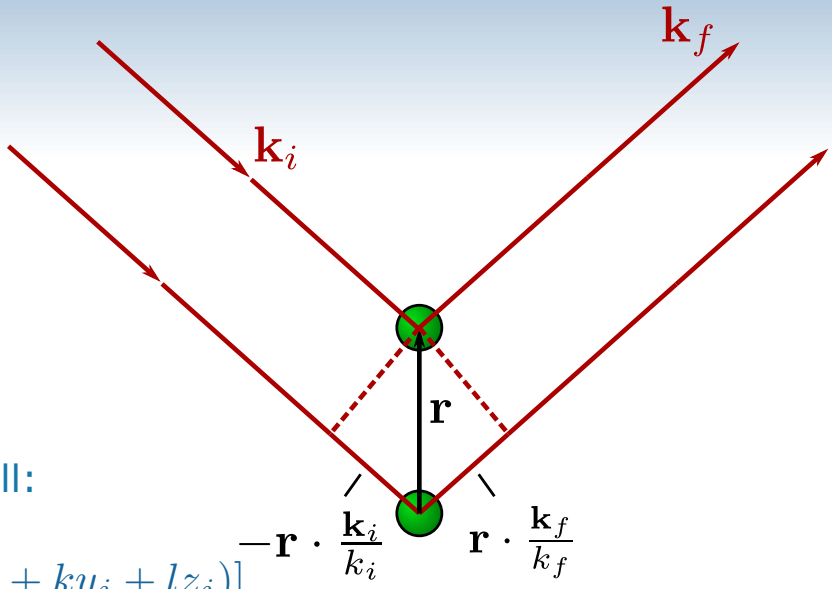
$$\Delta s(\mathbf{r}) = \mathbf{r} \cdot \frac{\mathbf{k}_f}{k_f} - \mathbf{r} \cdot \frac{\mathbf{k}_i}{k_i}$$

Therefore, the phase difference is:

$$\varphi(\mathbf{r}) = 2\pi \frac{\Delta s}{\lambda} = k\Delta s = (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} = \mathbf{G} \cdot \mathbf{r}$$

Sum up phase differences over atoms in unit cell:

$$F(hkl) = \sum_j b_j \exp(i\mathbf{G}\mathbf{r}_j) = \sum_j b_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$



Structure factor *F(hkl)* is the Fourier transform of the unit cell scattering potential.

Scattering from a unit cell

The phase problem

Now we know how to calculate the structure factor:

$$F(hkl) = \sum_j b_j \exp(i\mathbf{G}\mathbf{r}_j) = \sum_j b_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

BUT… a diffraction experiment yields the intensity of the scattered wave:

$$I \sim F^2$$

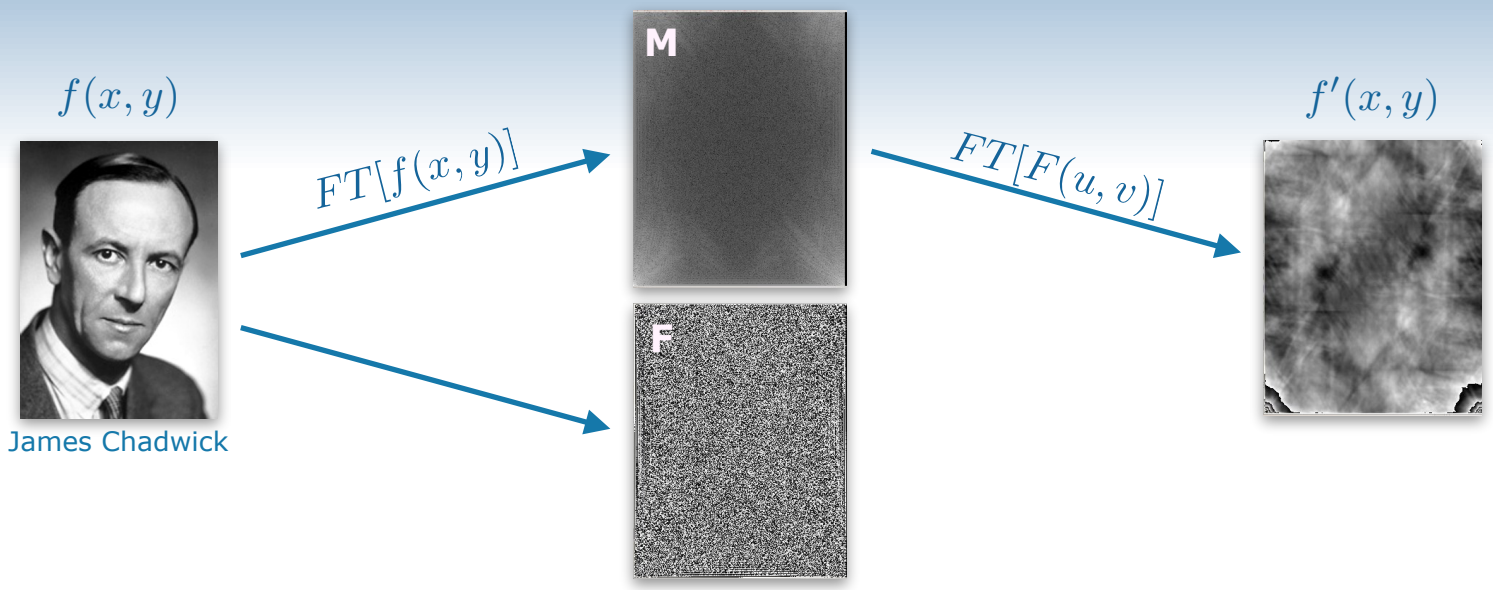
Important information is lost as only the amplitude can be recovered.
This is known as the phase problem in crystallography.

Consequence: The scattering potential cannot be determined without a model.

Scattering from a unit cell

The phase problem

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



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Scattering from a unit cell

Debye-Waller factor

Until now our derivation of the structure factor is only valid for fixed atomic positions, i.e. T = 0 K.

One has to consider the atomic displacement due to thermal motion!
Atoms may have very large displacements with respect to the Fermi length (up to 10% of atomic distance).

Atomic position can be separated into an equilibrium position and a time-dependent displacement:

$$F = \sum_j \exp(i\mathbf{Gr}) = \sum_j \exp[i\mathbf{G}(\mathbf{r}_{j,0}+\mathbf{u}_j(t))] = \sum_j \exp(i\mathbf{Gr}_{j,0})\langle\exp[i\mathbf{Gu}_j(t)]\rangle$$

Debye-Waller factor

For small displacements:

$$\langle\exp[i\mathbf{Gu}_j(t)]\rangle \approx 1+i\langle\mathbf{Gu}_j(t)\rangle-\tfrac{1}{2}\langle[\mathbf{Gu}_j(t)]^2\rangle$$

Scattering from a unit cell

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$$\langle\exp[i\mathbf{Gu}_j(t)]\rangle \approx 1+\underbrace{i\langle\mathbf{Gu}_j(t)\rangle}_{0}-\tfrac{1}{2}\langle[\underbrace{\mathbf{Gu}_j(t)}_{\langle\cos\theta\rangle=1}]^2\rangle = 1-\tfrac{1}{2}G^2\langle u_j^2(t)\rangle \approx \exp[-\tfrac{1}{2}G^2\langle u_j^2(t)\rangle]$$

Scattering from a unit cell

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Atoms may have very large displacements with respect to the Fermi length (up to 10% of atomic distance)

Atomic position can be separated into an equilibrium position and a time-dependent displacement:

$$F = \sum_j \exp(i\mathbf{Gr}) = \sum_j \exp[i\mathbf{G}(\mathbf{r}_{j,0}+\mathbf{u}_j(t))] = \sum_j \exp(i\mathbf{Gr}_{j,0})\langle\exp[i\mathbf{Gu}_j(t)]\rangle$$

Debye-Waller factor

For small displacements:

$$\langle\exp[i\mathbf{Gu}_j(t)]\rangle \approx 1+\underbrace{i\langle\mathbf{Gu}_j(t)\rangle}_{0}-\tfrac{1}{2}\langle[\underbrace{\mathbf{Gu}_j(t)}_{\langle\cos\theta\rangle=1}]^2\rangle = 1-\tfrac{1}{2}G^2\langle u_j^2(t)\rangle \approx \exp[-\tfrac{1}{2}G^2\langle u_j^2(t)\rangle]$$

With $G = \frac{4\pi\sin\theta}{\lambda}$:

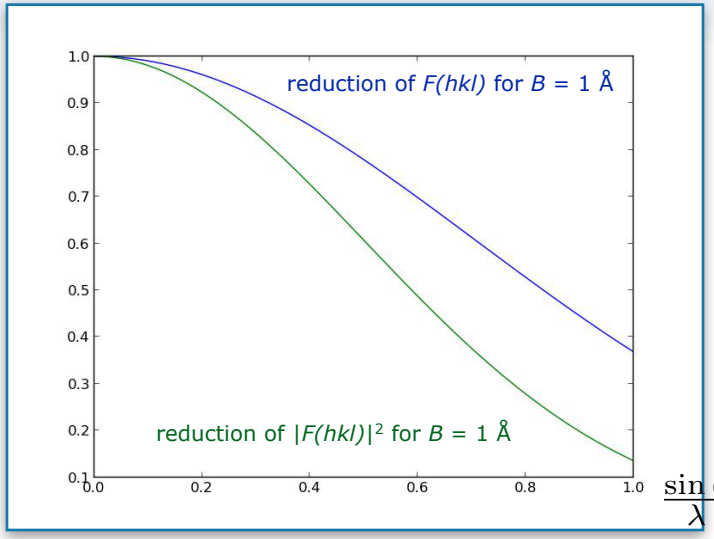
$$F = \sum_j \exp(i\mathbf{Gr}_{j,0})\exp(-8\pi^2\langle u_j^2\rangle\tfrac{\sin^2\theta}{\lambda^2}) = \sum_j \exp(i\mathbf{Gr}_{j,0})\exp(-B_j\tfrac{\sin^2\theta}{\lambda^2})$$

with the isotropic displacement parameter: $B_j = 8\pi^2\langle u_j^2\rangle$

Scattering from a unit cell

Debye-Waller factor

Scattering function is damped at high momentum transfer

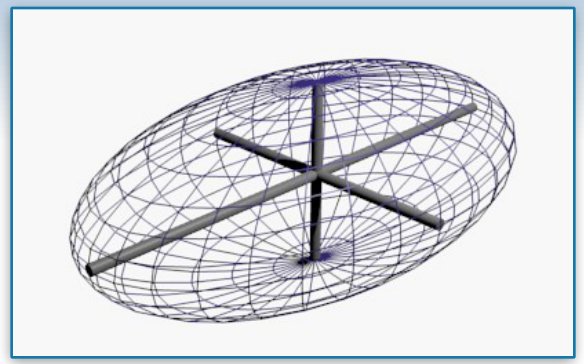


Effect on measured peaks:

Intensity is reduced, but the peak width and the position stay the same!

Scattering from a unit cell

Anisotropic displacement parameters



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).

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

$$F(hkl) = \sum_j \exp(i\mathbf{G}\mathbf{r}_{j,0}) \exp[-2\pi^2 \langle (\mathbf{u}\mathbf{G})^2 \rangle]$$

Summary

What have we learned so far?

Crystals have a 3D periodicity and further symmetry properties.
Classification into crystal systems, Bravais lattices and space groups.

Every direct lattice has a reciprocal lattice. It consists of the **k** vectors of the scattered waves.
a* is perpendicular to b and c, b* is perpendicular to c and a, …

The scattering length is the Fourier transform of the potential function.
The structure factor is the Fourier transform of the unit cell potential functions.

Atomic displacements reduce the scattered intensity due to the Debye-Waller factor.
Crystal structures need to be solved using models (phase problem).

Outline

Yesterday

- Crystallography

Direct lattice, symmetry operations, reciprocal lattice, Miller indices, ...

- Interaction neutron-sample

scattering by a potential, scattering length, form factor, structure factor, Debye Waller factor, …

- Diffraction condition

Bragg's law, Laue condition

Today

- Symmetry in reciprocal space

Friedel law, Laue groups, forbidden reflections, Ewald construction

- Basic diffractometer

monochromators, collimators, detectors, …

- Diffraction techniques

powder diffraction, single crystal diffraction, Laue diffraction, …

- Examples

Symmetry in reciprocal space

Friedel law

… relates inverse Q points and stems from the property of Fourier transforms of real functions:

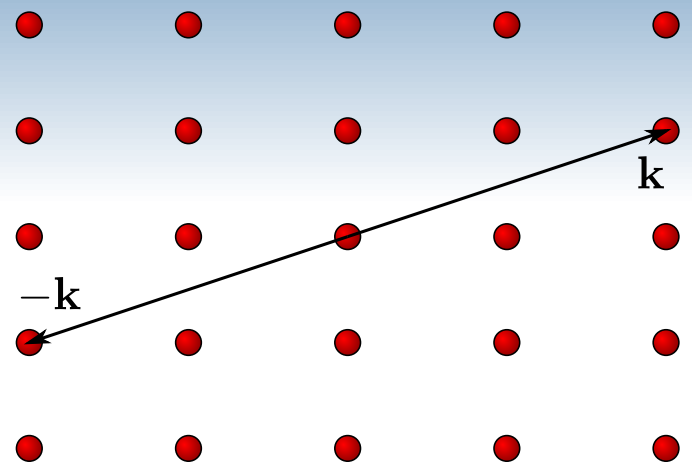
$$F(\mathbf{k}) = \sum_j b_j \exp(i\mathbf{k}\mathbf{r}_j)$$

if b_j is real then:

$$F(-\mathbf{k}) = \sum_j b_j \exp(-i\mathbf{k}\mathbf{r}_j) = F^*(\mathbf{k})$$

since the scattered intensity is proportional to FF^*

$$I(\mathbf{k}) = F(\mathbf{k})F^*(\mathbf{k}) = F^*(-\mathbf{k})F(-\mathbf{k}) = I(-\mathbf{k})$$



→ scattered intensities of Friedel pairs are equal if b_j are real
reciprocal space has inversion symmetry even if the real space has not

Symmetry in reciprocal space

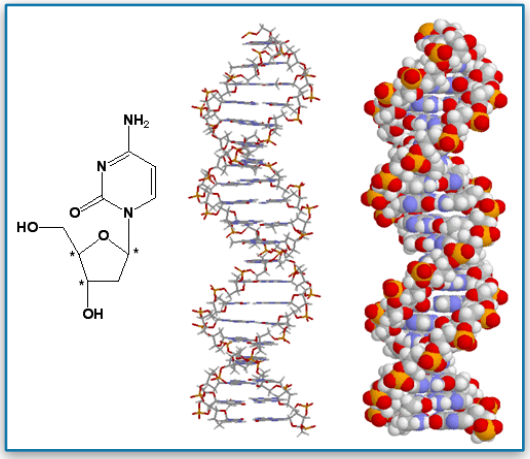
Friedel law

… is violated when the neutron energy is close to a resonance of the scatterer, in which case the anomalous scattering length $b = b' + ib''$ has to be considered

Without inversion symmetry in real lattice:

$$F(-\mathbf{k}) = \sum_j b_j \exp(-i\mathbf{k}\mathbf{r}_j) \neq F^*(\mathbf{k})$$

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 law holds almost all of the time
  (especially in neutron scattering unless very high incident energies are used)
- Symmetries in real space are also valid in reciprocal space (without the translation)
- Combining the two above ⟶ 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*

crystal system can only be determined by the Laue symmetry (symmetry of intensities)

Example: lattice parameters nearly orthorhombic

$$a = 10.097\ \text{Å} \quad b = 13.978\ \text{Å} \quad c = 18.123\ \text{Å}$$
$$\alpha = 90.00° \quad \beta = 90.10° \quad \gamma = 90.00°$$

2/m: (h k l) = (-h -k -l) = (h -k l) = (-h k -l)

mmm: (h k l) = (-h -k -l) = (h -k l) = (-h k -l)
= (-h k l) = (h -k -l) = (-h -k l) = (h k -l)

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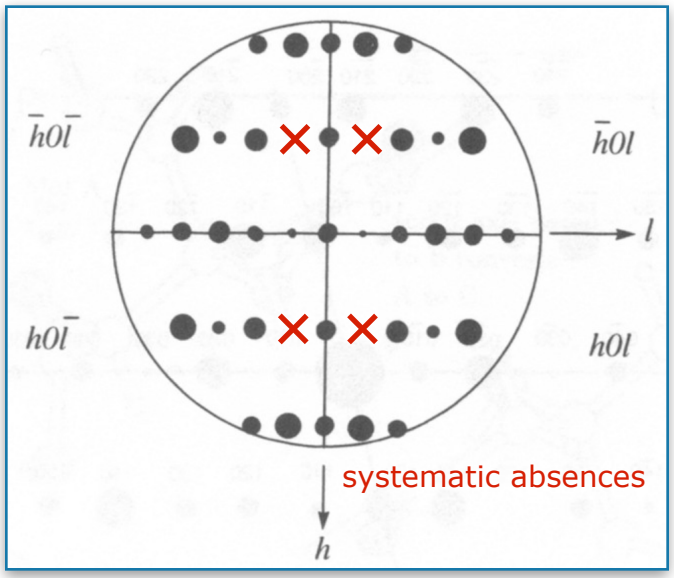

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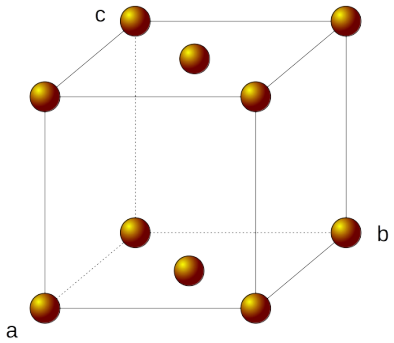
Symmetry in reciprocal space

Systematic absences

Systematic lack of scattered intensity due to translational crystal symmetry:

- lattice centering
- screw axes
- glide planes

Direct consequence of exact cancellation of structure factors. Example C-centering:



$$F(hkl) = b[e^{2\pi i(hx+ky+lz)} + e^{2\pi i[h(x+1/2)+k(y+1/2)+lz]})$$

$$= be^{2\pi i(hx+ky+lz)} \cdot (1 + e^{\pi i(h+k)})$$

$$= \begin{cases} 2b & \text{, if } \quad h+k = 2n \\ 0 & \text{, if } \quad h+k = 2n+1 \end{cases}$$

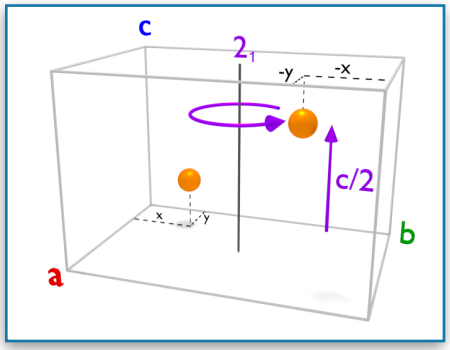
Symmetry in reciprocal space

Systematic absences

Systematic lack of scattered intensity due to translational crystal symmetry:

- lattice centering
- screw axes
- glide planes

Direct consequence of exact cancellation of structure factors. Example screw axis:



$$F(hkl) = b[e^{2\pi i(hx+ky+lz)} + e^{2\pi i[-hx-ky+l(z+1/2)]}]$$

$$= be^{2\pi ilz} \cdot (1 + e^{\pi il}) \qquad \text{(for } h\text{=}k\text{=0)}$$

$$\Rightarrow \text{only } (00l) \text{ reflections with } l = \text{even}$$

Ewald construction

Monochromatic source

- simple method to find out which scattered $\mathbf{k}_f$ are possible
- the idea of P. P. Ewald was to decouple real and reciprocal lattice
- use incident wave number

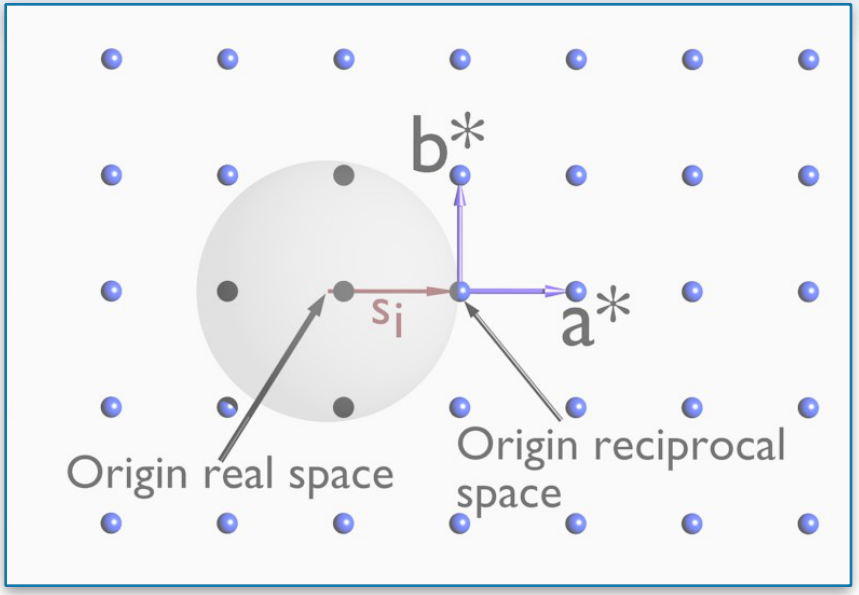
$$s_i = k_i/2\pi$$

- draw a sphere of radius

$$s = 2\pi/\lambda$$

- origin of reciprocal space is at extreme point of *s*

- reflection condition fulfilled for reciprocal space points lying on the surface of the Ewald sphere



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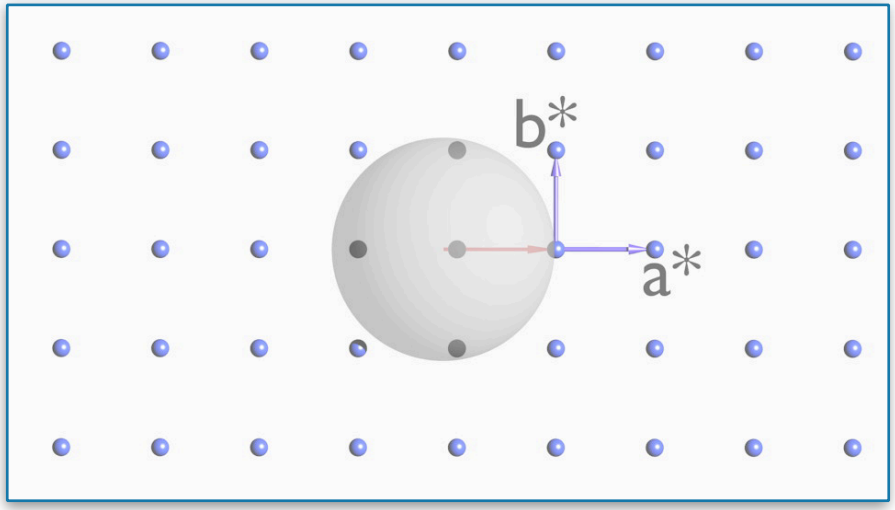


ω scan

Ewald construction

Polychromatic source (Laue method)

- simple method to find out which scattered $\mathbf{k}_f$ are possible
- the idea of P. P. Ewald was to decouple real and reciprocal lattice
- use incident wave number

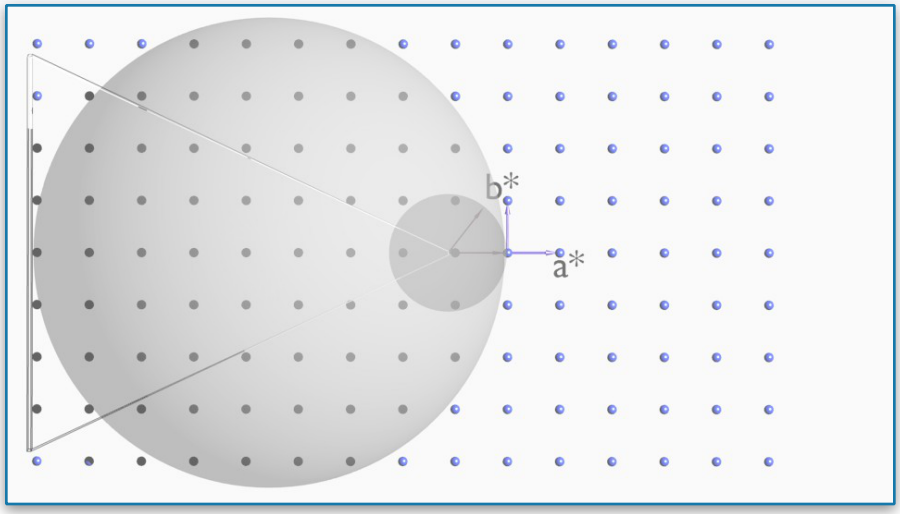
$$s_i = k_i/2\pi$$

- draw two spheres of radius

$$s_1 = 2\pi/\lambda_{min} \qquad s_2 = 1/\lambda_{max}$$

- origin of reciprocal space is at extreme point of *s*

- reflection condition fulfilled for reciprocal space points lying between the two Ewald spheres



Ewald construction

Monochromatic source (Powder method)

- simple method to find out which scattered $\mathbf{k}_f$ are possible
- the idea of P. P. Ewald was to decouple real and reciprocal lattice
- use incident wave number

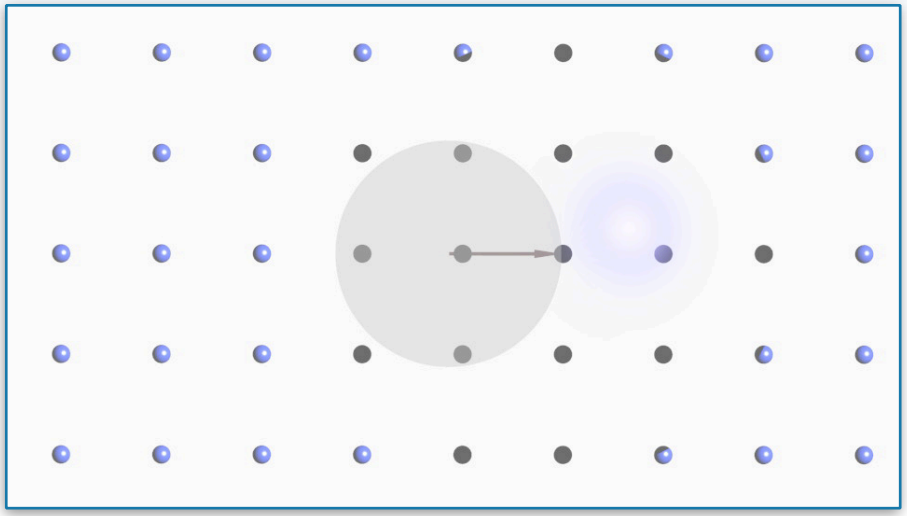
$$s_i = k_i/2\pi$$

- draw a sphere of radius

$$s = 2\pi/\lambda$$

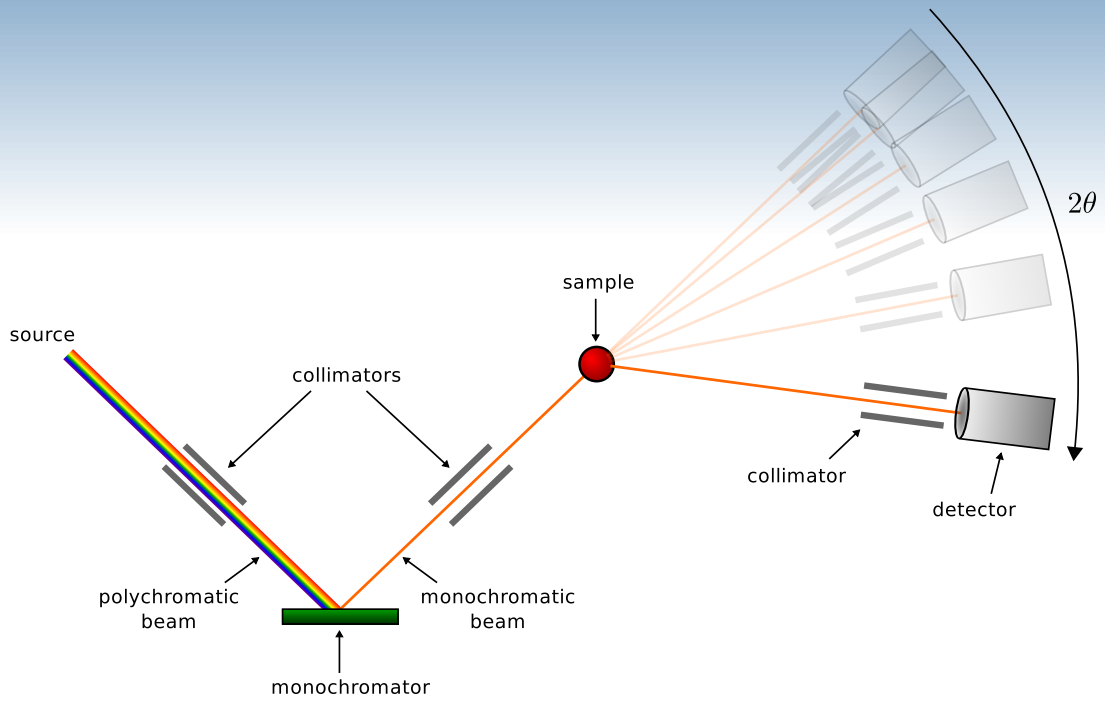
- origin of reciprocal space is at extreme point of *s*

- reflection condition fulfilled for the intersection of the Ewald sphere with spheres around 0 with radii *Q(hkl)*



The basic diffractometer

Constant wavelength (reactor source)



The basic diffractometer

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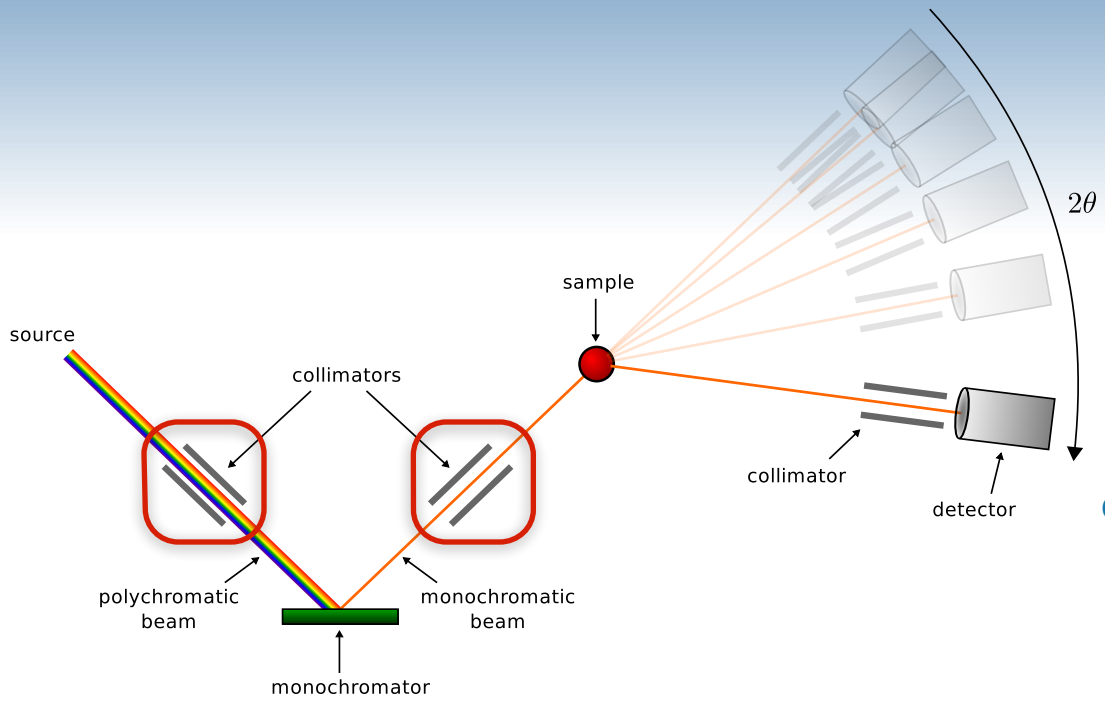
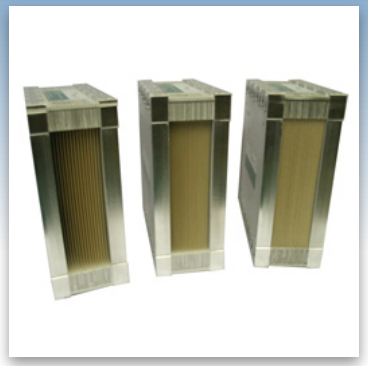


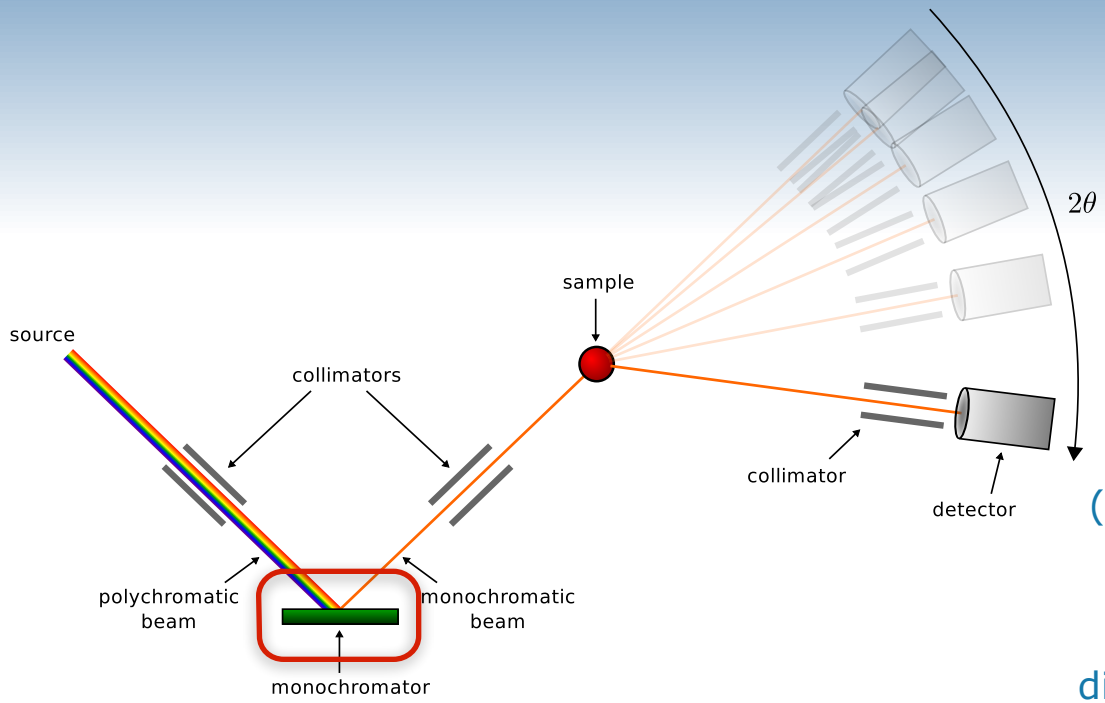


collimator

defines the beam shape and divergence
Soller collimators, slits

The basic diffractometer

Constant wavelength (reactor source)



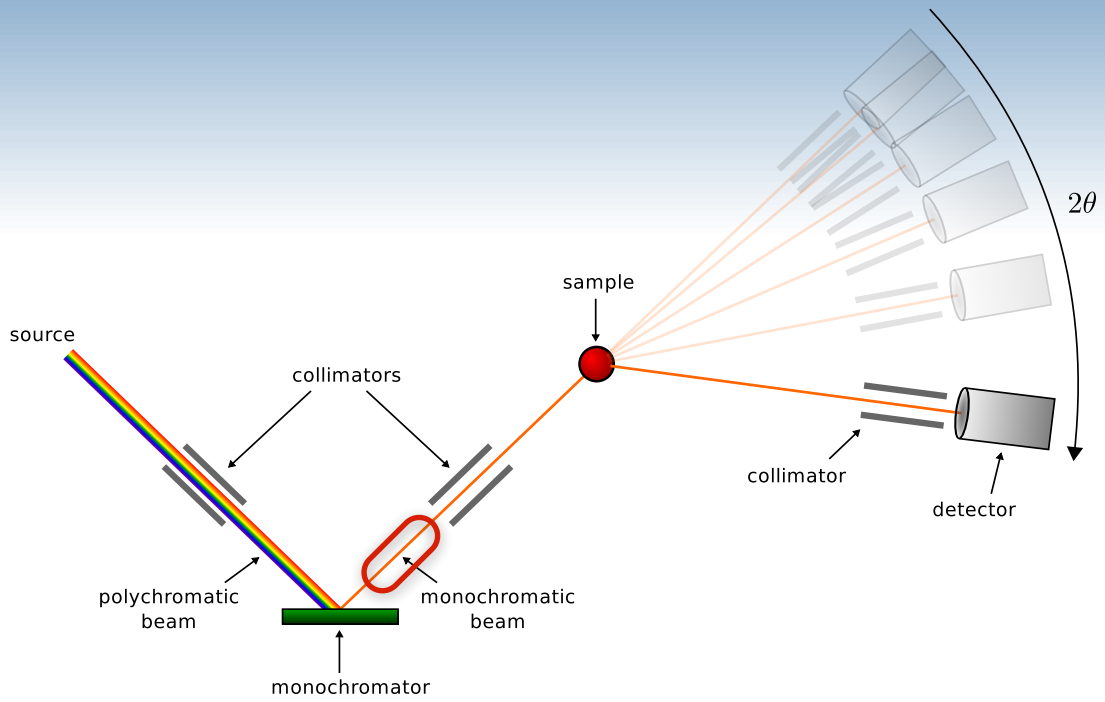
monochromator

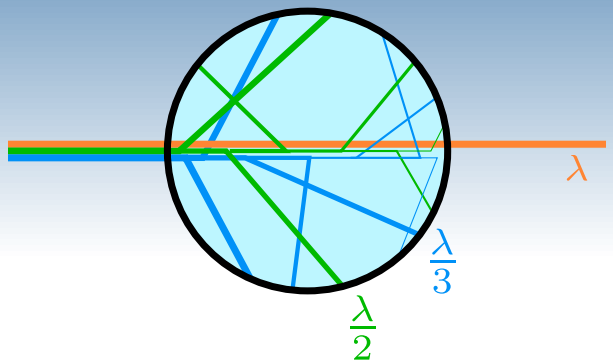
(assembly of) high quality single crystals
choice of wavelength
choice of resolution (take-off angle)
typically Cu, Ge, HOPG, Si
diffracts also higher harmonics $\lambda/2$, $\lambda/3$, …

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

The basic diffractometer

Constant wavelength (reactor source)





filter

diffracts shorter λ out of the beam

$\lambda/2d_{Filter}>1$

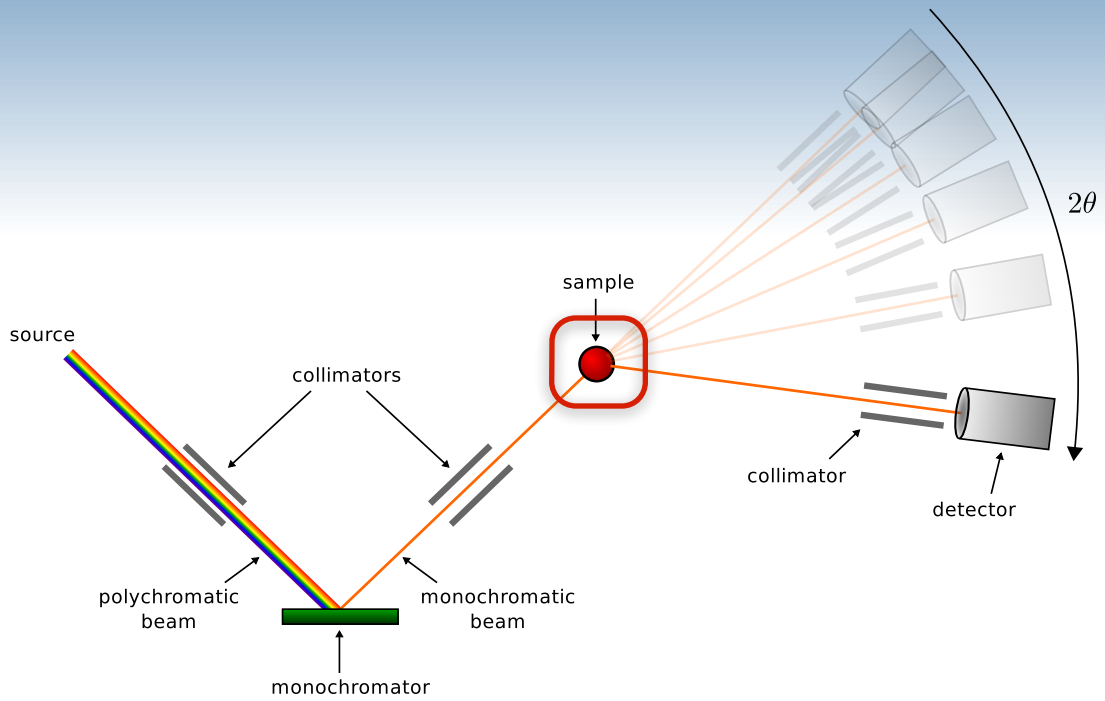
typically PG, Be

no $\lambda/2$ filter needed for Si, Ge

(111) is used, because (222) is forbidden

The basic diffractometer

Constant wavelength (reactor source)

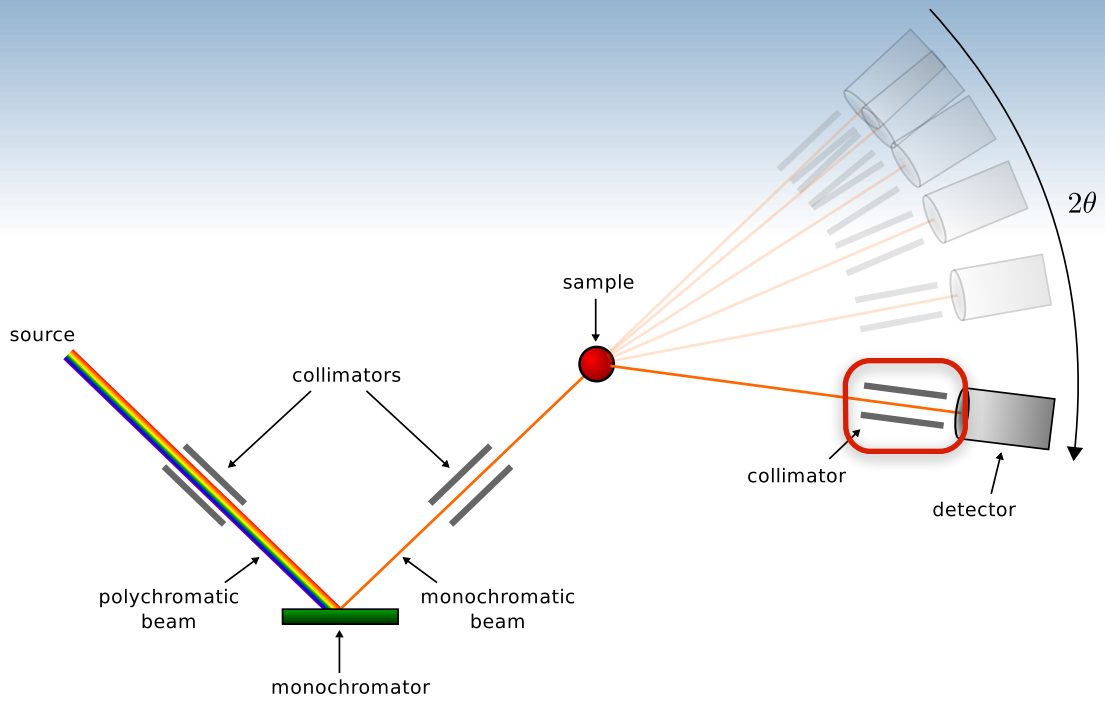


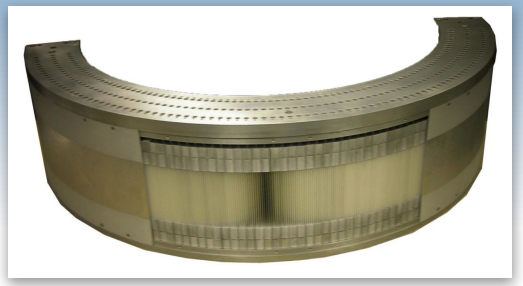
sample environment

cryostat, cryomagnet,
furnace, pressure cell, CryoPAD

The basic diffractometer

Constant wavelength (reactor source)





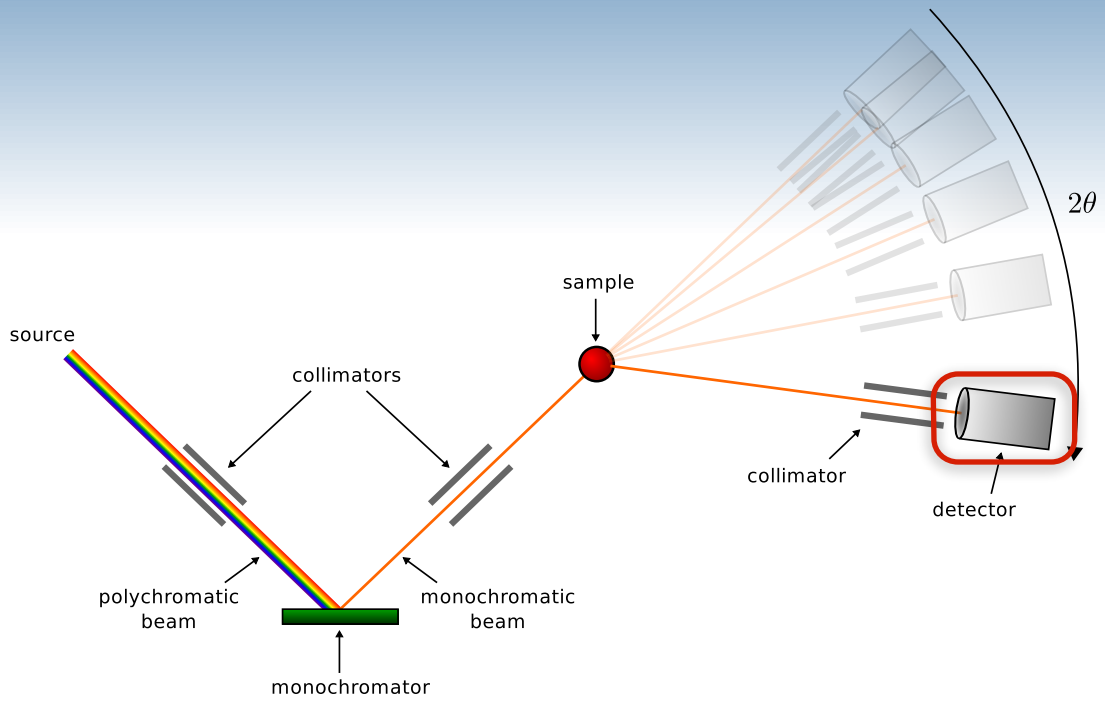
collimator

e.g. radial oscillating collimator reduces background from sample environment

or another Soller collimator to increase resolution

The basic diffractometer

Constant wavelength (reactor source)



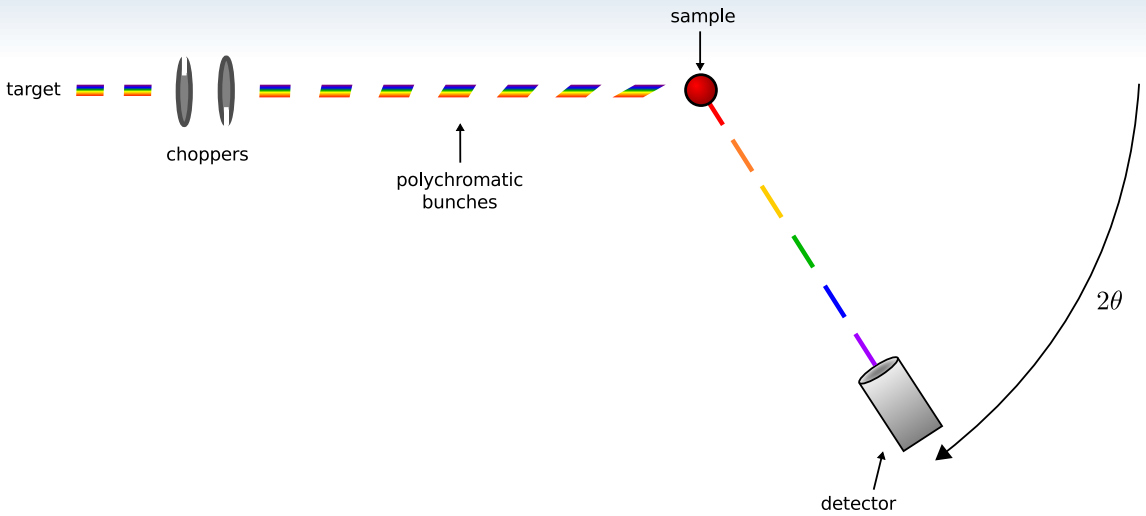
detector

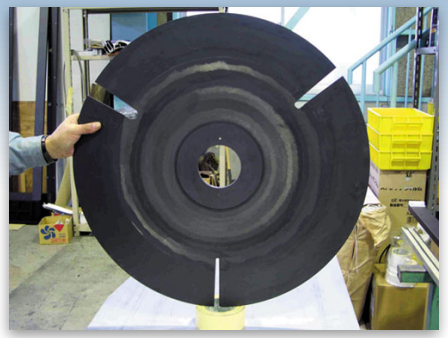
gas cells in which an incoming neutron triggers a nuclear reaction producing a charged particle which then is detected typically ^3He or B_3F

save time by large-area detectors (153.6° on D20)

Time-of-flight diffractometer

Polychromatic (spallation source)



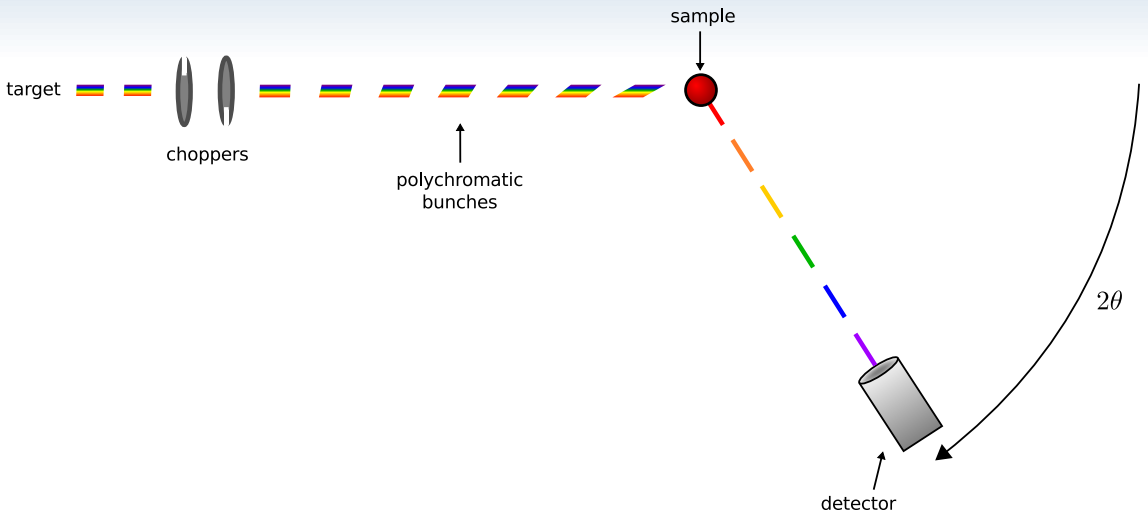


chopper

defines the wavelength band
avoids frame overlap

Time-of-flight diffractometer

Polychromatic (spallation source)



time of flight of the neutrons is related to the their wavelength

$$t = \frac{m_n}{h}\lambda L$$

diffraction pattern is recorded at constant scattering angle (close to 180° for best resolution, small Δt/t)

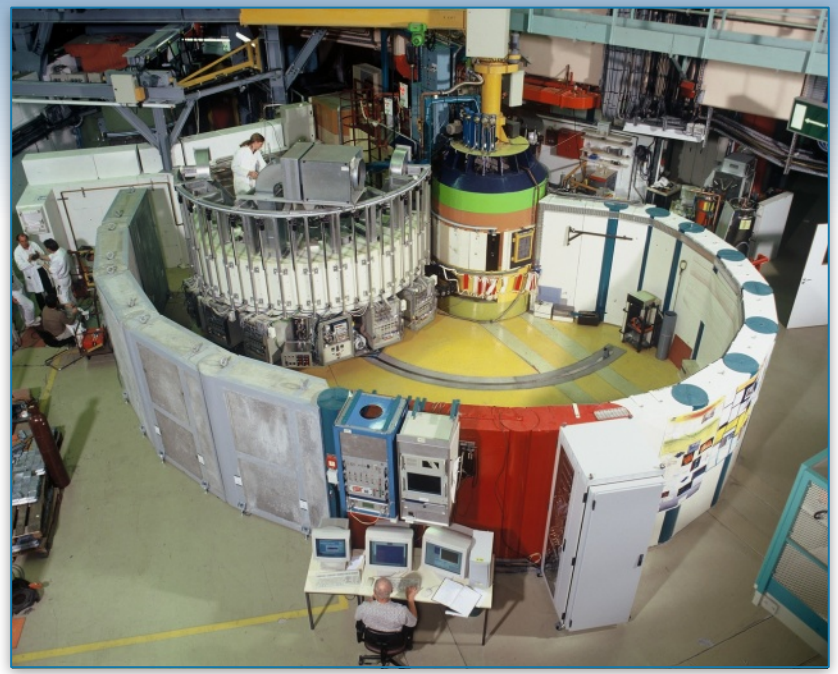
$$\frac{\Delta\lambda}{\lambda} = \Delta\theta_M \cot\theta_M$$

Diffraction techniques

Powder diffraction

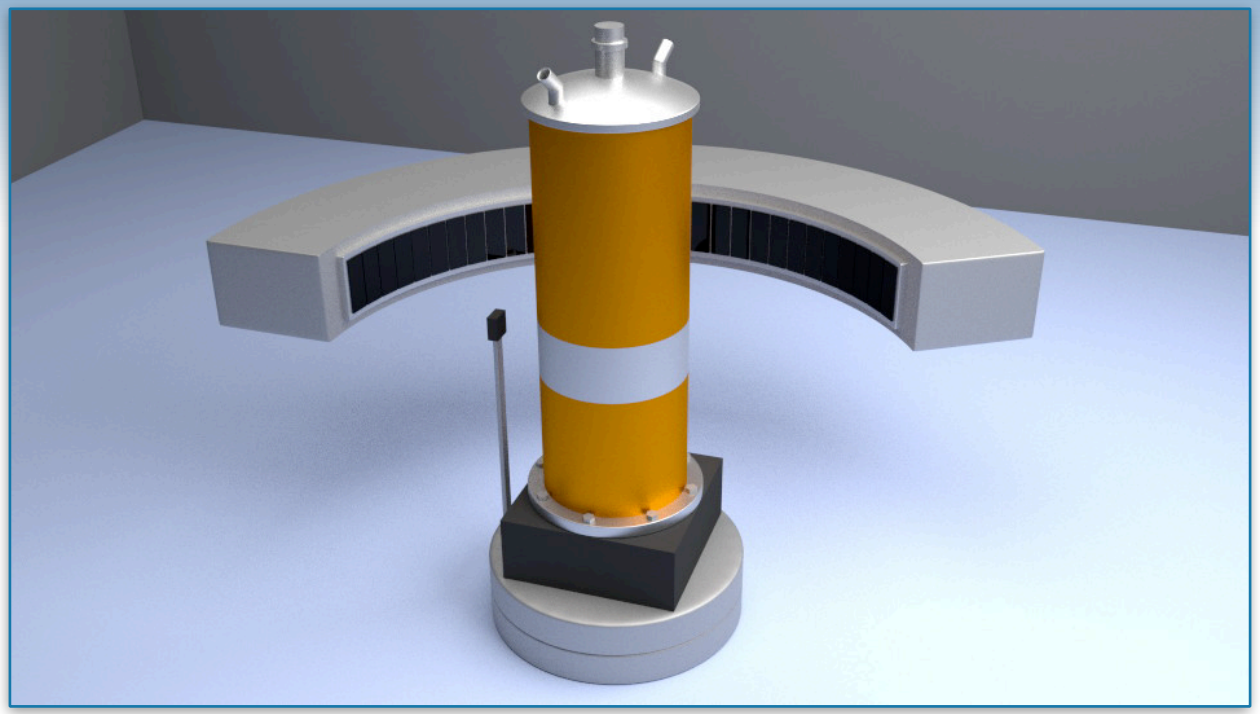
D20 (high flux)

sample in a vanadium container
V scatters only incoherently



Diffraction techniques

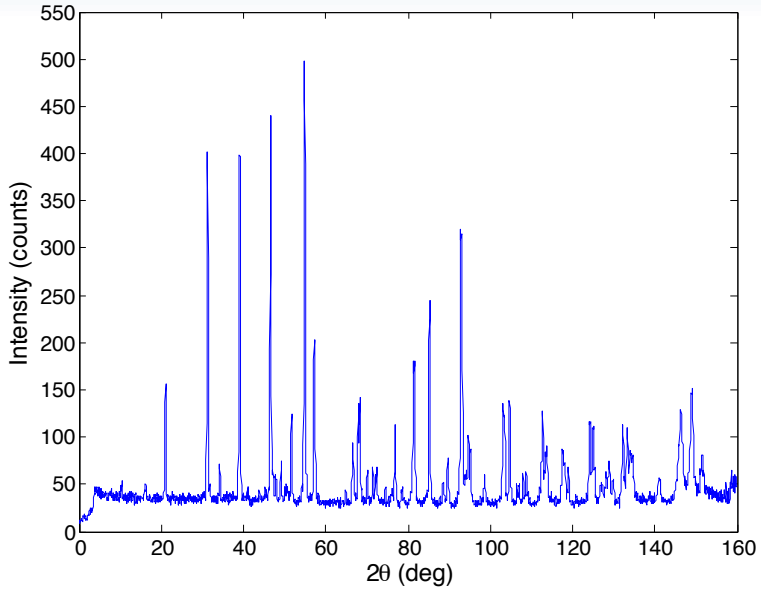
Powder diffraction



Diffraction techniques

Powder diffraction

Result: Diffraction pattern



Useful information lies in the

- position (or t.o.f)
- the intensity
- the shape and width

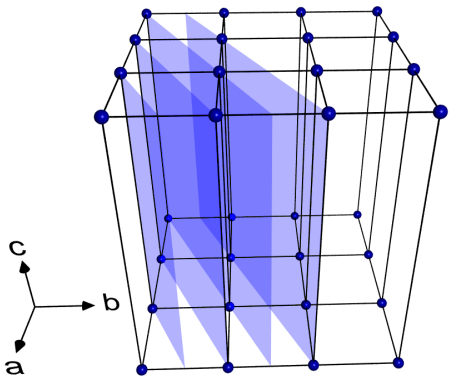
of the reflections.

Diffraction techniques

Powder diffraction

1. Position (or t.o.f)

Bragg's law $n\lambda = 2d\sin\theta$



monoclinic

$$d = \left(\frac{h^2}{a^2 \sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta} \right)^{-\frac{1}{2}}$$

orthorhombic

$$d = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}$$

cubic

$$d = a(h^2 + k^2 + l^2)^{-\frac{1}{2}}$$

with θ and λ known → able to obtain lattice parameters

Diffraction techniques

Powder diffraction

magnetic form factor

$$f(\mathbf{k}) = \int_{-\infty}^{\infty} \rho_{mag}(\mathbf{r}) \exp(i\mathbf{kr}) d\mathbf{r}$$

2. Intensity $I \sim F^2$

nuclear structure factor

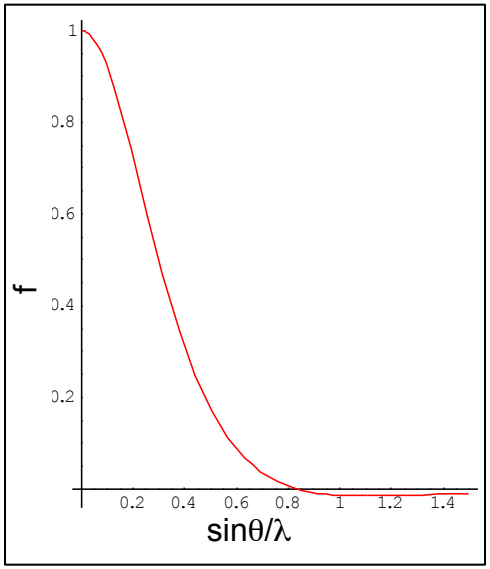
(interaction between neutron and core potential of nuclei)

$$F_N(\mathbf{k}) = \sum_j b_j \exp(i\mathbf{kr}_j) \exp(-B_j \tfrac{\sin^2\theta}{\lambda^2})$$

magnetic structure factor

(interaction between neutron and electron's magnetic field)

$$\mathbf{F}_M(\mathbf{k}) = \sum_j \boldsymbol{\mu}_j f_j(\mathbf{k}) \exp(i\mathbf{kr}_j) \exp\left(-B_j \frac{\sin^2\theta}{\lambda^2}\right)$$



Diffraction techniques

Powder diffraction

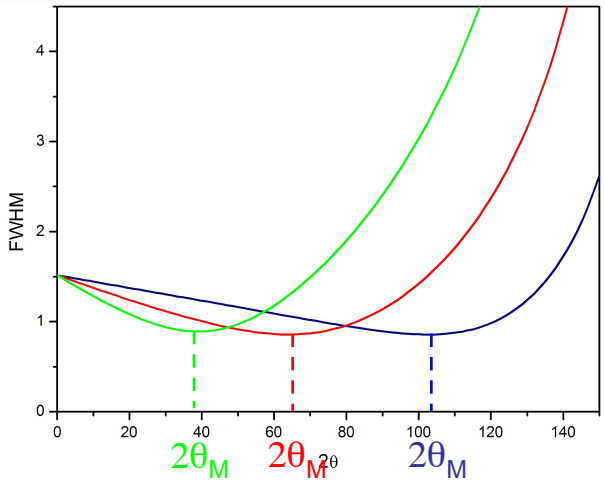
3. Peak width and shape

source, monochromator, slits, collimators,
sample strain, stress, etc. have an influence on the peak shape and the peak width

Caglioti formula

$$FWHM^2 = u\tan^2\theta + v\tan\theta + w$$

resolution function minimum at the take-off angle $2\theta_M$
(focussing effect)

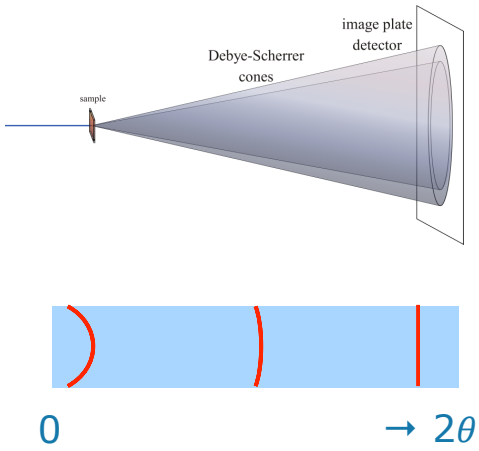


T.O.F.: The resolution function is a constant for a given scattering angle

Diffraction techniques

Powder diffraction - Corrections

Lorentz factor
Asymmetry



Plane multiplicity

example:

$$F_{(200)} = F_{(220)} = F_{(222)}$$

	(220)	$(222)\,(22\bar{2})$
(200)	$(\bar{2}20)$	$(\bar{2}22)\,(\bar{2}2\bar{2})$
$(\bar{2}00)$	$(2\bar{2}0)$	$(2\bar{2}2)\,(2\bar{2}\bar{2})$
	$(\bar{2}\bar{2}0)$	$(\bar{2}\bar{2}2)\,(\bar{2}\bar{2}\bar{2})$

$$4I_{(200)} = 2I_{(220)} = I_{(222)}$$

Preferred orientation

needles, platelets, etc. tend to have a preferred orientation

no statistical orientation of crystallites

some (hkl) families like e.g. (hk0), (00l), etc. might be favoured

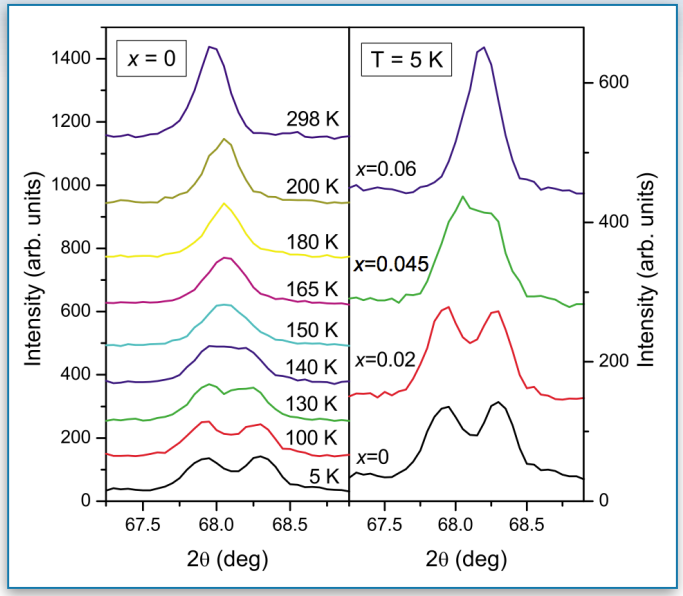
Absorption

sample absorption is angle dependent

Diffraction techniques

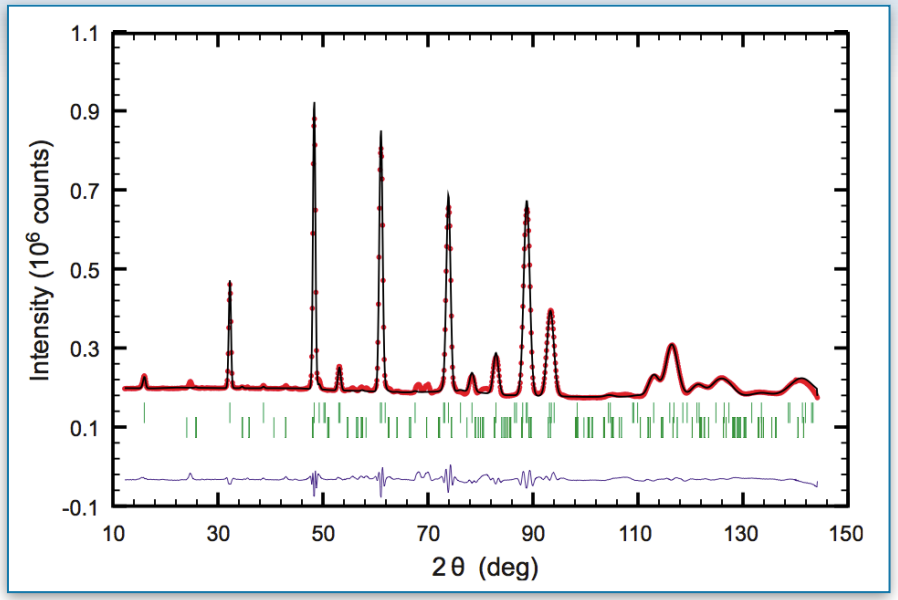
Which powder diffractometer? Example: $LaO_{1-x}F_xFeAs$

orthorhombic distortion as seen by the splitting of the $(220)_T$ into the $(400)_O$ and $(040)_O$ reflections



high resolution needed

weak magnetic reflections at low 2θ angles compared to strong nuclear reflections.



high flux needed

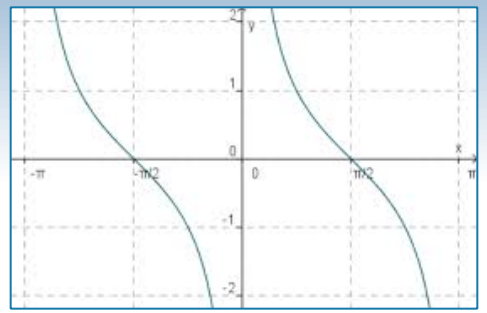
Diffraction techniques

High resolution vs. high flux (reactor source)

$$\frac{\Delta\lambda}{\lambda} = \Delta\theta_M \cot\theta_M$$

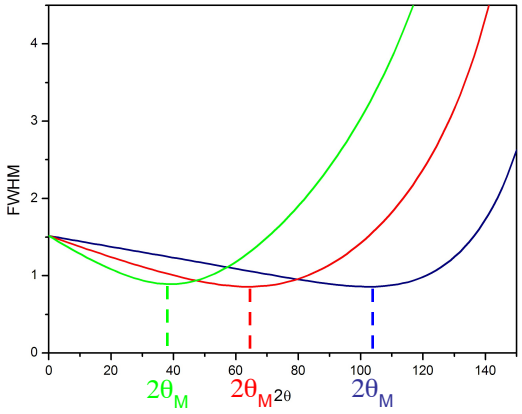
High-resolution diffractometer (e.g. D2B)

- large take-off angle → resolution minimum at high 2θ, small $\Delta\lambda/\lambda$
- Soller collimators to decrease (α_1, α_2, α_3) divergence
- bigger sample does not influence resolution



High-flux diffractometer (e.g. D20)

- low take-off angle → resolution minimum at low 2θ, high $\Delta\lambda/\lambda$
- large focusing monochromator with large mosaic spread
- no collimation
- monochromator reflectivity increases with λ^3
- increasing sample size → more intensity → less resolution

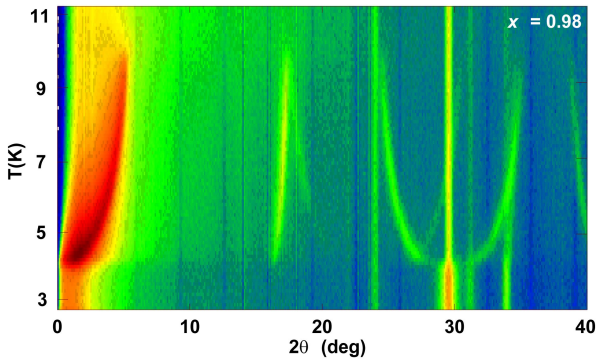


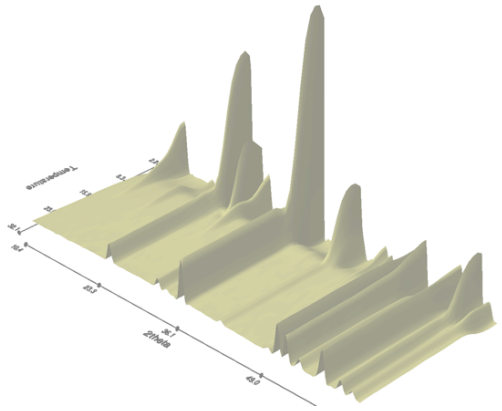
Diffraction techniques

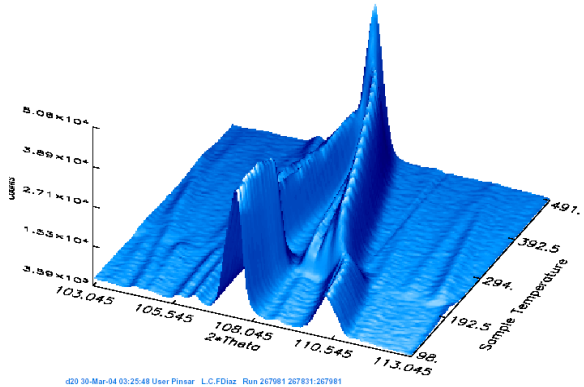
Powder diffraction

Thermodiffraction

Collection of diffraction patterns as a function of temperature.
Clearly reveals structural and magnetic phase transitions.







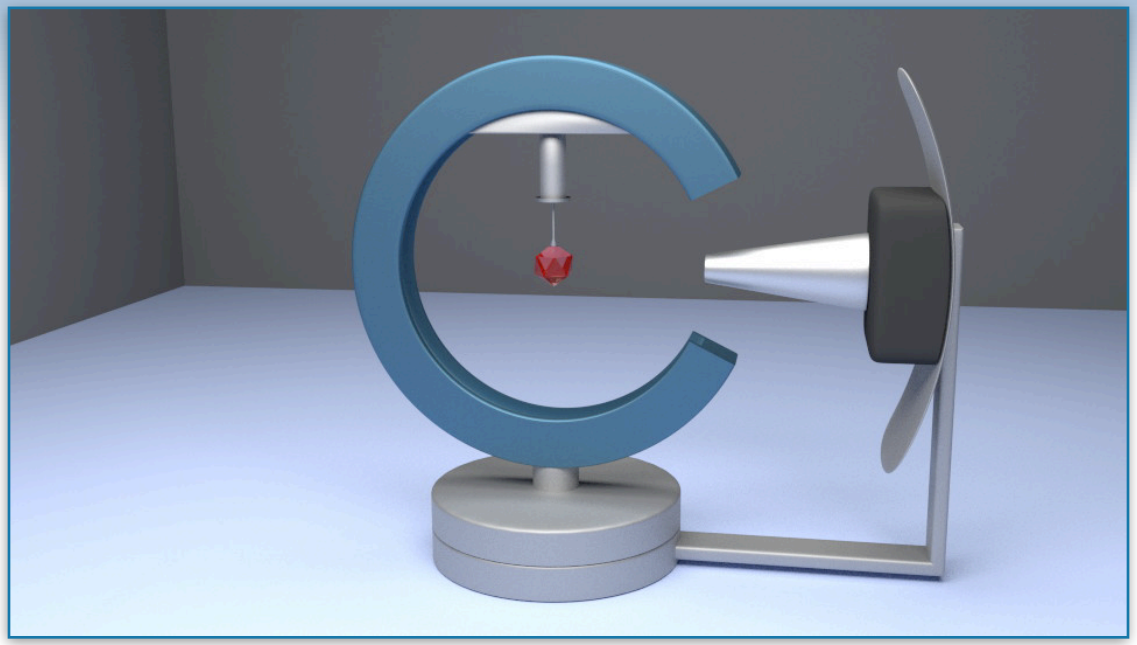
Diffraction techniques

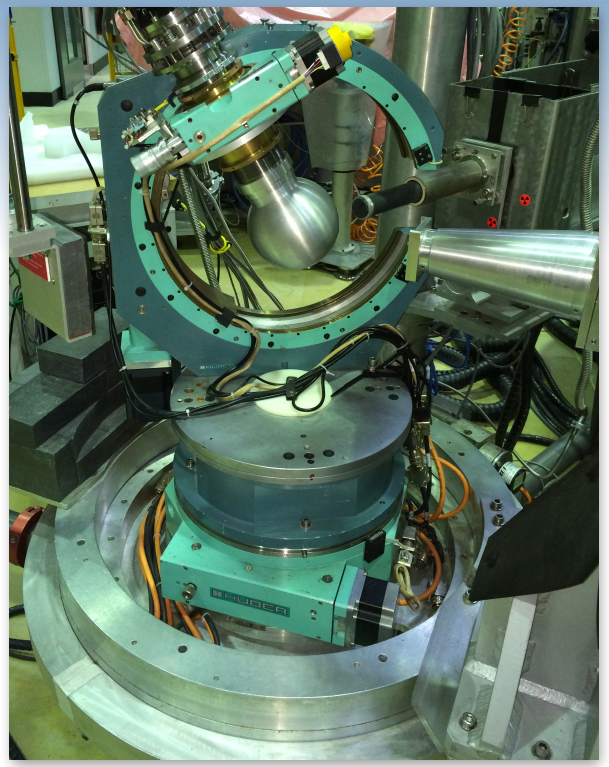
Single crystal diffraction

- single crystal experiments take 3-10 days
- only if neutron powder and X-ray single crystal experiments fail
- lattice parameters and rough orientation need to be known (not for Laue)
- different techniques: normal beam, 4 circle, Laue, …

Diffraction techniques

Single crystal diffraction - 4 circle mode

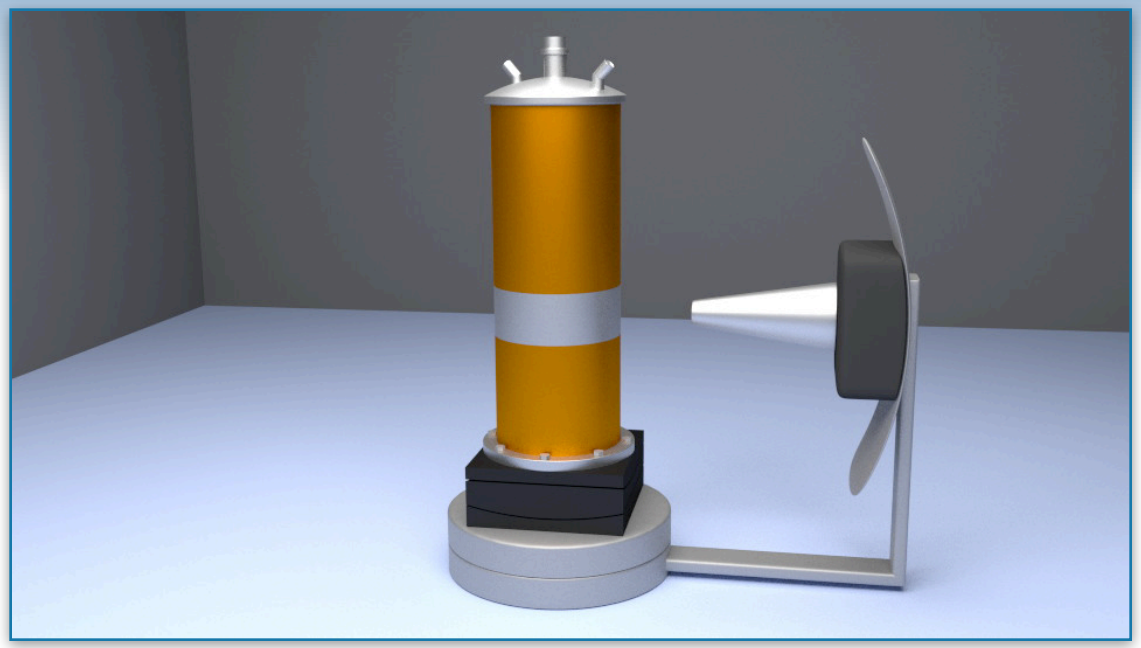




D10 (ILL)

Diffraction techniques

Single crystal diffraction - Normal beam mode



cryostats, cryomagnets, …
cannot be tilted much

→ confined to the scattering plane
e.g. only (*hk*0) reflections

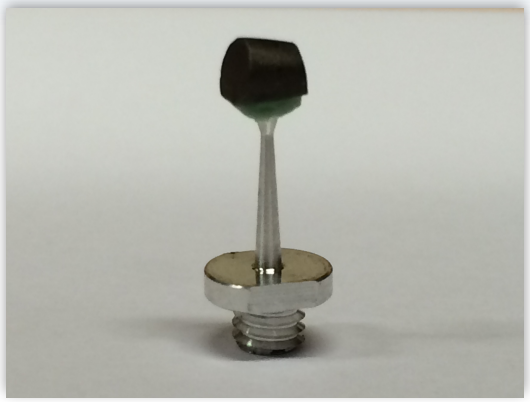
→ lifting counter
able to reach *l*=1, 2…

Diffraction techniques

Single crystal diffraction - experimental procedure

- mount the sample

- align it in the center of the Eulerian cradle
- find the first reflection and index it correctly
- find the second reflection and index it correctly
- calculate a rough UB matrix
- measure more reflections and refine the UB matrix
- set the temperature, magnetic field, pressure etc.
- collect many reflections at constant conditions
- integrate the measured reflections
- merge and average symmetry-equivalent reflections
- make necessary corrections
- refine a (magnetic) structure model



single crystal glued on
an aluminium sample holder

Diffraction techniques

Single crystal diffraction - experimental procedure

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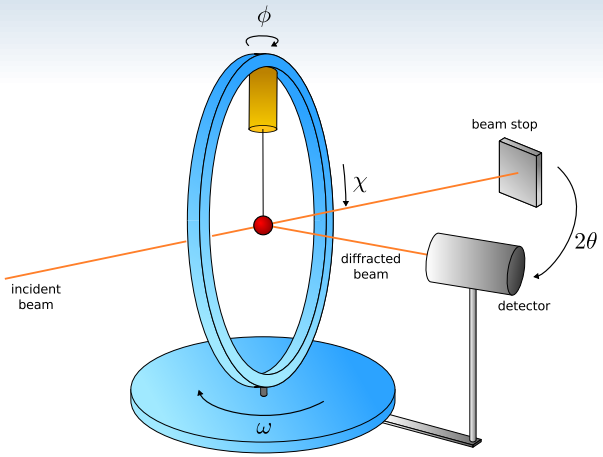

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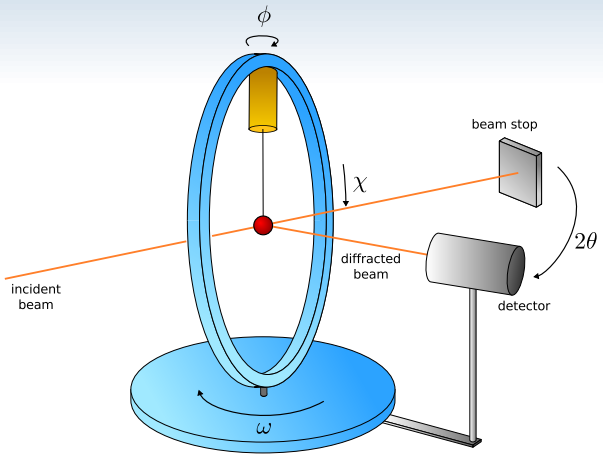

set 2θ and adjust χ, ϕ

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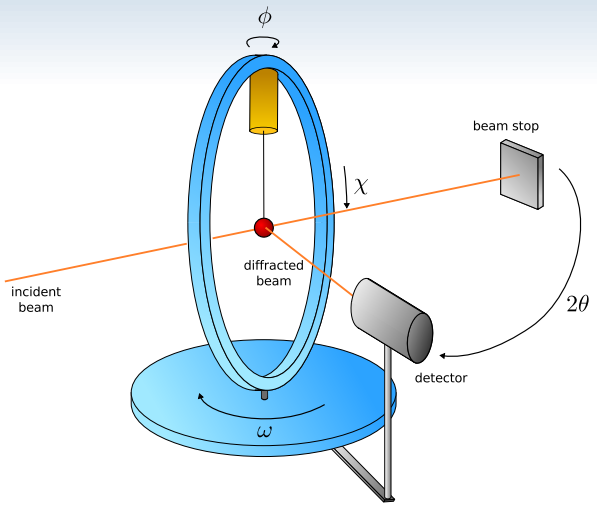

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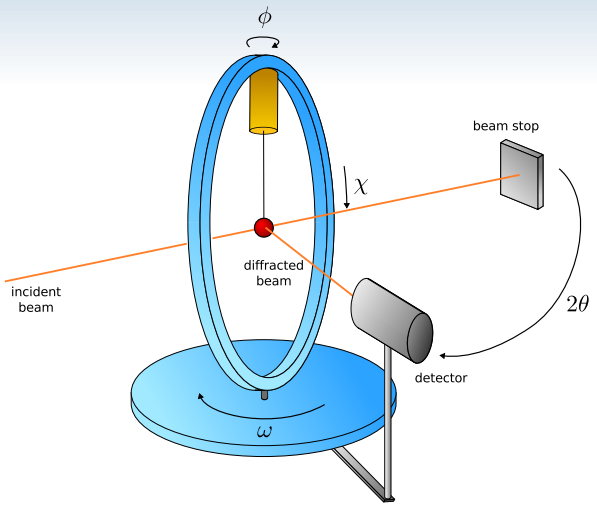

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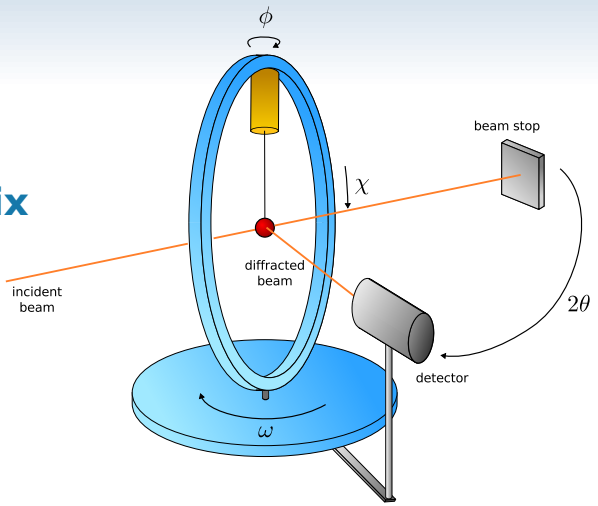

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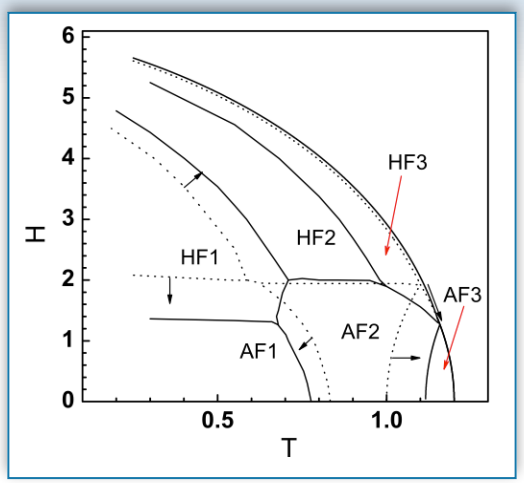

phase diagram of CuO
Villareal et al., PRL **109** 167206 (2012)

Diffraction techniques

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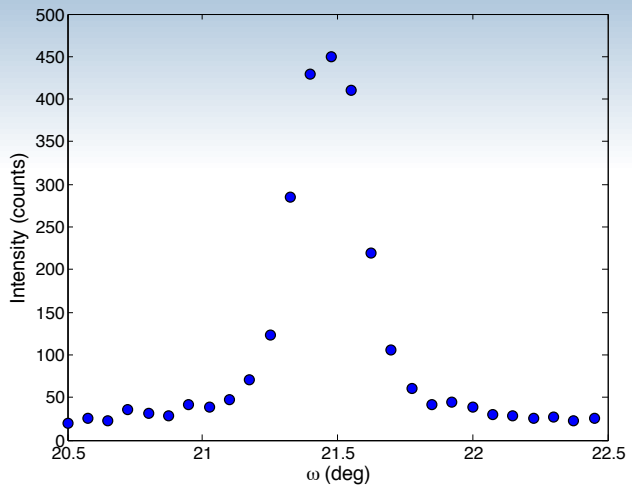

move crystal through reflection position by scanning ω (or ω-xθ)

Diffraction techniques

Single crystal diffraction - experimental procedure

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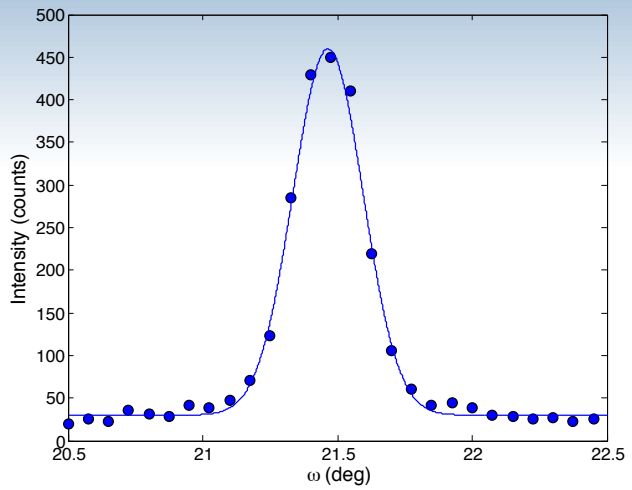

sophisticated fitting routines
e.g. COLL5, RACER

Diffraction techniques

Single crystal diffraction - experimental procedure

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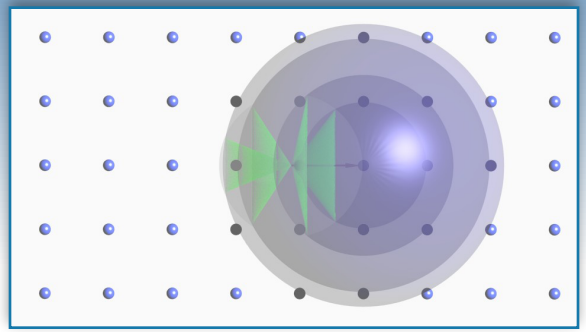

(120) $(1\bar{2}0)$

$(\bar{1}20)$ $(\bar{1}\bar{2}0)$

(120)

Diffraction techniques

Single crystal diffraction - experimental procedure

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- **make necessary corrections**
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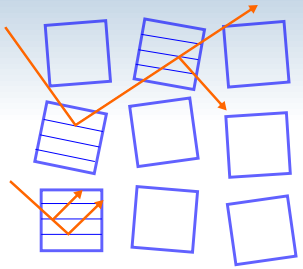
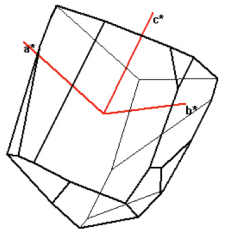
Lorentz factor

Extinction



Absorption



Multiple scattering

$(h_2 - h_1 \quad k_2 - k_1 \quad l_2 - l_1)$

Diffraction techniques

Single crystal diffraction - experimental procedure

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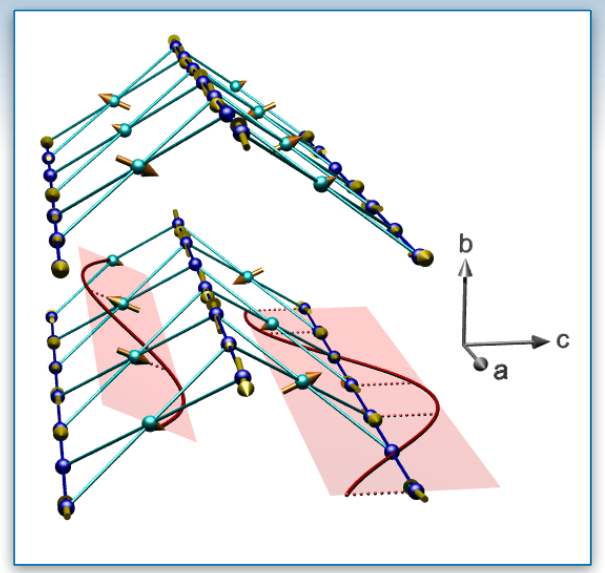
- make necessary corrections
- **refine a (magnetic) structure model**

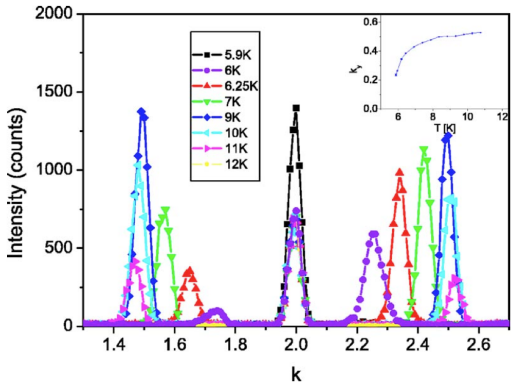


magnetic structure of $(Co_{0.1}Ni_{0.9})_3V_2O_8$

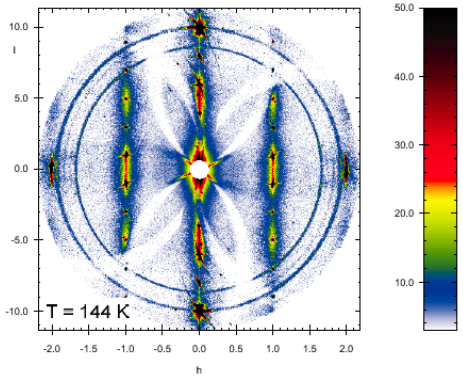
Diffraction techniques

Single crystal diffraction - other types of experiments

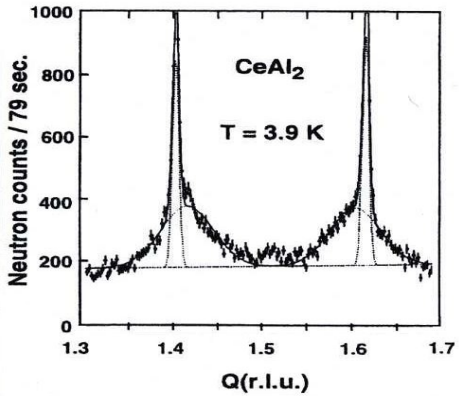
phase transitions as function of T, H, p
propagation vectors



volumetric mapping
diffuse/weak scattering
superlatice/satellite reflections

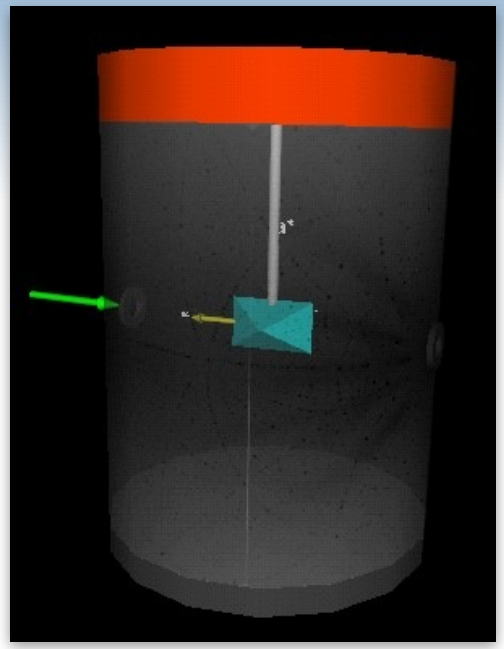


study of individual
reflection profiles

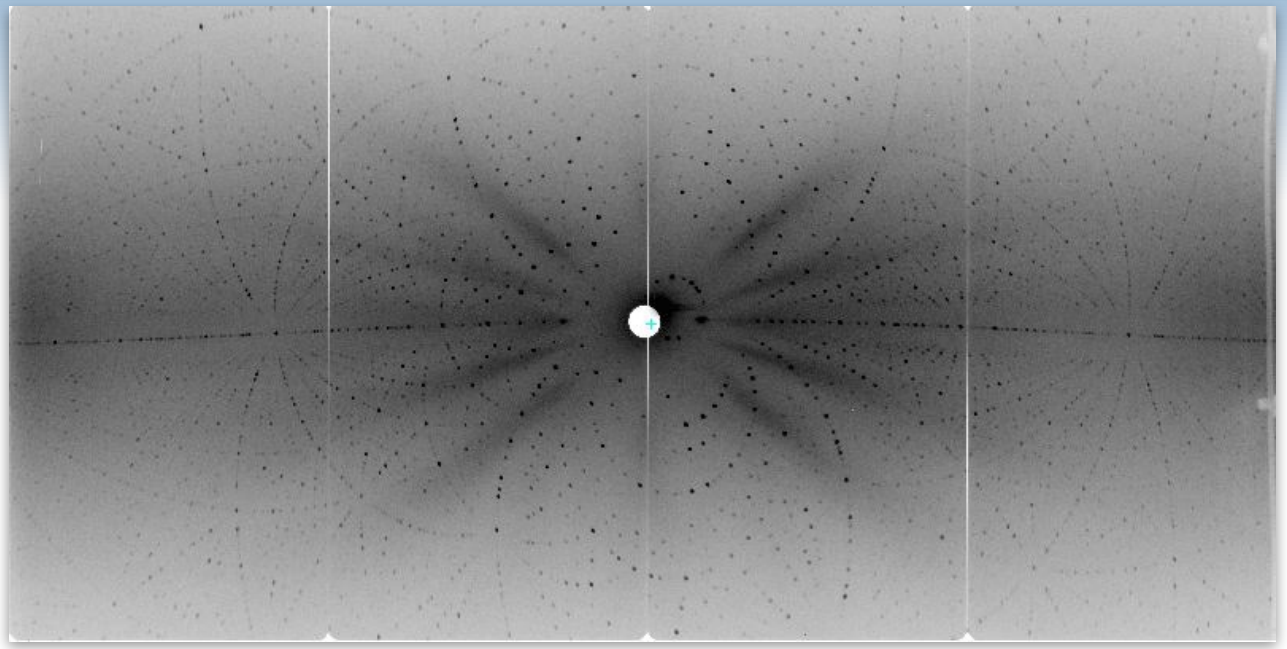


Diffraction techniques

Single crystal diffraction - Laue method



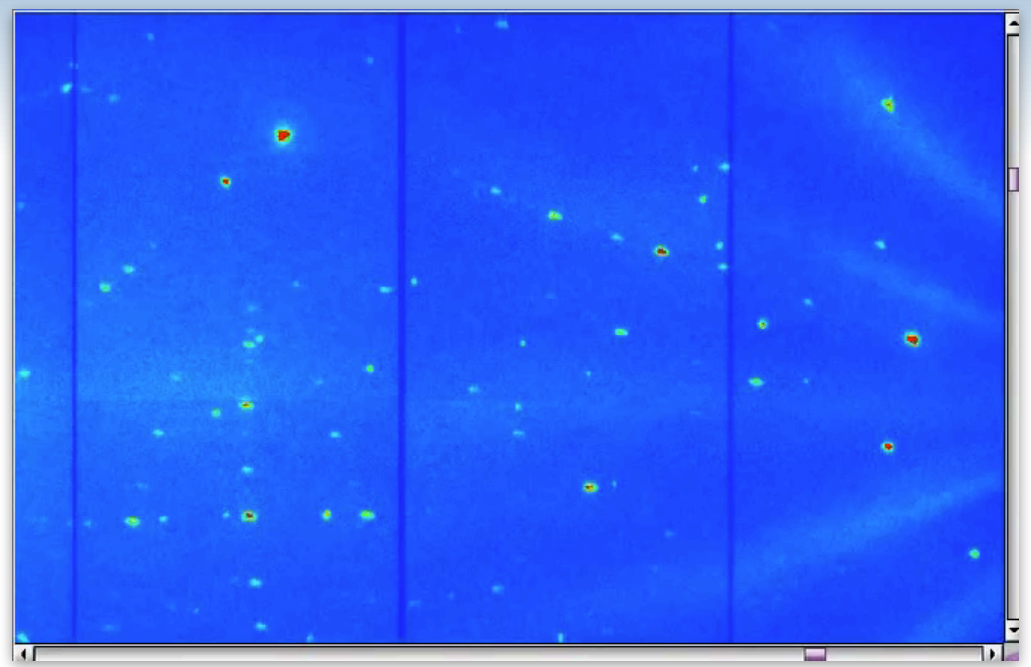
polychromatic beam



→ every accessible *hkl* plane is in reflection position for a particular wavelength

Diffraction techniques

Single crystal diffraction - Laue method



- quickly orient single crystals
- observe phase transitions
- magnetic satellites
- find propagation vectors

Examples

Antiferromagnetism in MnO

Detection of Antiferromagnetism by Neutron Diffraction*

C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee
AND
J. SAMUEL SMART
Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
August 29, 1949

Additional peaks in the neutron diffraction pattern confirm Louis Néel's suggestion of an antiferromagnetic state (1932).

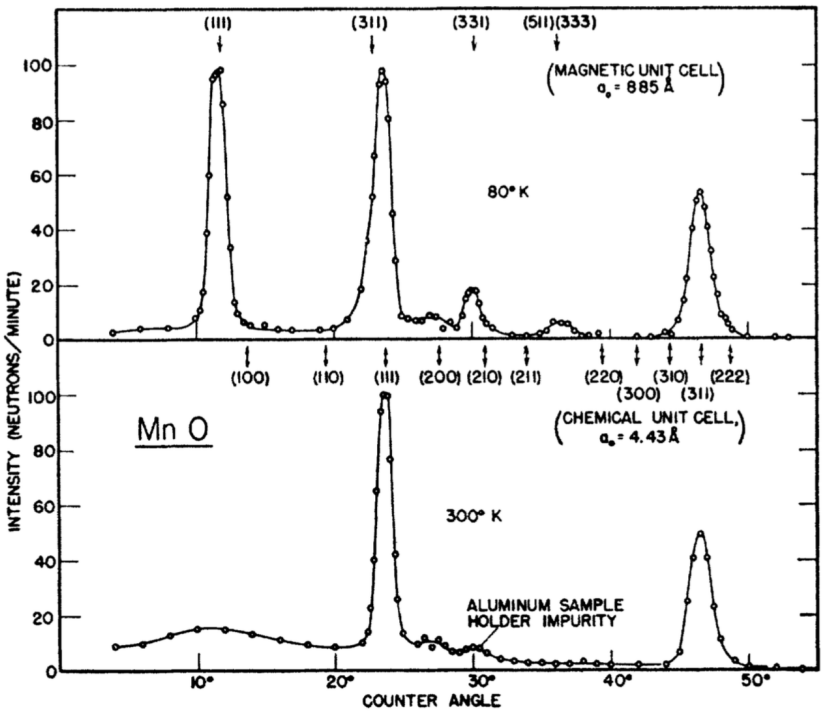


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

Examples

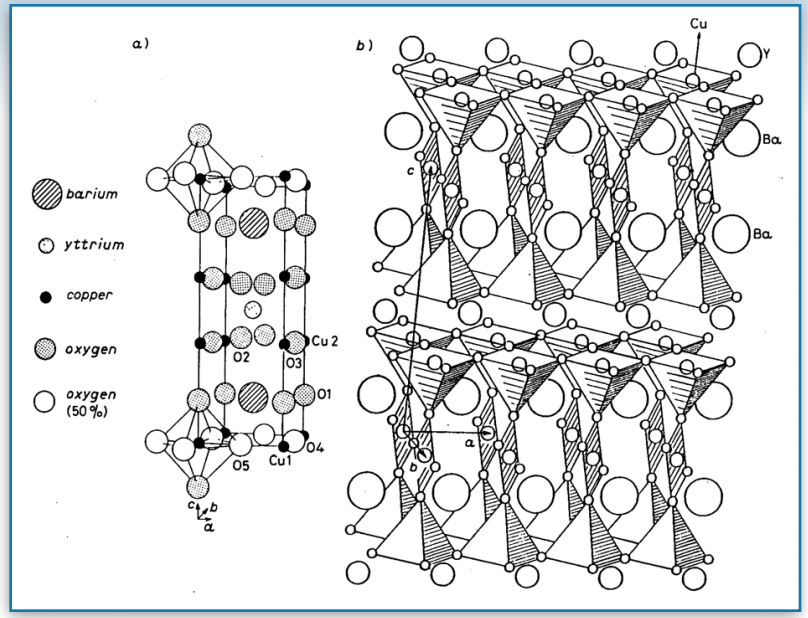
Crystal structure in HT superconductors

CuO_6 octahedra were at the heart of Bednorz and Müller's idea for HT superconductors in 1986.

X-rays indeed yield an octahedral coordination, but X-rays are mainly scattered by heavy elements.

Neutron diffraction yields the widely-accepted structure with oxygen squares and CuO_5 pyramids.

X-rays neutrons



Siegrist et al., Phys. Rev. B **35** (1987)

Capponi et al., Europhys. Lett. **3** (1987)

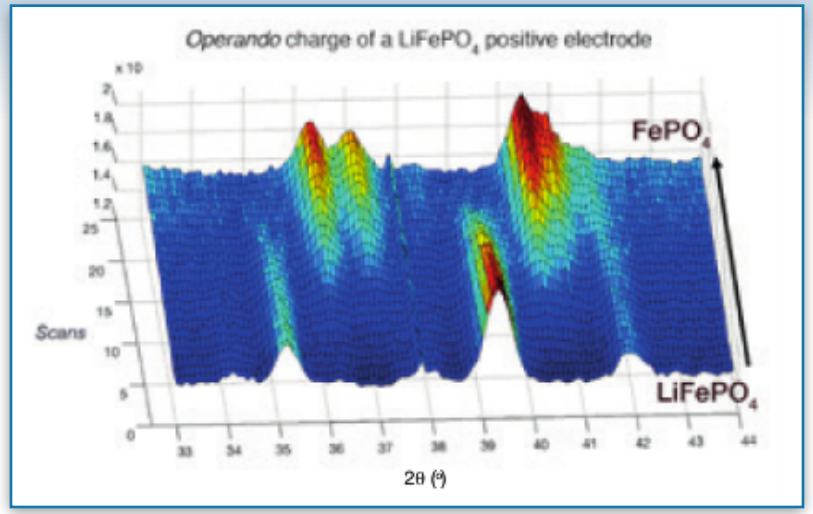
Examples

Li batteries

X-rays have a poor sensibility for Li

Knowing exactly what the Li does while charging and operating the battery is crucial to relate the Li concentration with the electrochemical features

key importance for understanding and improving Li-ion batteries



M. Bianchini and E. Suard, ILL Annual report 2014, p. 16

Summary

Diffraction yields structural information: lattice constants, atomic positions, atomic displacement factors, occupations, space group symmetry, stress and strain, magnetic structures

Advantages of neutrons with respect to X-rays: sensitive to the nuclei position, contrast of scattering lengths, isotope effect, isotropic scattering, sensitive to magnetic moment

The **scattering length/form factor** is the Fourier transform of the atomic scattering potential function.

The **structure factor** is the Fourier transform of the unit cell scattering potential functions.

We measure $I \sim F^2$ ⟶ phase information is lost ⟶ models necessary