MSE-238
Structure of Materials

Week 6 – crystallography IV
Spring 2025

Marianne Liebi (MX/PSI)

Ecole Polytechnique Fédérale de Lausanne

EPFL

General Outline

- introduction and reminder of atomic bonds, crystals – week 1

Part I: crystallography - weeks 2-6

- packing of spheres, constructing crystal structure
- crystal lattice and symmetry operations
- mathematical description of the lattice, Miller indices
- reciprocal space

Part II: characterization – week 6-8

- diffraction
- scattering

BREAK 18.4. & 25.4.

Part III: amorphous & hierarchical structures – week 9-12

- glasses
- polymers
- biological and hybrid materials

Recap – week 13

General Outline (adapted)

- introduction and reminder of atomic bonds, crystals – week 1

Part I: crystallography - weeks 2-6

- packing of spheres, constructing crystal structure week 2
- crystal lattice and symmetry operations week 3
- mathematical description of the lattice, Miller indices week 4
- reciprocal space (&diffraction) week 6
- characterization I: diffraction week 7
- diffraction & recap of crystallography week 8

BREAK 18.4. & 25.4.

Part III: amorphous & hierarchical structures – week 9-12

- glasses
- polymers
- Characterization II: scattering
- biological and hybrid materials

Recap – week 13

Overview today

- Diffraction on planes of crystals

- Reciprocal lattice

- d-spacing of planes

- Young's double slit experiment and Bragg's law

- Laue's condition: connection between diffraction and reciprocal lattice

- Diffraction as Fourier Transform of the crystal (=lattice & motif)

- Hammond Chapter 6-8

- Jens Als-Nielsen & Des McMorrow "Elements of Modern X-ray Physics" Chapter 5

https://lampz.tugraz.at/~hadley/ss1/skriptum/outline.php for some nice visualization and interactive plots!

- **Crystal structure**
  - ○ Crystal structure   W
  - ○ Unit cell   W
  - ○ Bravais lattices   W
  - ○ Miller indices   W
  - ○ Wigner Seitz cell   W
    - ▪ Drawing Wigner-Seitz cells in two dimensions
    - ▪ Drawing Wigner-Seitz cells in three dimensions
  - ○ Asymmetric unit
  - ○ Symmetries
    - ▪ Point groups   W
    - ▪ Space groups   W
    - ▪ Space Group → Bravais Lattice, Point Group
  - ○ Examples of crystal structures
    - ▪ simple cubic, fcc, bcc, hcp, dhcp, diamond, silicon, zincblende, ZnO wur...

X-ray diffraction: crystal planes
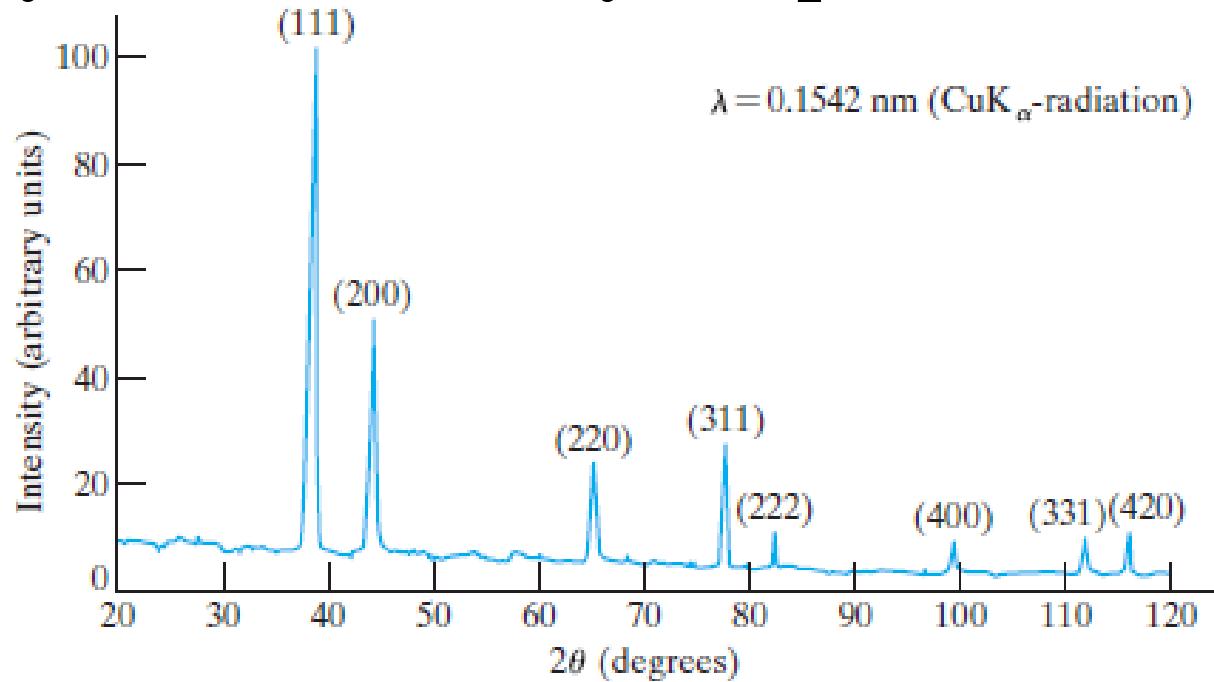
Diffraction pattern of Al (FCC crystal)

An X-ray diffraction pattern reflects the lattice and symmetry of the crystalline material.

The diffraction peaks are indexed, these indices tell you which crystal planes are reflecting the X-rays

Electron diffraction: crystal planes

beam falls in parallel to
the [110] zone axis.
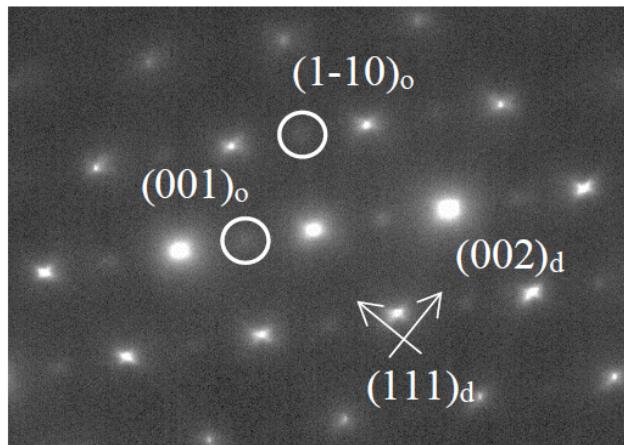
Images of same sample
with incident electron beam
parallel to other crystallographic
directions
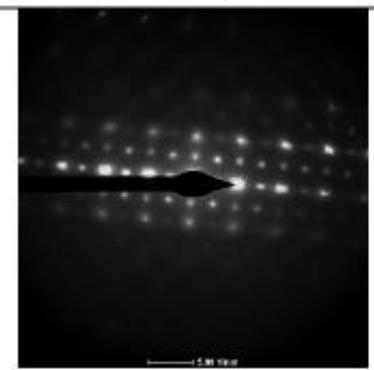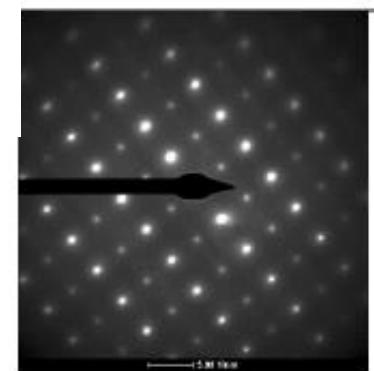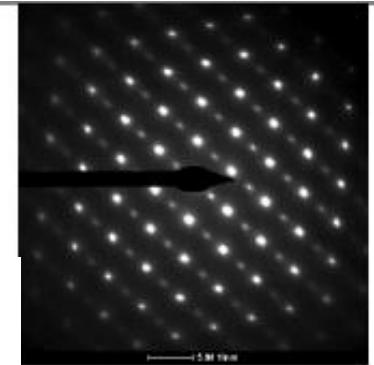
Depending on how the sample is oriented
relative to the incoming beam, the diffraction
pattern will be different and allow to recognize
the symmetry of the crystal

[110]

[112]

[001]

Au alloy

Reciprocal lattice and diffraction

- the electron diffraction patterns or the X-ray diffraction patterns are simply sections through the reciprocal lattice of a crystal—the pattern of spots on the screen or area detector and the pattern of reciprocal lattice points in the corresponding plane or section through the crystal are identical.

- which section of the 3D reciprocal lattice is probed is defined by the Ewald sphere (as will be discussed in coming weeks)

Reciprocal lattice vectors

direction normal to plane

length inversely proportional to lattice spacing d

$$\|\mathbf{d}_1^*\| = C/d_1$$
$$\|\mathbf{d}_2^*\| = C/d_2$$

$$C = 2\pi$$
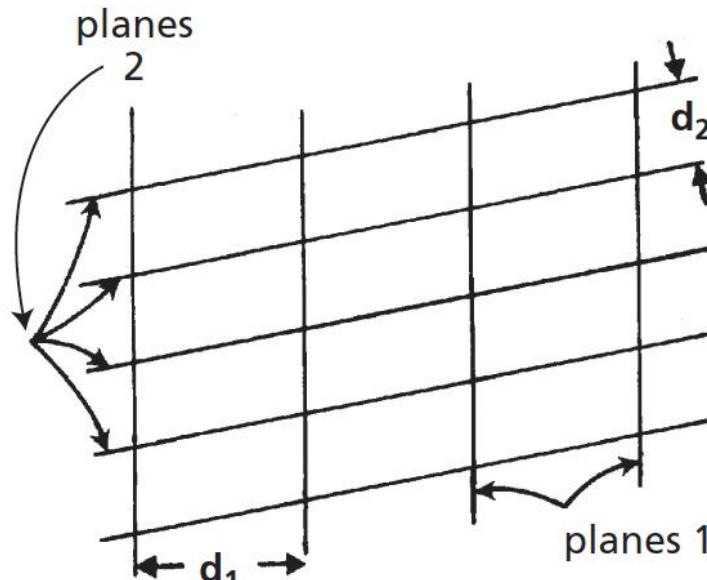
(a) two families of planes with d-spacing d_1 and d_2
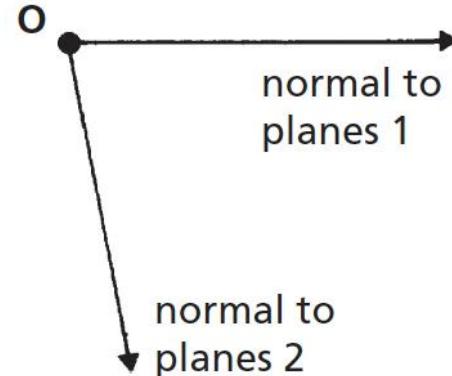
(b) normals to the family of planes from common origin O
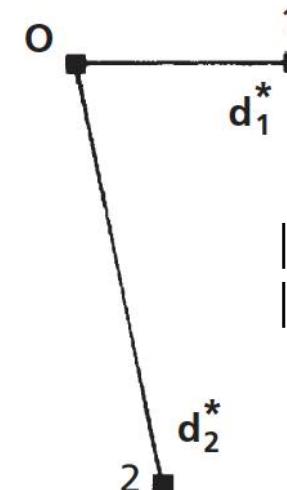
(c) reciprocal (lattice) vectors

longer vector for smaller d-spacing

Reciprocal lattice

(a)

(b)

(c)
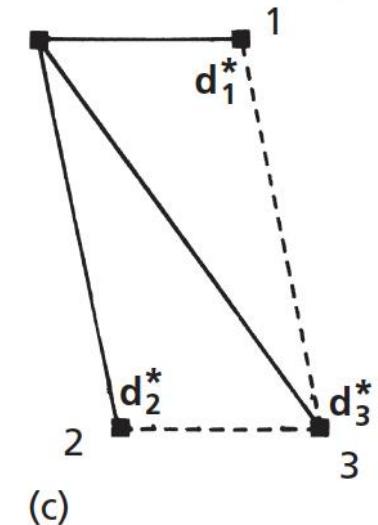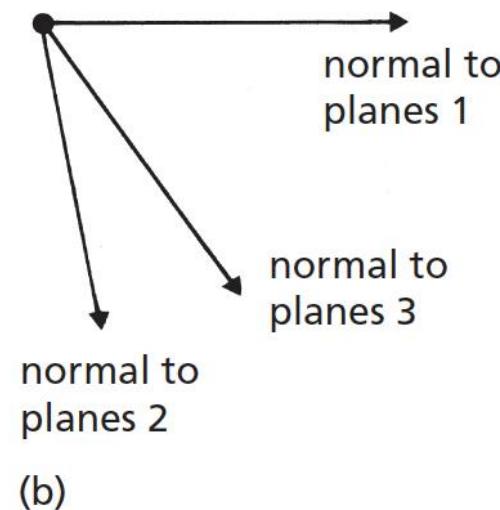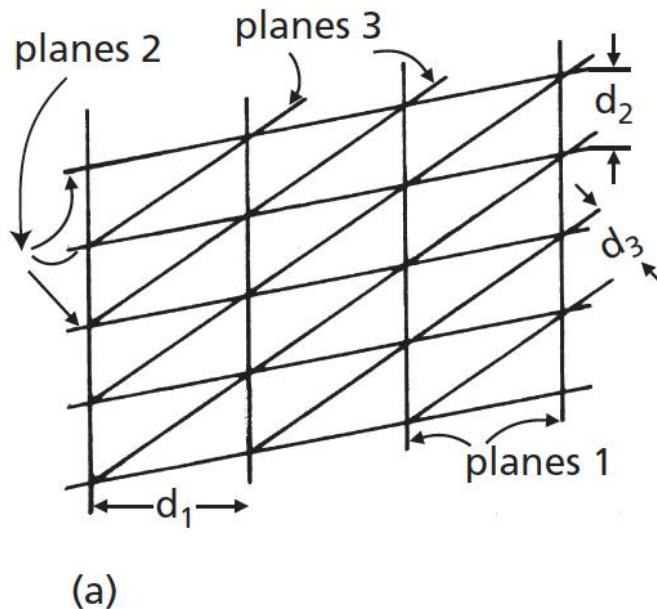
scale in reciprocal space
is 1/length
Å^{-1}, or nm

third family of planes, the reciprocal vectors start to form a grid or lattice

The five plane lattices and their corresponding reciprocal lattice
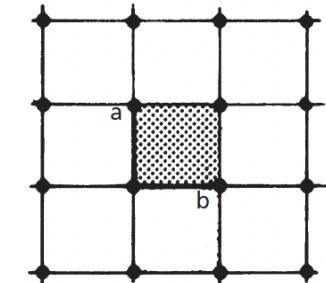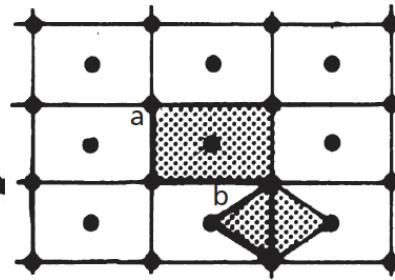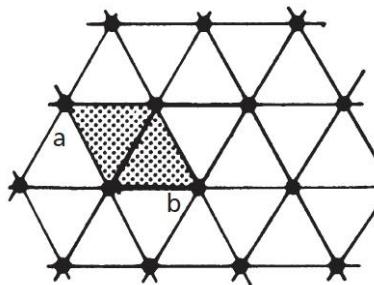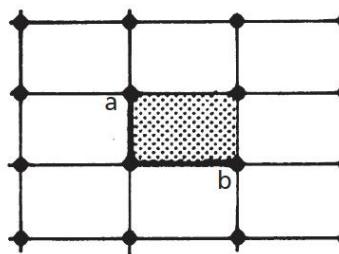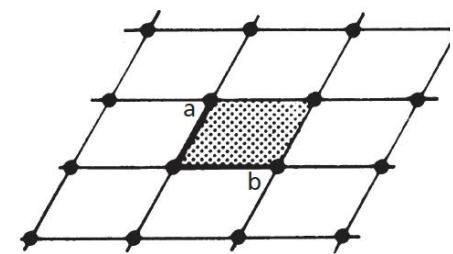
unit cell specified by lattice vectors **a** and **b**
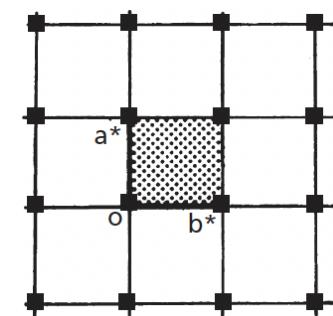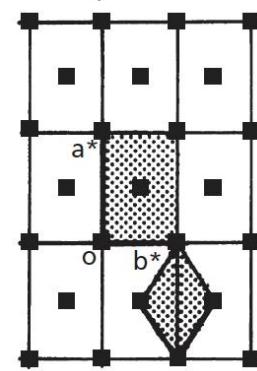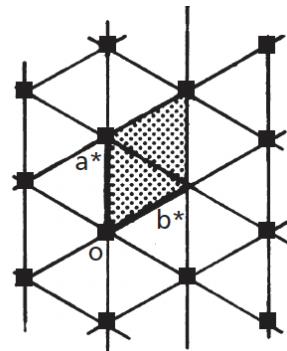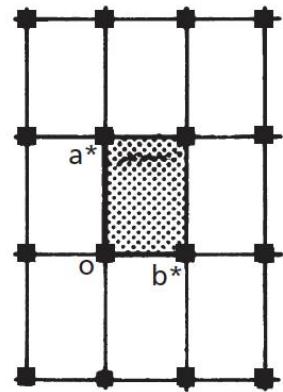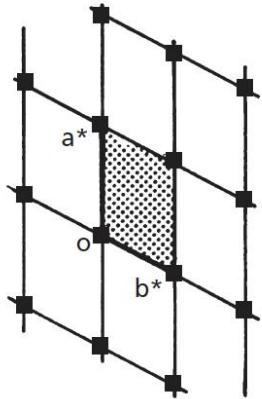
unit cell specified by reciprocal lattice vectors **a*** and **b***

Reciprocal lattice

Plan of a monoclinic P unit cell
perpendicular to the y-axis
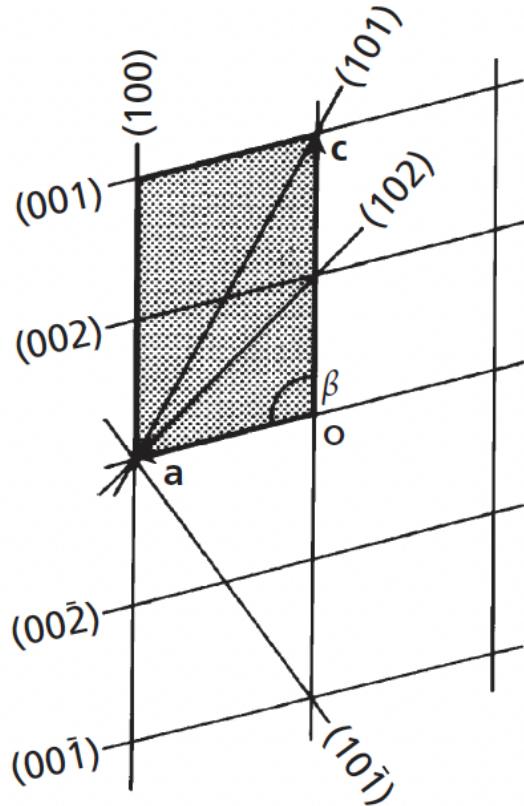
planes (hok)
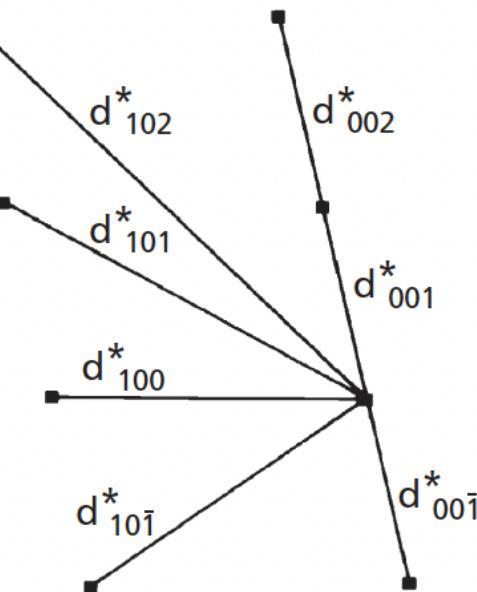
Note that $\mathbf{a^*}$ and $\mathbf{c^*}$ are not parallel to $\mathbf{a}$ and $\mathbf{c}$, respectively, because the normals to the (100) and (001) planes in the monoclinic lattice are not parallel to $\mathbf{a}$ and $\mathbf{c}$, respectively.
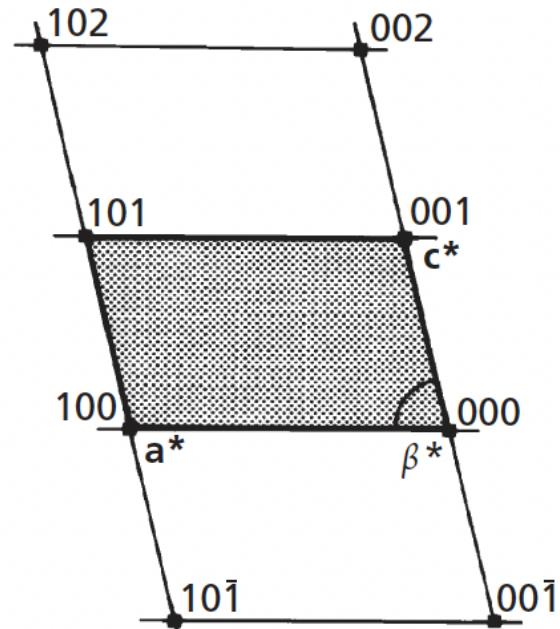
$$\mathbf{a^*} = \mathbf{d^*_{100}} \quad \text{and} \quad ||\mathbf{a^*}|| = 2\pi/d_{100}$$

$$\mathbf{c^*} = \mathbf{d^*_{001}} \quad \text{and} \quad ||\mathbf{c^*}|| = 2\pi/d_{001}$$

Reciprocal lattice

for the (102) planes:

$$\mathbf{d}^*_{102} = 1\mathbf{a}^* + 0\mathbf{b}^* + 2\mathbf{c}^*$$

for the (hkl) planes:

$$\mathbf{d}^*_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$

plane indices are components of the $\mathbf{d}^*_{hkl}$ vector
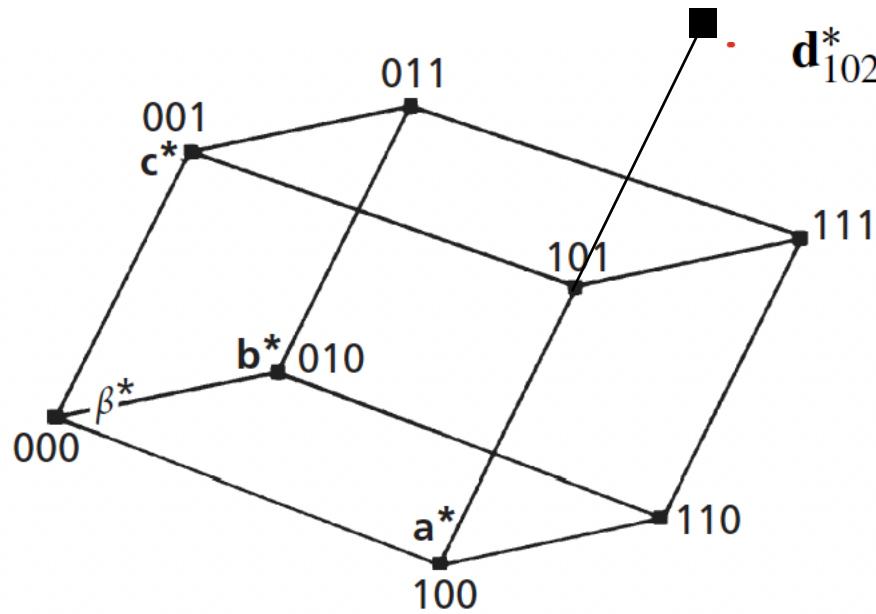
The reciprocal lattice unit cell of a monoclinic P crystal defined by reciprocal lattice vectors **a***, **b*** and **c***

direct lattice vector: directions are its components

$$\mathbf{r}_{uvw} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

Reciprocal lattice

Plan of a monoclinic unit cell
perpendicular to the y-axis

c^* is perpendicular to both **a** and **b**, which means their dot products are zero

$c^* \cdot a = 0$ and $c^* \cdot b = 0$

$c^* \cdot c = cc^* \cos\phi$

with $||c^*|| = 2\pi/d_{001}$ and from drawing: $c \cos\phi = d_{001}$

$c^* \cdot c = 2\pi d_{001}/d_{001} = 2\pi$

does we have:

$\vec{a^*}\cdot\vec{a} = 2\pi$	$\vec{b^*}\cdot\vec{a} = 0$	$\vec{c^*}\cdot\vec{a} = 0$
$\vec{a^*}\cdot\vec{b} = 0$	$\vec{b^*}\cdot\vec{b} = 2\pi$	$\vec{c^*}\cdot\vec{b} = 0$
$\vec{a^*}\cdot\vec{c} = 0$	$\vec{b^*}\cdot\vec{c} = 0$	$\vec{c^*}\cdot\vec{c} = 2\pi$

We have a new basis new basis (O, a^*, b^*, c^*) in which a vector $N^*_{hkl} = ha^* + kb^* + lc^*$ is perpendicular to the plane (hkl)

If we consider any vector in the direct space $\boldsymbol{R} = r_1\boldsymbol{a} + r_2\boldsymbol{b} + r_3\boldsymbol{c}$ and one in the reciprocal space $\boldsymbol{N^*} = n_1\boldsymbol{a^*} + n_2\boldsymbol{b^*} + n_3\boldsymbol{c^*}$, we have:

$$\boldsymbol{R} \cdot \boldsymbol{N^*} = r_1 n_1 \boldsymbol{a} \cdot \boldsymbol{a^*} + r_2 n_2 \boldsymbol{b} \cdot \boldsymbol{b^*} + r_3 n_3 \boldsymbol{c} \cdot \boldsymbol{c^*} = 2\pi(r_1 n_1 + r_2 n_2 + r_3 n_3)$$

an integer

Reciprocal lattice – Notations...

- A note on Notations:
- the reciprocal space vector (which points from one reciprocal lattice point to some other reciprocal lattice point) is called
- $\mathbf{d^*}_{hkl}$
- $\mathbf{N^*}$

or in particular when we talk about diffraction often

- $\mathbf{G}$ or $\mathbf{K}$

also

$\mathbf{a^*} \cdot \mathbf{a} = \mathbf{b^*} \cdot \mathbf{b} = \mathbf{c^*} \cdot \mathbf{c} = C$, C a constant

Often C is often noted as 2π (and we will see soon why it is very convenient to do so) in some text books (including Hammond) C= 1

# Find the reciprocal space vectors from direct lattice vectors

find **a*** which is orthogonal to **b** and **c** → cross product!
and fullfills **a** · **a*** = 2π

$$\text{with } \mathbf{a^*} = (\mathbf{b} \times \mathbf{c}) \frac{2\pi}{V}$$

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

Reminder Volume:

$$V = (\vec{a}, \vec{b}, \vec{c}) = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$$
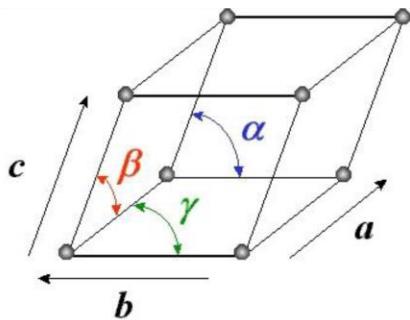
so we can find the reciprocal space vectors by:

$$\vec{a^*} = 2\pi \frac{\vec{b} \times \vec{c}}{V} \qquad \vec{b^*} = 2\pi \frac{\vec{c} \times \vec{a}}{V} \qquad \vec{c^*} = 2\pi \frac{\vec{a} \times \vec{b}}{V}$$

For cubic structure

primitive cubic:

$V = a^3$ $\qquad$ $\mathbf{a} = a\mathbf{x}$ $\qquad$ $\mathbf{b} = a\mathbf{y}$ $\qquad$ $\mathbf{c} = a\mathbf{z}$

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

$$\mathbf{a^*} = \frac{2\pi}{a^3}\begin{pmatrix} 0 \\ a \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ a \end{pmatrix} = \frac{2\pi}{a^3}\begin{pmatrix} a^2 \\ 0 \\ 0 \end{pmatrix} = \frac{2\pi}{a}\mathbf{x} = \frac{2\pi}{a^2}\mathbf{a} \qquad \text{and} \qquad \mathbf{b^*} = = \frac{2\pi}{a}\mathbf{y}$$

$$\mathbf{c^*} = = \frac{2\pi}{a}\mathbf{z}$$

→ another cubic
→ $\mathbf{a^*}, \mathbf{b^*}, \mathbf{c^*}$ are parallel to $\mathbf{a}, \mathbf{b}, \mathbf{c}$

face-centred cubic reciprocal lattice (cubic F) for the body-centred cubic (direct) lattic (cubic I)

reciprocal lattice of the face-centred cubic lattice is body-centred

Example

HM:F m -3 m #225
a=5.639Å
b=5.639Å
c=5.639Å
α=90.000°
β=90.000°
γ=90.000°
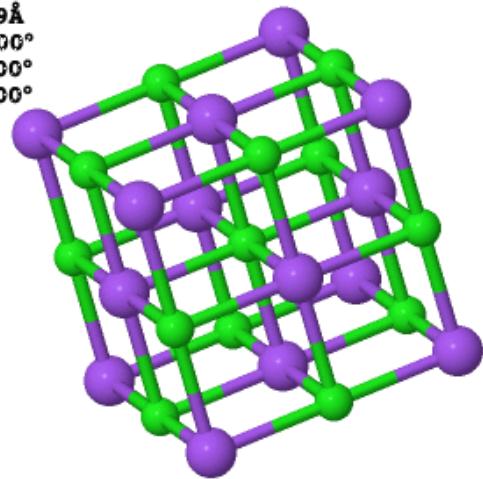
NaCl
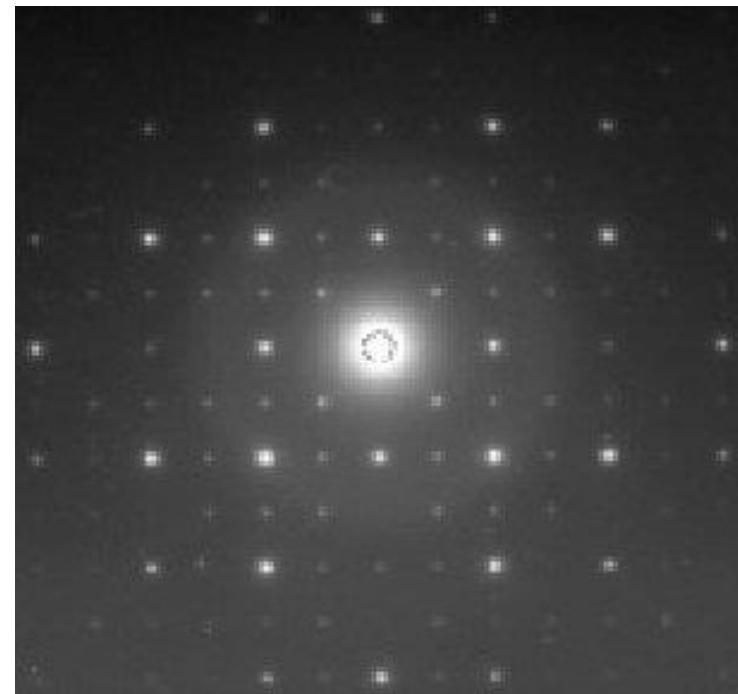
Distances between (hkl) planes

The reciprocal space formalism facilitates the derivation of the interplane distance of parallel (hkl) planes.

$$OA = \frac{1}{h}a \qquad OB = \frac{1}{k}b \qquad OC = \frac{1}{l}c$$

distance $d_{(hkl)}$ is the projection of **OA** (or **OB** or **OC**) onto the normal of the plane → the scalar product

$$N^* = ha^* + kb^* + lc^*$$
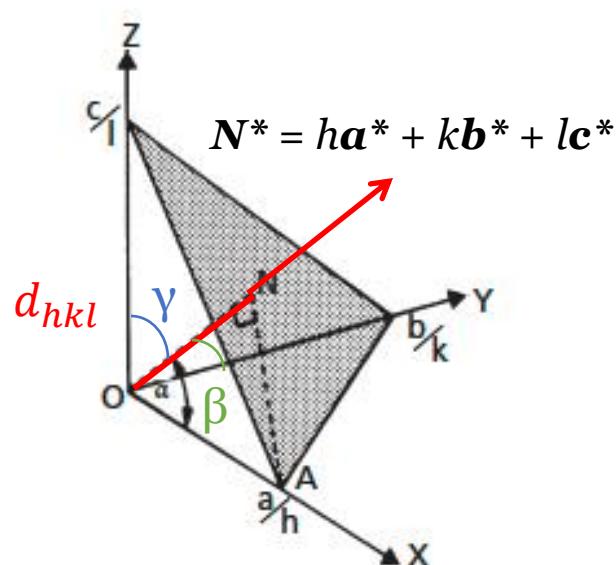
now we have the reciprocal lattice vector $N^*_{(hkl)}$ which is perpendicular to the (hkl) plane

does we can now calculate the distance by projection of OA onto the unit vector along $N^*_{(hkl)}$

$$d_{(hkl)} = OA \cdot \frac{N^*_{(hkl)}}{\|N^*_{(hkl)}\|}$$

as we have seen before, for any vector (e.g. **OA**) in real space it holds

$$OA \cdot N^*_{(hkl)} = OB \cdot N^*_{(hkl)} = OC \cdot N^*_{(hkl)} = 2\pi$$

$$\boxed{d_{(hkl)} = \frac{2\pi}{\|N^*_{(hkl)}\|}}$$

- Calculate the reciprocal lattice vectors a^*, b^*, c^* and the vector $N^*_{(hkl)}$

- Find the norm of $N^*_{(hkl)}$ -→ find the distance.

Distance between (hkl) planes: cubic system

$$d_{(hkl)} = \frac{2\pi}{\left\| N^*_{(hkl)} \right\|}$$

$$||\mathbf{N}^*{}_{(hkl)}|| = \sqrt{(h\boldsymbol{a}* + k\boldsymbol{b}* + l\boldsymbol{c}*) \cdot (h\boldsymbol{a}* + k\boldsymbol{b}* + l\boldsymbol{c}*)}$$

for crystals with orthogonal axis, for example cubic
also reciprocal basis is orthogonal $\mathbf{a}^* \cdot \mathbf{b}^* = 0$ etc.

$$||\mathbf{N}^*{}_{(hkl)}|| = \sqrt{h\boldsymbol{a}* \cdot h\boldsymbol{a}* + k\boldsymbol{b}* \cdot k\boldsymbol{b}* + l\boldsymbol{c}* \cdot l\boldsymbol{c}*)}$$

as we have seen before for cubic $\quad \mathbf{a}^* = \dfrac{2\pi}{a}\mathbf{x} \quad \mathbf{b}^* = \dfrac{2\pi}{a}\mathbf{y} \quad \mathbf{c}^* = \dfrac{2\pi}{a}\mathbf{z}$

orthonormal basis → norm of vector as square root of components

$$||\mathbf{N}^*|| = \sqrt{\left(\frac{2\pi}{a}h\right)^2 \left(\frac{2\pi}{a}k\right)^2 + \left(\frac{2\pi}{a}l\right)^2} = 2\pi\frac{\sqrt{h^2+k^2+l^2}}{a} \qquad d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Reminder distance in direct lattice

- The plane parallel to the plane (ABC) and passing through the origin O is a crystal plane belonging to the family of planes $\{hkl\}$.

- Assuming that the distance between two (hkl) planes is the same for all consecutive planes, this distance is given by **ON,** which is the projection of the vector **OA** on the normal to the plane

- $ON = d_{(hkl)} = \boldsymbol{OA} \cdot \boldsymbol{n_{hkl}}$

$\boldsymbol{a} \cdot \boldsymbol{b} = ab \cos\alpha$
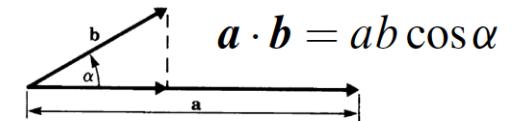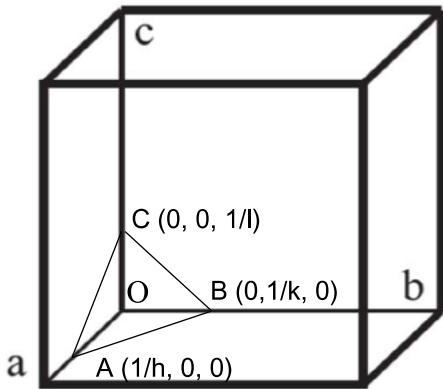
$OA \cos\alpha = ON$ or $(a/h)\cos\alpha = d_{hkl}$ or $\cos\alpha = \left(\dfrac{h}{a}\right) d_{hkl}.$

$\cos\beta = \left(\dfrac{k}{b}\right) d_{hkl}$ and $\cos\gamma = \left(\dfrac{l}{c}\right) d_{hkl}.$
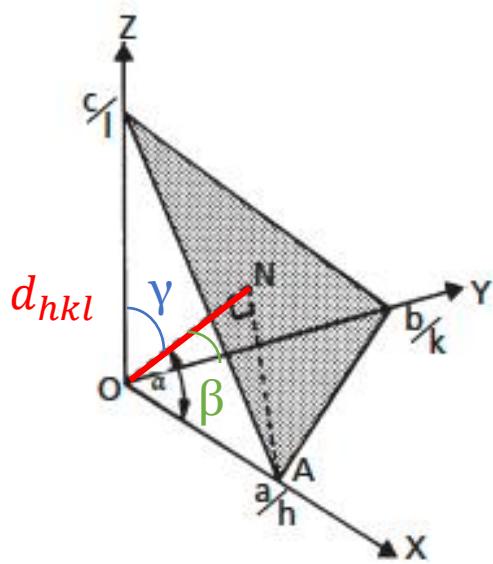
For orthogonal axes $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ (Pythagoras' theorem).

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

For a cubic crystal $a = b = c$, $\dfrac{1}{d_{hkl}^2} = \dfrac{h^2 + k^2 + l^2}{a^2}.$ $d_{(hkl)} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

→ for cubic both works, for non-orthogonal lattice it is much easier in the reciprocal space   21

Distance between (hkl) planes

$$d_{(hkl)} = \frac{2\pi}{\|N^*_{(hkl)}\|}$$

$$||N^*_{(hkl)}|| = \sqrt{(h\boldsymbol{a}* + k\boldsymbol{b}* + l\boldsymbol{c}*) \cdot (h\boldsymbol{a}* + k\boldsymbol{b}* + l\boldsymbol{c}*)}$$

watch out, **a***, **b*** and **c*** are not orthogonal to each other for many of the crystal lattices!
but the reciprocal space lattice helps to get back some orthogonality since we defined **a*** to be orthogonal to **a** and **b** etc.

→ exercise to calculate for hexagonal lattice

Distances betweek (hkl) planes

– Monoclinic:
$$d_{hkl} = \cfrac{1}{\sqrt{\left(\cfrac{h^2}{a^2} + \cfrac{l^2}{c^2} - \cfrac{2\,hl}{a\,c}\cos b\right)\cfrac{1}{\sin^2 b} + \cfrac{k^2}{b^2}}}$$

– Orthorhombic:
$$d_{hkl} = \cfrac{1}{\sqrt{\cfrac{h^2}{a^2} + \cfrac{k^2}{b^2} + \cfrac{l^2}{c^2}}}$$

–Tetragonal:
$$d_{hkl} = \cfrac{1}{\sqrt{\cfrac{h^2 + k^2}{a^2} + \cfrac{l^2}{c^2}}}$$

– Hexagonal:
$$d_{hkl} = \cfrac{1}{\sqrt{\cfrac{4}{3\,a^2}(h^2 + k^2 + hk) + \cfrac{l^2}{c^2}}}$$

– Cubic:
$$d_{hkl} = \cfrac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

Young's double slit experiment
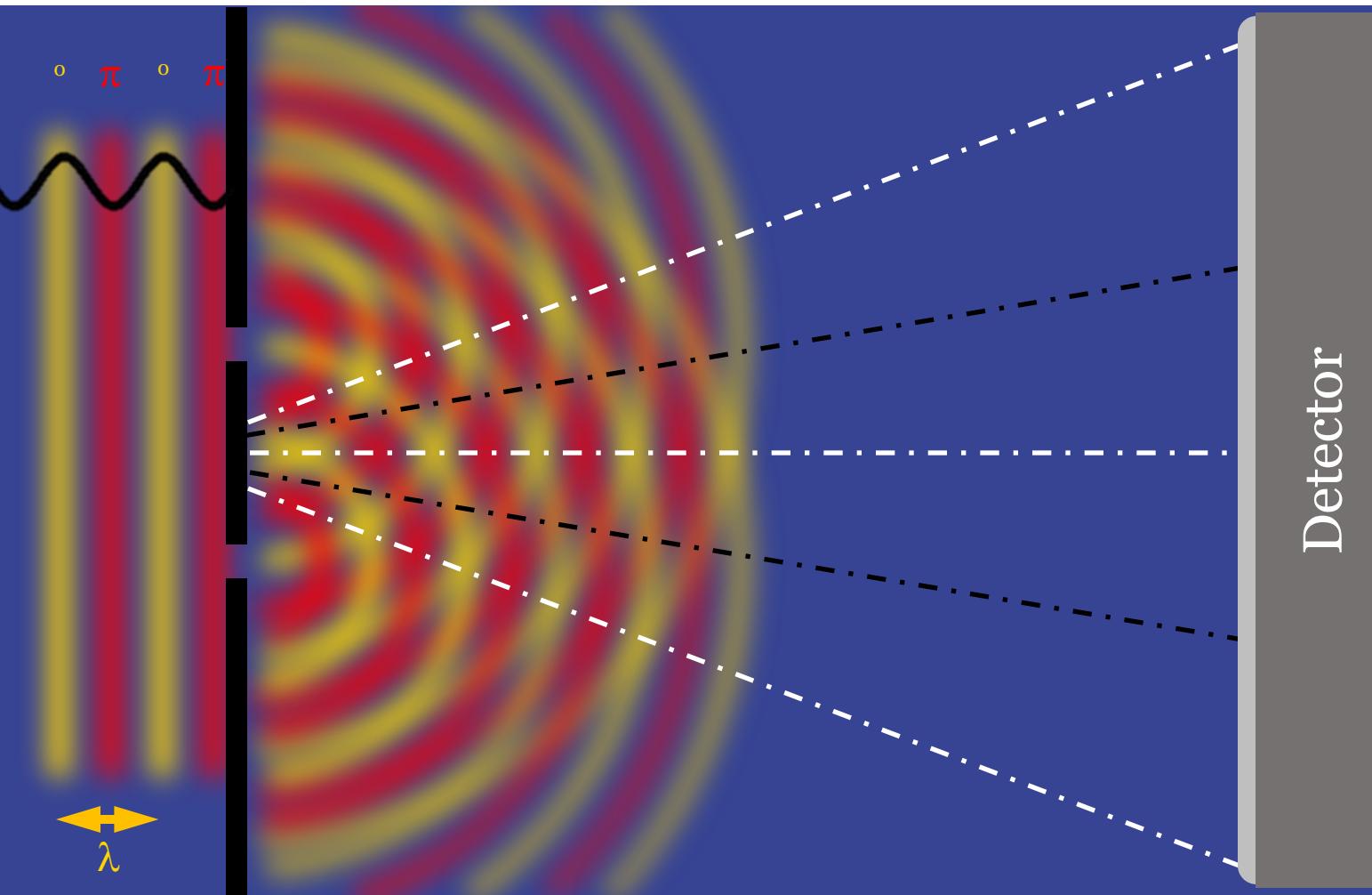
to get such an interference pattern we need a wavelength that is of the order of the distance between the slits.

by Phil Willmott

Young's double slit experiment

P

Path 1

Path 2

2θ

2θ

S_1

d

S_2

OPD
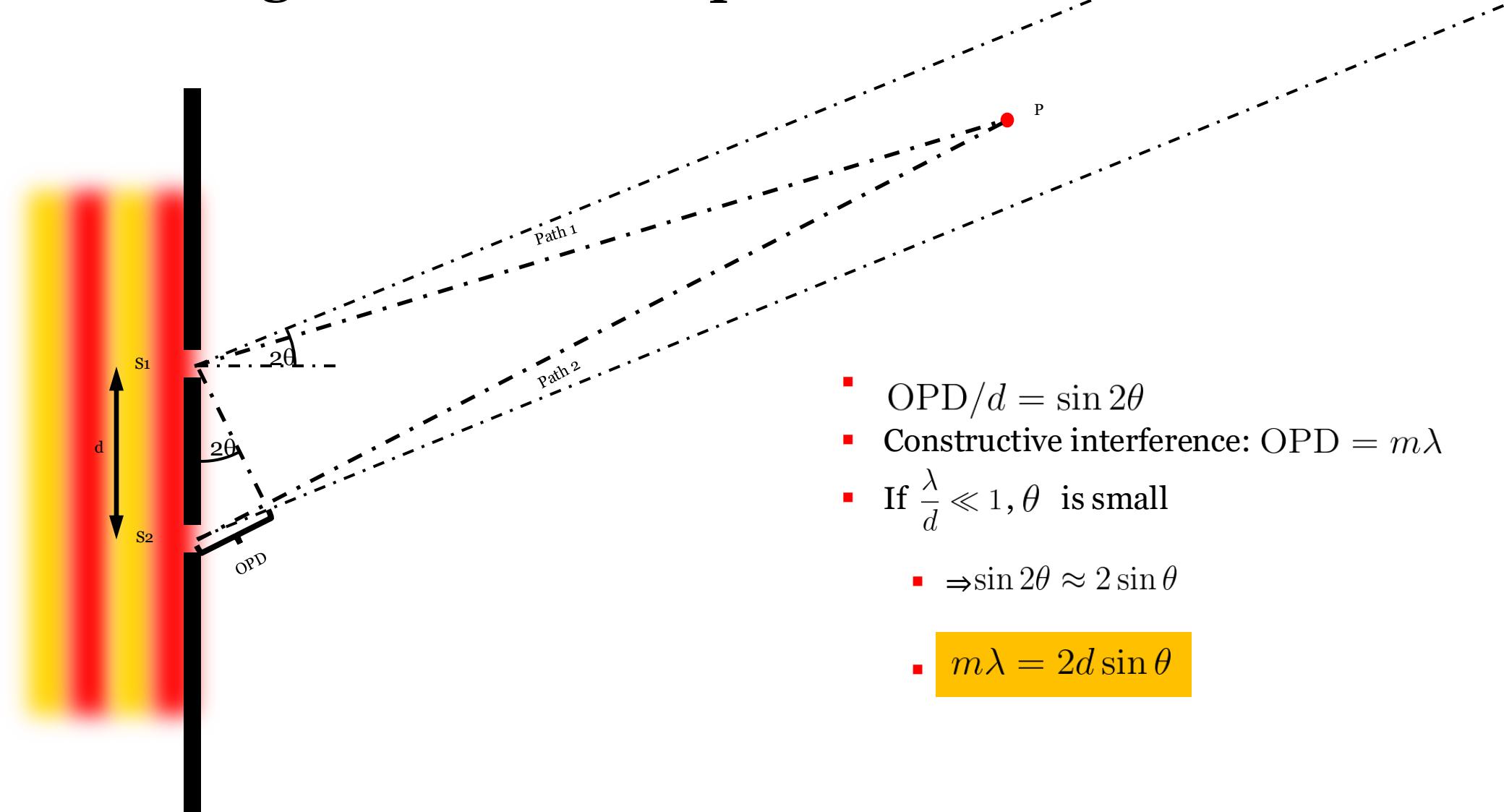
- $\text{OPD}/d = \sin 2\theta$
- Constructive interference: $\text{OPD} = m\lambda$
- If $\dfrac{\lambda}{d} \ll 1$, θ is small
  - $\Rightarrow \sin 2\theta \approx 2\sin\theta$
  - $m\lambda = 2d\sin\theta$

by Phil Willmott

Young's double slit experiment

$$m\lambda = 2d \sin\theta$$
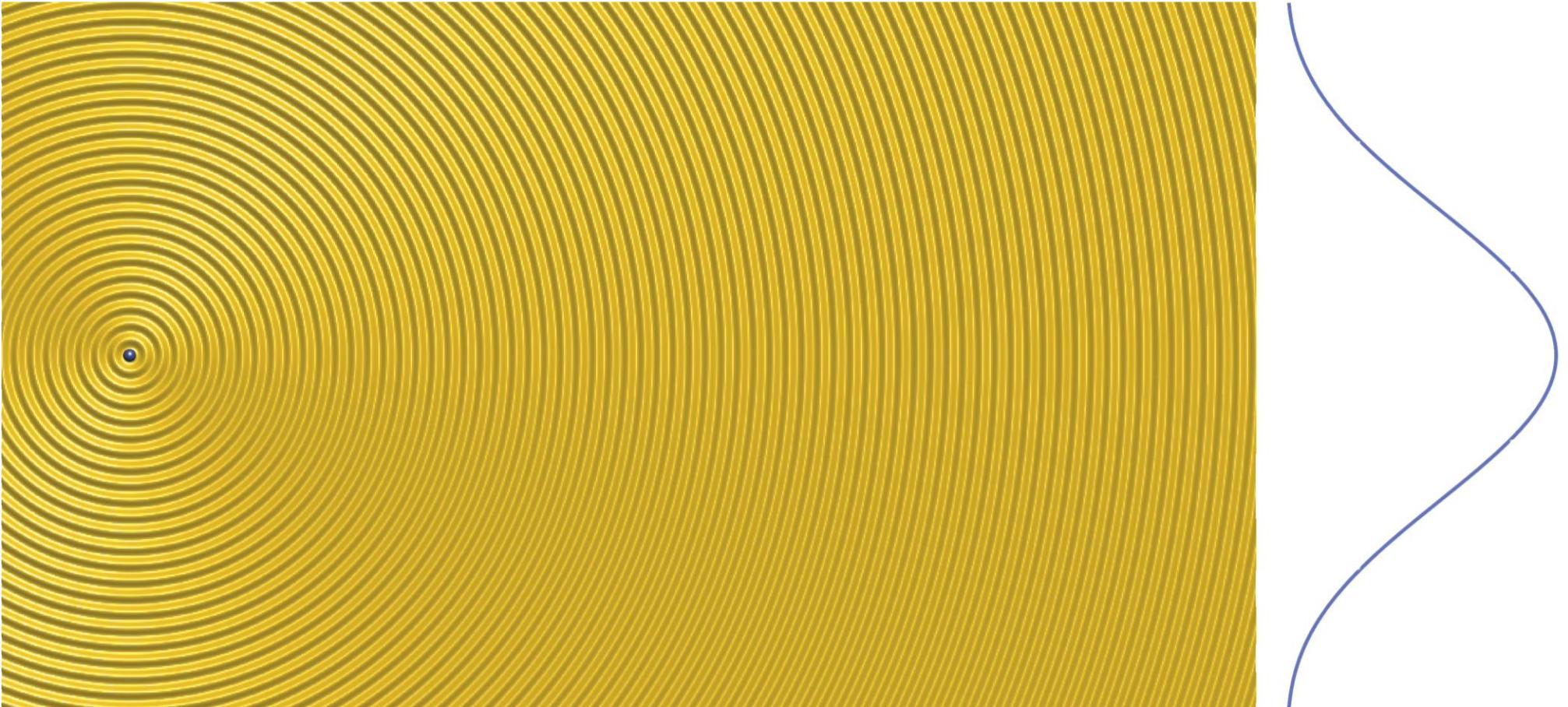
distance between two scattering centers or slits increases
the angle between maxima become narrower

by Phil Willmott

Crystal instead of double slit
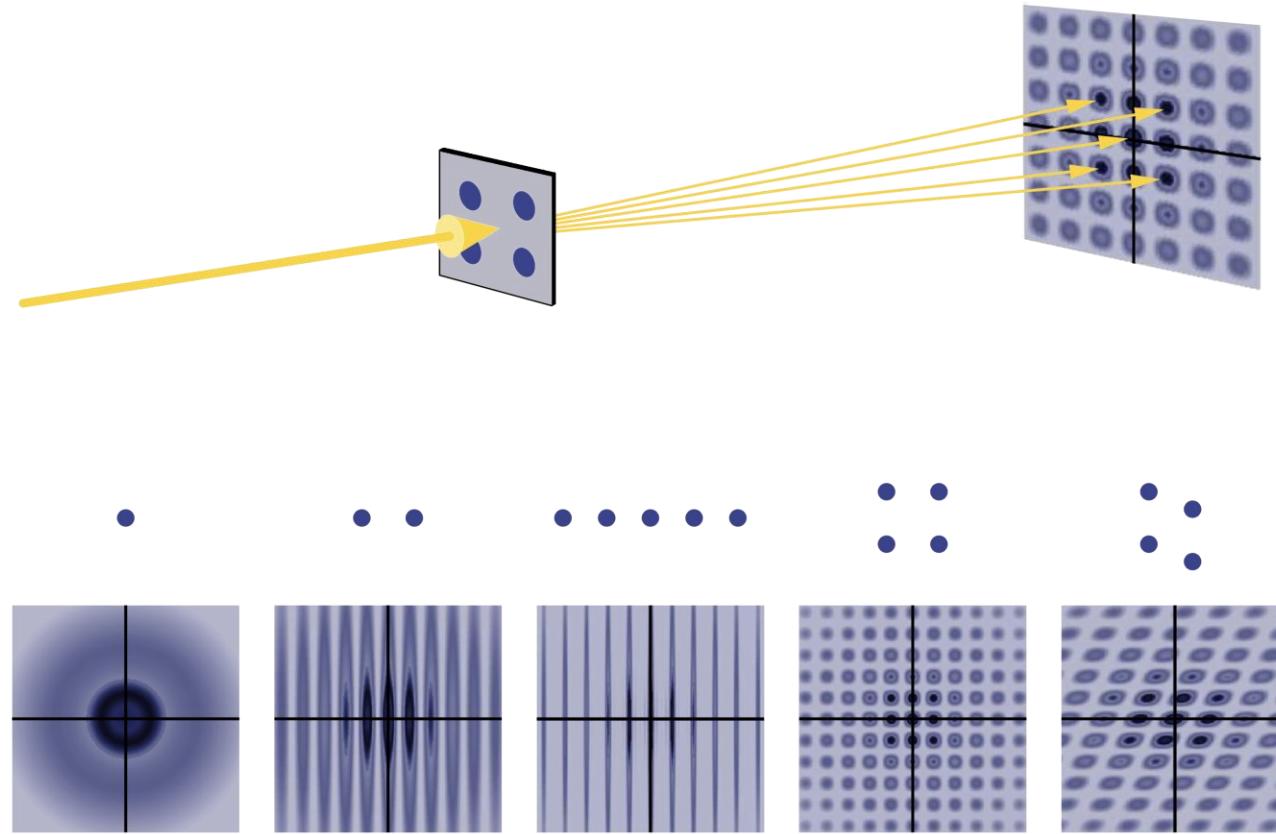
Which radiation?

visible light will not be a good probe since the wavelength is 400nm-700nm, which is much bigger than the distance between the atoms, typically of the order of a few 10^{-10}m. For instance,
- the lattice parameter of the element Ni is 3.6 10^{-10}m,
- the size of an atom is about 1.4 10^{-10}m.

	Energy	wavelength
Neutrons	1 – 5 meV (cold)	9 - 4 A
	25 – 50 meV (thermal)	1.8 – 1.3 A
Xrays	100keV	0.12 A (hard Xrays)
	40 keV	0.31 A
	5 keV	2.48 A (soft Xrays)
Electrons	200 keV	0.025 A

Bragg's law
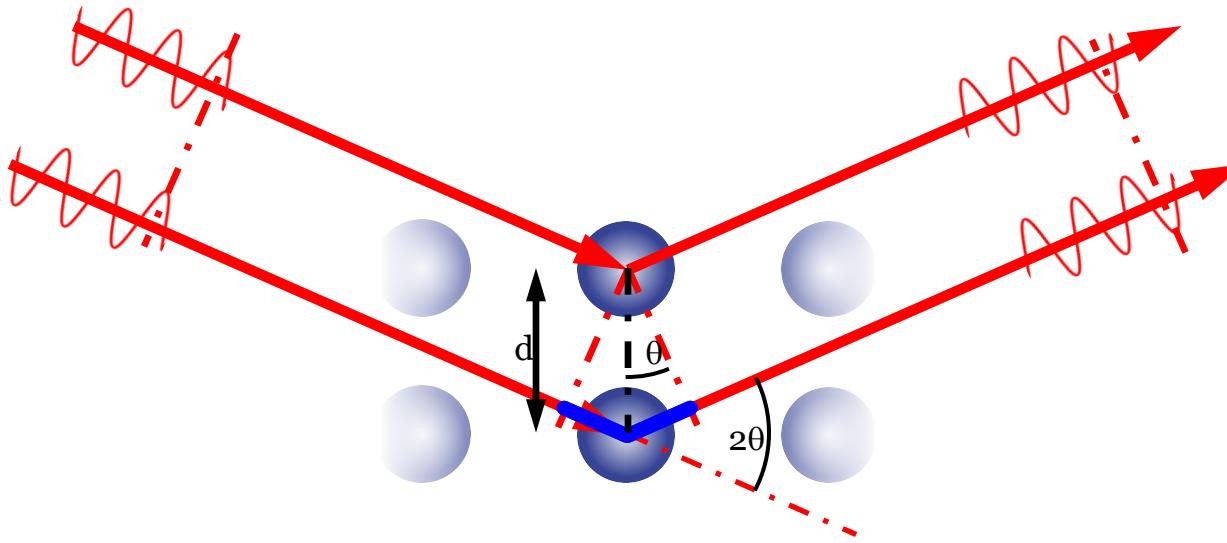
Again, $\boxed{m\lambda = 2d\sin\theta}$ or $\boxed{\lambda = 2d_{hkl}\sin\theta}$

Bragg's law

2θ

d
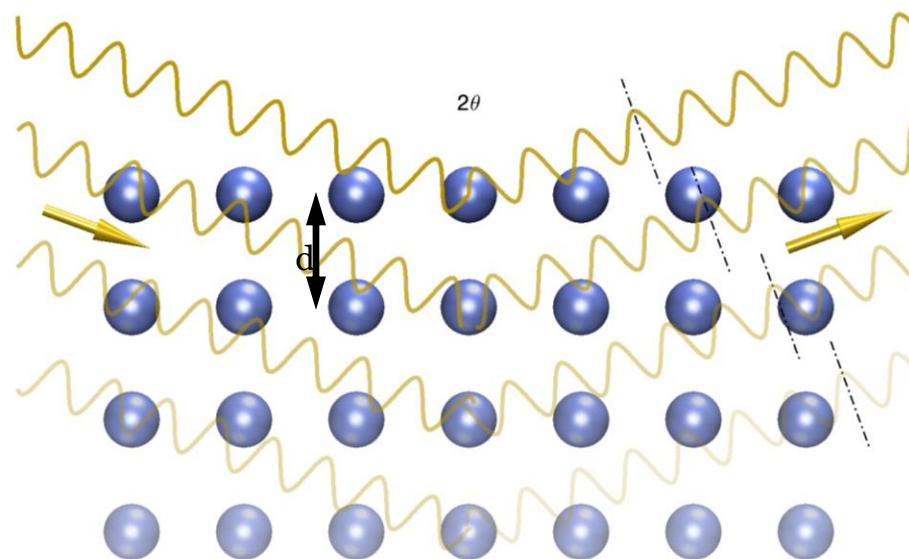
Bragg's law

higher orders m (or n):
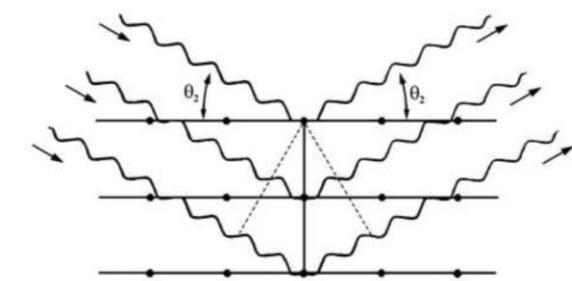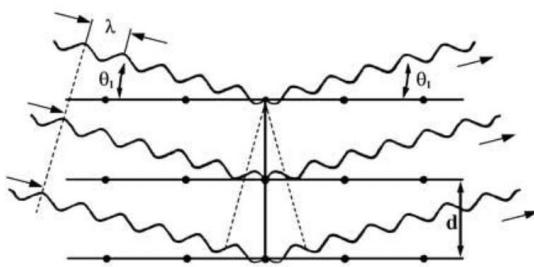
$$m\lambda = 2d \sin\theta$$

$$\lambda = 2d_{hkl} \sin\theta \qquad \text{what happened to } m?$$

it usually is incorporated into (hkl)

$$m\lambda = 2d_{hkl} \sin\theta$$
$$\lambda = 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = 2d_{nh\,nk\,nl}\sin\theta$$

for example third order reflection of the plane (111) is represented as a first order of the plane (333)

Bragg's law

$$\Delta L = d_2 - d_1 = 0$$

$$d_2 = dcos(\theta)$$
$$d_1 = dcos(\theta)$$
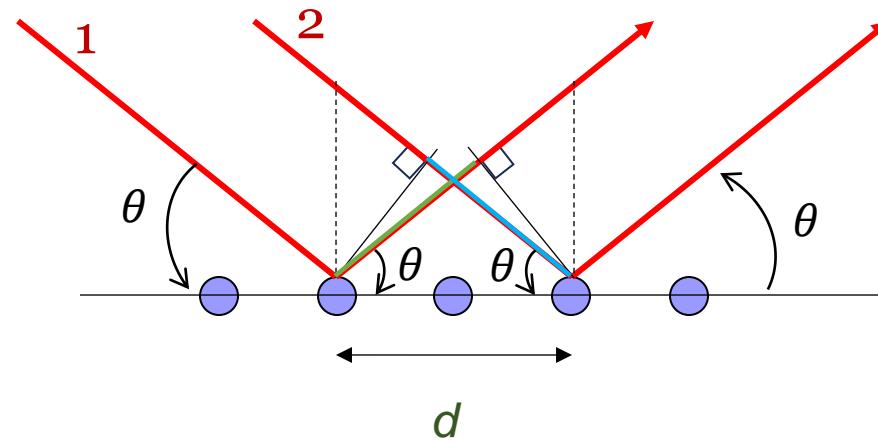
only atoms on different planes can scatter out of phase! So we can consider entire planes as scatterers.
geometrical view, simple expression

what if we look at a crystal as a three-dimensional lattice with atoms located in a certain motif? We can look at the lattice as a 3D diffraction grating → view of Max von Laue (1912)

Reminder complex numbers

Designation	Formulae
Imaginary unit j	$j^2 = -1$
Imaginary number η	$\eta = jy \quad (y \text{ real})$
Complex number z in arithmetic form	$z = x + jy \quad (x, y \text{ real})$ $x = \text{real part}$ $y = \text{imaginary part}$
Complex conjugate	$z^* = x - jy$
Complex numbers in polar form	$z = r(\cos\alpha + j\sin\alpha)$
Transformation $(x, y) \leftrightarrow (r, \alpha)$	$\left. \begin{array}{l} x = r\cos\alpha \\ y = r\sin\alpha \end{array} \right\} \quad \left. \begin{array}{l} r = \sqrt{x^2 + y^2} \\ \tan\alpha = y/x \end{array} \right\}$
Complex number in exponential form Euler's formula	$z = re^{j\alpha}$ $e^{j\alpha} = \cos\alpha + j\sin\alpha$
Exponential form for cosine and sine functions	$\cos\alpha = \dfrac{1}{2}(e^{j\alpha} + e^{-j\alpha}) = \cosh j\alpha$ $\sin\alpha = \dfrac{1}{2j}(e^{j\alpha} - e^{-j\alpha}) = \dfrac{1}{j}\sinh j\alpha$
Periodicity of complex numbers	$\begin{aligned} z &= re^{j\alpha} \\ &= re^{j(\alpha + 2k\pi)} \quad (k = \pm 1, \pm 2, \pm 3, \cdots) \end{aligned}$

Reminder complex numbers

Designation	Formulae
Multiplication and division in exponential form	$z_1 = r_1 e^{j\alpha_1}, z_2 = r_2 e^{j\alpha_2}$ $z_1 z_2 = r_1 r_2 e^{j(\alpha_1 + \alpha_2)}$ $\dfrac{z_1}{z_2} = \dfrac{r_1}{r_2} e^{j(\alpha_1 - \alpha_2)}$
Raising to a power and extracting roots in exponential form	$z = r e^{j\alpha}$ $z^n = r^n e^{jn\alpha}$ $\sqrt[n]{z} = \sqrt[n]{r} e^{j[(\alpha + 2\pi k)/n]} \; (k = 0, \pm 1, \pm 2, \cdots)$
Multiplication and division in polar form	$z_1 = r_1 (\cos\alpha_1 + j \sin\alpha_1)$ $z_2 = r_2 (\cos\alpha_2 + j \sin\alpha_2)$ $z_1 z_2 = r_1 r_2 [\cos(\alpha_1 + \alpha_2) + j \sin(\alpha_1 + \alpha_2)]$ $\dfrac{z_1}{z_2} = \dfrac{r_1}{r_2} [\cos(\alpha_1 - \alpha_2) + j \sin(\alpha_1 - \alpha_2)]$
Raising to a power and extracting roots in polar form	$z = r(\cos\alpha + j \sin\alpha)$ $z^n = r^n [\cos n\alpha + j \sin n\alpha]$ $\sqrt[n]{z} = \sqrt[n]{r} \left[\cos\left(\dfrac{\alpha}{n} + \dfrac{2\pi k}{n} \right) + j \sin\left(\dfrac{\alpha}{n} + \dfrac{2\pi k}{n} \right) \right]$ $(k = 0, \pm 1, \pm 2, \cdots)$

Reminder complex numbers

- The polar form :
$$z = r\cos\theta + ir\sin\theta = re^{i\theta}$$

- The relation $e^{i\theta} = \cos\theta + i\sin\theta$ is called the Euler relation

- Link with the algebraic form:

$$r = \sqrt{x^2 + y^2} \text{ and } \tan\theta = \frac{y}{x}$$

$$\cos\theta = \frac{x}{\sqrt{x^2+y^2}} \text{ and } \sin\theta = \frac{y}{\sqrt{x^2+y^2}}$$

- Remember that $e^{i\theta}$ is periodic ! So:

$$e^{i\theta} = e^{i(\theta+2p\pi)}, p \in \mathbb{Z}$$

- $|e^{i\theta}| = 1 = \sqrt{x^2 + y^2}$, with

$x = \cos\theta$ and y= $\sin\theta$

So the x coordinate are the cosine of the angle;
The y coordinates are the sine of the angle.

Example: $\cos\left(\frac{\pi}{3}\right) = \frac{1}{2}$; $\sin\left(\frac{\pi}{3}\right) = \frac{\sqrt{3}}{2}$
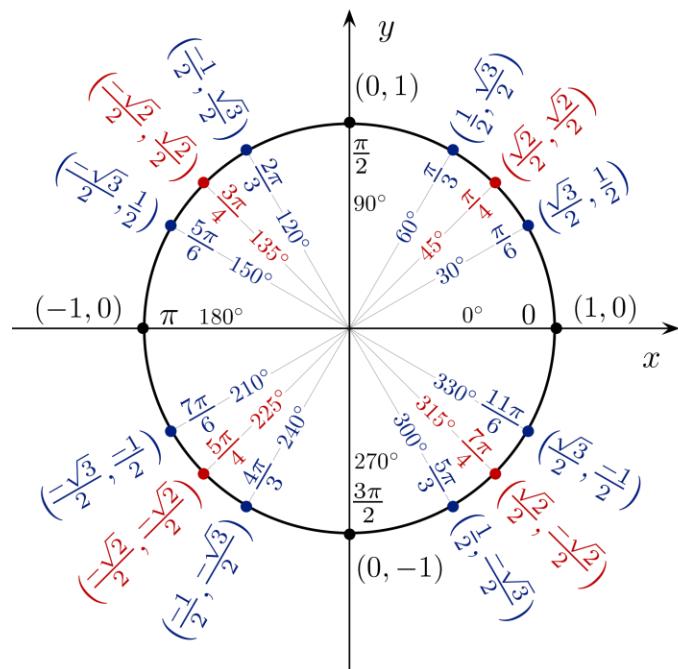
Plane wave equation

$$\psi(\boldsymbol{r},t) = Ae^{i\Phi} = Ae^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_0)} = A'e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\psi(\boldsymbol{r},t) = A\cos(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_0)$$

$\boldsymbol{r}$ is the position vector (x,y,z)
t is the time
Φ the (total) phase
A is the amplitude of the wave (in electromagnetism often noted as $\boldsymbol{E}_o$, the electric field amplitude)

A' is the complex amplitude $A' = e^{i\phi}$
which includes the phase shift ϕ_0

$\boldsymbol{k}$ is the wave vector $\boldsymbol{k} = \frac{2\pi}{\lambda}\hat{n}$
λ is the wave length, $\hat{n}$ a unit vector pointing in the direction of propagation

ω is the angular frequency, with $\omega = 2\pi f$

Laue's condition

- scattering of an electromagnetic plane wave

$\vec{E} = \vec{E_0}e^{i(\boldsymbol{k.r}-\omega t)}$ where $\boldsymbol{k}$ is the wave vector on a crystal, $|\mathbf{k}|=2\pi/\lambda$, $\omega = 2\pi/T$

- consider simplified crystal where motif = 1 atom, located at lattice points

- each atom acts like an independent source that scatters the incoming light in different directions
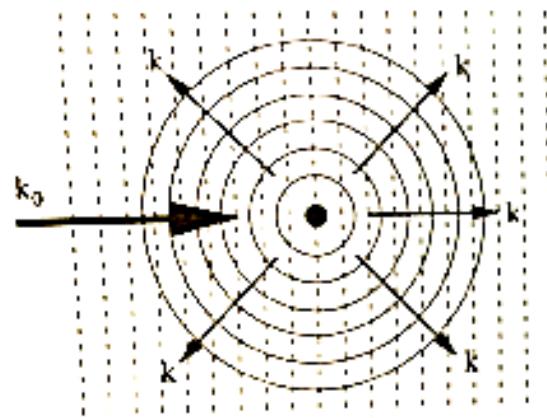
look at any 2 points on the lattice, not two planes
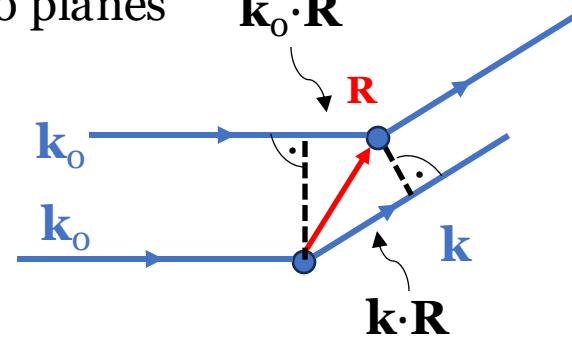
- diffraction peaks will be observed in directions that the rays scattered from all lattice points interfere constructively

Laue's condition

two (random) lattice points on the crystal lattice
any lattice vector $\boldsymbol{R} = r_1\boldsymbol{a} + r_2\boldsymbol{b} + r_3\boldsymbol{c}$
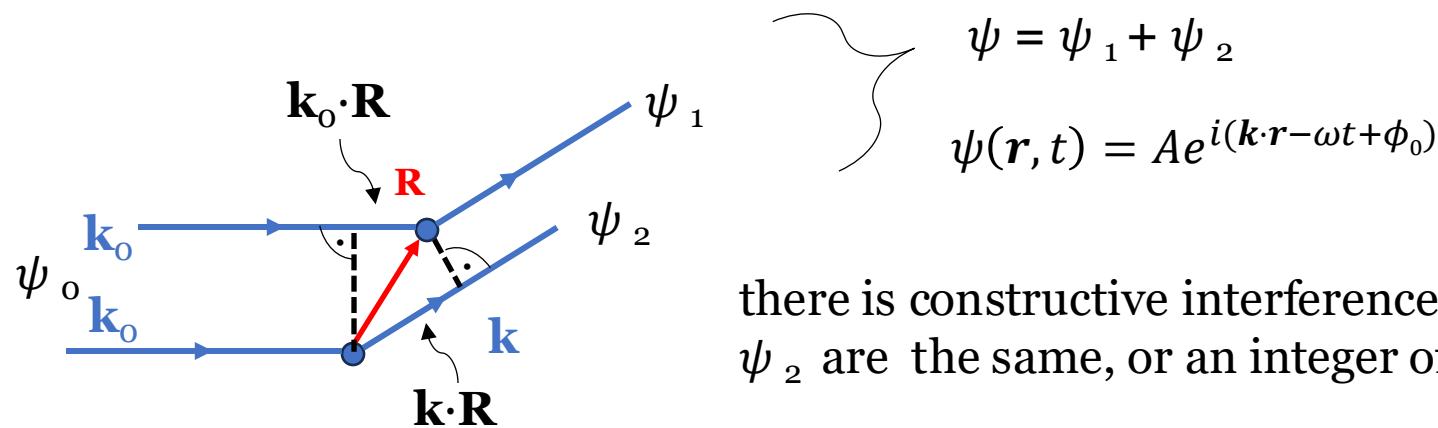
$$\psi = \psi_1 + \psi_2$$

$$\psi(\boldsymbol{r}, t) = Ae^{i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t + \phi_0)}$$

there is constructive interference if the phase of ψ_1 and ψ_2 are the same, or an integer of 2π

$$\boldsymbol{k} \cdot \boldsymbol{R} - \omega t = \boldsymbol{k_0} \cdot \boldsymbol{R} - \omega t + 2\pi N$$
$$(\boldsymbol{k} - \boldsymbol{k_0)} \cdot \boldsymbol{R} = 2\pi N$$

Reciprocal lattice

Plan of a monoclinic unit cell
perpendicular to the y-axis

c^* is perpendicular to both **a** and **b**, which means their dot products are zero

$c^* \cdot a = 0$ and $c^* \cdot b = 0$

$c^* \cdot c = cc^* \cos \phi$

with $|c^*| = 2\pi/d_{001}$ and from drawing: $c \cos \phi = d_{001}$

$c^* \cdot c = 2\pi d_{001} / d_{001} = 2\pi$

does we have:

$\vec{a^*} \cdot \vec{a} = 2\pi$	$\vec{b^*} \cdot \vec{a} = 0$	$\vec{c^*} \cdot \vec{a} = 0$
$\vec{a^*} \cdot \vec{b} = 0$	$\vec{b^*} \cdot \vec{b} = 2\pi$	$\vec{c^*} \cdot \vec{b} = 0$
$\vec{a^*} \cdot \vec{c} = 0$	$\vec{b^*} \cdot \vec{c} = 0$	$\vec{c^*} \cdot \vec{c} = 2\pi$

We have a new basis new basis (O, **a***, **b***, **c***) in which a vector $N^*_{hkl} = h a^* + k b^* + l c^*$ is perpendicular to the plane (hkl)

If we consider any vector in the direct space $R = r_1 a + r_2 b + r_3 c$ and one in the reciprocal space $N^* = n_1 a^* + n_2 b^* + n_3 c^*$, we have:

$$R \cdot N^* = r_1 n_1 a \cdot a^* + r_2 n_2 b \cdot b^* + r_3 n_3 c \cdot c^* = 2\pi(r_1 n_1 + r_2 n_2 + r_3 n_3)$$

→ an integer

Laue's condition

two (random) lattice points on the crystal Bravais lattice
any lattice vector $\mathbf{R} = r_1 \mathbf{a} + r_2 \mathbf{b} + r_3 \mathbf{c}$
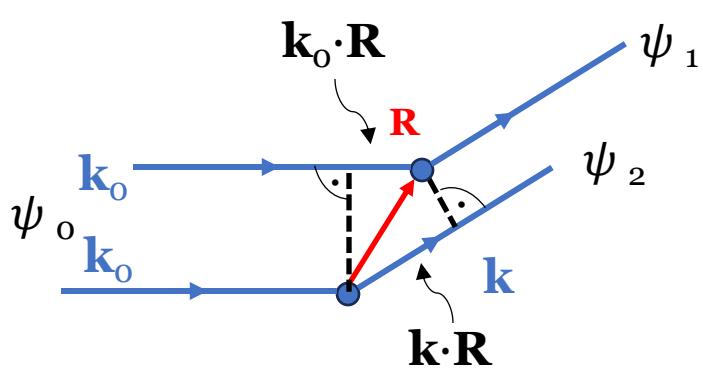
$$\psi = \psi_1 + \psi_2$$

$$\psi(\mathbf{r}, t) = A' e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

there is constructive interference if the phase of ψ_1 and ψ_2 are the same, or an integer of 2π

$$\mathbf{k} \cdot \mathbf{R} - \omega t = \mathbf{k_0} \cdot \mathbf{R} - \omega t + 2\pi N$$

$$(\mathbf{k} - \mathbf{k_0}) \cdot \mathbf{R} = 2\pi N$$

$\mathbf{R} \in \mathcal{D}$ the (direct) Bravais lattice
$\mathbf{N}^* \in \mathcal{R}$ the reciprocal lattice

this is fullfilled if
$$\mathbf{k} - \mathbf{k_0} = \mathbf{N}^*$$

→ Laue's condition: for constructive interference, the difference between incident wave vector $\mathbf{k_o}$ and scattered wave vector $\mathbf{k}$ must be a reciprocal lattice vector $\mathbf{N}^*$

Laue's condition and Bragg's law

$\boldsymbol{k} - \boldsymbol{k_0} = \mathbf{N^*}$

$\boldsymbol{k_0} = \boldsymbol{k} - \mathbf{N^*}$

$\|\boldsymbol{k_0}\|^2 = \|\boldsymbol{k}\|^2 - 2\|\boldsymbol{k}\|\|\mathbf{N^*}\|\cos\varphi + \|\mathbf{N^*}\|^2$
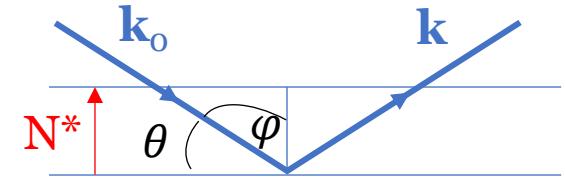
$$\cos\left(\frac{\pi}{2} - \theta\right) = \sin\theta$$

wave only changes direction, thus $\|\boldsymbol{k_0}\| = \|\boldsymbol{k}\| = \frac{2\pi}{\lambda}$

and using $\|\mathbf{N^*}\| = \frac{2\pi}{d}$

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

Laue's condition and Bragg's law

Bragg

$\lambda = 2d\sin\theta$

Real

Laue

$Q = \mathbf{N}^*$
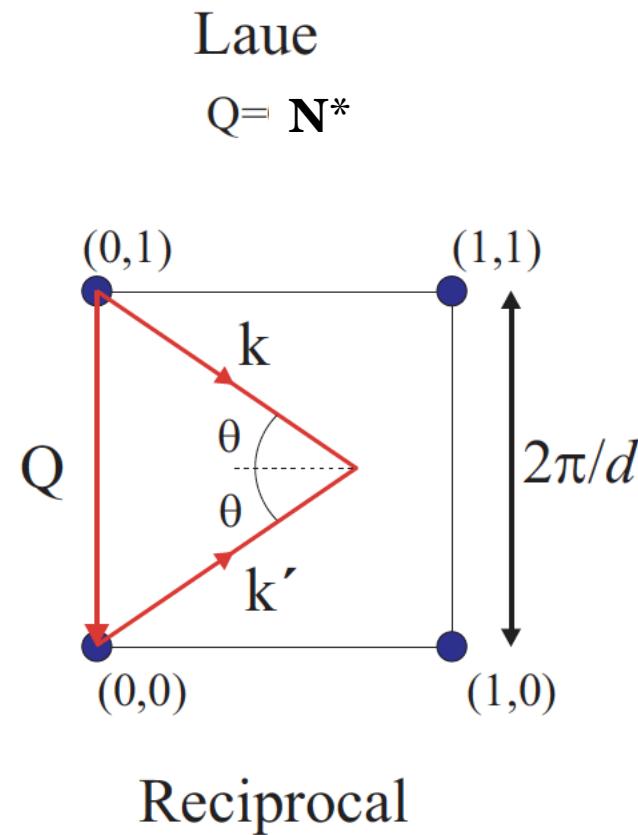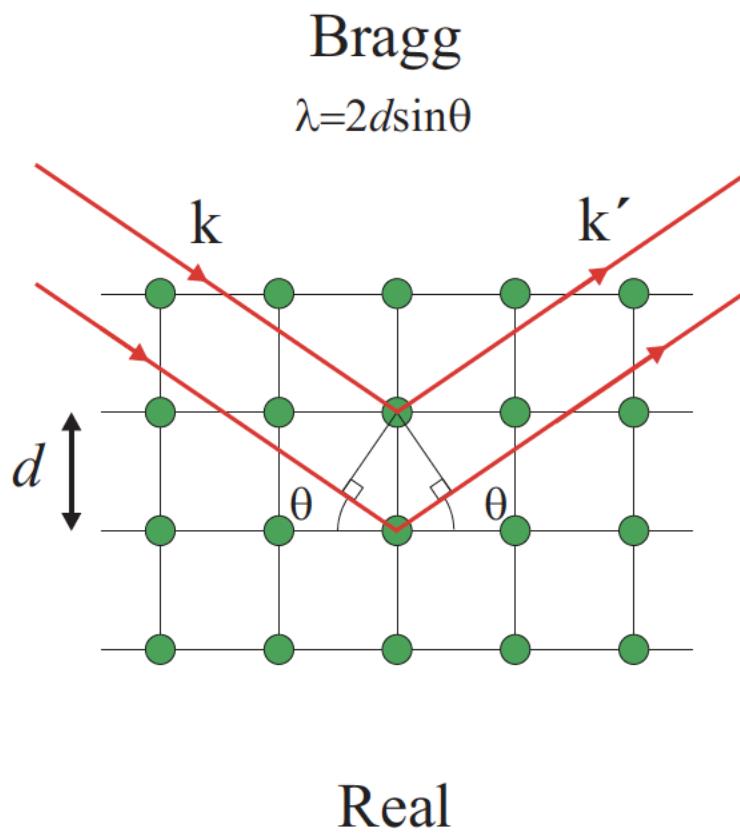
Reciprocal

Reciprocal space lattice → diffraction pattern

The reciprocal lattice represents the framework and components of the diffraction pattern

e.g. $a < b < c$
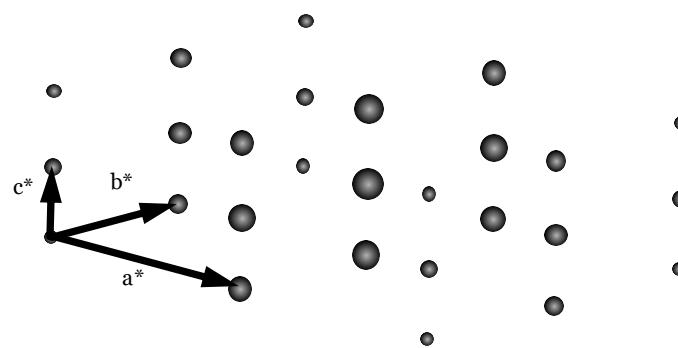
Real space

$a^* > b^* > c^*$

Reciprocal space

The reciprocal lattice is the Fourier transform of the direct lattice!

The spacings between peaks in reciprocal lattice (a^*, b^*, c^*) are inversely proportional to the corresponding dimensions in real space (a, b, c)

Fourier series in one dimension

$$f(x) = A_0 + \sum_{\sim} A_n \left(\cos(\theta_n) \cos(2\pi n x/a) + \sin(\theta_n) \sin(2\pi n x/a) \right)$$
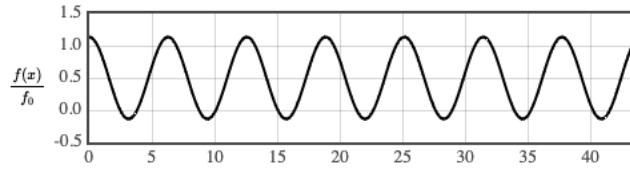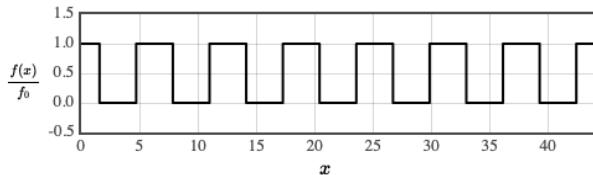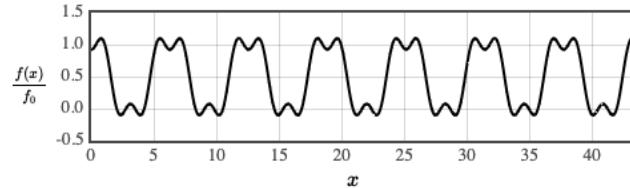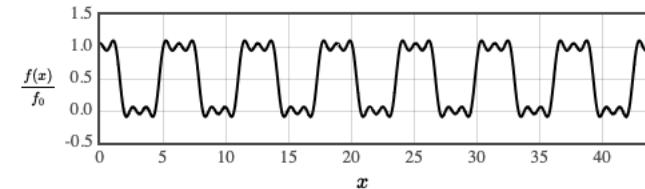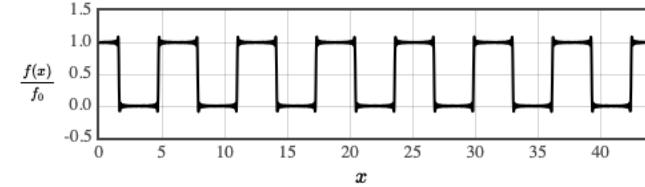
the resulting curve depend on the amplitude A and the phase between the waves

$n_{max} = 1$

$n_{max} = 3$

$n_{max} = 5$

$n_{max} = 50$
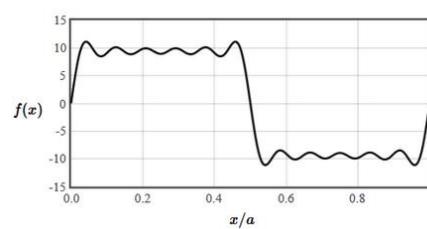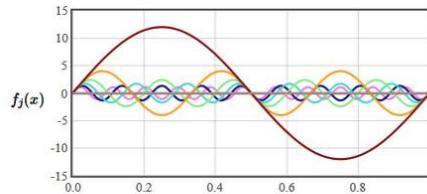
can also be expressed in exponential form

$$f(x) = \sum_{n=-\infty}^{\infty} f_{G_n} e^{iG_n x}, \qquad f_{G_n} = \frac{c_n}{2} - i\frac{s_n}{2}.$$

$$G_n = 2\pi n/a$$

Fourier series and Fourier transform

Fourier series: for periodic functions, discrete sum of harmonics

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} \exp\left(i\vec{G} \cdot \vec{r}\right)$$

sum over the reciprocal lattice vectors $\mathbf{G}$

$f_{\mathbf{G}}$ complex coefficients (called structure factors)

Fourier transform extends also to non periodic functions, integral
Fourier transform of one-dimensional function $f(x)$ is
$$F(k) = \int_{-\infty}^{+\infty} f(x) e^{ikx} \, dx$$

Diffraction and Fourier transform

$$\psi(system) \propto [\mathcal{FT}(system)]$$
$$\psi(crystal) \propto [\mathcal{FT}(crystal)]$$

The reciprocal lattice is the Fourier transform of the direct lattice

→ what is missing for a crystal?

Bravais lattice

$\otimes$ Basis

= Crystal

by Phil Willmott
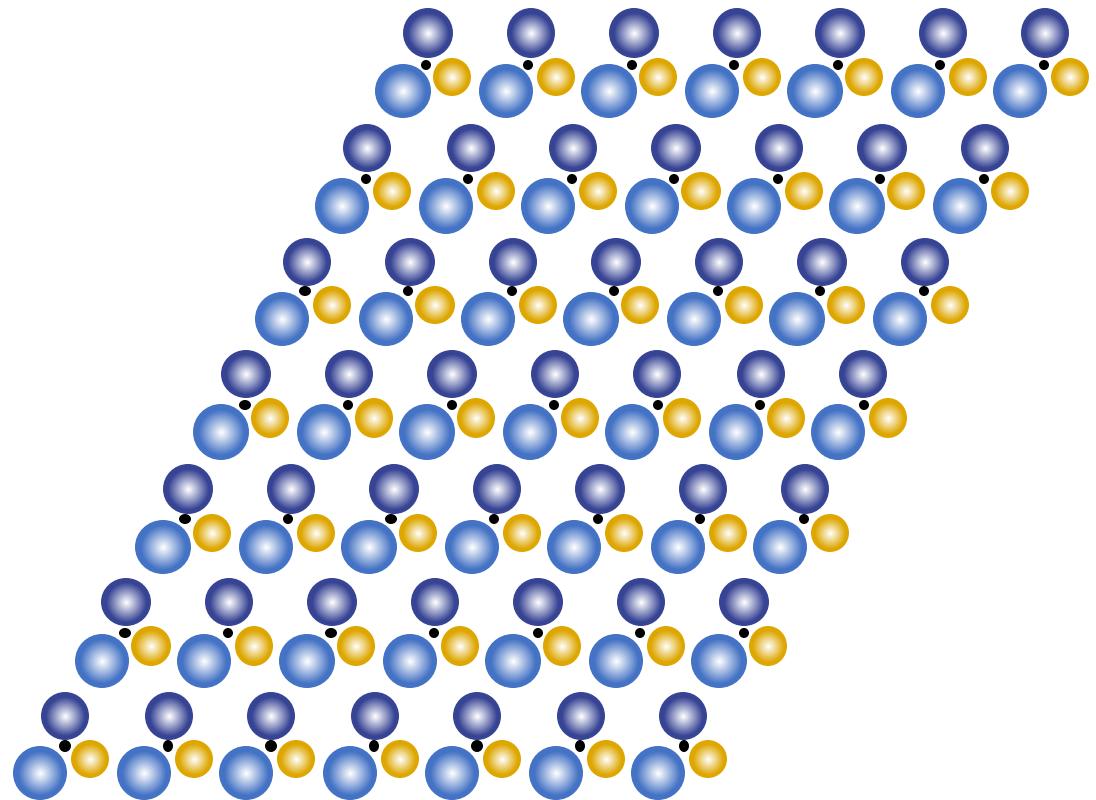
Diffraction

- Bragg's law: simple geometric consideration if a constructive interference CAN occur

- Crystal is not just the lattice (and lattice planes) but also consists of a motif!

- it is the lattice which determines the geometry of the pattern and the motif which determines the intensities of the X-ray diffracted beams.
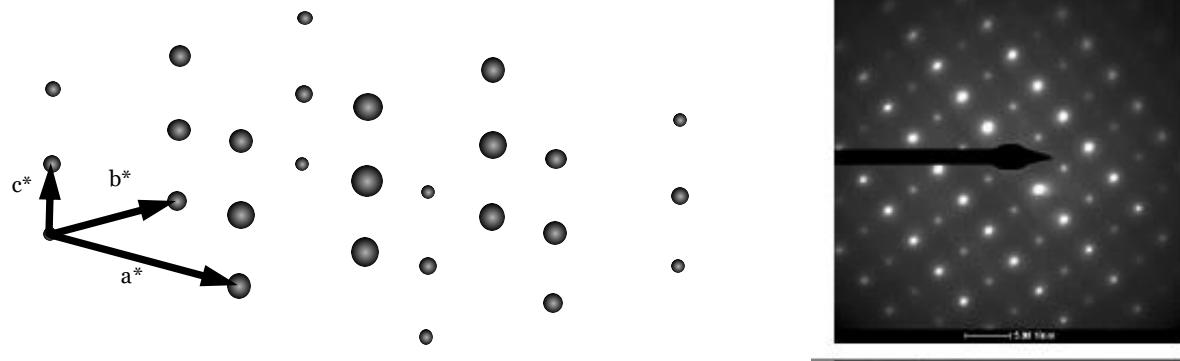
- The diffraction pattern is the is the square of the Fourier transform of that system

Diffraction and Fourier transform

scattering amplitude from a crystalline material

$$F^{crystal}(\boldsymbol{q}) = \overset{all\ atoms}{\underset{l}{\sum}} f_l(\boldsymbol{q})e^{i\boldsymbol{q}\cdot r_l} = \overset{all\ atoms}{\underset{\boldsymbol{R}n+rj}{\sum}} f_l(\boldsymbol{q})e^{i\boldsymbol{q}\cdot(\boldsymbol{R}n+rj)} = \underset{n}{\sum} e^{i\boldsymbol{q}\cdot\boldsymbol{R}n} + \underset{j}{\sum} f_l(\boldsymbol{q})e^{i\boldsymbol{q}\cdot rj}$$

atomic form factor of the
atom situated at position $\boldsymbol{r}_l$

→ see next week

$\boldsymbol{r}_l = \boldsymbol{R}_n + \boldsymbol{r}_j$

$\boldsymbol{R}_n$ lattice vector
$\boldsymbol{r}_j$ position vector of the
atoms in the unit cell
(= the motif)

lattice

unit cell structure factor
→ see next week

Reciprocal lattice and Fourier transform
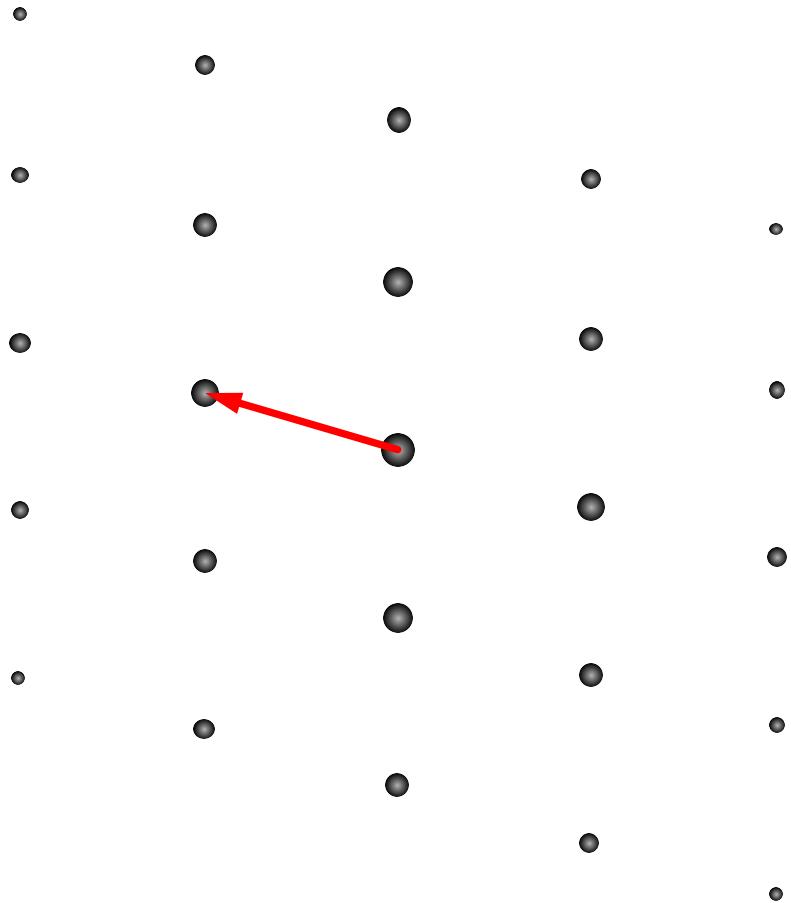
a diffraction pattern is the Fourier Transform of the object that produces it

- Each point in the reciprocal lattice is therefore a "Fourier component" of the diffraction pattern
- The position of each point in the RL defines the frequency and direction of a sinusoidal wave of electron density

by Phil Willmott

# Reciprocal lattice and Fourier transform

by Phil Willmott
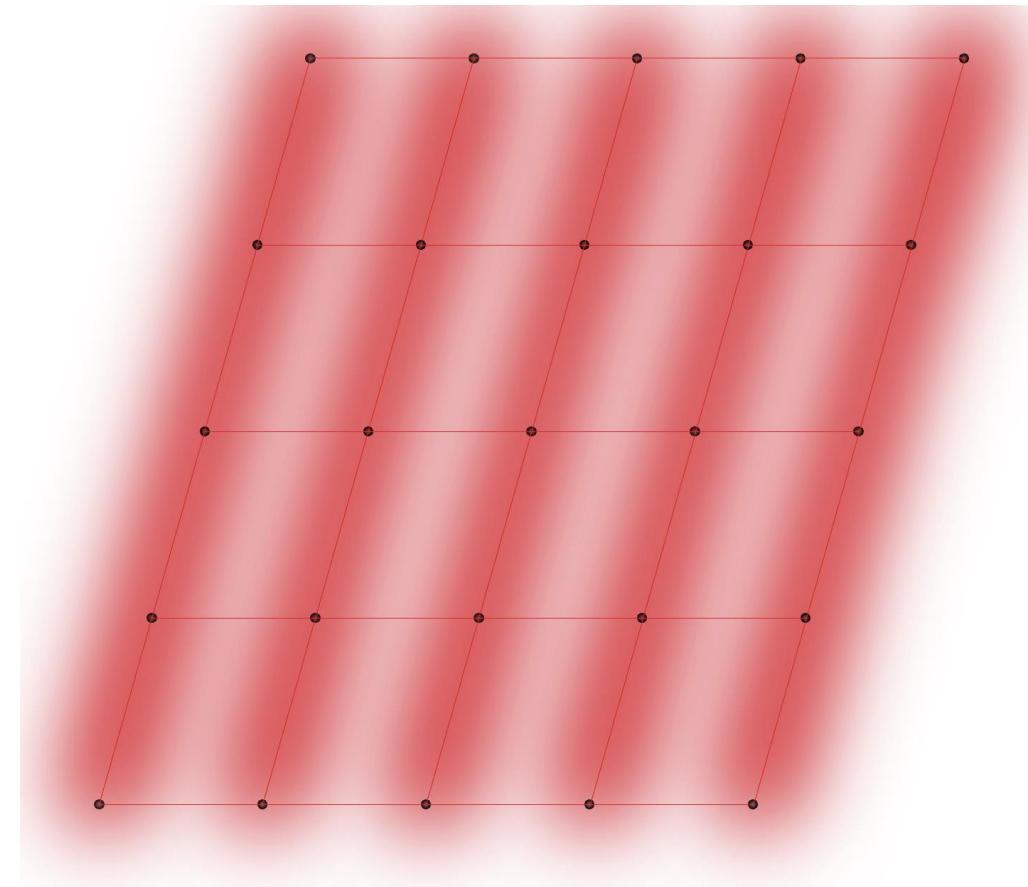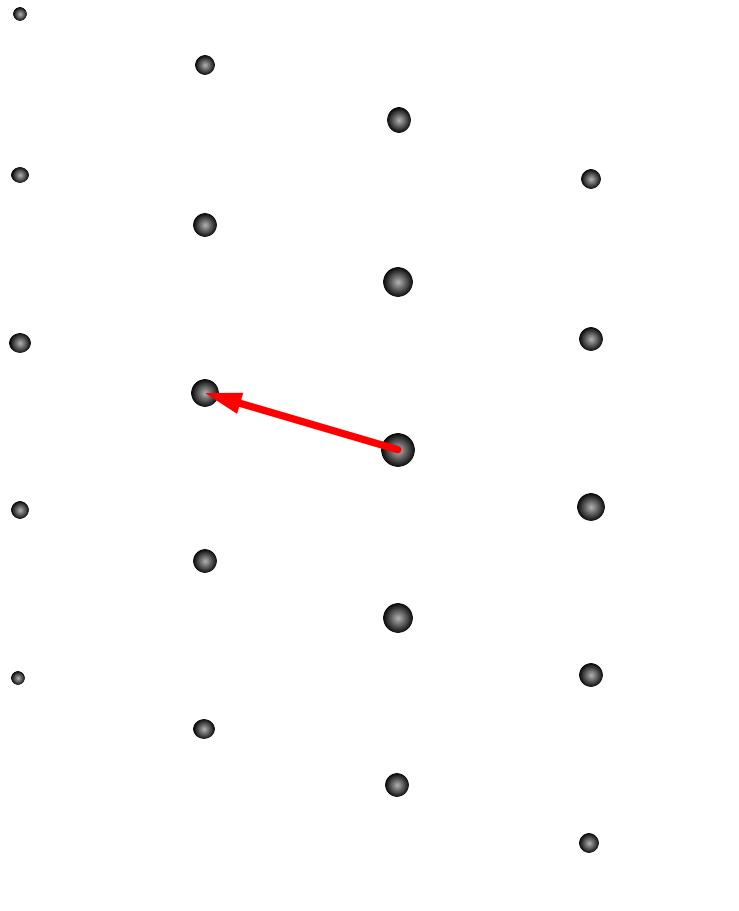
Reciprocal lattice and Fourier transform
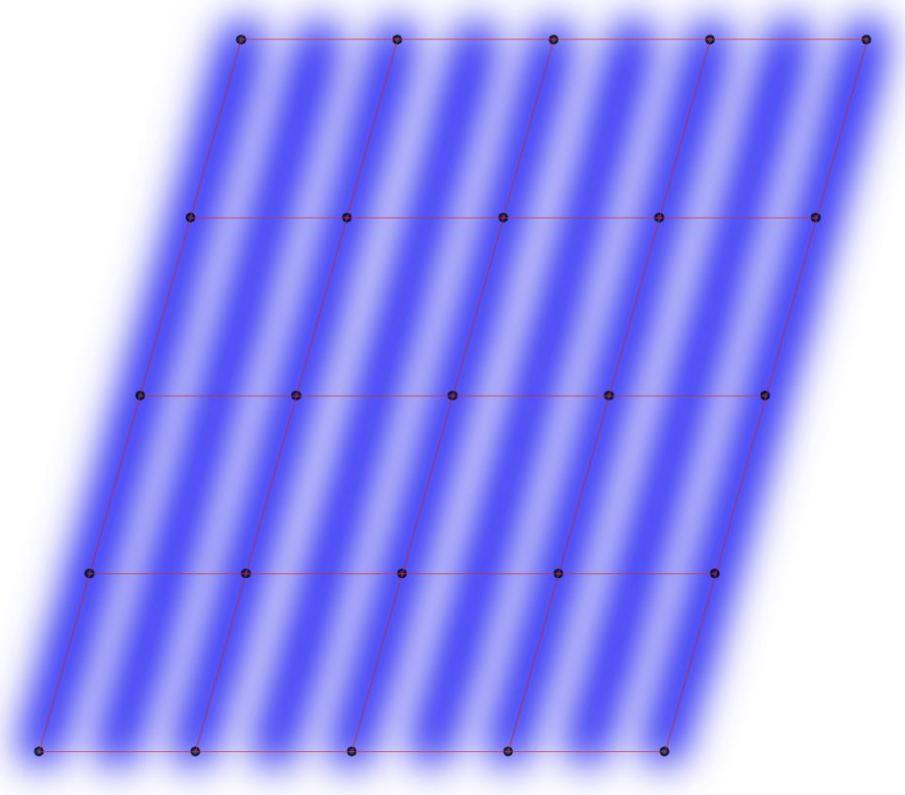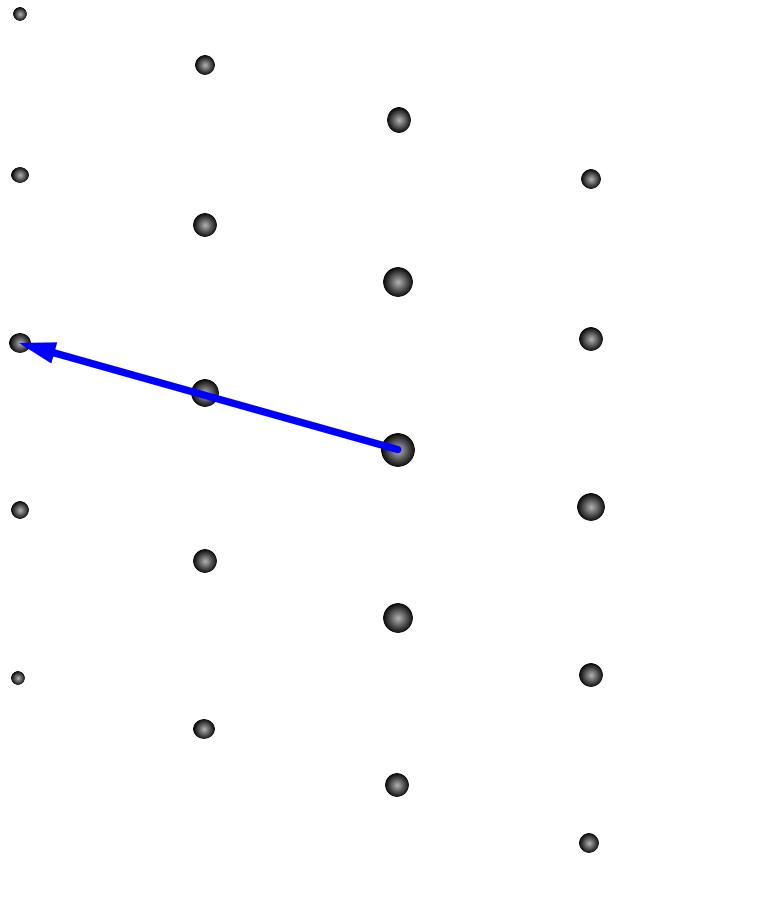
diffraction peak (reciprocal space vector) in the same direction from the diffraction peak centre but twice the distance or length→ corresponding electron wave has double the frequency

Reciprocal lattice and Fourier transform

a diffraction pattern is the Fourier Transform of the object that produces it

- Each point in the reciprocal lattice is therefore a "Fourier component" of the diffraction pattern
- The position of each point in the RL defines the frequency and direction of a sinusoidal wave of electron density
- **The intensity at each point defines the amplitude of the wave**

by Phil Willmott

Reciprocal lattice and Fourier transform

a diffraction pattern is the Fourier Transform of the object that produces it

- Each point in the reciprocal lattice is therefore a "Fourier component" of the diffraction pattern
- The position of each point in the RL defines the frequency and direction of a sinusoidal wave of electron density
- The intensity at each point defines the amplitude of the wave
- The phase ϕ of that wave is fixed for that wave relative to all the other waves but cannot be measured directly

$$I_{\mathrm{rec}}(\mathrm{system}) \propto [\mathcal{FT}(\mathrm{system})]^2$$

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Reciprocal lattice and Fourier transform

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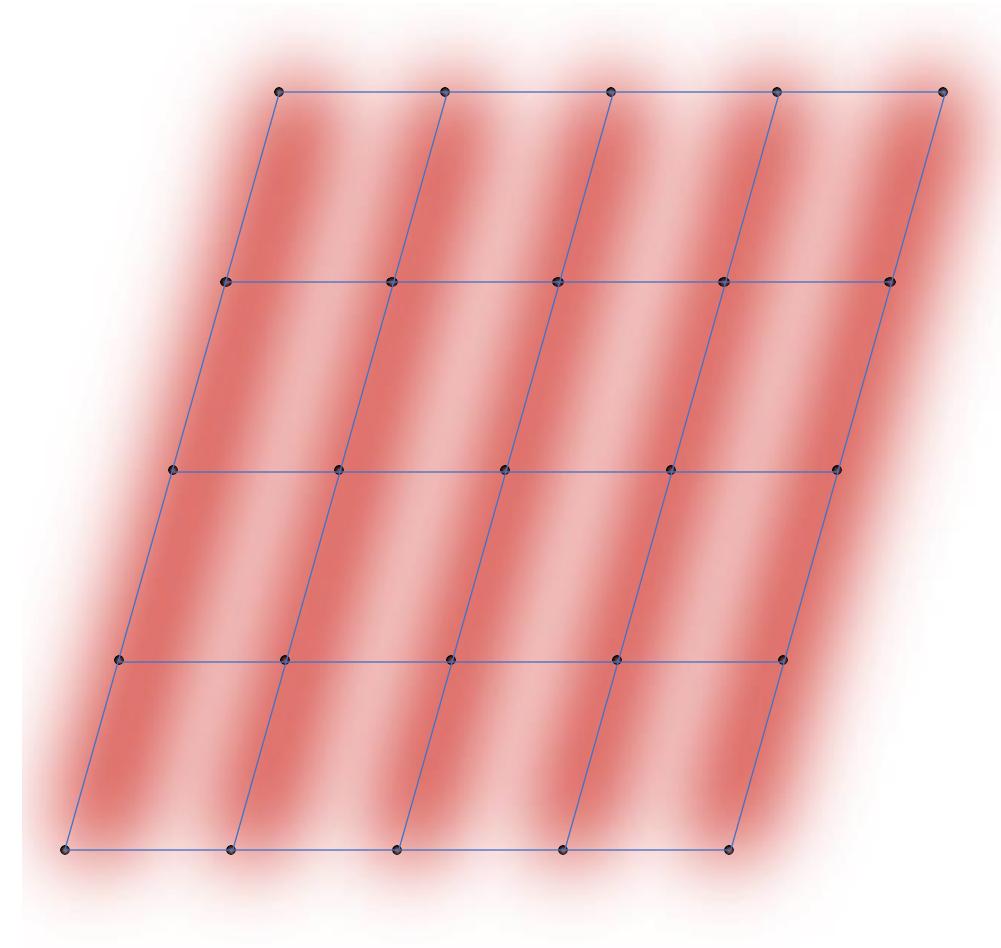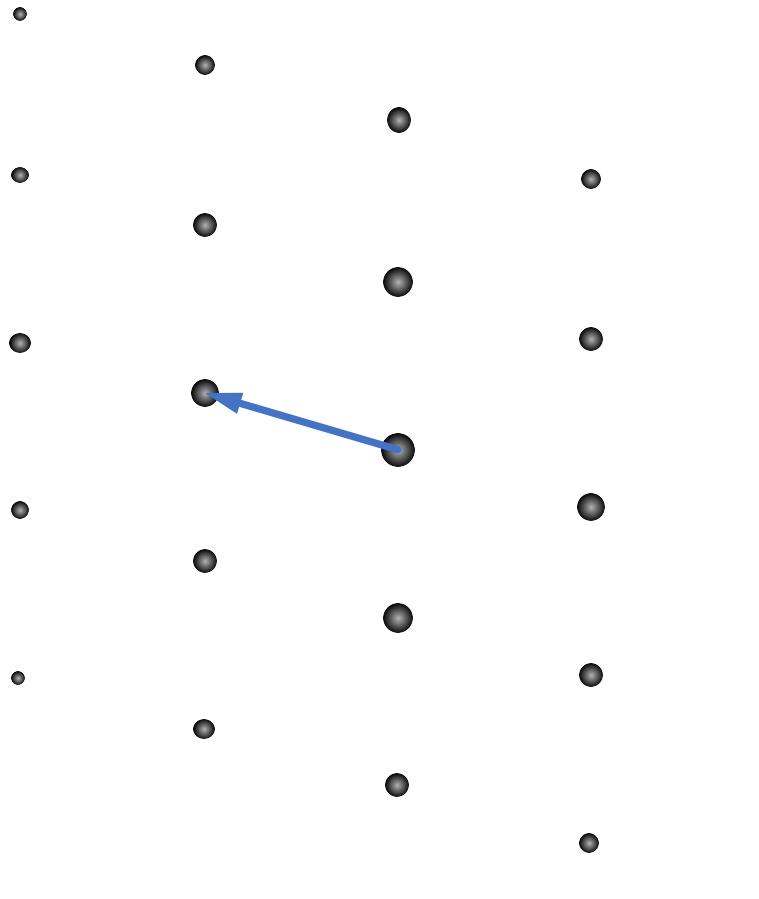
Electromagnetic wave and measured intensity

$\psi(\boldsymbol{r}, t) = A e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \phi)}$

what we can measure is the intensity I

$I \propto |\psi(\boldsymbol{r}, t)|^2$

$|\psi(\boldsymbol{r}, t)|^2 = \left| A e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \phi)} \right|^2$ with $\left| e^{i\theta} \right| = 1 = \sqrt{x^2 + y^2}$

$|\psi(\boldsymbol{r}, t)|^2 = |A|^2$

$I \propto |A|^2$ → measured intensity only depends on amplitude, not the phase

we know the direction of the wave and its amplitude over the measured intensity

we cannot just take the Fourier transform to get back to the direct lattice & motif since we don't know the phase

→generally know as "**the phase problem**"

Full information content of reciprocal lattice

 … take the information provided by each diffraction point in the reciprocal lattice

- The direction (angle) of the wave relative to the origin of the RL

- The frequency (given by the distance from origin of the RL, proportional to 1/l)

- The amplitude of the wave, given by the square root of the intensity

- **if** one can work out the phase ϕ associated with each of these points (techniques exist, but not covered in this course)

- … draw the corresponding wave $\psi(A,\lambda,\phi)$ in real space and add them all together

Example: the scattering of collagen
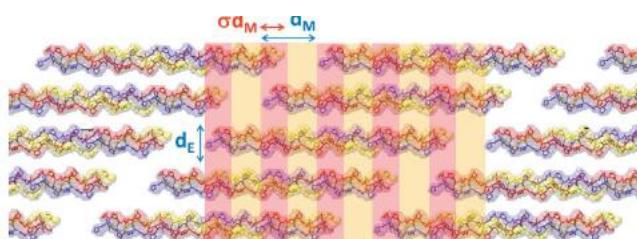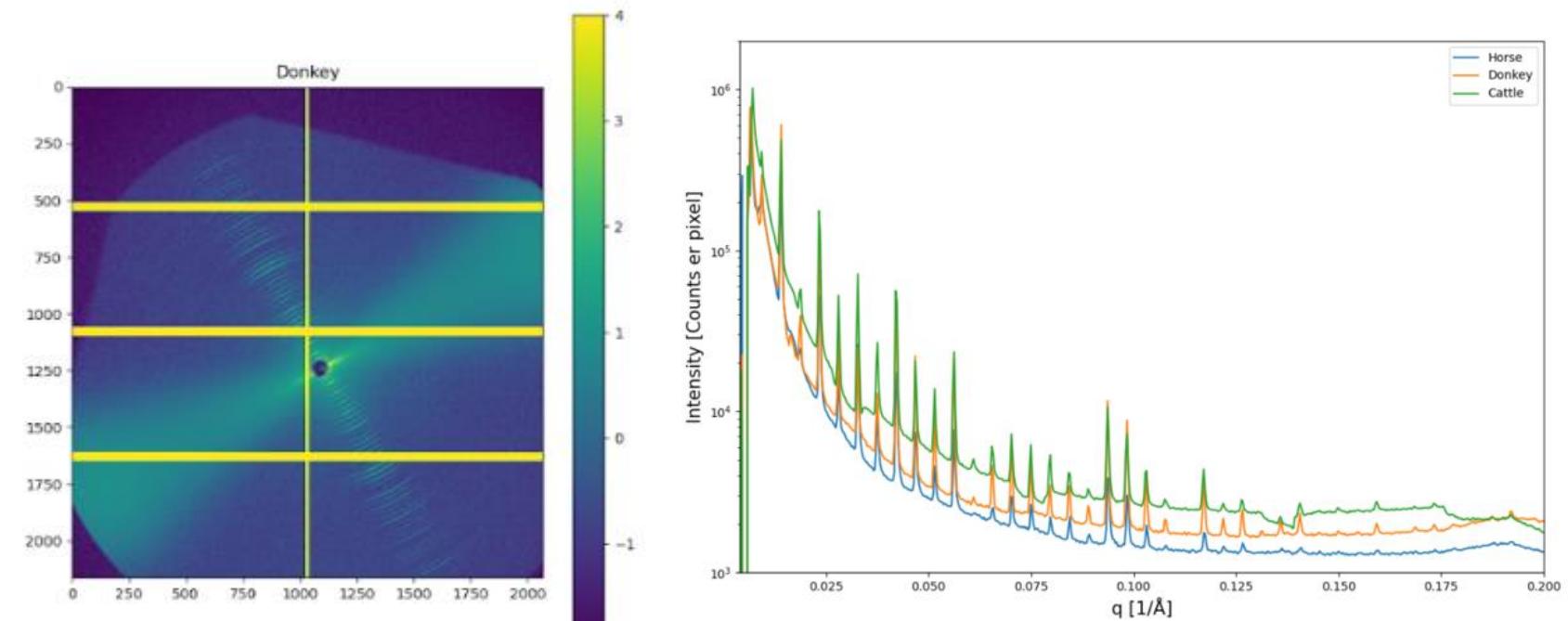
Figure 1
Schematic of the staggered repetition unit of the triple-helix collagen structure. The fiber axis is along the arrow indicating dense σd_M-wide regions with five nanofibrils overlapping alternately with less dense $(1 - \sigma)d_M$-wide regions of one gap and four nanofibrils overlapping.
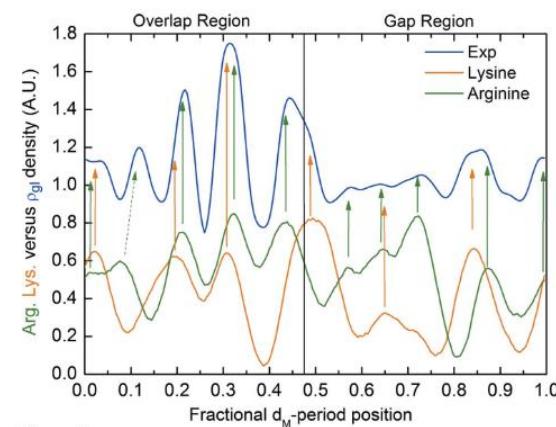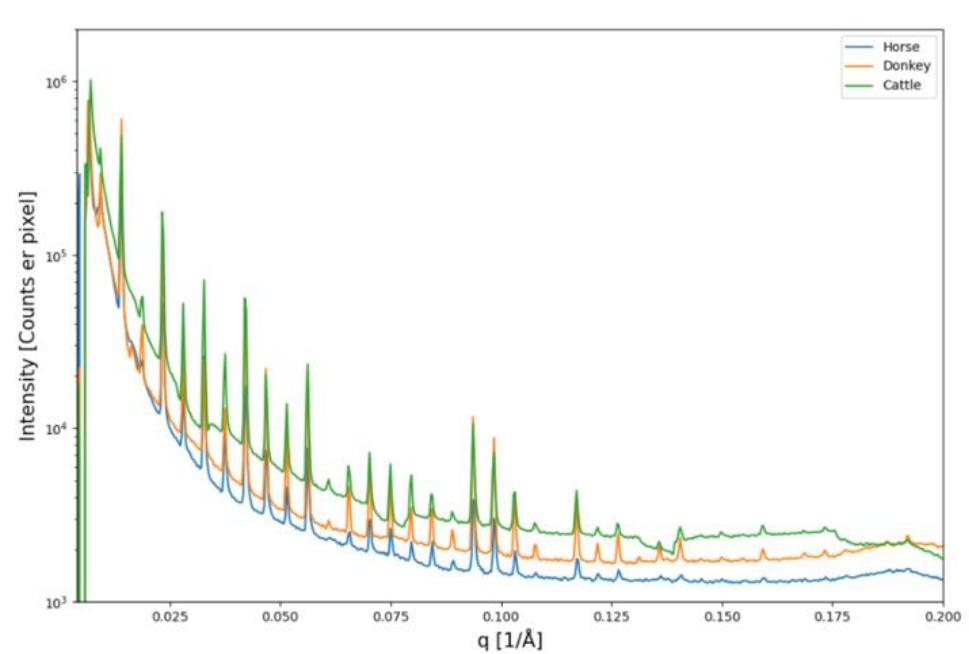
Figure 5
Linear densities of lysine/hydroxylysine and arginine amino acids as a function of the fractional d_M-period coordinate along the collagen fibril versus the electron density obtained by the Fourier difference phasing.

De Caro, L., Terzi, A., Fusaro, L., Altamura, D., Boccafoschi, F., Bunk, O. & Giannini, C. (2021). *IUCrJ* **8**, 1024–1034.

Electron density profile of each unit cell

Electron density profile of each unit cell

by Phil Willmott

Summary