MSE-238
Structure of Materials

Week 7 – crystallography V

Spring 2025

Marianne Liebi (MX/PSI)

Ecole Polytechnique Fédérale de Lausanne

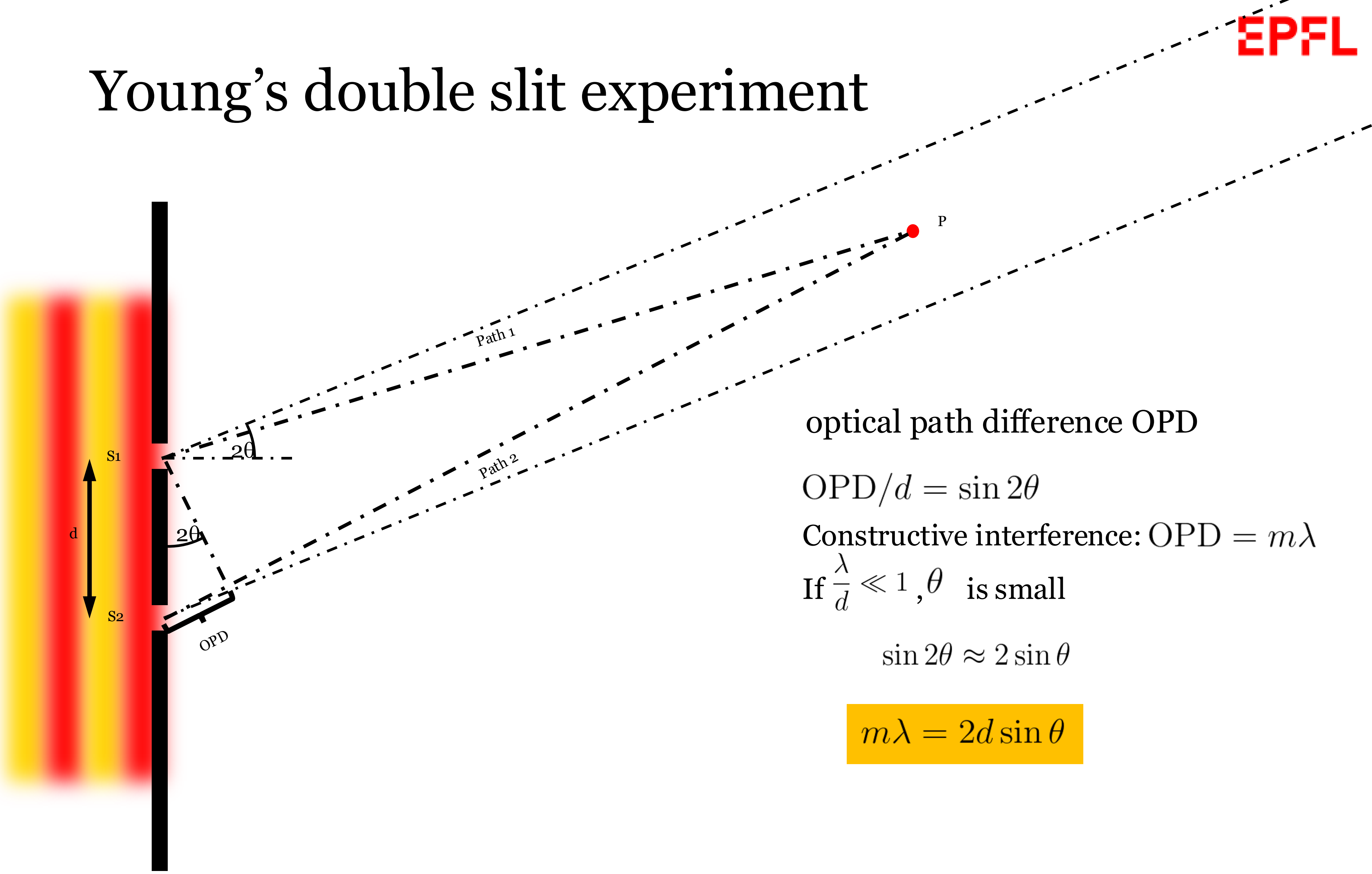
Overview

- Repetition Bragg law, Laue condition and reciprocal lattice
- Diffraction as Fourier transform of a crystal
- Interaction of material with different radiation → focus on X-rays
- Interaction of X-rays with electrons
- Interactions of X-rays with atoms → atomic form factor
- Interaction of X-rays with a unit cell of a crystal → structure factor
- Diffraction pattern and systematic absences

→(Hammond Chapter 9)

→Jens Als-Nielsen & Des McMorrow "Elements of Modern X-ray Physics" Chapter 5
→ Phil Willmott, "Introduction to Synchrotron Radiation" Chapter 6

Young's double slit experiment



optical path difference OPD

$$\mathrm{OPD}/d = \sin 2\theta$$

Constructive interference: $\mathrm{OPD} = m\lambda$

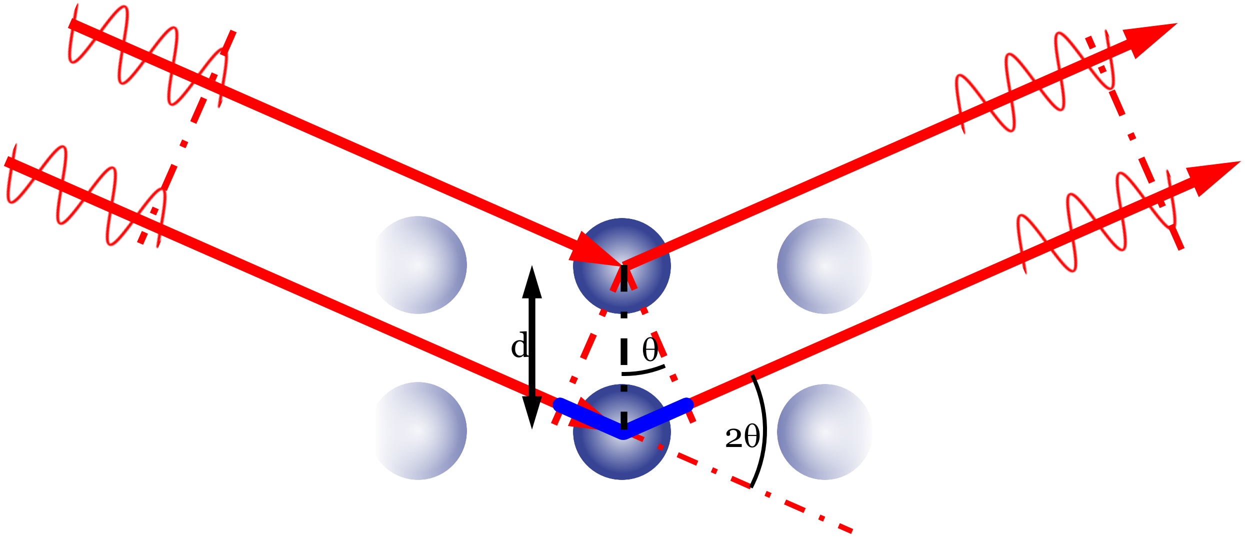
If $\frac{\lambda}{d} \ll 1$, θ is small

$$\sin 2\theta \approx 2\sin\theta$$

$$\boxed{m\lambda = 2d\sin\theta}$$

by Phil Willmott

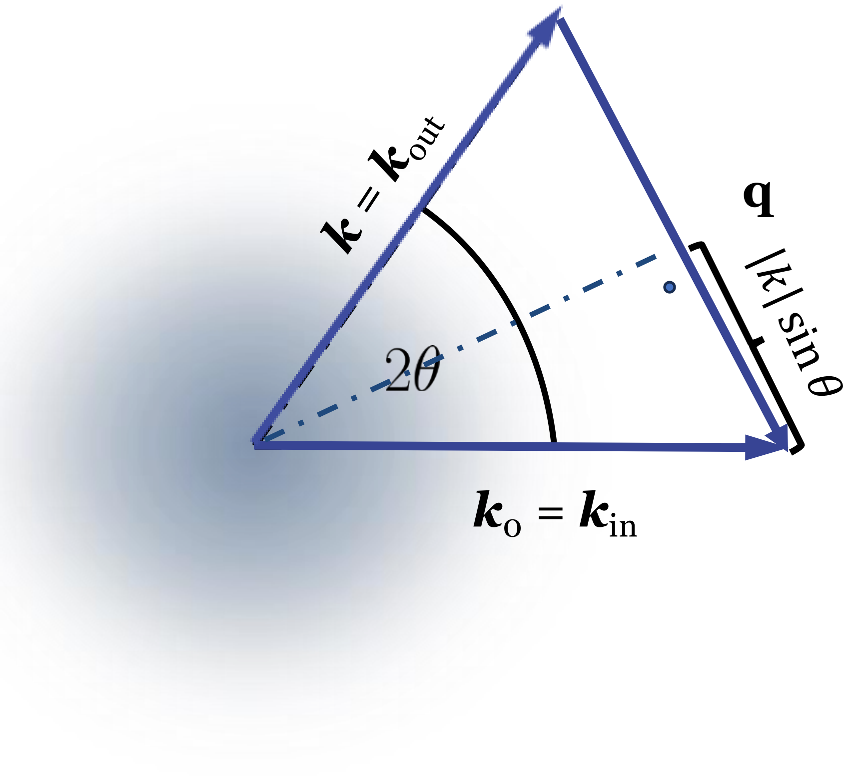
Bragg's law



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

→ exercise 4

Elastic scattering



wave vector $\boldsymbol{k} = \frac{2\pi}{\lambda}$

elastic scattering: no loss in photon energy but direction of the photon can change with a scattering angle 2θ

$$|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}|$$

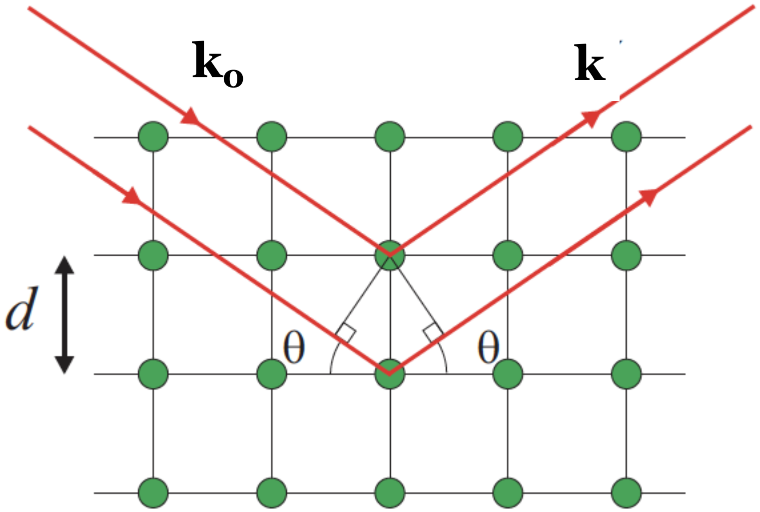
scattering vector $\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$

$$q = 2|k| \sin\theta = \frac{4\pi \sin\theta}{\lambda}$$

Laue's condition and Bragg's law

Bragg

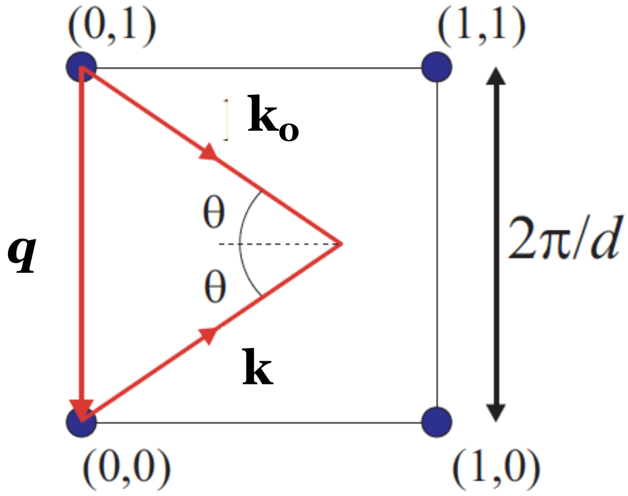
$\lambda = 2d\sin\theta$



Real

Laue

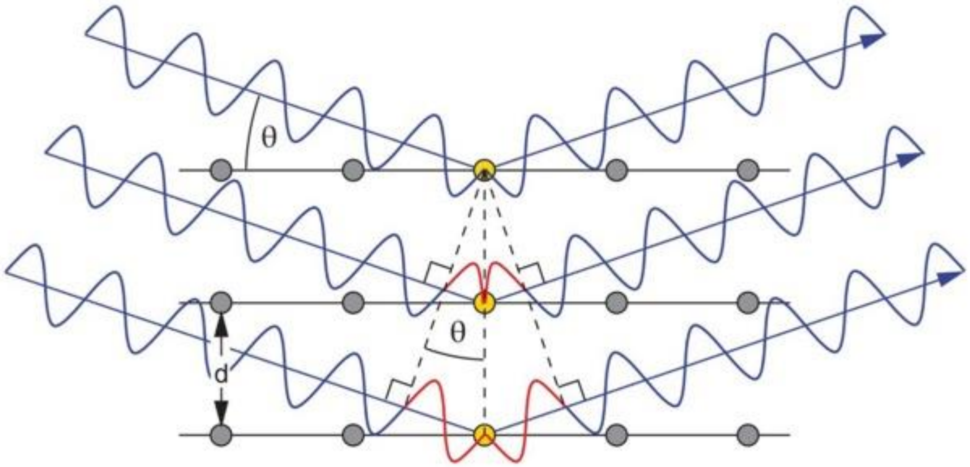
$\mathbf{q} = \mathbf{k} - \mathbf{k_o} = \mathbf{N}^* = \mathbf{K}$

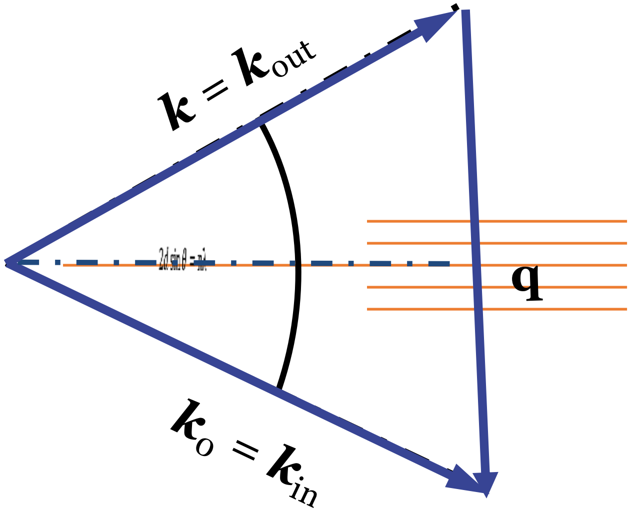


Reciprocal

$$q = \frac{2\pi}{d}$$

Bragg law





The scattering vector ***q*** always lies perpendicular to the scattering planes if the Bragg condition is fullfilled

the angle subtended by $\mathbf{k}_{in} = 2\pi/\lambda$ (or $\mathbf{k}_{out}$) and the scattering planes is θ.

The scattering angle is 2θ

Bragg law: $2d \sin\theta = \mathrm{n}\lambda$

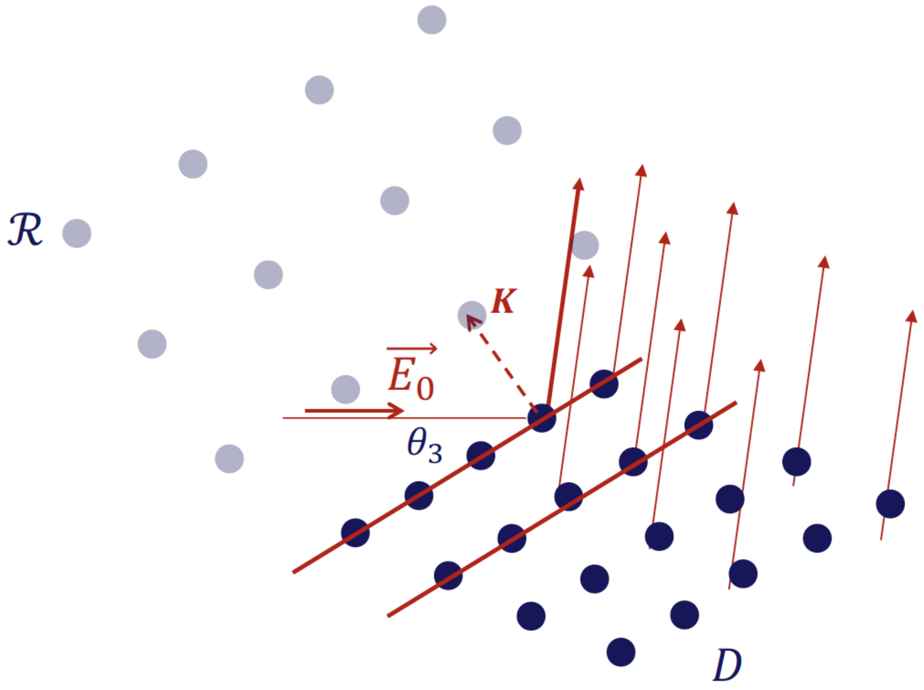
$$|\boldsymbol{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

$$d = \mathrm{n}\frac{2\pi}{q}$$

independent of wave length (experimental condition)

Laue condition → The reciprocal space lattice

$2d_{(hkl)} sin(\theta_3) = n\lambda$

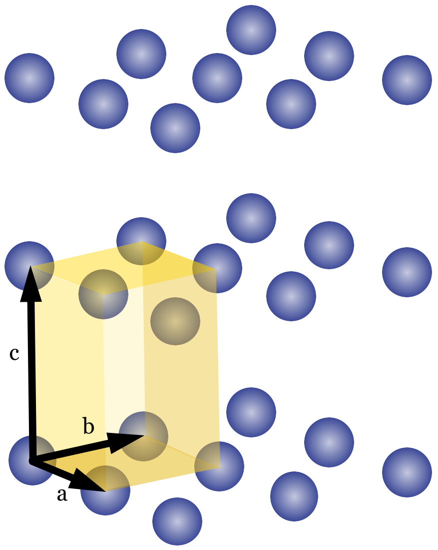


reciprocal lattice vector $\mathbf{N}^* = \boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}_0$

Laue condition

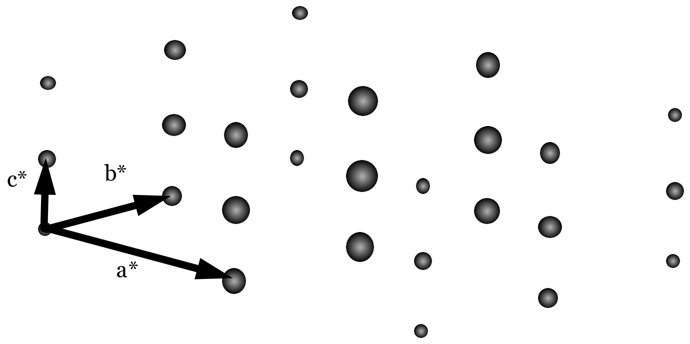
Reciprocal space lattice → diffraction pattern

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



e.g. $a < b < c$

Real space



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

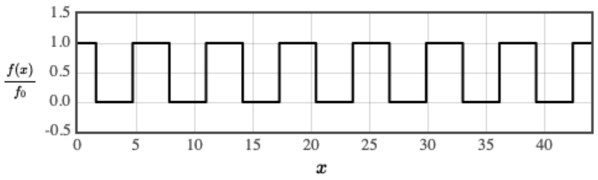
Reciprocal space

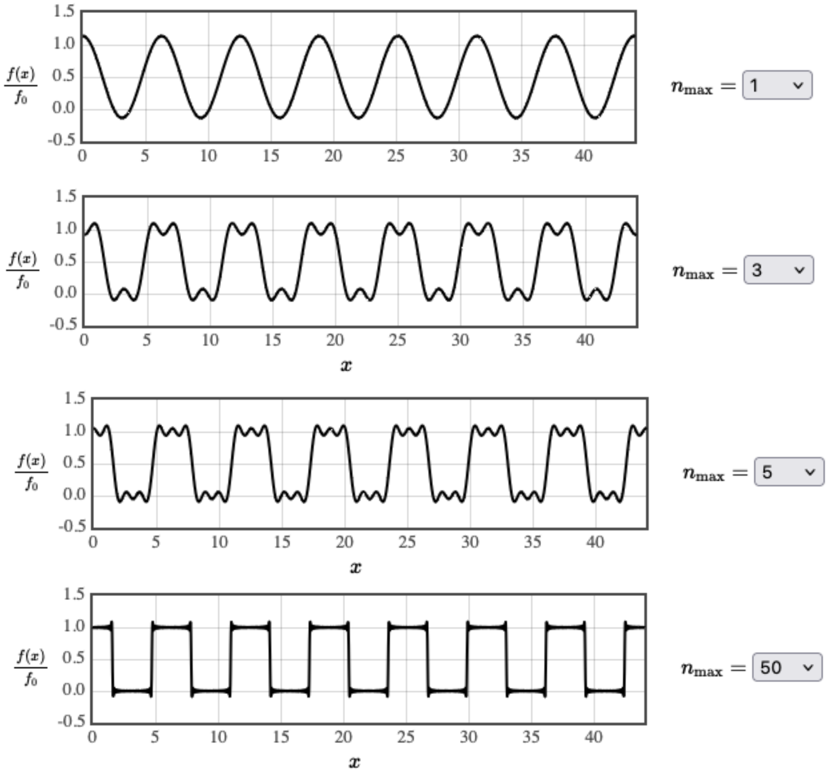
The reciprocal lattice is the Fourier transform of the direct lattice!

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

$$f(x) = A_0 + \sum_n A_n \left(\cos(\theta_n)\cos(2\pi n x/a) + \sin(\theta_n)\sin(2\pi n x/a)\right)$$





can also be expressed in exponential form

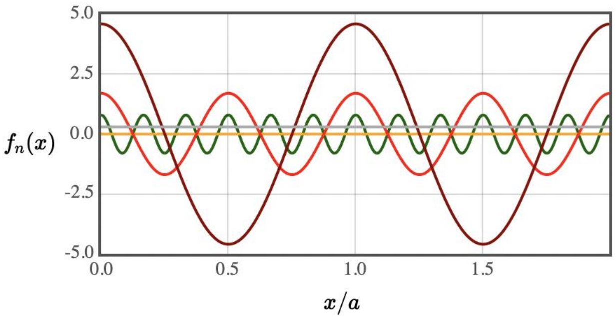
$$f(x) = \sum_{n=-\infty}^{\infty} f_{G_n} e^{iG_n x}, \qquad f_{G_n} = \frac{c_n}{2} - i\frac{s_n}{2}.$$

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

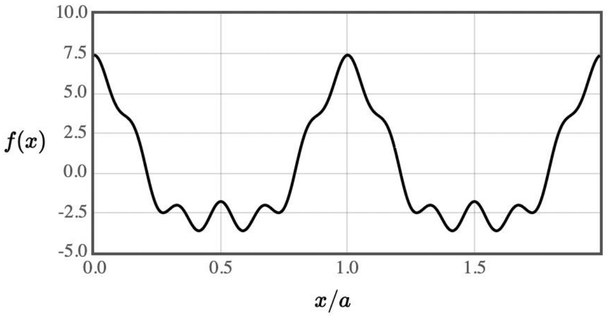
https://lampz.tugraz.at/~hadley/ss1/skriptum/outline.php

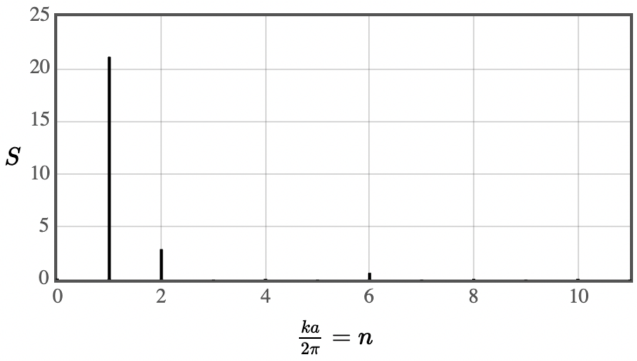
Fourier series

$$f(x) = A_0 + \sum_n A_n \left(\cos(\theta_n)\cos(2\pi n x/a) + \sin(\theta_n)\sin(2\pi n x/a)\right).$$



the resulting curve depend on the amplitude A and the phase between the waves





https://lampz.tugraz.at/~hadley/ss1/skriptum/outline.php

Fourier series and Fourier transform

Fourier series: for periodic functions, discrete sum of harmonics

$$S(\boldsymbol{K}) = \sum_{j} f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j}$$

sum over the reciprocal lattice vectors **K**

$f_{\boldsymbol{G}}$ 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

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

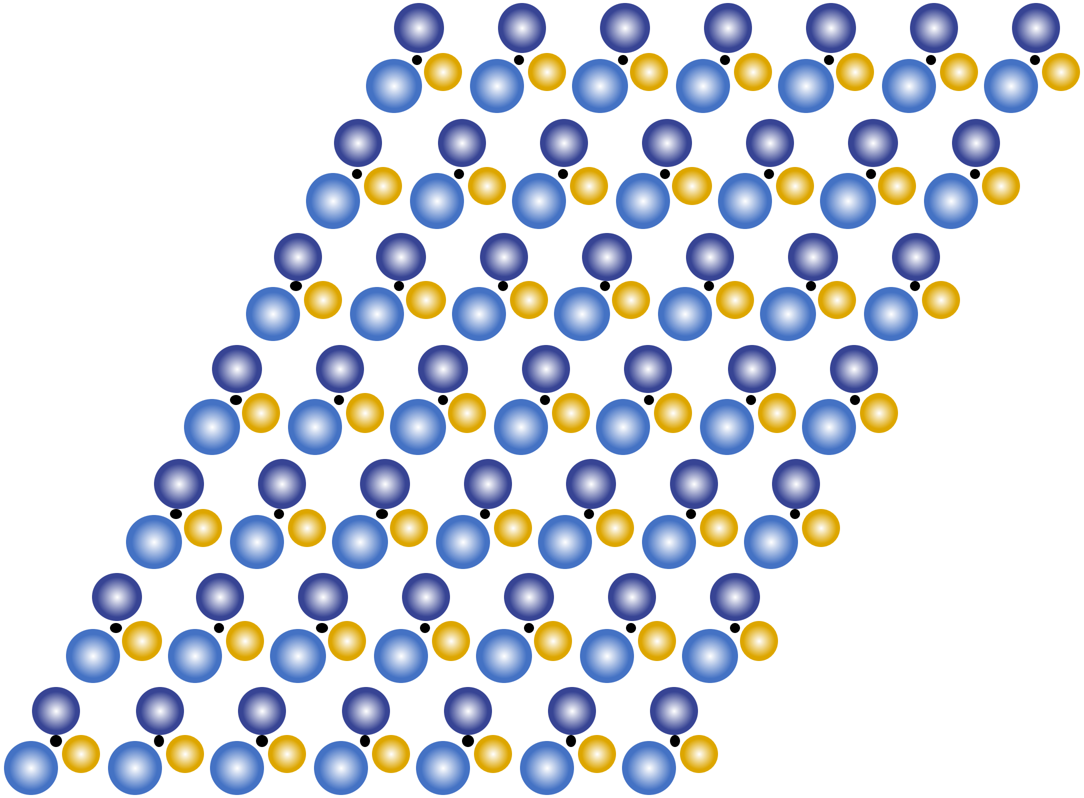
The reciprocal lattice is the Fourier transform of the direct lattice

→ what is missing for a crystal?

Bravais lattice

⊗ Basis

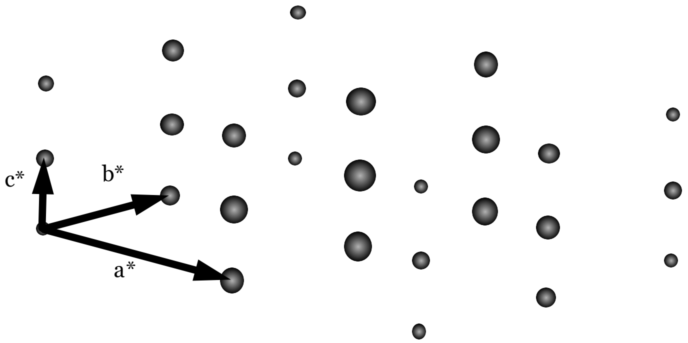
= Crystal

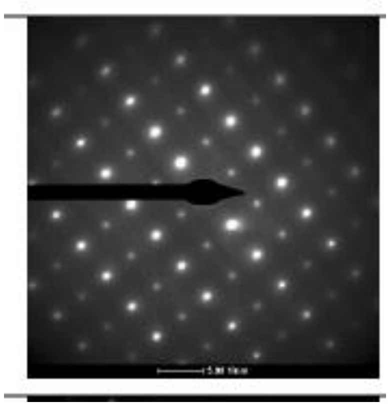


by Phil Willmott

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

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

scattering amplitude from a crystalline material

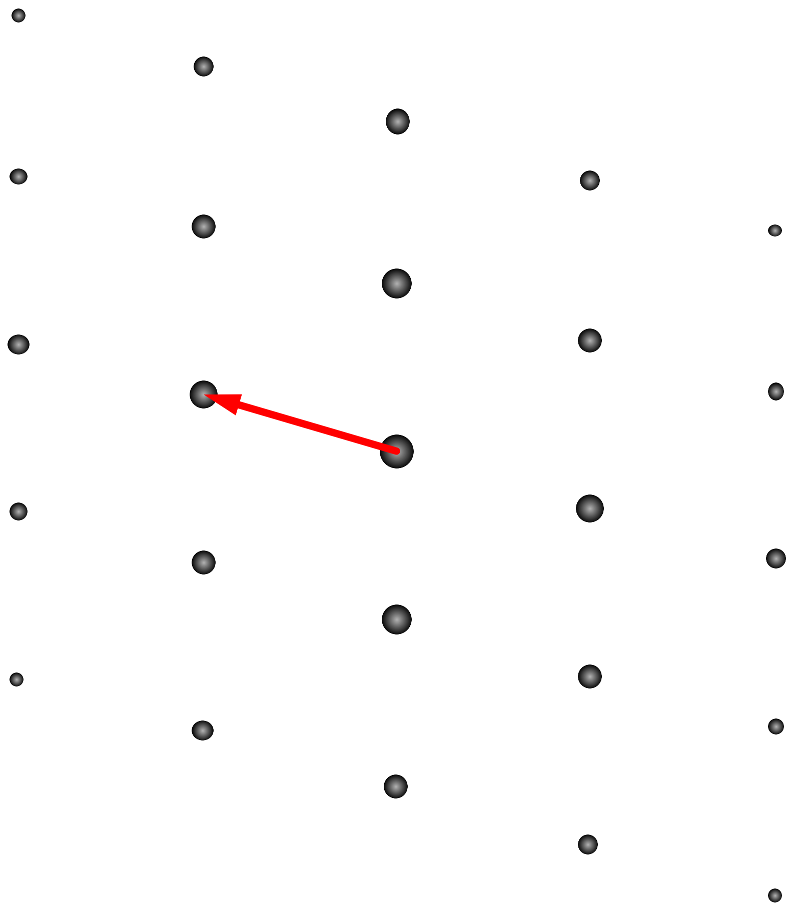
$$F^{crystal}(\boldsymbol{q}) = \sum_{l}^{all\ atoms} f_l(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} = \sum_{\boldsymbol{R}n+\boldsymbol{r}j}^{all\ atoms} f_l(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot(\boldsymbol{R}n+\boldsymbol{r}j)} = \underbrace{\sum_{n} e^{i\boldsymbol{q}\cdot\boldsymbol{R}n}}_{\text{lattice}} \underbrace{\sum_{j} f_l(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}j}}_{\text{unit cell structure factor}}$$

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

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

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

Reciprocal lattice and Fourier transform

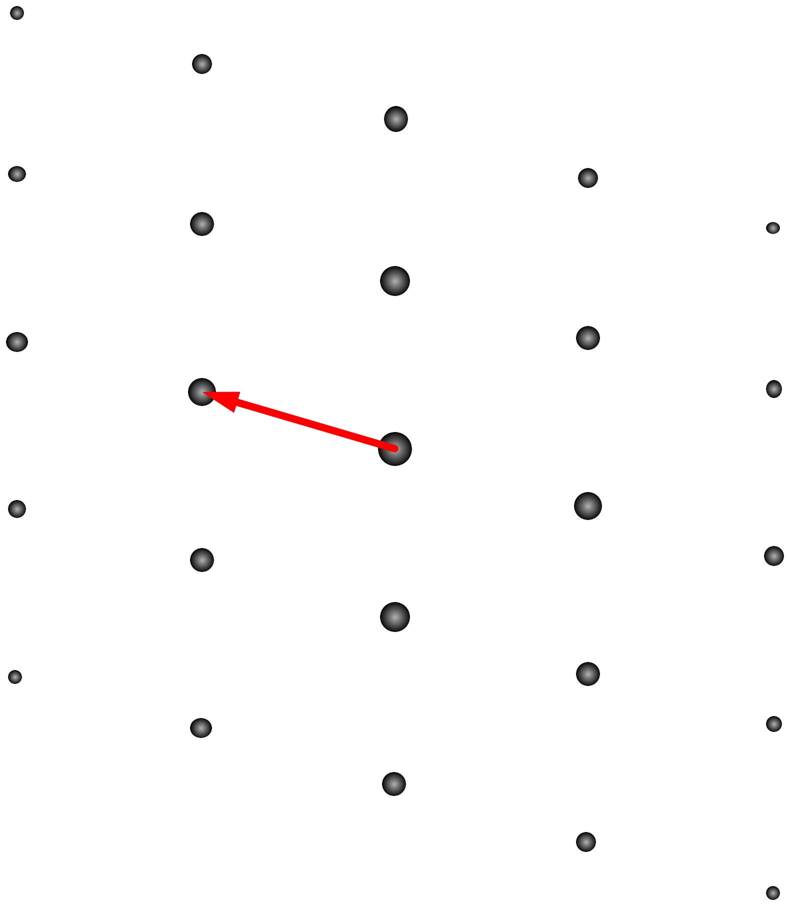


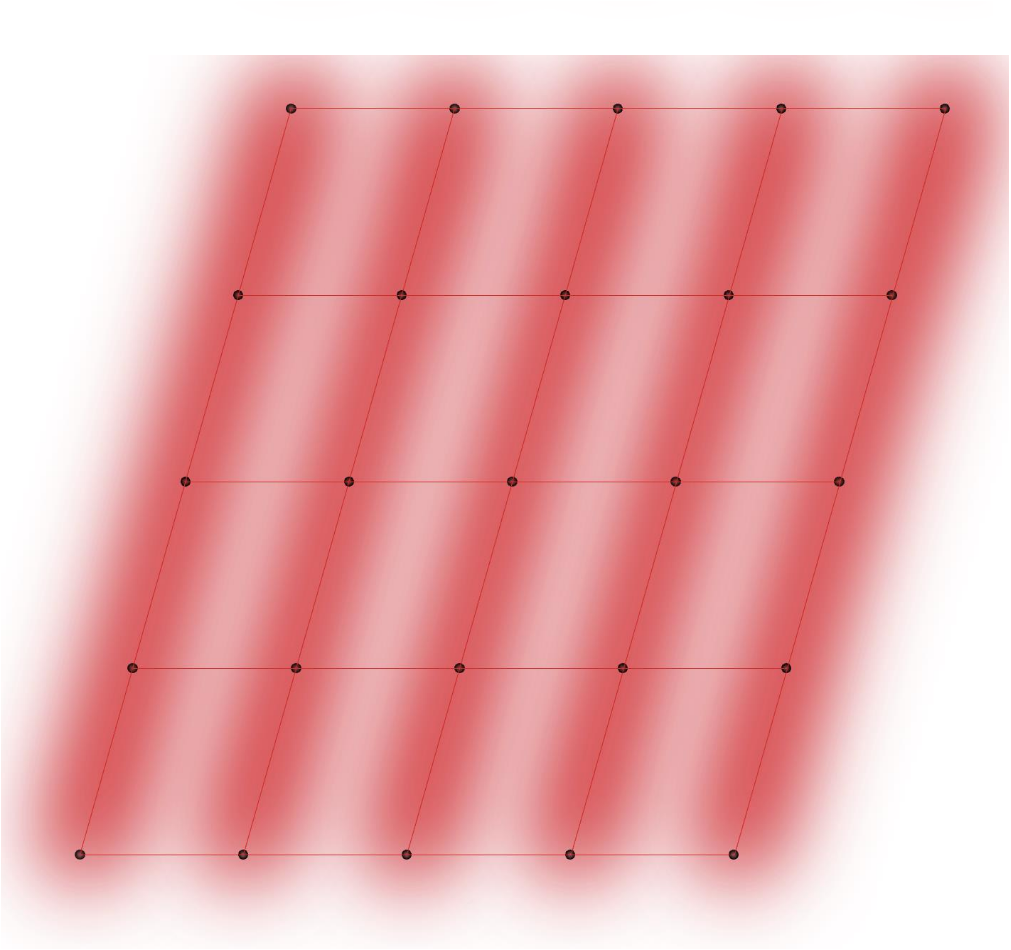
a diffraction pattern is the Fourier Transform of the object that produces it

- 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

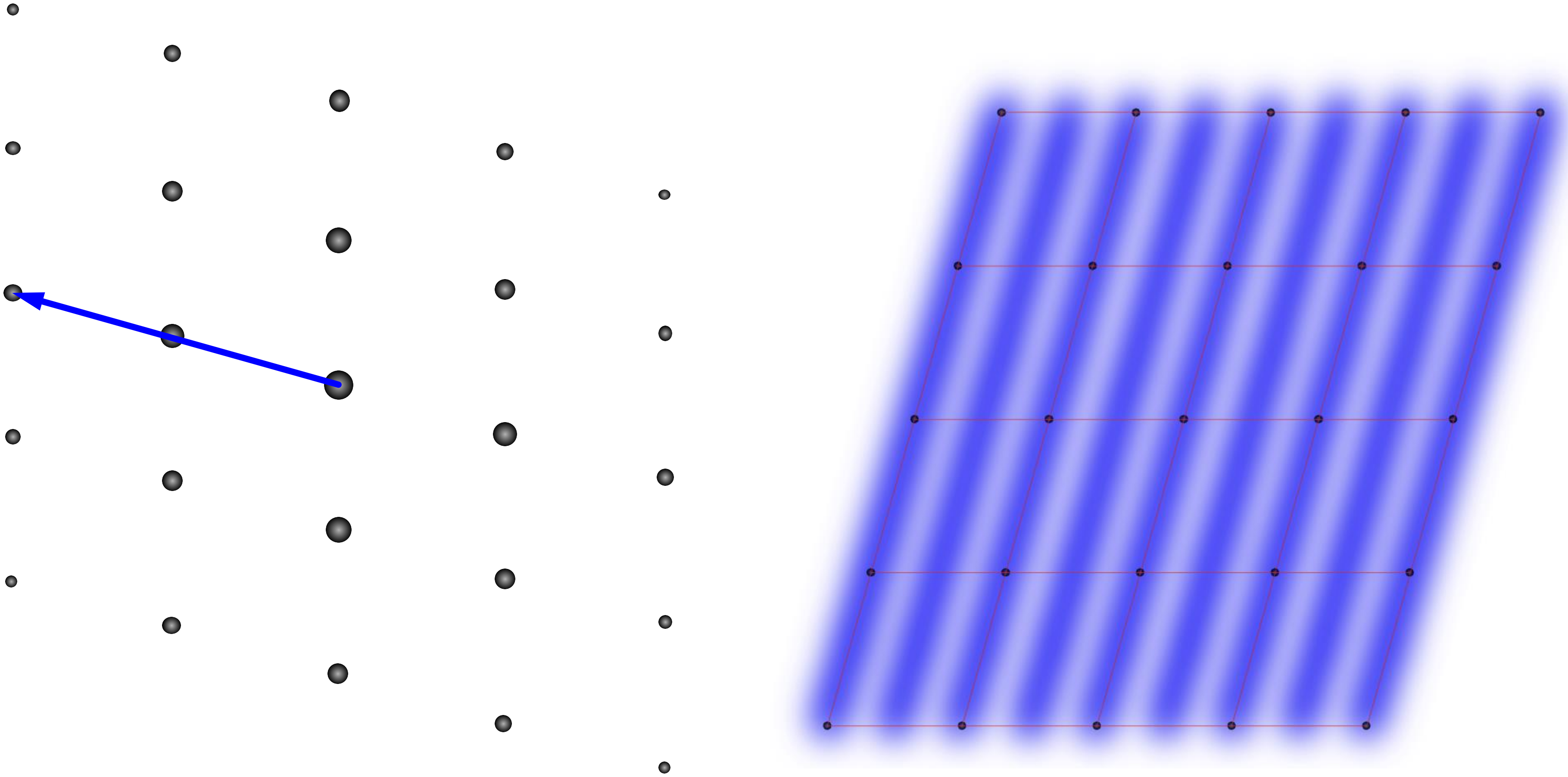
Reciprocal lattice and Fourier transform





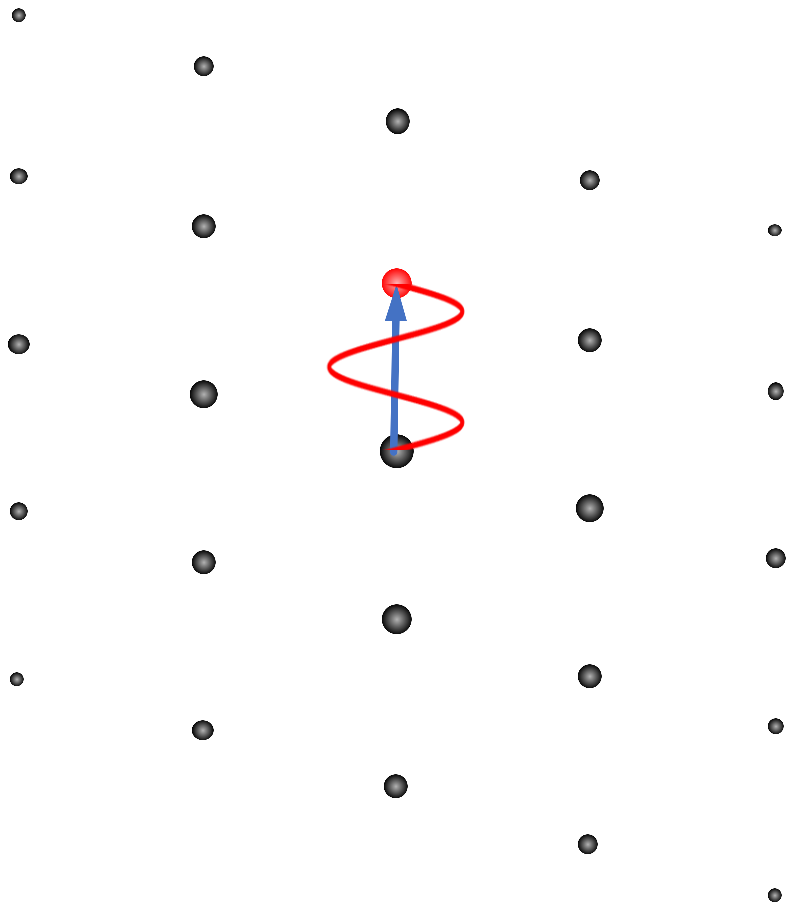
by Phil Willmott

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

Electromagnetic wave and measured intensity

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

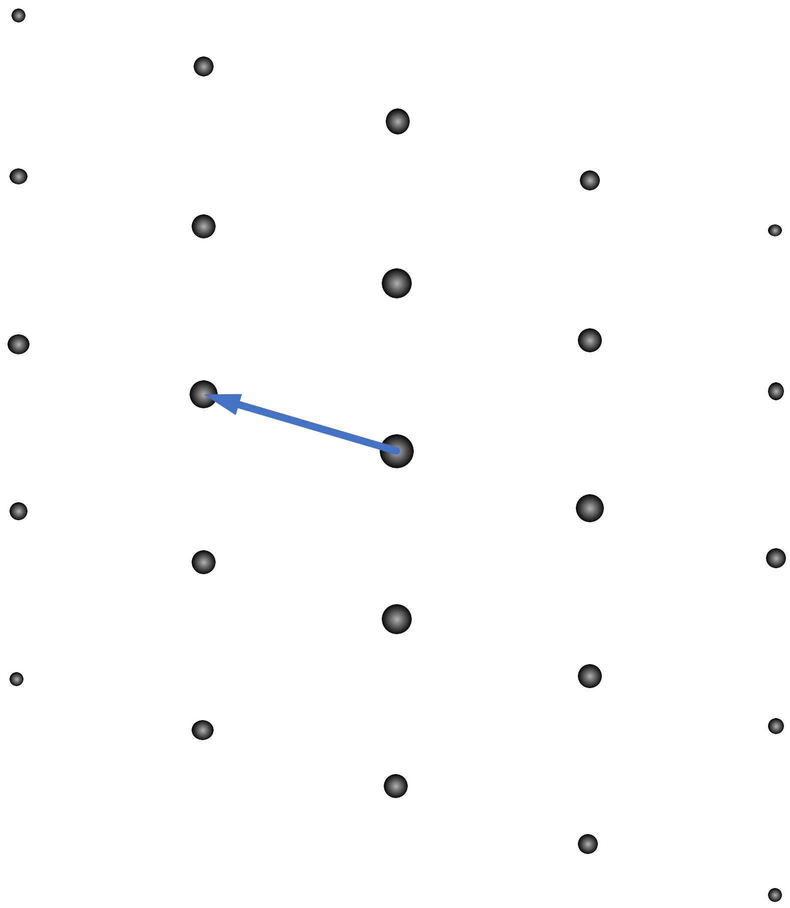
what we can measure is the intensity I

$I \propto |\psi(\boldsymbol{r}, t)|^2$
$|\psi(\boldsymbol{r}, t)|^2 = \left|Ae^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi)}\right|^2$ 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**”

Reciprocal lattice and Fourier transform



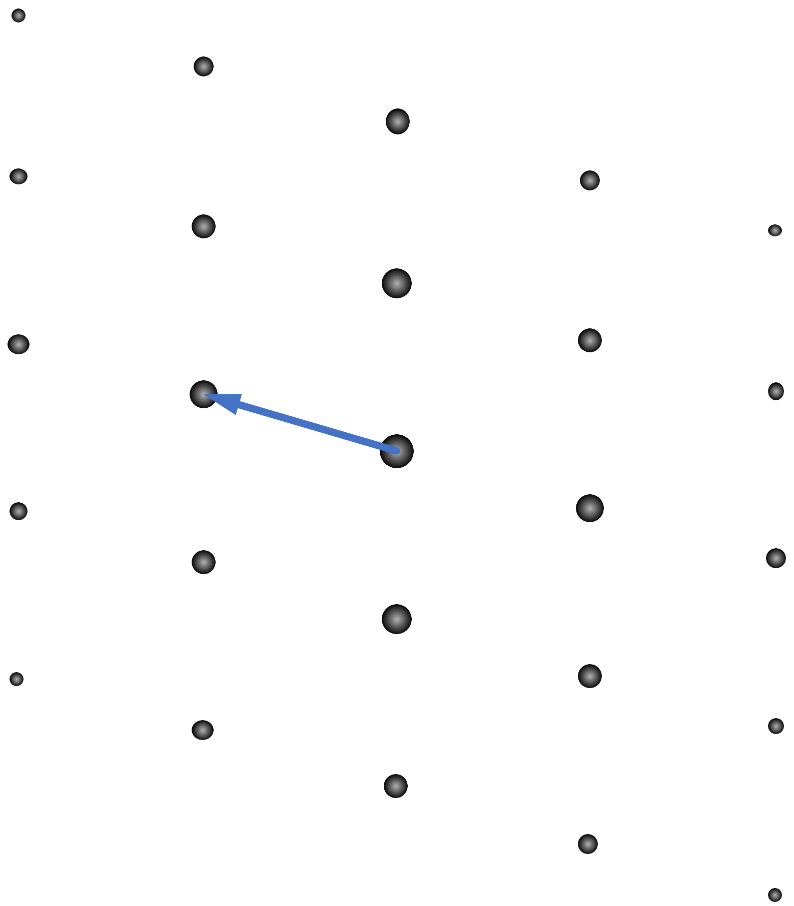
a diffraction pattern is the Fourier Transform of the object that produces it

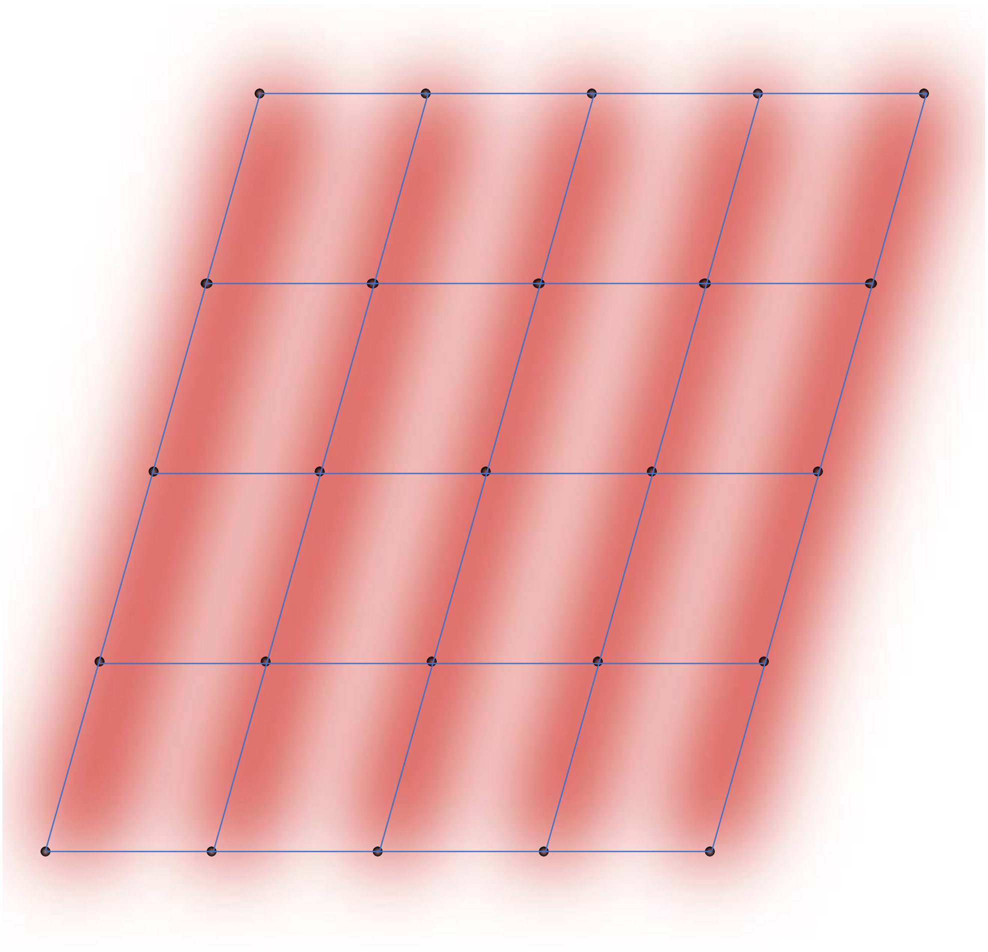
- Each point in the reciprocal lattice is therefore a "Fourier component" of the diffraction pattern
- The position of each point in the RL defines the frequency and direction of a sinusoidal wave of electron density
- The intensity at each point defines the amplitude of the wave
- The phase ϕ of that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

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

by Phil Willmott

Reciprocal lattice and Fourier transform





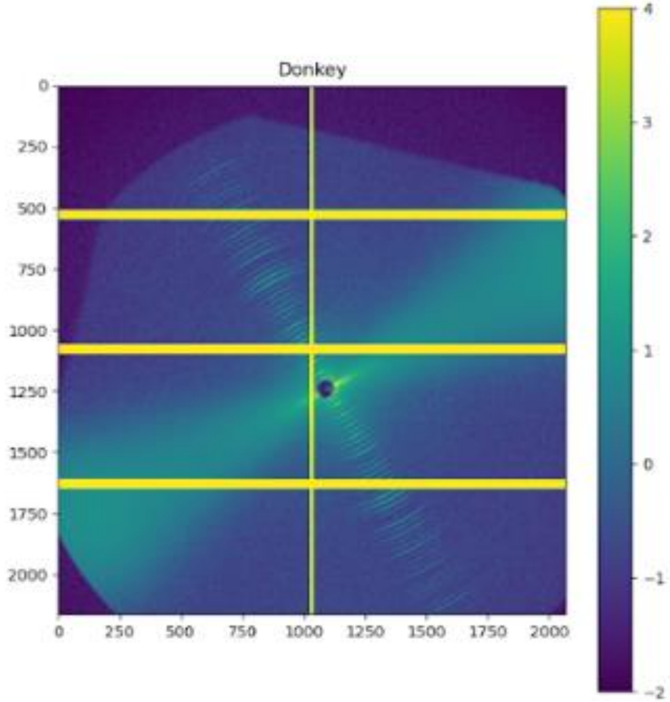
by Phil Willmott

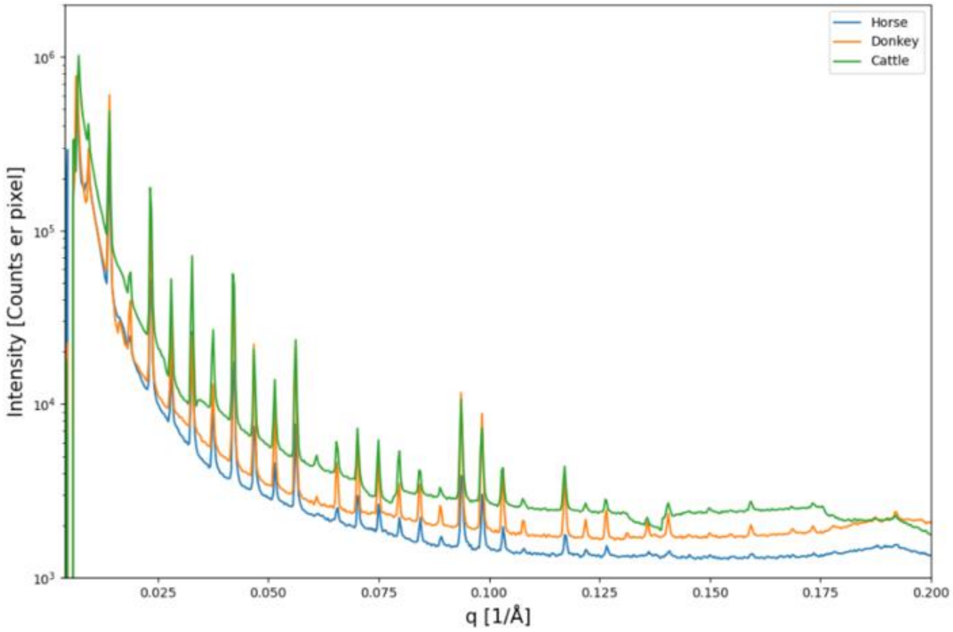
Full information content of reciprocal lattice

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

- The direction (angle) of the wave relative to the origin of the reciprocal lattice
- The frequency (given by the distance from origin of the reciprocal lattice, 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





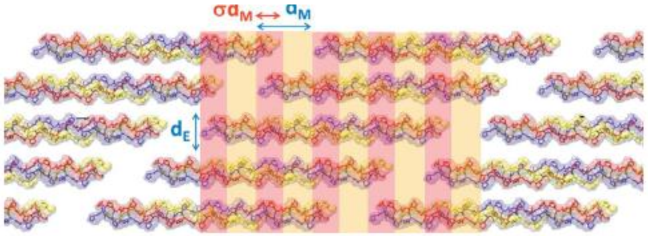


Figure 1

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.

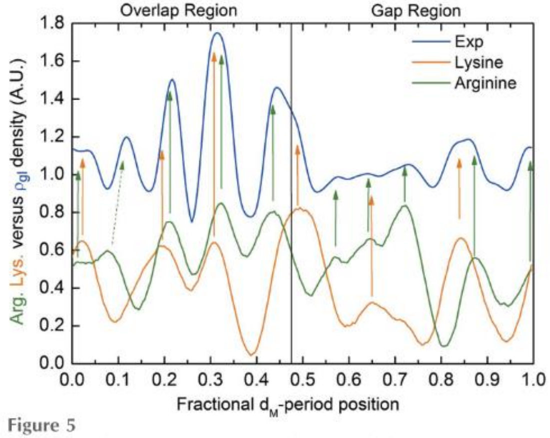
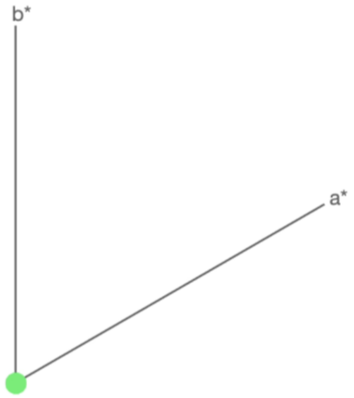


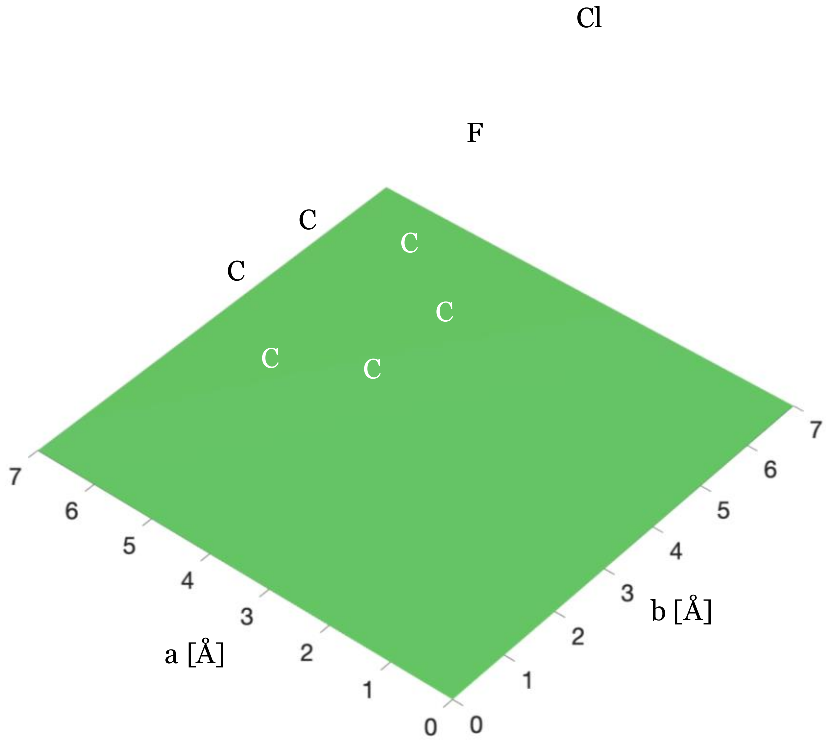
Figure 5

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.

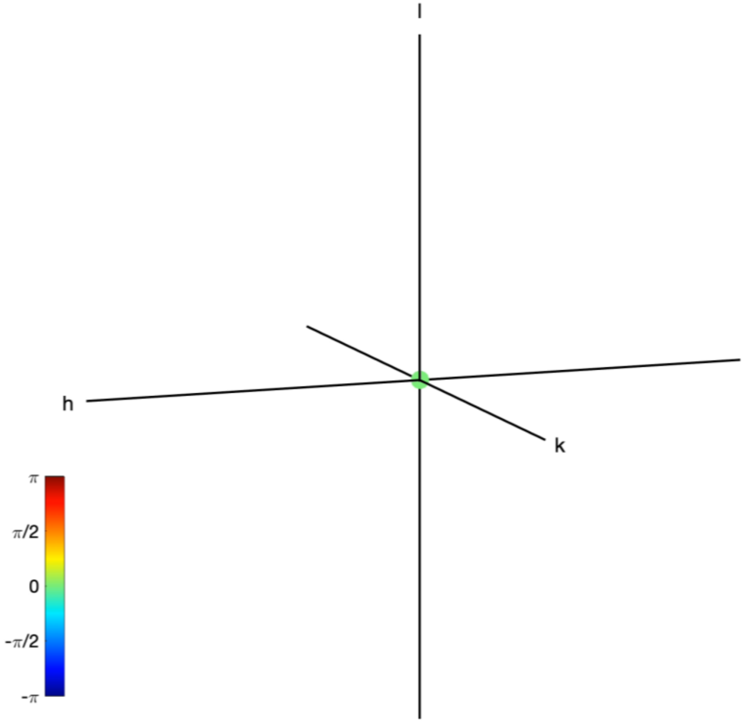
Electron density profile of each unit cell

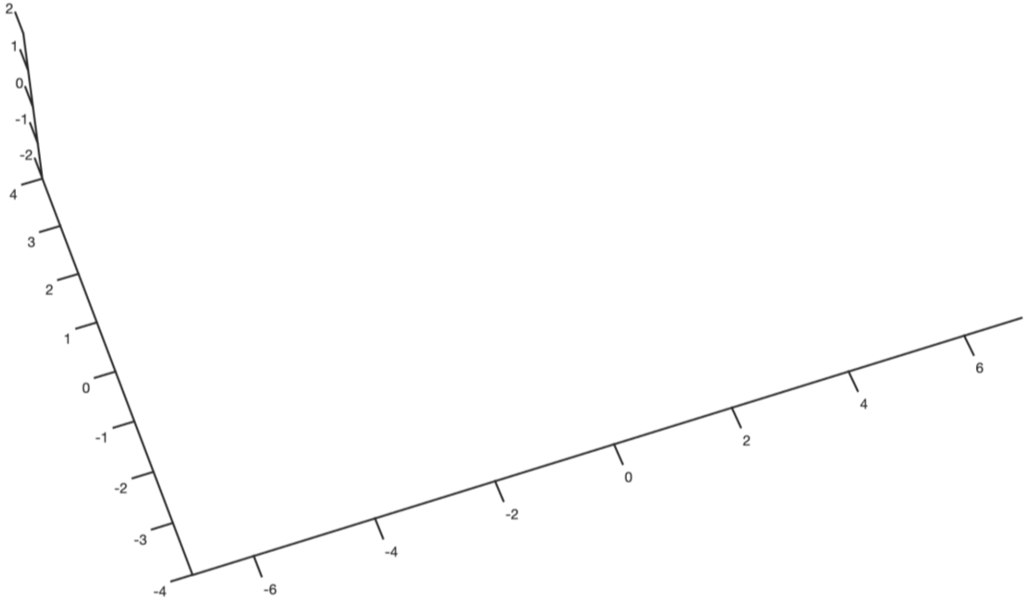




by Phil Willmott

Electron density profile of each unit cell





by Phil Willmott

Diffraction and Fourier transform

The diffraction pattern of a homogenously illuminated system is the square of the Fourier transform of that system

$$I(crystal) \propto [\mathcal{FT}(crystal)]^2$$

scattering amplitude from a crystalline material

$$F^{crystal}(\boldsymbol{q}) = \sum_{l}^{all\ atoms} f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} = \sum_{\boldsymbol{R}n+\boldsymbol{r}j}^{all\ atoms} f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot(\boldsymbol{R}n+\boldsymbol{r}j)} = \underbrace{\sum_{n} e^{i\boldsymbol{q}\cdot\boldsymbol{R}n}}_{\text{lattice}} \underbrace{\sum_{j} f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}j}}_{\text{unit cell structure factor}}$$

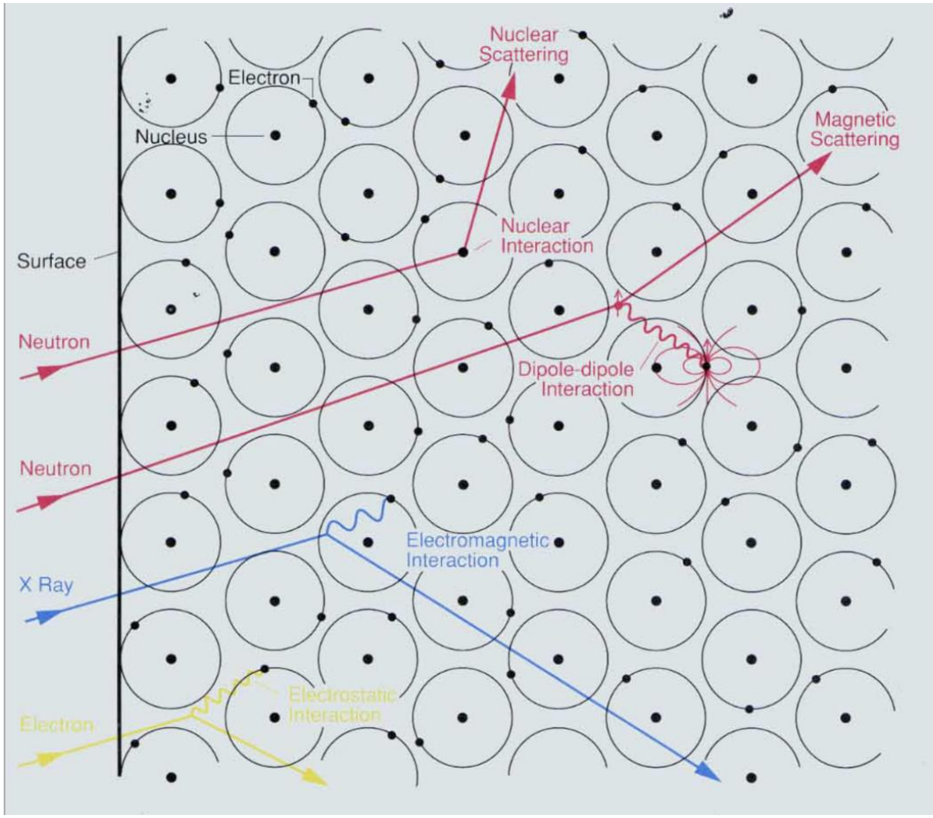
atomic form factor of the atom situated at position $\boldsymbol{r}_l$

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

$\boldsymbol{R}_n$ lattice vector

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

Interaction of material with different radiation



https://www.ncnr.nist.gov/summerschool/ss16/pdf/NeutronScatteringPrimer.pdf

X-rays and electron-beam interact with electrons in the materials, neutrons with the atomic nuclei

electron beam: electrostatic (electrostatic potential from positively charged nucleus and surrrounding electron cloud, strong interaction, very low penetration depth

X-ray: electromagnetic, rather strong, intermediate penetration depth

Neutrons: short-range strong nuclear interaction, large penetration depth, (for unpaired electrons: magnetic scattering)

Interaction of material with different material

electron

interact with the variation
in electrostatic potential
coulomb interaction

$$f \propto \sqrt[3]{Z}$$

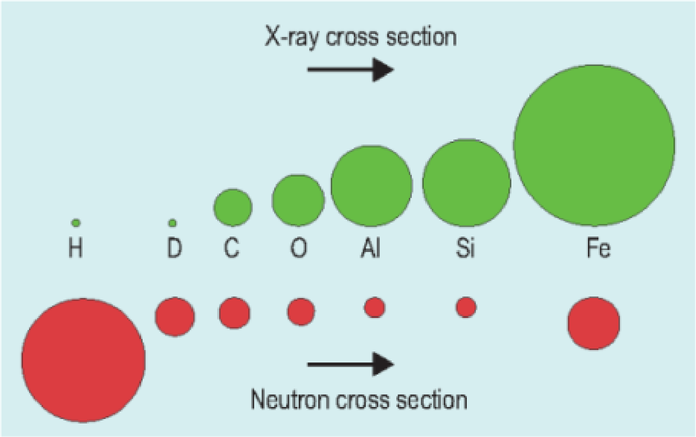
strong interaction:
multiple scattering needs
to be considered
(dynamical diffraction
theory)

neutron

interact with nuclei

point scattering

no clear trend with Z



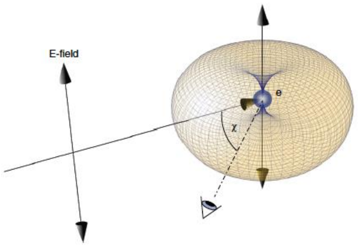
X-ray

interact with variation
in electron density
Thomson scattering

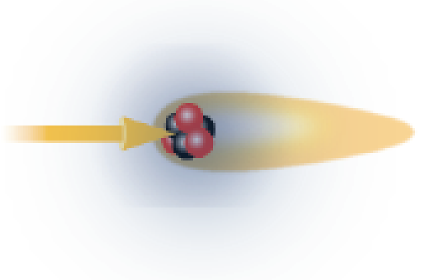
$$f \propto Z$$

most diffraction
experiments can be
explained by
kinematical diffraction
theory (neglecting
multple diffraction)

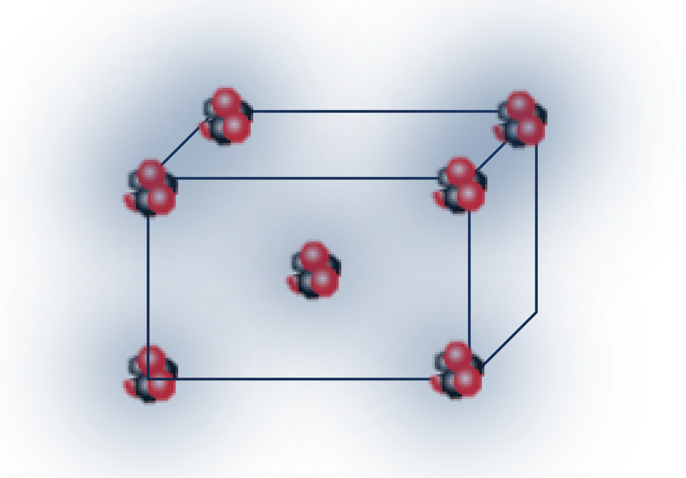
Interaction of X-rays with a crystal



interaction with
electron



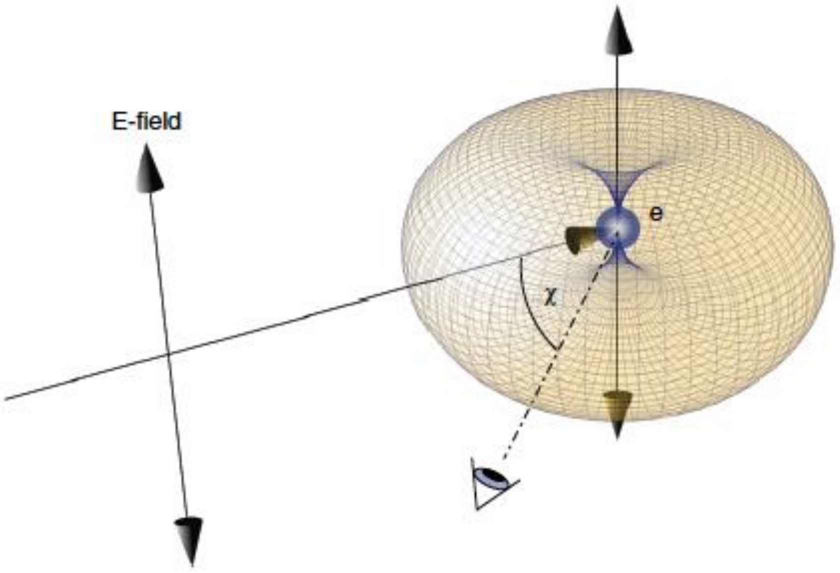
scattering from an atom



scattering from unit cell

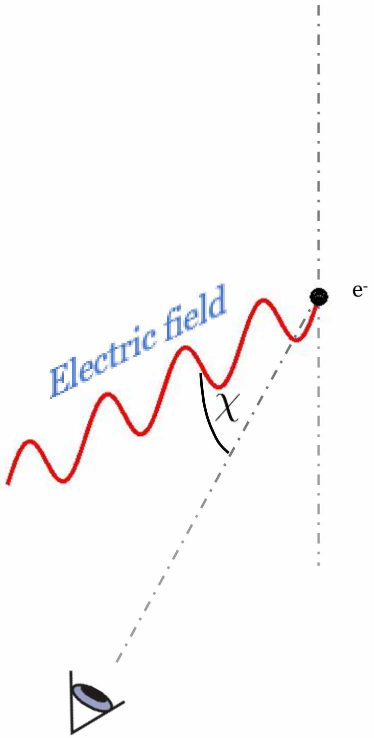
Elastic scattering from a single scatterer

- X-ray scattering from a single electron: Thomson scattering



- electromagnetic dipole radiation (non-isotropic) for polarized X-rays

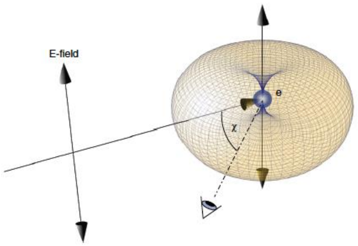
Interaction with electron: dipole radiation



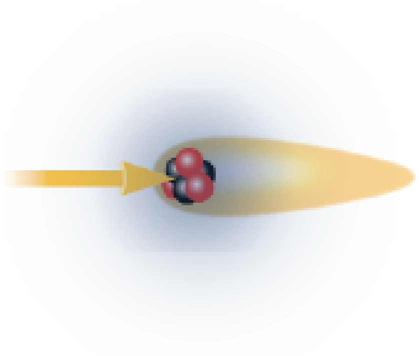
$$I(\chi) = E_0^2 \cos^2 \chi$$

Philip Willmott: Synchrotron and X-ray Free Electron Laser

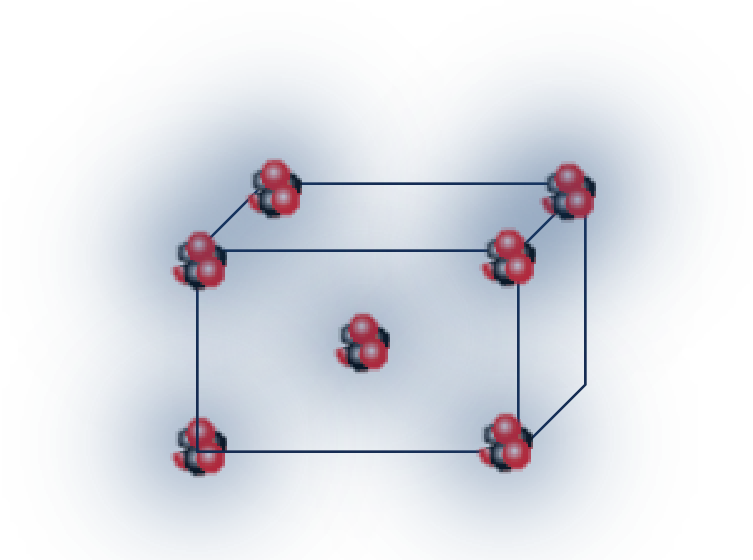
Interaction of X-rays with a crystal



interaction with electron
polarization factor
(decreases intensity at
higher angles)



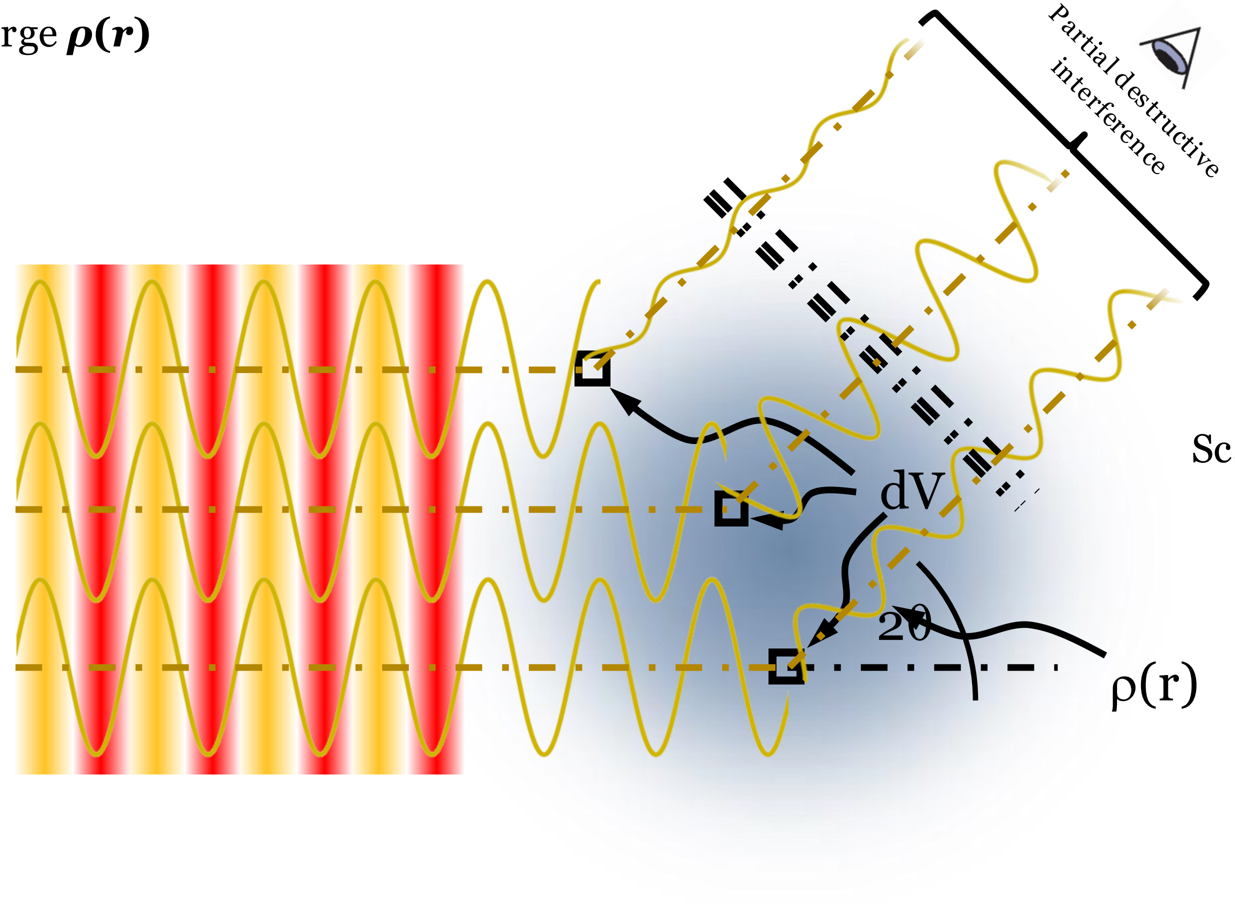
scattering from an atom
atomic form factor f



scattering from unit cell

Scattering from an atom

The orbital electrons in an atom move very fast (of the order of 10-^{18} sec for one orbital) and therefore an impinging wave sees only an average electron cloud which is characterized by an electron density of charge $\boldsymbol{\rho(r)}$

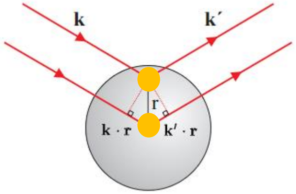


Scattering amplitude decreases with increasing angle 2θ

Philip Willmott: Synchrotron and X-ray Free Electron Laser

Scattering and Fourier Transform

2 electrons



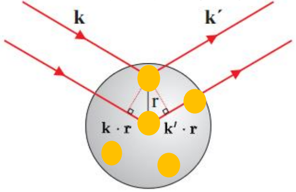
Phase difference of electron placed at position $\vec{r}$:
$\Delta\varphi(\boldsymbol{r}) = (\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{r} = \boldsymbol{q} \cdot \boldsymbol{r}$

Phase *factor* : $e^{\Delta\varphi(\boldsymbol{r})} = e^{\boldsymbol{iq \cdot r}}$

Scattering amplitude: $A(\boldsymbol{q}) = -r_0(1 + e^{\boldsymbol{iq \cdot r}})$

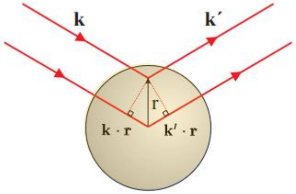
contribution of electron placed at origin $(\boldsymbol{r} = \vec{0})$

N electrons



Scattering amplitude: $A(\boldsymbol{q}) = -r_0 \sum_j e^{\boldsymbol{iq \cdot r}}$

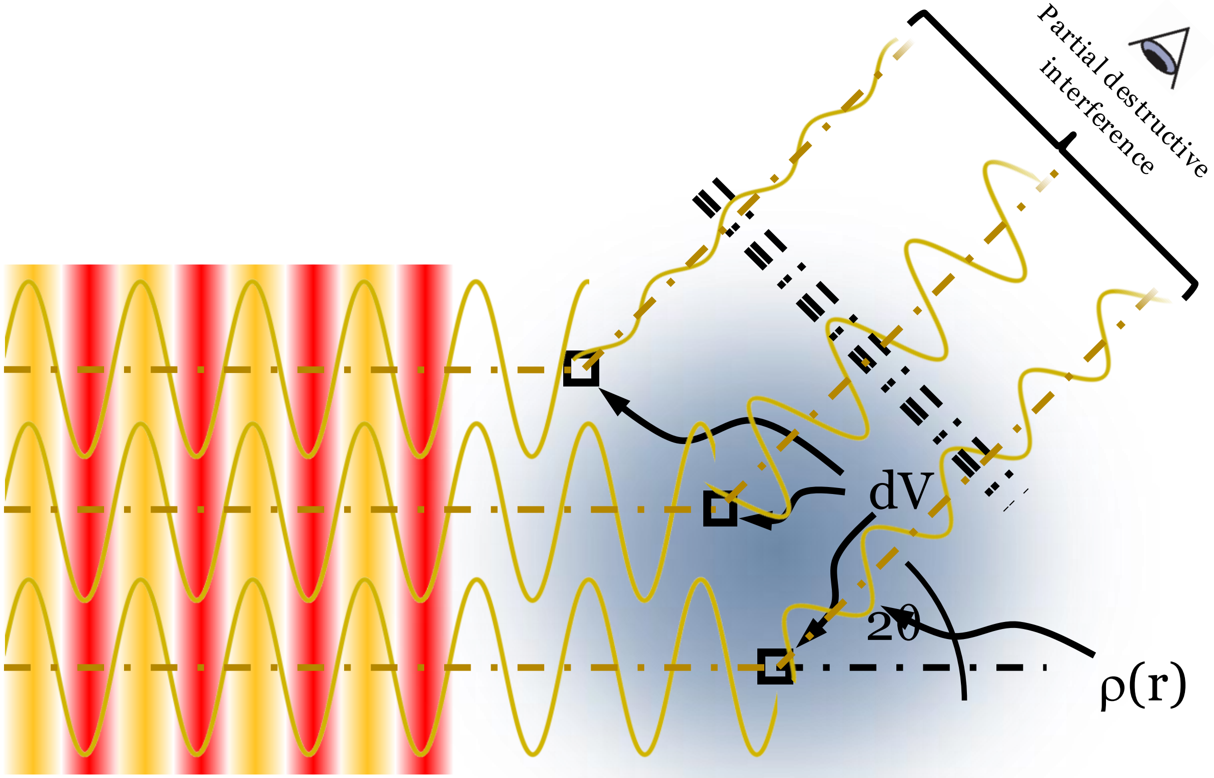
Electron distribution $\rho(\vec{r})$



atomic form factor: $f^0(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{\boldsymbol{iq \cdot r}} d\boldsymbol{r}$

Fourier Transform of electron density distribution !

Scattering from an atom



quantify phase difference between scattered radiation from any two dV and integrate contributions from all the volume elements

→ scattering amplitude of an atom as a function of the scattering angle and photon energy

→ in forward direction no phase difference, no destructive interference

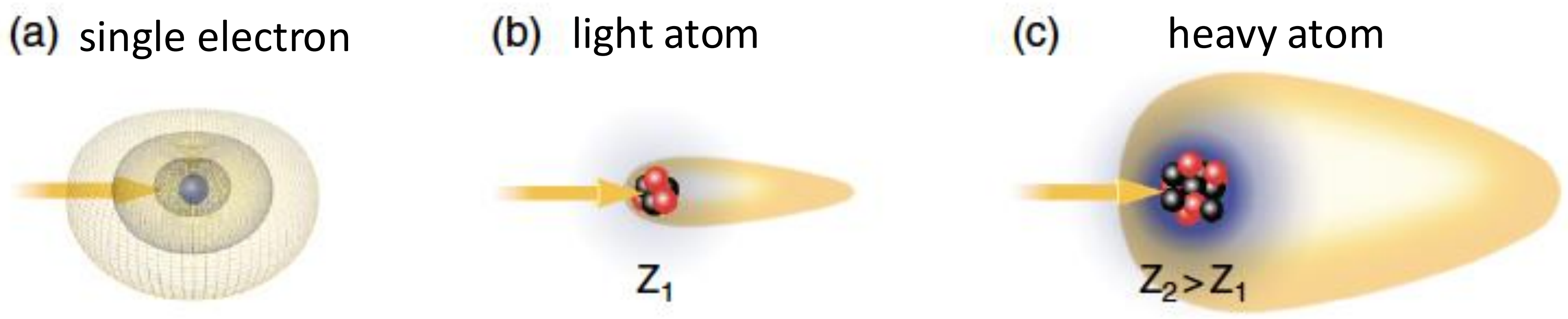
→ **atomic form/scattering factor**

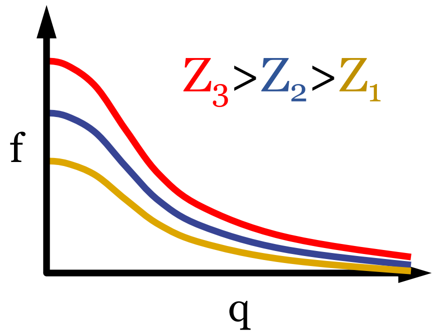
→ **Fourier transform of electron density distribution ρ(r)**

Philip Willmott: Synchrotron and X-ray Free Electron Laser

Elastic scattering and atomic form factor

photon wave length < electron cloud





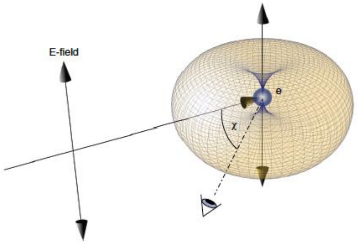
forward direction $f^0(0)$: integral of the electron density over the atom’s electron cloud: atomic number Z

for q≠0 scattering amplitude decreases with increasing 2θ

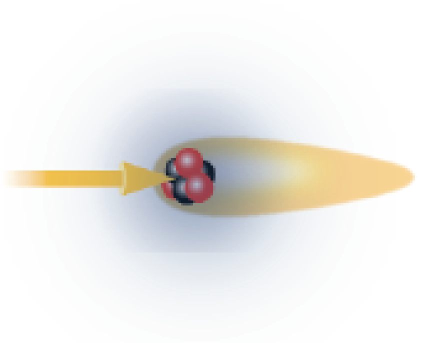
drop off is steeper for Z_1 (core electrons are closer to nuclear core, heavy atoms have electron density concentrated in a smaller central volume)

Willmott, P. (2019). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

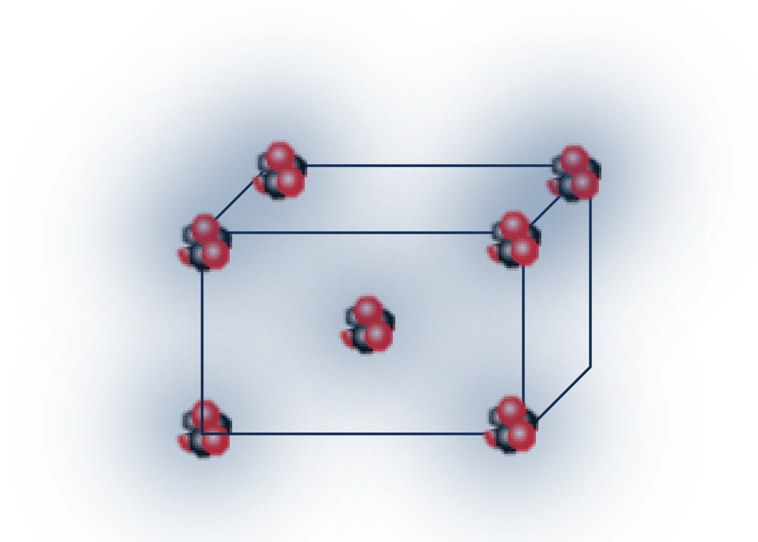
Interaction of X-rays with a crystal



interaction with electron
polarization factor



scattering from an atom
atomic form factor f



scattering from unit cell
structure factor F

Diffraction and Fourier transform

scattering amplitude from a crystalline material

$$F^{crystal}(\boldsymbol{q}) = \sum_{l}^{all\ atoms} f_l(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} = \sum_{\boldsymbol{R}n+\boldsymbol{r}j}^{all\ atoms} f_j(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot(\boldsymbol{R}n+\boldsymbol{r}j)} = \underbrace{\sum_{n} e^{i\boldsymbol{q}\cdot\boldsymbol{R}n}}_{\text{lattice}} \underbrace{\sum_{j} f_j(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}j}}_{\textbf{unit cell structure factor}}$$

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

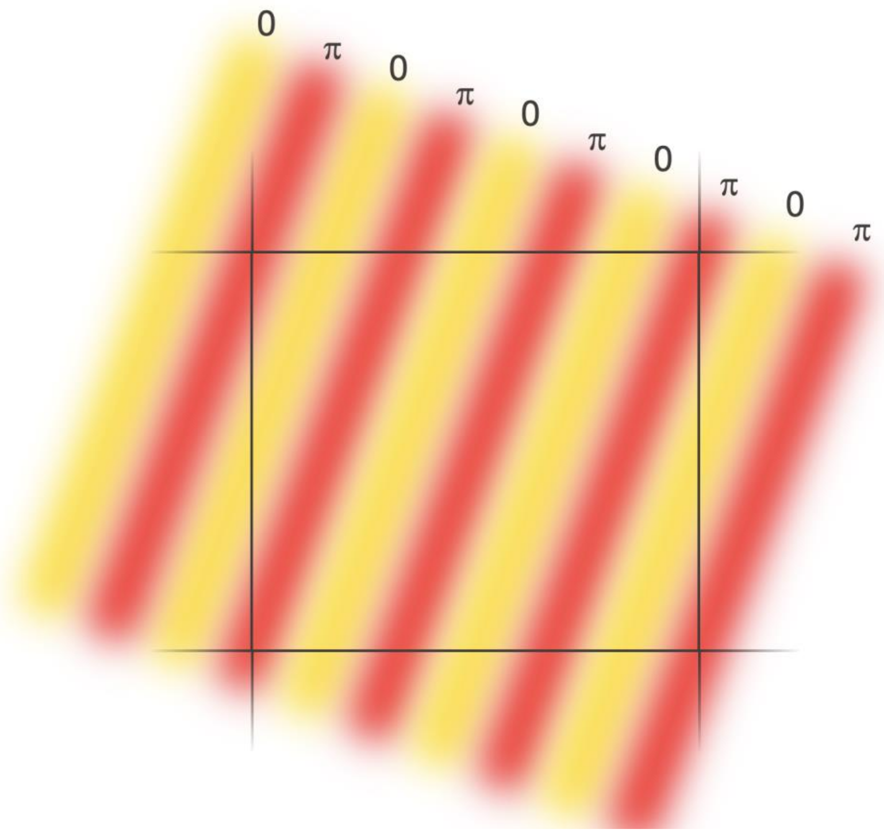
$\boldsymbol{r}_l = \boldsymbol{R}_n + \boldsymbol{r}_j$

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

with Laue's condition for constructive interference
$\boldsymbol{q} = \boldsymbol{K}$, with $\boldsymbol{K} \in \mathcal{R}$
at any other scattering vector q, the intensity is zero

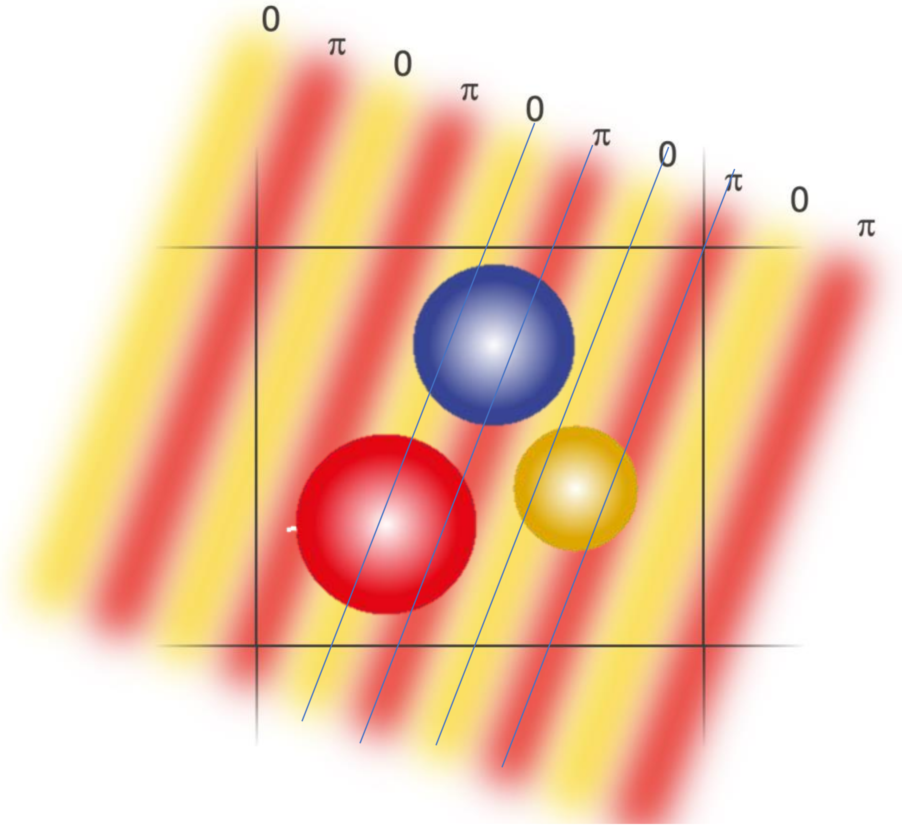
$$S(\boldsymbol{K}) = \sum_{j} f_j(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}j}$$

Interaction with a unit cell



Unit cell in Bragg condition:
phase must be the same from one unit cell to the next: corners have the same phase

Interaction with a unit cell



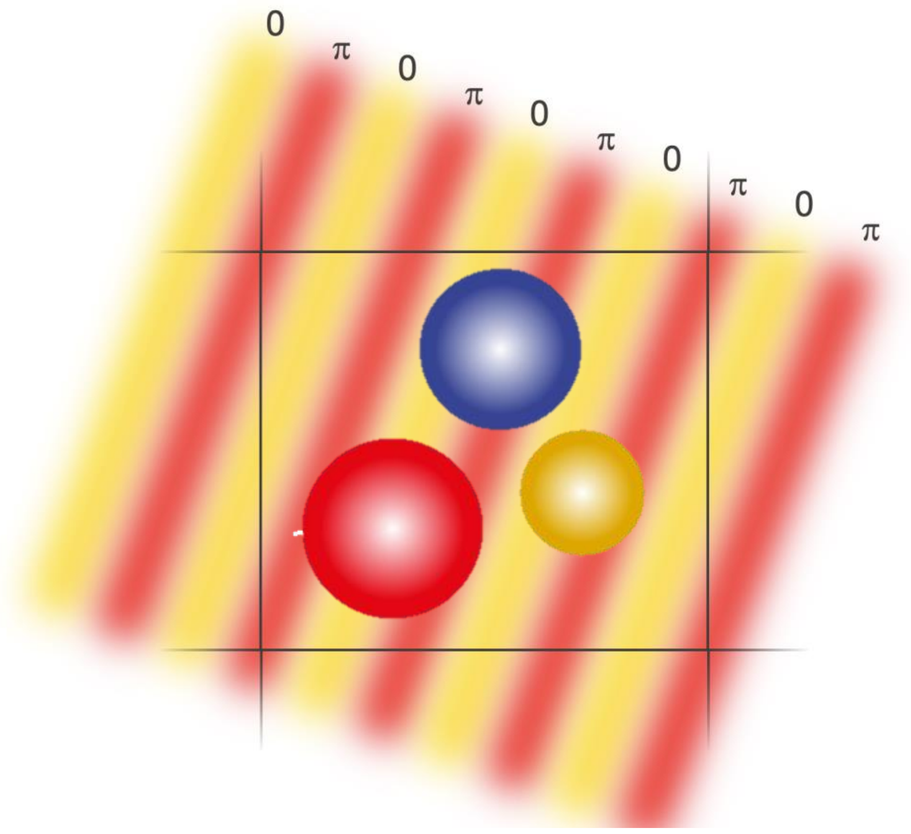
Scattering atoms associated with basis in unit cell

Phases of scattered waves

Depends on their location within the unit cell

Atom 1: $\phi_1 \simeq \pi/6$ (30°)
Atom 2: $\phi_2 \simeq 2\pi/3$ (120°)
Atom 3: $\phi_3 \simeq \pi/2$ (90°)

Interaction with a unit cell



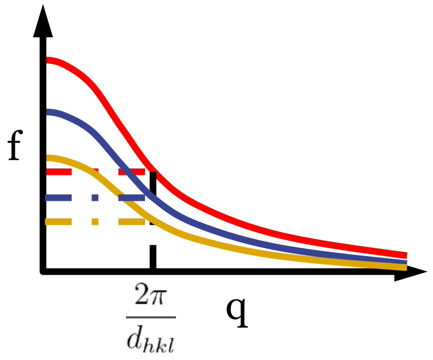
Scattering atoms associated with basis in unit cell

Phases of scattered waves

  Depends on their location within the unit cell

Amplitudes of scattered waves

  Given by atomic form factors for $q = 2\pi/d_{\mathrm{hkl}}$



Interaction with a unit cell: the structor factor

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\underbrace{\boldsymbol{K}\cdot\boldsymbol{r}j}_{\text{phase } \phi}}$$

$$\boldsymbol{K} \in \mathcal{R}$$
$$\boldsymbol{r_j} \in \mathcal{D}$$

$$\boldsymbol{K} \cdot \boldsymbol{r} = (\mathrm{h}\boldsymbol{a}{*}{+}k\boldsymbol{b}{*}{+}l\boldsymbol{c}{*}) \cdot (x_j\boldsymbol{a}{+}yj\boldsymbol{b}{+}\ zj\boldsymbol{c})$$

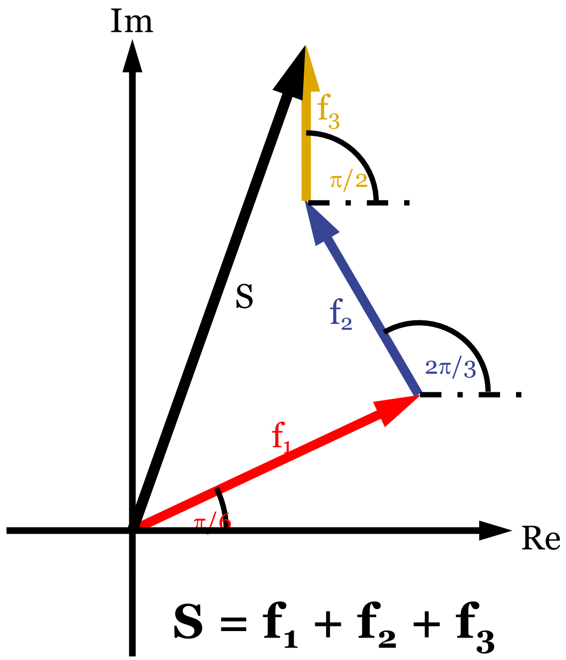
with $\boldsymbol{a}^*\boldsymbol{a}=\boldsymbol{b}^*\boldsymbol{b}=\mathbf{c}^*\mathbf{c}= \mathbf{2}\boldsymbol{\pi}$ and
$\boldsymbol{a}^*\boldsymbol{b}=\boldsymbol{b}^*\boldsymbol{a}=\boldsymbol{c}^*\boldsymbol{a}$ ... =0

$$\boldsymbol{K} \cdot \boldsymbol{r} = 2\pi(hx_j + ky_j + lz_j)$$

Intensity of measured Bragg peak (hkl) is proportional to $|S_{hkl}|^2$
All phase information is lost!

Interaction with a unit cell: the structor factor

One can also consider S as the vector sum of atomic form factors



$$\mathbf{S} = \mathbf{f_1} + \mathbf{f_2} + \mathbf{f_3}$$

Argand diagram

Example
Phases of scattered waves

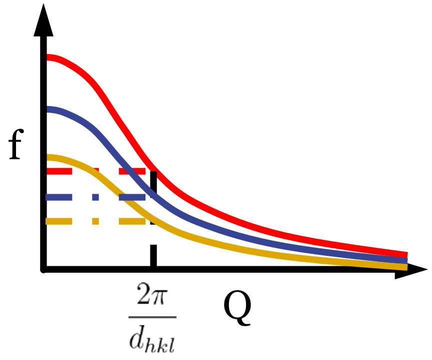
Atom 1: $\phi_1 \simeq \pi/6$ (30°)

Atom 2: $\phi_2 \simeq 2\pi/3$ (120°)

Atom 3: $\phi_3 \simeq \pi/2$ (90°)

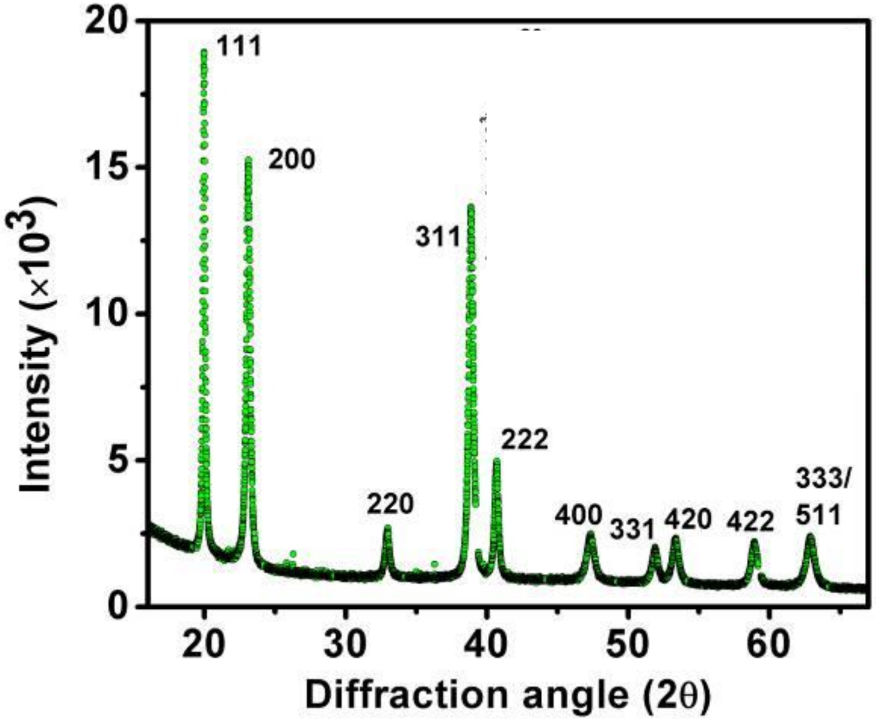
Amplitudes of scattered waves

Atomic form factors for
$q = 4\pi/\lambda \sin\theta$



Diffraction pattern and systematic absences

For a given peak, $\boldsymbol{K} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$ in the reciprocal space, and an associated perpendicular plane (hkl)



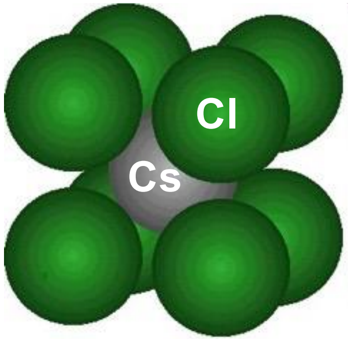
nanocrystalline Ni

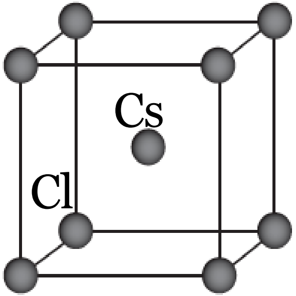
but why is there no (001) reflection?

Structure factor

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j} \qquad \boldsymbol{K}\cdot\boldsymbol{r} = (\mathrm{h}\boldsymbol{a}{*}+k\boldsymbol{b}{*}+l\boldsymbol{c}{*})\cdot(x_j\boldsymbol{a}+yj\boldsymbol{b}+zj\mathbf{c}) = 2\pi(hx_j + ky_j + lz_j)$$

- The $\boldsymbol{r}_j$ are the vector position of the atoms in the motifs.





$\boldsymbol{r}_{CL} =$

$\boldsymbol{r}_{Cs} =$

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j} = f_{Cl}(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}Cl} + f_{Cl}(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}\,Cl}$$

$$\boldsymbol{K}\cdot\boldsymbol{r}_{Cl} = 0 \qquad \boldsymbol{K}\cdot\boldsymbol{r}_{Cs} = (\mathrm{h}\boldsymbol{a}{*}+k\boldsymbol{b}{*}+l\boldsymbol{c}{*})\cdot\left(\frac{1}{2}\boldsymbol{a}+\frac{1}{2}\mathbf{b}+\frac{1}{2}\mathbf{c}\right) = \pi(h+k+l)$$

$$e^{i0} = 1 \qquad e^{i\pi} = e^{-i\pi} = -1$$

$$S(\boldsymbol{K}) = f_{Cl} + f_{Cs}(-1)^{(h+k+l)}$$

Structure factor and diffraction peak

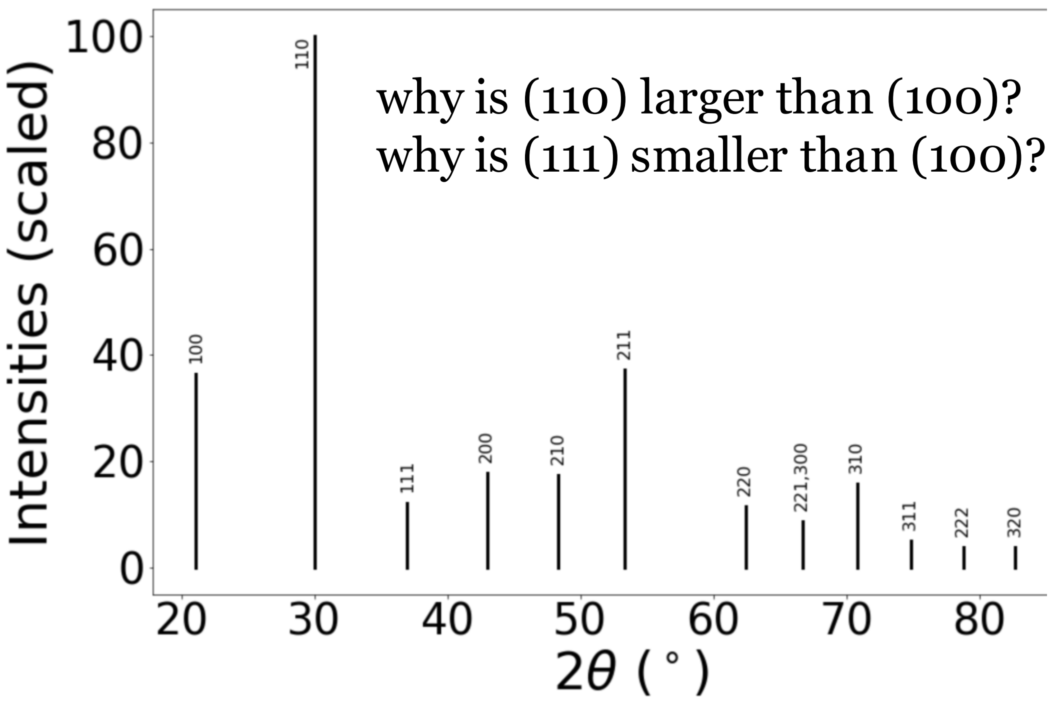
- Hence for CsCl we have:

$$\boxed{\begin{cases} S(\boldsymbol{K}) = f_{Cl} + f_{Cs} & \text{for } (h+k+l) \text{ even} \\ S(\boldsymbol{K}) = f_{Cl} - f_{Cs} & \text{for } (h+k+l) \text{ odd} \end{cases}}$$

$$f_{Cl} \neq f_{Cs}$$

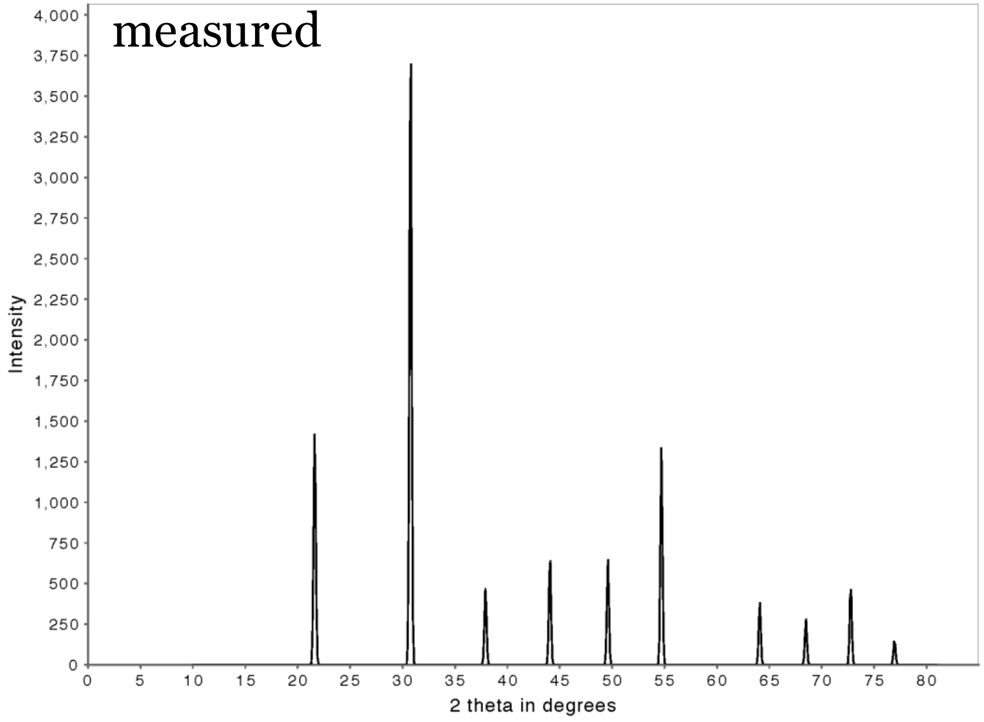
Intensity is proportional to the square of the structure factor $I(hkl) \propto |S(hkl)|^2$

XRD peaks calculated

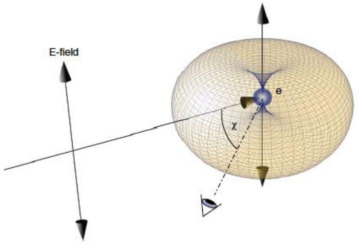


why is (110) larger than (100)?
why is (111) smaller than (100)?

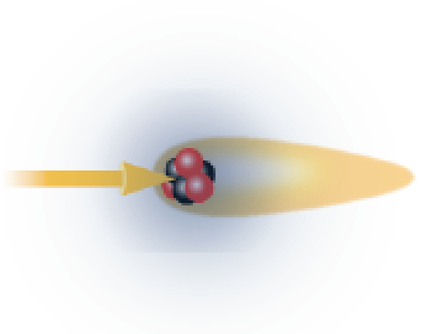
*-Cs Cl-[PM3-M]Cortona, P.[1992]



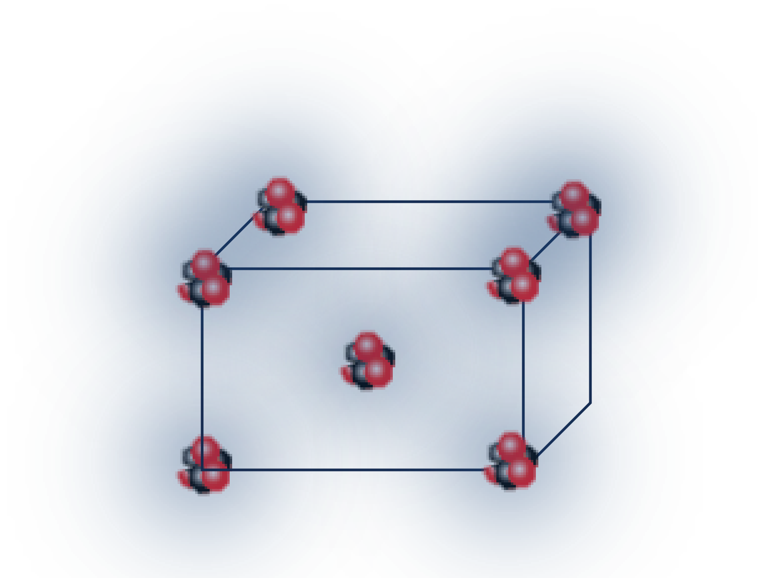
Interaction of X-rays with a crystal



interaction with electron
polarization factor
(decreases intensity at
higher angles)



scattering from an atom
atomic form factor f



scattering from unit cell

Structure factor and diffraction peak

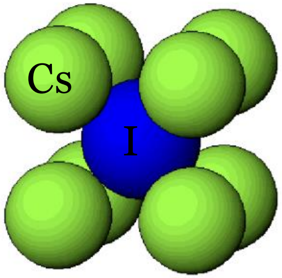
- Hence for CsCl we have:

$$\boxed{\begin{cases} S(\boldsymbol{K}) = f_{Cl} + f_{Cs} & \text{for } (h+k+l) \text{ even} \\ S(\boldsymbol{K}) = f_{Cl} - f_{Cs} & \text{for } (h+k+l) \text{ odd} \end{cases}}$$

- Peaks observed:

$$f_{Cl} \neq f_{Cs}$$

(hkl)	CsCl	CsI
(100)	√	
(110)	√	√
(111)	√	
(200)	√	√
(210)	√	
(211)	√	√
(220)	√	√
(221)	√	

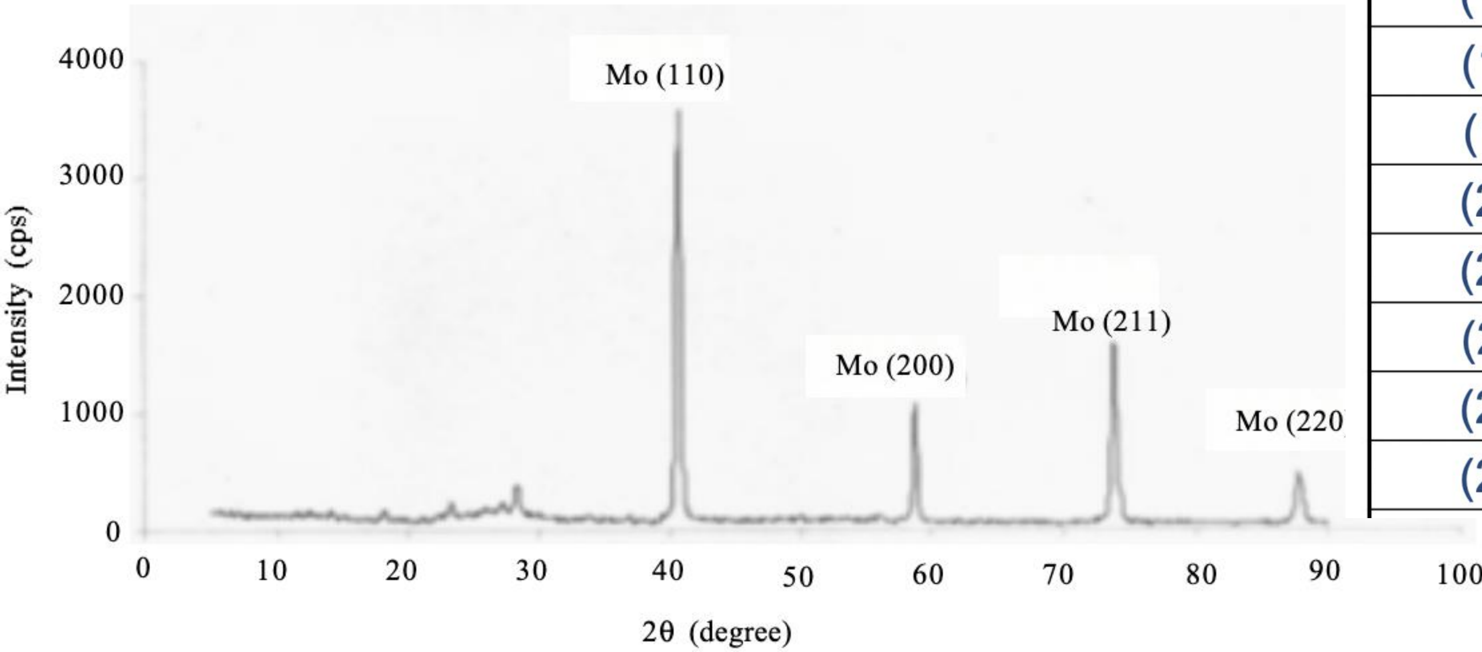


- For CsI, many peaks disappear ! Cs and I are isoelectronic: $f_I = f_{Cs}$!

X-ray diffraction and systematic absences

Some peaks are also systemically absent from diffraction patterns also in single atom motifs

Example BCC Molybdenum (Mo) metal.



(hkl)	CsI
(100)	
(110)	√
(111)	
(200)	√
(210)	
(211)	√
(220)	√
(221)	

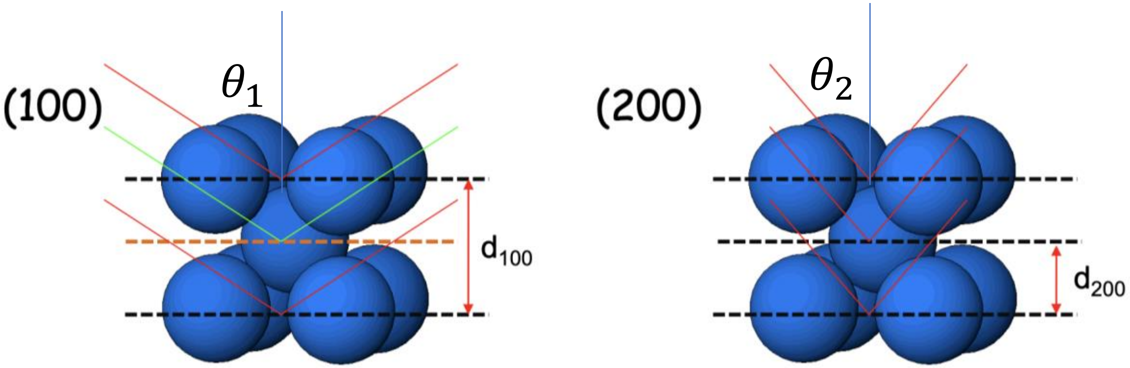
This is surprising since for a single atom motif, $S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j} = f_{M_0}$.

X-ray diffraction and systematic absences

Some peaks are also systemically absent from diffraction patterns in single atom motifs

This is surprising since for a single atom motif, $S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j} = f_{M_0}$.

However, the (h,k,l) intercepts here defined on the conventional cell, which means there is more than one motif in this cell!

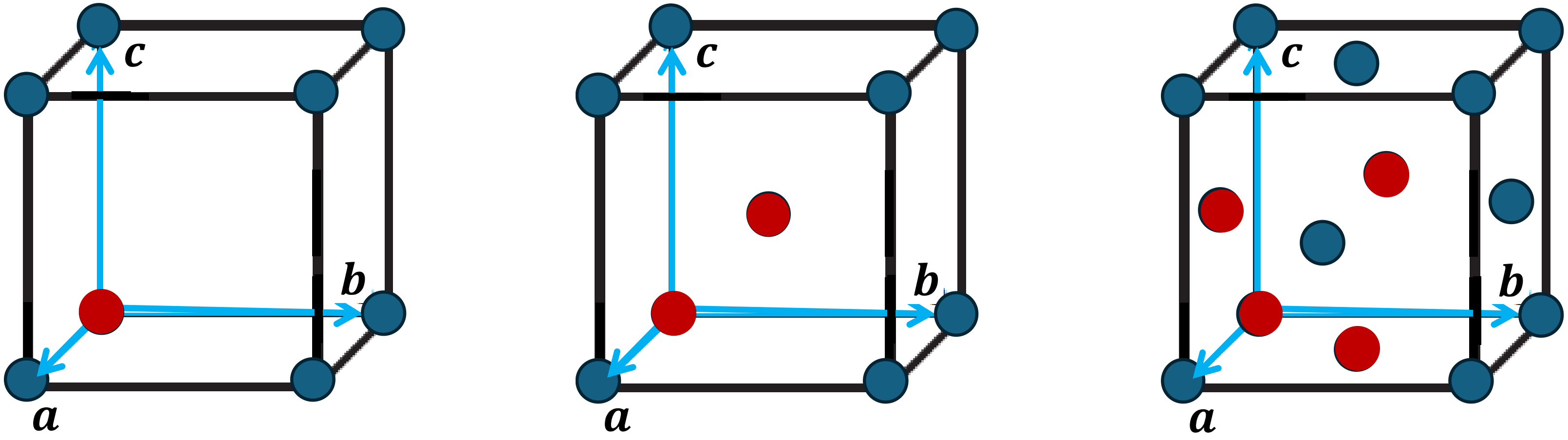


At θ_1 where Bragg law is fullfilled for the (100) planes diffraction, the parallel planes (200) diffract out of phase, resulting in destructive interferences.

At θ_2 where Bragg law is fullfilled for the (200) planes diffraction, the parallel planes (100) diffract inf phase, resulting in constructive interferences.

X-ray diffraction and systematic absences

We can view non-primitive crystal structures as being defined by the conventional cell, and a motif with a number of atoms equal to the number of atoms per conventional cell.



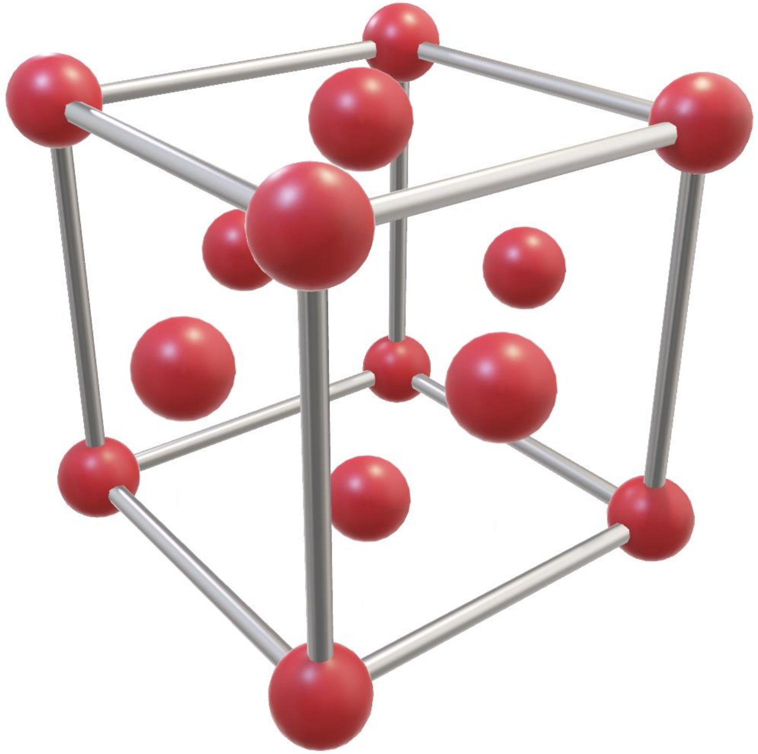
- Be careful: while it describes a similar crystal, it is not a rigorous way to look at crystal structures, as it leads to believe that the BCC and FCC don't have their own Bravais Lattice prime vectors. Also, it leads to believe that planes like the (200) planes are not crystal planes for the BCC and FCC structures !

It is however a good way to treat diffraction and understand systematic absences.

- Indeed, to these multiple atoms motifs, we can now apply the formalism of structure factors developed for CsCl:
- $S(\boldsymbol{K}) = f_{Mo}\left(1 + (-1)^{(h+k+l)}\right)$

$$\begin{cases} S(\boldsymbol{K}) = 2f_{Mo} & \text{for } (h+k+l) \text{ even} \\ S(\boldsymbol{K}) = 0 & \text{for } (h+k+l) \text{ odd} \end{cases}$$

Interaction with a unit cell: the structor factor



Face-centered cubic (fcc): 4 identical atoms/unit cell at positions:

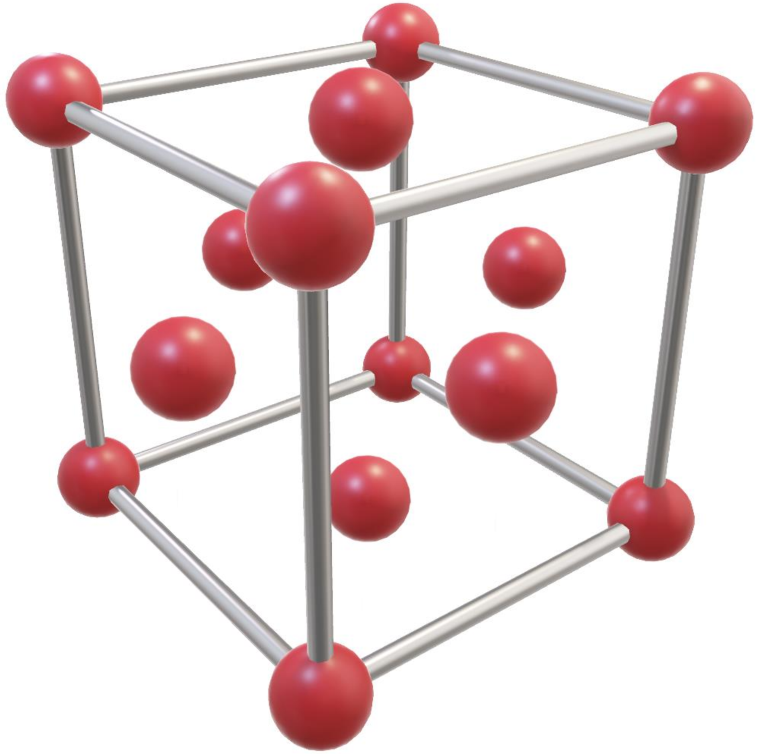
- 0, 0, 0 (corner)
- ½ ½ 0 (face centre)
- ½ 0 ½ (face centre)
- 0 ½ ½ (face centre)

S_{001}?

$$S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{r}j}$$

$$\boldsymbol{K}.\boldsymbol{r} = 2\pi(hx_l + ky_l + lz_l)$$

Interaction with a unit cell: the structor factor



Face-centered cubic (fcc): 4 identical atoms/unit cell at positions:

0, 0, 0 (corner)
½ ½ 0 (face centre)
½ 0 ½ (face centre)
0 ½ ½ (face centre)

S_{001}?

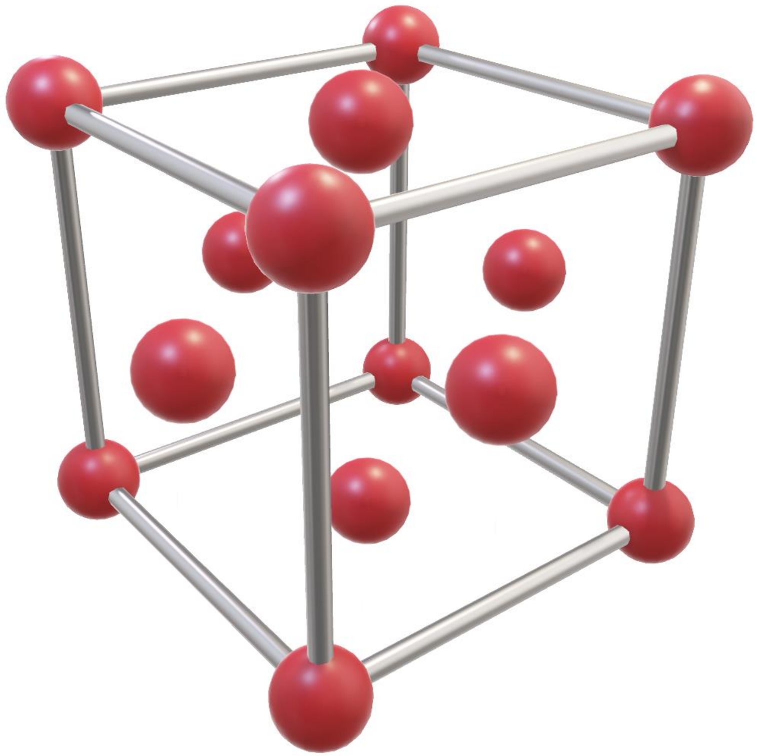
$$S_{001} = f_{atom}[\exp(0) + \exp(0) + \exp(-i\pi) + \exp(-i\pi)]$$
$$= f_{atom}[1 + 1 - 1 - 1] = 0!!$$

Bragg's law tells you that you will see a Bragg peak at (hkl) = (001)

But structure factor here = 0 "systematic absence"

General rule for fcc crystals: only Bragg peak intensity if : h,k,l all odd, or h,k,l all even

Interaction with a unit cell: the structor factor



Face-centered cubic (fcc): 4 identical atoms/unit cell at positions:

0, 0, 0 (corner)
½ ½ 0 (face centre)
½ 0 ½ (face centre)
0 ½ ½ (face centre)

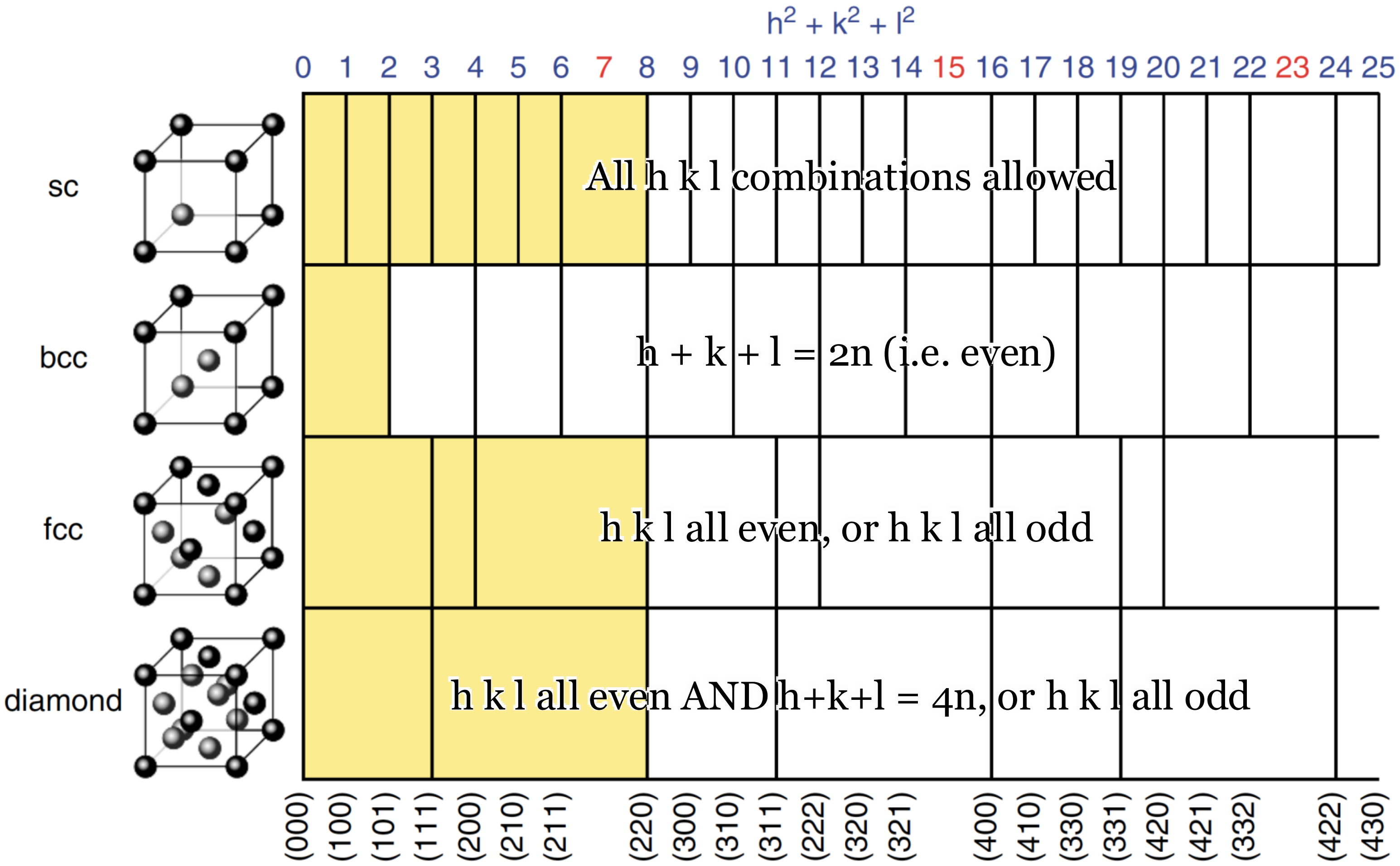
$$= f\left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{l+h}{2})]}\right]$$

$$= f[1+e^{i\pi(h+k)}+e^{i\pi(k+l)}+e^{i\pi(l+h)}]$$

remember that $e^{i\pi n}$ = 1 when n is an even integ
= -1 when n is an odd integer

General rule for fcc crystals: only Bragg peak intensity if : h,k,l all odd, or h,k,l all even

Interaction with a unit cell: systematic absences



All h k l combinations allowed

h + k + l = 2n (i.e. even)

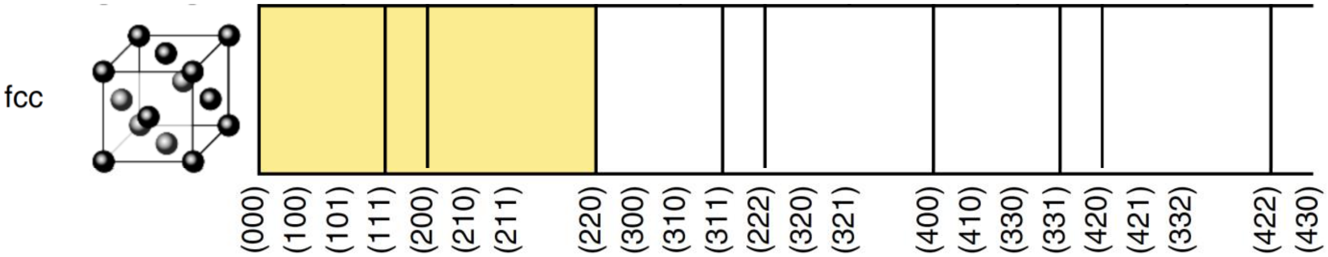
h k l all even, or h k l all odd

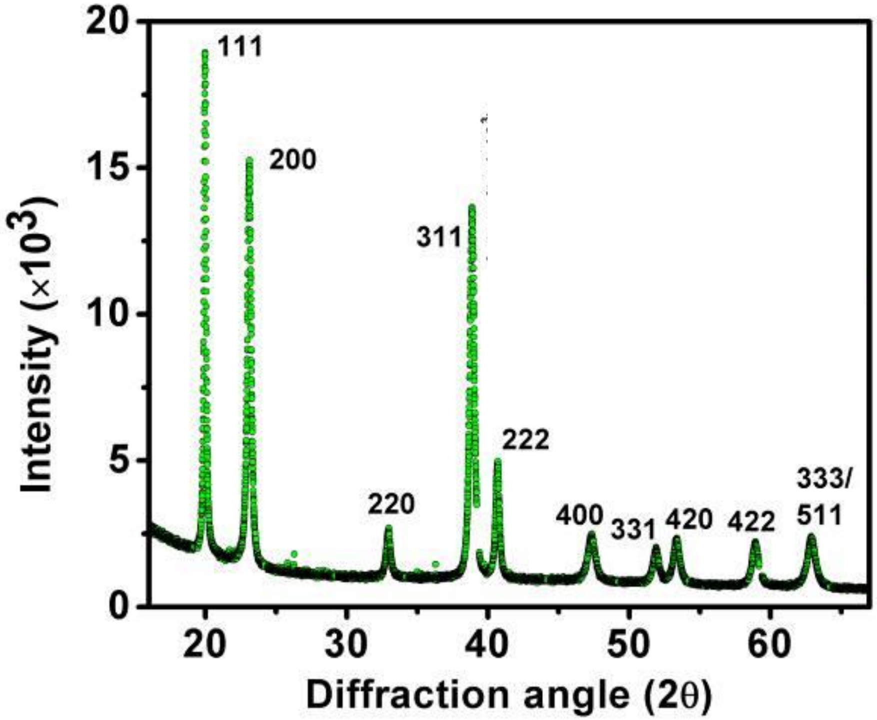
h k l all even AND h+k+l = 4n, or h k l all odd

Interaction with a unit cell

- Example: nanocrystalline Ni

Why is there no (001) reflection?





diffraction pattern gives “fingerprint” of the diffracting substance, peak position and height is used for phase identification

Summary

- Bragg law defined geometrically in direct lattice, Laue condition connects to the reciprocal lattice
- Diffraction as Fourier transform of a crystal = lattice & motif!
- Structure of the motif can be solved if the phase problem can be overcome
- Interaction of X-rays with electrons → polarization factor
- Interactions of X-rays with atoms → atomic form factor, FT of the electron density
- Interaction of X-rays with a unit cell of a crystal → structure factor
- Diffraction pattern
  - →position according to reciprocal lattice (Bragg, Laue)
  - →intensity depends on the motif, vector sum of atomic form factors, can lead to systematic absences due to destructive interference