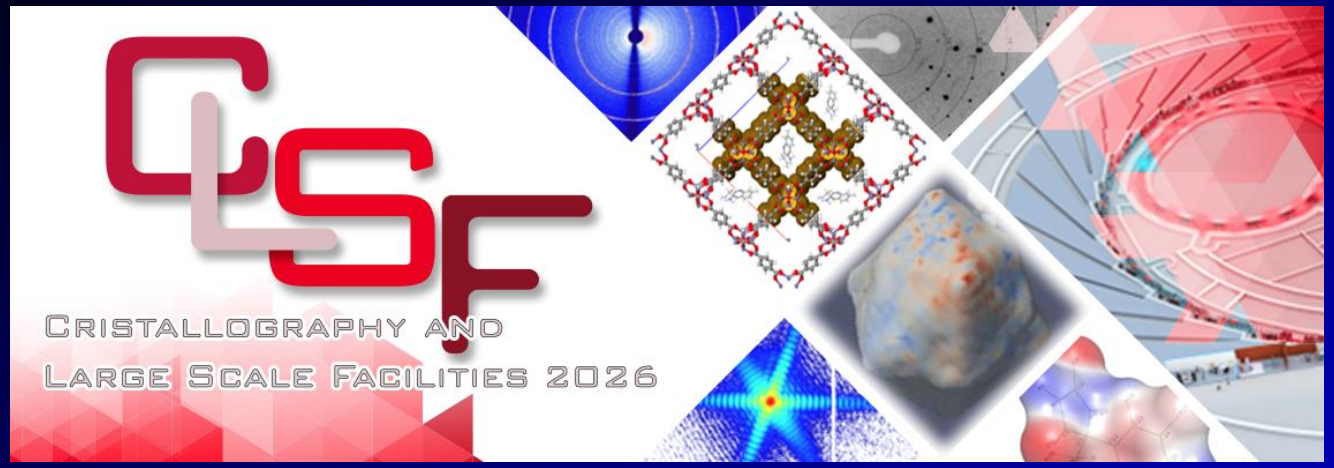


Scattering and Diffraction

A. Interaction of Radiation with Matter
   1. Wave and particles
   2. Absorption and Scattering
   3. Thomson scattering
B. Scattering by an atom
   1. Interferences
   2. Scattering Factor
   3. Resonant scattering
C. Diffraction
   1. Pair Distribution Function
   2. Scattering amplitude
   3. Periodic Crystals ; diffraction
   4. Disorder

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A- Interaction of Radiation with Matter

A-1 Wave and Particles

Caracteristics of particles

Particle	X photons	Neutrons	Electrons
Description	Electromagnetic Field $E = E_0 \exp(i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t))$	Particule $\psi \sim \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$	Particle $\psi \sim \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$
Energy E	$E = h\nu = hc/\lambda$ λ(Å)=12398/E(keV) λ=1 Å, E=12.4 keV (ν=10^{18} Hz)	$E=p^2/2m_n$ λ(Å)=0.286/$E^{0.5}$(eV) λ=1 Å, E=81.8 meV .	$E=p^2/2m_e$ λ(Å)=12.265/$E^{0.5}$(eV) λ=1 Å, E=150 eV (λ=0.04 Å, E=100 keV)
Momentum p	$p = \hbar k\ (= \frac{h\nu}{c})$	$p = \hbar k\ (= mv)$	$p = hk\ (= mv)$
$\frac{k_B T}{E}$ 300K	$3.10^{-6} << 1$	~ 1	~ 10^{-5}
Interaction	Charge $\sigma_{th} \sim Z^2$ barn Magnetic Moment $\sigma_d \sim 10^{-6}$ barn	Nuclei (strong) $\sigma_d \sim 5$ barn Magnetic moment $\sigma_d \sim 3$ barn	Electrostatic potential $\sigma_d \sim 10^8$ barn
Absorption	4700 barn (Z=28, 1.5 Å)	Typical : 0.1-1 barn	-

X Rays

Wave lengths

λ = 0,1 Å to 3 Å

Photon energy

$E = \hbar\omega$ = 120 keV to 4 keV

Typically : 4 keV (3.1 Å) to 30 keV (0.41 Å)

And remember: 1 Å=10^{-10} m, 1 eV = 1.6 10^{-19} J,

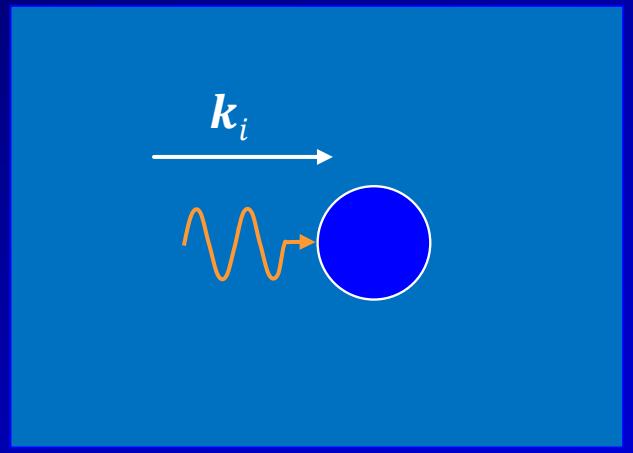
E[keV] = 12.398/λ[Å]

A-2 Absorption and scattering

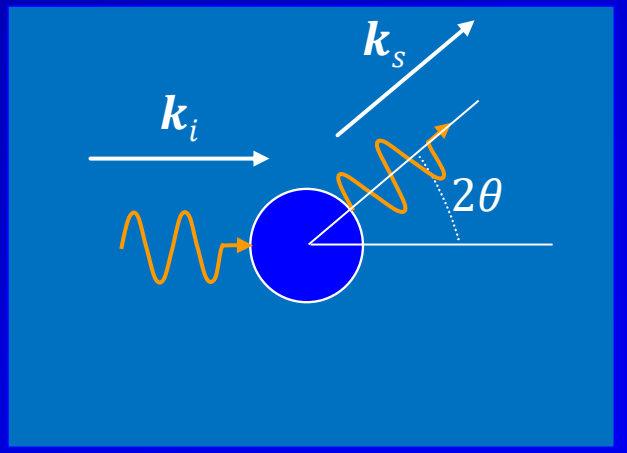
Interaction of Radiation with Matter

« Element of modern x-ray physics »
J. Als-Nielsen et D. McMorrow

Two process of interaction
Absorption and scattering



The particle/wave **disappears**
(conservation E and p…)



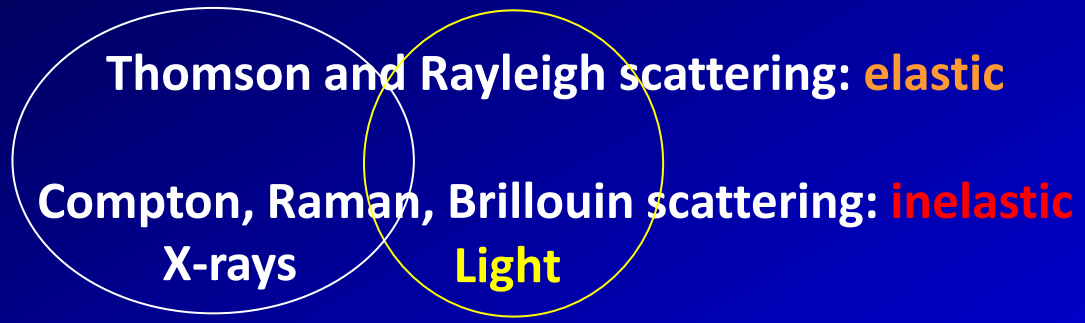
The particle/wave
changes its
direction of propagation
(interference, diffraction)

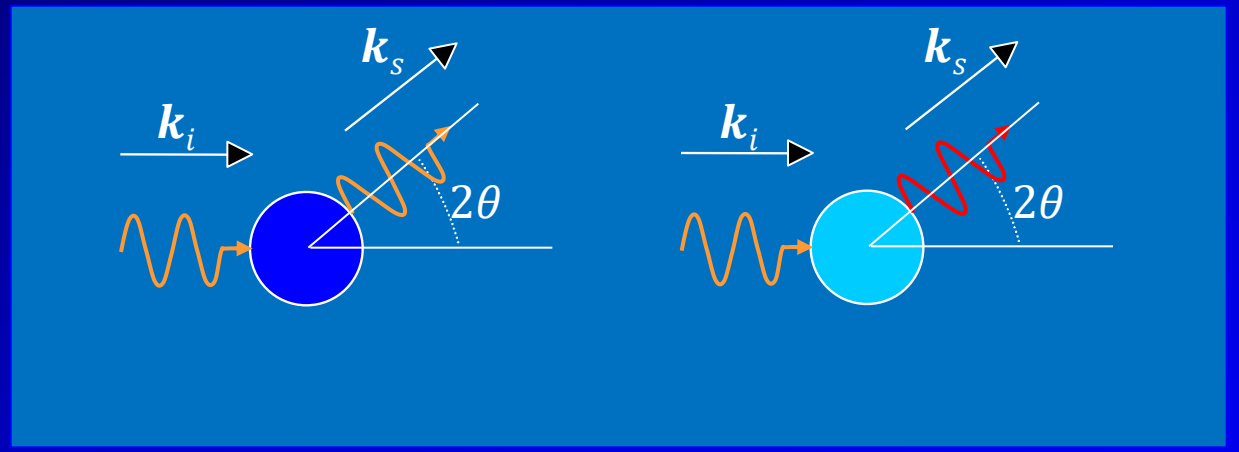
2θ: scattering angle
(k_i, k_s) define
the scattering plane

Elastic and Inelastic Scattering

Elastic scattering :
Does not change nature or state of the particle and the target

Quantum Mechanics II, p. 894
C. Cohen-Tannoudji,
B. Diu, Frank Laloë





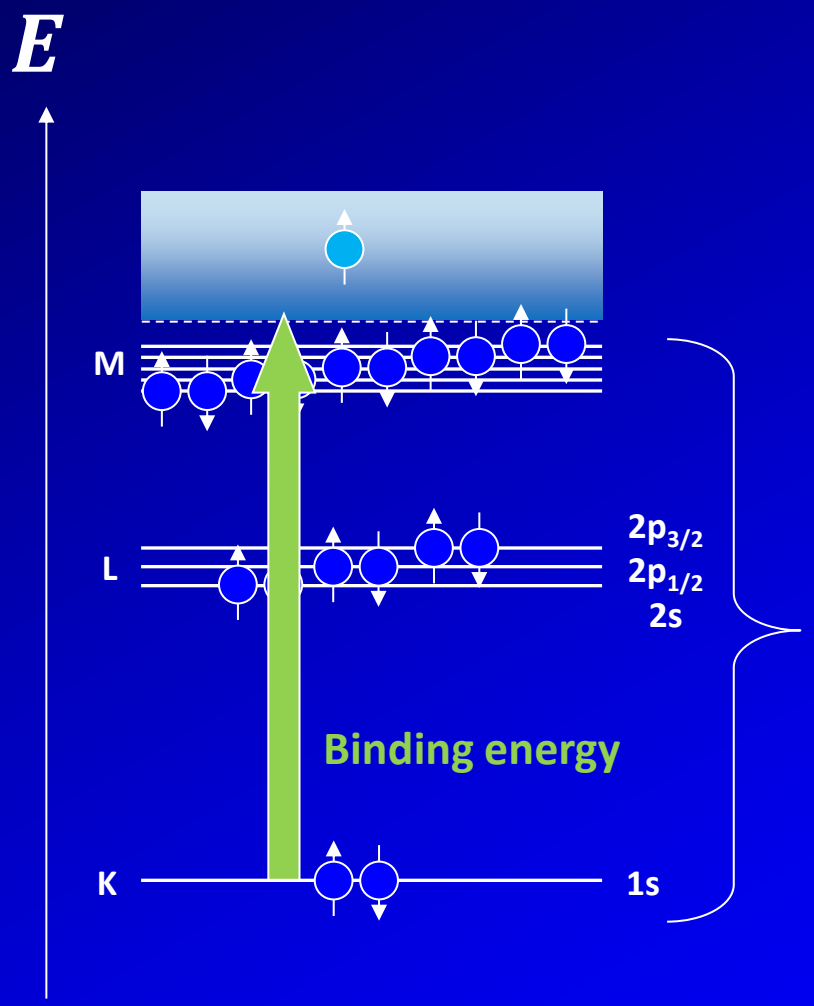
Target does not change state
$k_i = k_s$

Target does change state.
$k_i \neq k_s$

Electrons in Atoms

Vacuum
(continuum)
Free electrons

Core level
(discrete)
Bound electrons

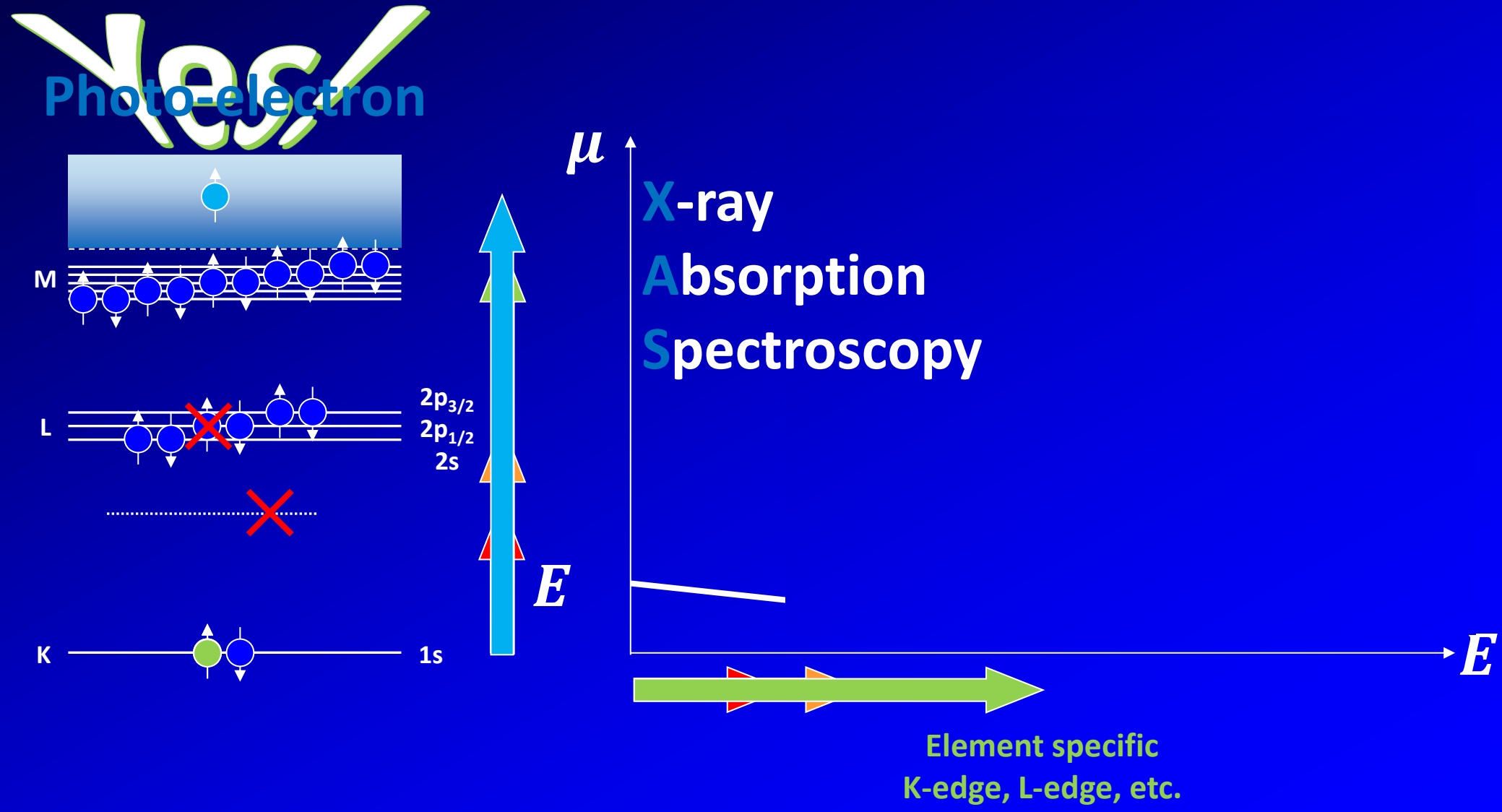


Examples of binding energies:

E_K(Ag) = 25 keV
E_K(Fe) = 7 keV
E_K(Ar) = 3.2 keV

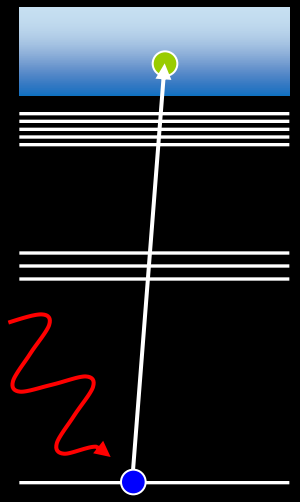
$E_{L_{I,II,III}}$(Au) = 14.3 ; 13.7 ; 11.5 keV

Absorption: increase of coefficient μ

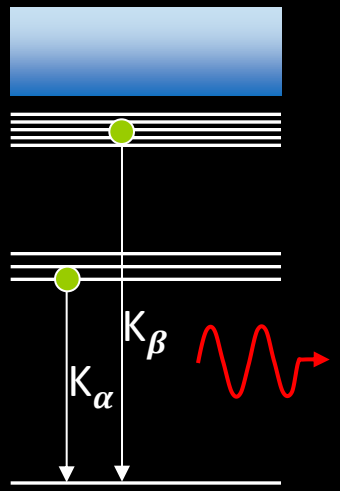


Absorption

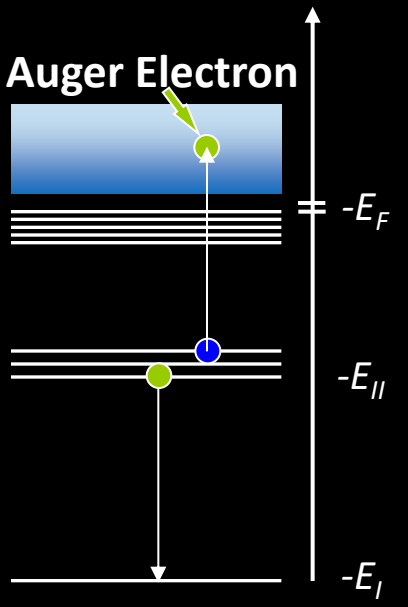
Photoelectric Effect



Fluorescence

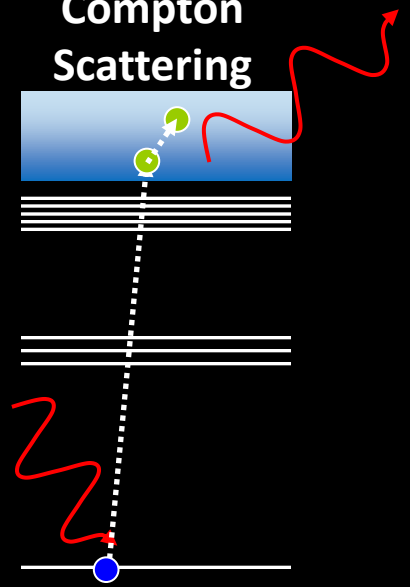


Auger Electron

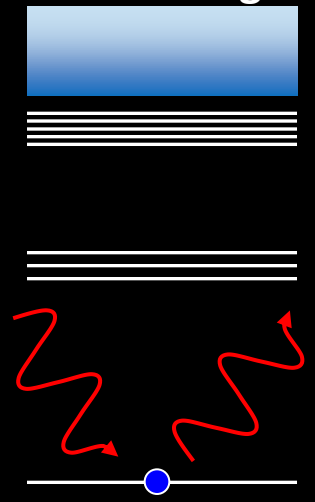


Scattering

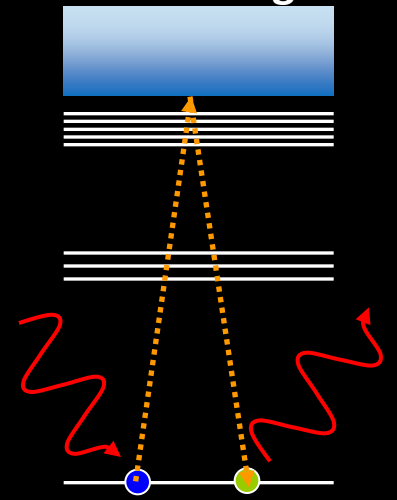
Compton Scattering



Thomson Scattering



Resonant Scattering



Cross sections

Scattering differential cross section

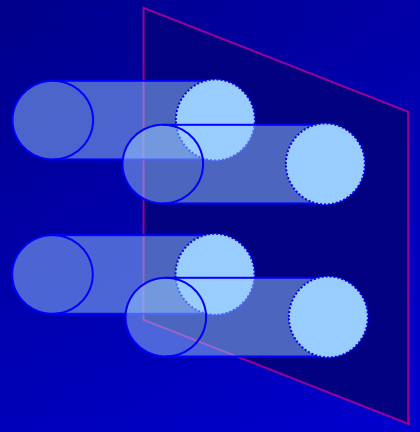
$$dN_s = \phi\, \Delta\Omega \frac{d\sigma}{d\Omega}$$

Incident Flux:
(Particle/s/cm²)

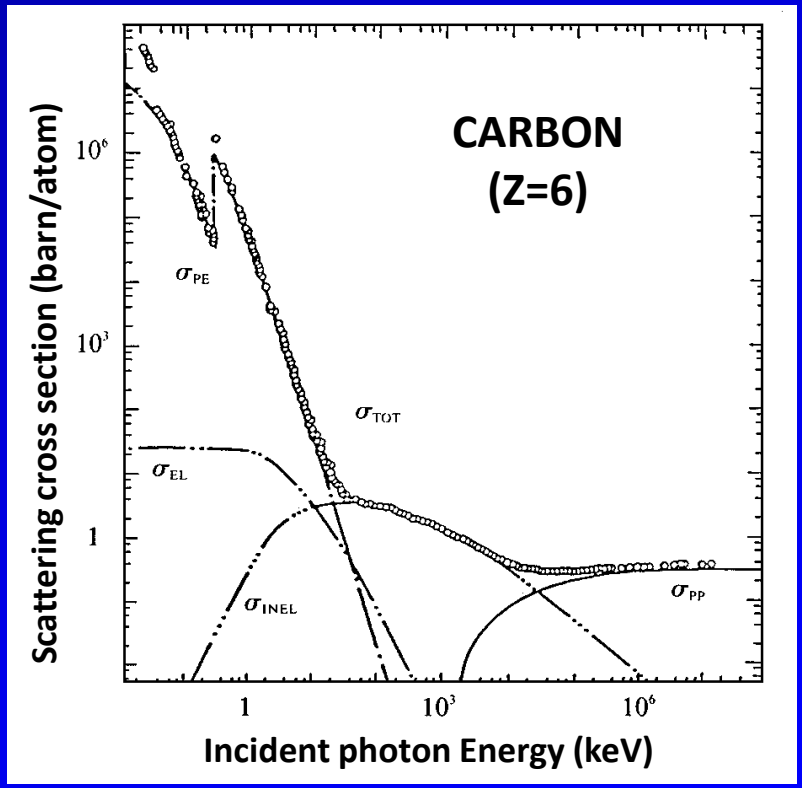
Absorption cross section

$$dN_a = \phi\, N(dz)\sigma_a$$

Measurable quantities

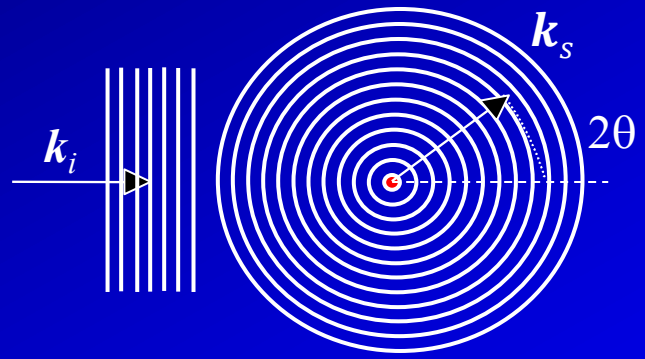


Unit: the barn (10^{-28} m²)



Scattering cross section

- **Scattering process**



$$dN_s = \phi \Delta\Omega \frac{d\sigma}{d\Omega}$$

Differential scattering cross section

- **Wave function of the scattered particle**

$$\psi_s = -\frac{b(\theta)}{r} e^{ik_s r}$$

$b(\theta)$: **scattering length**
Complex number: phase shift
Convention: $b > 0$ (out of phase)

- **Scattering**

$$\left(\frac{d\sigma}{d\Omega}\right)_{sca} = \frac{k_s}{k_i}|b|^2$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = |b|^2$$

A-3 Thomson Scattering

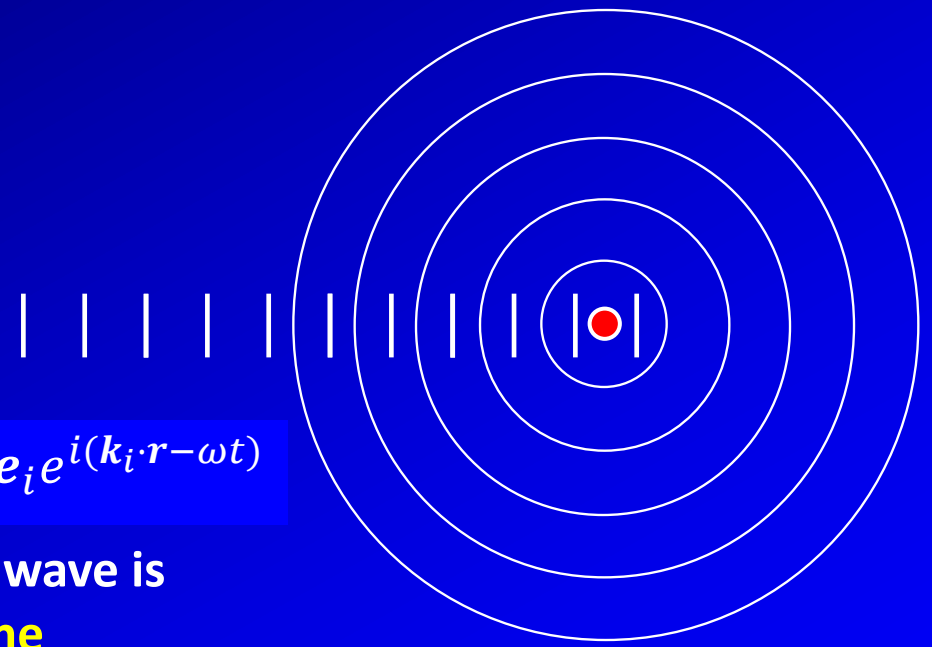
Thomson Scattering

Incident and scattered photons

$$\hbar\omega_i = \hbar\omega_f$$
$$k_i = k_s = \frac{2\pi}{\lambda}$$

Scattered wave is spherical

$$\boldsymbol{E}_s(r,t) = -E_0 \boldsymbol{e}_s \frac{b}{r} e^{i(k_s r - \omega t)}$$



$$\boldsymbol{E}_i(r,t) = E_0 \boldsymbol{e}_i e^{i(\boldsymbol{k}_i \cdot \boldsymbol{r} - \omega t)}$$

Incident wave is plane

Oscillating charge

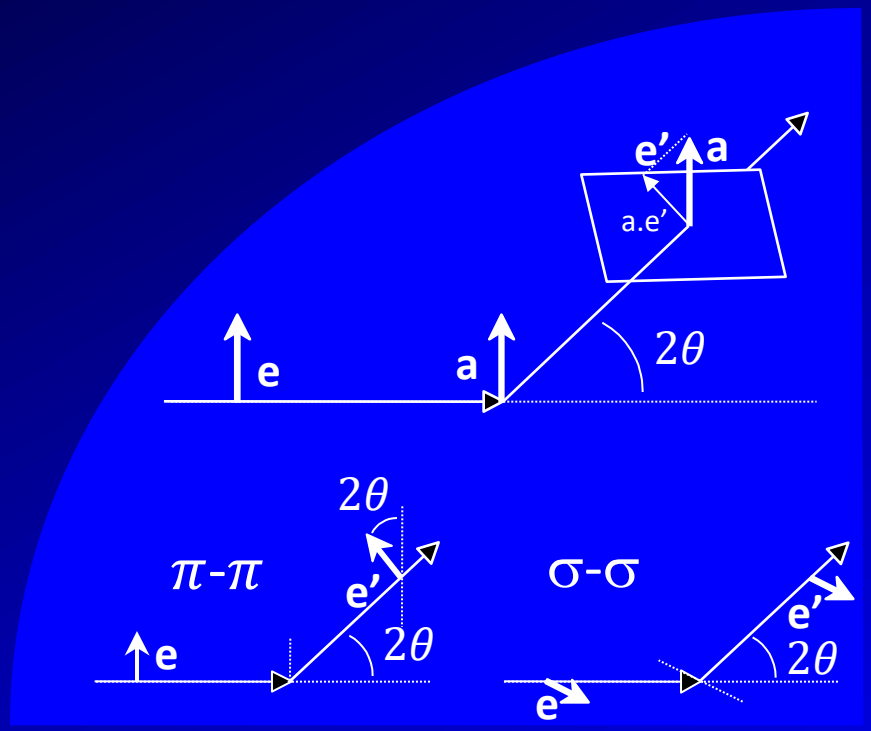


Radiation2D (field lines)

https://groups.oist.jp/qwmu/software

Thomson scattering

- Classical (intuitive but incorrect…) approach which does not explain Compton effect



Thomson Scattering length

- Incident plane wave

$$\boldsymbol{E}_i(r,t) = E_0 \boldsymbol{e} e^{i(\boldsymbol{k}_i \cdot \boldsymbol{r} - \omega t)}$$

- Electron experience a force:

$$\boldsymbol{F} = m\boldsymbol{a} = -e\boldsymbol{E}(0)$$

- This oscillating charge creates a field:

$$\boldsymbol{E}_s(\boldsymbol{r}) = \frac{\boldsymbol{e}}{4\pi\varepsilon_0 c^2 r}(\boldsymbol{a}(t - r/c) \cdot \boldsymbol{e}')\boldsymbol{e}'$$

$$\boldsymbol{E}_s(\boldsymbol{r}) = -\frac{b_{th}}{r} E_0 \boldsymbol{e}' e^{i(k_s r - \omega t)}$$

- The Thomson scattering length is:

$$b_{th} = \frac{e^2}{4\pi\varepsilon_0 mc^2}(\boldsymbol{e} \cdot \boldsymbol{e}')$$

Thomson scattering cross section

$$b_{th} = r_e\,(\boldsymbol{e}\cdot\boldsymbol{e}')$$

Characteristics

- **Classical electron radius**

$$r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.818\ 10^{-15}\ m$$

- **If the radiation is polarized (synchroton) :**

$$\sigma-\sigma:\ \left.\frac{d\sigma}{d\Omega}\right)_{dif} = r_e^2$$

$$\pi-\pi:\ \left.\frac{d\sigma}{d\Omega}\right)_{dif} = r_e^2\cos^2 2\theta$$

- **If the radiation is not polarized (lab)**

$$\left.\frac{d\sigma}{d\Omega}\right)_{dif} = r_e^2\,\frac{1+\cos^2 2\theta}{2}$$

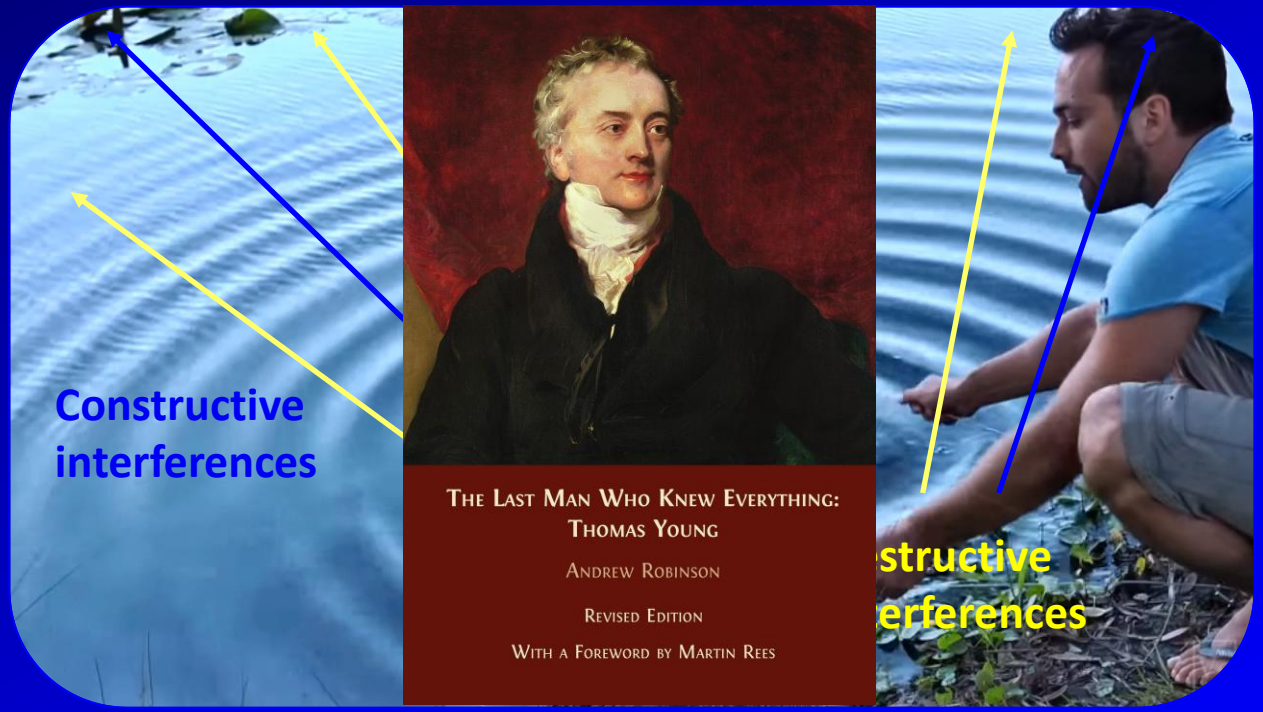
- **For a free electron:** $\sigma = 4\pi r_e^2 \sim 1\ barn$

B- Scattering by an atom

B-1 Interferences

1801: Thomas Young discovers the principle of interferences

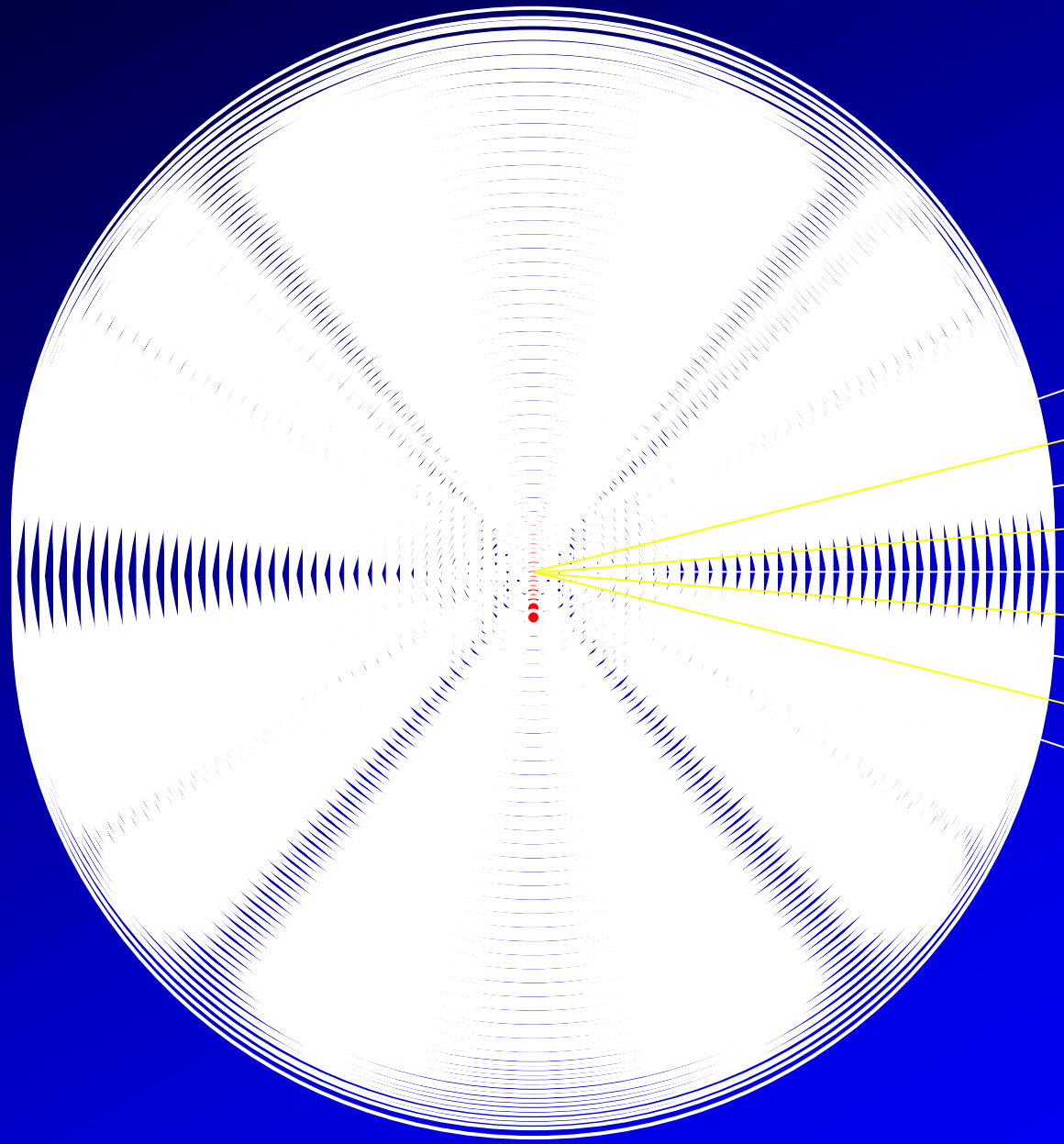
In 1802, he demonstrated interferences effects thanks to a ripple tank

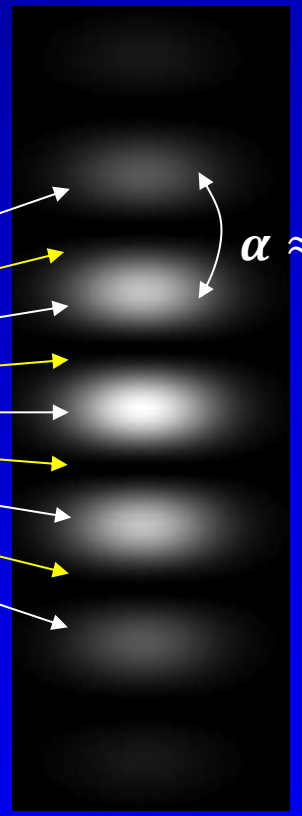


©Veritasium: https://www.youtube.com/watch?v=Iuv6hY6zsd0

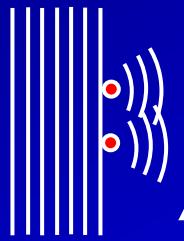
Idea
For waves, the principle of superposition brings a qualitatively different phenomena:
The interference fringes

Interferences





$$\alpha \approx \frac{\lambda}{a}$$



$$\frac{a^2}{4\lambda}$$

Fresnel (near-field)

Fraunhofer (far-field)

1. Diffraction iff: $\lambda < a$
2. Two regimes of diffraction
3. Real space and space of diffraction are ''reciprocal''

Definitions

$$\boldsymbol{a}(\boldsymbol{r}, t) = \boldsymbol{A_0}\, cos(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \varphi)$$

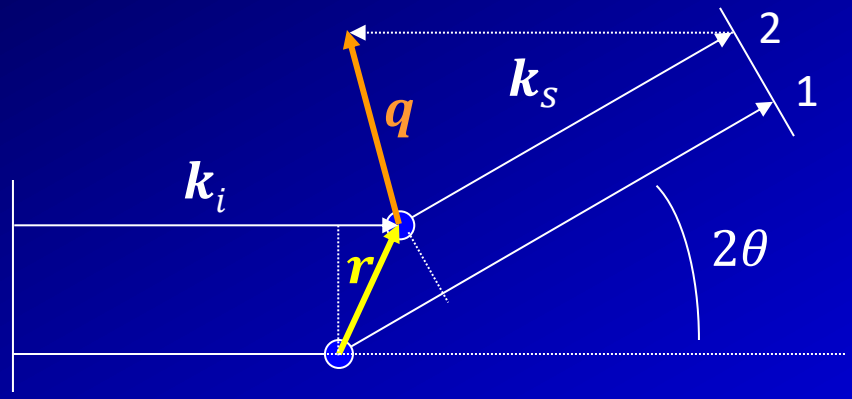
$\boldsymbol{k}$**: wave vector (**$k = 2\pi/\lambda$**)**

ω**: angular frequency or speed** ($\omega = 2\pi\nu = 2\pi/T$) **(rad/s)**

$\boldsymbol{k} \cdot \boldsymbol{r} - \omega t + \varphi$**: phase**

Phase difference in far-field

FF: Scattered beams are parallel



Phase difference between paths 2 and 1:

$$\Delta\phi = \boldsymbol{k}_i \cdot \boldsymbol{r} - \boldsymbol{k}_s \cdot \boldsymbol{r} \qquad \Delta\phi = -\boldsymbol{q} \cdot \boldsymbol{r}$$

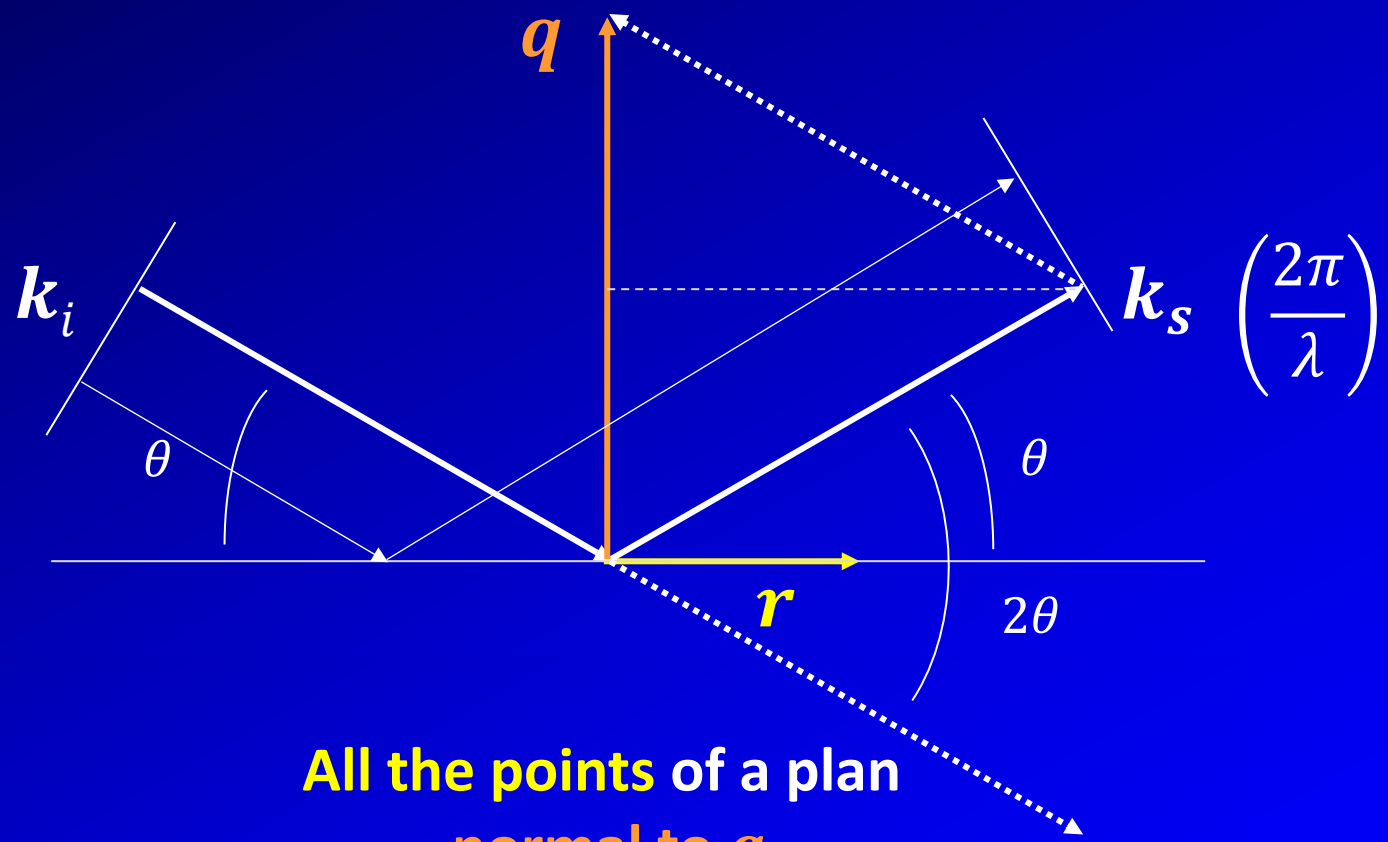
Only depends on the:

Scattering vector

$$\boldsymbol{q} = \boldsymbol{k}_s - \boldsymbol{k}_i$$

Scattering vector

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



All the points of a plan
normal to q
scatter in phase

Expression of the scattered wave

$$a(r,t) = A_1\, cos(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t - \boldsymbol{q} \cdot \boldsymbol{r}_1) + A_2\, cos(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t - \boldsymbol{q} \cdot \boldsymbol{r}_2) + \cdots$$

In practice, the complex exponential notation is used

$$a(\boldsymbol{r},t) = Re\left(A_1 e^{i(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t - q \cdot r_1)} + A_2 e^{i(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t - \boldsymbol{q} \cdot \boldsymbol{r}_2)} + \cdots\right)$$

$$a(\boldsymbol{r},t) = Re\left(e^{i(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t)} \underbrace{\left(A_1 e^{-i\boldsymbol{q} \cdot \boldsymbol{r}_1} + A_2 e^{-i\boldsymbol{q} \cdot \boldsymbol{r}_2} + \cdots\right)}_{a = |a| e^{i\varphi}}\right)$$

a is the complex amplitude

$$a(\boldsymbol{r},t) = |a|\, cos(\boldsymbol{k}_s \cdot \boldsymbol{r} - \omega t + \varphi)$$

The complex amplitude

$$a = A_1 e^{-iq\cdot r_1} + A_2 e^{-iq\cdot r_2} + \cdots$$

The square of the modulus gives the intensity

$$I = |a|^2$$

Its phase is the phase of the scattered wave
with respect to the origin
and it is lost!

With these notations, diffraction calculations consist in
calculating Fourier series (discret case)

$$a = \sum_i \ldots e^{-iq\cdot r_i}$$

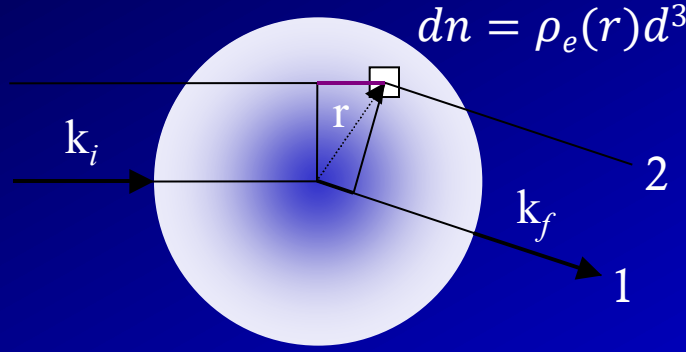
or Fourier transform (continuous case)

$$\boldsymbol{a} = \int \ldots e^{-iq\cdot r}\, d^3\boldsymbol{r}$$

B-2 Atomic scattering factor

Atomic scattering factor

- **Scattering by a distribution of charge**



Scattered wave is the sum of the waves scattered by the electrons in volume $d^3\boldsymbol{r}$

$$\boldsymbol{b} = \boldsymbol{b_{th}} \qquad \rho_e(\mathbf{r})d^3\mathbf{r}$$

$$\Delta\varphi = -\mathbf{q}\cdot\mathbf{r}$$

- **Atomic scattering factor**

$$f(\mathbf{q}) = \int \rho_e(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{r}$$

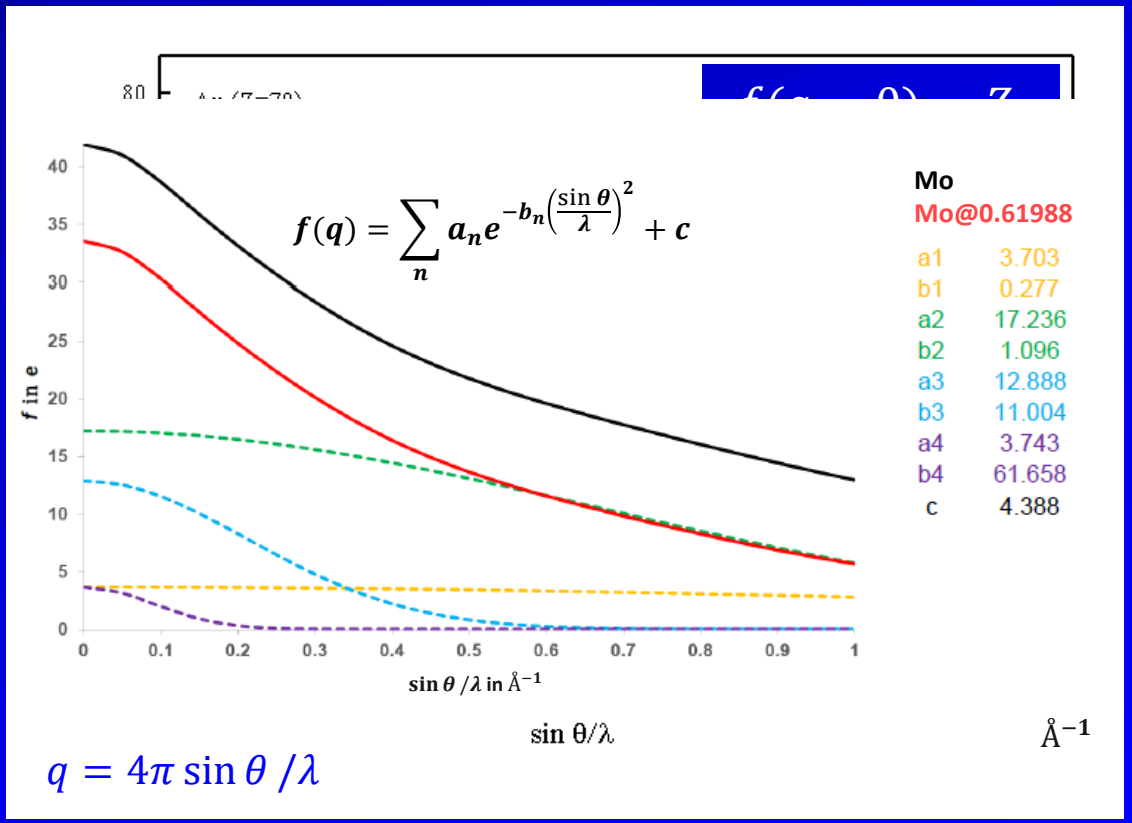
$\rho_e(r)$ is the electron density of the atom
q scattering vector

Atomic scattering factor

$$f(\mathbf{q}) = \int \rho_e(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}$$

$f(\mathbf{q})$: Fourier transform of $\rho_e(r)$

$f(\mathbf{q})$:
International tables of crystallography
[SHELXL]



$q = 4\pi \sin\theta\ /\lambda$

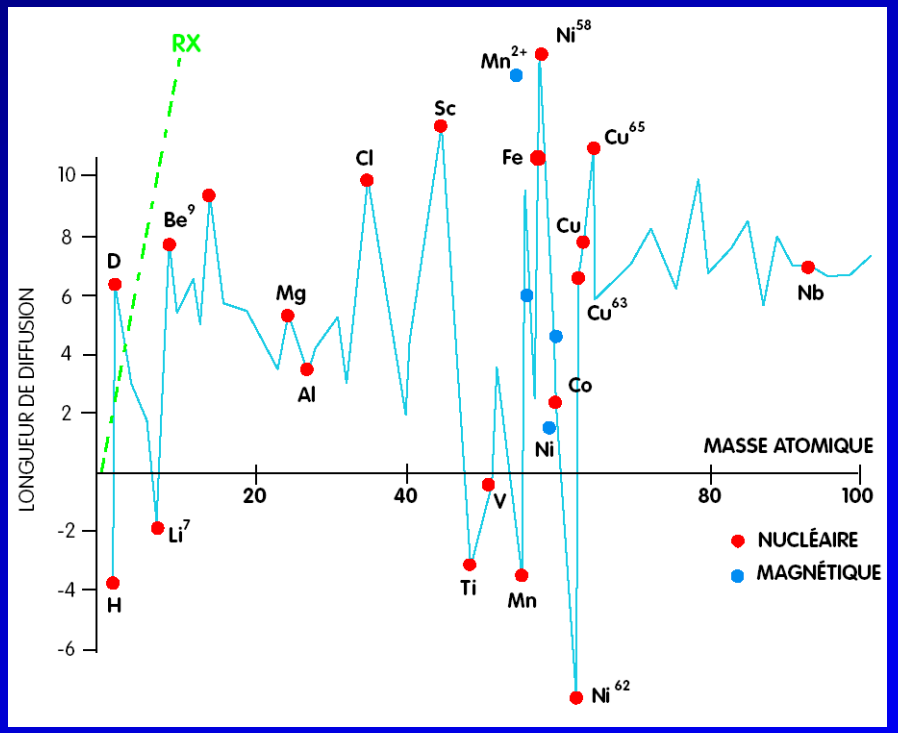
Neutron scattering length

$$b = \left(\frac{2\pi\hbar^2}{M}\right)\int v(r)e^{-iq\cdot r}d^3r$$

Fermi pseudo potential
Short range (fm).

$$b \sim 5\ fm \Rightarrow$$
$$\sigma = 4\pi b^2 \sim \textbf{3 barn}$$

$$\sigma_X = Z^2 \textbf{ barn}$$



- b does not depend on q
- b is large for light elements
- b depends on the isotope
- b can be negative

Limits of the classical theory (RX)

$f(\mathbf{q})$ (Thomson) depends on the:

i) Electron density
ii) Scattering vector

and not (directly) on energy...

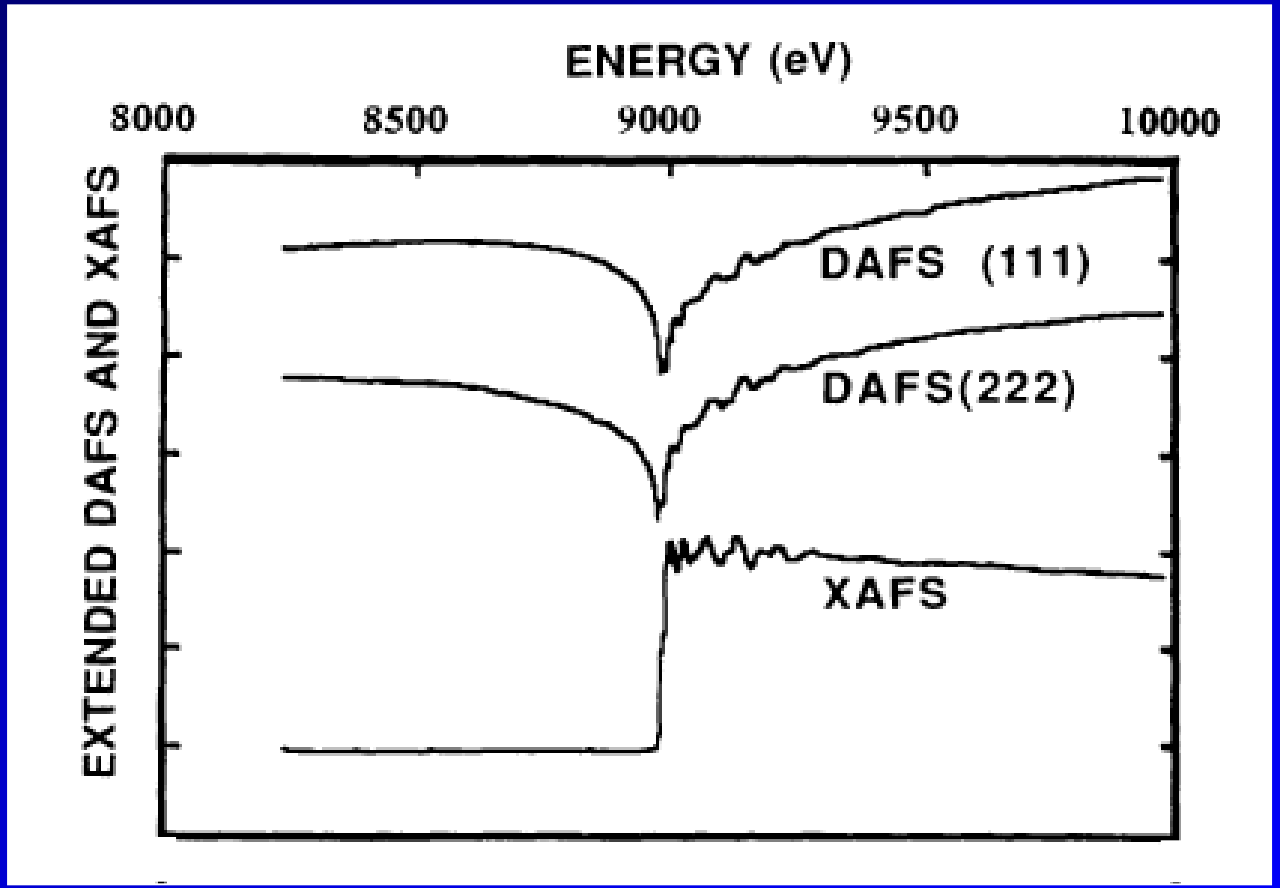
But!...

DAFS: Diffraction Anomalous Fine Structure

Intensity of Bragg reflections (111) and (222) of Cu (25 mm x 200 nm) for energies close to the K-Edge of Cu.

$$2d_{111}\sin\theta = \lambda$$

$$q = 4\pi\frac{\sin\theta}{\lambda} = \frac{2\pi}{d_{111}}$$



H. Stragier *et al.*, PRL69, 3064 (1992)

B-3 Resonant Scattering

Resonant scattering factor

(anomalous)

$$f'(\mathbf{q},\omega) = f_0(\mathbf{q}) + f'(\mathbf{q},\omega) + if''(\mathbf{q},\omega)$$

$f'(\mathbf{q},\omega)$ **associated to dispersion (n index)**



$f''(\mathbf{q},\omega)$ **associated to absorption (optical theorem)**



Both are related by the Kramers-Kronig relations





Resonant scattering

Classical model: damped oscillator

Restoring force $m\omega_0^2 r$, friction $-Kv$

More important with Synchrotron radiation

$$\boldsymbol{F} = m\boldsymbol{a} = -e\boldsymbol{E}(0) - K\mathbf{v} - m\omega_0^2\boldsymbol{r}$$

With $\boldsymbol{r} = \boldsymbol{r_0}e^{-i\omega t}$

$$\boldsymbol{a} = -\omega^2\boldsymbol{r_0}e^{-i\omega t} = \frac{\boldsymbol{e}\omega^2\boldsymbol{E}_0 e^{-i\omega t}}{m(\omega_0^2 - \omega^2) - i\omega K}$$

The scaterred field writes

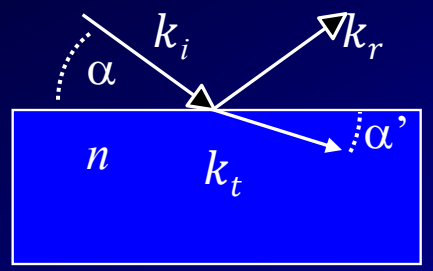
$$\boldsymbol{E}_d(\boldsymbol{r}) = \frac{\boldsymbol{e}}{4\pi\varepsilon_0 c^2 r}(a(t - r/c)\cdot\boldsymbol{e}')\boldsymbol{e}'$$

$$\boldsymbol{E}_d(\boldsymbol{r}) = -\frac{\boldsymbol{b_{an}}}{r}E_0\boldsymbol{e}'e^{i(k_d r - \omega t)}$$

Scattering length is modified : real part and imaginary part

$$b_{an} = b_{th}\left(\frac{\omega^2}{\omega^2 - \omega_0^2 + i\omega K/m}\right)$$

Refraction index



It can be shown that:

$$n(\omega) = 1 - \frac{2\pi\rho_s r_0 f(\boldsymbol{q} = 0, \omega)}{k^2}$$

$$n = n_r + i\beta = 1 - \delta + i\beta$$

$$e^{inkz} = e^{in_r kz} e^{-\beta kz} \qquad \beta k = \mu/2$$



$$n_r = 1 - \frac{2\pi\rho_s r_0}{k^2}(f_0 + f'(\omega))$$

Refraction : $\boldsymbol{\delta = 10^{-5}}$



$$\beta = -\frac{2\pi\rho_s r_0}{k^2} f''(\omega)$$

Absorption :

$$f''(\omega) = \frac{\mu(\omega)k}{4\pi\rho_s r_0}$$

Kramers-Kronig relation (1926)

Causality principle gives a relation between f' et f''

$$f'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' f''(\omega')}{(\omega'^2 - \omega^2)} d\omega'$$

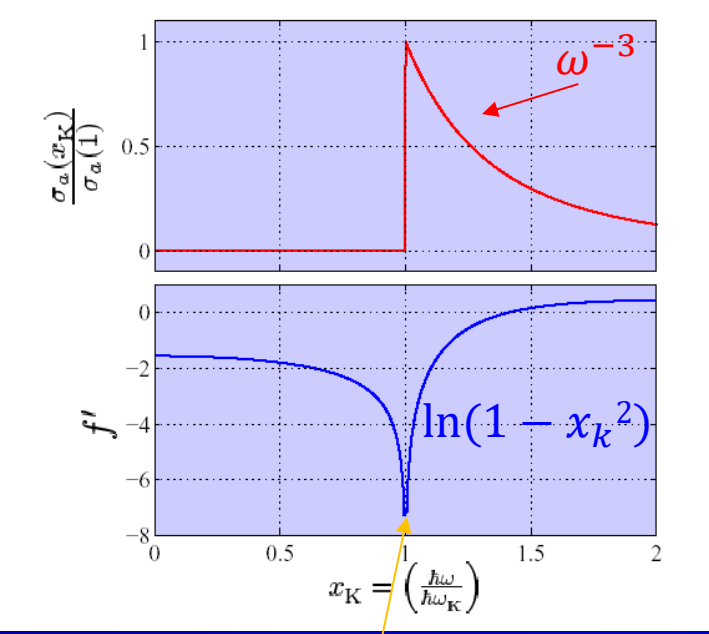
$$f''(\omega) = \frac{2\omega}{\pi} P \int_0^\infty \frac{f'(\omega')}{(\omega^2 - \omega'^2)} d\omega'$$

Once you have measured one, you can calculate the other one.

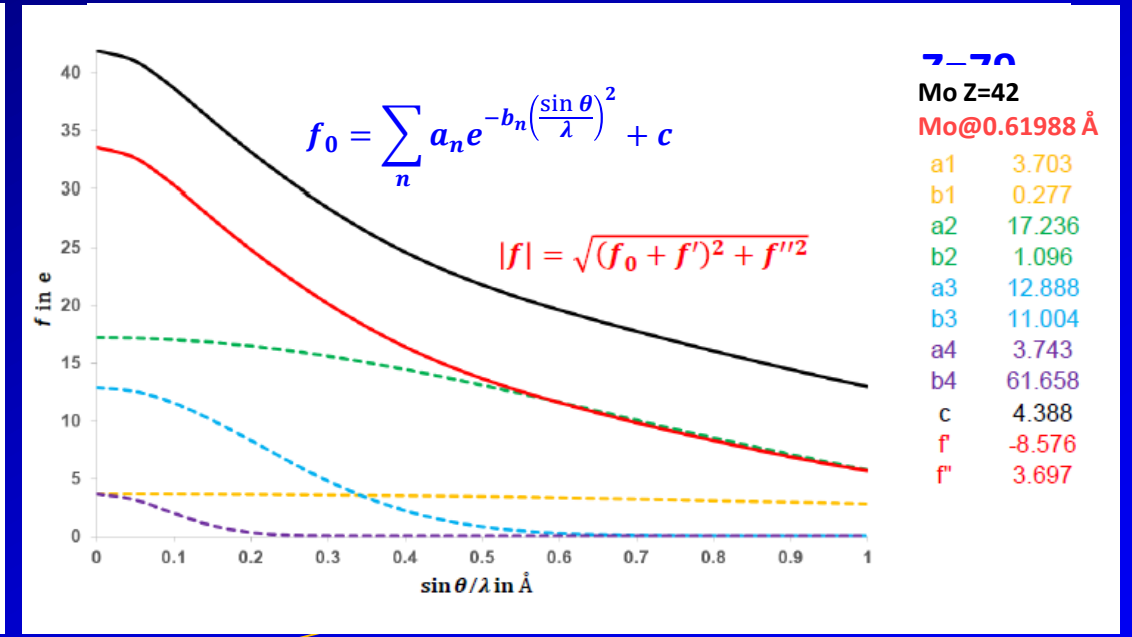
P is the Cauchy principal value $\lim_{\varepsilon \to 0} \int_{\omega-\varepsilon}^{\omega+\varepsilon} \dots$

Kramers-Kronig relation

Theoretical calculation with 2 K electrons



KK from absorption



Corrections can be very important close to an edge (see the example of Au L-edges)

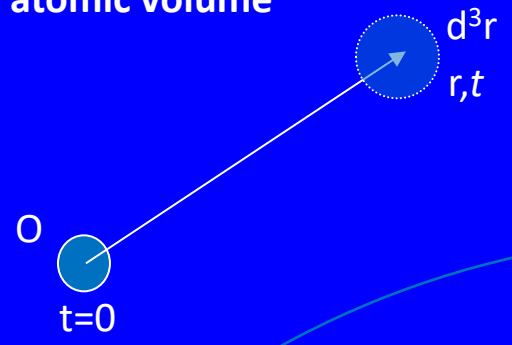
It is necessary to take them into account for structure refinements
Can be used to enhance contrast between elements

C- Scattering by an arbitrary structure

C-1 Pair Correlation Function

Pair Correlation Function

$v_a = V/N$
Average
atomic volume



Time dependent pair correlation function

$$\langle dn(\boldsymbol{r},t)\rangle = G(\boldsymbol{r},t)d^3\boldsymbol{r}$$

Spatial, statistical, temporal average

$G(r,t)$: Space and time Fourier Transform can be obtained by neutron scattering

Pair Distribution Function $g(r)$ (PDF)

$$G(\boldsymbol{r},t=0) = G(\boldsymbol{r})$$

$$\langle dn(\boldsymbol{r},t=0)\rangle = G(\boldsymbol{r})d^3\boldsymbol{r} = \delta(\boldsymbol{r})d^3\boldsymbol{r} + \frac{g(\boldsymbol{r})}{v_a}d^3\boldsymbol{r}$$

FT of $g(r)$ can be obtained by X-ray diffraction

Density-density correlation function:

$$G(\boldsymbol{r}) = \frac{1}{N}\left\langle \int \rho(\boldsymbol{u})\rho(\boldsymbol{u}+\boldsymbol{r})d^3\boldsymbol{u}\right\rangle = \frac{1}{N}\langle \rho(\boldsymbol{r}) * \rho(-\boldsymbol{r})\rangle$$

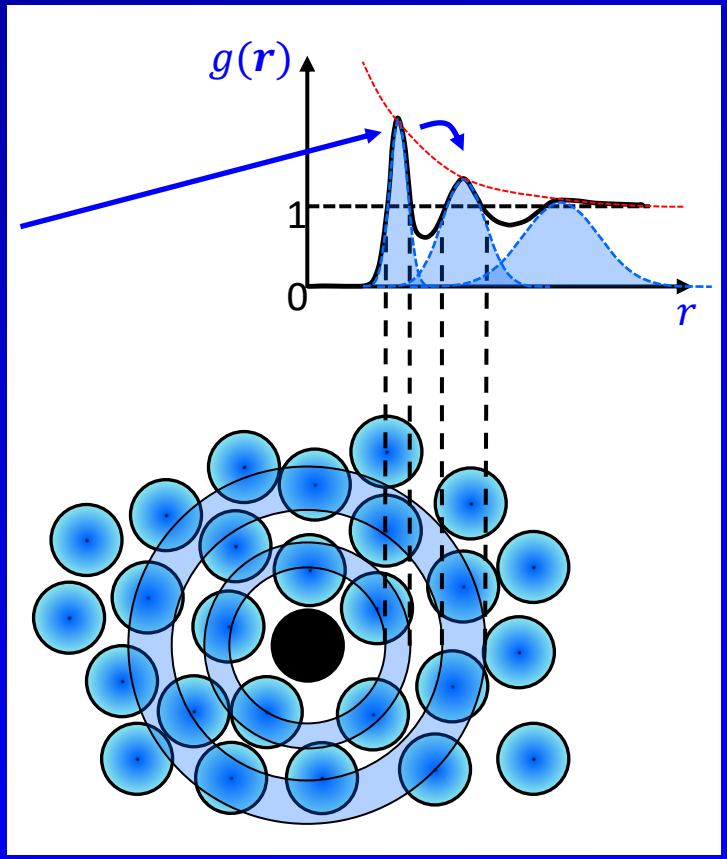
Pair distribution function

$$dn(\boldsymbol{r}) = \delta(r)d^3\boldsymbol{r} + g(\boldsymbol{r})\rho_a d^3\boldsymbol{r}$$

Peaks:
First neighbour
Second neighbour
etc.

Peak width:
Distance fluctuation

Peak integral:
Number of neighbours



Three types of order

$$dn(\boldsymbol{r}) = \delta(r)d^3\boldsymbol{r} + g(\boldsymbol{r})\rho_{\boldsymbol{a}}d^3\boldsymbol{r}$$

- **Large distance behaviour of $g(r)$ defines three types of order:**

Short-Range Order (SRO)

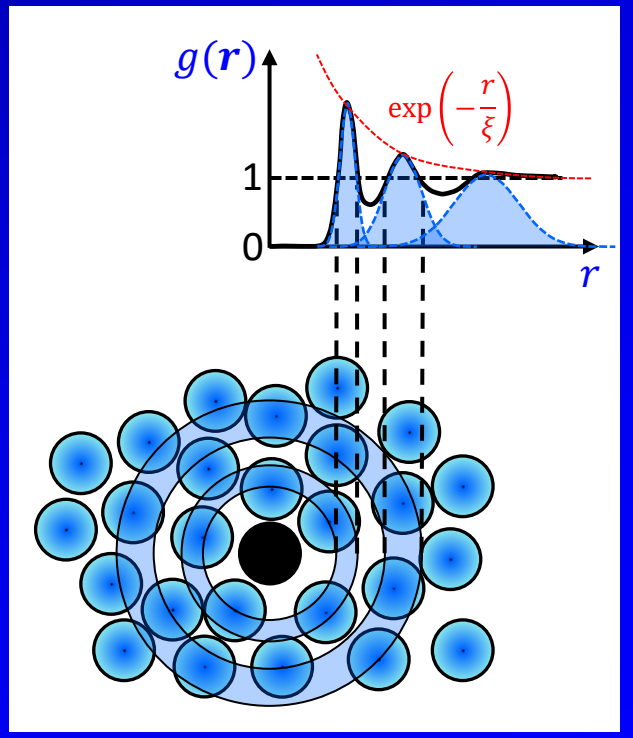
- $g(r) \sim exp\left(-\frac{r}{\xi}\right)$
- ξ : correlation length
- Ex: glass, liquids
- Maximum order in 1D

Quasi Long-Range Order (QLRO)

- $g(\boldsymbol{r}) \sim |\boldsymbol{r}|^{-\eta}$
- No length scale
- Ex: Smectics, 2D crystals
- Maximum order in 2D

Long-Range Order (LRO)

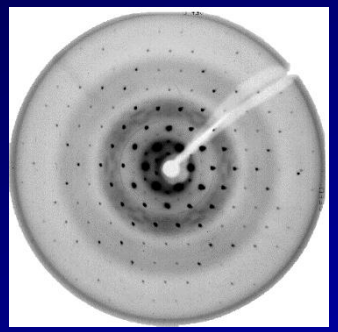
- $g(r)$ has no limit
- Ex: Crystals
- Bragg peaks



Experimental evidence of order

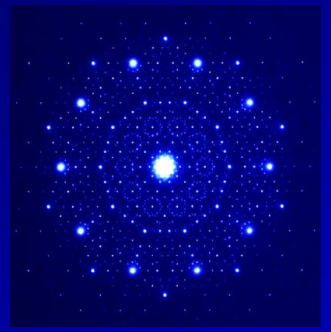
Long-range Order: diffraction

X-rays



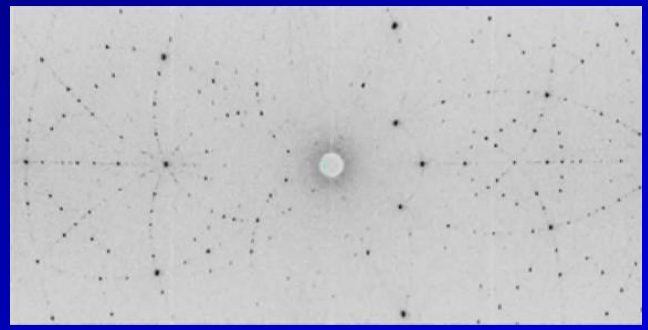
C_{60} crystal

Electrons



Quasi-crystal

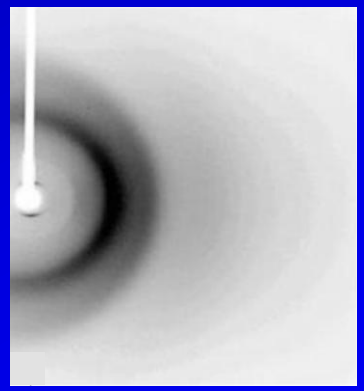
Neutrons



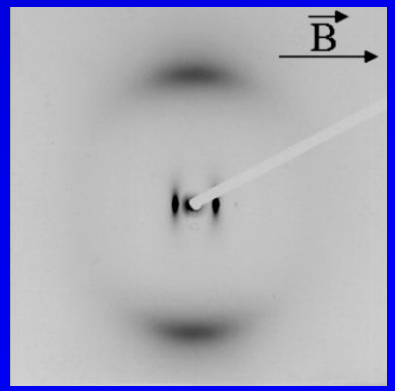
Existence of Bragg reflections
Widths are resolution limited

Otherwise: diffuse scattering

Continuous Scattering



Water



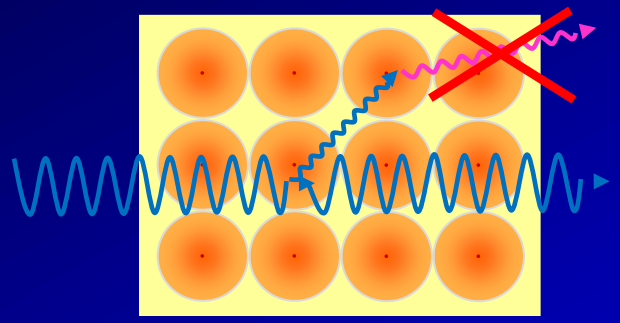
Smectic liquid crystal

C-2 Scattering amplitude

Scattering by an arbitrary structure

Kinematic approximation

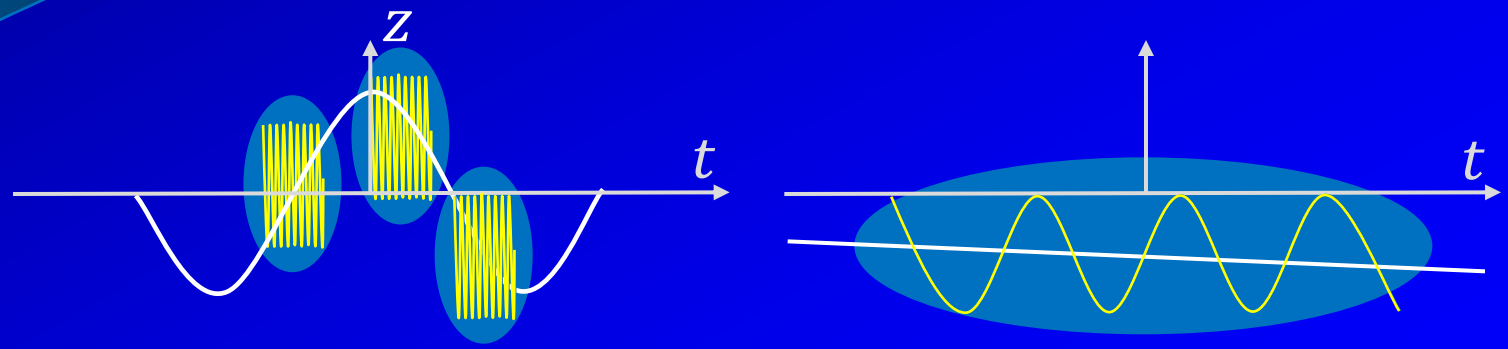
- Intensity of the diffracted beam is much smaller than the incident beam intensity
- No multiple diffraction, no intensity loss



- Approximation is valid for small crystals (1 µm) or mosaic crystals.
- No approximation → Dynamical theory

Static approximation

- Frequencies of X-rays: 10^{18} Hz
- Frequencies of atomic vibrations: 10^{12} Hz (THz)



- Energy of X-rays is larger than the energy of elementary excitations
- X-ray make an average of the intensity of « snapshots »

Calculation of the scattering amplitude

Kinematical approximation

$$A(q) = \int \rho_{tot}(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}$$

- Integration on all the crystal
- r = r(t)...

$A(q)$ is the complex scattering amplitude

It is the Fourier transform of the total electron density

$\rho(r)_{tot} \equiv \rho(r)$

Total scattering cross section

$$\frac{d\sigma}{d\Omega}\Big) = \frac{d\sigma}{d\Omega}\Big)_{th} \left\langle \left| \int \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r} \right|^2 \right\rangle_t$$

Scattering Intensity

$$I(q) = \langle |A(q)|^2 \rangle$$

Ergodicity: $\langle \dots \rangle_t = \langle \dots \rangle$

Scattering function

Scattering function $S(q)$ is:

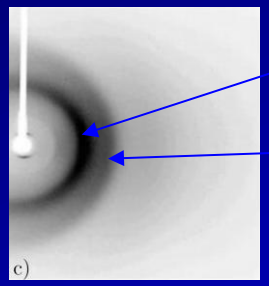
$$S(\boldsymbol{q}) = \frac{I(\boldsymbol{q})}{Nf^2} = 1 + \rho_a \int (g(\mathbf{r}) - 1) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}$$

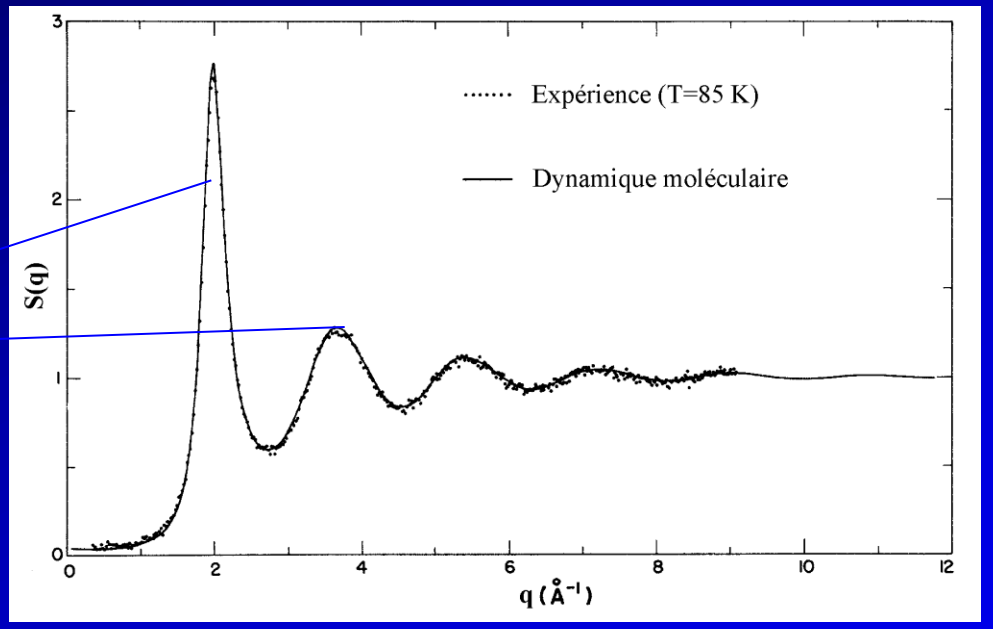
The only quantity directly measurable by diffraction methods is the pair distribution function $g(\mathbf{r})$

$$g(\mathbf{r}) = 1 + \frac{v_a}{(2\pi)^3} \int (S(\boldsymbol{q}) - 1) e^{i\mathbf{q}\cdot\mathbf{r}} d^3\boldsymbol{q}$$

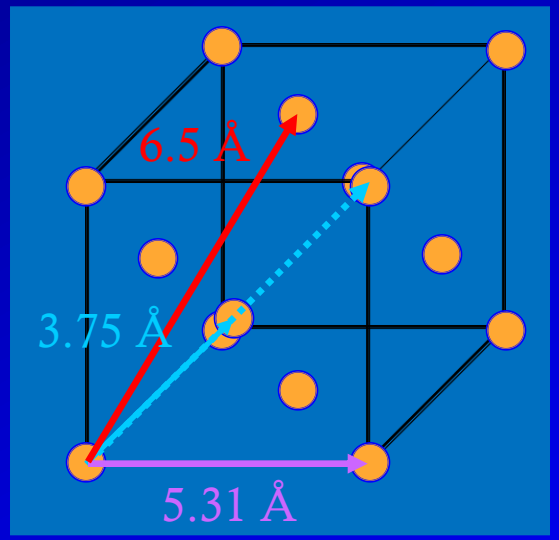
Example

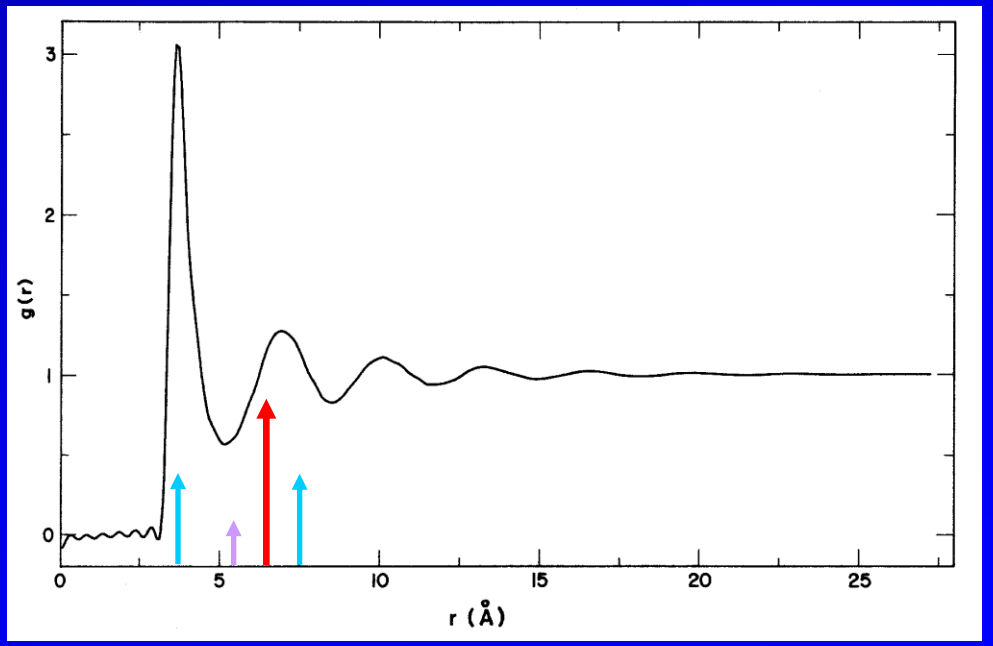
Liquid argon
85 K
Neutrons





Solid Argon
f.c.c





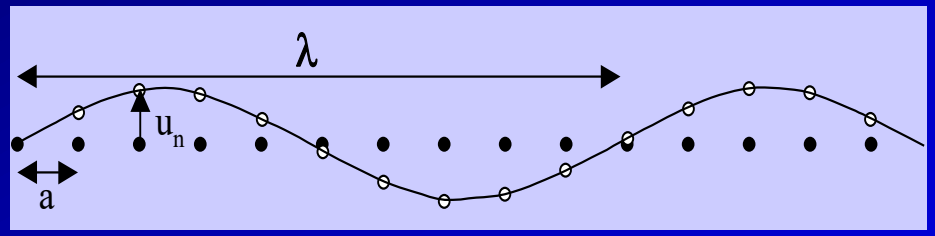
C-3 Periodic Crystals

All crystals are not periodic!

Aperiodic crystals

Incommensurate crystals

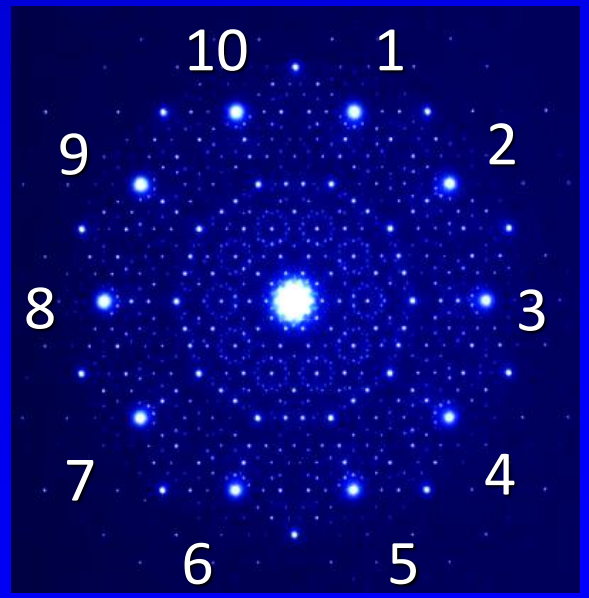
Local property (ex: polarisation) has a periodicity incommensurate with the l attice periodicity.



λ and a have an irrationnal ratio

Crystallographic methods must be changed

Quasi-cristals (AlPdMn)

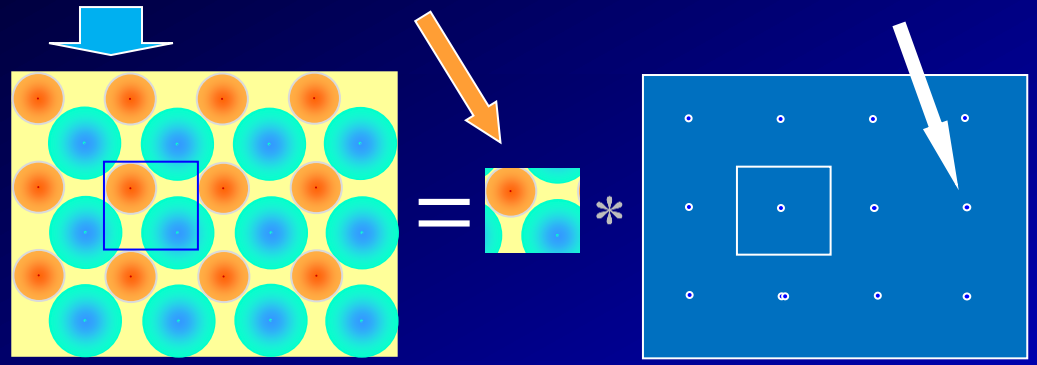


Sharp diffraction peaks

Long-range order
AND
5-fold symmetry
(not consistent with periodicity)

Periodic crystals

Crystal: motif (or basis) associated to a lattice

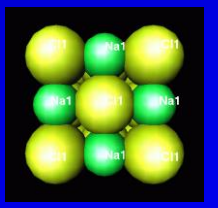


Na

Atom



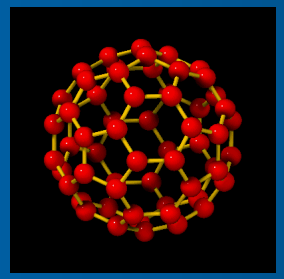
NaCl

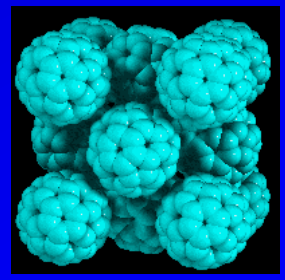


Group of atoms

C_{60}

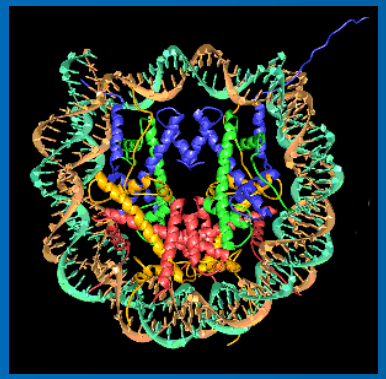
Molecule

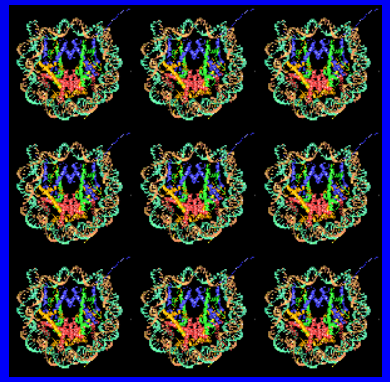




Nucleosome

Macromolecule





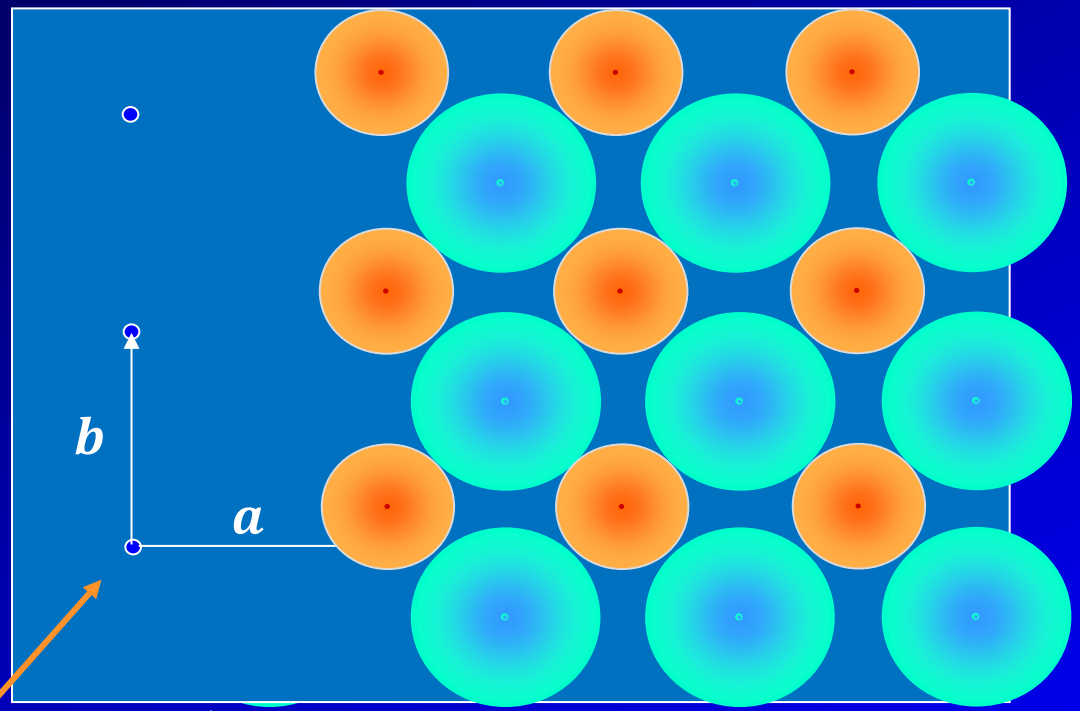
Motif

Crystal

Periodic crystals

Reduced coordinates

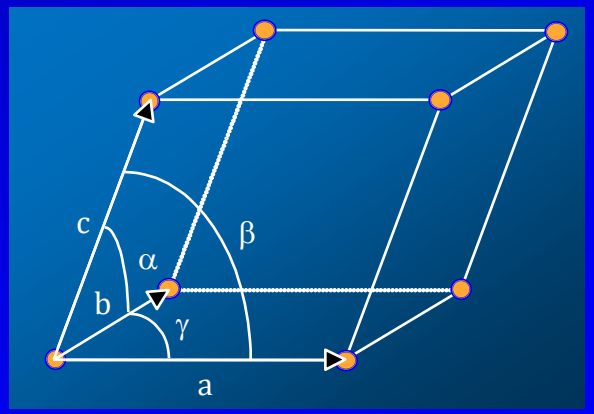
Nodes positions: $\boldsymbol{r}_{uvw} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$



$$\left(\rho_A(\boldsymbol{r}) + \rho_B(\boldsymbol{r})\right) * \sum_{uvw} \delta(\boldsymbol{r} - \boldsymbol{r}_{uvw})$$

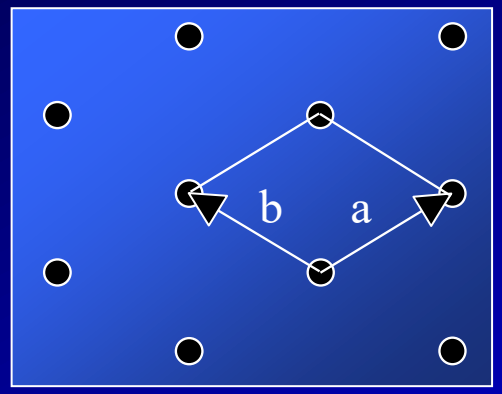
Cell parameters

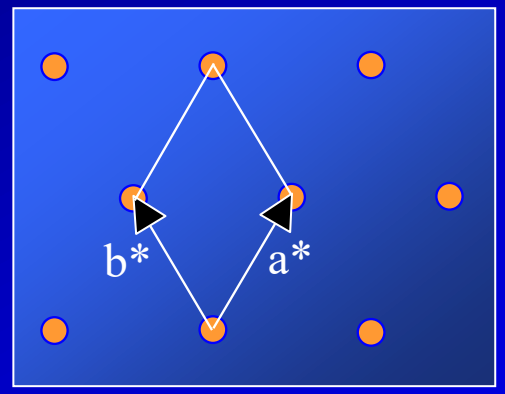
$a, b, c, \alpha, \beta, \gamma$



The reciprocal space

Is the Fourier transform of the direct space





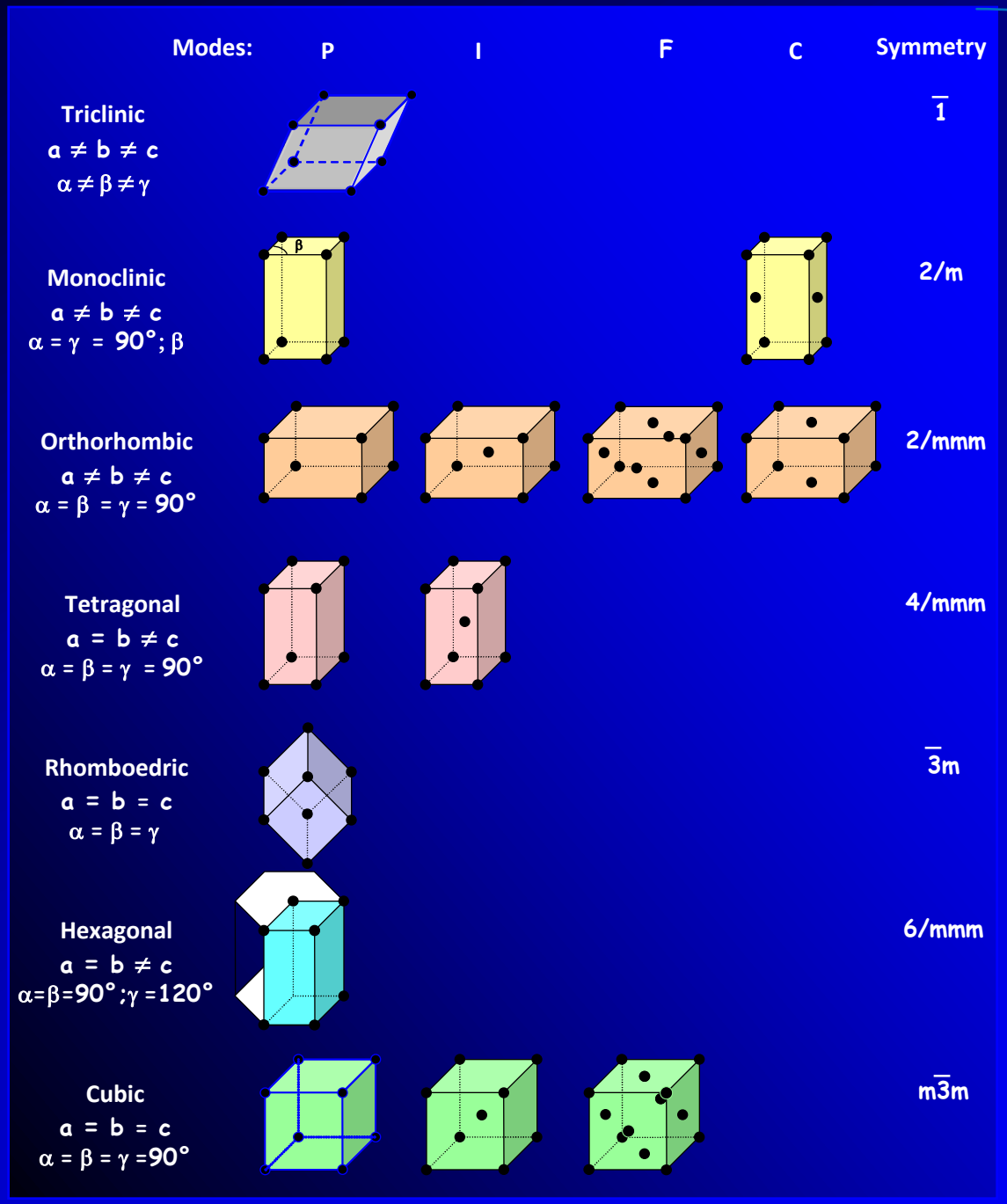
$$\boldsymbol{a}^* = 2\pi\frac{\boldsymbol{b}\wedge\boldsymbol{c}}{v};\ \boldsymbol{b}^* = 2\pi\frac{\boldsymbol{c}\wedge\boldsymbol{a}}{v};\boldsymbol{c}^* = 2\pi\frac{\boldsymbol{a}\wedge\boldsymbol{b}}{v}$$

$$FT\left(\sum_{uvw}\delta(\boldsymbol{r}-\boldsymbol{r}_{uvw})\right) = \frac{1}{v}\sum_{hkl}\delta(\boldsymbol{q}-\boldsymbol{Q}_{hkl})$$

$$\boldsymbol{Q}_{hkl} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$$

Miller indices

14 Bravais lattices



In 3D

7 systems (symmetry)
14 lattice modes

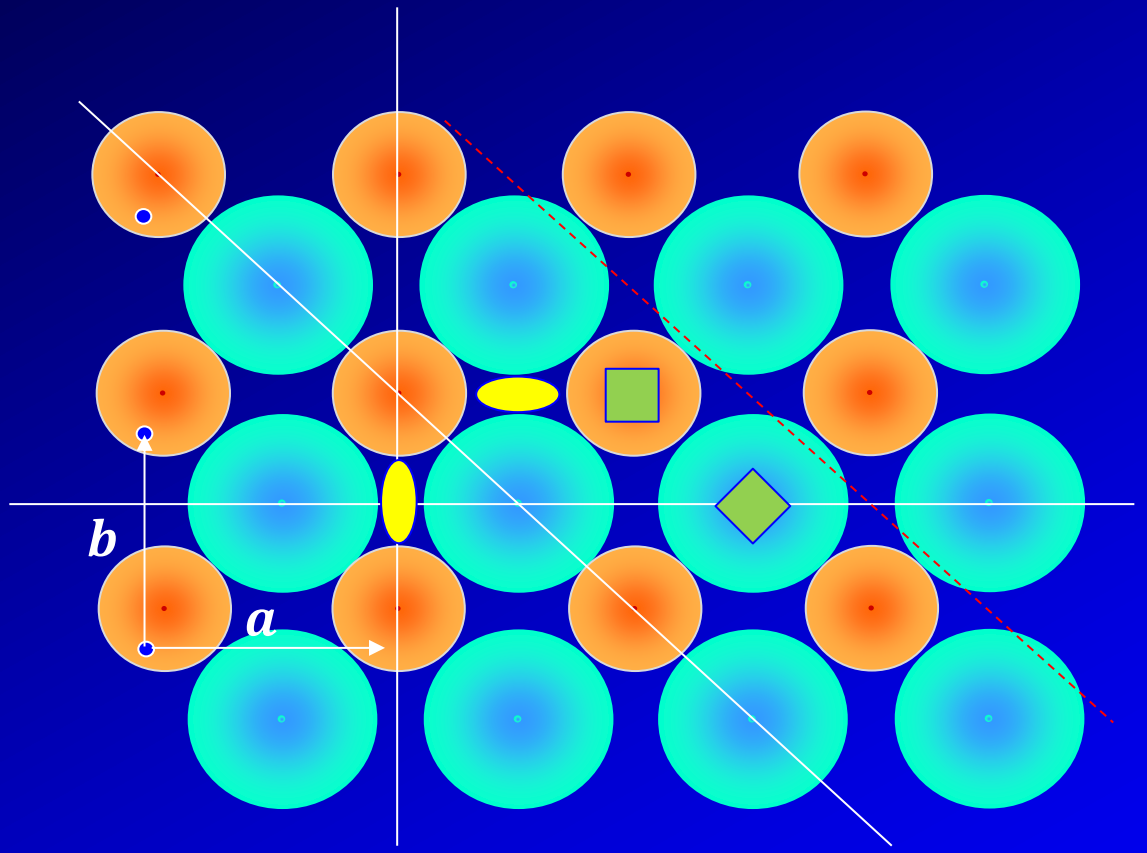
Only 1,2,3,4,6-fold

symmetries are
compatible with periodicity

Reciprocal Lattice has
the same symmetry
(not the same mode)

A little bit of symmetry

The symmetries of a crystal form a group, called « space group » (p4mm)



In 3D
230 space groups
7 crystalline systems

32 point groups
$I4_122\,;422$

Mirrors

4-fold symmetry

2-fold symmetry

Glide plane
(screw axis)

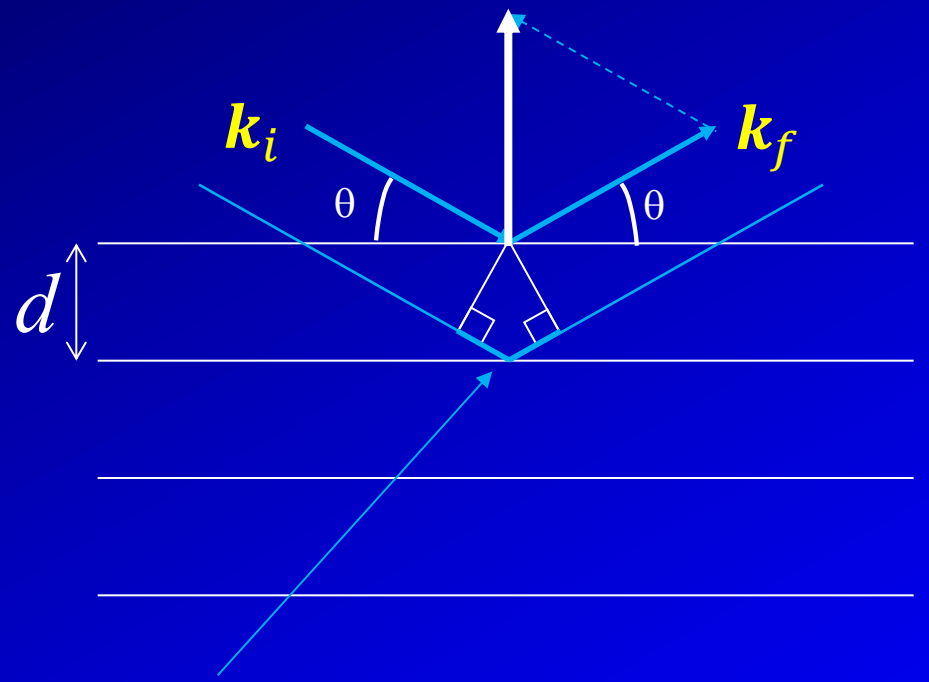
Symmetry of the Reciprocal Lattice is the Laue Group (point Group + center of symmetry)

$I4_122\,;422;4mm$

Bragg relation

Periodicity = Lattice planes
mirrors

$$q = k_f - k_i$$



$$2d \sin\theta = m\lambda$$
$$qd = m2\pi$$

The lower beam traverses an extra length of
$2d \sin\theta$

Constructive interference occurs when this length is equal to an integer multiple of the wavelength

Bragg relation gives a
geometric relation
for diffraction to happen
but no
quantitative information
on the diffracted intensity

Diffraction by a periodic crystal

Simple case: Crystal of $N \times N \times N$ cells

One atom/cell scattering factor f, amplitude is:

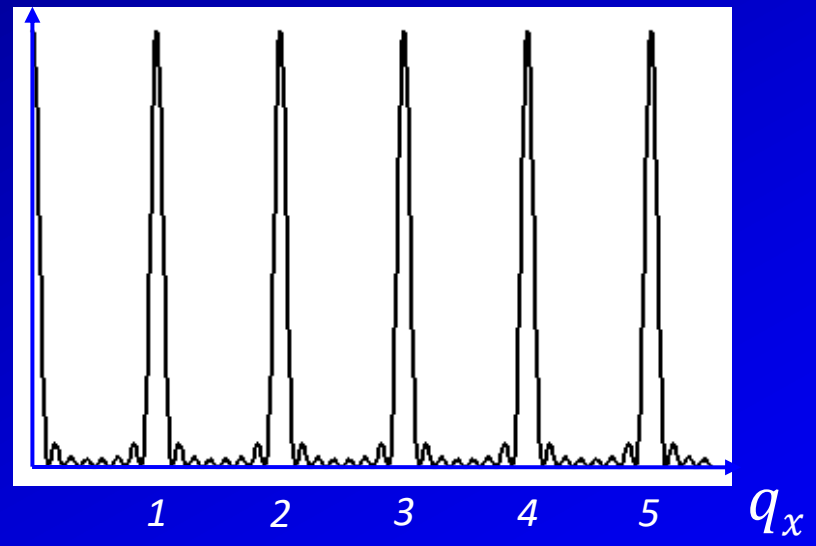
$$A(\boldsymbol{q}) = \sum_{u=1}^{N} \sum_{v=1}^{N} \sum_{w=1}^{N} f e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_{uvw}}$$

Calculation of a geometric sum

$$\boldsymbol{q} = q_x \boldsymbol{a}^* + q_y \boldsymbol{b}^* + q_z \boldsymbol{c}^*$$

$$\sum_{u=1}^{N} e^{-2i\pi q_x u} = e^{-i\pi(N+1)q_x} \frac{\sin(\pi N q_x)}{\sin(\pi q_x)}$$

$N = 8$



Scattering amplitude max at:

$$\boldsymbol{q} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$$

$\boldsymbol{q}$ **belongs to the reciprocal lattice**

$$I(\boldsymbol{q}) = f^2 \frac{\sin^2(\pi N q_x)}{\sin^2(\pi q_x)} \frac{\sin^2(\pi N q_y)}{\sin^2(\pi q_y)} \frac{\sin^2(\pi N q_z)}{\sin^2(\pi q_z)}$$

Laue equations- 1

- Kinematic approximation
- Perfect periodicity

Crystal

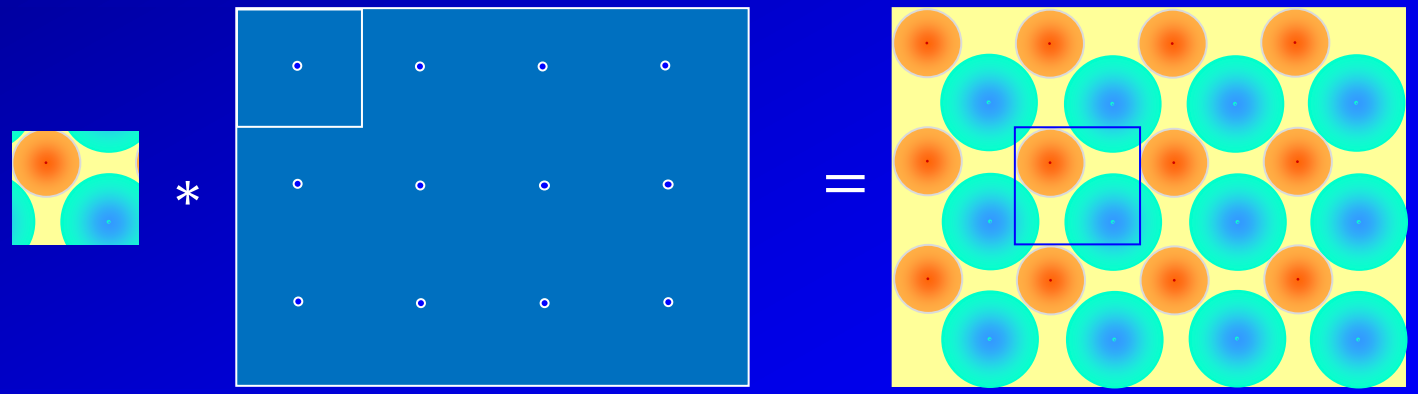
- Total electron density $\rho_{tot}(r)$

$$\rho_{tot(r)} = \sum_{uvw} \rho_{uvw}(r - R_{uvw})$$

- Electron density of a unit cell $\rho(r)$ (no disorder)

$$\rho_{uvw}(r) = \rho(r)$$

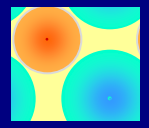
$$\rho(\boldsymbol{r}) * \sum_{uvw} \delta(\boldsymbol{r} - \boldsymbol{R}_{uvw})\, \sigma(\boldsymbol{r}) = \rho_{tot}\ (\boldsymbol{r})$$



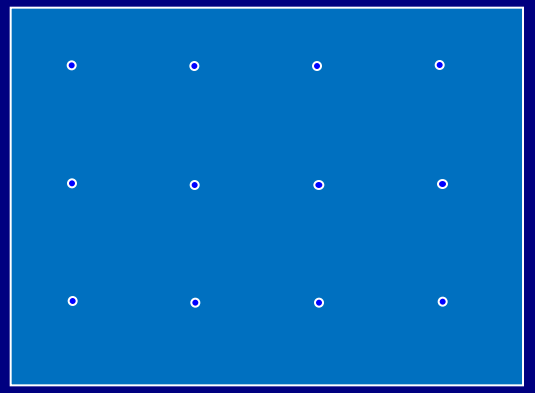
Laue equation - 2

FT of $\rho_{tot}(\boldsymbol{r})$

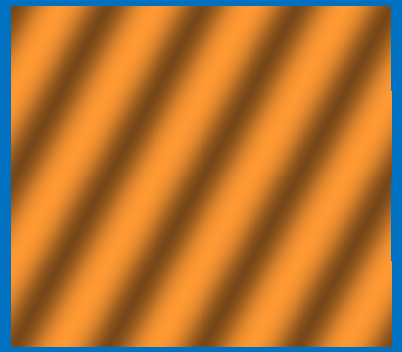
$$\rho_{tot}(\boldsymbol{r}) = \rho(\boldsymbol{r}) * \sigma(\boldsymbol{r}) \times \sum_{uvw} \delta(\boldsymbol{r} - \boldsymbol{r}_{uvw})$$



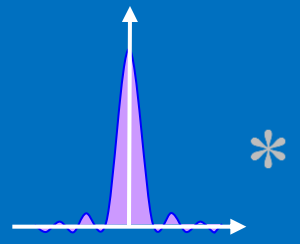
$*$



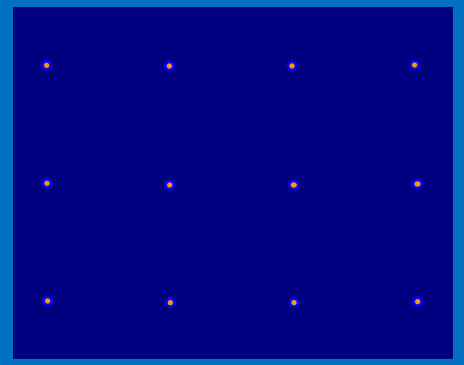
$$A(\boldsymbol{q}) = F(\boldsymbol{q}) \times (2\pi)^3 \left(\Sigma(\boldsymbol{q}) * \frac{1}{v} \sum_{hkl} \delta(\boldsymbol{q} - \boldsymbol{Q}_{hkl}) \right)$$



$\times$



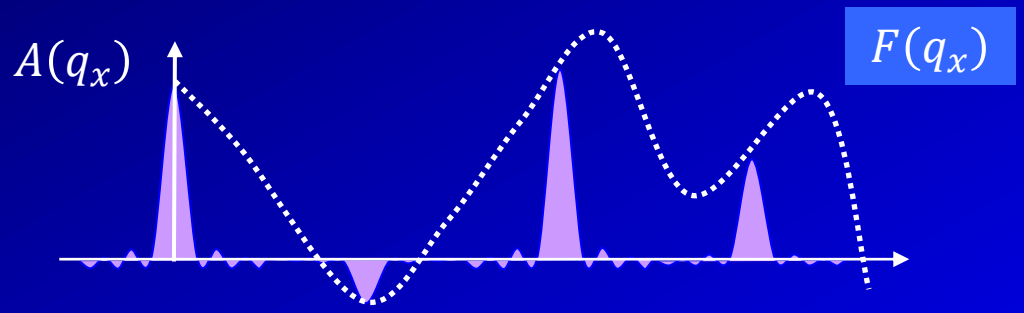
$*$



Laue equations - 3

$$A(\boldsymbol{q}) = F(\boldsymbol{q}) \times \left(\Sigma(\boldsymbol{q}) * \frac{1}{v} \sum_{hkl} \delta(\boldsymbol{q} - \boldsymbol{Q}_{hkl}) \right)$$

Each node of the RS replaced by $\Sigma(\boldsymbol{q})$

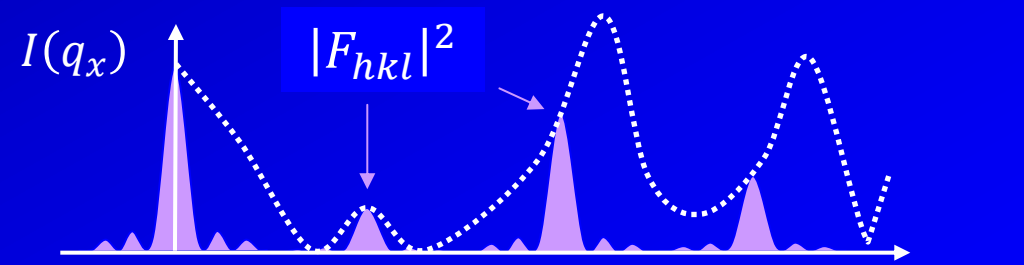


Crystal size cell parameters, no cross terms:

Intensity is max when $\boldsymbol{q}$ belongs to the RL

$$I(\boldsymbol{q}) = |F(\boldsymbol{q})|^2 \times \left(\frac{1}{v^2} \sum_{hkl} |\Sigma(\boldsymbol{q} - \boldsymbol{Q}_{hkl})|^2 \right)$$

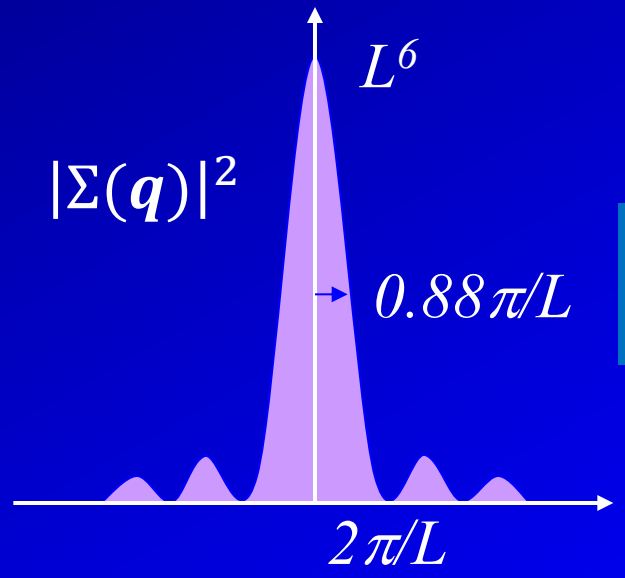
$$F(\boldsymbol{Q}_{hkl}) = F_{hkl}$$



Fourier Transform of $\sigma(\mathbf{r})$

Fourier Transform
of the « volume » function

$$\Sigma(\boldsymbol{q}) = \int \sigma(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \mathrm{d}^3\boldsymbol{r}$$



Exemple of a cube

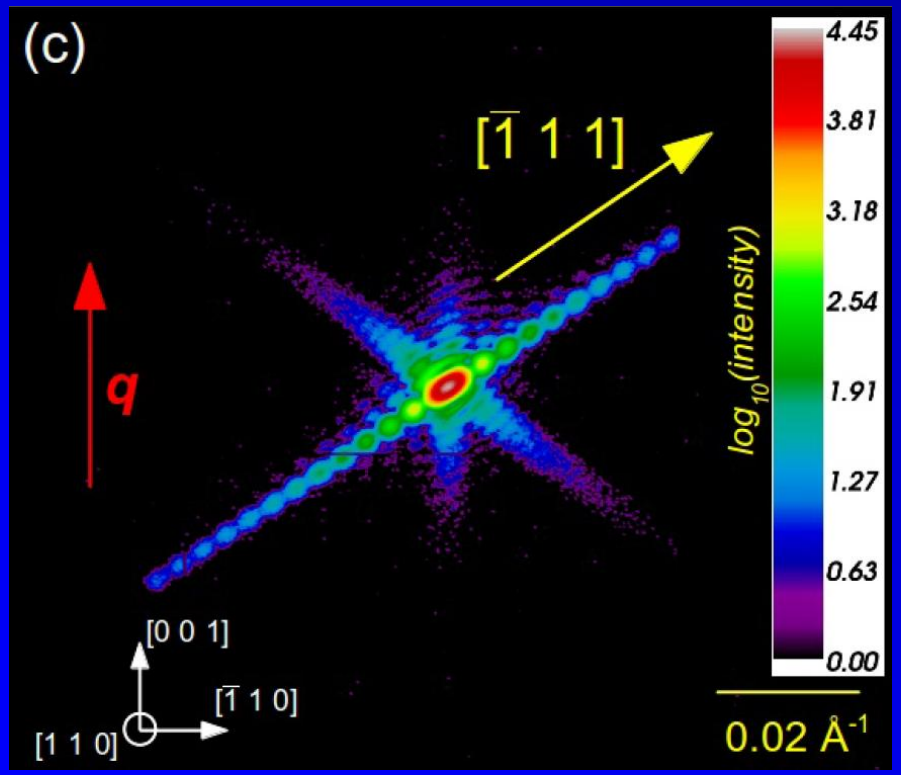
$$\Sigma(\boldsymbol{q}) = \left(\frac{\sin(Lq_x/2)}{q_x/2}\right)\left(\frac{\sin(Lq_y/2)}{q_y/2}\right)\left(\frac{\sin(Lq_z/2)}{q_z/2}\right)$$

Measure of $\Sigma(q)$

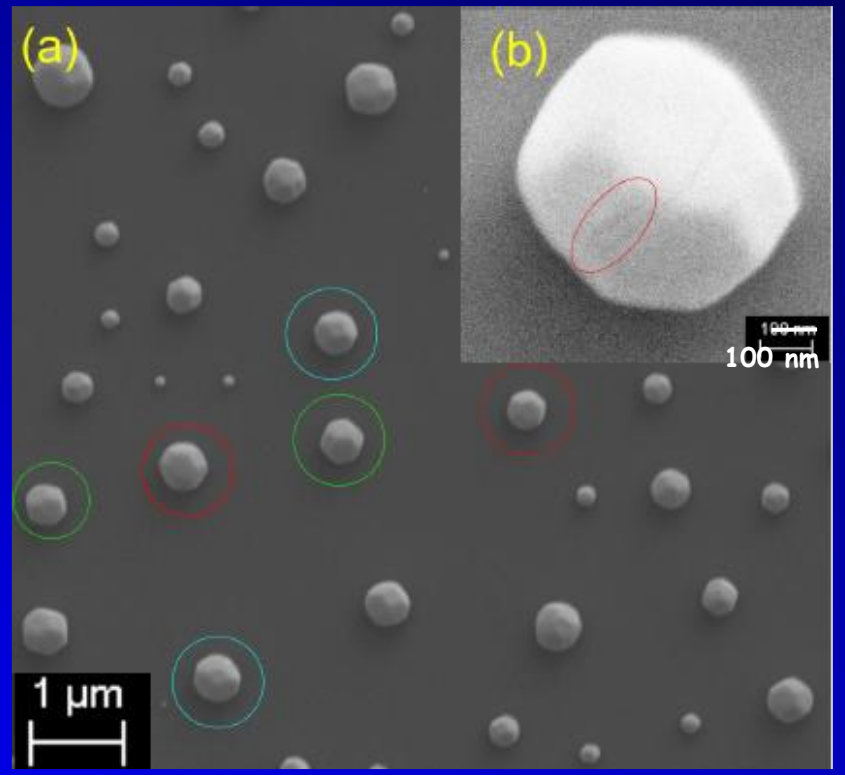
In order to measure $\Sigma(q)$, X-ray must interfere **on the whole crystal**:

→ Transverse coherence length > crystal size (1µm)

→ At least 3rd generation x-ray source



Intensity around the 002 Bragg reflexion mesured on a synchrotron radiation facility.
From Maxime Dupraz Thesis, 2015



Gold on sapphire
SEM image

Structure factor

$$F(\boldsymbol{Q}_{hkl}) = F_{hkl}$$

TF of the electron density of the unit cell

$$F(\boldsymbol{q}) = \int \rho_{uvw}(\boldsymbol{r})\, e^{-i\boldsymbol{q}.\boldsymbol{r}}$$

Spherical approximation

$$\rho_{uvw}(r) = \sum_j \rho_j(\boldsymbol{r} - \boldsymbol{r}_j)$$

Atoms j, position $\boldsymbol{r}_j$
density ρ_j , scattering factor $\boldsymbol{f}_j$

$$F(\boldsymbol{q}) = \sum_j f_j e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_j}$$

$$F_{hkl} = \sum_j f_j e^{-2i\pi(hu_j + kv_j + lw_j)}$$

- h, k, l, **Miller indices,**
- u_j, v_j, w_j, **reduced coordinates of atoms ($\boldsymbol{r}_j = u_j\boldsymbol{a} + v_j\boldsymbol{b} + w_j\boldsymbol{c}$)**

Friedel law

$$F_{\bar{h}\bar{k}\bar{l}} = F^*_{hkl} \qquad I_{\bar{h}\bar{k}\bar{l}} = I_{hkl}$$

Centrosymmetric or non-centrosymmetric (neglecting resonant effects)

The electron density is periodic

therefore admits a Fourier series expansion

$$\rho(\boldsymbol{r}) = \frac{1}{v}\sum_{hkl} F_{hkl} e^{i\boldsymbol{Q}_{hkl}\cdot\boldsymbol{r}}$$

Fourier coefficients (with a phase)

Spatial frequencies $\frac{2\pi}{|\boldsymbol{Q}_{hkl}|}$

This is obtained from: $\rho(\boldsymbol{r}) = \int A(\boldsymbol{q}) d\boldsymbol{q} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ **by using:** $A(\boldsymbol{q}) = F(\boldsymbol{q})\frac{1}{v}\sum_{hkl}\delta(\boldsymbol{q}-\boldsymbol{Q}_{hkl})$

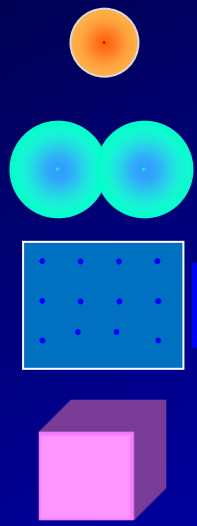
X-rays/Neutrons

For neutrons,
just replace f by b

$$F_{hkl} = \sum_j b_j e^{-2i\pi(hu_j + kv_j + lw_j)}$$

…if one considers only elastic scattering

Diffracted intensity

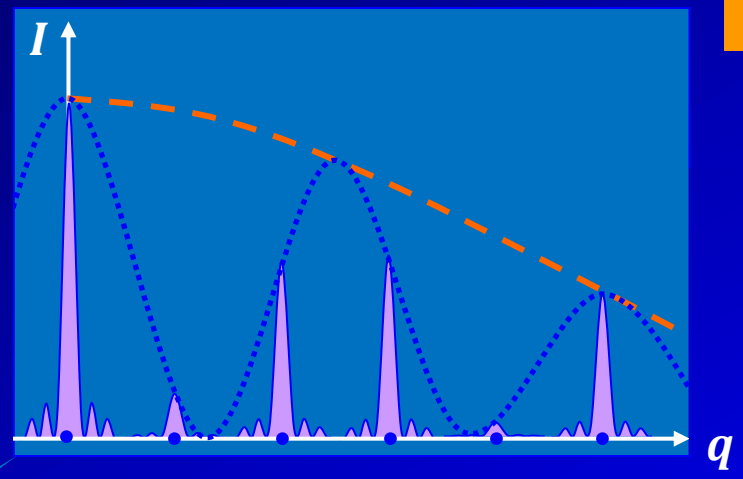


Atom

Motif

Direct lattice

Crystal



Atomic scattering factor

Structure factor

Reciprocal lattice

Form factor

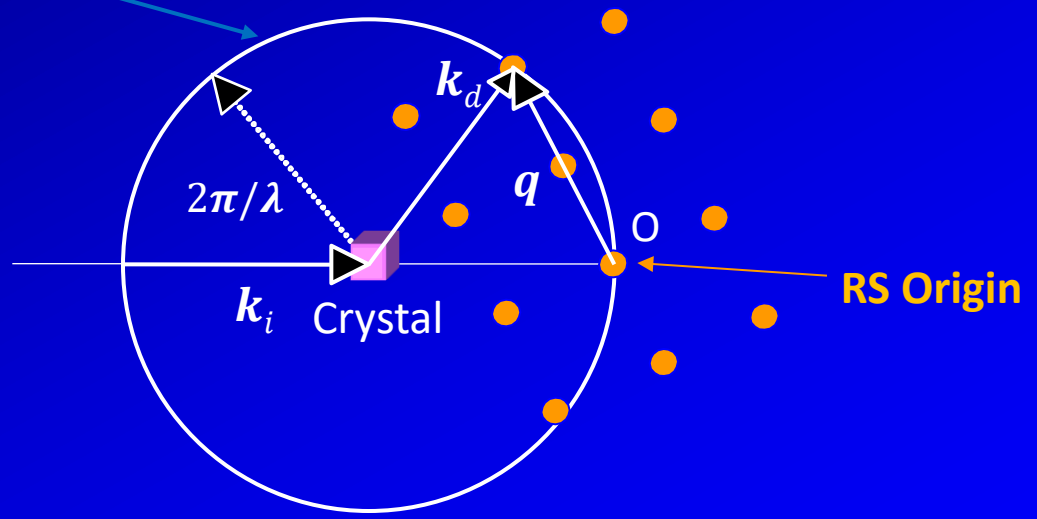
Position of Bragg spots: lattice
Intensity: motif
Profile: Shape/size of grains/crystals

Ewald construction

Geometrical interpretation of diffraction

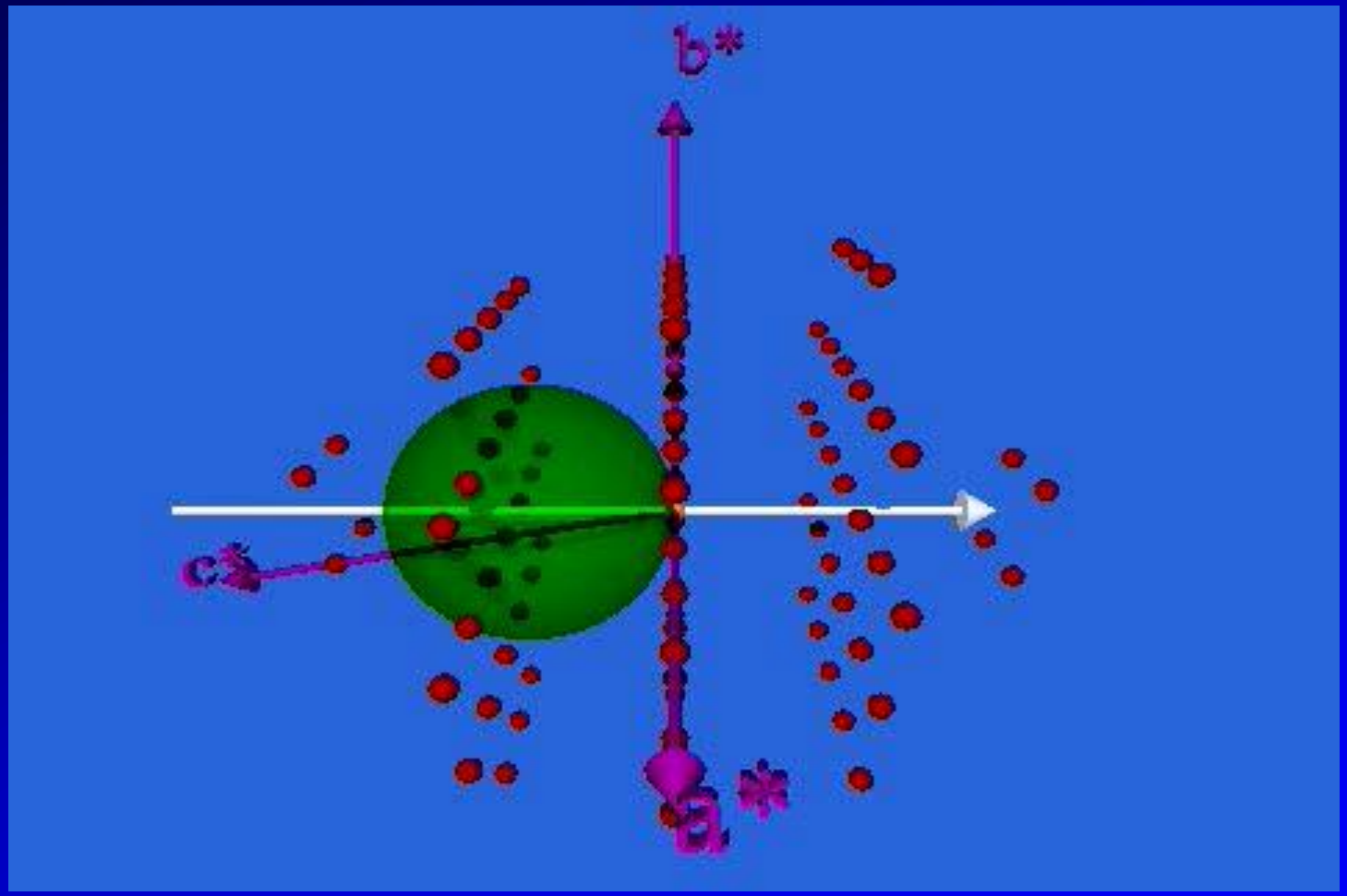
- Elastic scattering : $k_i = k_d = 2\pi/\lambda$
- Laue equations: scattering vector q belongs to RL

Ewald's sphere of reflexion



Diffraction occurs for nodes that lie on the sphere

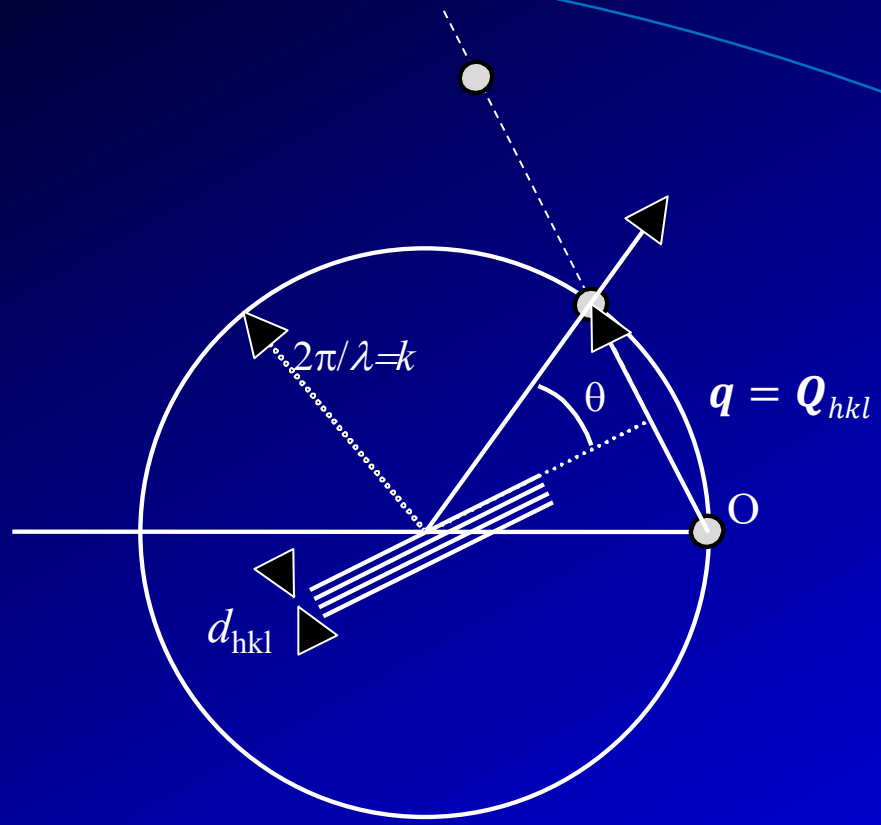
Ewald sphere



© Gervais Chapuis

Not all nodes are accessible

Laue ⇔ Bragg

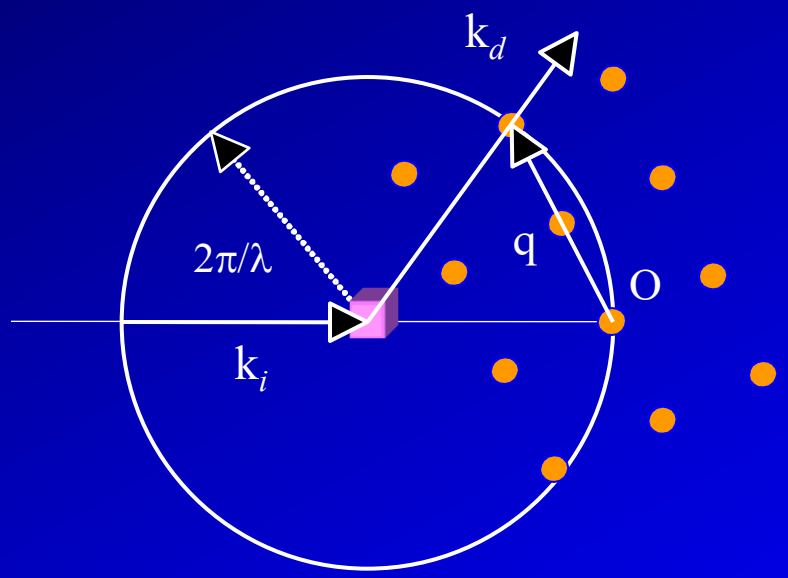


$$q = Q_{hkl} = \frac{2\pi}{d_{hkl}}$$

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

Experimental methods

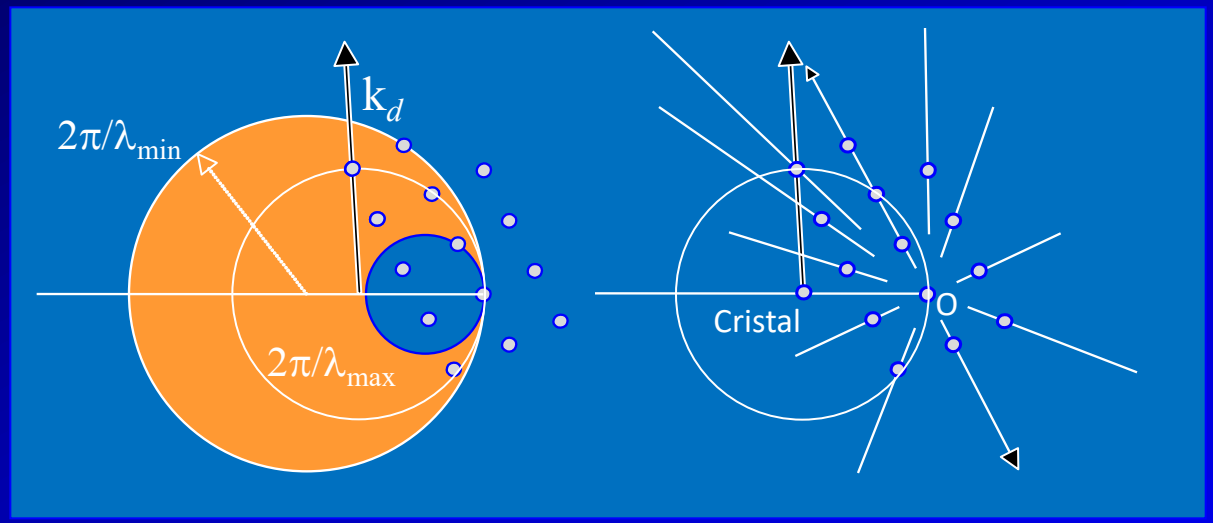
In a 3D crystal, the number of nodes in reflection is small.



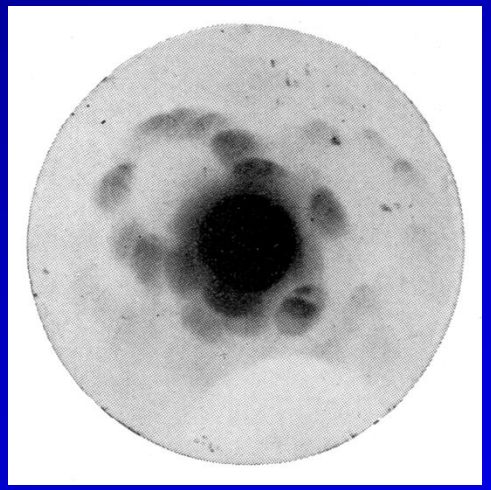
- **Laue method (many λ)**
- **Powder method (many crystals)**
- **Rotating crystal (many orientations)**

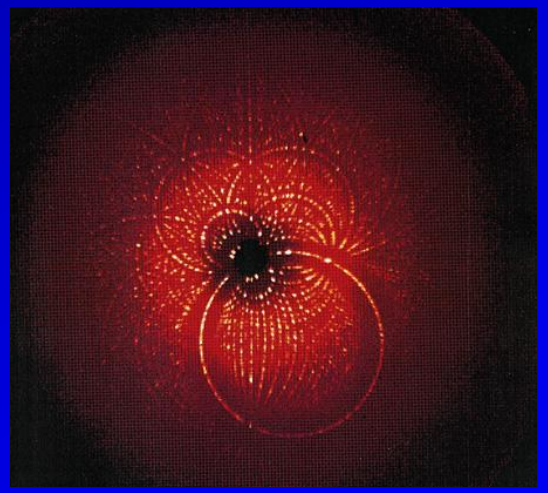
Laue method

Diffraction with white beam



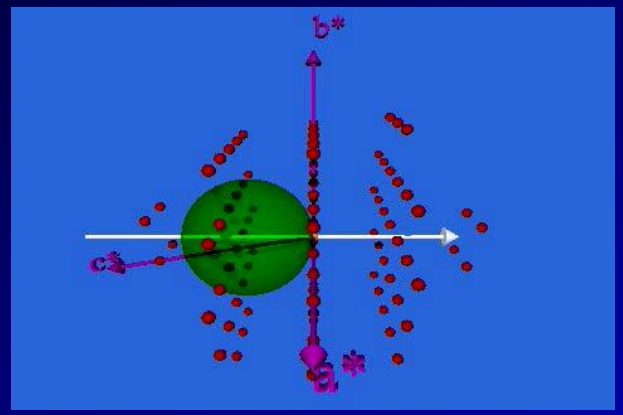
First diffraction 1912 ($CuSO_4$)
Von Laue, Friedrich, Knipping



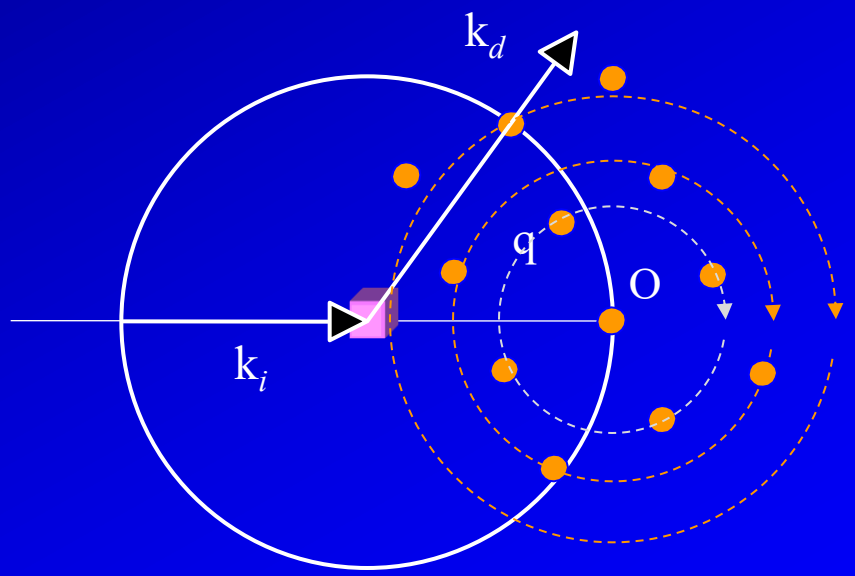


Laue diffraction pattern of MbCO
150 ps pulse (ESRF ID13)
2000 reflections (E=7-38 keV)

Rotating crystal

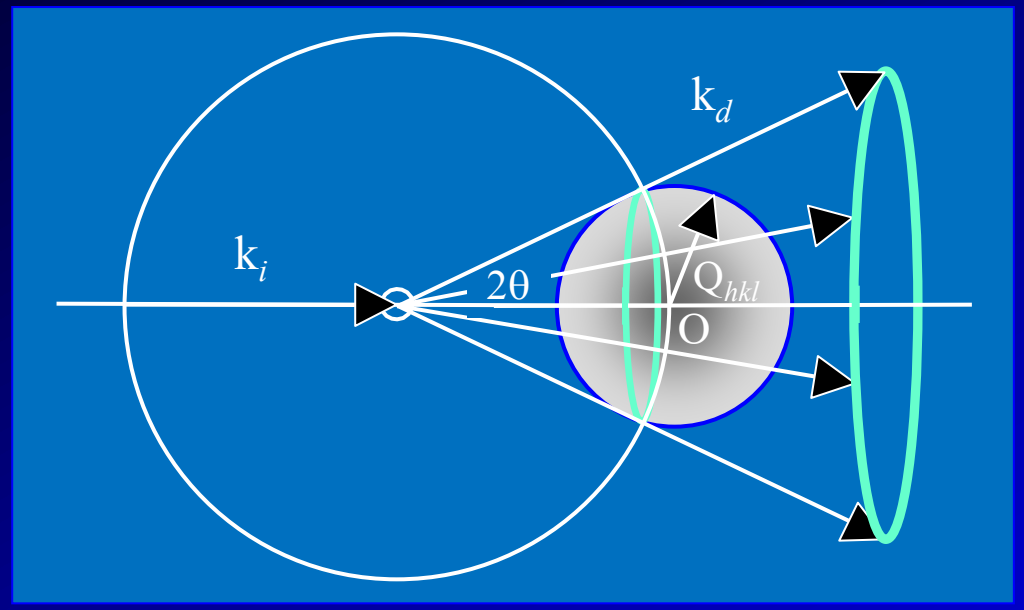


All accessible nodes
Pass through the Ewald sphere

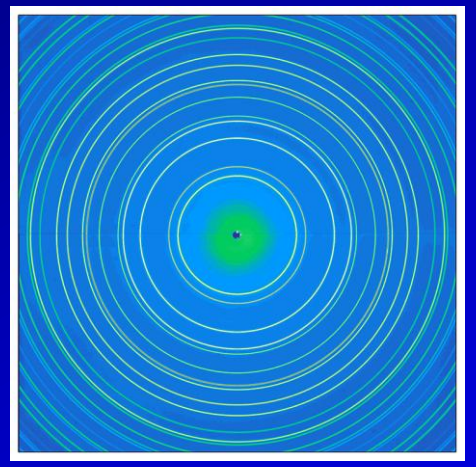


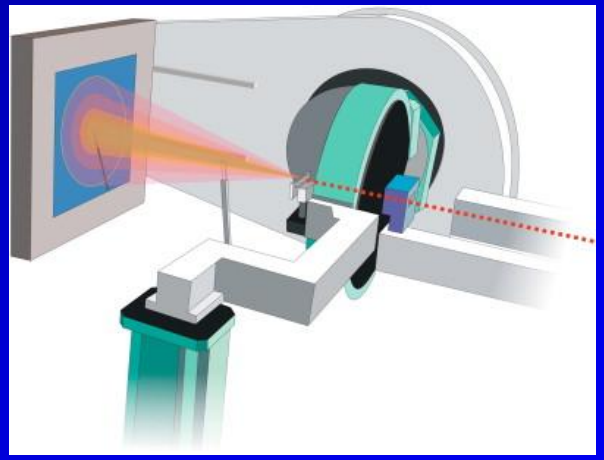
Powder method

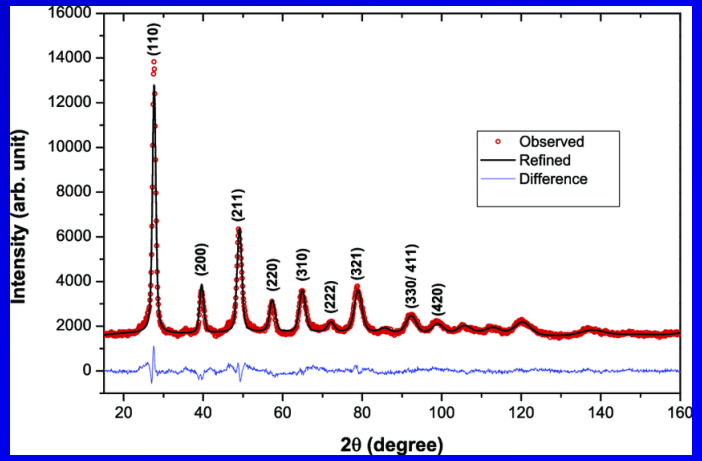
Powder: Set of small crystals (0.1-10 µm) in every possible orientations.



Each node Q_{hkl} on a sphere





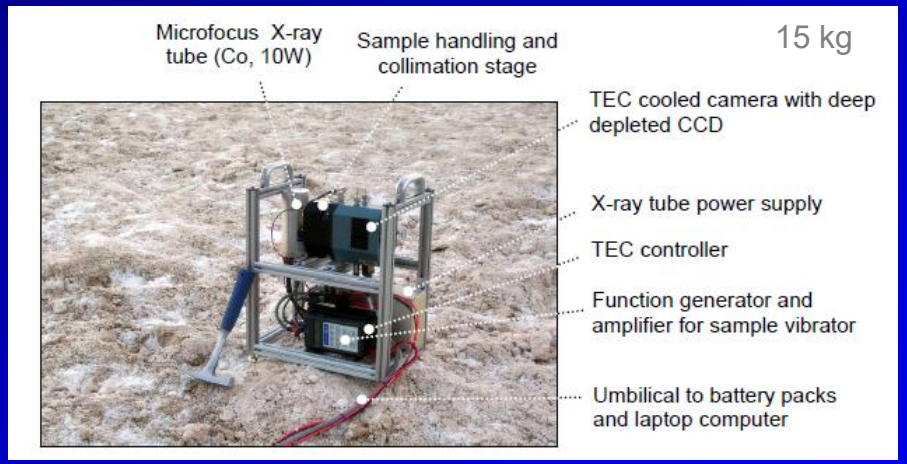


One line: one θ ; distance d_{hkl}

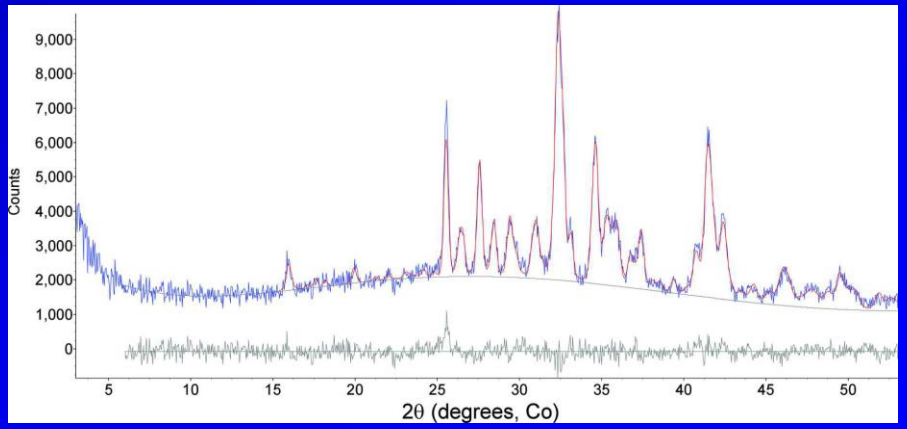
Debye-Scherrer method

Powder diffraction… on Mars in 2012!





Rocks similar to Mauna Loa, Hawaii



David Bish, et al. IUCrJ. 2014 Nov 1; 1(Pt 6): 514–522

Principle of structure determination

Measure the positions of Bragg spots and their intensity

Determine lattice parameter, symmetry, space group (if possible)

Extract the Bragg spots intensity: $|F_{hkl}|^2$

Solve the phase problem (!)
to get the electron density

$$\rho_{tot}(x,y,z) = \frac{1}{v}\sum_{hkl} F_{hkl} e^{2i\pi(hx+ky+lz)}$$

Example: Structure of phthalocyanin

J. Monteath Robertson, J. Chem. Soc. 615, (1935); 1185 (1936)





Metal (Cu, Ni, Pt)

Determination of phases of 150 hk0 Bragg reflections by comparison.

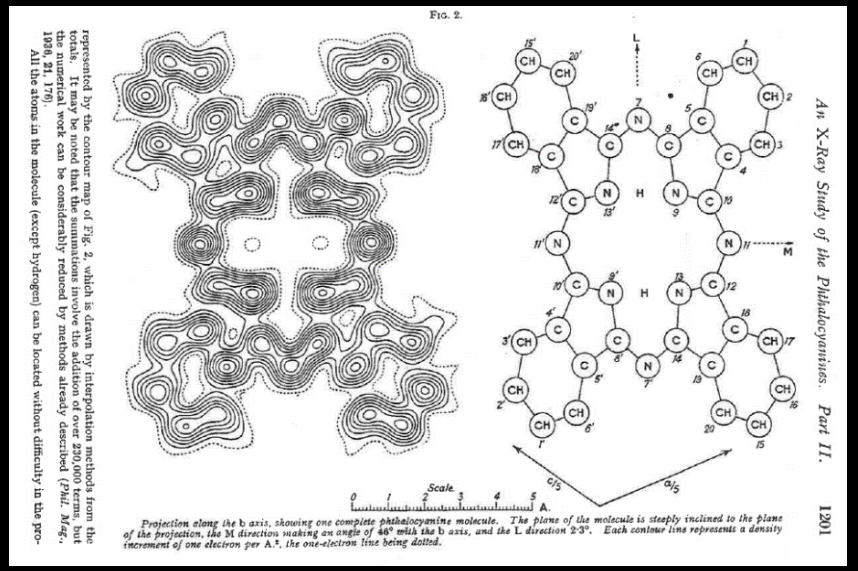


FIG. 2.

Projection along the b axis, showing one complete phthalocyanine molecule. The plane of the molecule is steeply inclined to the plane of the projection, the M direction making an angle of 46° with the b axis, and the L direction 2·3°. Each contour line represents a density increment of one electron per A.², the one-electron line being dotted.

Scale. 0 1 2 3 4 5 A.

An X-Ray Study of the Phthalocyanines. Part II. 1201

represented by the contour map of Fig. 2, which is drawn by interpolation methods from the totals. It may be noted that the summations involve the addition of over 220,000 terms, but the numerical work can be considerably reduced by methods already described (*Phil. Mag.*, 1933, 21, 176). All the atoms in the molecule (except hydrogen) can be located without difficulty in the pro-

Electron density map

Calculation of 1800 sums of 150 terms (270 000)!

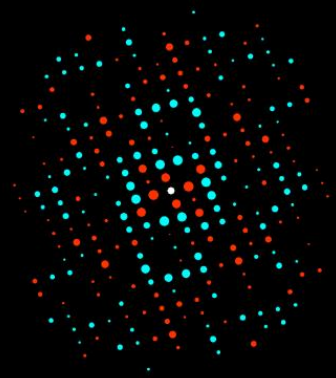
Without computers…

Use of the Fourier series

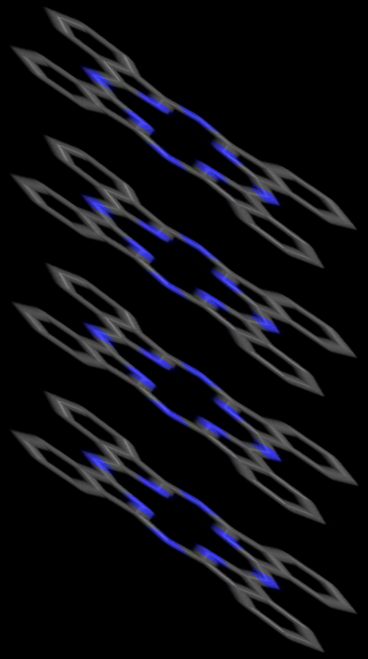
$$\text{resolution} = \frac{2\pi}{q_{Max}} = \frac{\lambda}{2\sin\theta}$$

Fourier series

sine **component**



resolution = 0.95 Å



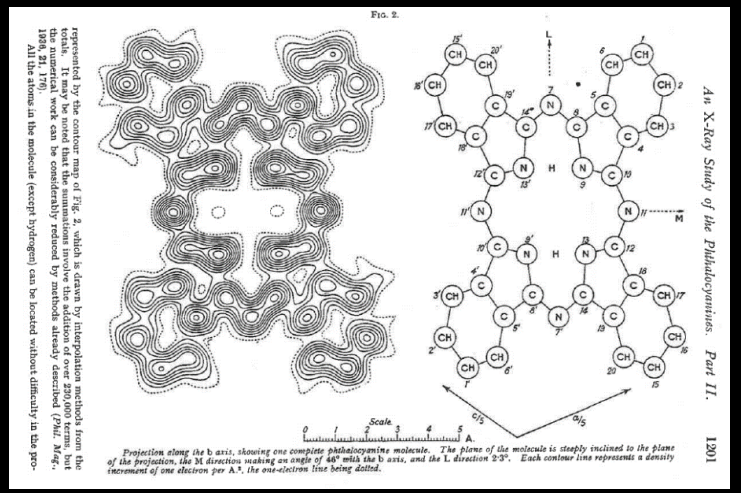


Fig. 2.

An X-Ray Study of the Phthalocyanines. Part II. 1201

represented by the contour map of Fig. 2, which is drawn by interpolation methods from the totals. It may be noted that the summations involve the addition of over 200,000 terms; but the numerical work can be considerably reduced by methods already described (*Phil. Mag.*, 1935, **19**, 1161).

All the atoms in the molecule (except hydrogen) can be located without difficulty in the pro-

Scale 0 1 2 3 4 5 Ångström Å

Projection along the b axis, showing one complete phthalocyanine molecule. The plane of the molecule is steeply inclined to the plane of the projection, the M direction making an angle of 46° with the b axis, and the L direction 2·3°. Each contour line represents a density increment of one electron per A.², the one-electron line being dotted.

The molecule is tilted



This is a 3D problem!

Fourier transform of a CUT Is the PROJECTION of the FT

Better resolution:

Smaller wavelength
Better crystal quality
Lower temperature

Electron density

$$\rho_{tot}(x,y,z) = \frac{1}{v}\sum_{hkl} F_{hkl}\, e^{2i\pi(hx+ky+lz)}$$

X-ray give access to
Electron density
and not to
Atom density (neutron)

Precise measurements of intensities → Electron density

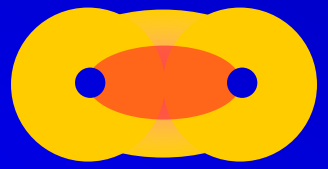
Chimical bonding
Electrostatic potential, charge transfer, dipolar moment, etc.

Calculation of F_{hkl} in the spherical approximation

$$F_{hkl}^{calc} = \sum_{j} f_j\, e^{-2i\pi(hu_j+kv_j+lw_j)}$$

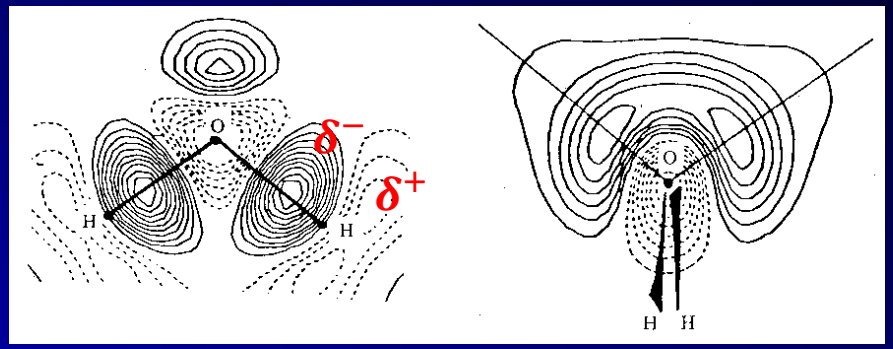
Deformation map of electron density

$$\rho_{def}(x,y,z) = \frac{1}{v}\sum_{hkl} (F_{hkl} - F_{hkl}^{calc})\, e^{2i\pi(hx+ky+lz)}$$



Examples of maps

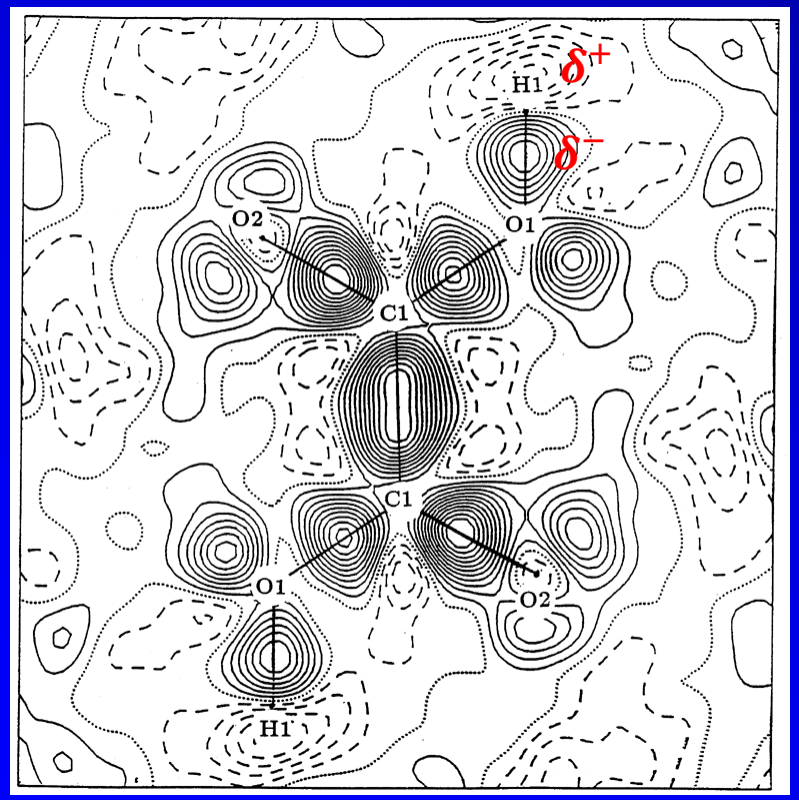
Contour 0.005 eÅ^{-3}



H_2O in $LiOH.H_2O$

From Vainshtein

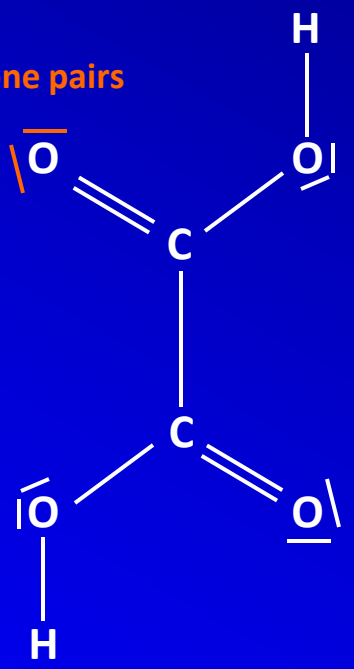
Oxalic acid 15 K



Contour 0.05 eÅ^{-3}

(Zobel et al. 1992)

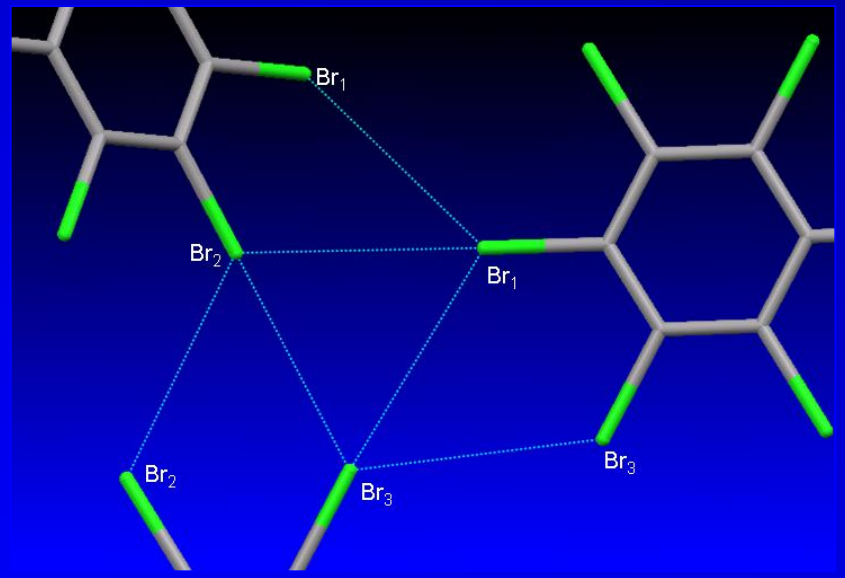
Lone pairs



Multipolar development of electron density (Hansen-Coppens model)

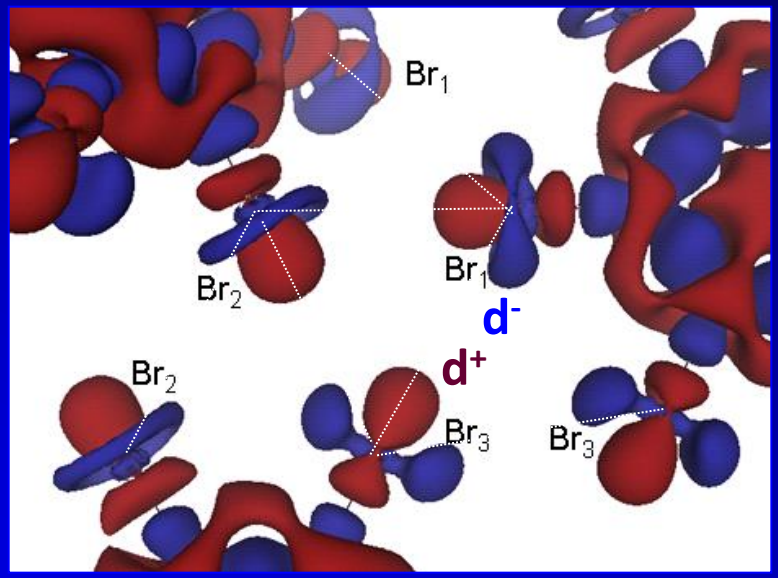
$$\rho_{mul}(r) = \rho_{core}(r) + P_v \kappa^3 \rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{+l} P_{lm\pm} y_{lm\pm}(\theta, \varphi)$$

Hexabromobenzène C_6Br_6



From S. Dahaoui *et al.*,
Angew. Chem. Int. Ed., 2009, 48, 3838

Static deformation map



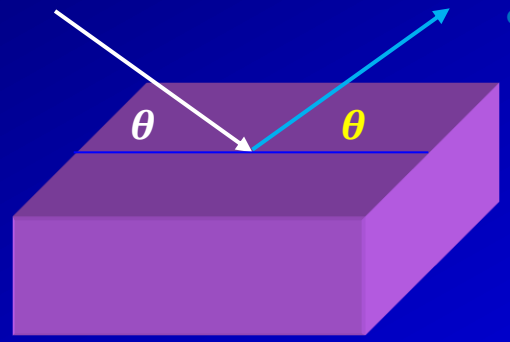
$\Delta\rho_{stat}(r) = \rho_{multipole}(r) - \rho_{spherical}(r)$

The anisotropic distribution electron density around halogen atom originates the halogen-halogen interaction

Dynamical theory

Diffraction on perfect crystals

- Dynamical theory (M. Von Laue, P. Ewald, G. Darwin)
- Depends on the diffraction geometry



- Same diffraction condition (Laue, Bragg) but refraction ($n = 1 - \delta$)

$$2d_{hkl}\sin\left(\theta - 2\frac{\delta}{\sin 2\theta}\right) = \lambda$$

Reflected power (Bragg reflections)

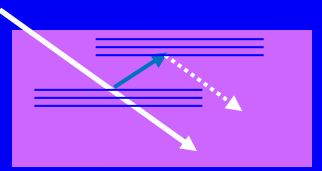
Kinematic Theory

$$P_{ciné.} = r_e^2 \frac{(1+\cos^2 2\theta)}{2\sin 2\theta}\frac{\lambda^3}{v^2}|F_{hkl}|^2\frac{1}{2\mu}$$

Dynamical Theory

$$P_{dyn.} = \frac{8}{3\pi}r_e\frac{(1+|\cos 2\theta|)}{2\sin 2\theta}\frac{\lambda^2}{v}|F_{hkl}|$$

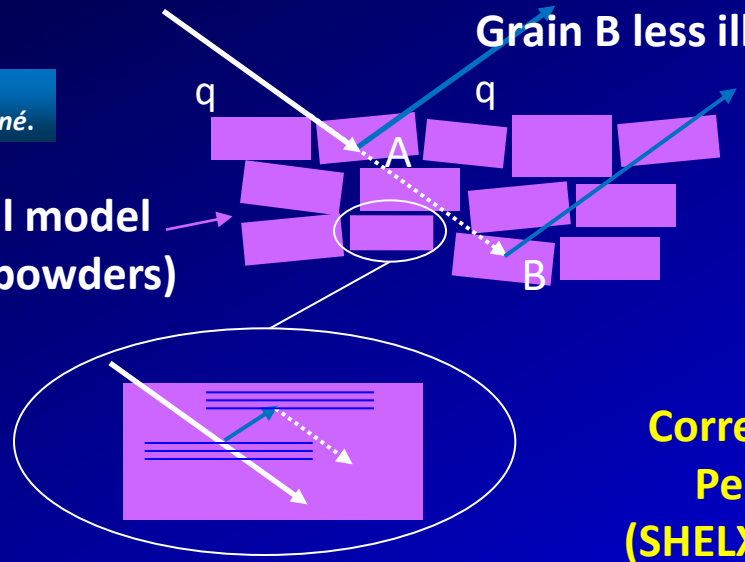
Dynamical results is much smaller: Extinction



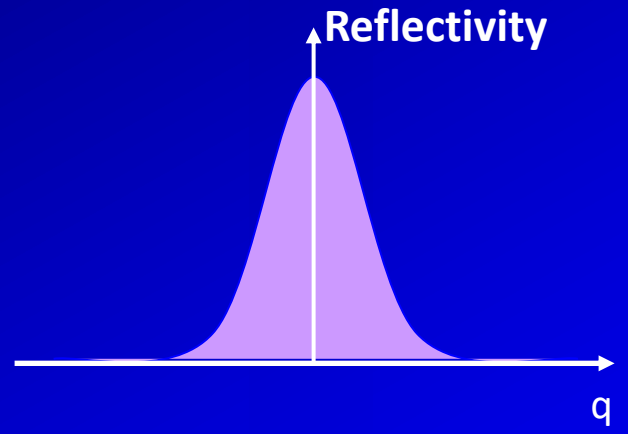
Dynamical theory-2

$P_{dyn.} < P_{ciné.}$

Secondary extinction:
Grain B less illuminated than grain A



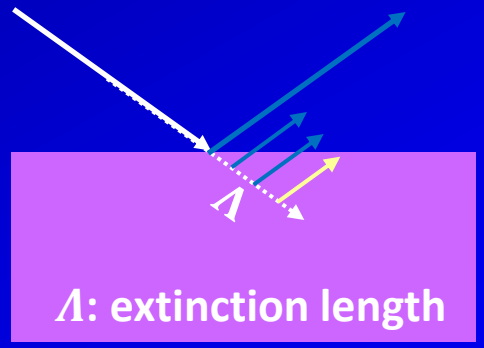
Mosaic crystal model
(small crystal, powders)



« Rocking curves »

Correction to be Performed!
(SHELXTL package)

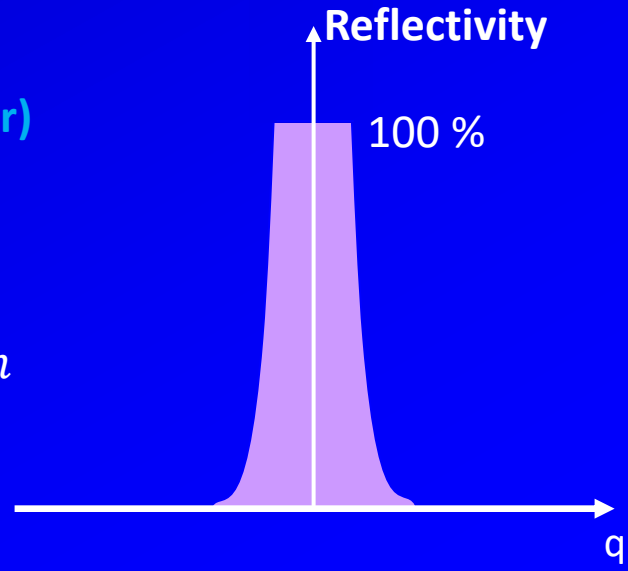
Primary extinction:
Destructive interferences between beams diffracted n-times



Λ: extinction length

Perfect crystals
(Si, Ge, monochromator)
Darwin Curve

$$\Lambda = \frac{1}{2d_{hkl}} \frac{v}{r_e |F_{hkl}|} \sim 1\ \mu m$$



C-4 Disorder

Two types of disorder

- Disorder of second kind (liquid-like) :

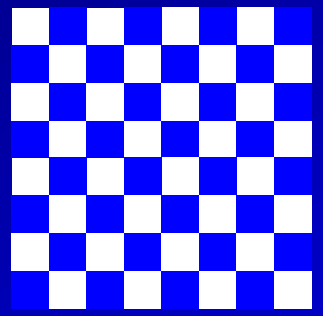
Pair Distribution Function $g(\mathrm{r})$ tends to 0
No diffraction peaks

- Desorder of first kind (disordered crystal):

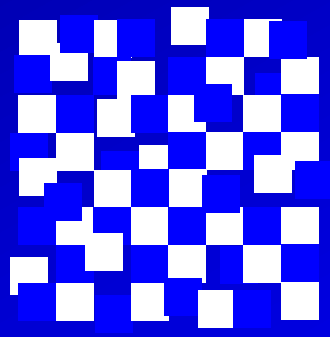
Long range order

Diffraction peak intensity (smaller intensity)
AND
Diffuse scattering

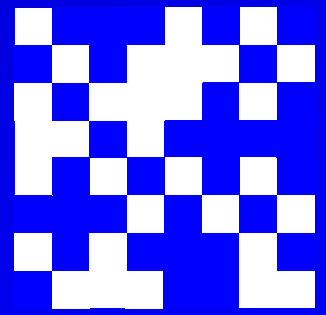
Two types of disordered crystals



Displacement disorder



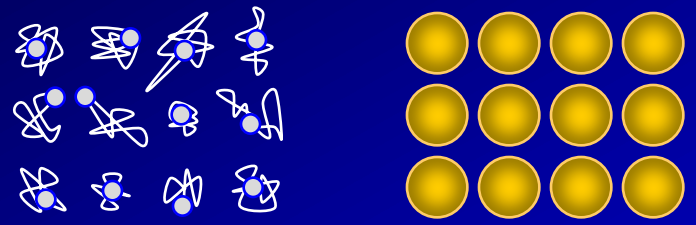
Substitution disorder



Disorder 1-Effect of temperature

Thermal motion

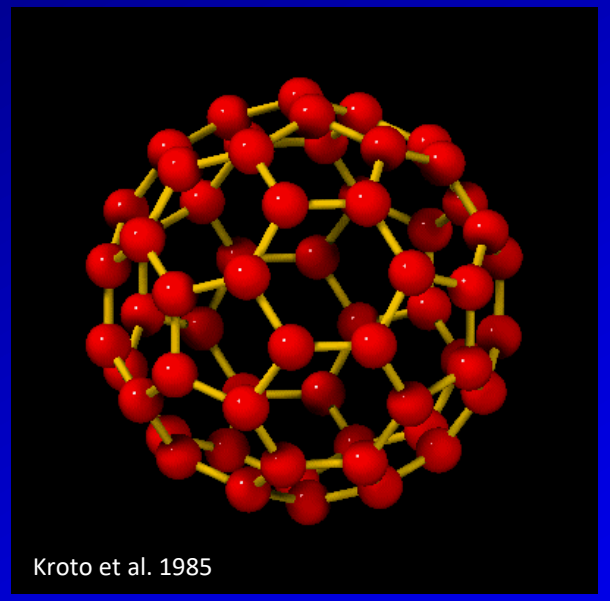
- At a given time, no perfect periodicity
- Periodicity is recovered on average

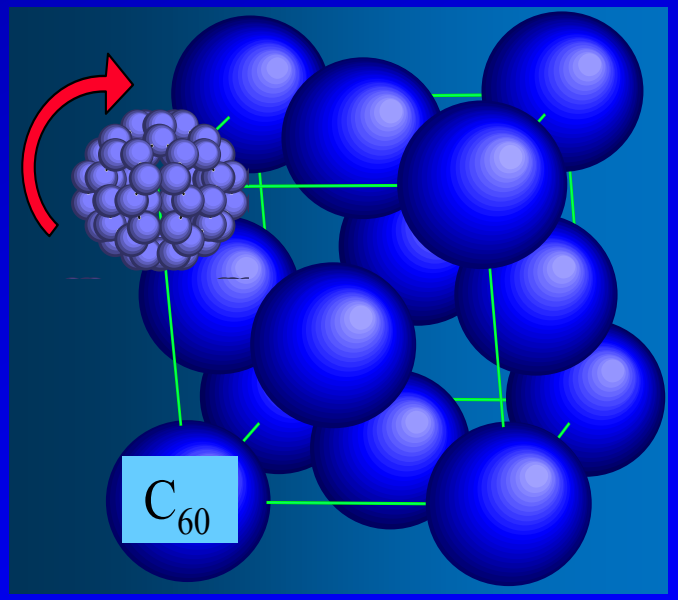


- Average structure is periodic
- Statistical average ↔ time average (Ergodic hypothesis)

Orientational disorder

- Ex : C_{60}, plastic crystals





T=300 K
fcc

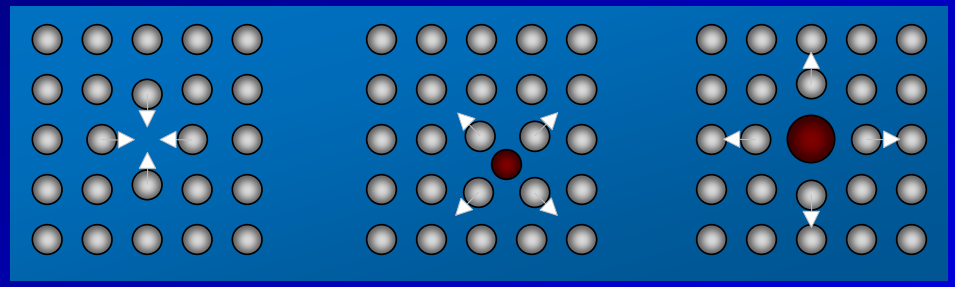
Real crystals: 2-Defects

www.techfak.uni-kiel.de/matwis/amat/def_en/makeindex.html

- **Topological defects**
  - Deformations which change the local atomic environment, such as the number of neighbors

Dimension 0

- Vacancies, intersticials



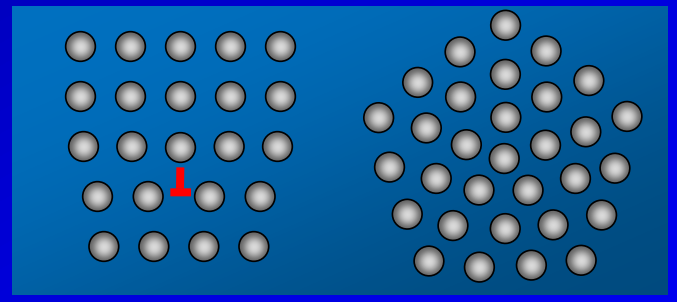
Vacancy
- Always present (2.10^{-4} Cu at 300 K)
- Diffusion, colored centers

Intersticial
- Plasticity

(Impurety)
- semi-cond. doping
- Colors of jewels
- Plasticity

Dimension 1

- Dislocations (metal plasticity)
- Disclinations (2D, liquid crystals)

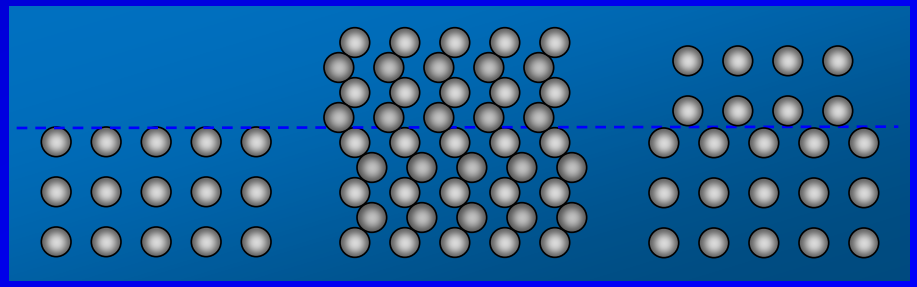


Dislocation

Disclination

Dimension 2

- Surfaces, stacking faults
- Grain boundaries, twins



Surface

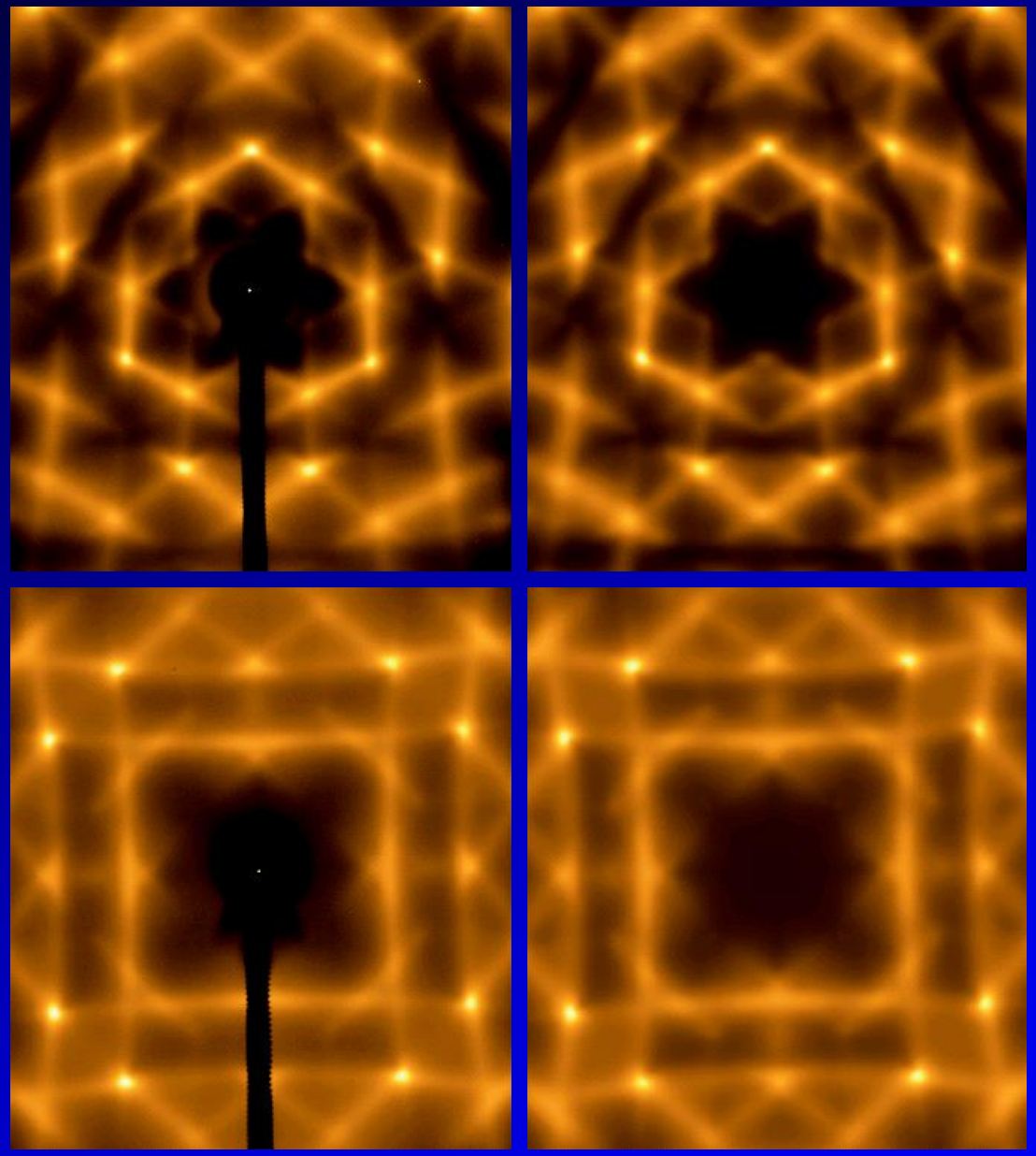
Stacking faults

Grain boundary

Thermal Diffuse Scattering (TDS)

Experiment

Simulation



Not elastic…

Si 300 K

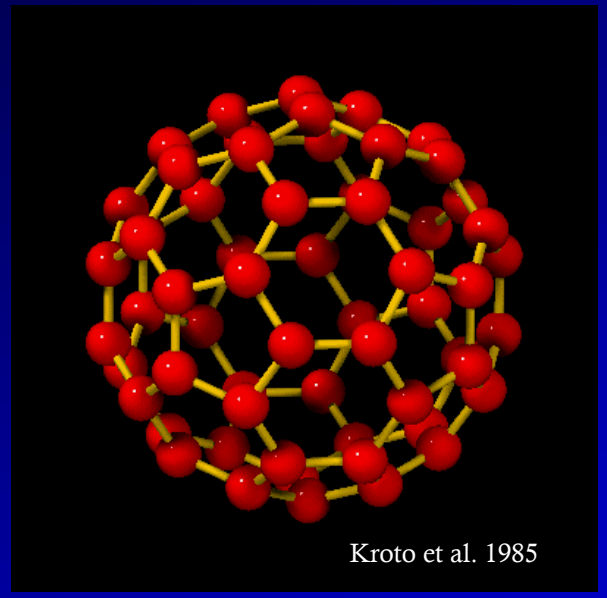
XRay // <111>

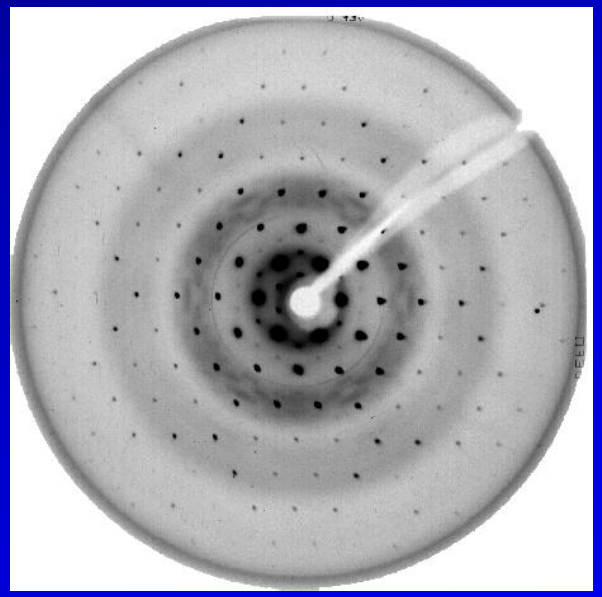
False colors,
Log scale.

X-Ray // <100>

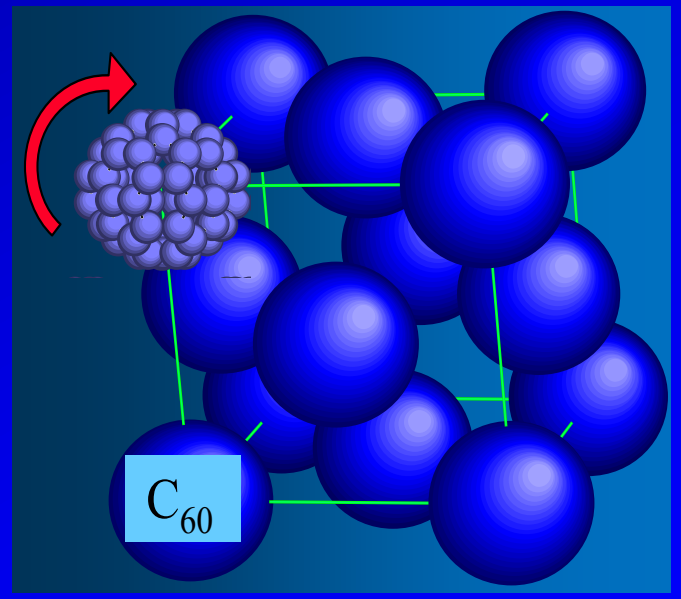
M. Holt, Phys. Rev. Lett 83, 3317 (1999)

C_{60} Crystal



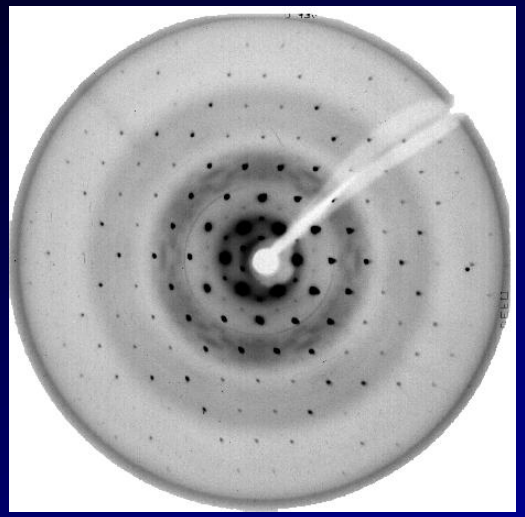


R. Moret, P. Launois, S. Ravy



T=300 K
c.f.c.

General effect of disorder



Bragg reflection

Diffuse scattering

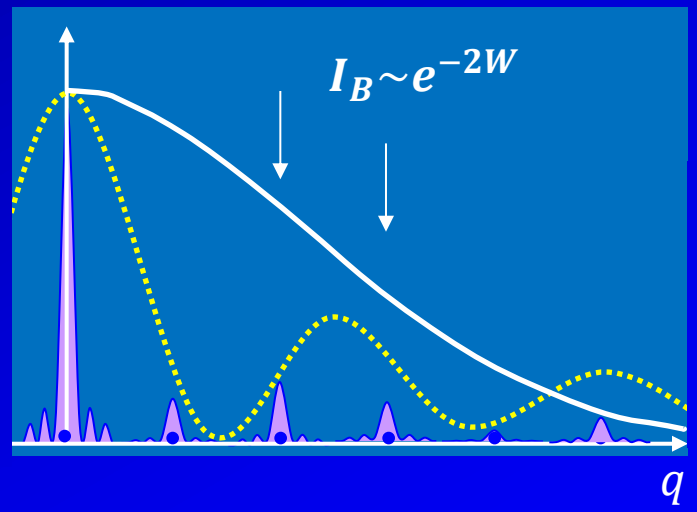
Decreases the Bragg intensity;

Appeance/Increase of ”diffuse scattering”

Very important case: thermal agitation

Debye-Waller factor

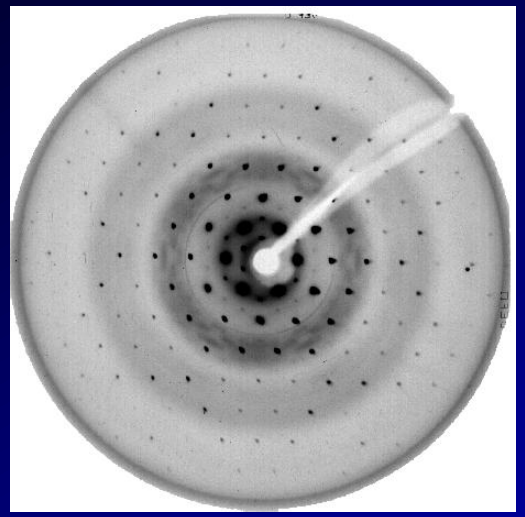
$$e^{-W(q,T)}$$



The larger the temperature
The larger the scattering vector

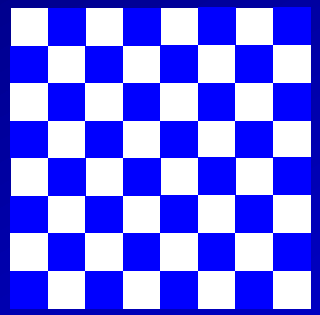
The larger the decrease of Bragg intensities

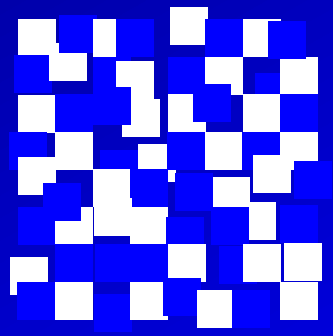
Calculation



Bragg reflection

Diffuse scattering





Complex scattering amplitude

$$A(\boldsymbol{q}) = \sum_{uvw} F_{uvw} e^{-iq\cdot \boldsymbol{R}_{uvw}} = \sum_{n} F_n e^{-iq\cdot \boldsymbol{R}_n}$$

Long-range order but
the structure factor depends on $\boldsymbol{R}_{uvw}$
and cannot be factorized

General expression of scattered intensity

$$I(\boldsymbol{q}) = A^*(\boldsymbol{q})A(\boldsymbol{q}) = \sum_{n,\,n'} F_n^* F_{n'} e^{-i\boldsymbol{q}\cdot(\boldsymbol{r}_{n'}-\boldsymbol{r}_n)}$$

$\langle \ldots \rangle$: space and time average

$$I(q) = N \sum_m \langle F_n^* F_{n+m} \rangle e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_m}$$

N = number of unit cells

Diffuse scattering

$$\Phi_n = F_n - \langle F_n \rangle$$

ϕ_n: **deviation from average value** F_n

$$\langle F_n^* F_{n+m} \rangle = |\langle F \rangle|^2 + \langle \Phi_n^* \Phi_{n+m} \rangle$$

$$I(\boldsymbol{q}) \cong |\langle F(\boldsymbol{q}) \rangle|^2 \sum_{hkl} \frac{|\Sigma(\boldsymbol{q} - \boldsymbol{Q}_{hkl}|^2}{v^2} + N \sum_m \langle \Phi_n^* \Phi_{n+m} \rangle e^{-i\mathbf{q}\cdot\mathbf{r}_m}$$

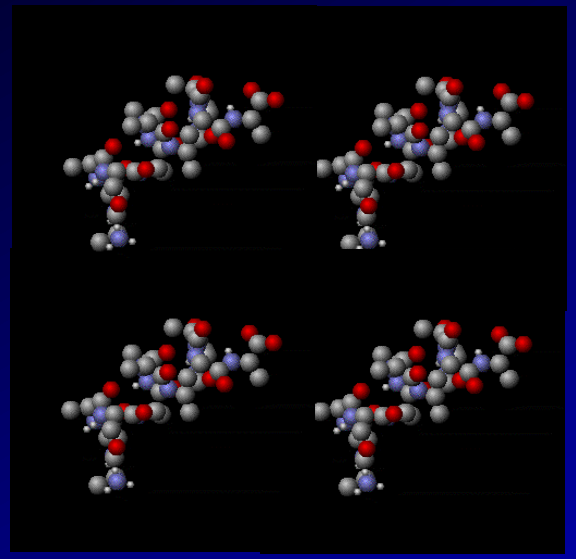
$I_D(\boldsymbol{q})$:
Diffraction

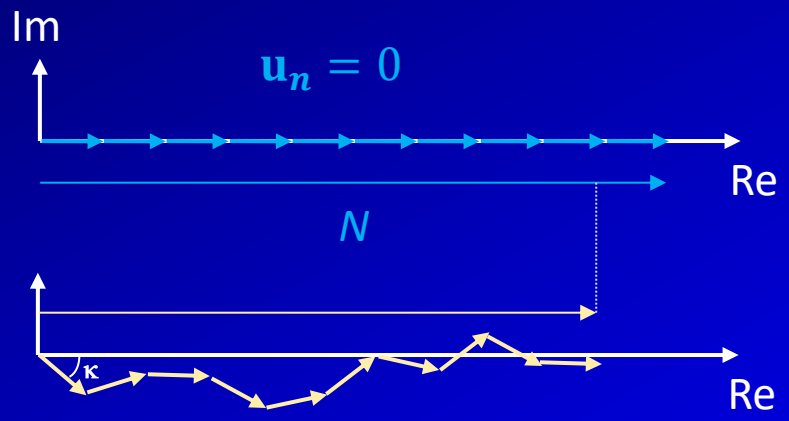
$I_{DD}(\boldsymbol{q})$:
Diffuse scattering

Average structure factor

Disorder (deviation from average)

Debye-Waller factor 1





T large, $\mathbf{u}_n$ large, ⇒ κ large

q large ⇒ κ large

One atom: $\langle F_n(\mathbf{q})\rangle = f\langle e^{-i\mathbf{q}\cdot\mathbf{u}_n}\rangle$

Harmonic crystal $\langle e^{-i\mathbf{q}\cdot\mathbf{u}_n}\rangle = e^{-1/2\langle(\mathbf{q}\cdot\mathbf{u}_n)^2\rangle} = e^{-W}$

$$I(\mathbf{q}) = N^2|\langle F_n(\mathbf{q})\rangle|^2 = N^2 f^2 e^{-2W}$$

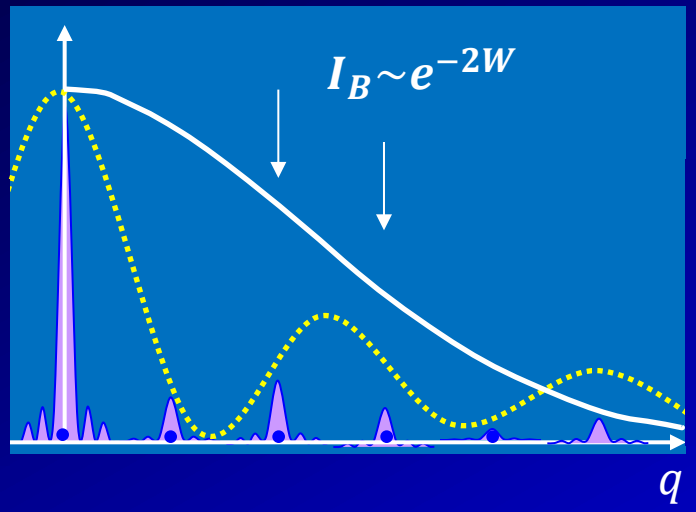
Intensity decreased by factor e^{-2W}

e^{-W}

is the Debye-Waller factor

The lost intensity goes in the TDS

Debye-Waller factor 2



Unit cell with *n* atoms in $\mathbf{r}_j$

$$\langle F_n(\mathbf{q})\rangle = \sum_j f_j e^{-W_j} e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

$$W_j = \frac{1}{2}\left\langle (\mathbf{q}\cdot\boldsymbol{u}_j)^2 \right\rangle = \frac{1}{2} q^2 \langle u_{jq}^2 \rangle$$

For isotropic vibrations

$$\langle u_j^2 \rangle = \langle u_{xj}^2 + u_{yj}^2 + u_{zj}^2 \rangle = 3\langle u_{jq}^2 \rangle$$

$$W_j = \frac{1}{6}\left(\frac{4\pi \sin\theta}{\lambda}\right)^2 \langle u_j^2 \rangle \equiv B_{j,T,iso}\left(\frac{\sin\theta}{\lambda}\right)^2$$

Diffraction allows one to get:

$$B_{j,T,iso} = \frac{8\pi^2}{3}\langle u_j^2 \rangle$$

Example 1: Lindemann criterion

Solide melts when the ”root mean square”:

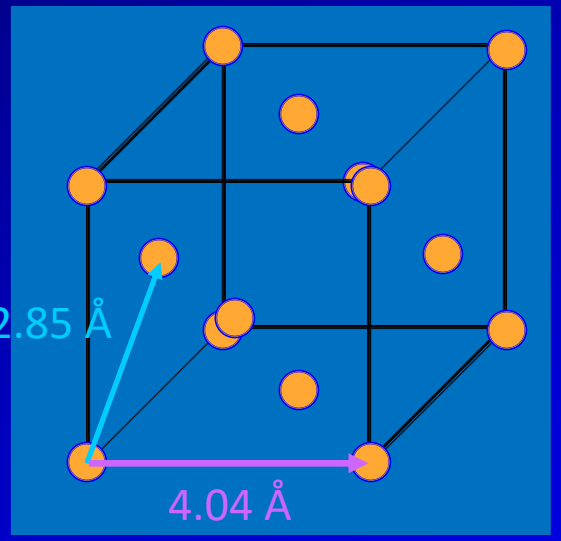
$$\sqrt{\langle u^2 \rangle} = 10\%\ d_{1^{st}\ neighbour}$$

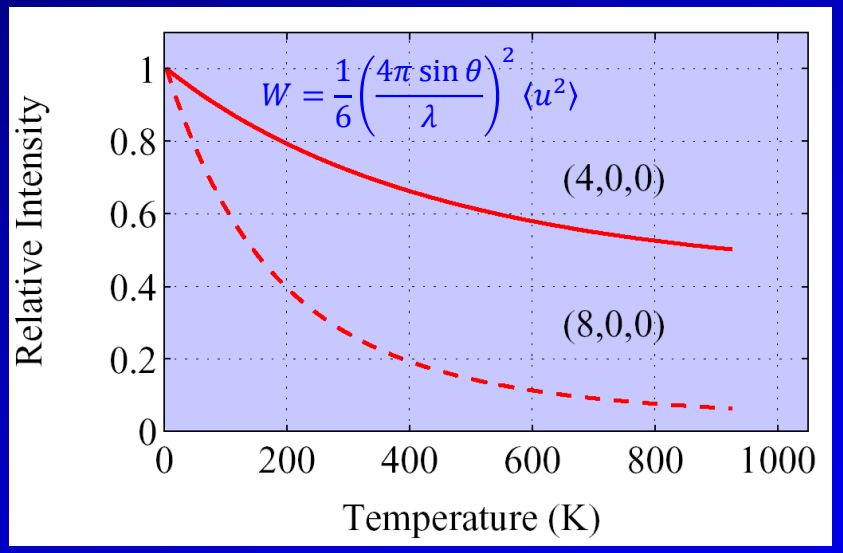
Aluminium (f.c.c.)

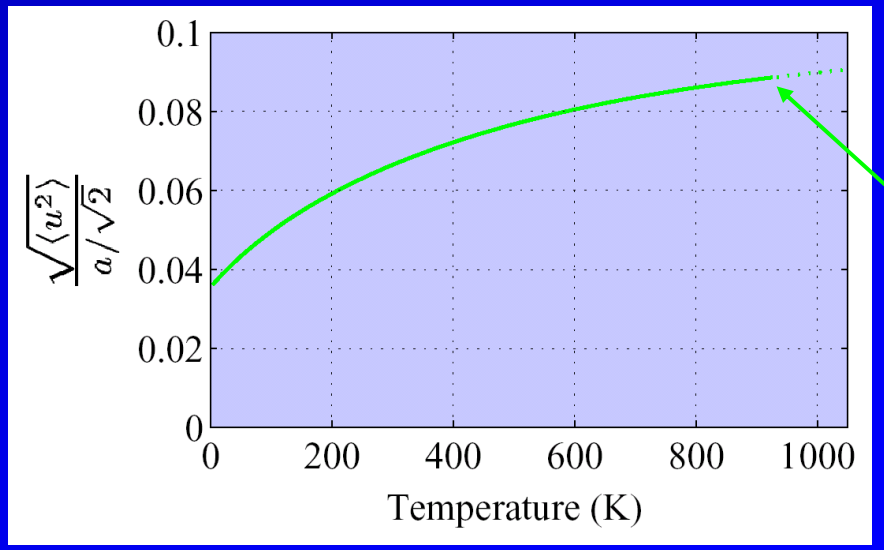
$a = 4.04$ Å

First neighbour

$\frac{a}{\sqrt{2}} = 2{,}85$ Å







Example 2:

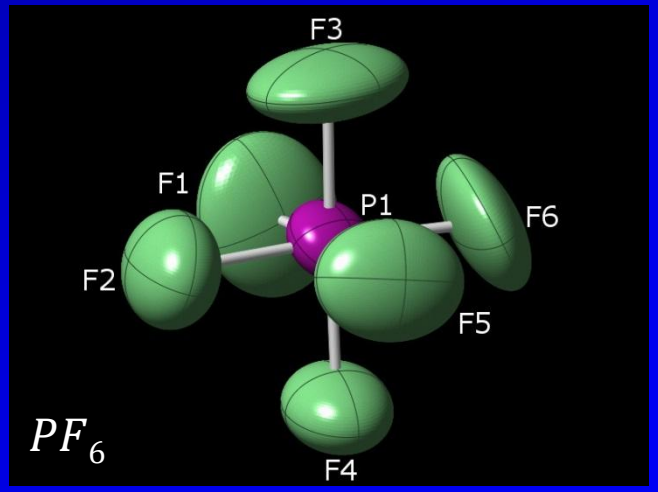
$$W_j = B_{j,T,iso}\left(\frac{\sin\theta}{\lambda}\right)^2$$

$$B_{j,T,iso} = \frac{8\pi^2}{3}\langle u_j^2\rangle$$

Simple metals: $\sqrt{\langle u^2\rangle} = 0,05 - 0,2$ Å

Organic compounds: $\sqrt{\langle u^2\rangle} = 0,5$ Å

Anisotropic *B*:
$\langle u^2\rangle$ **depends on the directions**



Thermal ellipsoids

3D-ΔPDF

Pair Correlation Function

$$P(\boldsymbol{r}) = FT^{-1}\left(I_{Tot}(\mathbf{q})\right) = \langle \rho(r) * \rho(-r) \rangle$$

Patterson

$$P_{Pat}(\boldsymbol{r}) = FT^{-1}\left(I_{Bragg}(\mathbf{q})\right) = \langle \rho(r) \rangle * \langle \rho(-r) \rangle$$

Difference: 3D-ΔPDF

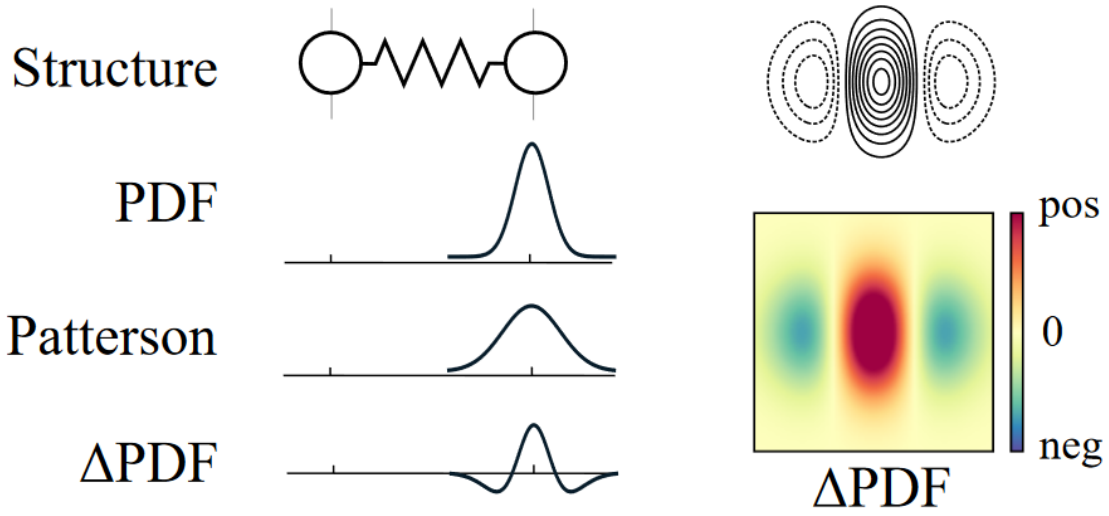
$$\Delta PDF(\boldsymbol{r}) = FT^{-1}\left(I_{Diff}(\mathbf{q})\right)$$

Now measurable in 3D

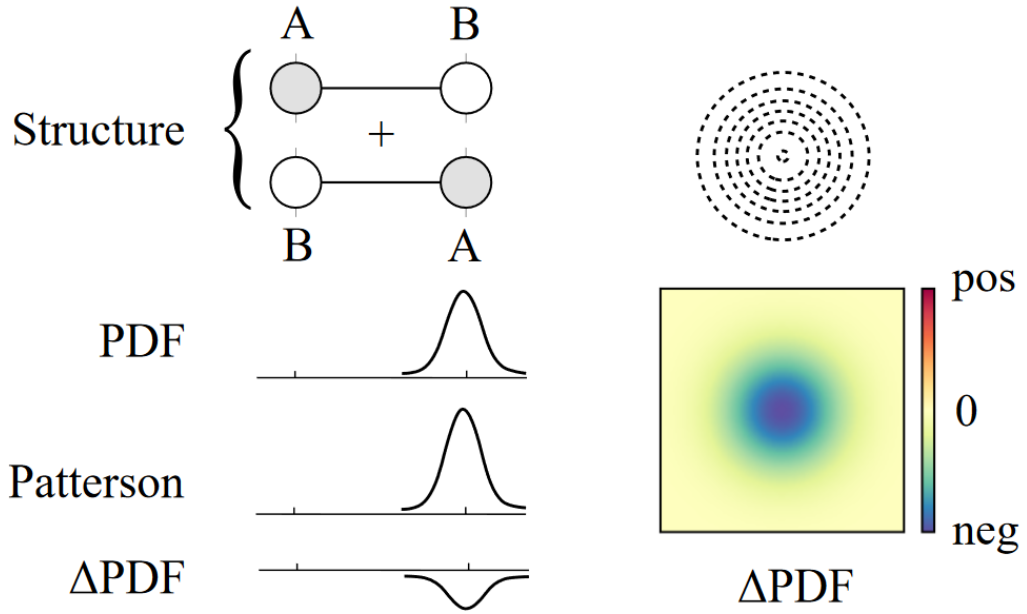
Examples

Each type of disorder has a signature in the 3D-ΔPDF

Displacement correlation

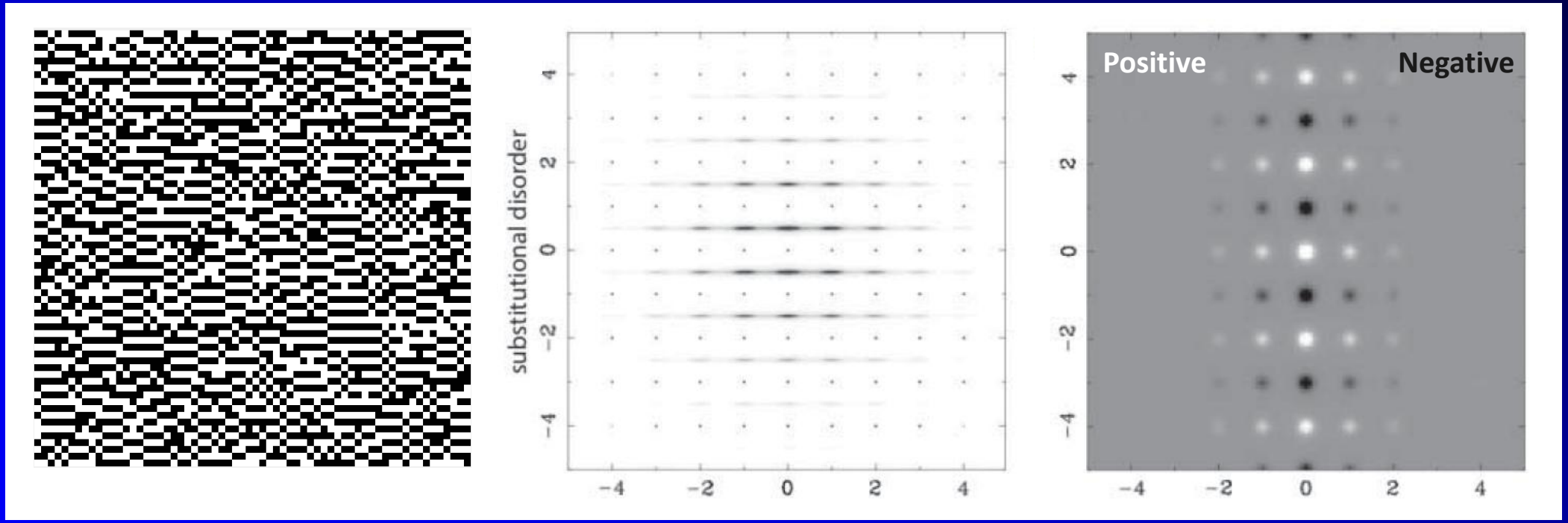


Substitutional correlation



From https://workshops.ill.fr/event/306/attachments/225/853/3DdPDF_Pair_distribution_function_analysis_for_single_crystals_Arkadiy_Simonov_.pdf

Example of short-range order



Local ordering

Total scattering

2D-ΔPDF
Substitution disorder (obviously)

T.R. Welberry & T. Weber (2016) One hundred years of diffuse scattering, Crystallography Reviews, 22:1, 2-78
Welberry TR. Diffuse X-ray scattering and models of disorder (Second edition). Oxford: Oxford University Press; 2022

The end!