Scattering
and
Diffraction

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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** $\boldsymbol{\psi} \sim \exp(i\boldsymbol{k} \cdot \boldsymbol{r})$	**Particle** $\boldsymbol{\psi} \sim \exp(i\boldsymbol{k} \cdot \boldsymbol{r})$
Energy E	$E = h\nu = hc/\boldsymbol{\lambda}$ $\lambda(\text{Å})=12398/E(\text{keV})$ $\lambda=1$ Å, E=12.4 keV ($\nu=10^{18}$ Hz)	$E=p^2/2m_n$ $\lambda(\text{Å})=0.286/E^{0.5}(\text{eV})$ $\lambda=1$ Å, E=81.8 meV .	$E=p^2/2m_e$ $\lambda(\text{Å})=12.265/E^{0.5}(\text{eV})$ $\lambda=1$ Å, E=150 eV ($\lambda=0.04$ Å, E=100 keV)
Momentum p	$\boldsymbol{p} = \hbar \boldsymbol{k}\ (= \frac{h\nu}{c})$	$\boldsymbol{p} = \hbar \boldsymbol{k}\ (= m\boldsymbol{v})$	$\boldsymbol{p} = \boldsymbol{hk}\ (= \boldsymbol{mv})$
$\frac{k_B T}{E}$ **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]

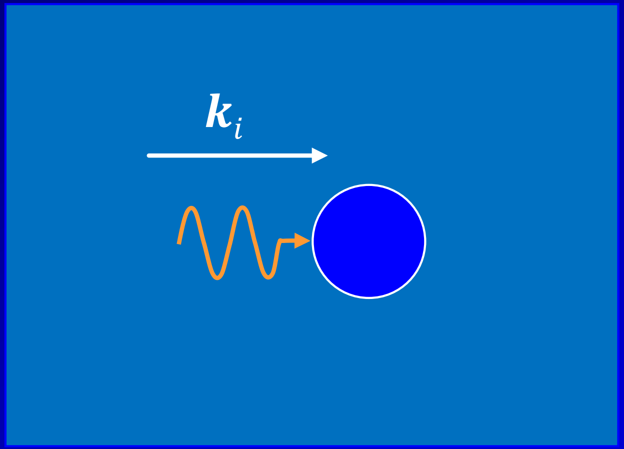
A-2 Absorption and scattering

Interaction of Radiation with Matter

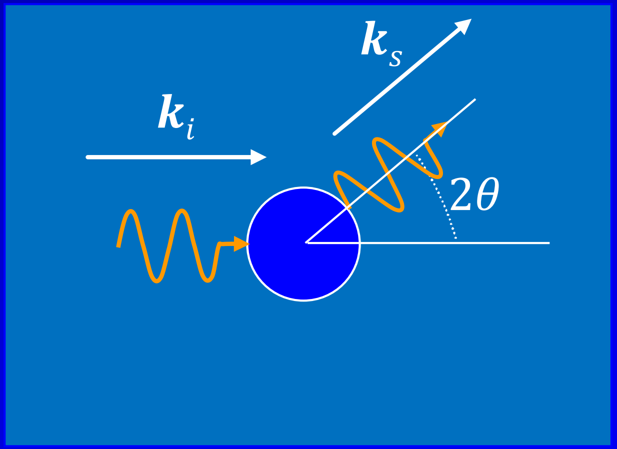
« Element of modern x-ray physics »
J. Als-Nielsen et D. McMorrow

Two process of interaction

Absorption and scattering



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



2θ: scattering angle
$(\boldsymbol{k}_i, \boldsymbol{k}_s)$ define
the scattering plane

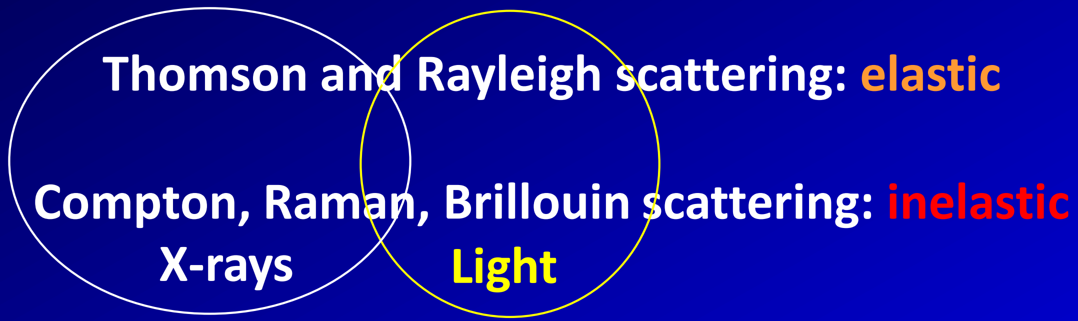
The particle/wave
changes its
direction of propagation
(interference, diffraction)

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

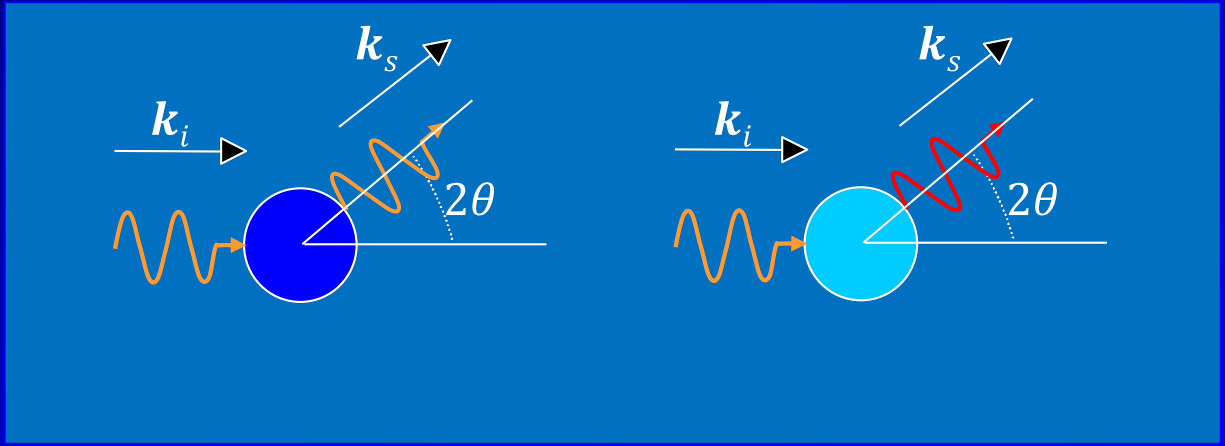


Thomson and Rayleigh scattering: elastic

Compton, Raman, Brillouin scattering: inelastic

X-rays

Light



Target does not change state

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

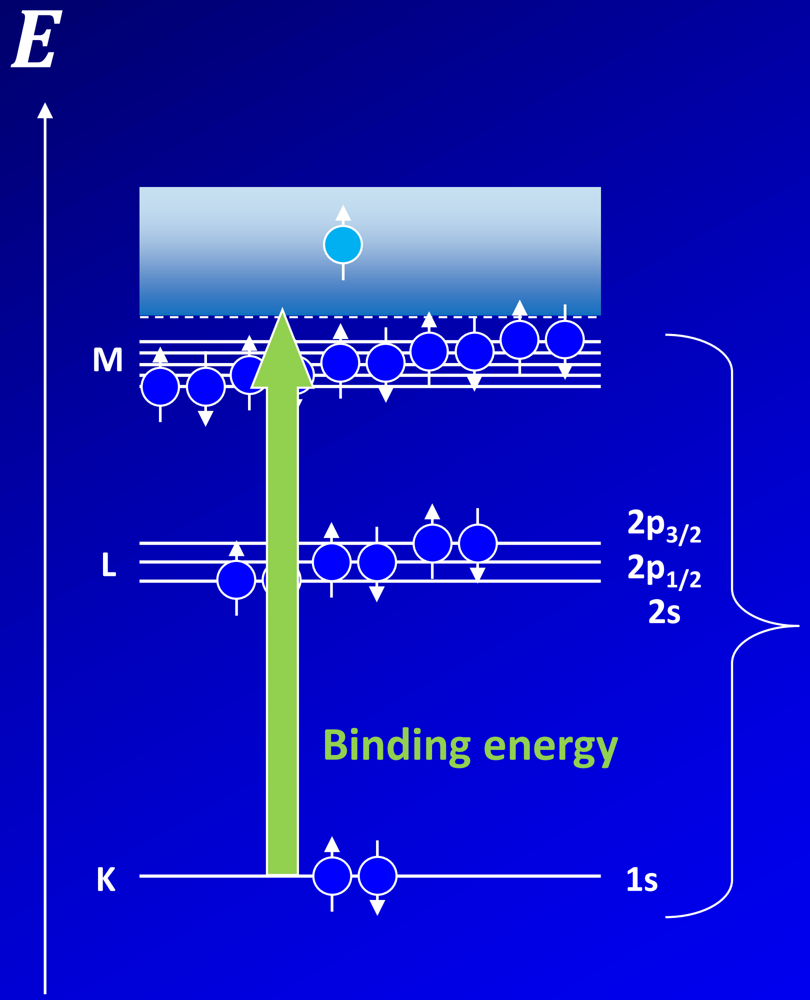
Target does change state.

$$\boldsymbol{k}_i \neq \boldsymbol{k}_s$$

Electrons in Atoms

Vacuum
(continuum)
Free electrons

Core level
(discrete)
Bound electrons



Examples of binding energies:

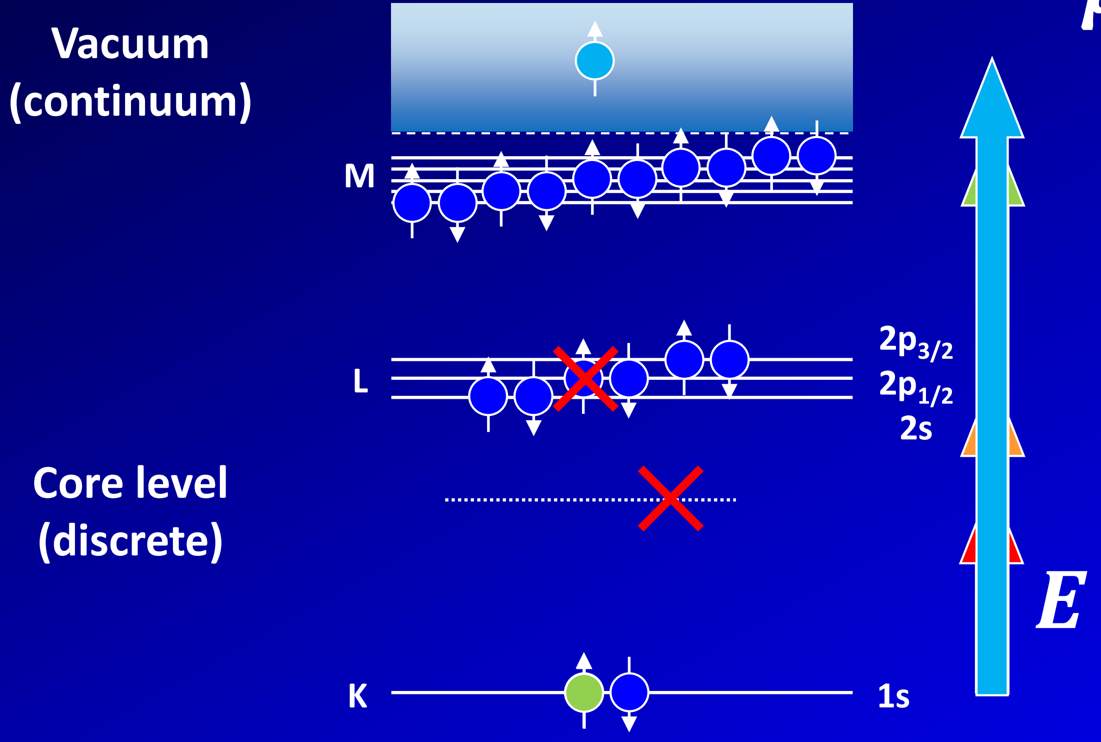
E_K(Ag) = 25 keV
E_K(Fe) = 7 keV
E_K(Ar) = 3.2 keV

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

Absorption: increase of coefficient μ

Yes!

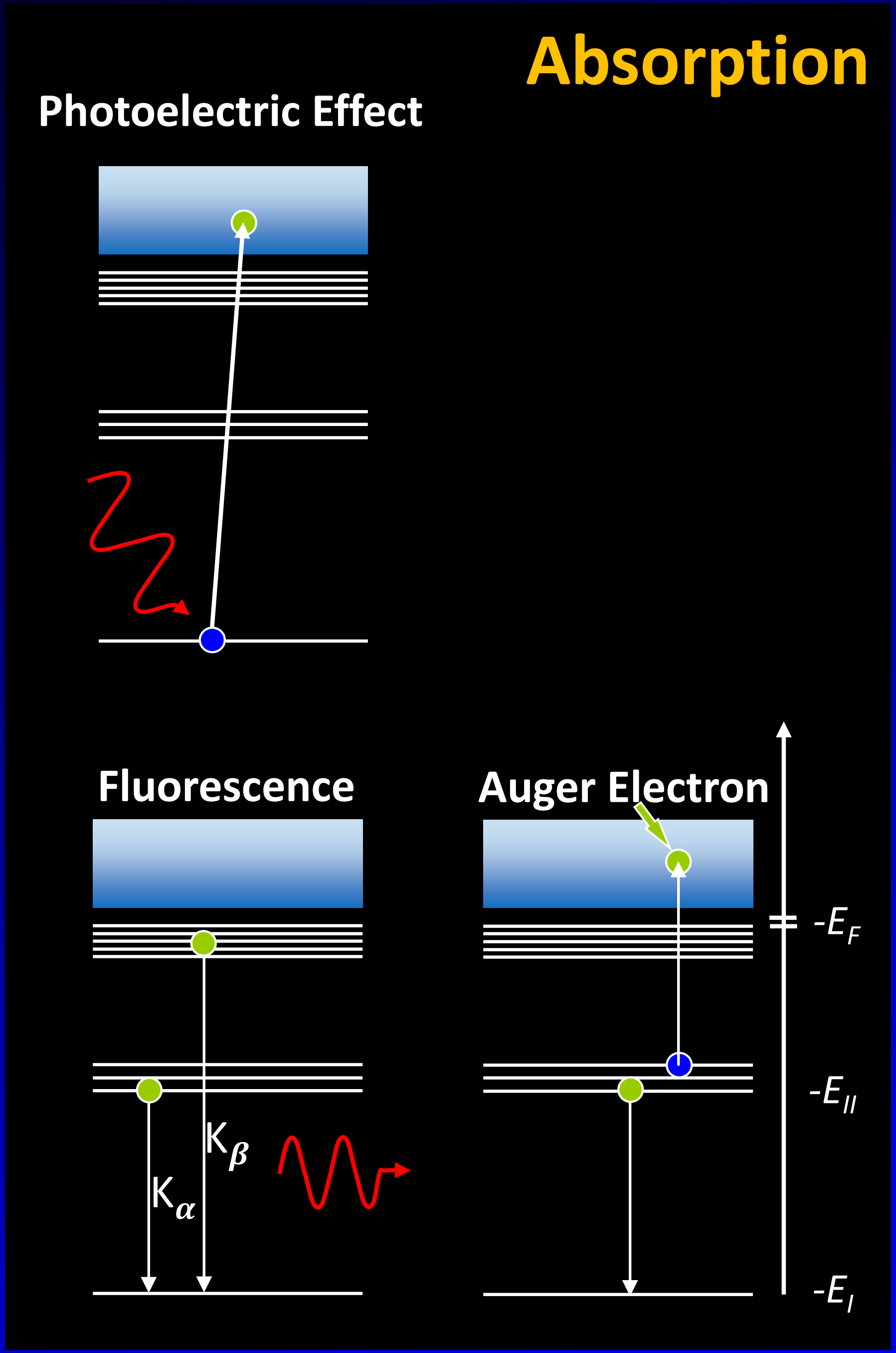
Photo-electron



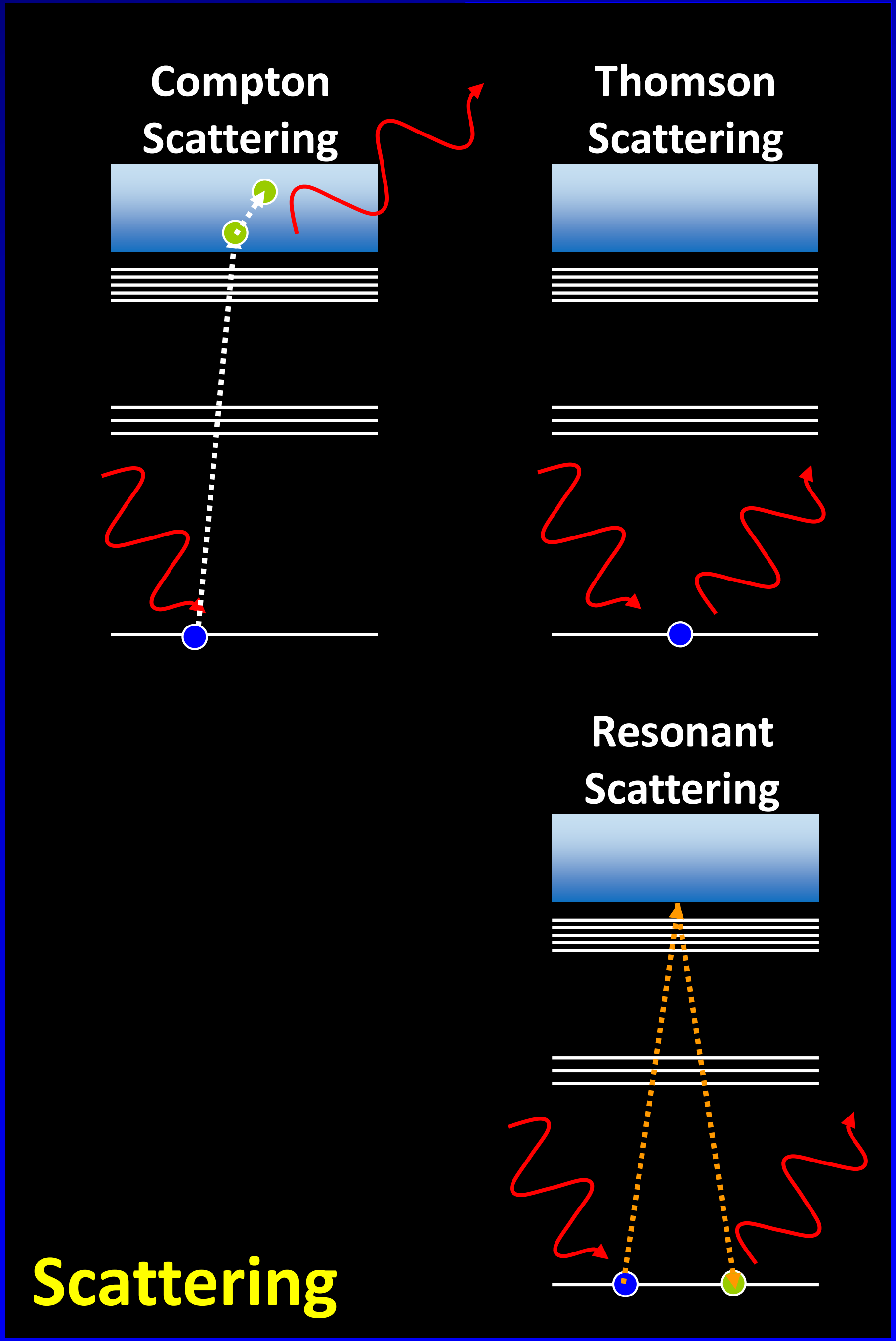
X-ray
Absorption
Spectroscopy

Element specific
K-edge, L-edge, etc.

Absorption



Scattering



Cross sections

Scattering differential cross section

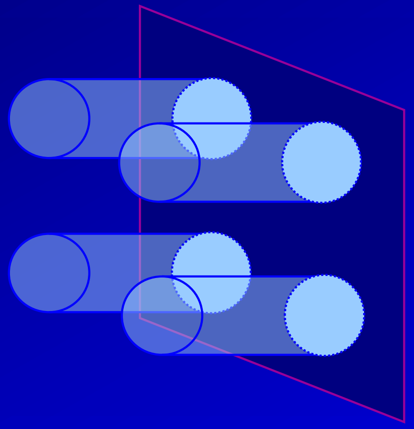
$$dN_s = \phi\;\Delta\Omega\,\frac{d\sigma}{d\Omega}$$

Incident Flux:
(Particle/s/cm^2)

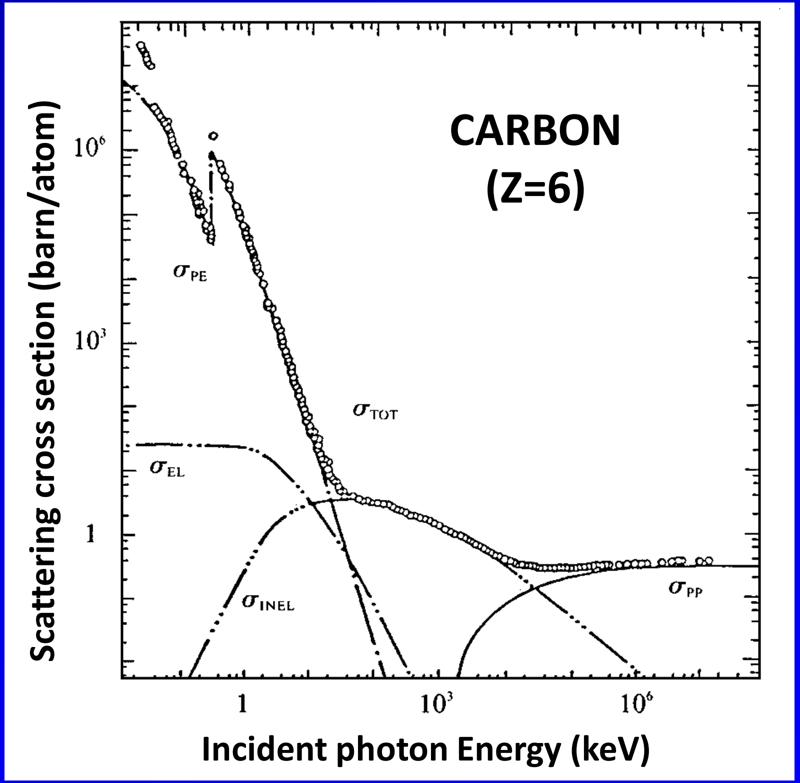
Absorption cross section

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

Measurable quantities



Unit: the barn (10^{-28} m^2)

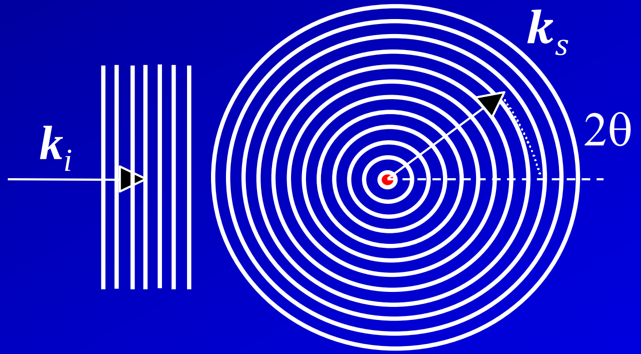


Scattering cross section

- **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

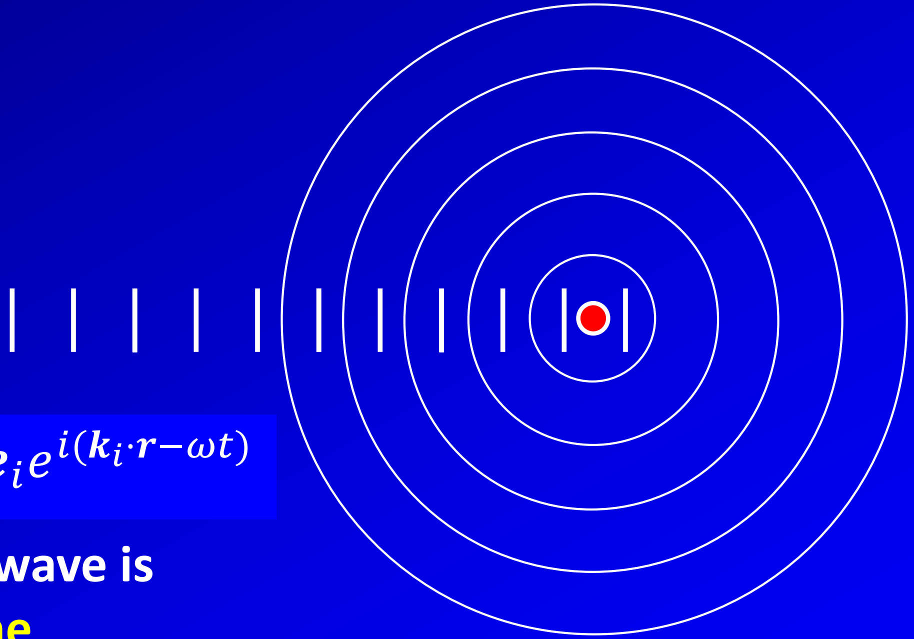
Incident and scattered photons

$$\hbar\omega_i = \hbar\omega_f$$

$$k_i = k_s = \frac{2\pi}{\lambda}$$

Scattered wave is
spherical

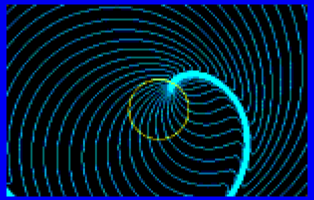
$$\boldsymbol{E}_s(r,t) = -E_0\boldsymbol{e}_s\frac{b}{r}e^{i(k_s r-\omega t)}$$



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

Incident wave is
plane

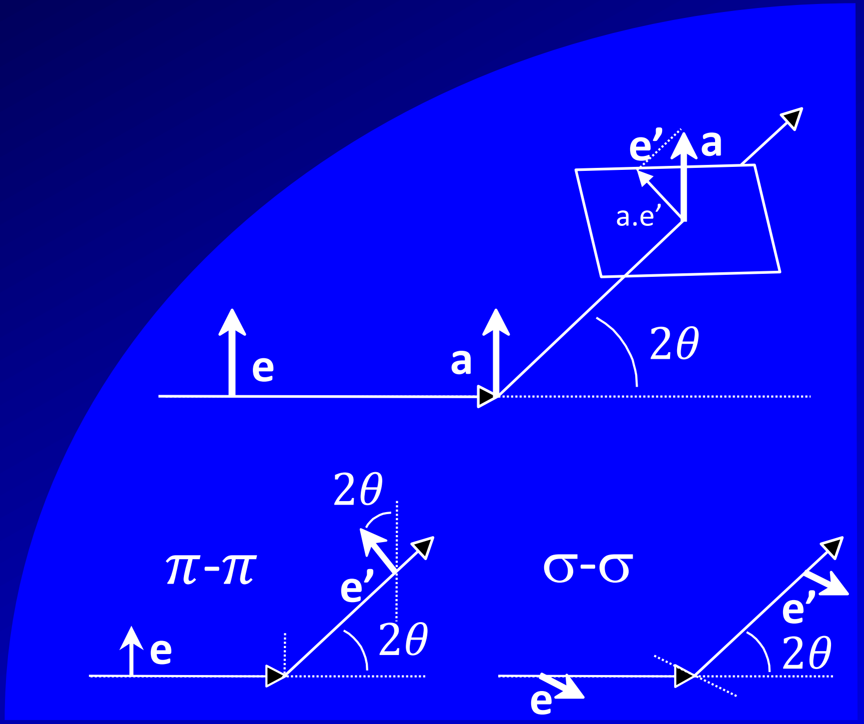
Oscillating charge



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:

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

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

- 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)

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

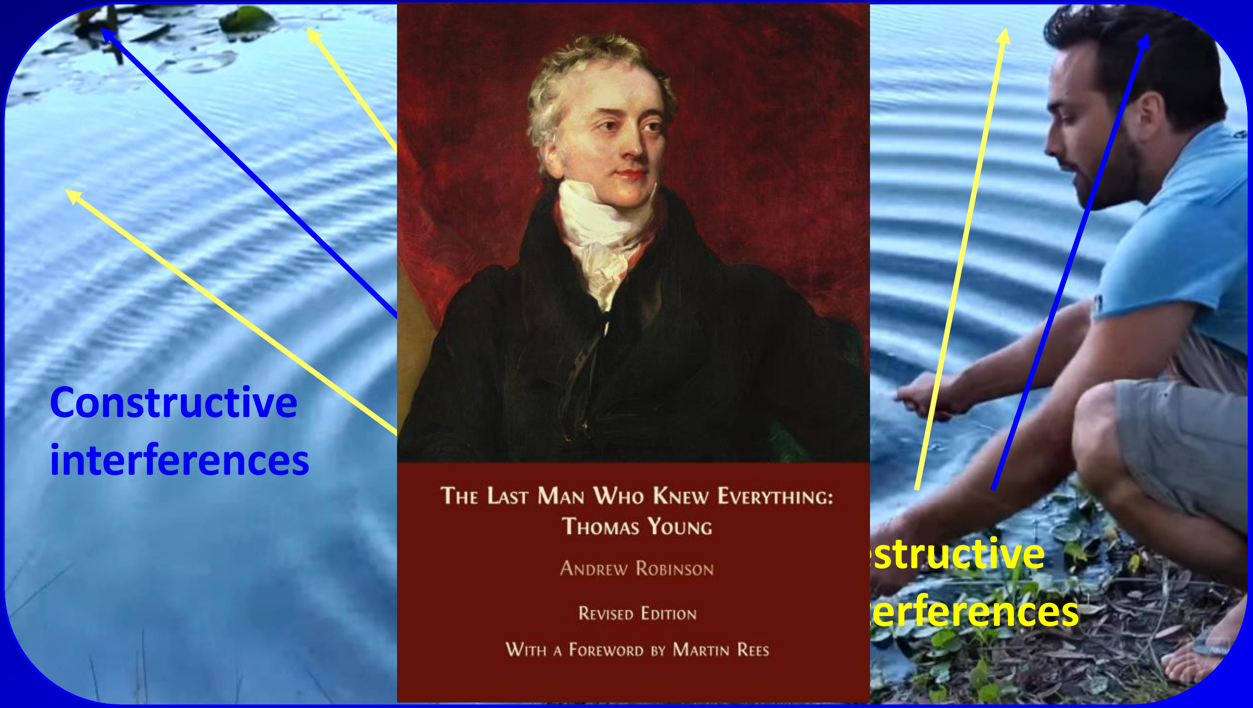
- For a free electron: $\sigma = 4\pi r_e^2 \sim 1\ barn$

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



The Last Man Who Knew Everything:
Thomas Young

Andrew Robinson

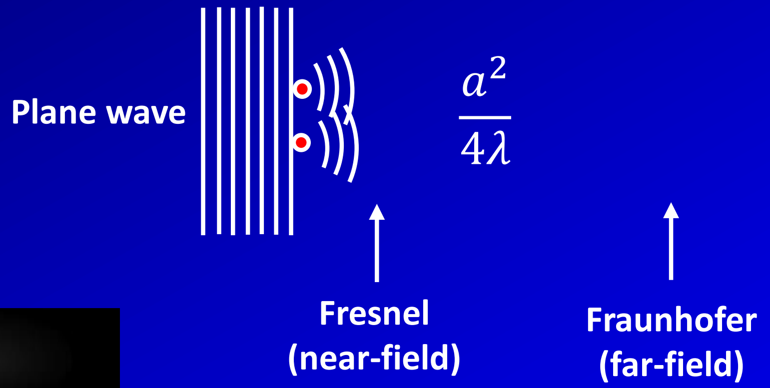
Revised Edition

With a Foreword by Martin Rees

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

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

Interferences

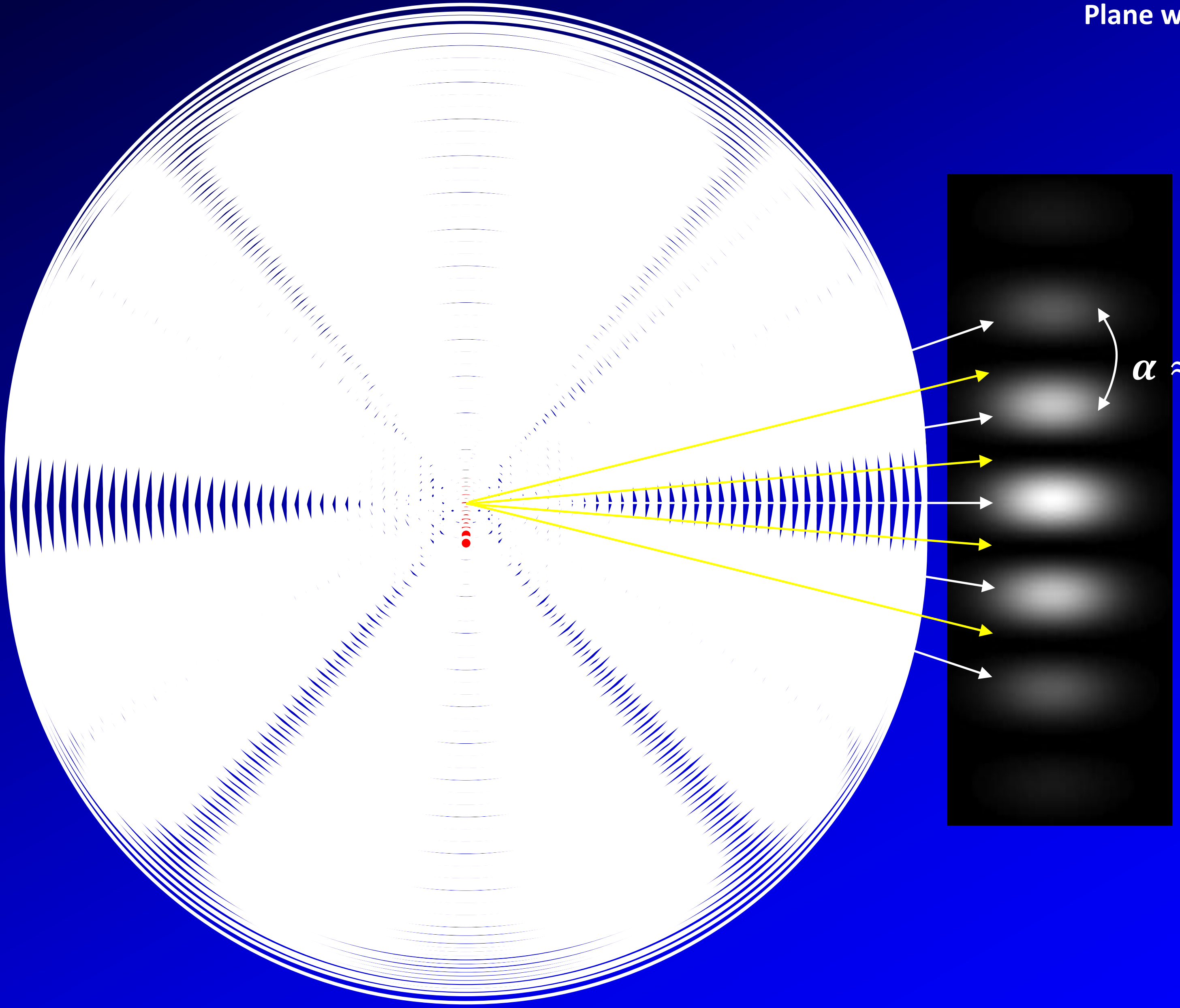


Plane wave

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

Fresnel
(near-field)

Fraunhofer
(far-field)



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

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

Definitions

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

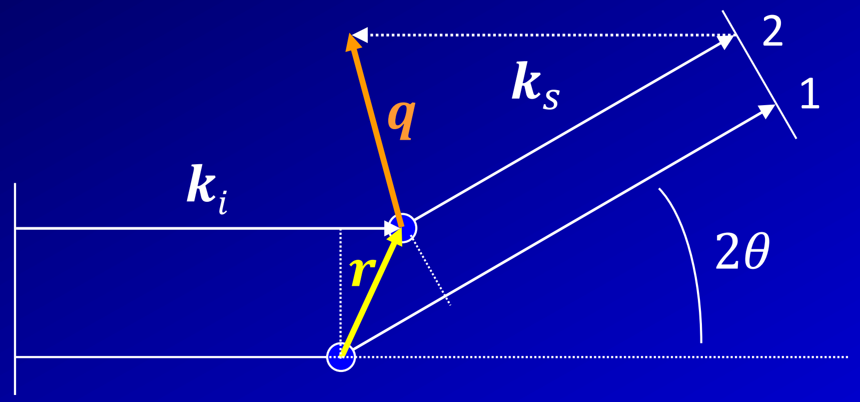
$\boldsymbol{k}$: wave vector ($k = 2\pi/\lambda$)

$\boldsymbol{\omega}$: 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:

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

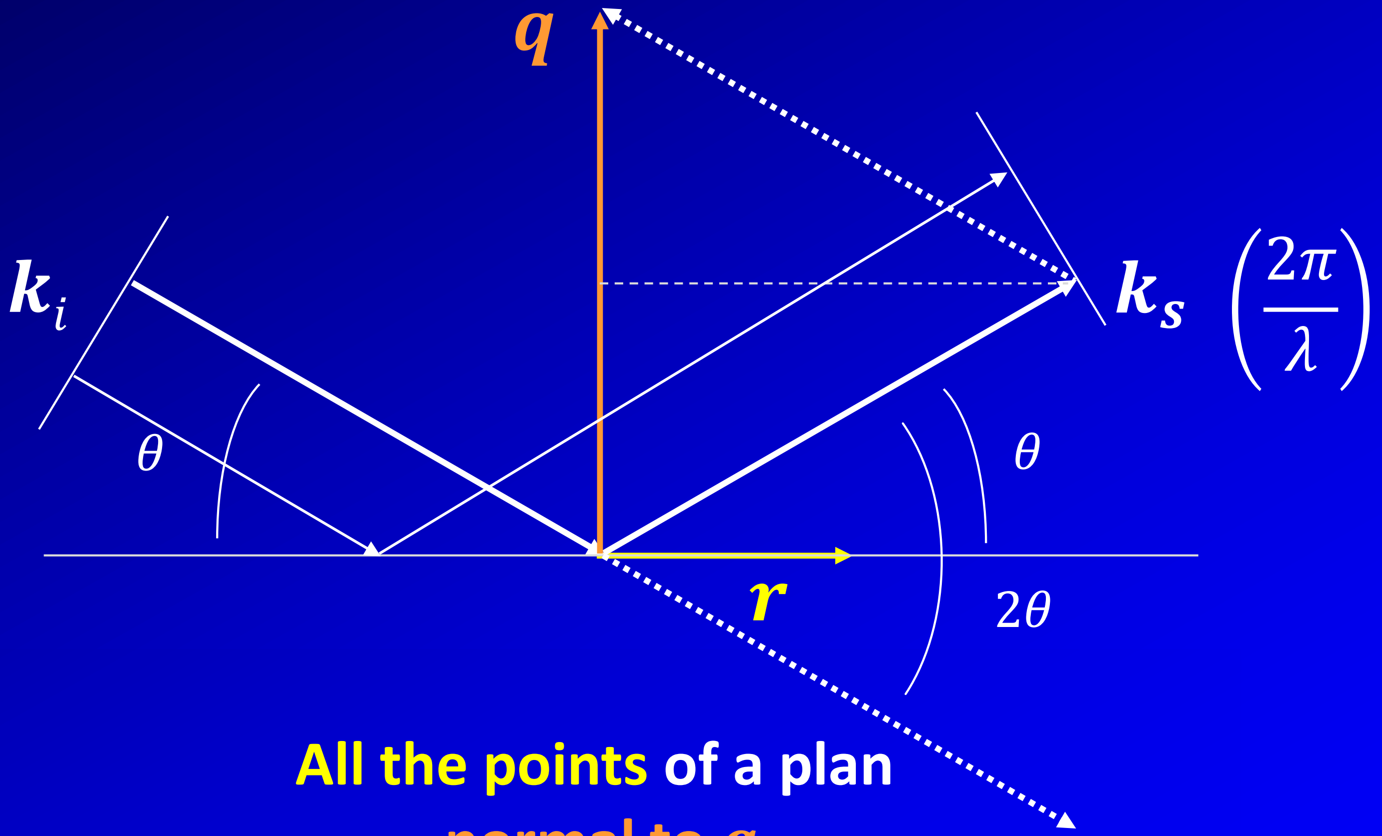
Only depends on the:

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 $\boldsymbol{q}$ scatter in phase

Expression of the scattered wave

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

In practice, the complex exponential notation is used

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

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

$\boldsymbol{a}$ **is the complex amplitude**

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

The complex amplitude

$$a = A_1 e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_1} + A_2 e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_2} + \cdots$$

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)

$$a = \sum_{\boldsymbol{i}} \dots e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_i}$$

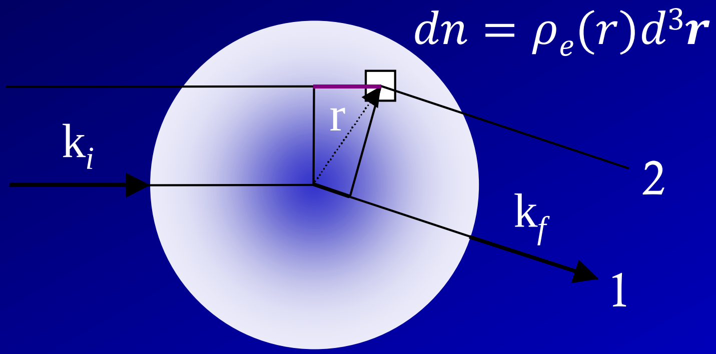
or Fourier transform (continuous case)

$$\boldsymbol{a} = \int \dots e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, d^3\boldsymbol{r}$$

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^3r

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

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

- Atomic scattering factor

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

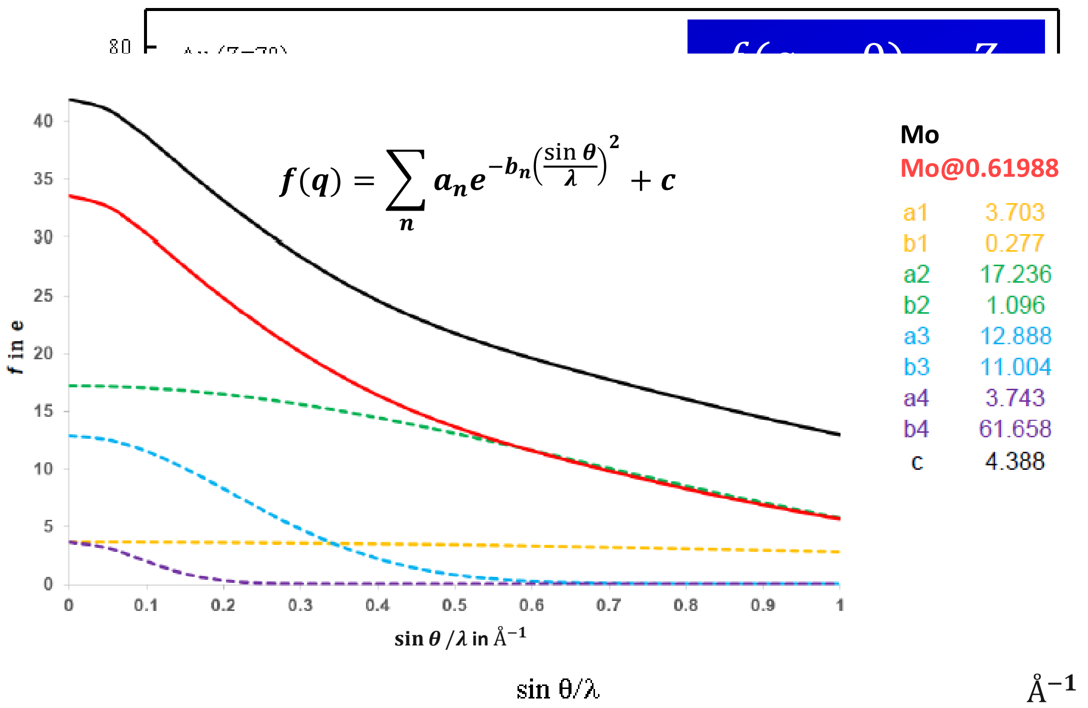
$\rho_e(r)$ is the electron density of the atom
q scattering vector

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]



$$f(q) = \sum_n a_n e^{-b_n\left(\frac{\sin\theta}{\lambda}\right)^2} + c$$

Mo
Mo@0.61988

a1	3.703
b1	0.277
a2	17.236
b2	1.096
a3	12.888
b3	11.004
a4	3.743
b4	61.658
c	4.388

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

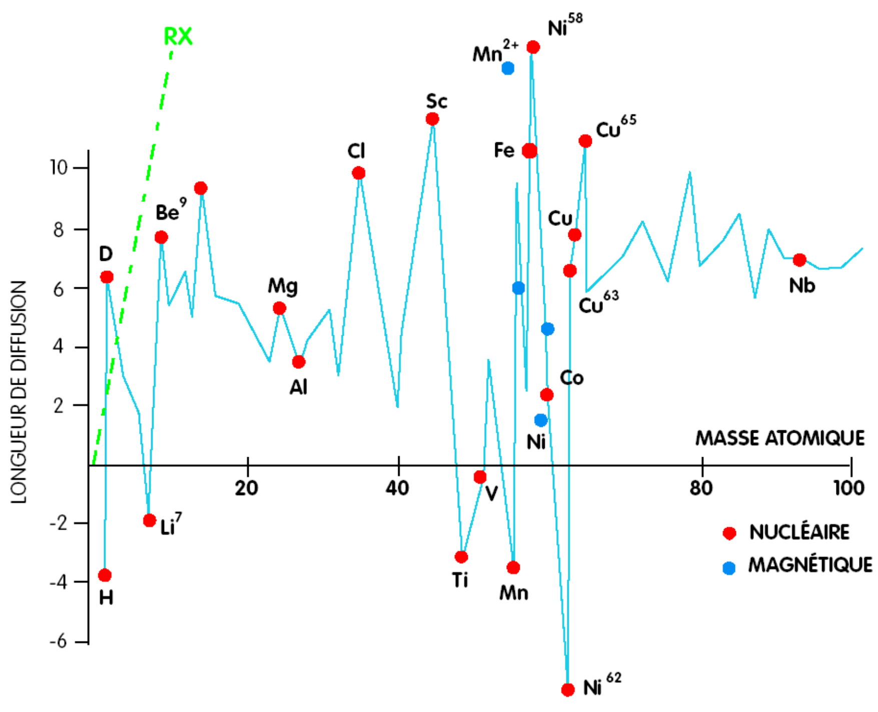
Neutron scattering length

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

Fermi pseudo potential
Short range (fm).

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

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



- 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...

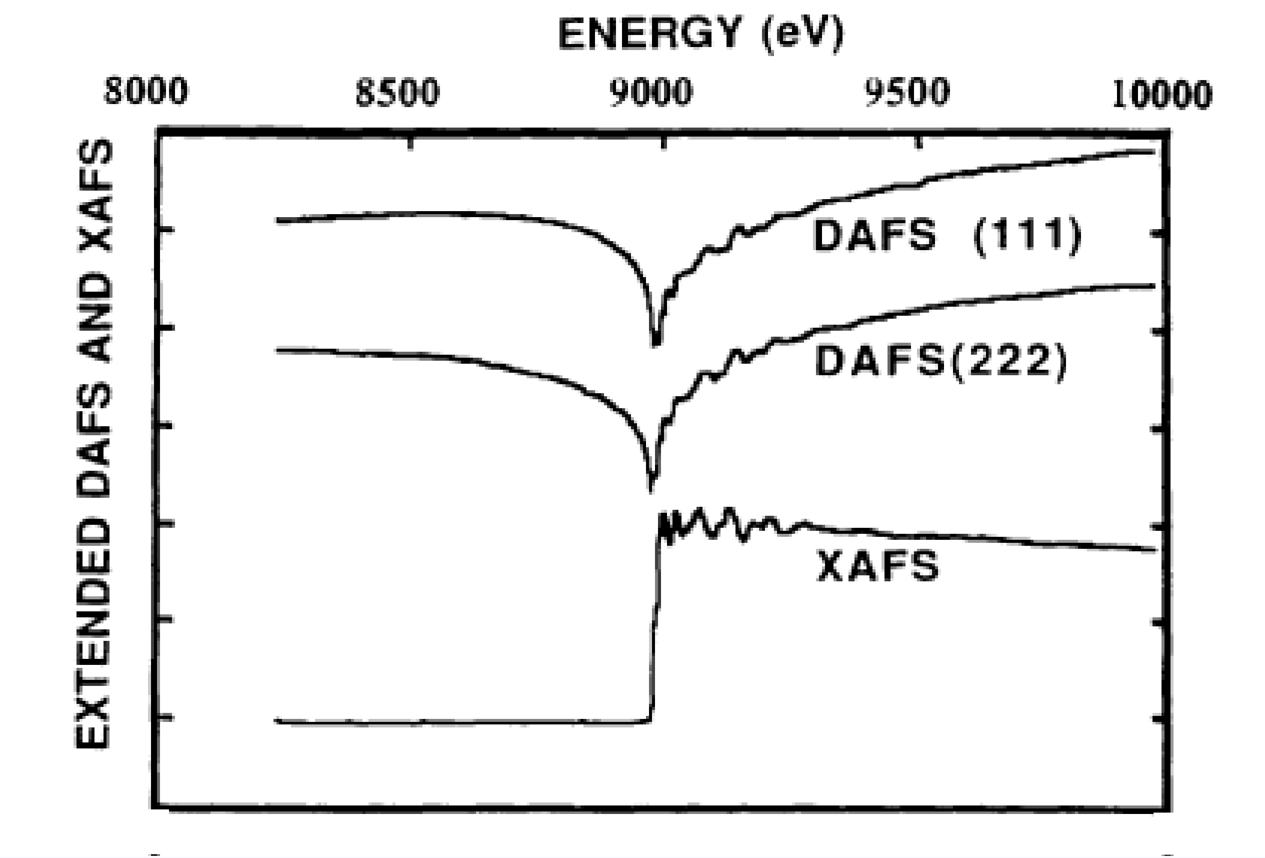
But!...

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)

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

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

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

Both are related by the Kramers-Kronig relations

Resonant scattering

More important with Synchrotron radiation

Classical model: damped oscillator

Restoring force mw_0^2r, friction $-Kv$

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

With $\boldsymbol{r} = \boldsymbol{r}_0\boldsymbol{e}^{-i\omega t}$

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

The scaterred field writes

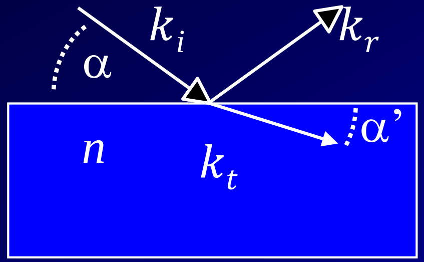
$$\boldsymbol{E}_d(\boldsymbol{r}) = \frac{\boldsymbol{e}}{4\pi\varepsilon_0 c^2 r}(a(t - r/c)\cdot\boldsymbol{e}')\boldsymbol{e}'$$

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

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:

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

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

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

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

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

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

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''

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

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

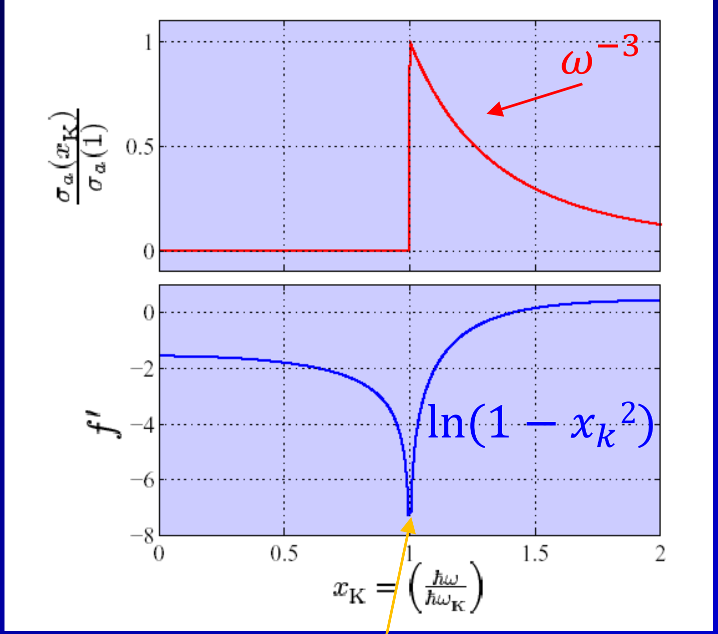
Once you have measured one, you can calculate the other one.

P is the Cauchy principal value

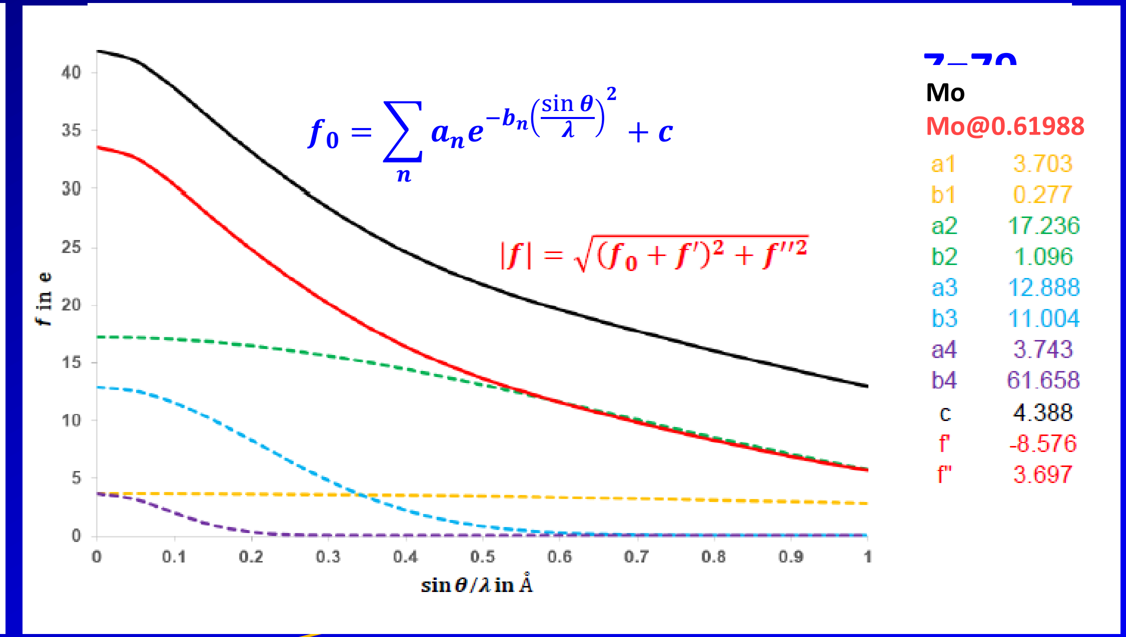
$$\lim_{\varepsilon \to 0} \int_{\omega-\varepsilon}^{\omega+\varepsilon} \ldots$$

Kramers-Kronig relation

Theoretical calculation with 2 K electrons



KK from absorption



Mo

Mo@0.61988

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b1	0.277
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a4	3.743
b4	61.658
c	4.388
f'	-8.576
f"	3.697

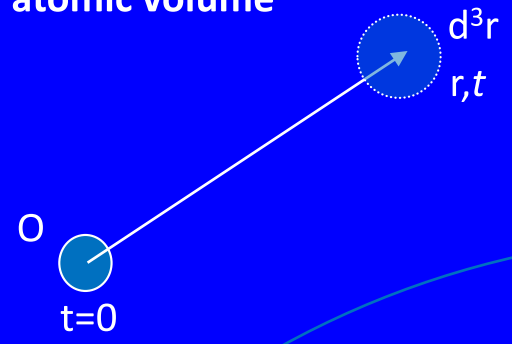
Corrections can be very important
close to an edge
(see the example of Au L-edges)

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 $g(\boldsymbol{r})$ (PDF)

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

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

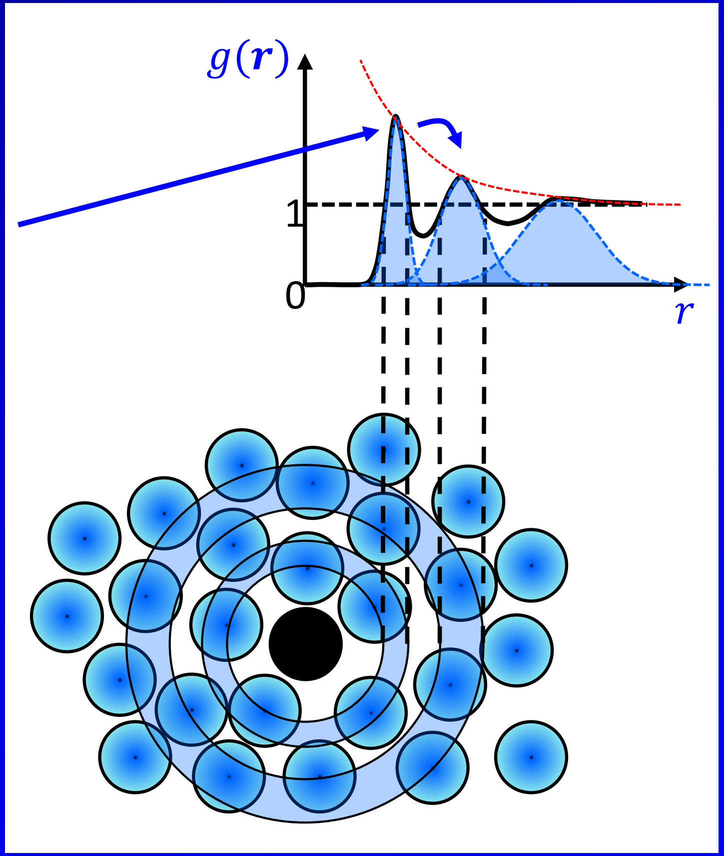
FT of $g(r)$ can be obtained by X-ray diffraction

Density-density correlation function:

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

Pair distribution function

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



Peaks:
First neighbour
Second neighbour
etc.

Peak width:
Distance fluctuation

Peak integral:
Number of neighbours

Three types of order

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

- Large distance behaviour of $g(\mathbf{r})$ defines three types of order:

Short-Range Order (SRO)

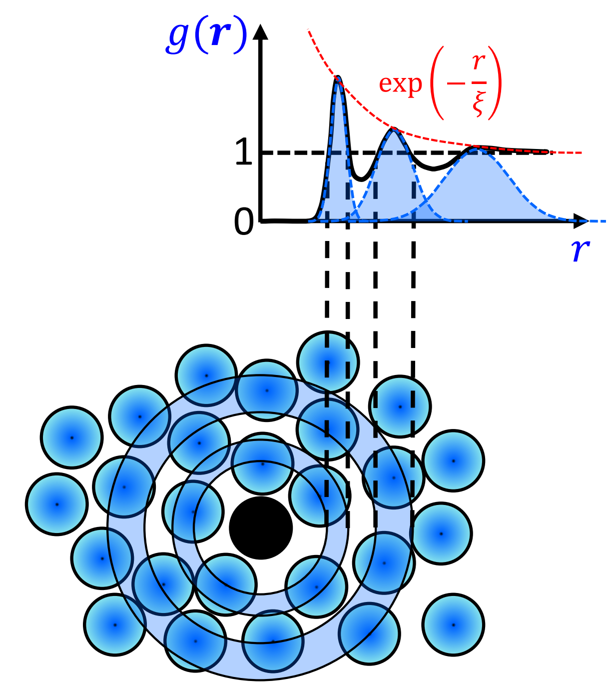
- $g(\mathbf{r}) \sim exp\left(-\frac{r}{\xi}\right)$
- ξ : correlation length
- Ex: glass, liquids
- Maximum order in 1D

Quasi Long-Range Order (QLRO)

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

Long-Range Order (LRO)

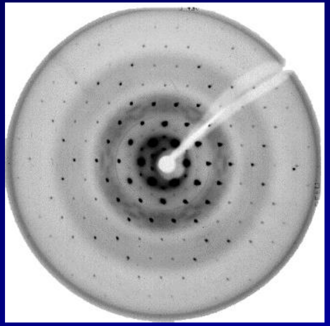
- $g(\mathbf{r})$ has no limit
- Ex: Crystals
- Bragg peaks



Experimental evidence of order

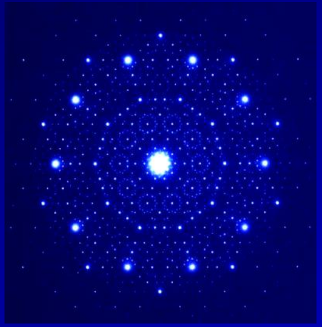
Long-range Order: diffraction

X-rays



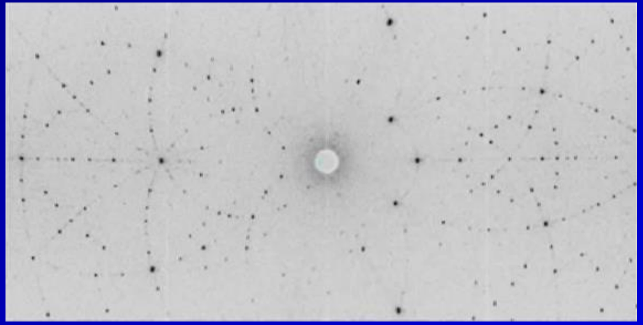
C_{60} crystal

Electrons



Quasi-crystal

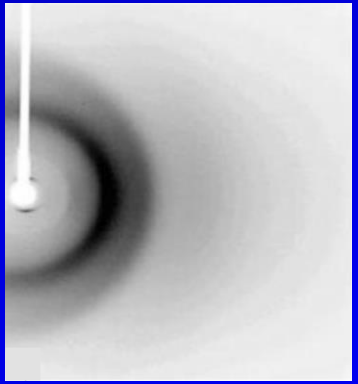
Neutrons



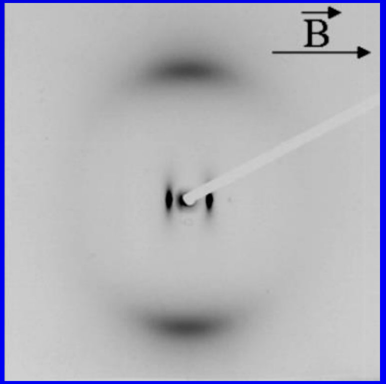
Existence of Bragg reflections
Widths are resolution limited

Otherwise: diffuse scattering

Continuous Scattering



Water



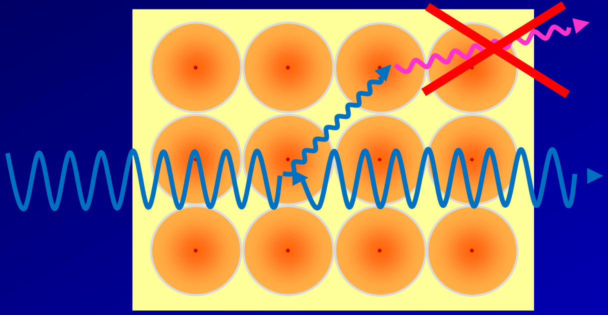
Smectic liquid crystal

C-2 Scattering amplitude

Scattering by an arbitrary structure

Kinematic approximation

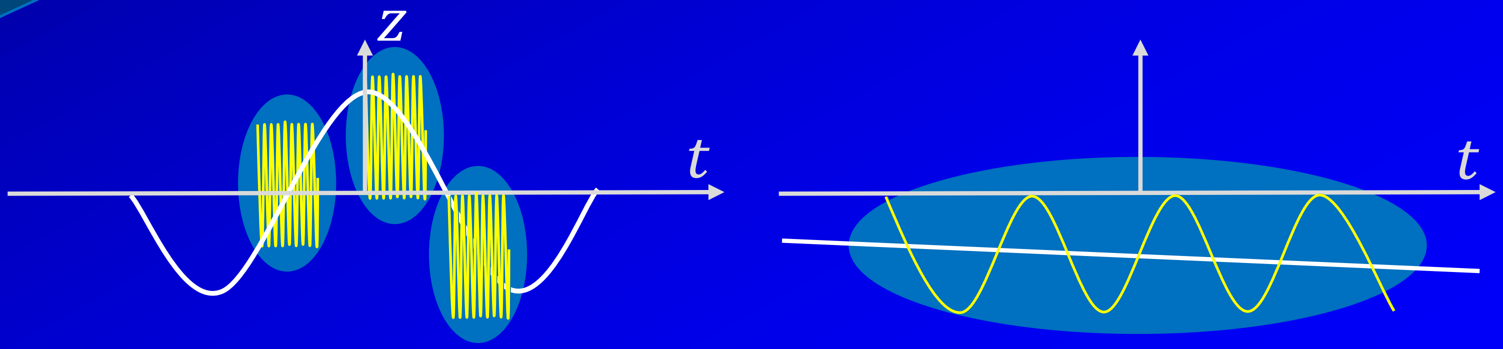
- Intensity of the diffracted beam much samller than the incident beam energy
- No multiple diffraction, no intensity loss



- Approximation is valid for small crystals (mosaic)
- 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

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

- 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

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

Total scattering cross section

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

Scattering Intensity

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

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

Scattering function

Scattering function $S(q)$ is:

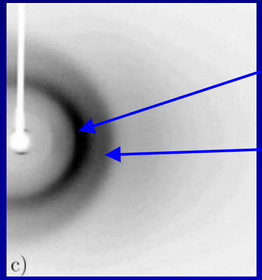
$$S(\boldsymbol{q}) = \frac{I(\boldsymbol{q})}{Nf^2} = 1 + \rho_a \int (g(\mathbf{r}) - 1) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}$$

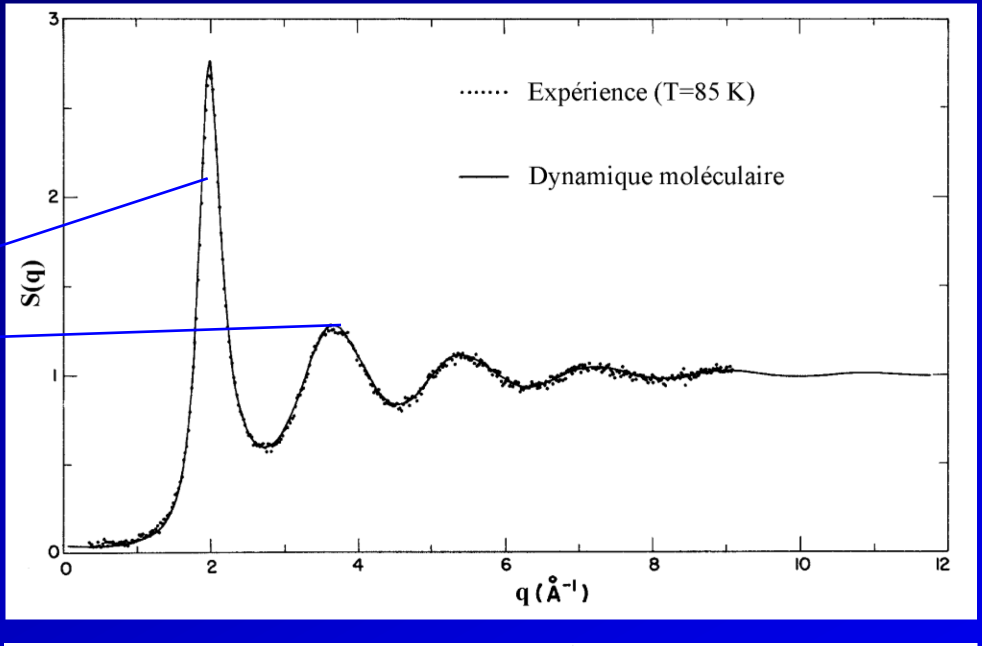
The only quantity directly measurable by diffraction methods is the pair distribution function $g(\mathbf{r})$

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

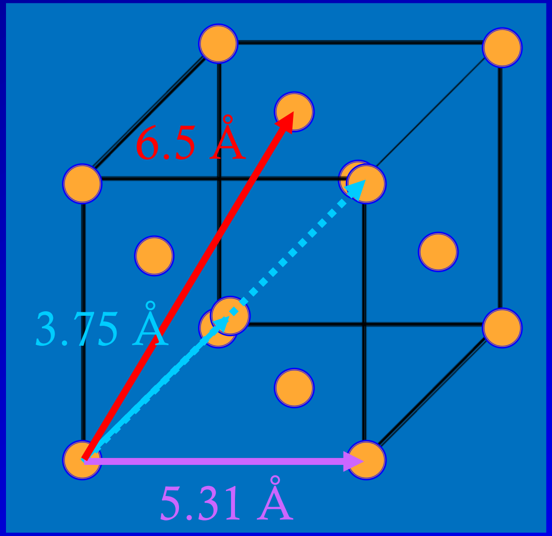
Example

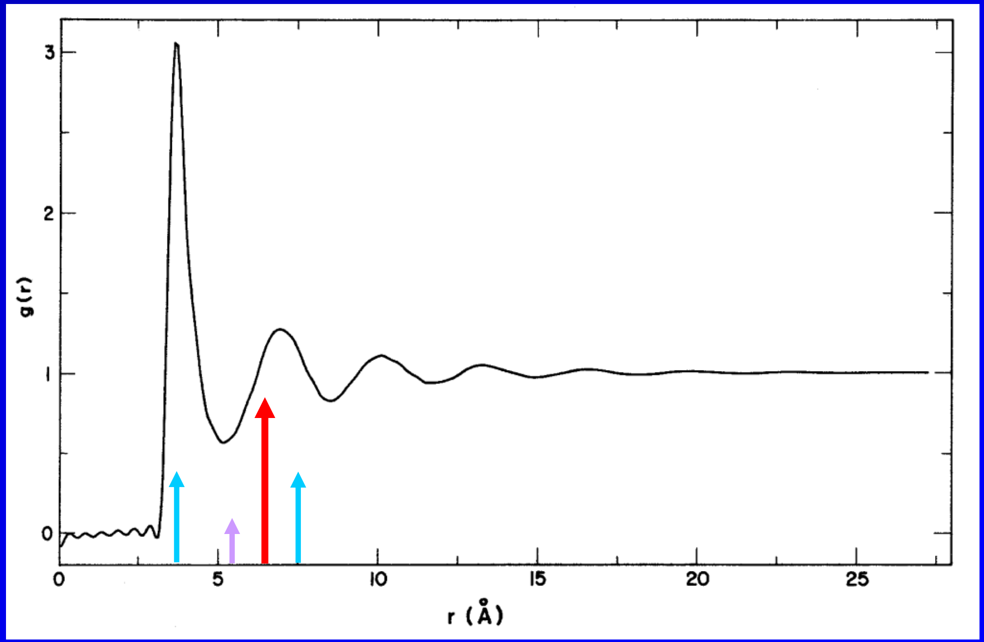
Liquid argon
85 K
Neutrons





Solid Argon
f.c.c





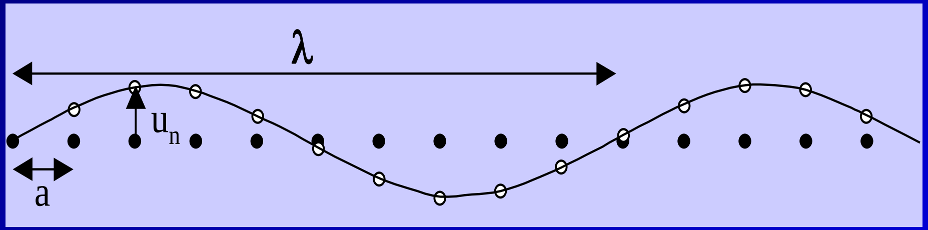
C-3 Periodic Crystals

All crystals
are not
periodic!

Aperiodic crystals

Incommensurate crystals

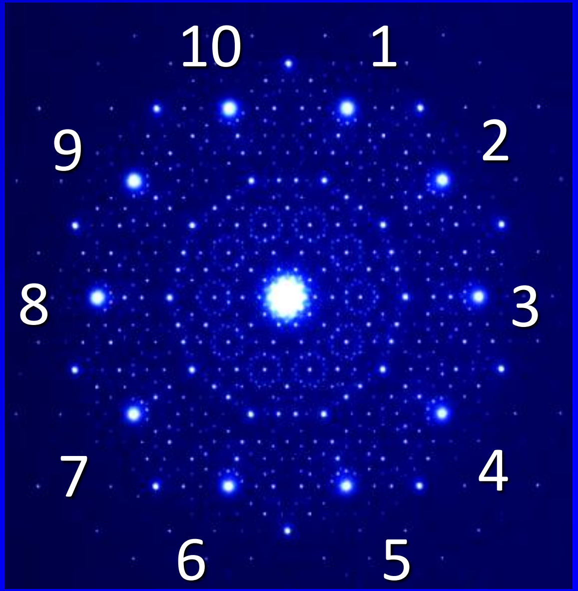
Local property (ex: polarisation)
has a periodicity
incommensurate with the l
attice periodicity.



λ and a have an irrationnal ratio

Crystallographic methods must be changed

Quasi-cristals (AlPdMn)

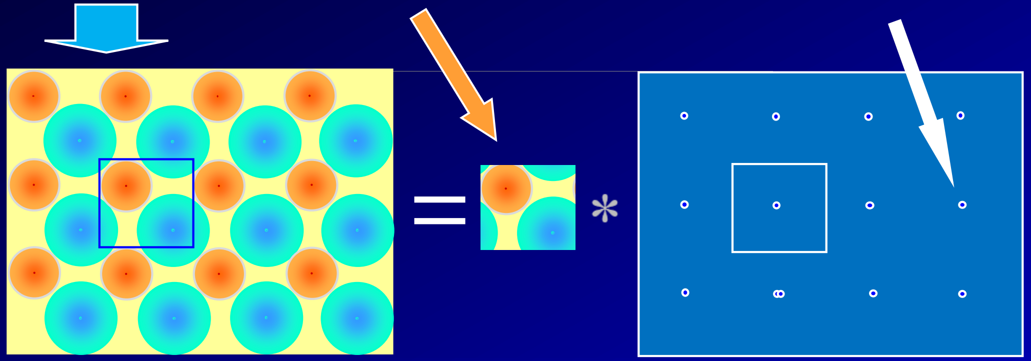


Sharp diffraction peaks

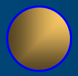
Long-range order
AND
5-fold symmetry
(not consistent with periodicity)

Periodic crystals

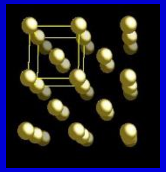
Crystal: motif (or basis) associated to a lattice



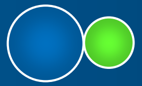
Na



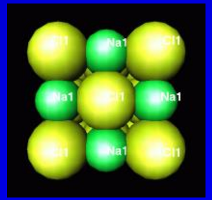
Atom



NaCl

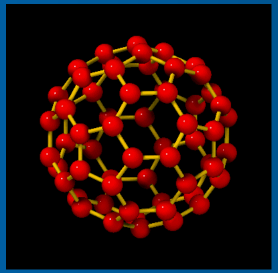


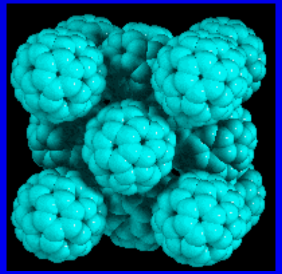
Group of atoms



C_{60}

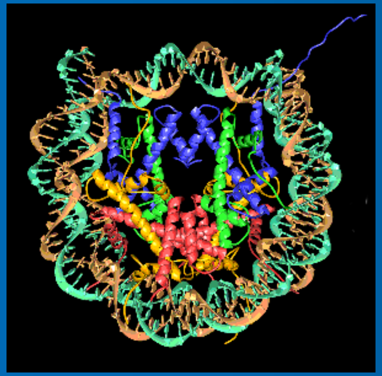
Molecule

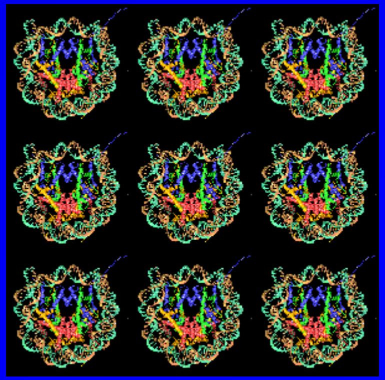




Nucleosome

Macromolecule





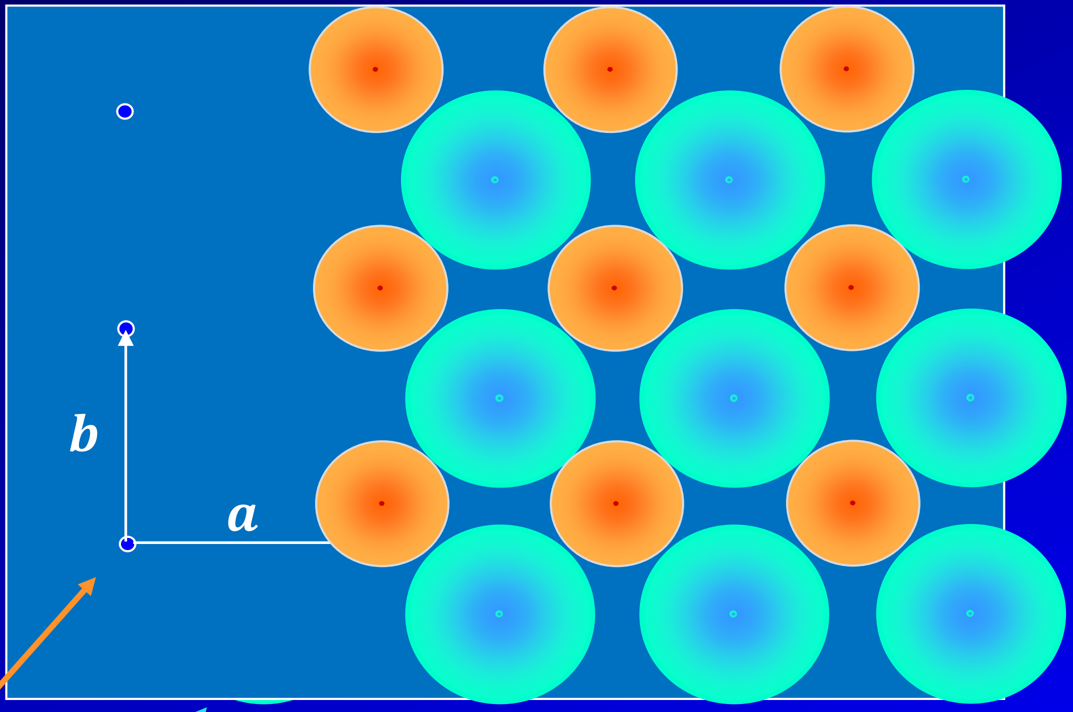
Motif

Crystal

Periodic crystals

Reduced coordinates

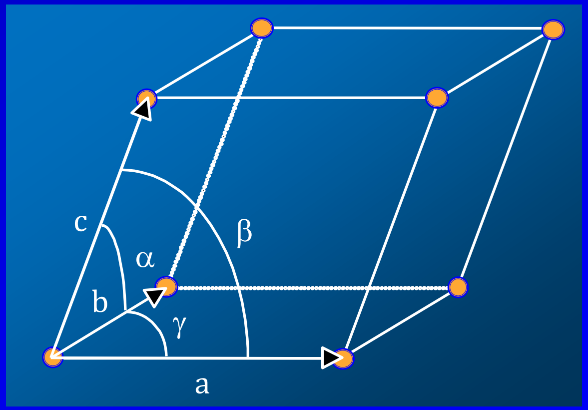
Nodes positions: $\boldsymbol{r}_{uvw} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$



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

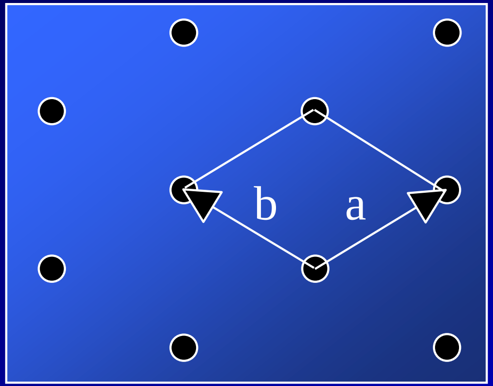
Cell parameters

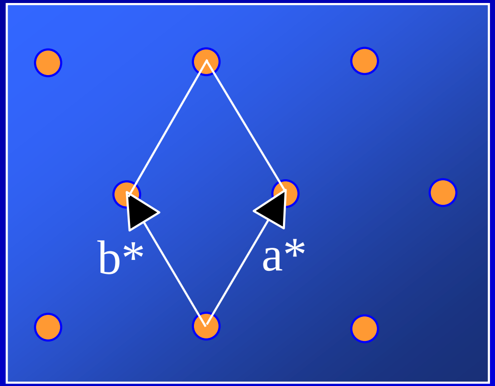
$a, b, c, \alpha, \beta, \gamma$



The reciprocal space

Is the Fourier transform of the direct space





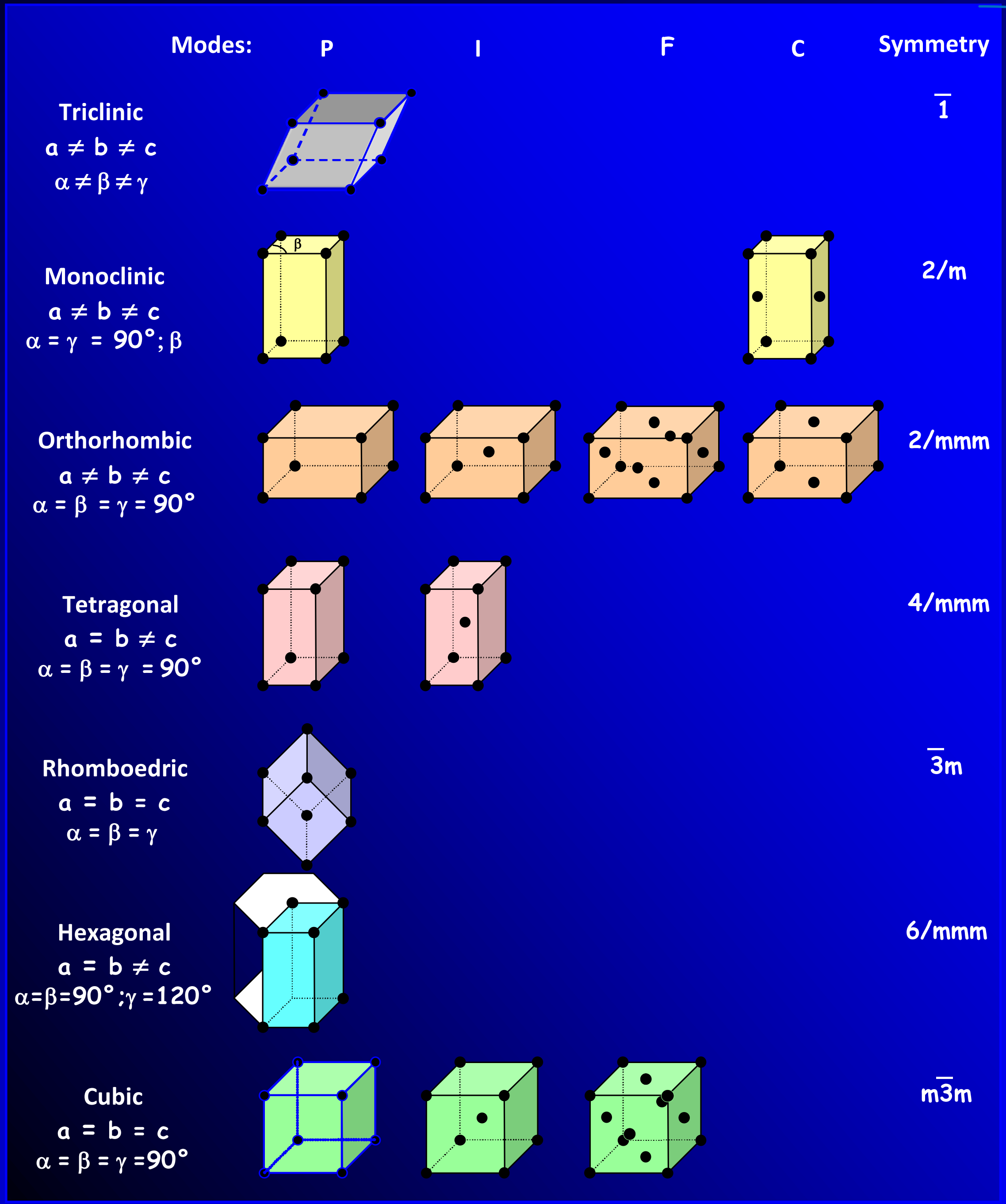
$$\boldsymbol{a}^* = 2\pi\frac{\boldsymbol{b}\wedge\boldsymbol{c}}{v};\ \boldsymbol{b}^* = 2\pi\frac{\boldsymbol{c}\wedge\boldsymbol{a}}{v};\ \boldsymbol{c}^* = 2\pi\frac{\boldsymbol{a}\wedge\boldsymbol{b}}{v}$$

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

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

Miller indices

14 Bravais lattices



Modes:	P	I	F	C	Symmetry
Triclinic a ≠ b ≠ c $\alpha \neq \beta \neq \gamma$					$\bar{1}$
Monoclinic a ≠ b ≠ c $\alpha = \gamma = 90°; \beta$					2/m
Orthorhombic a ≠ b ≠ c $\alpha = \beta = \gamma = 90°$					2/mmm
Tetragonal a = b ≠ c $\alpha = \beta = \gamma = 90°$					4/mmm
Rhomboedric a = b = c $\alpha = \beta = \gamma$					$\bar{3}$m
Hexagonal a = b ≠ c $\alpha=\beta=90°; \gamma=120°$					6/mmm
Cubic a = b = c $\alpha = \beta = \gamma = 90°$					m$\bar{3}$m

In 3D

7 systems (symmetry)
14 lattice modes

Only 1,2,3,4,6-fold
symmetries are
compatible with periodicity

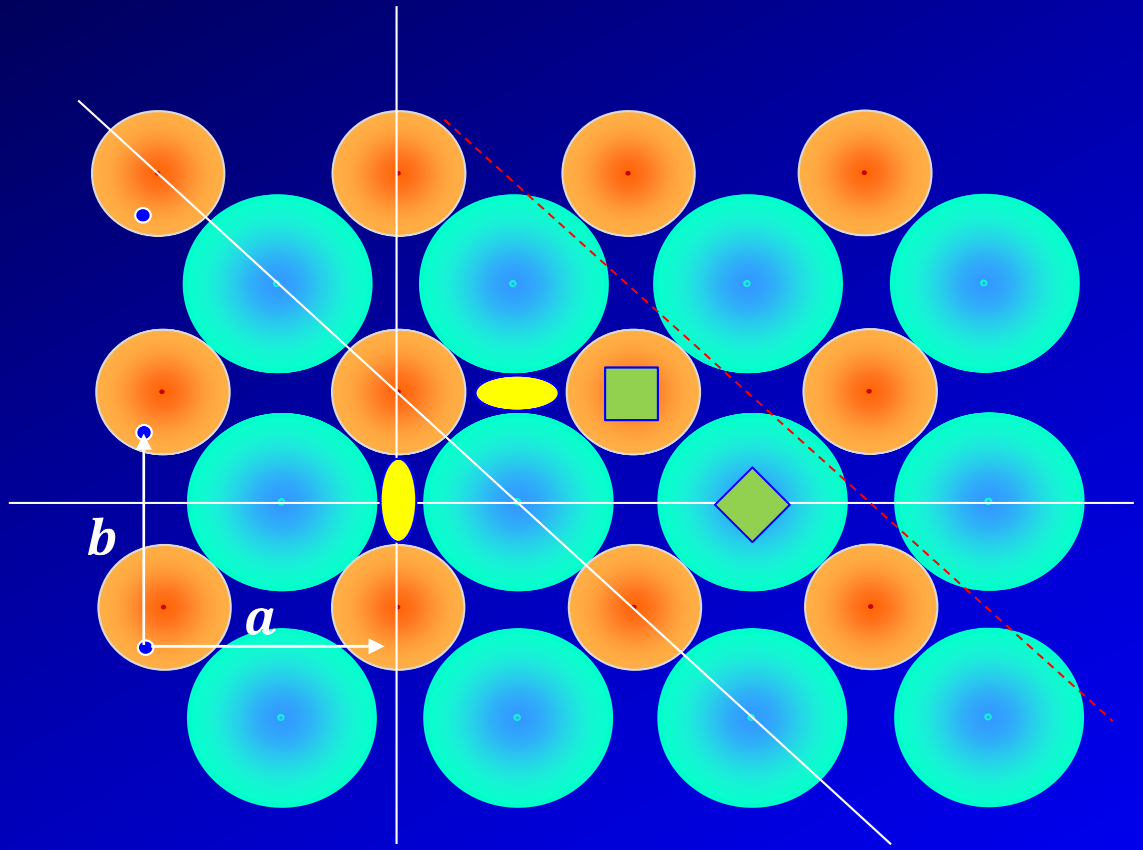
Reciprocal Lattice has
the same symmetry
(not the same mode)

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
$I4_1 22\ ; 422$



Mirrors

4-fold symmetry

2-fold symmetry

Glide plane
(screw axis)

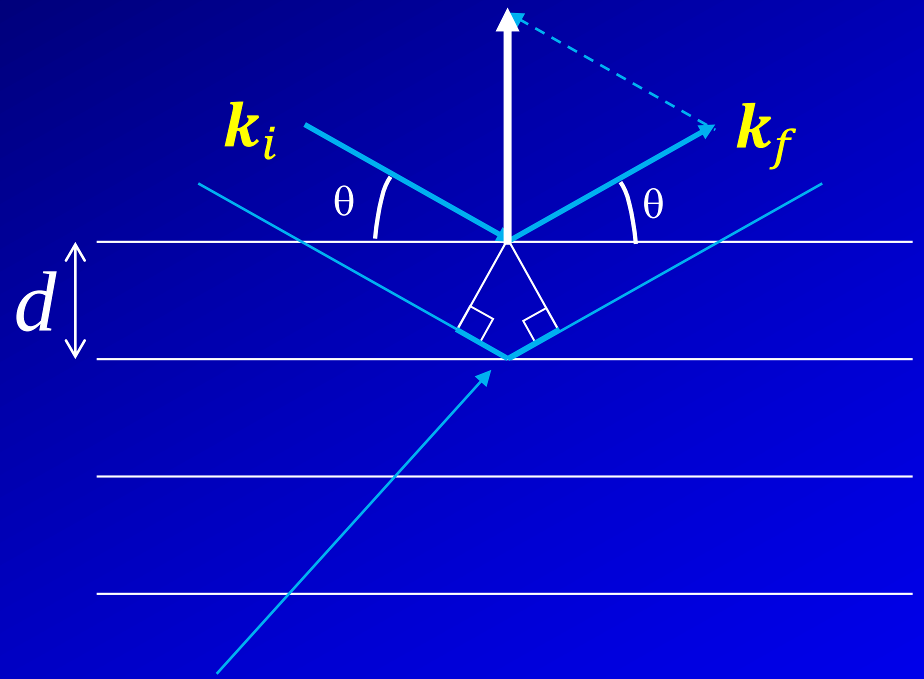
Symmetry of the Reciprocal Lattice is the Laue Group (point Group + center of symmetry)

$I4_1 22\ ; 422; 4\mathrm{mm}$

Bragg relation

Periodicity = Lattice planes
mirrors

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



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

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:

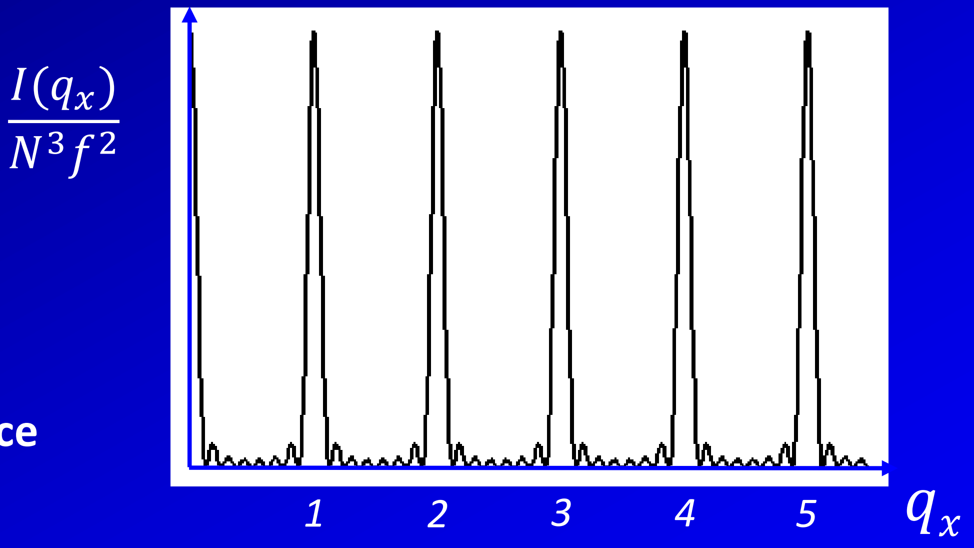
$$A(\boldsymbol{q}) = \sum_{u=1}^{N}\sum_{v=1}^{N}\sum_{w=1}^{N} f e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_{uvw}}$$

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

Crystal

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

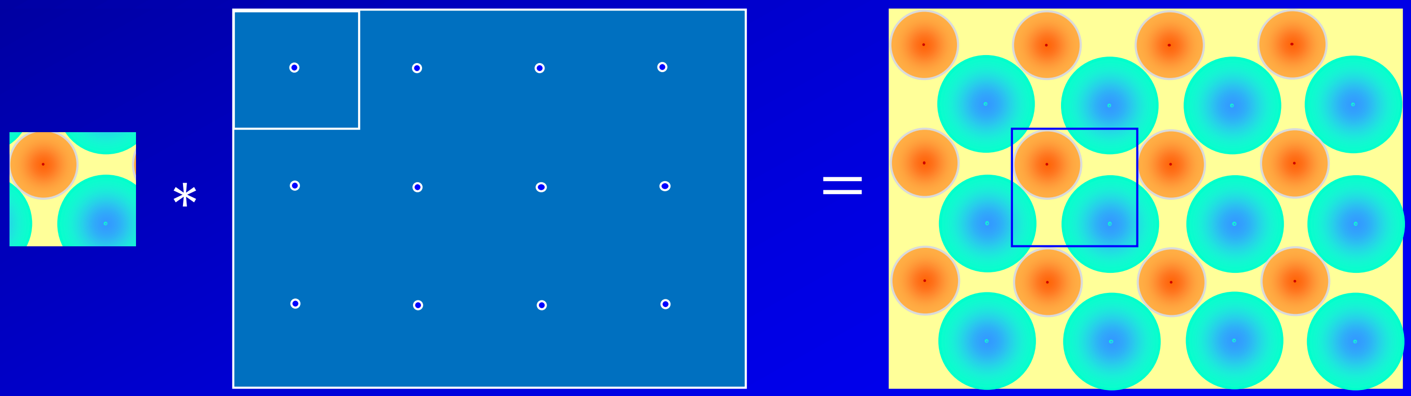
$$\boldsymbol{\rho_{tot}(r) = \sum_{uvw} \rho_{uvw}(r - R_{uvw})}$$

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

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

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

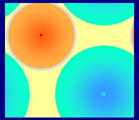
- Kinematic approximation
- Perfect periodicity



Laue equation - 2

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

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



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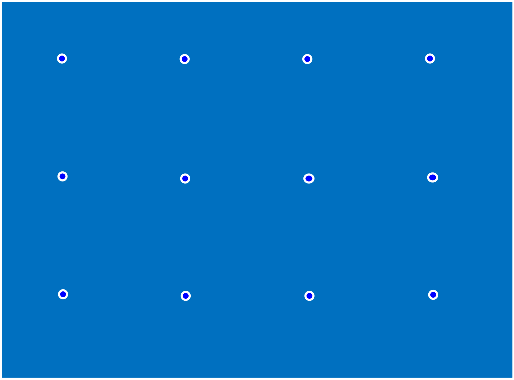
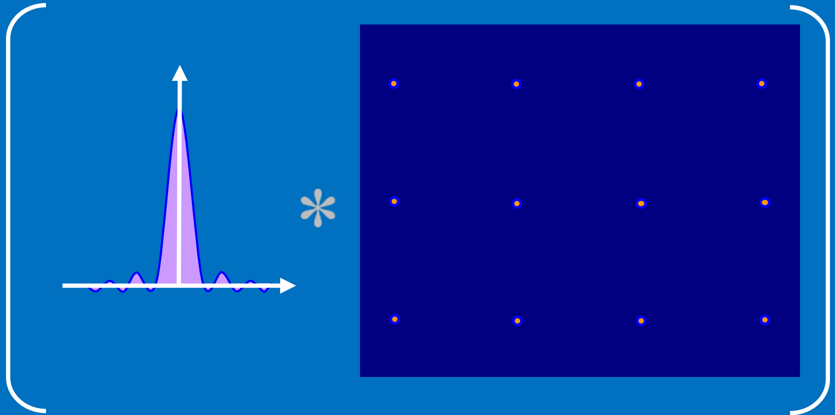


$$A(\boldsymbol{q}) = F(\boldsymbol{q}) \times (2\pi)^3 \left(\Sigma(\boldsymbol{q}) * \frac{1}{v} \sum_{hkl} \delta(\boldsymbol{q} - \boldsymbol{Q}_{hkl}) \right)$$

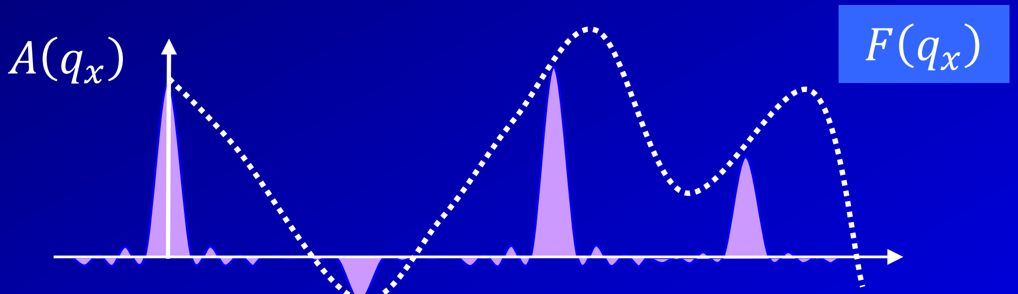
$\times$



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 $\Sigma(\boldsymbol{q})$

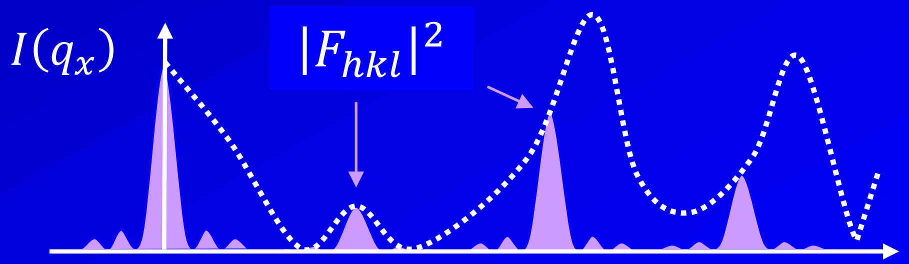


Crystal size cell parameters, no cross terms:

Intensity is max when q belongs to the RL

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

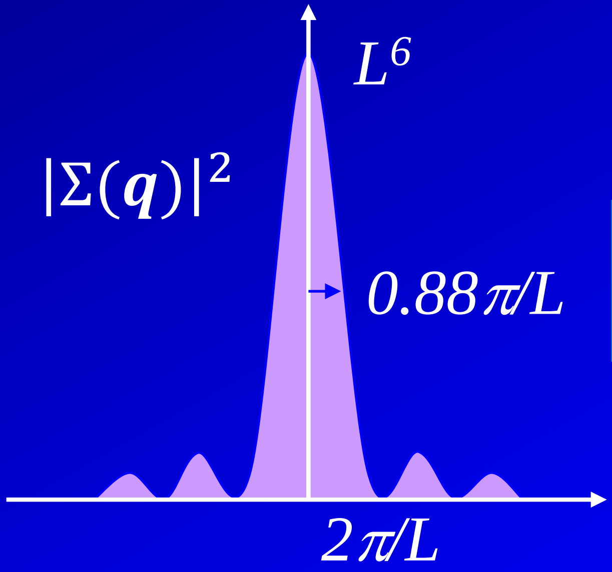
$$F(\boldsymbol{Q}_{hkl}) = F_{hkl}$$



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

Fourier Transform of the « volume » function

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

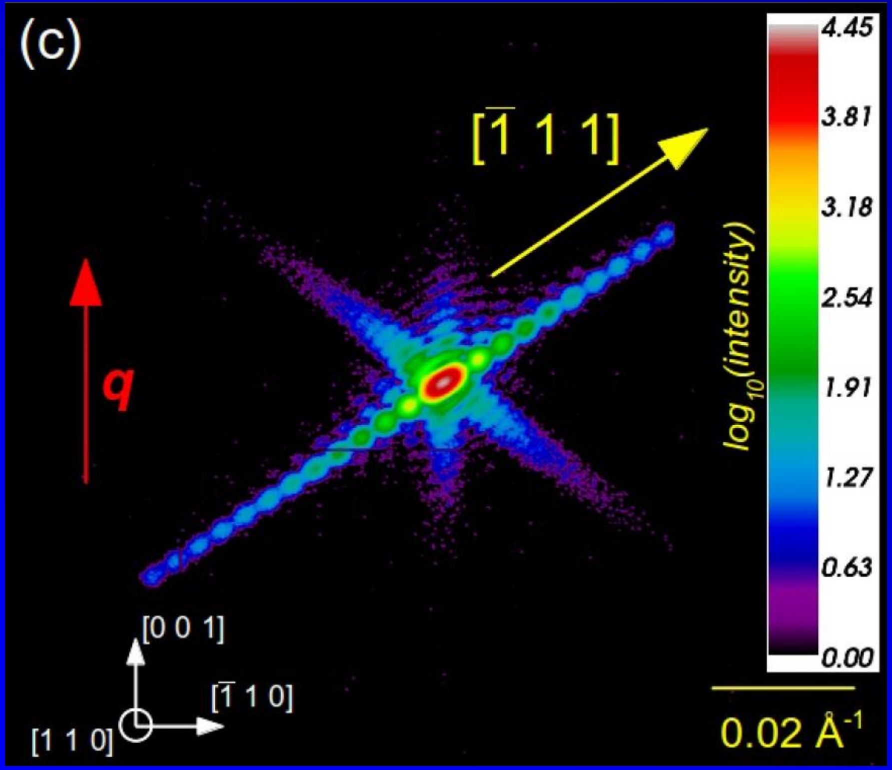


Exemple of a cube

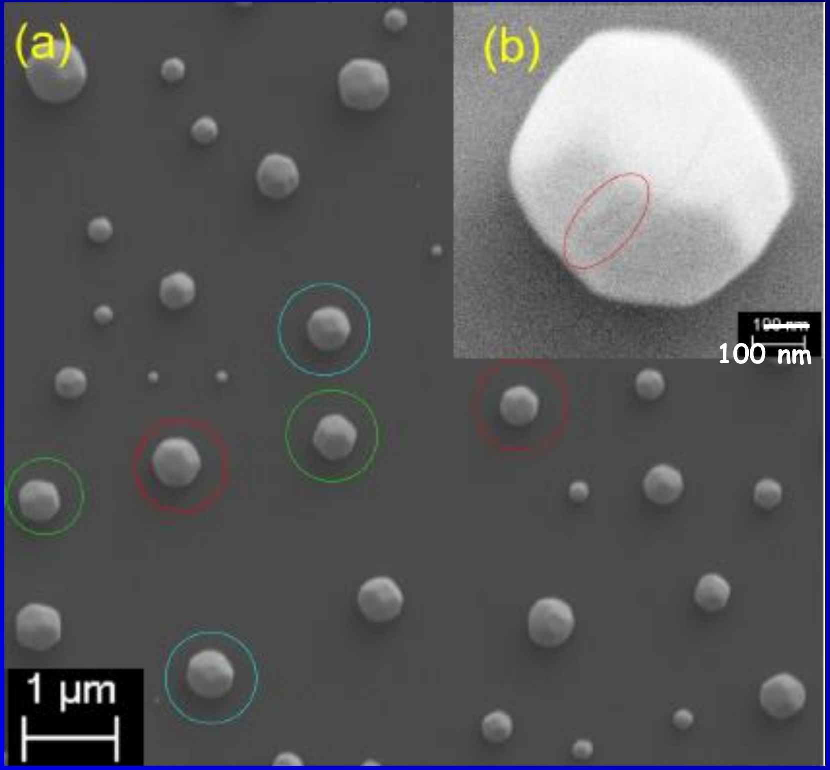
$$\Sigma(\boldsymbol{q}) = \left(\frac{\sin(Lq_x/2)}{q_x/2}\right)\left(\frac{\sin(Lq_y/2)}{q_y/2}\right)\left(\frac{\sin(Lq_z/2)}{q_z/2}\right)$$

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

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

Spherical approximation

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

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

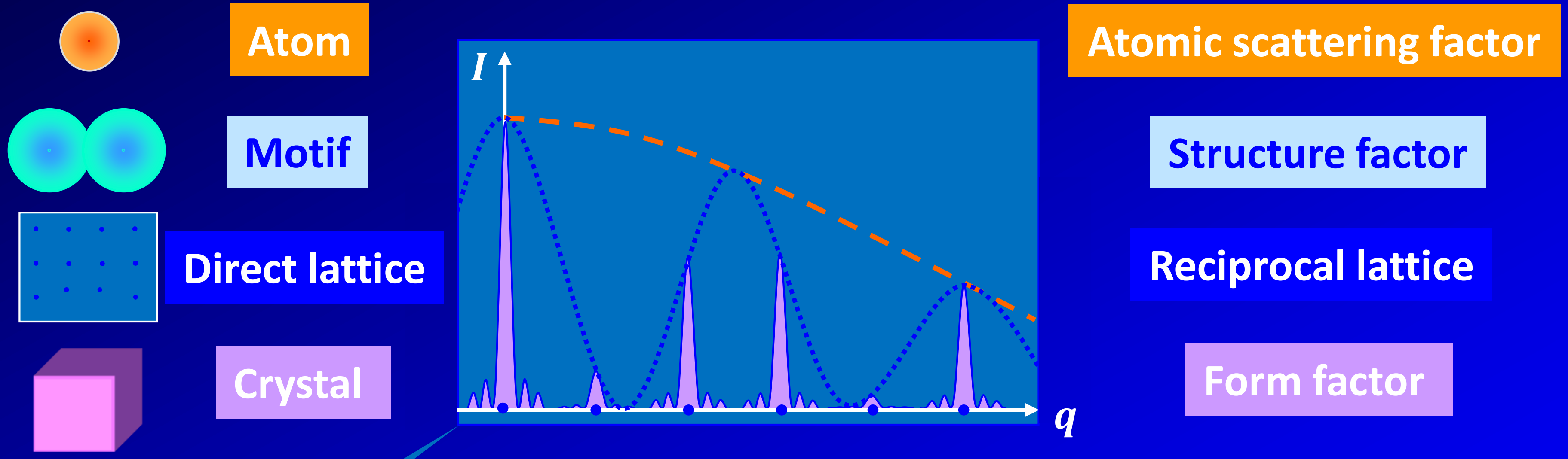
X-rays/Neutrons

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	Atomic scattering factor
Motif	Structure factor
Direct lattice	Reciprocal lattice
Crystal	Form factor

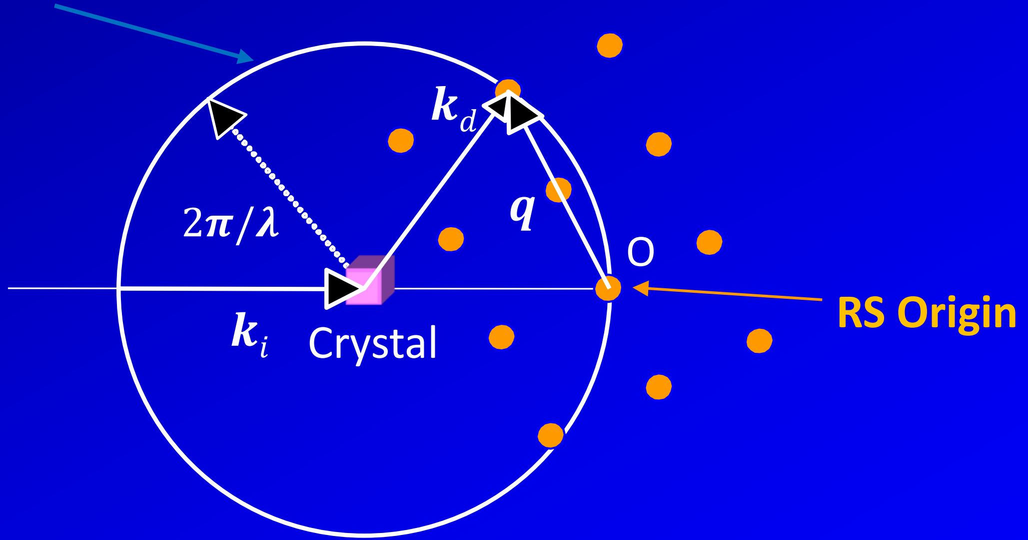
Position of Bragg spots: lattice
Intensity: motif
Profile: Shape/size of grains/crystals

Ewald construction

Geometrical interpretation of diffraction

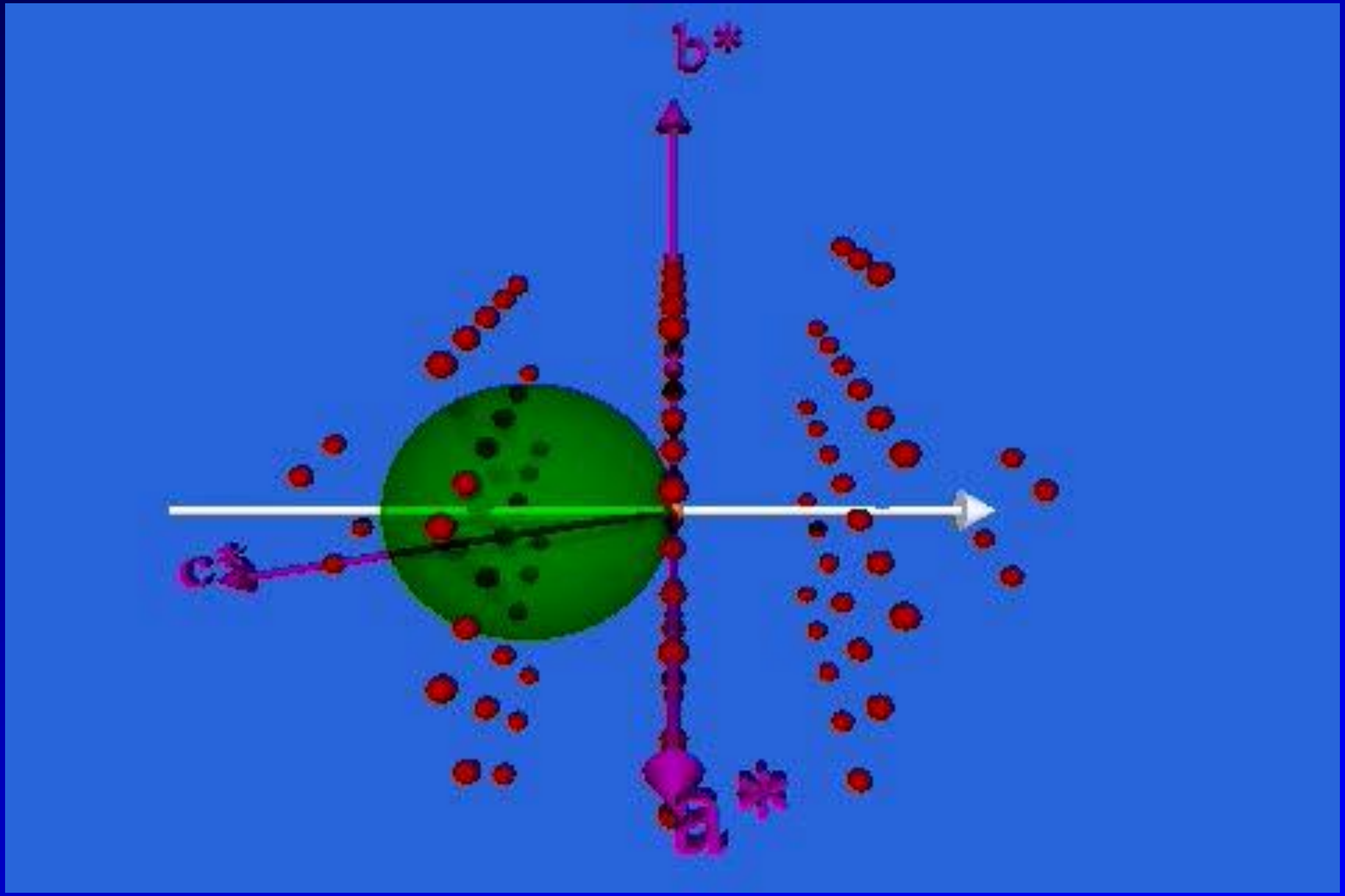
- Elastic scattering : $\boldsymbol{k_i} = \boldsymbol{k_d} = 2\pi/\lambda$
- Laue equations: scattering vector $\boldsymbol{q}$ belongs to RL

Ewald's sphere of reflexion



Diffraction occurs for nodes that lie on the sphere

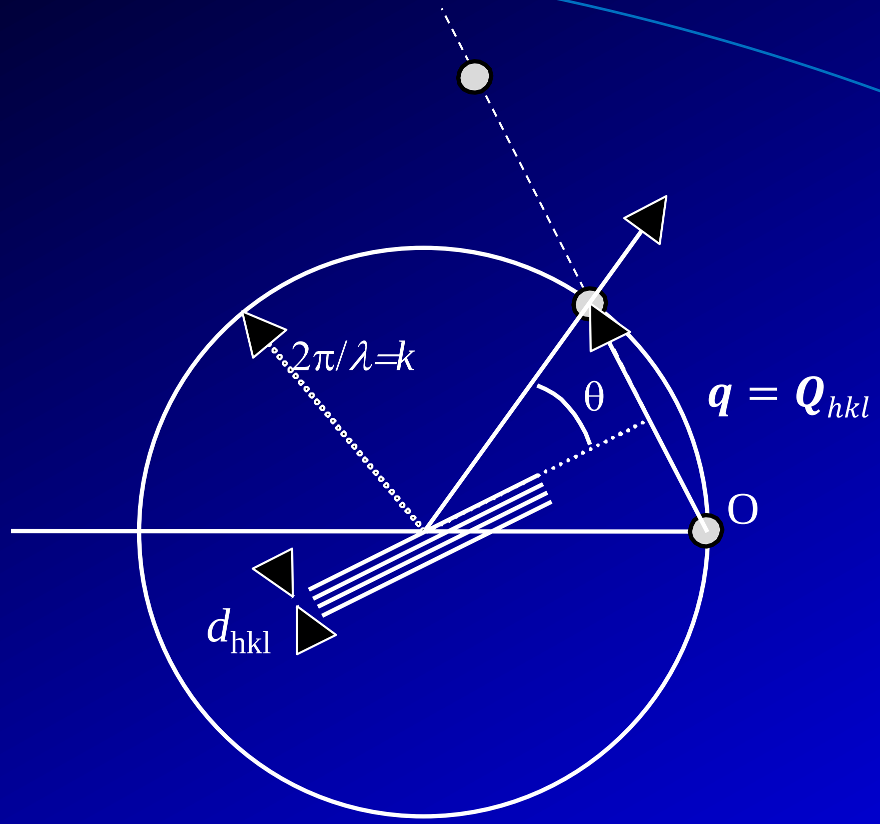
Ewald sphere



© Gervais Chapuis

Not all nodes are accessible

Laue ⇔ Bragg

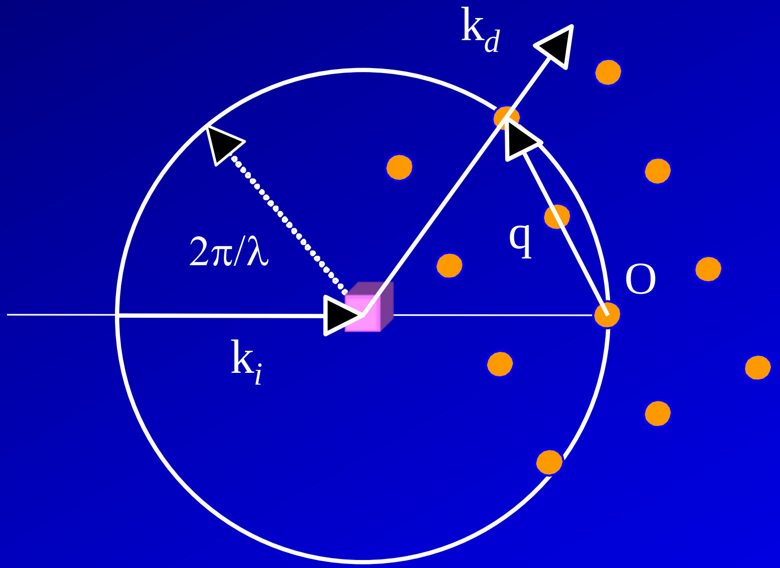


$$q = Q_{hkl} = \frac{2\pi}{d_{hkl}}$$

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

Experimental methods

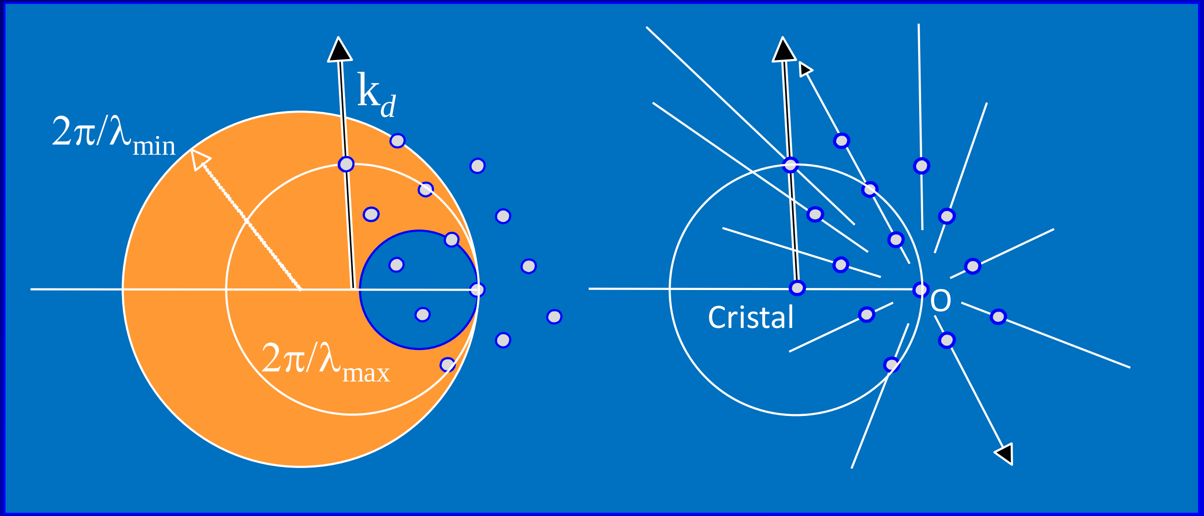
In a 3D crystal, the number of nodes in reflection is small.



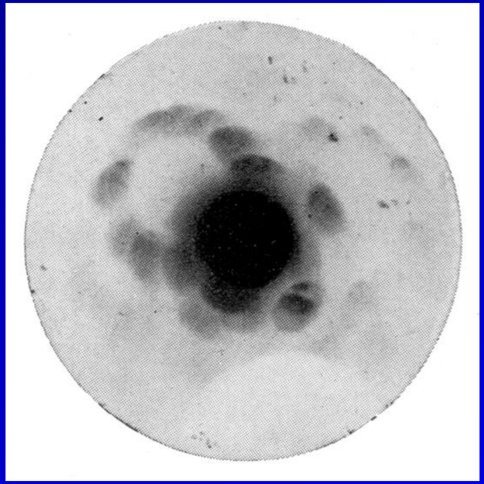
- Laue method (many λ)
- Powder method (many crystals)
- Rotating crystal (many orientations)

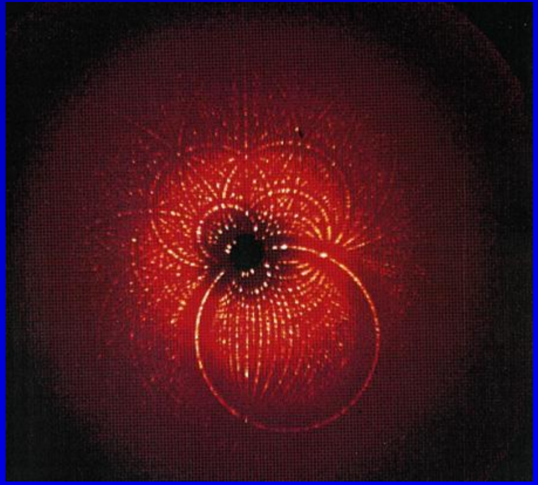
Laue method

Diffraction
with white beam



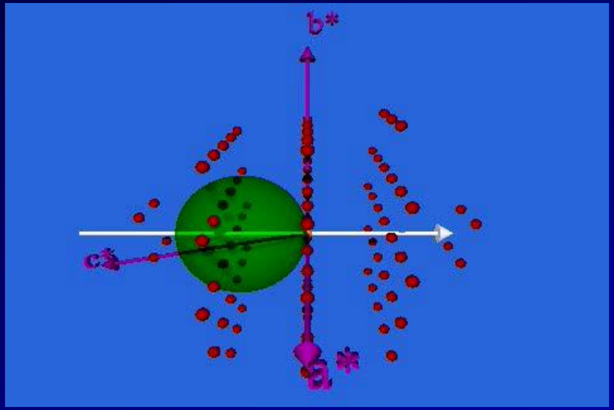
First diffraction 1912 ($CuSO_4$)
Von Laue, Friedrich, Knipping



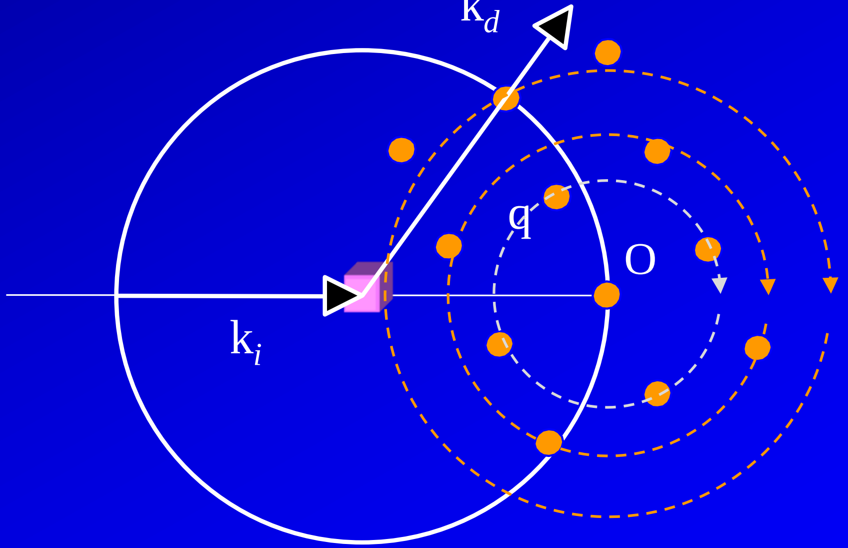


Laue diffraction pattern of MbCO
150 ps pulse (ESRF ID13)
2000 reflections (E=7-38 keV)

Rotating crystal

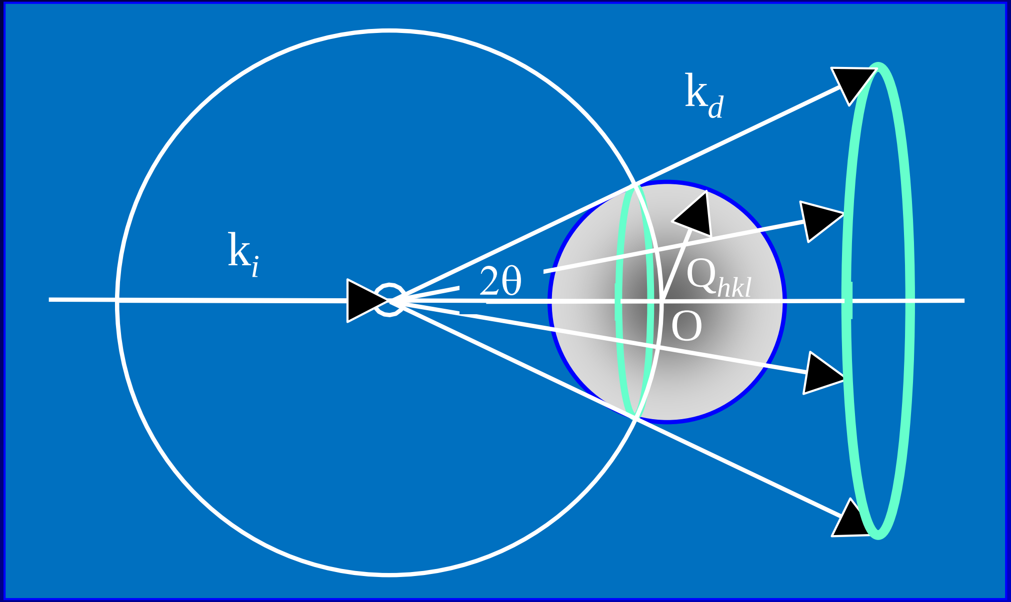


All accessible nodes
Pass through the Ewald sphere



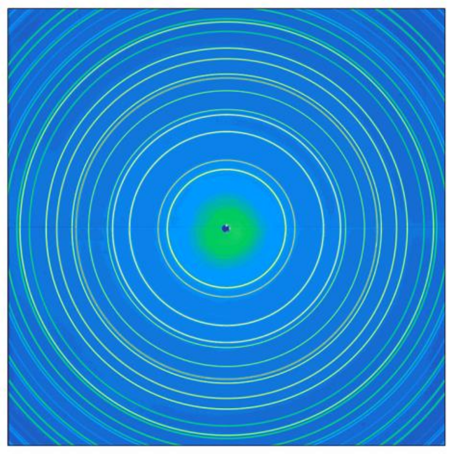
Powder method

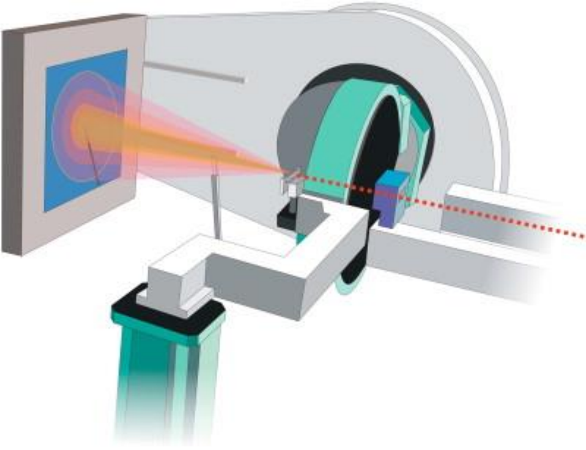
Powder: Set of small crystals (0.1-10 µm) in every possible orientations.

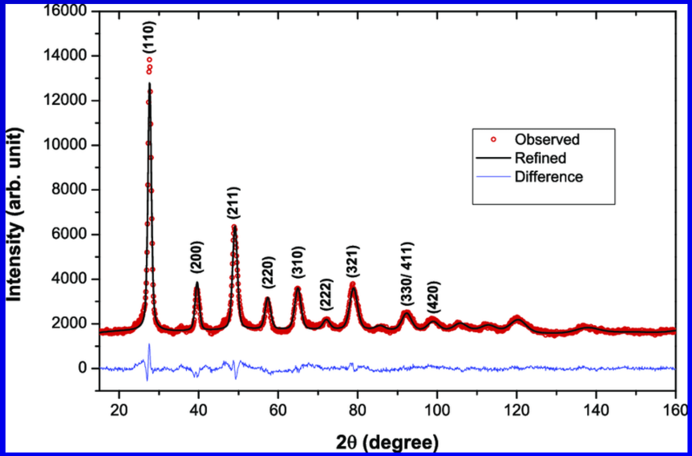


Each node Q_{hkl} on a sphere

Debye-Scherrer method

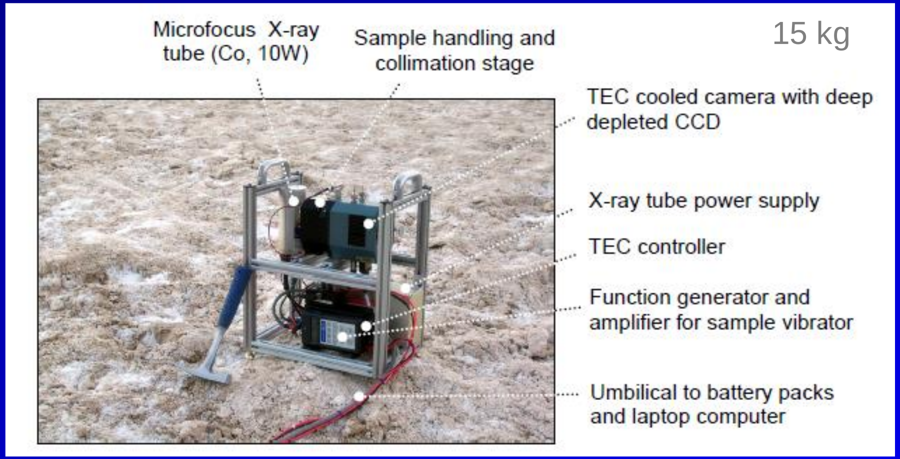




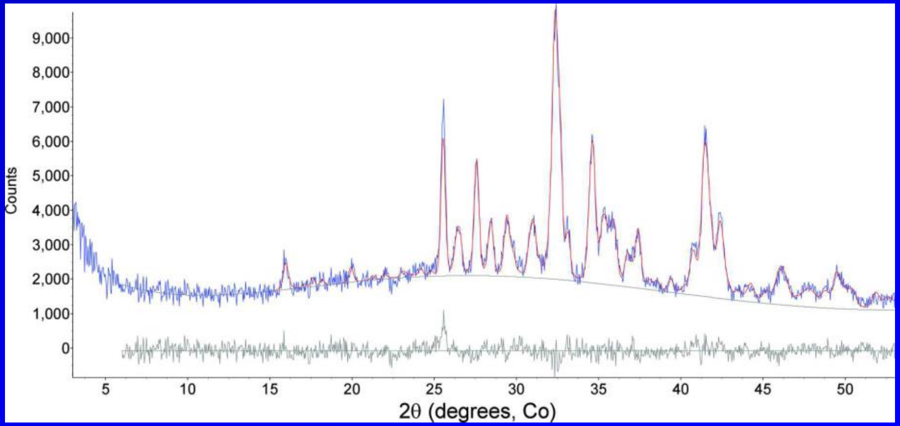


One line: one θ ; distance d_{hkl}

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)

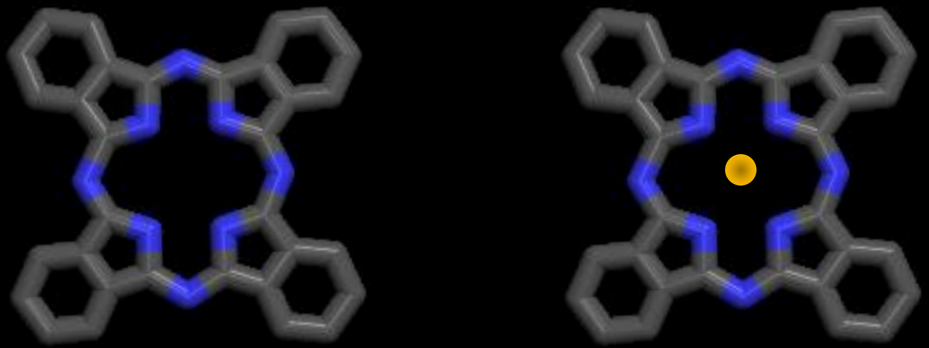
Extract the Bragg spots intensity: $|F_{hkl}|^2$

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

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

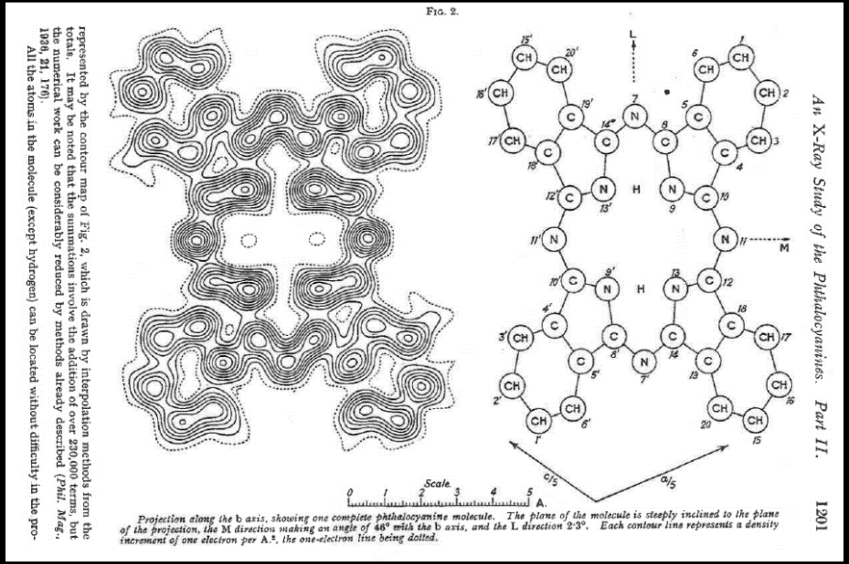
Example: Structure of phthalocyanin

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



Metal (Cu, Ni, Pt)

Determination of phases of 150 hk0 Bragg reflections by comparison.



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

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.*

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 230,000 terms, but the numerical work can be considerably reduced by methods already described (*Phil. Mag.*, 1936, 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)!

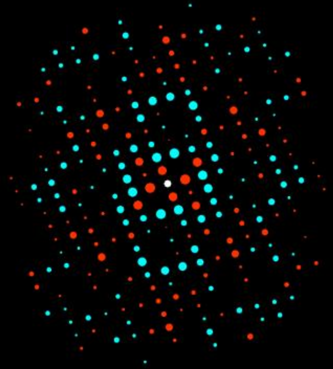
Without computers…

Use of the Fourier series

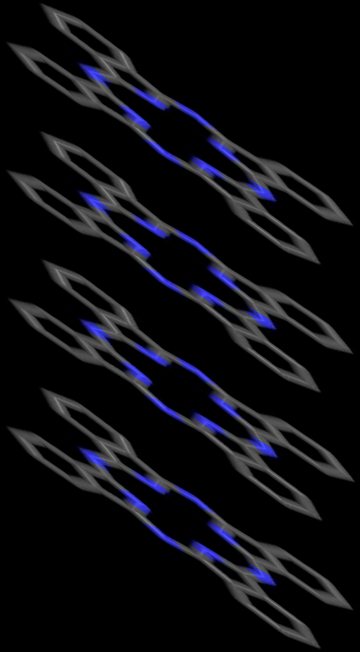
$$\text{resolution} = \frac{2\pi}{q_{Max}} = \frac{\lambda}{2\sin\theta}$$

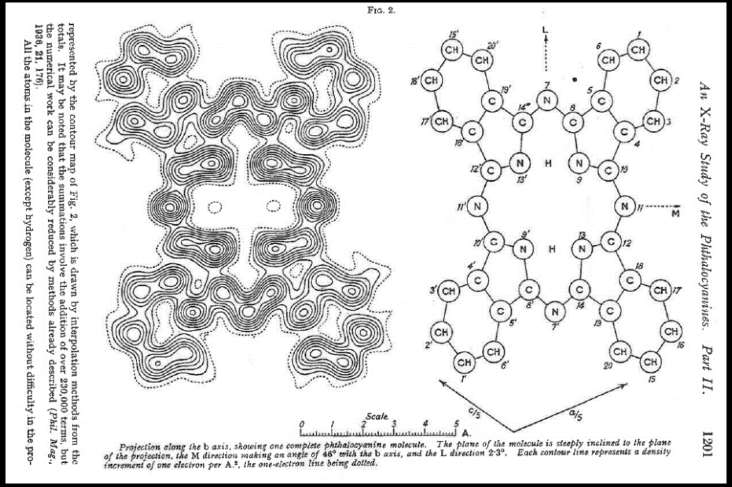
Fourier series

sine **component**



resolution = 0.95 Å





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

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

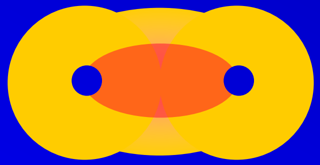
Chemical bonding
Electrostatic potential, charge transfer, dipolar moment, etc.

Calculation of F_{hkl} in the spherical approximation

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

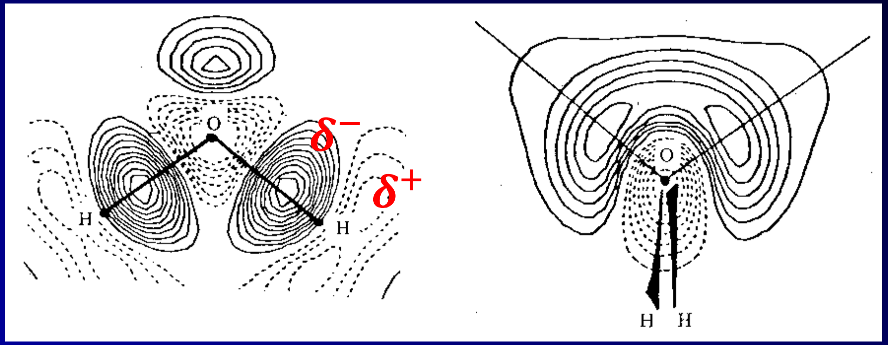
Deformation map of electron density

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



Examples of maps

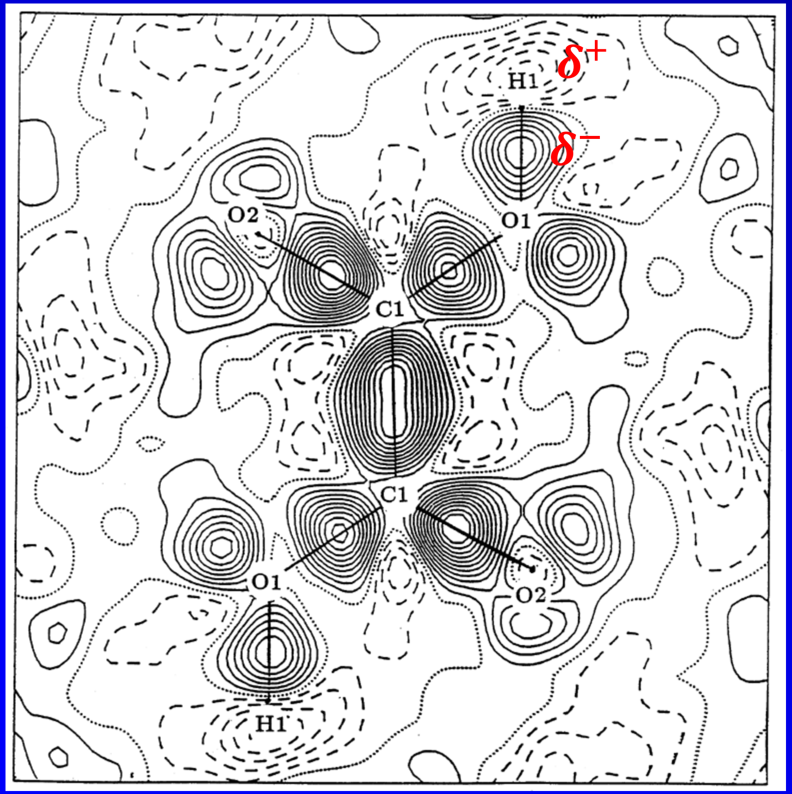
Contour 0.005 eÅ^{-3}



H_2O in $LiOH.H_2O$

From Vainshtein

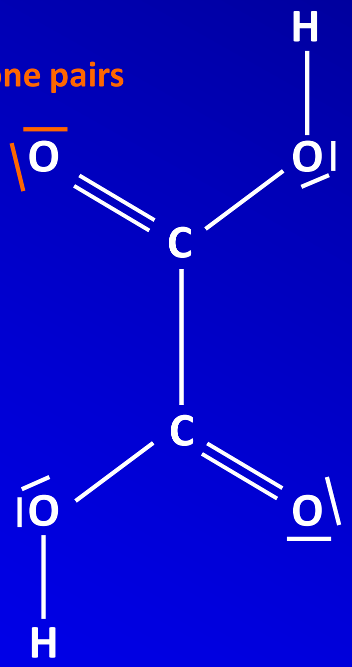
Oxalic acid 15 K



Contour 0.05 eÅ^{-3}

(Zobel et al. 1992)

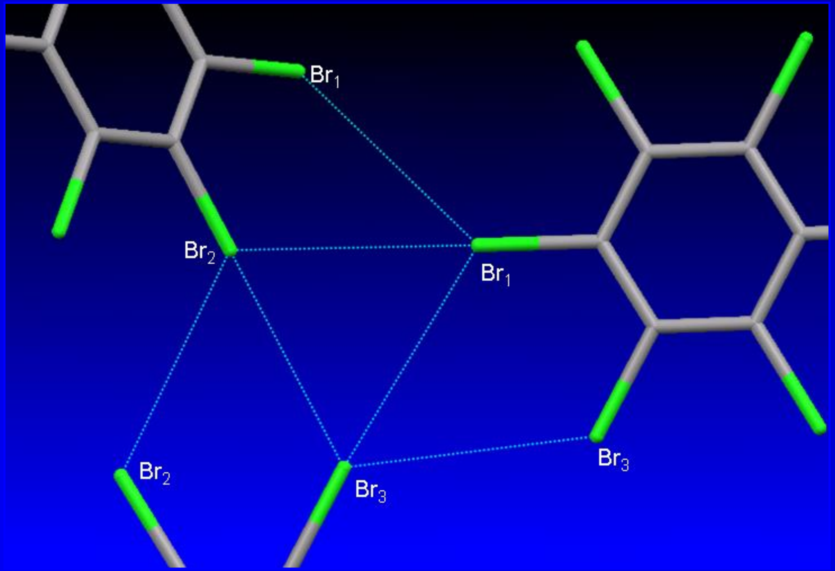
Lone pairs



Multipolar development of electron density (Hansen-Coppens model)

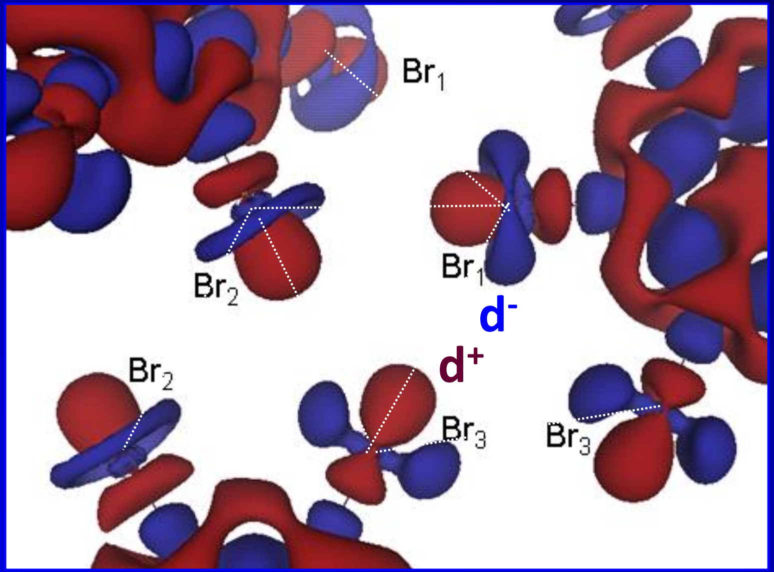
$$\rho_{mul}(r) = \rho_{core}(r) + P_v \kappa^3 \rho_{val}(\kappa r) + \sum_{l=0}^{l_{\max}} \kappa'^3 R_l(\kappa'.r) \sum_{m=0}^{+l} P_{lm\pm} y_{lm\pm}(\theta,\varphi)$$

Hexabromobenzène C_6Br_6



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

Static deformation map



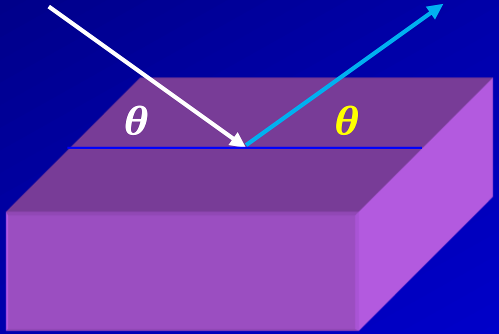
$\Delta\rho_{stat}(r) = \rho_{multipole}(r) - \rho_{spherical}(r)$

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**



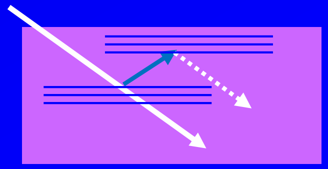
- **Same diffraction condition (Laue, Bragg) but refraction** $(n = 1 - \delta)$

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

Reflected power (Bragg reflections)

Kinematic Theory

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



Dynamical Theory

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

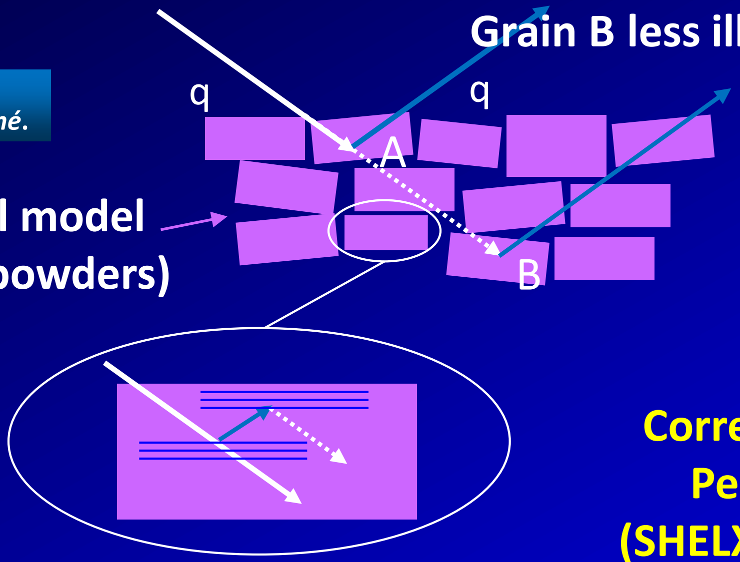
Dynamical results is much smaller: Extinction

Dynamical theory-2

$P_{dyn.} < P_{ciné.}$

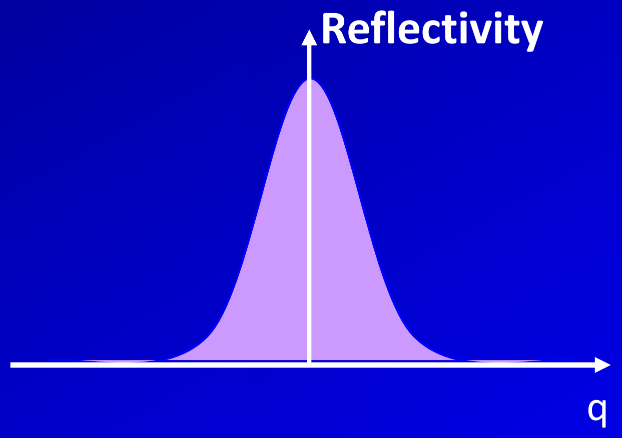
Secondary extinction:
Grain B less illuminated than grain A

Mosaic crystal model
(small crystal, powders)



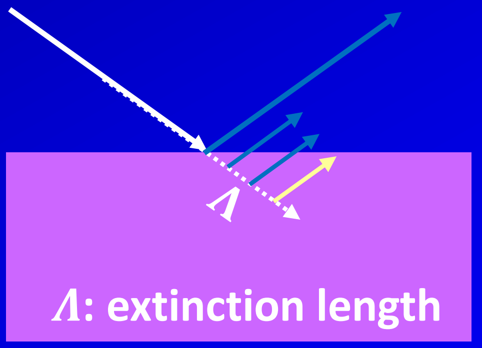
Primary extinction:
Destructive interferences
between beams diffracted n-times

Correction to be
Performed!
(SHELXTL package)

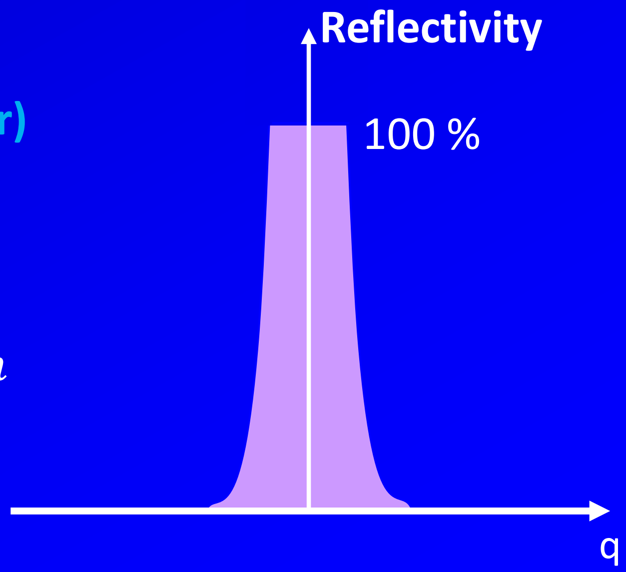


« Rocking curves »

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) :

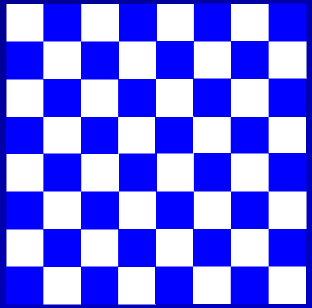
Pair Distribution Function $g(\mathrm{r})$ tends to 0
No diffraction peaks

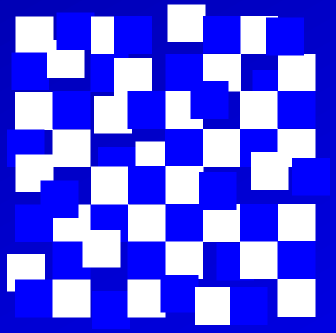
- Desorder of first kind (disordered crystal):

Long range order

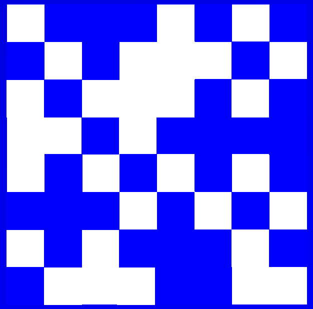
Diffraction peak intensity (smaller intensity)
AND
Diffuse scattering

Two types of disordered crystals





Displacement disorder



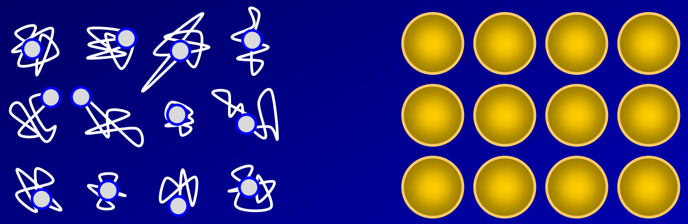
Substitution disorder

Disorder 1-Effect of temperature

Thermal motion

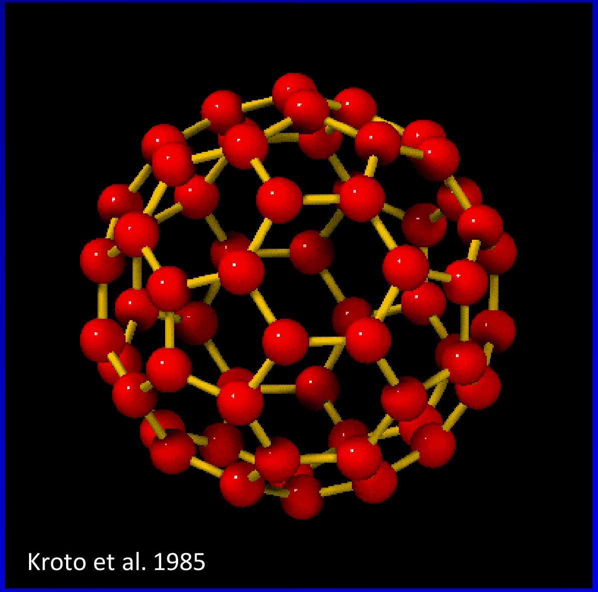
- At a given time, no perfect periodicity
- Periodicity is recovered on average

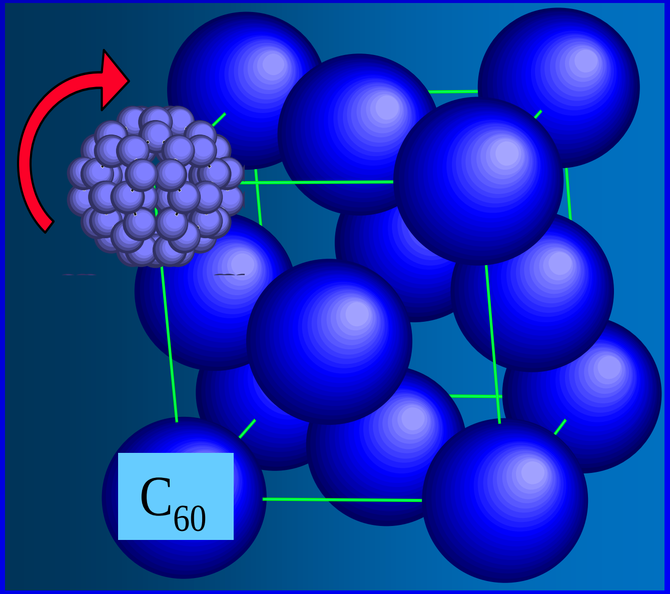
- Average structure is periodic
- Statistical average ↔ time average (Ergodic hypothesis)



Orientational disorder

- Ex : C_{60}, plastic crystals


Kroto et al. 1985



T=300 K
fcc

Real crystals: 2-Defects

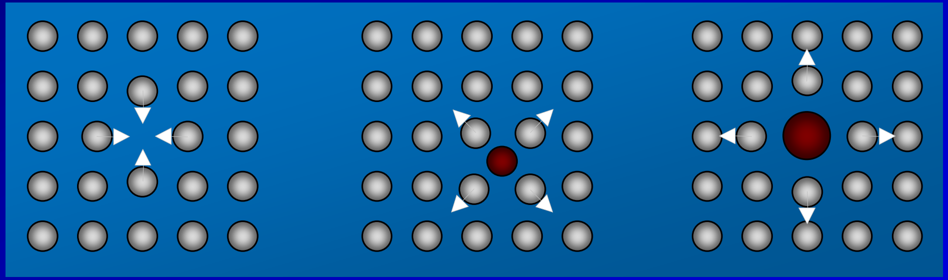
www.techfak.uni-kiel.de/matwis/amat/def_en/makeindex.html

Topological defects

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

Dimension 0

- Vacancies, intersticials



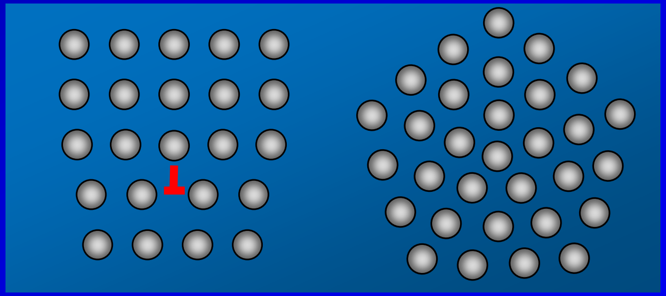
Vacancy
- Always present (${2.10}^{-4}$ Cu at 300 K)
- Diffusion, colored centers

Intersticial
- Plasticity

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

Dimension 1

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

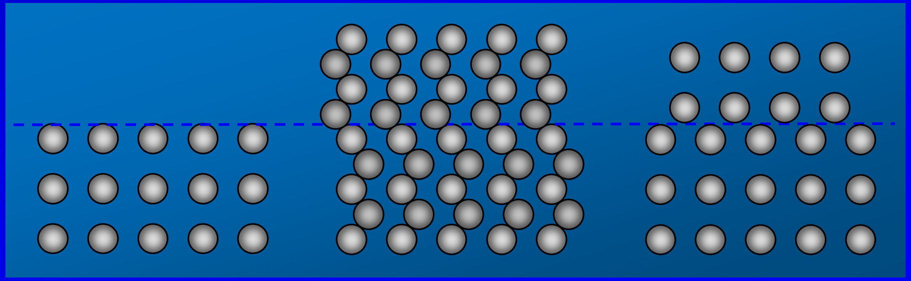


Dislocation

Disclination

Dimension 2

- Surfaces, stacking faults
- Grain boundaries, twins



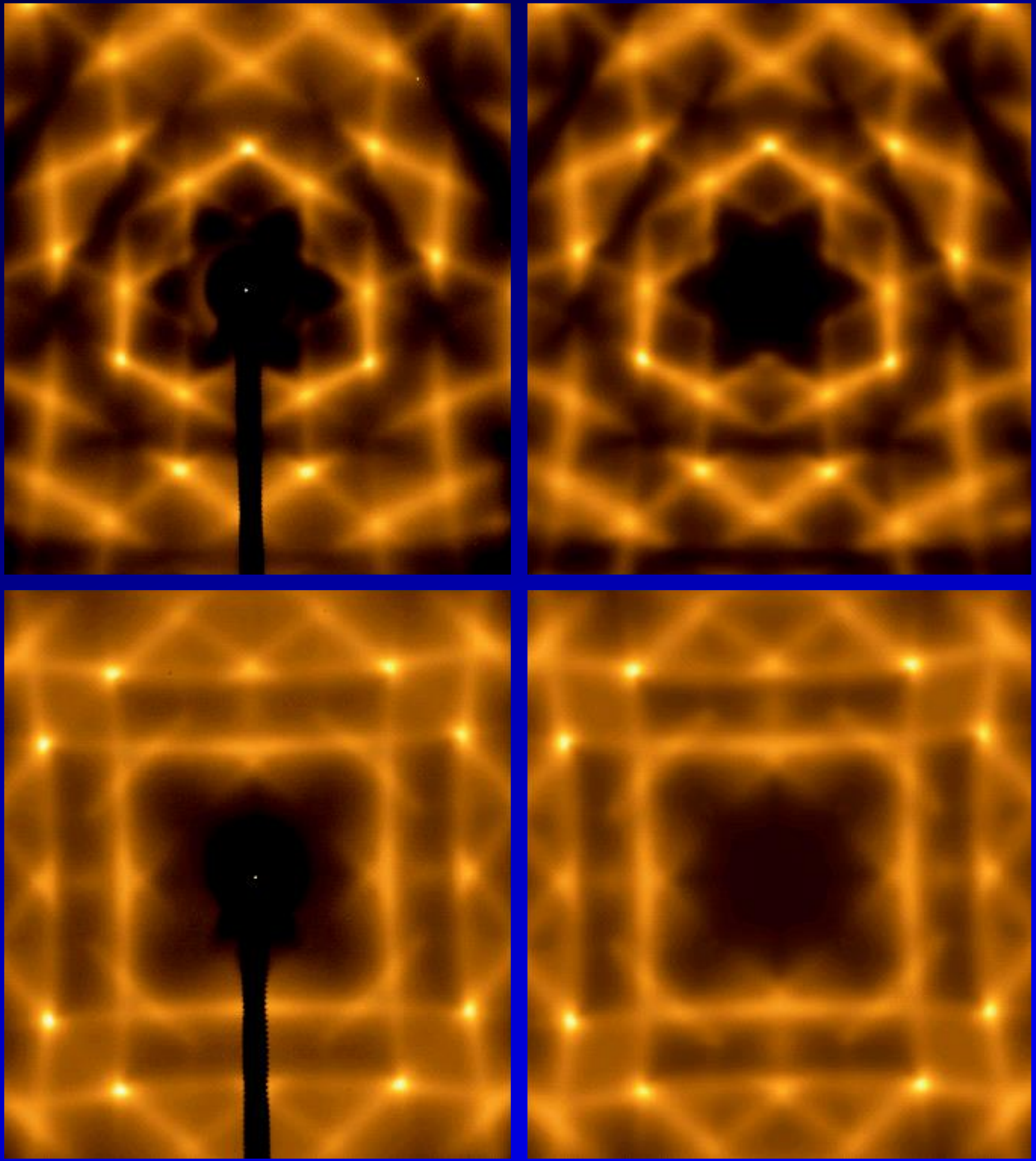
Surface

Stacking faults

Grain boundary

Thermal Diffuse Scattering (TDS)

Not elastic…



Experiment

Simulation

Si 300 K

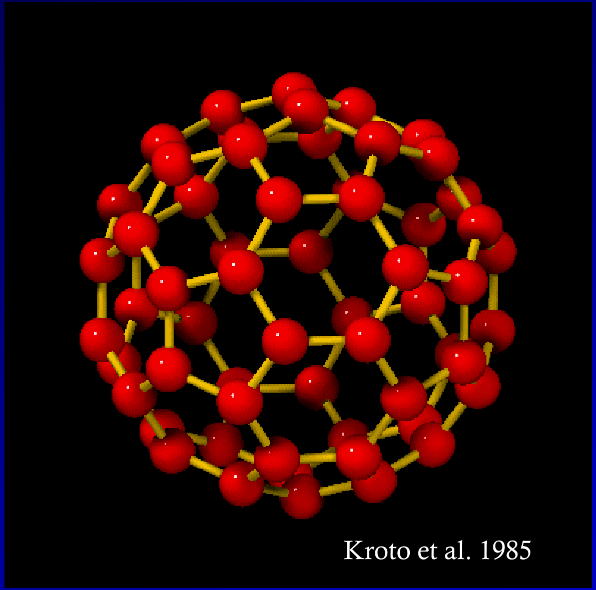
XRay // <111>

False colors,
Log scale.

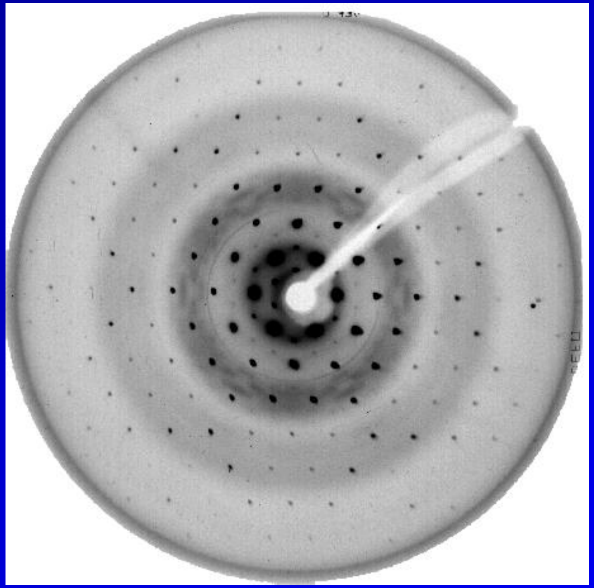
X-Ray // <100>

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

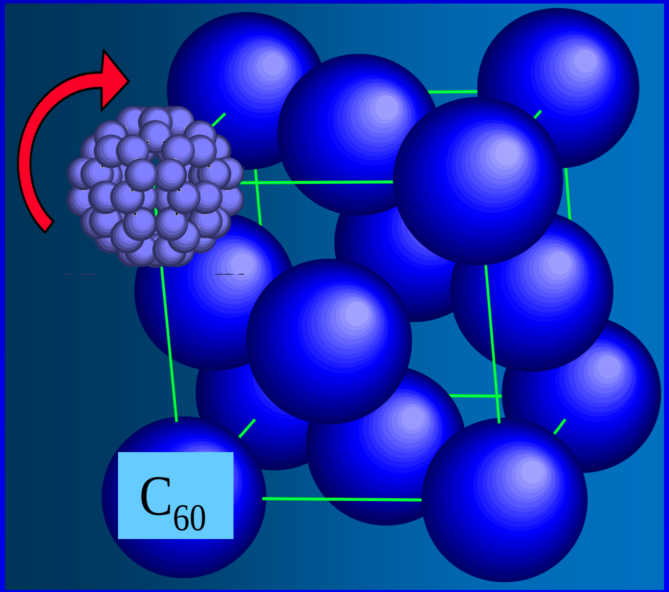
C_{60} Crystal



Kroto et al. 1985



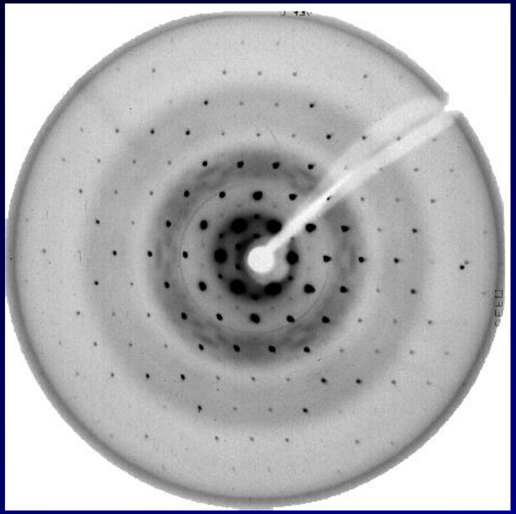
R. Moret, P. Launois, S. Ravy



T=300 K

c.f.c.

General effect of disorder



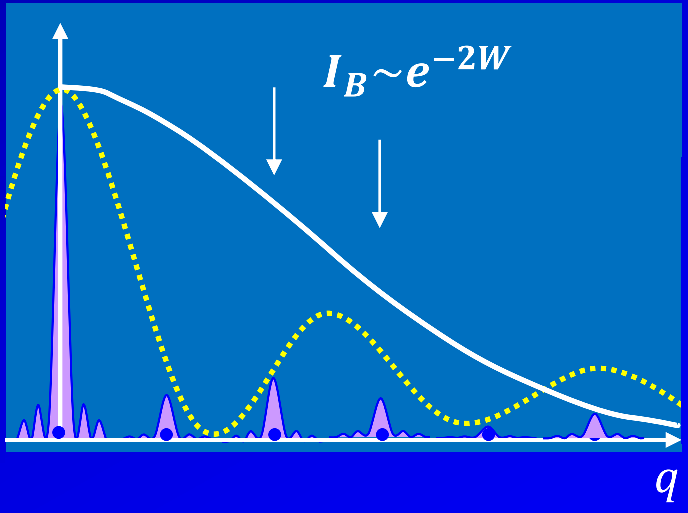
Bragg reflection Decreases the Bragg intensity;

Diffuse scattering Appeance/Increase of ”diffuse scattering”

Very important case: thermal agitation

Debye-Waller factor

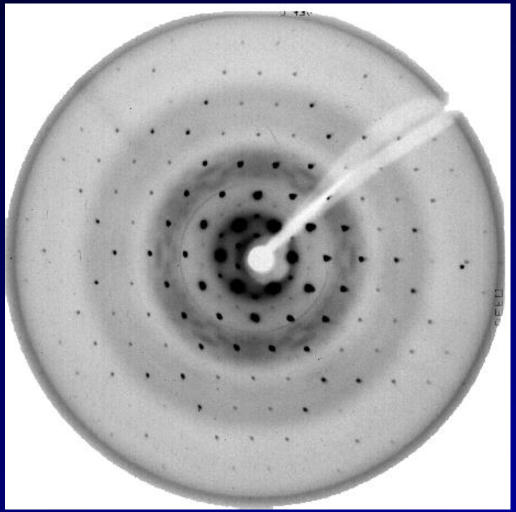
$$e^{-W(q,T)}$$



The larger the temperature
The larger the scattering vector

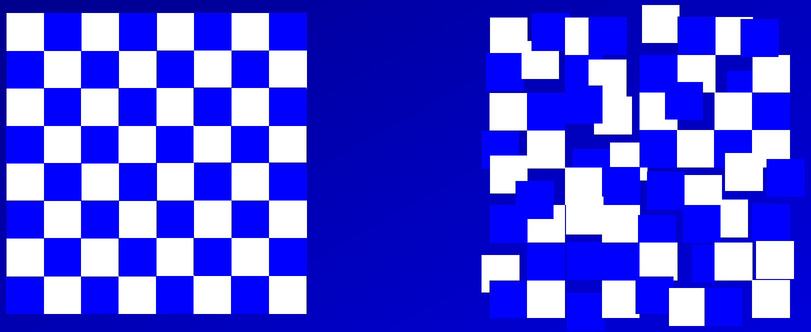
The larger the decrease of
Bragg intensities

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

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

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

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

N = number of unit cells

Diffuse scattering

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

ϕ_n: **deviation from average value** F_n

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

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

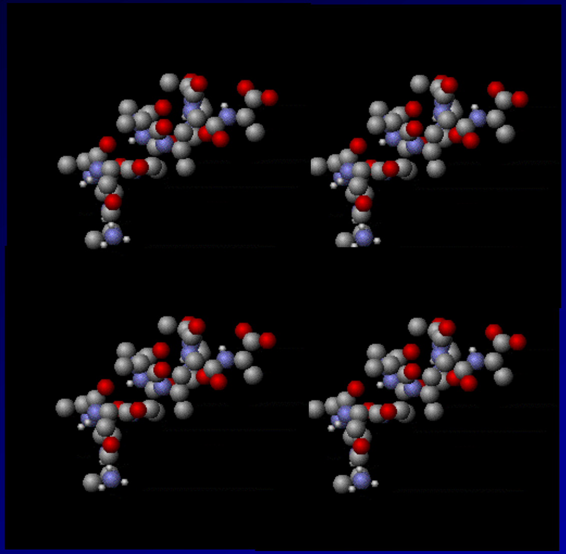
$I_D(\boldsymbol{q})$:
Diffraction

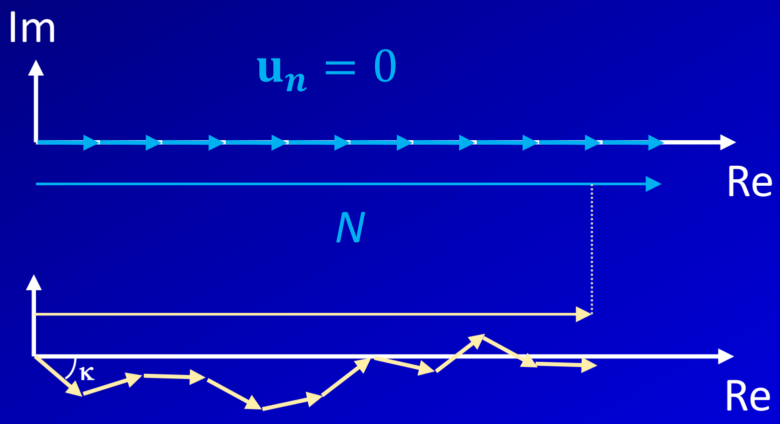
$I_{DD}(\boldsymbol{q})$:
Diffuse scattering

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

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

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

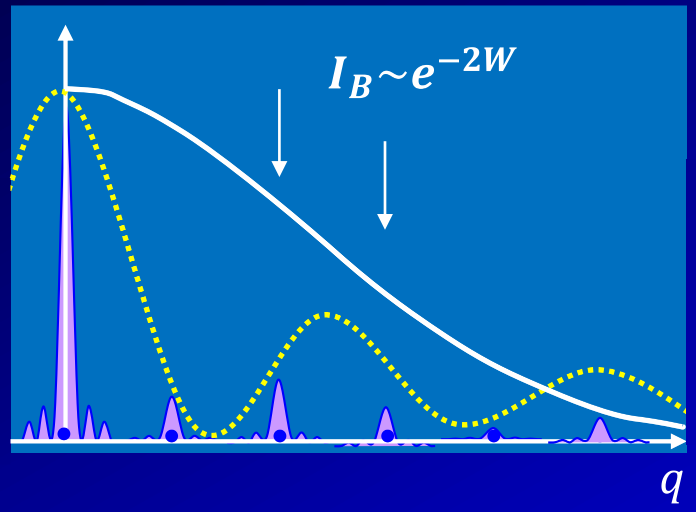
Intensity decreased by factor e^{-2W}

$$e^{-W}$$

is the Debye-Waller factor

The lost intensity goes in the TDS

Debye-Waller factor 2



Unit cell with *n* atoms in 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:

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

Example 1: Lindemann criterion

Solide melts when the ''root mean square'':

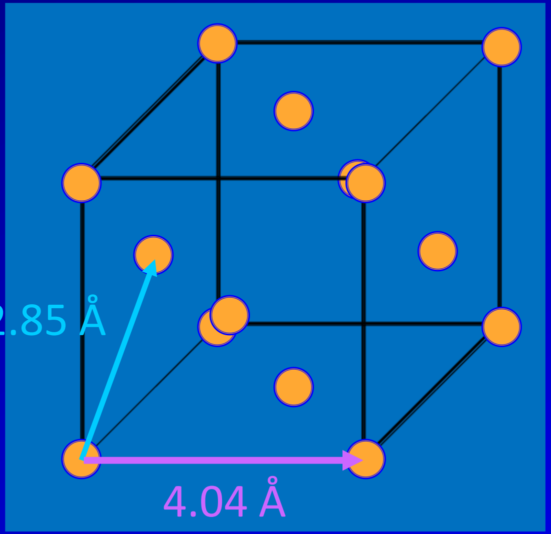
$$\sqrt{\langle u^2\rangle} = 10\%\ d_{1^{st}\ neighbour}$$

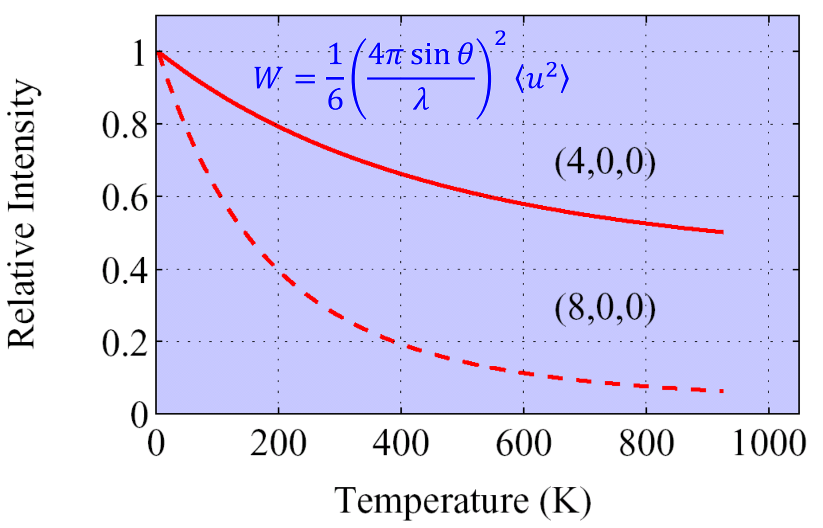
Aluminium (f.c.c.)

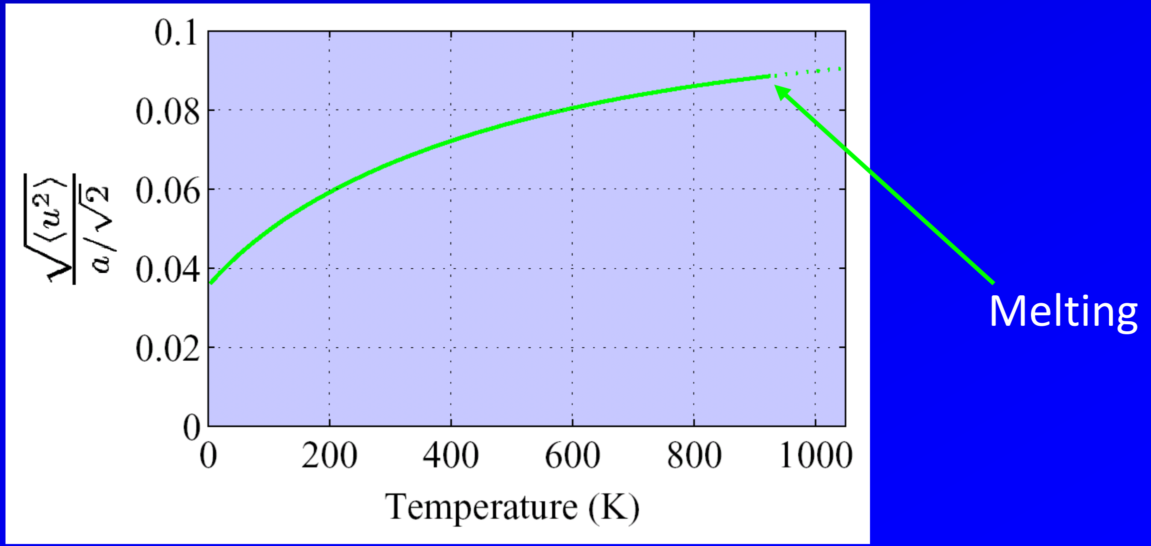
$$a = 4.04\ \text{Å}$$

First neighbour

$$\frac{a}{\sqrt{2}} = 2{,}85\ \text{Å}$$







Example 2:

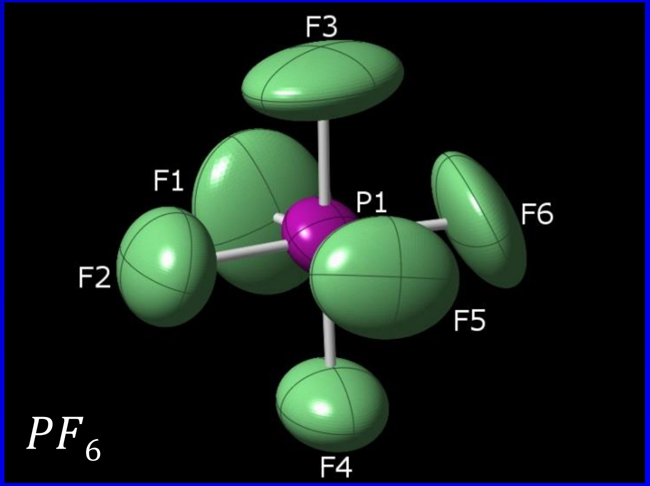
$$W_j = B_{j,T,iso}\left(\frac{\sin\theta}{\lambda}\right)^2$$

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

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

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

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

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

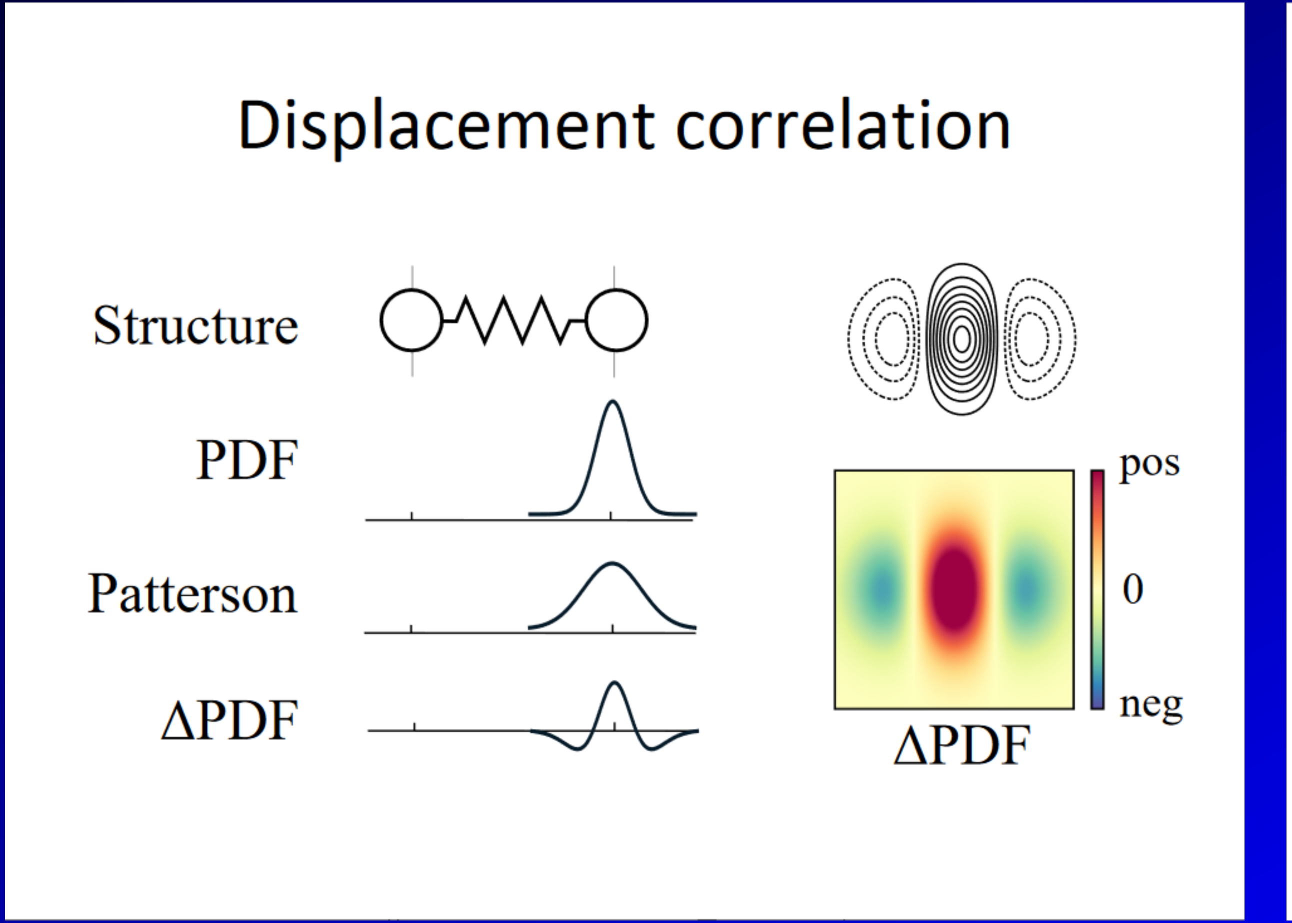
Difference: 3D-ΔPDF

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

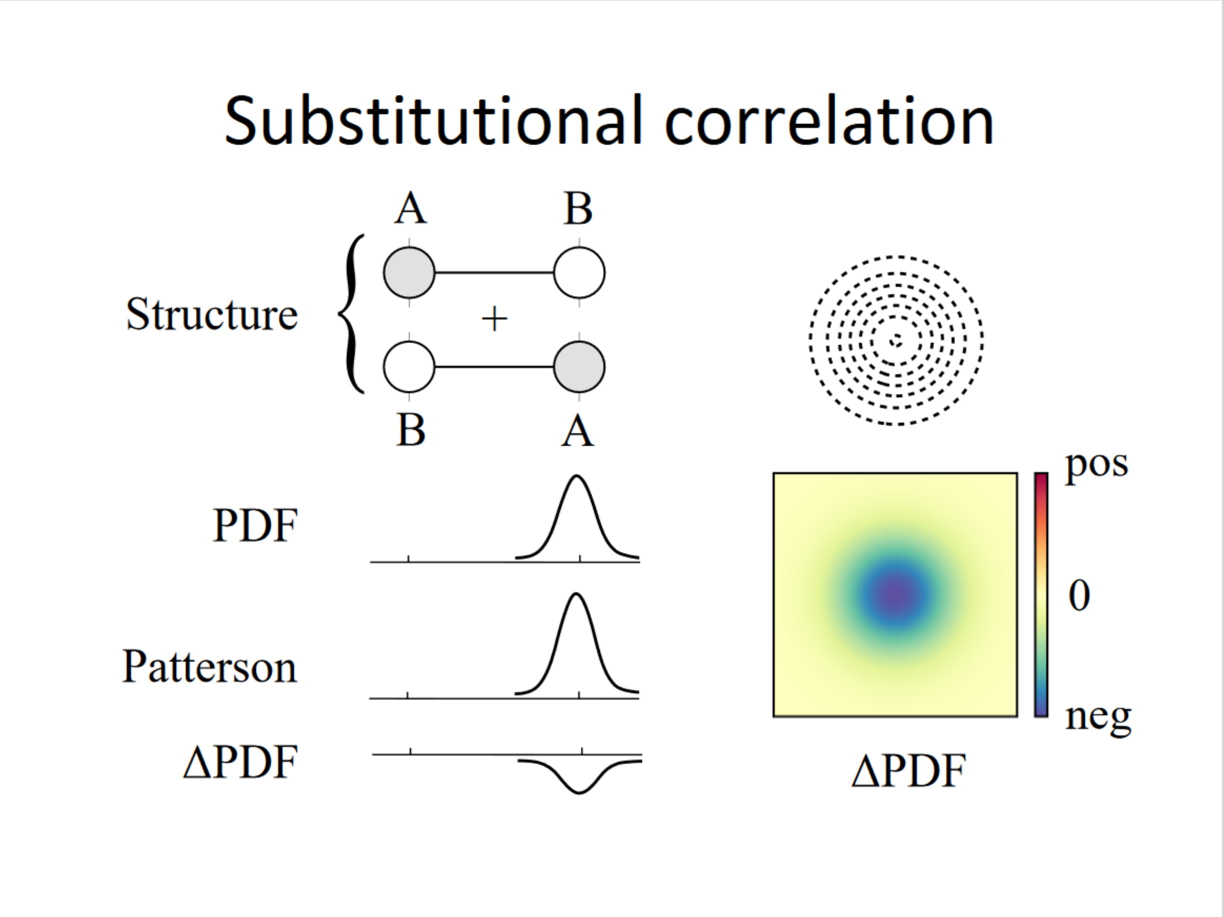
Now measurable in 3D

Examples

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



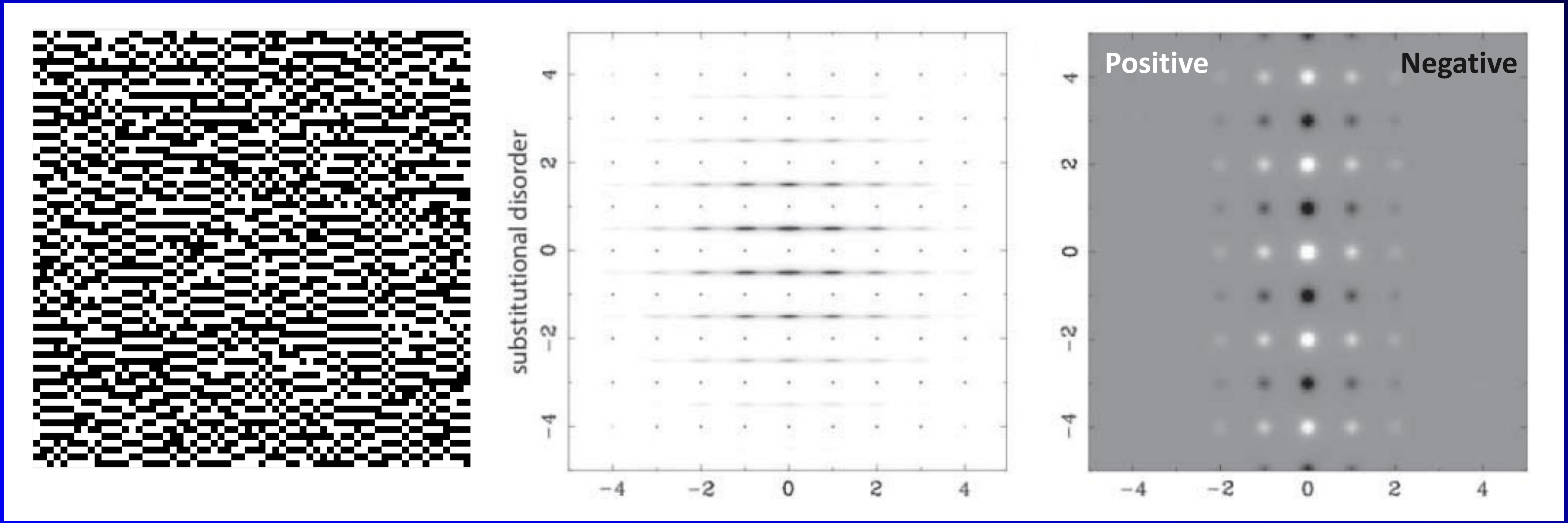
Displacement correlation



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!