Structural Analysis
Part III - X-ray tools

Session 3

X-ray scattering and diffraction

Intermezzo: Fourier Transform

Remember!

~~Alternative~~ approach: Fourier Transform (Infrared) Spectrometer)

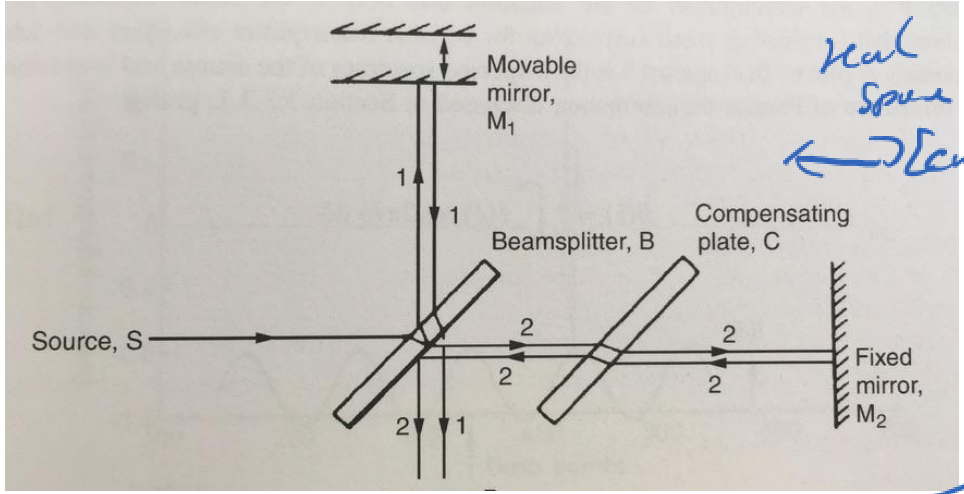
- Not a dispersive measurement but based on interferometry
- Use all wavelength at the same time
- Manipulation in x - cm (real space) to get information in wave numbers x^{-1} – cm^{-1} (frequencies)
- Measure interferogram, Fourier transform into spectrum

$\Downarrow$

Correlation between real & inverse space

$cm \leftrightarrow cm^{-1}$

Measuring an interferogram



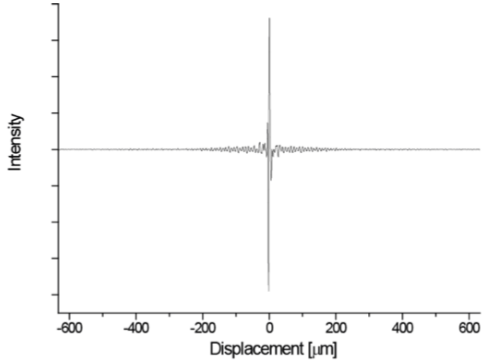
real space
⟵⟶ [cm]

Sample

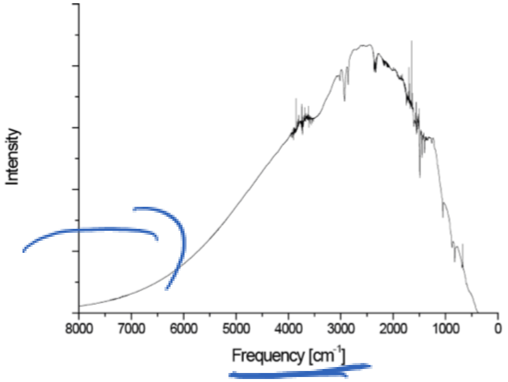
Detector

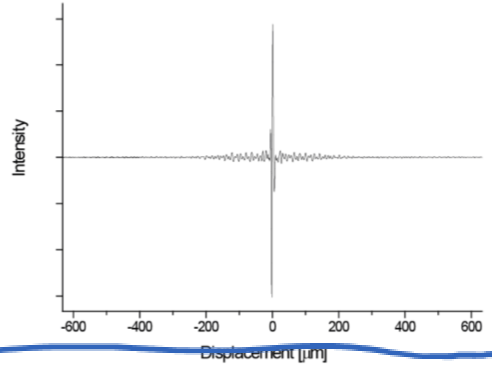
↓

Interferogram
→ Computer → FT → Spectra in $\frac{1}{cm}$ (frequency)

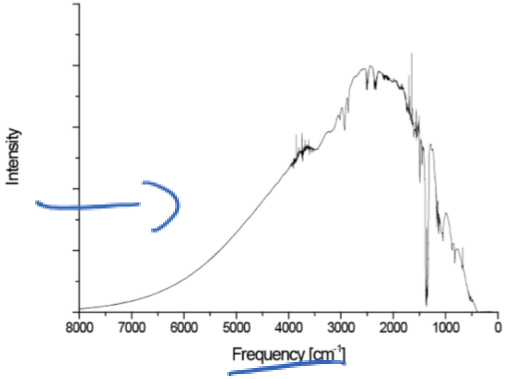


Empty Cell
FT →



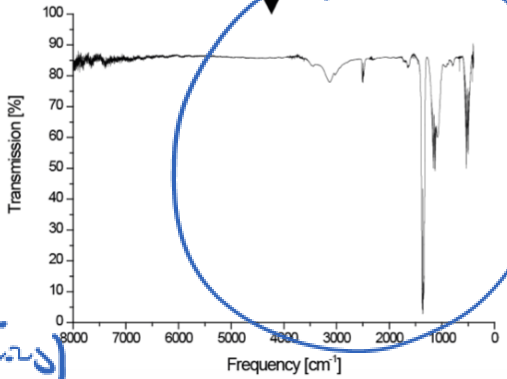


Filled Cell
FT →



FT → relationship
real space & inverse
(frequency) space

Divide



Prof. Emsley part of this class, 5 weeks ago!

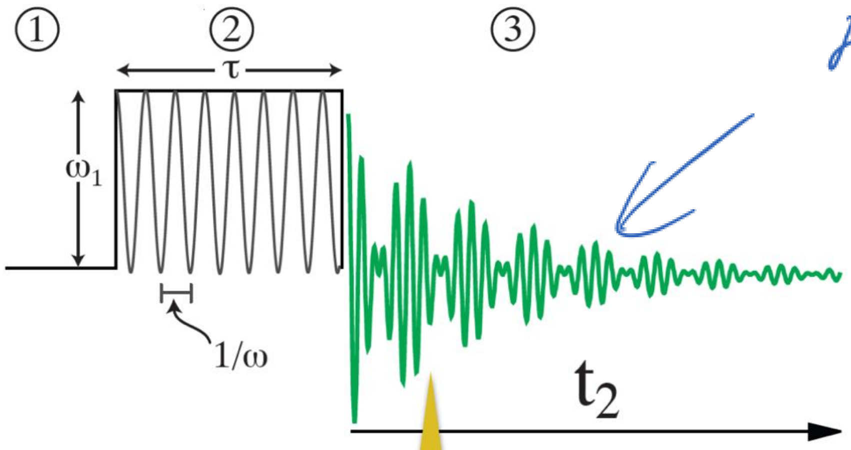
Pulsed FTNMR Spectroscopy

$\omega_1 = -\gamma B_1$

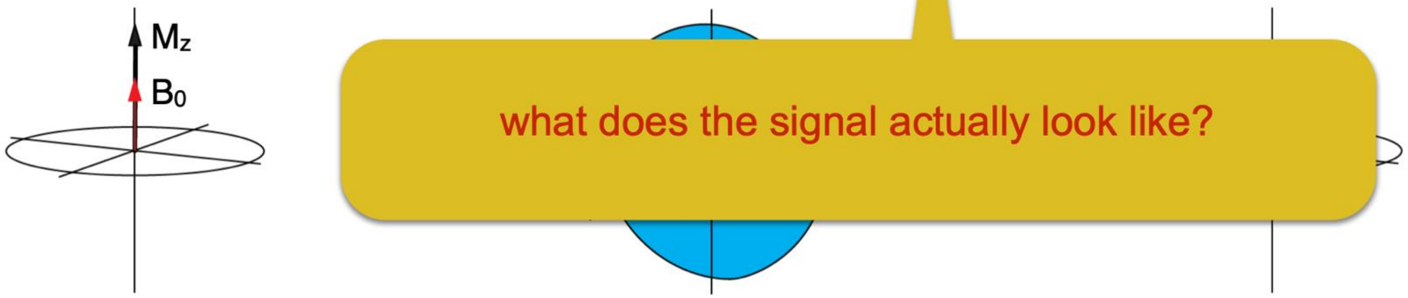
$\omega_1 \tau = \pi/2$

ω = carrier frequency, chosen by the operator to be near to the resonance frequencies

^{1}H



relationship
decay times
&
frequencies /
lifetimes

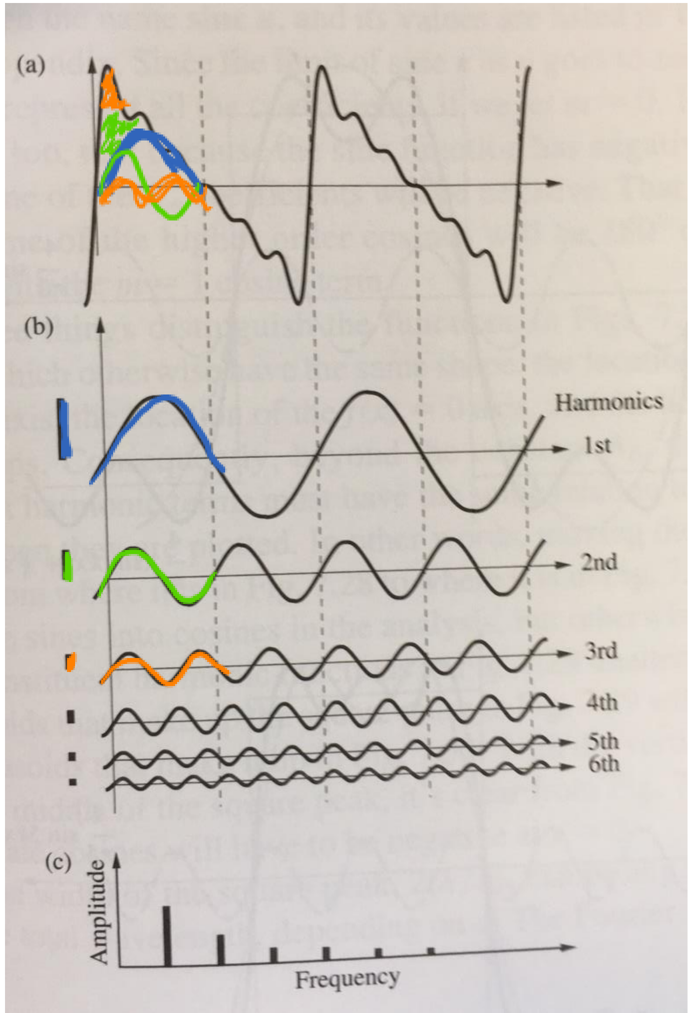


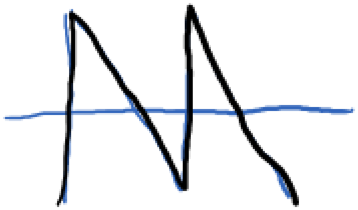
1. Equilibrium. The net magnetization is aligned along the direction of the main field (z-axis).

2. A field is applied in the transverse plane. The magnetization of the ensemble precesses around the field.

3. The field is removed leaving a net transverse component of the ensemble magnetization. This ***coherence*** then starts to precess around the main field.

Principle idea





initial fct

use Σ of harmonic fct

use each harmonic fct with a specific amplitude

Mathematical description

- The principle idea of the Fourier analysis / transformation is that any function can be represented by an (infinite) series of harmonic functions.
- The Fourier transform decomposes a function into its constituent frequencies.

Sum -> Integral over all frequencies

Function

Fourier transform describing f(x)

↳ "rule" how amplitudes & frequencies come together

Thus we can write

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} F(k)e^{-ikx}\,dk$$

harmonic fct

provided that

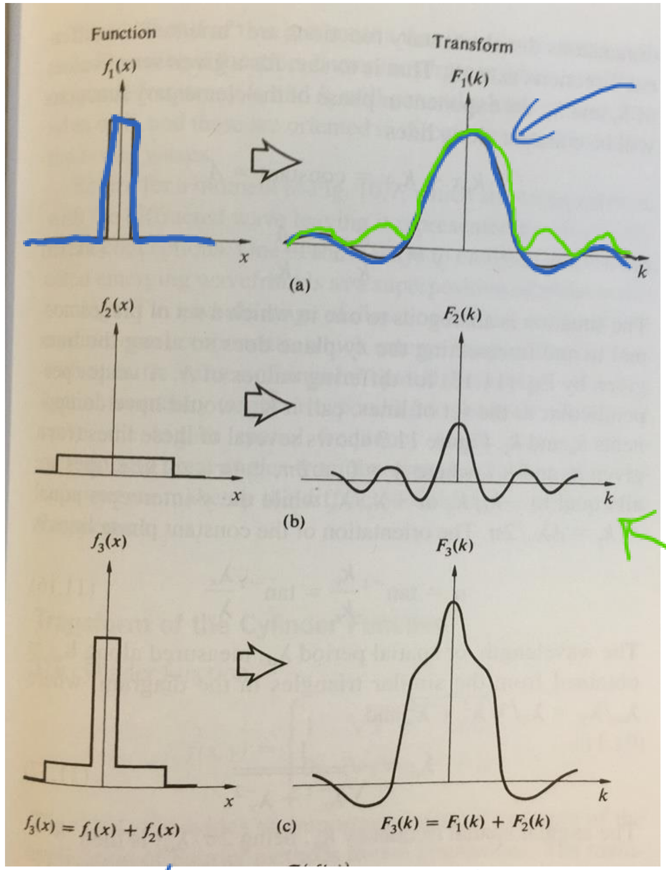
$$F(k) = \int_{-\infty}^{+\infty} f(x)e^{ikx}\,dx$$

↳ Fourier transform

Note computers can do this really well (GPU)

Examples → Some examples → for everything else there are computers

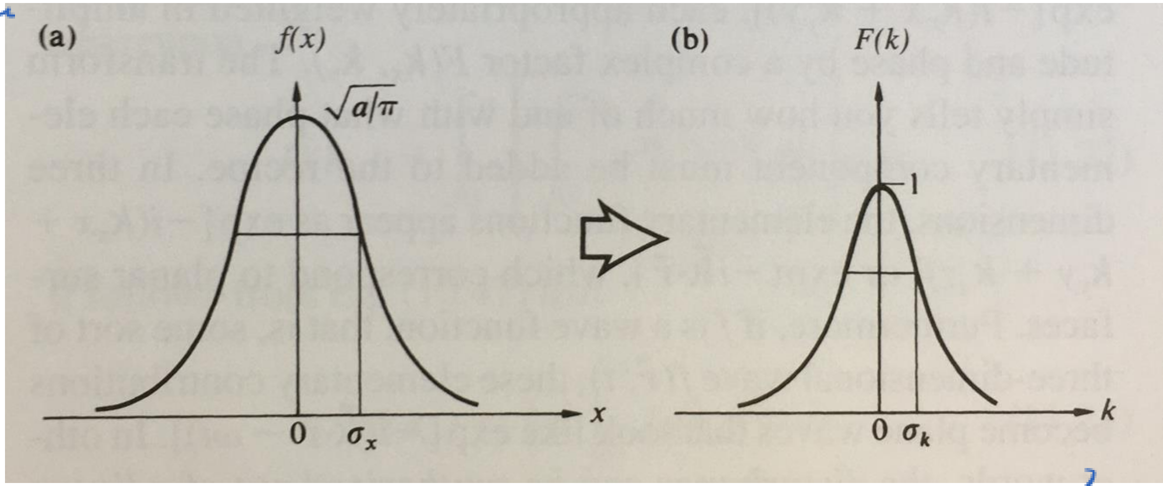
Squares and composite



sinc fct
c.f. interference from a slit
↓
in optics we measure
$I = |A|^2$

↳ composite fct

Gauss function

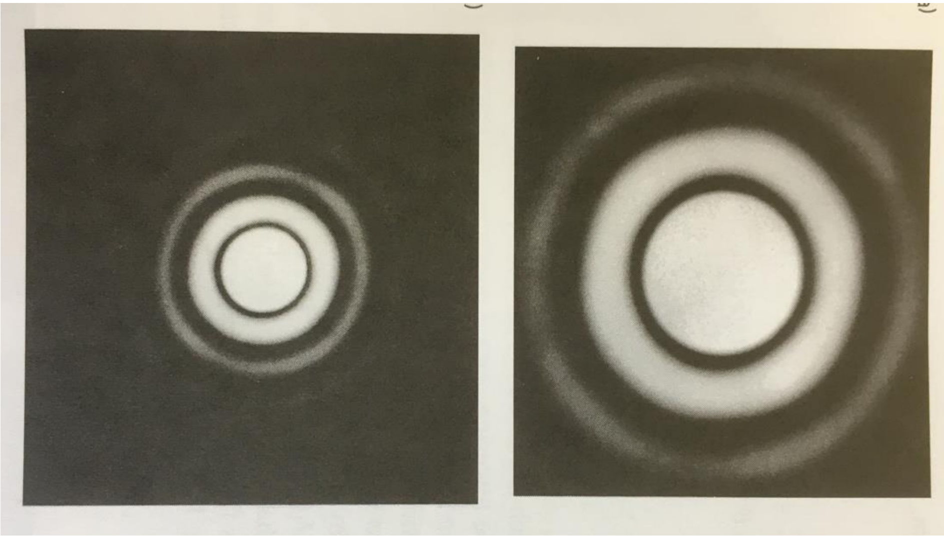


FT (Gauss) → Gaussian

→ Once a Gauss, always a Gauss!

Fourier transform of round aperture and airy pattern

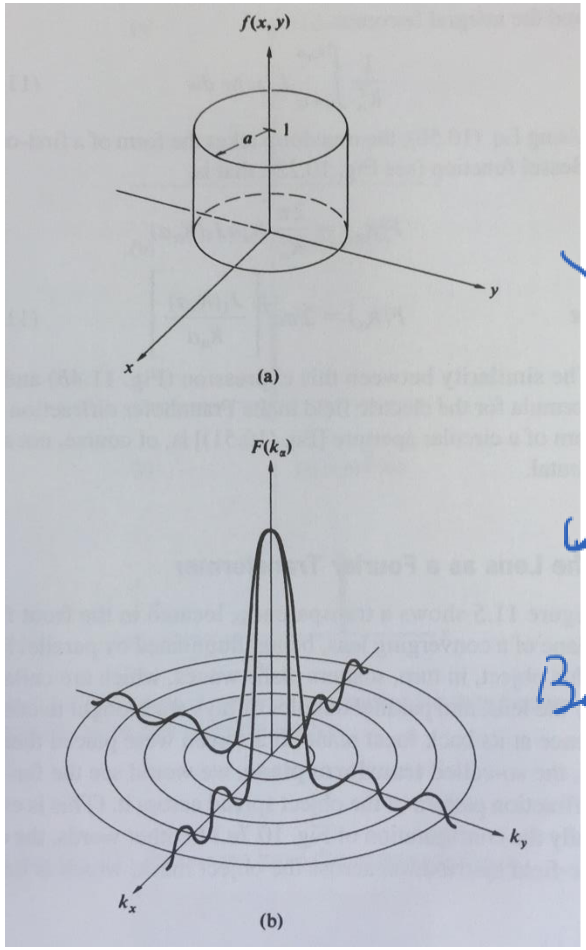
Experiment: Diffraction pattern of circular aperture, Airy pattern



Diffraction pattern ⇒ Bessel fct
That is not a coincidence!

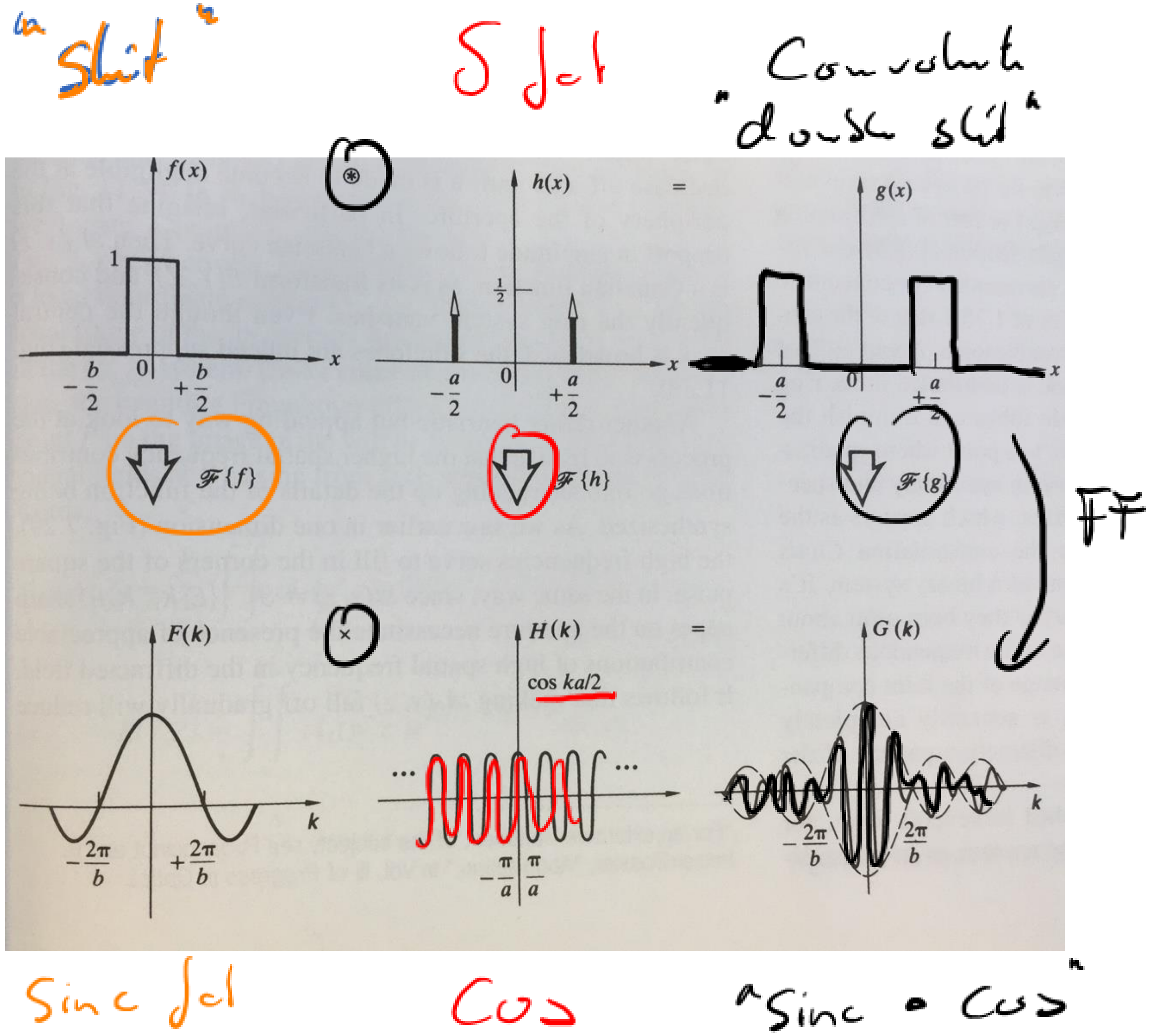
Generally The diffraction pattern of an object is described by its FT

Theory: Fourier transform of cylinder or "top-hat" function



Bessel fct

Diffraction as Fourier transform:



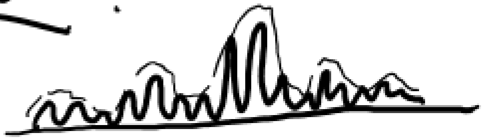
Convolution theorem

$$\mathcal{F}(f \circ g) = \mathcal{F}(f) \cdot \mathcal{F}(g)$$

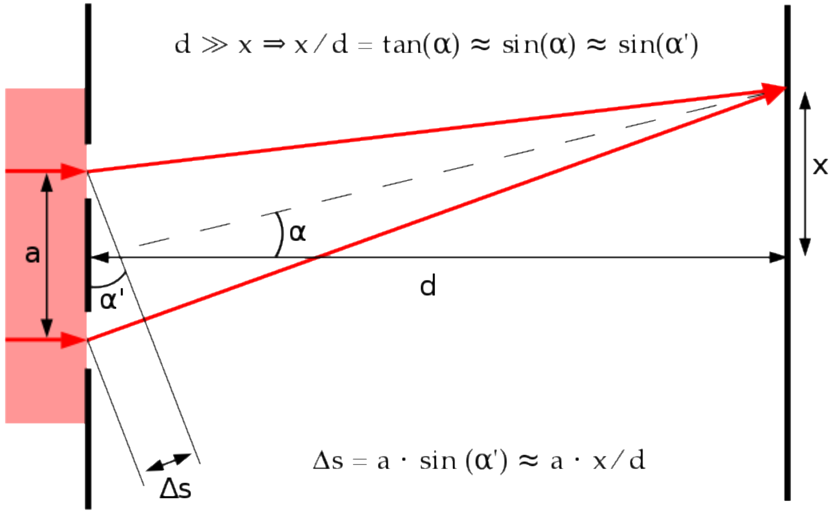
The FT of two convoluted fct is the point product of their FT

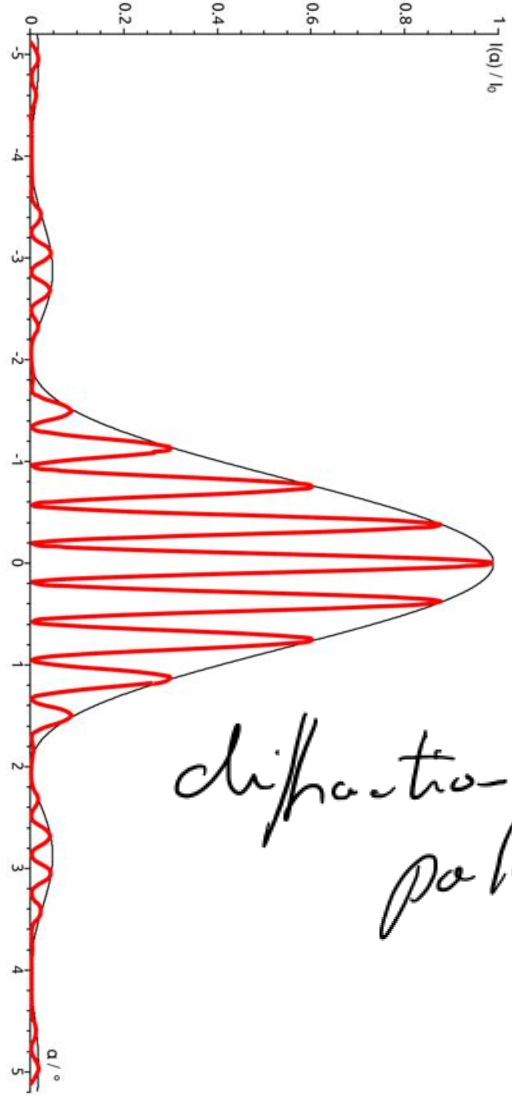
Reconstruct the double slit exp

but note: we measure $I = |A|^2$

$\Rightarrow$  > 0

The double slit





diffraction pattern

Convolution theorem

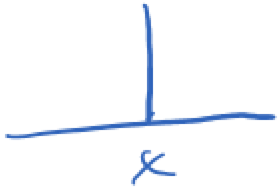
$$\mathcal{F}(f \circ g) = \mathcal{F}(f) \cdot \mathcal{F}(g)$$

Image source: wikipedia

Fourier relationships – some examples

Relationship between time domain — frequency domain

image space — spatial frequency

$\sin(x)$  $\rightarrow$ $\delta(x)$ 

Note: diffraction pattern is FT of object

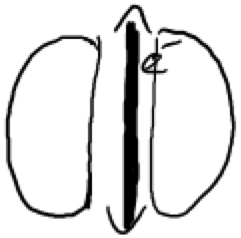
Lens is a FT $\rightarrow$ information inside focus is FT(object)

TEM, NMR

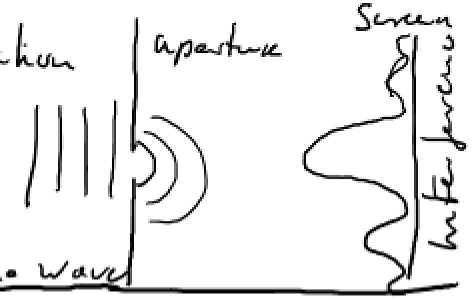
Building on session 1

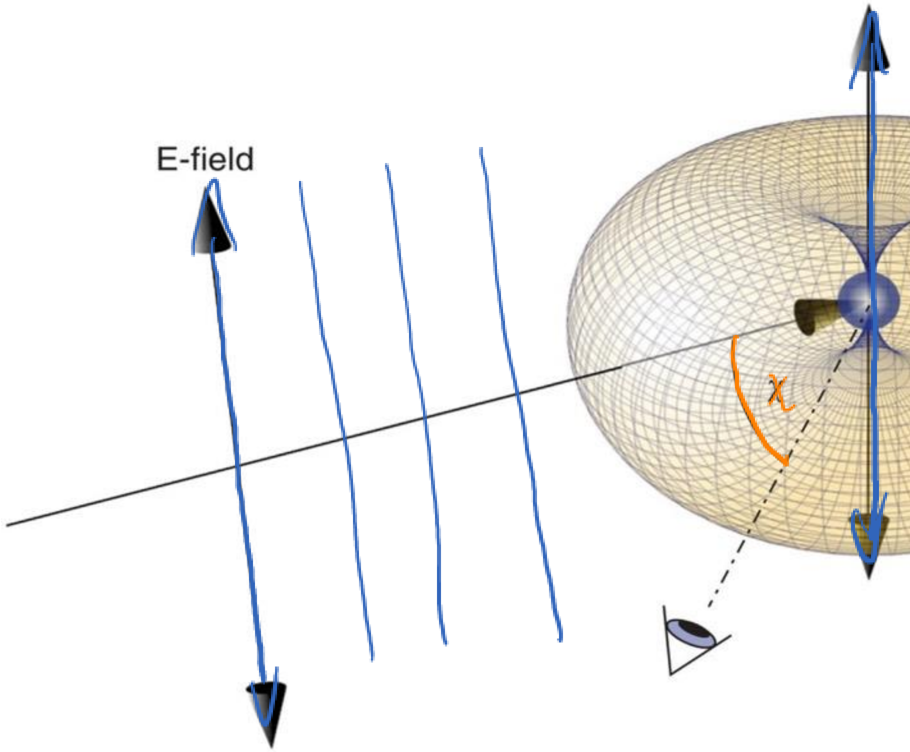
Thomson scattering

Remember from Physics : Dipole radiation



Diffraction





Dipole <u>no</u> intensity along axis

emission in 3D $\sim \cos^2\chi$

→ semi-classical description

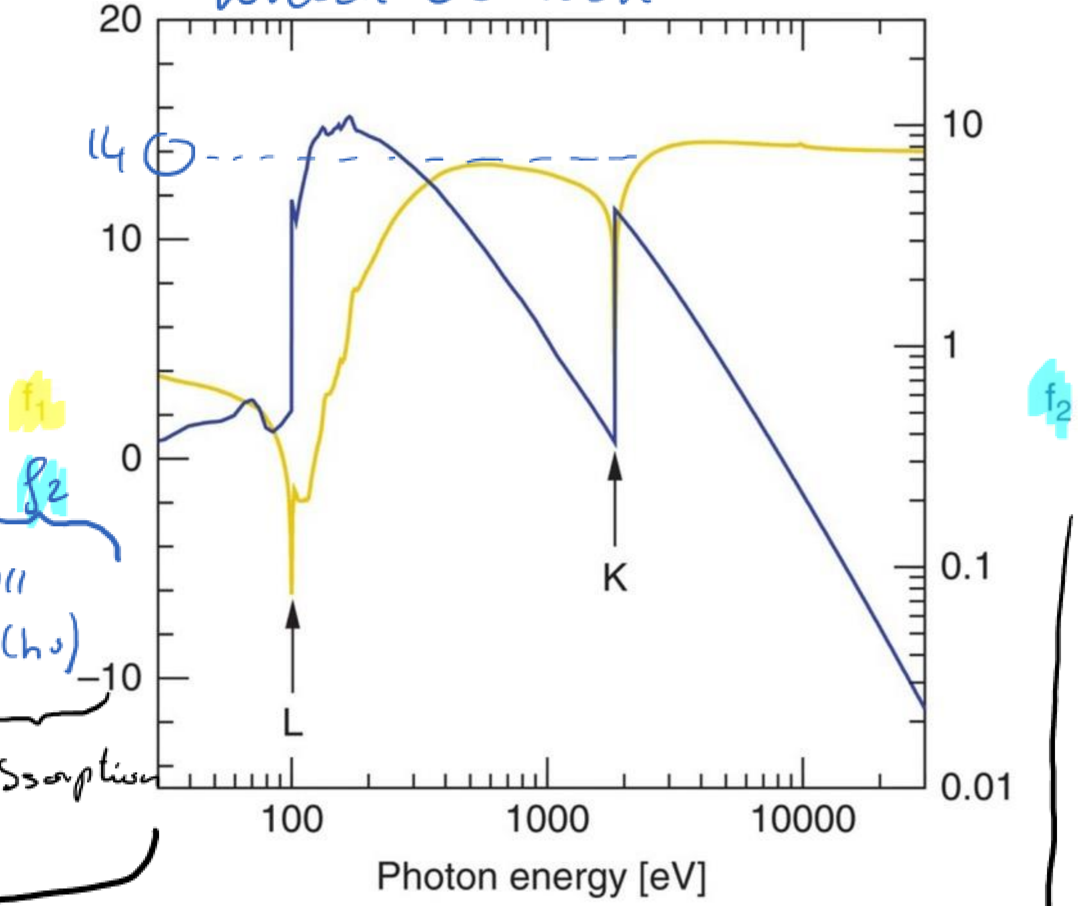
→ x-rays well approximated by <u>planar wave</u>

→ x-ray scattering process described by <u>dipole radiation</u>

Scattering process
- transfer incoming plane wave to dipole wave
- no frequency shift → elastic
- phase shift

Atomic scattering factors and refractive index

which element?



$$f(h\nu) = \overbrace{\underbrace{f_0 + f'(h\nu)}_{\#\text{ electrons}}}^{f_1} + i\,\overbrace{\underbrace{f''(h\nu)}_{\text{absorption}}}^{f_2}$$

x-ray analogue to "refraction index"

⇒ $f_1 \sim$ # electrons

⇒ 14

⇒ $1s^2\, 2s^2 2p^6\, 3s^2\, 3p^2$

⇒ Si

⇒ double check with absorption edge / f_2

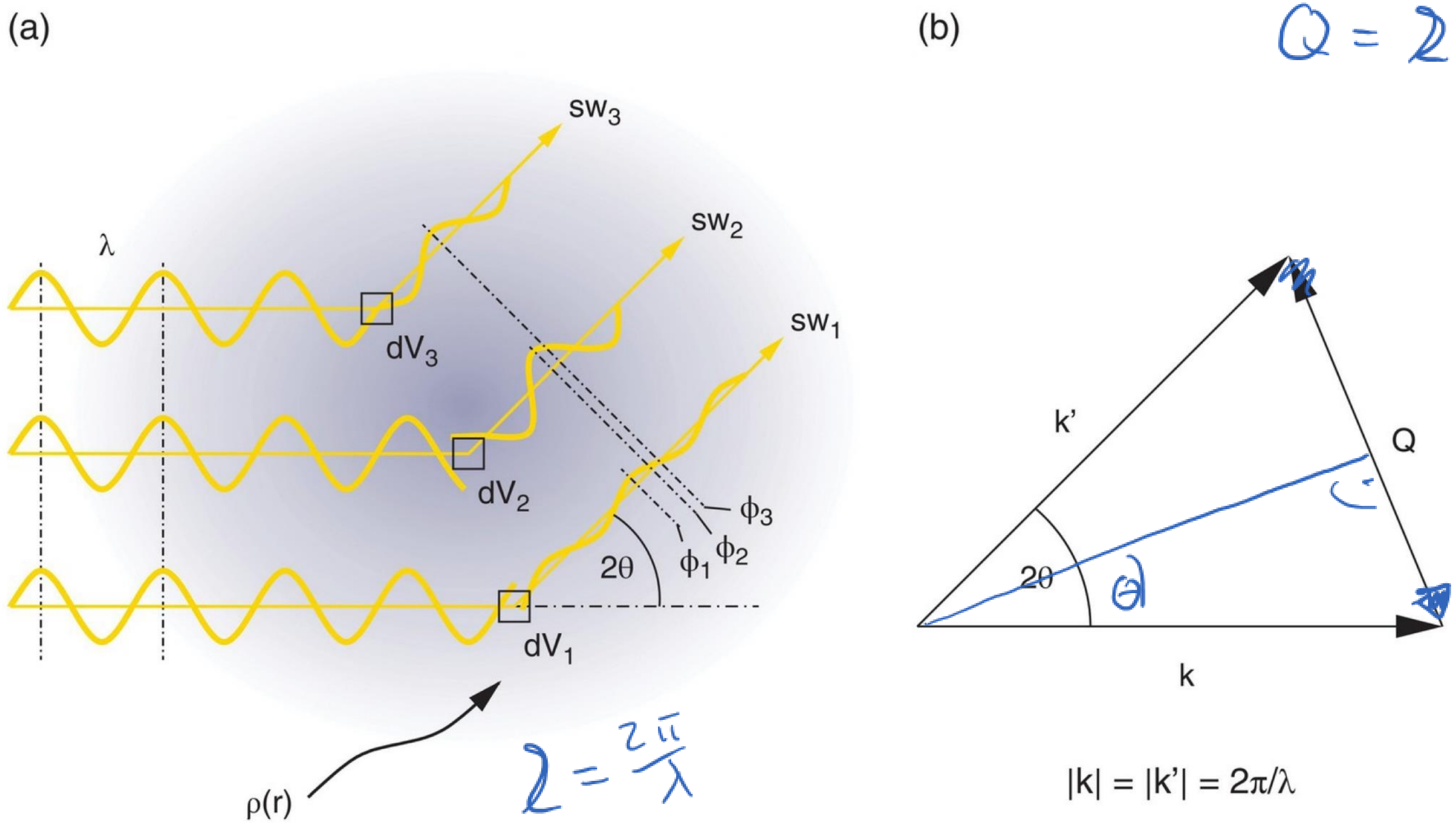
Relevance

absorption → electronic levels

Scattering → electronic information

Definition of the scattering vector Q

→ vectorial difference between incident & elastically scattered wave



$$Q = \vec{k} - \vec{k}'$$

$$k = \frac{2\pi}{\lambda}$$

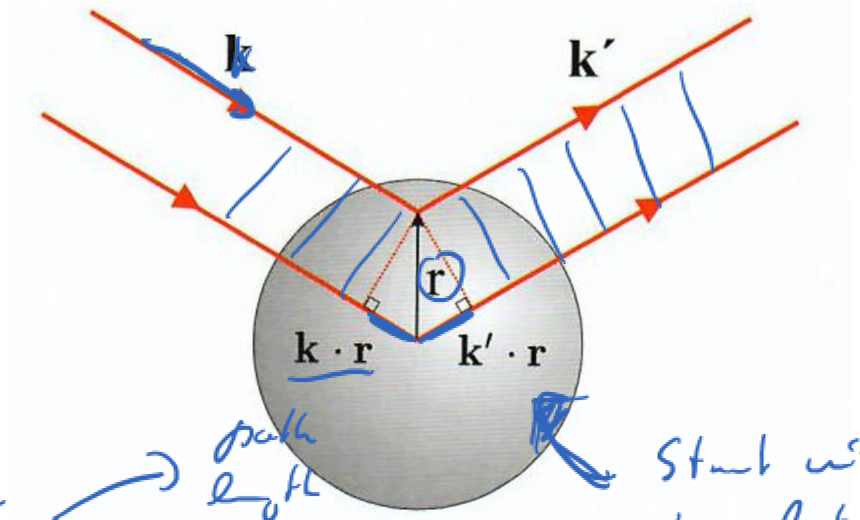
$$\frac{1}{2} Q \cdot \frac{1}{k} = \sin\theta$$

$$\sin\theta = \frac{Q}{2k}$$

$$\boxed{Q = 2k \sin\theta = \frac{4\pi}{\lambda}\sin\theta}$$

Scattering from an electron cloud

wave vector $\vec{k} \Rightarrow |\vec{k}| = \frac{2\pi}{\lambda}$



con-destructive → path length difference

Start with two electrons

$\lambda \Rightarrow$ constructive interference

equivalent to saying 2π phase shift

ultimately electron density distribution ρ

→ cloud: density ρ

→ constructive interference for phase shift 2π

→ $\vec{k}\vec{r} \sim$ phase

→ At observer the phase difference

$$\Delta\phi = \vec{k}\vec{r} - \vec{k}'\vec{r} = (\vec{k}-\vec{k}')\vec{r} = \vec{Q}\vec{r}$$

phase difference

→ elastic scattering $|\vec{k}| = |\vec{k}'|$

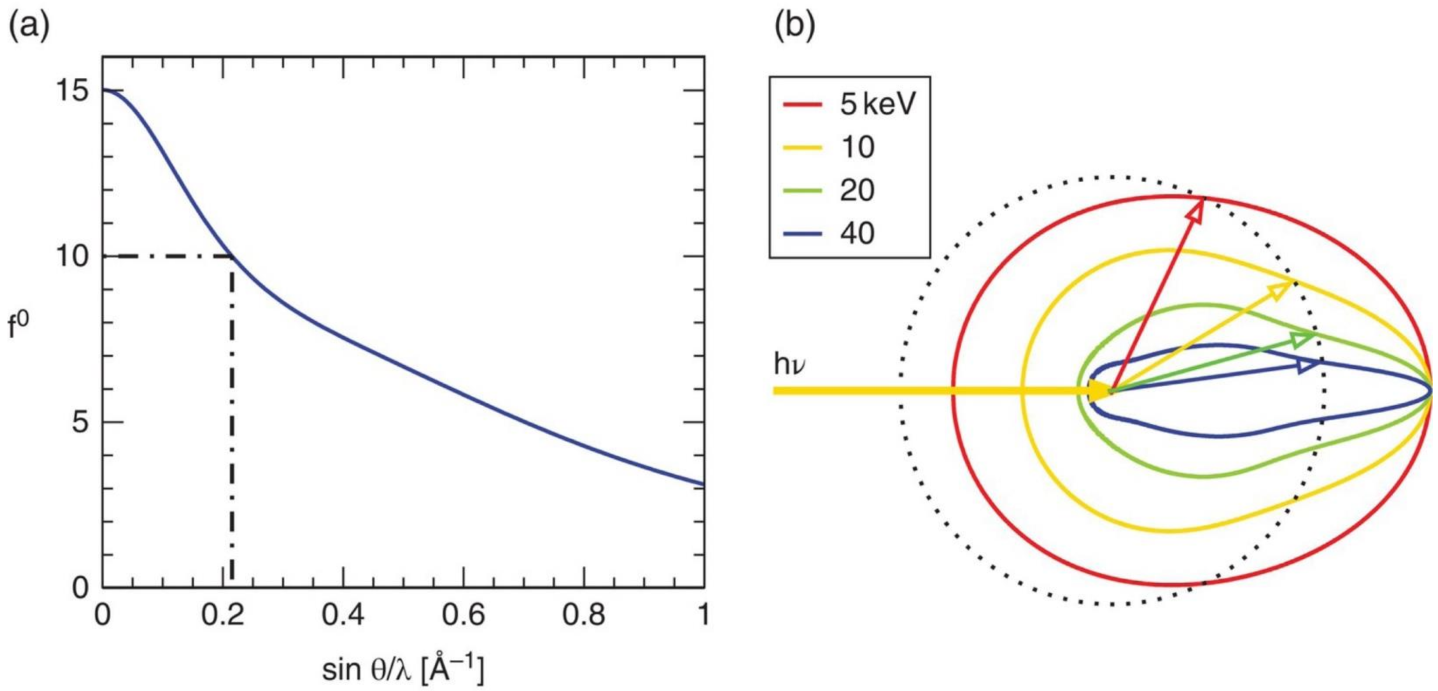
$$Q = 2k\sin\theta = \frac{4\pi}{\lambda}\sin\theta$$

→ lets look at volume dr at r

$r_0\,\rho(r)\,dr$ with e^{iQr}

$$\cancel{r_0}\, f(Q) = \cancel{r_0}\int \rho(r)\, e^{iQr}\, dr$$

Now full cross section / atomic scattering factors



$$f(Q) = \int \rho(r)\, e^{iQr}\, dr$$

FT of electron distribution

For $Q \to 0 \Rightarrow Z$

f^0 is fct of Q

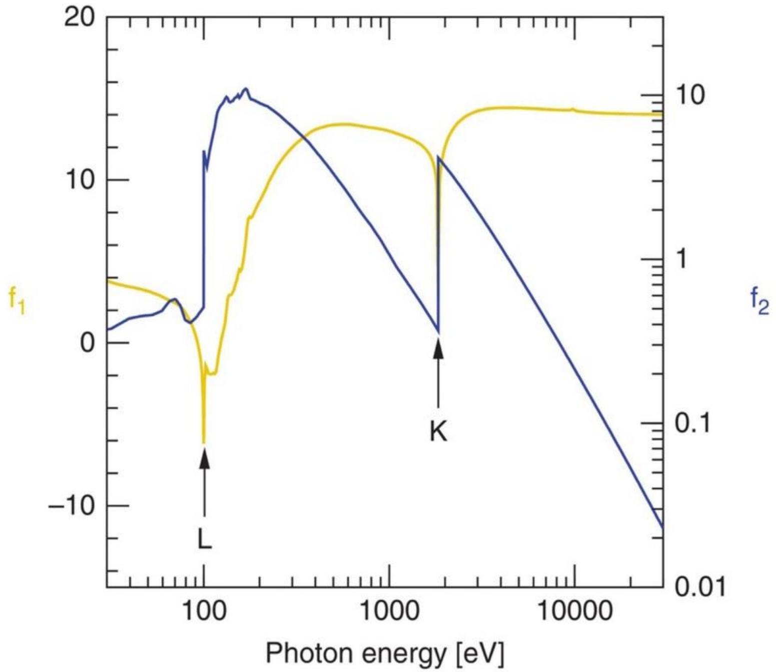
$f^0 \to$ is form factor of atoms

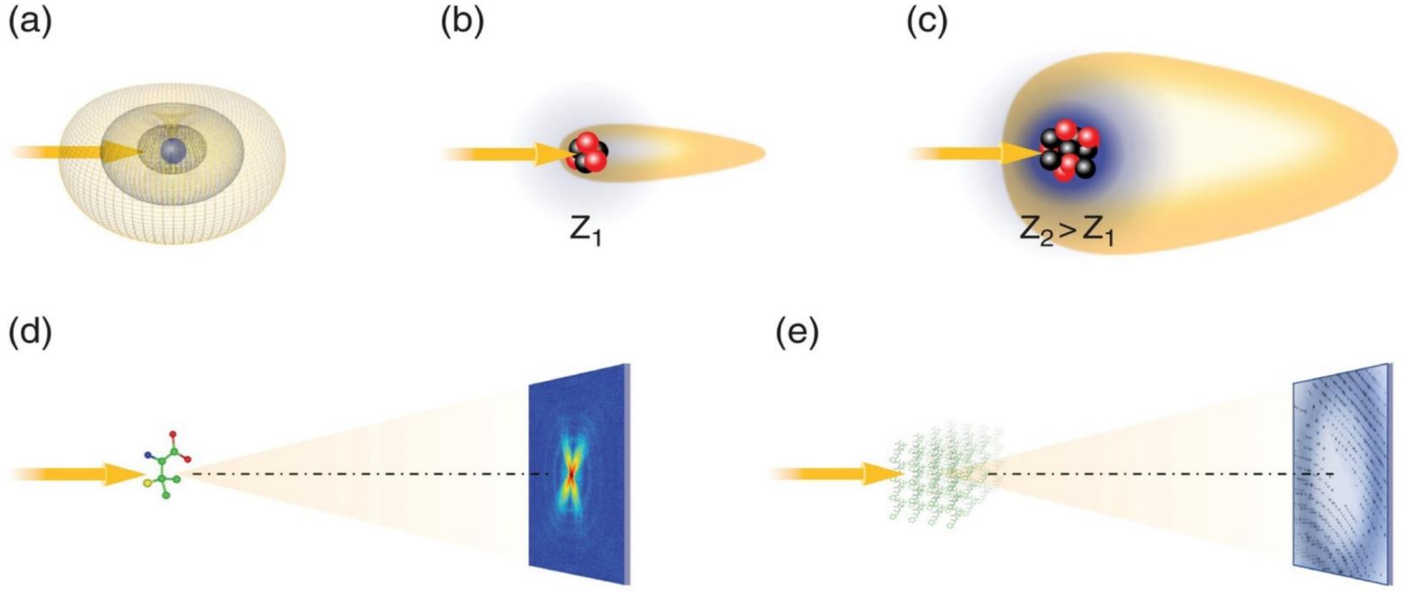
$\to Z$ in forward direction

$\to$ decreases with increasing scattering angles

(all tabulated)

Atomic scattering factors again





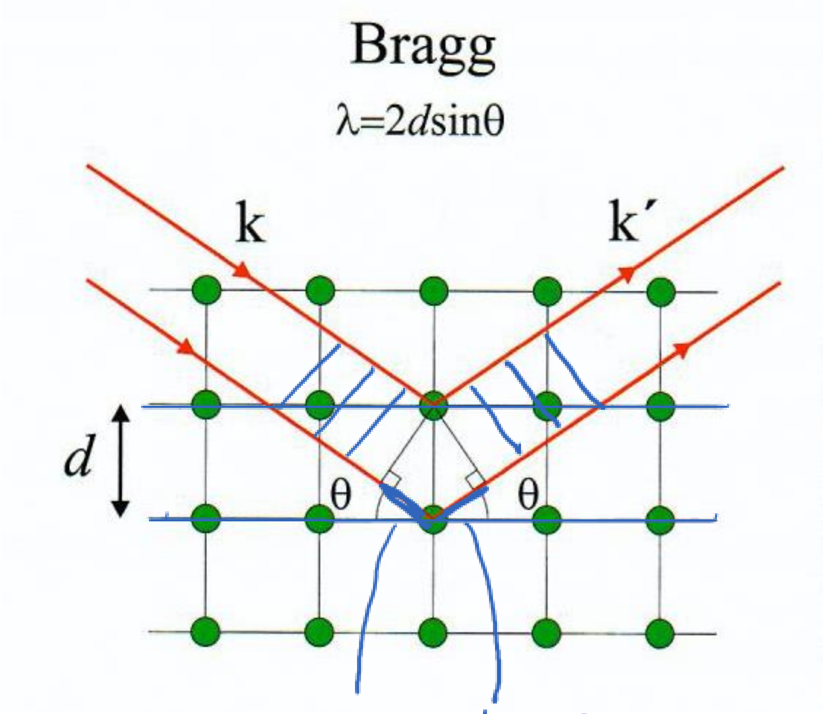
$Z \int \sim Q \rightarrow \sigma$

$$\boxed{f(Q, h\nu) = \underbrace{f^0(Q) + f'(h\nu)}_{\text{scatting}} + \underbrace{i f''(h\nu)}_{\text{absorptin}}}$$

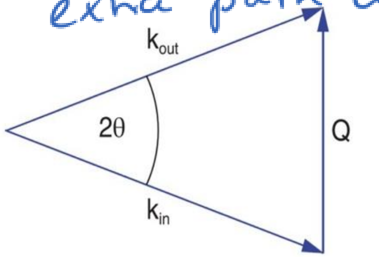
Building on session 2

Bragg scattering

The Nobel Prize in Physics 1915



$d \cdot \sin\theta + d \sin\theta$
extra path length



→ atoms in defined positions

→ defined crystal planes

→ x-rays can "reflect" from these planes

Main idea again: exploit interference phenomena

constitute positive interference

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

$$\sin\theta = \frac{n\lambda}{2d} \Rightarrow \boxed{2d\sin\theta = n\lambda}$$

Bragg law

Note: similar formalism applies to many other sample systems

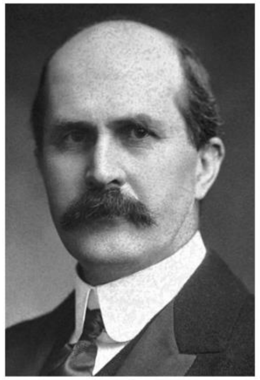


Photo from the Nobel Foundation archive.

Sir William Henry Bragg

Prize share: 1/2

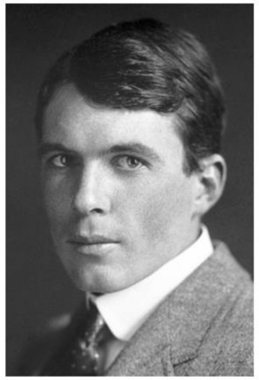
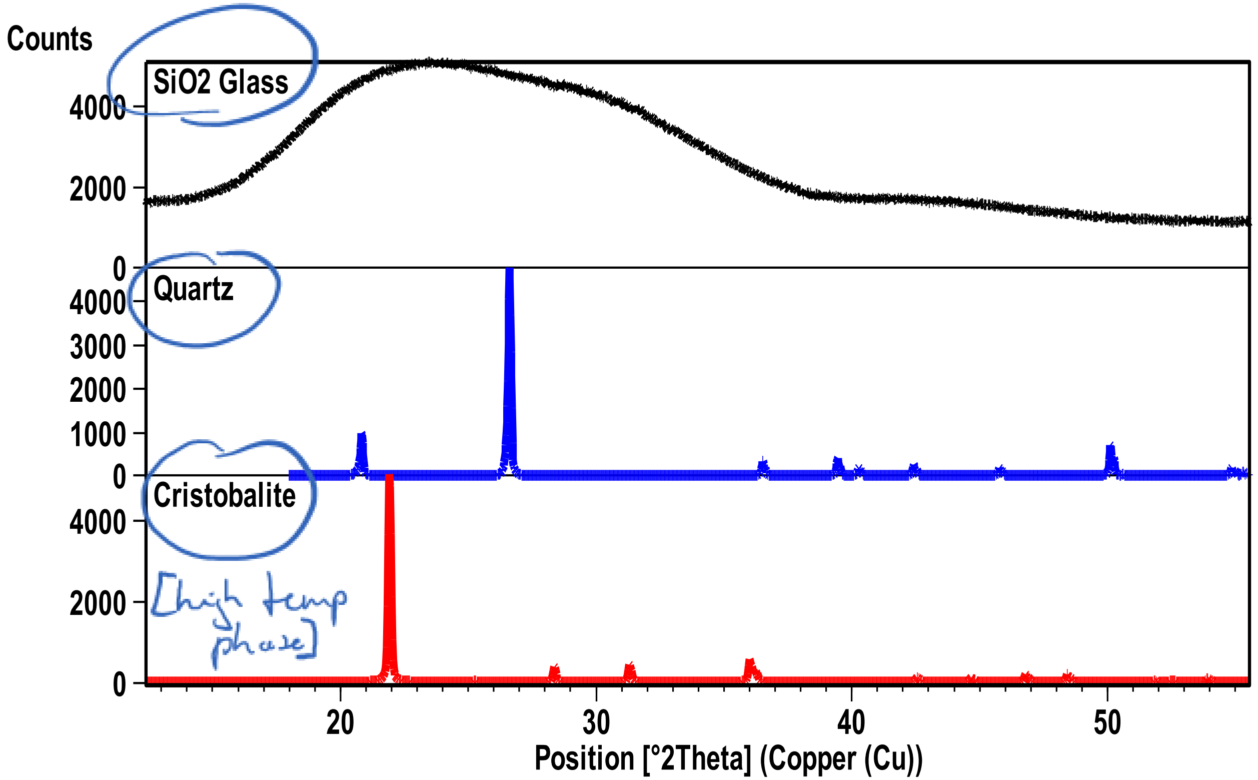


Photo from the Nobel Foundation archive.

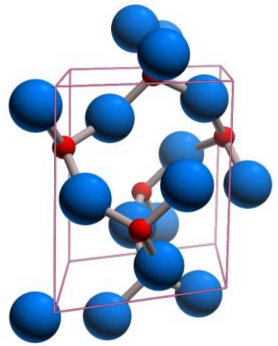
William Lawrence Bragg

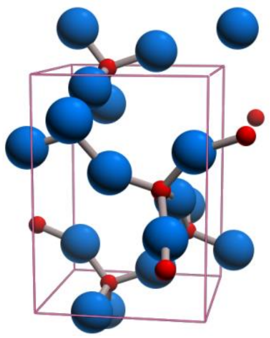
Prize share: 1/2

Characteristic signals from different – chemically identical – samples



no order (glass)



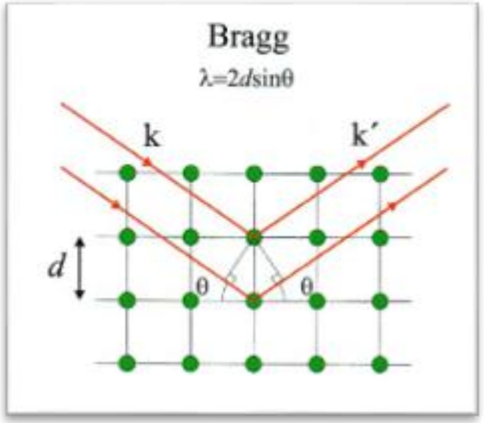


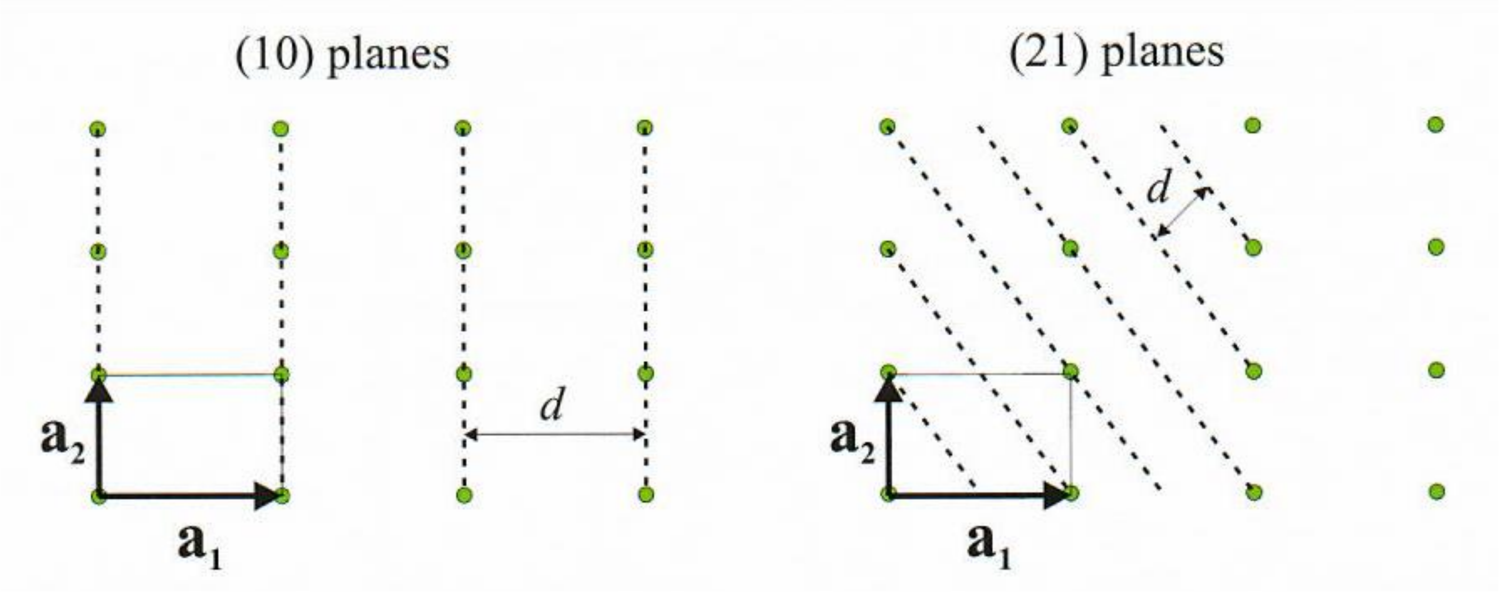
- all SiO_2 samples but different phases
- all structures are chemically identical but their structure order is different

⇓

XRD yields info about atomic arrangement

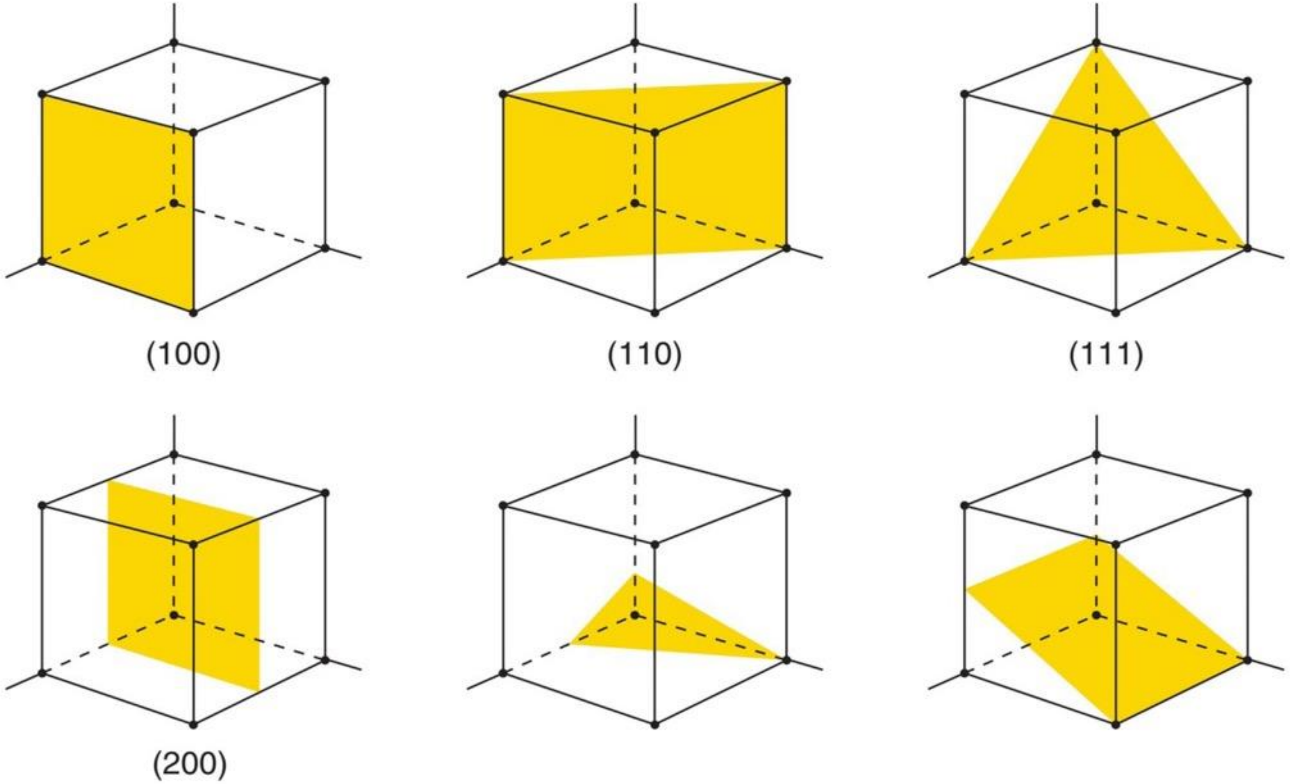
Lattice planes

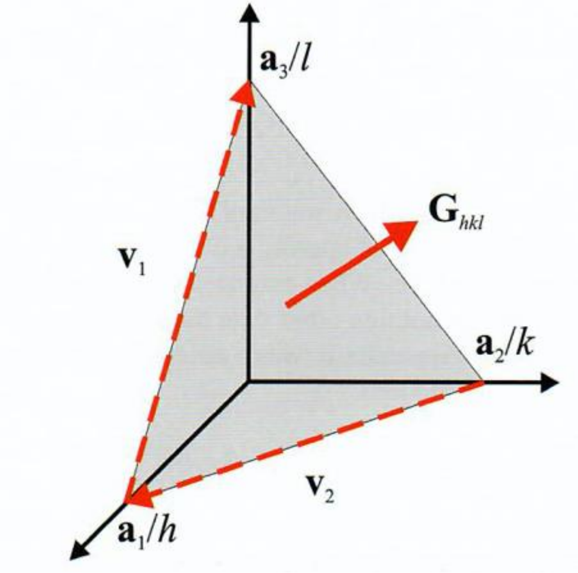




- Find the intercepts of the plane with the respective crystal axis
- Take the reciprocal of these numbers, reduce to smallest integer

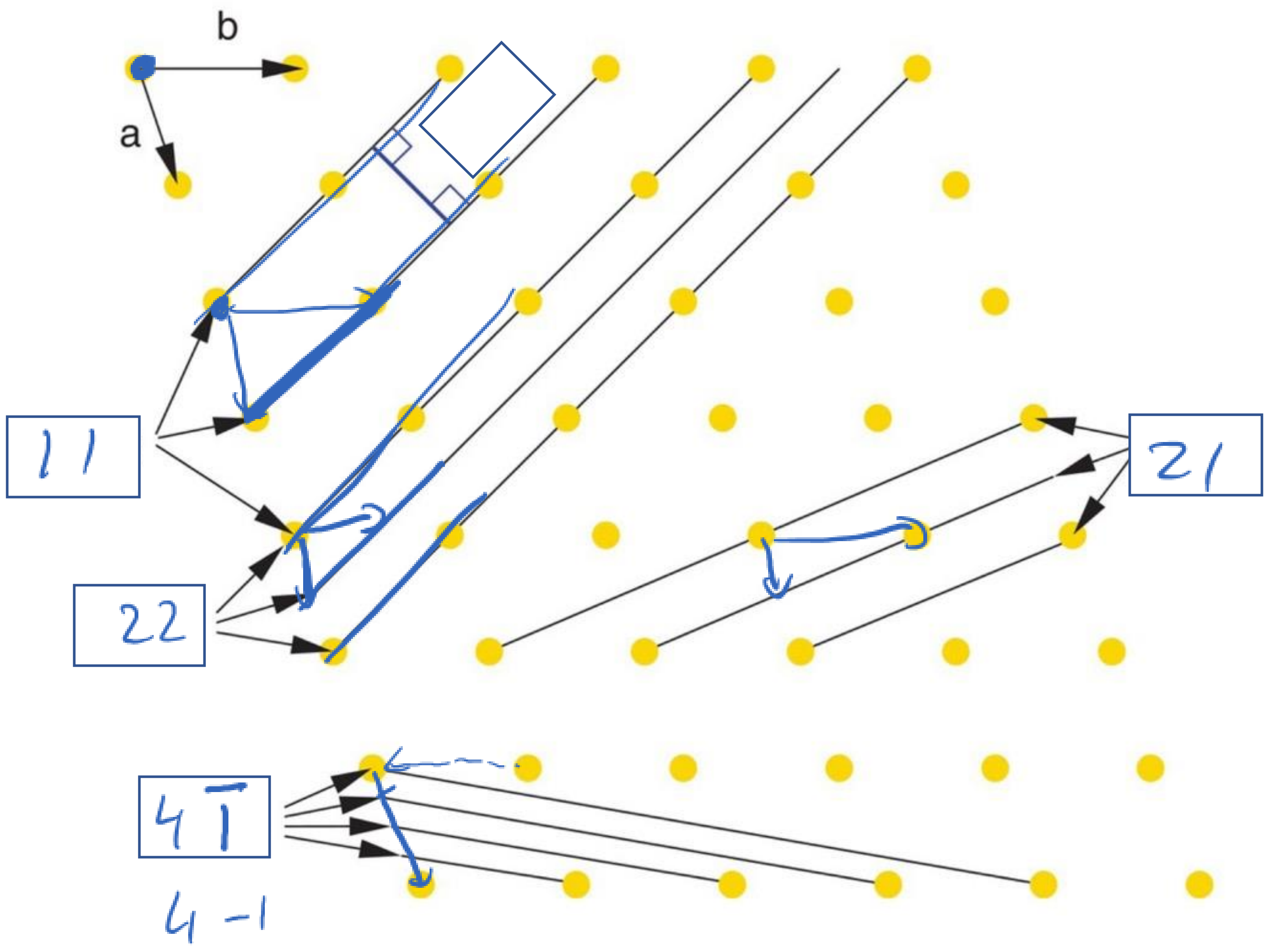
Miller indices





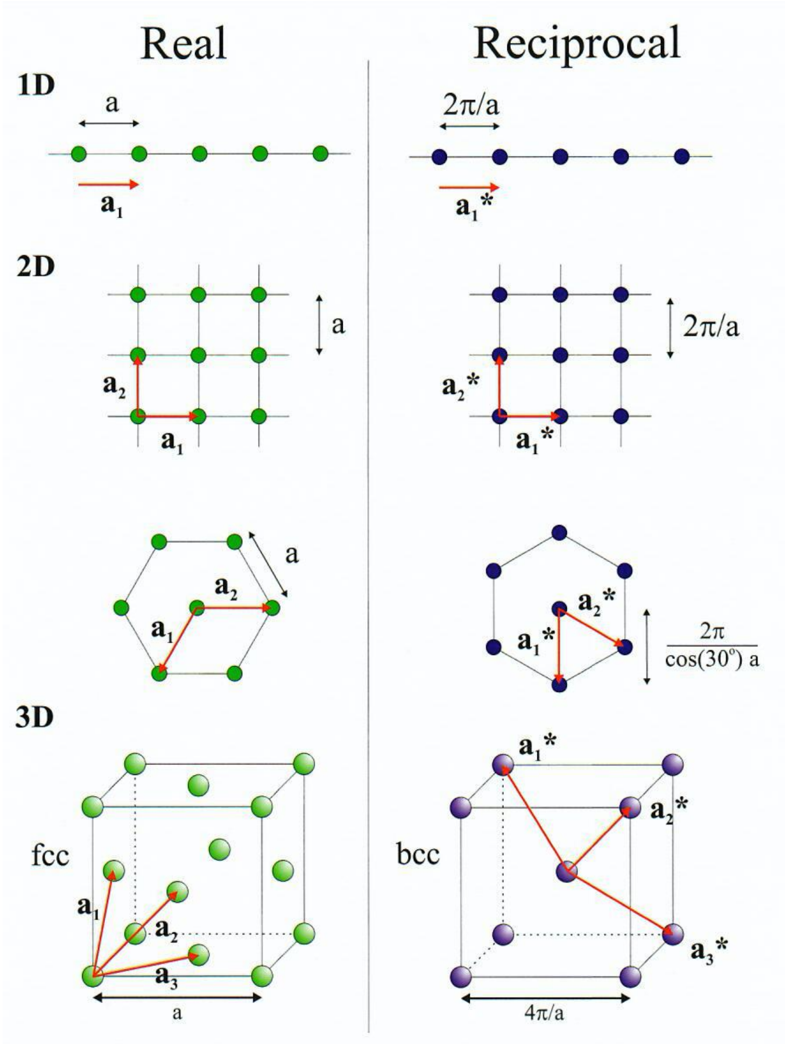
- Find the intercepts of the plane with the respective crystal axis
- Take the reciprocal of these numbers, reduce to smallest integer

Exercise: Identify lattice planes



More on diffraction of single crystals

For each lattice a reciprocal lattice can be defined



From physics

→ for each lattice there exist a so-called reciprocal lattice

→ the reciprocal lattice ~~th~~ is the Fourier transform of the direct lattice

→ reciprocal lattice is defined

$$\vec{G} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$

$$|\vec{G}| = \frac{2\pi}{d_{hkl}}$$

$\vec{G}$ → perpendicular on planes

hkl → Miller indices

Bargg and Laue conditions

Real Inverse

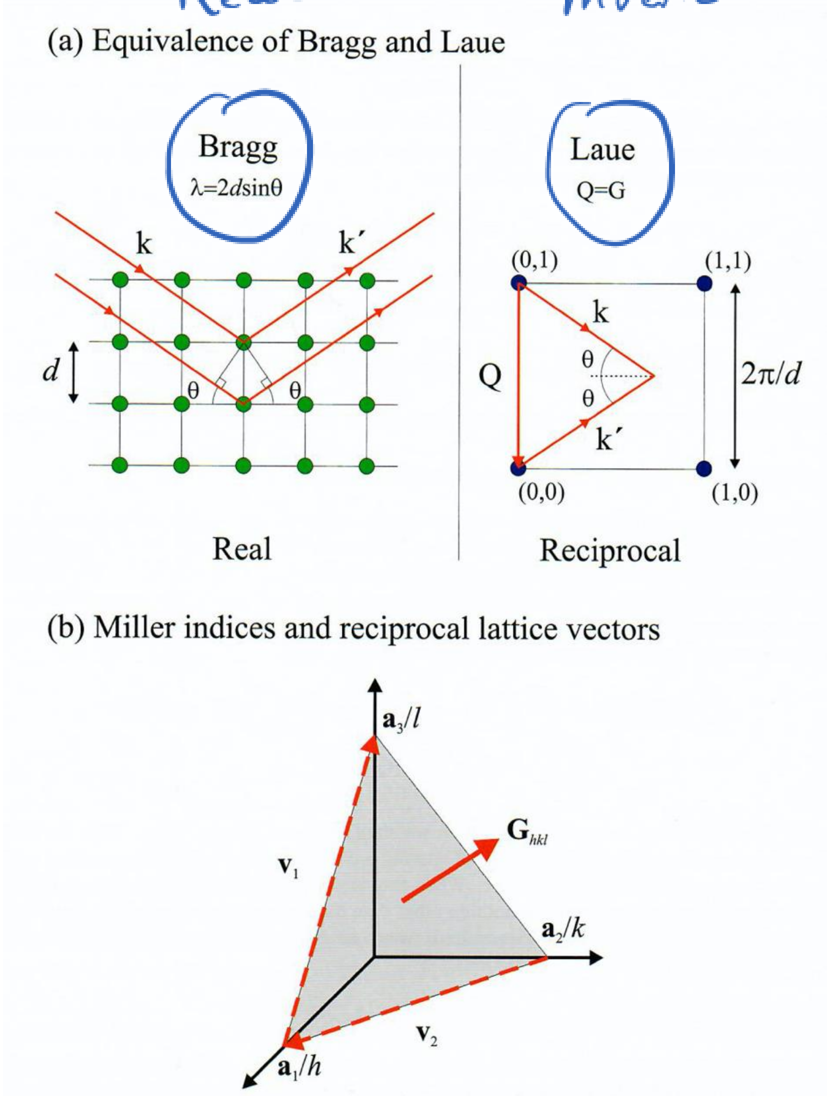


Photo from the Nobel Foundation archive.

Max von Laue

Prize share: 1/1

In reciprocal space one can show that for

$$\boxed{\vec{Q} = \vec{G}}$$

constructive interference is obtained

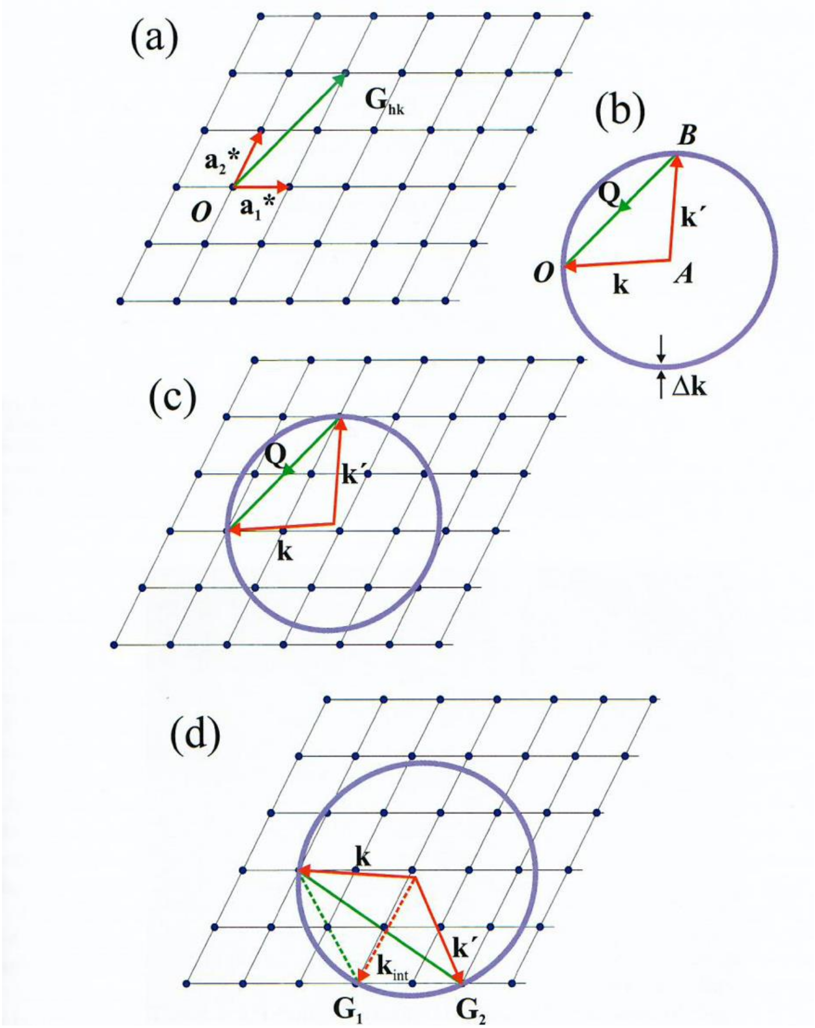
$\vec{G} \rightarrow$ perpendicular to lattice planes

$|\vec{G}| = \frac{2\pi}{d_{hkl}} \Rightarrow$ lattice spacing of hkl planes

The Ewald Sphere

→ Elegant geometric construction of relationship

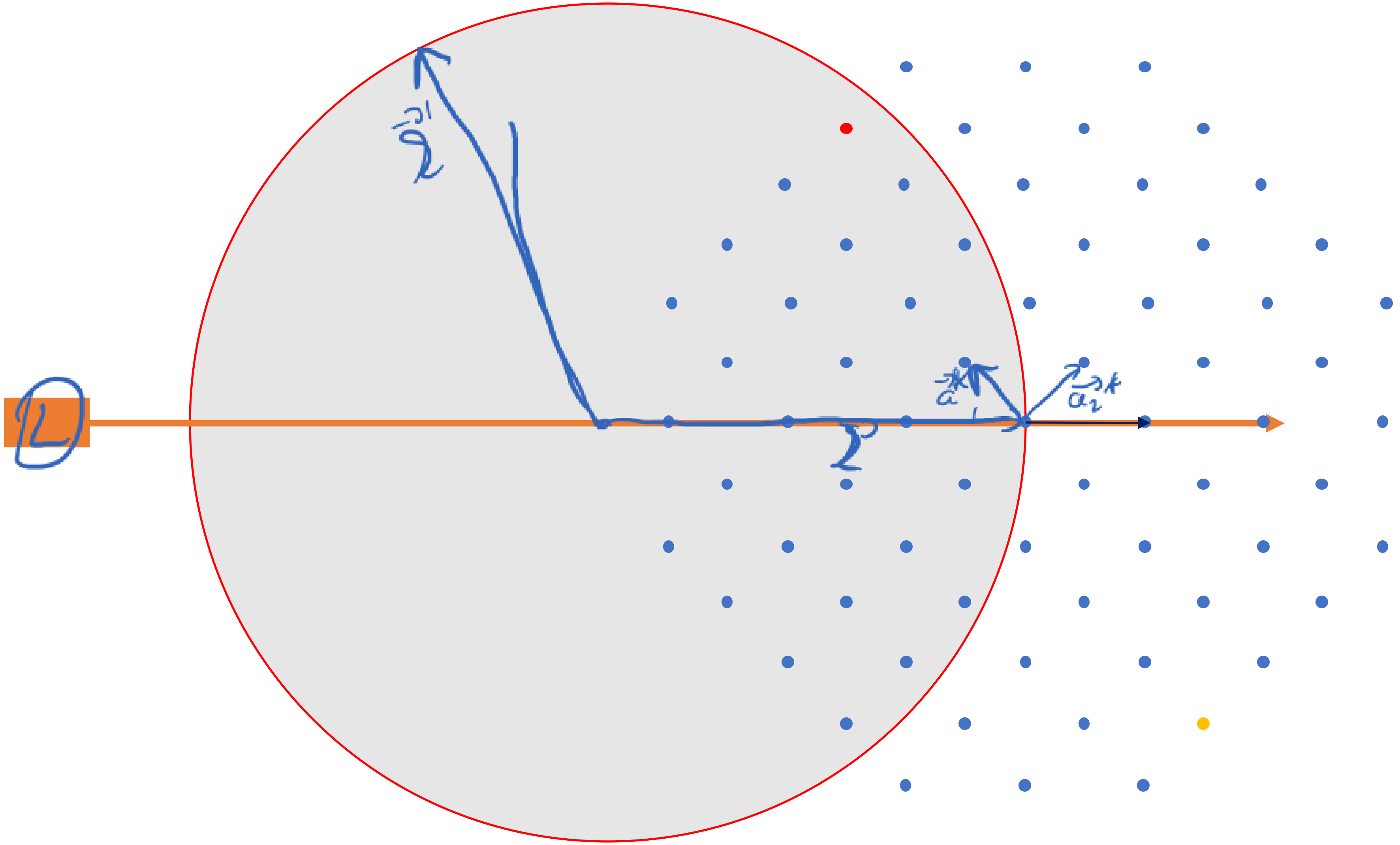
- $\vec{Q} = \vec{k} - \vec{k}'$ → wave vector $\vec{k}$
  → diffraction angle
  → in reciprocal lattice
- Laue condition $\vec{Q} = \vec{G}_{hkl}$
- Create sphere (in 2D: circle) with radius k
- Move sphere on origin O
- Monochromatic light can be scattered constructively ("signal") whenever sphere overlaps with reciprocal lattice point as here $\vec{Q} = \vec{G}$



A Laue diffraction experiment

A diffraction experiment

(41)



reciprocal lattice fixed with respect to real lattice

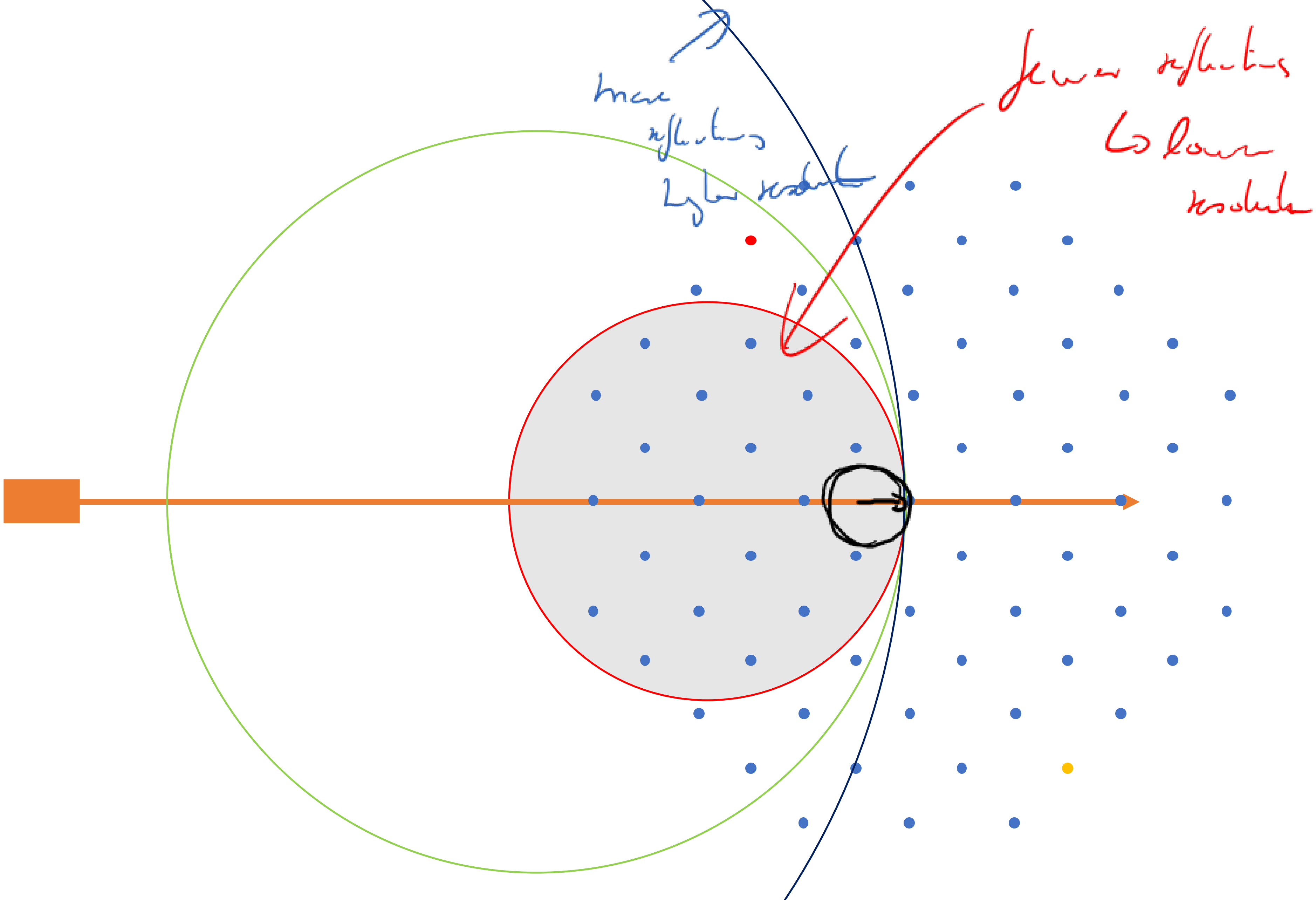
↓

rotate crystal until reflection is seen

↓

reflection angles from respective points

A diffraction experiment



There is a dependence of reflections and the $|\vec{k}|$, photon energy

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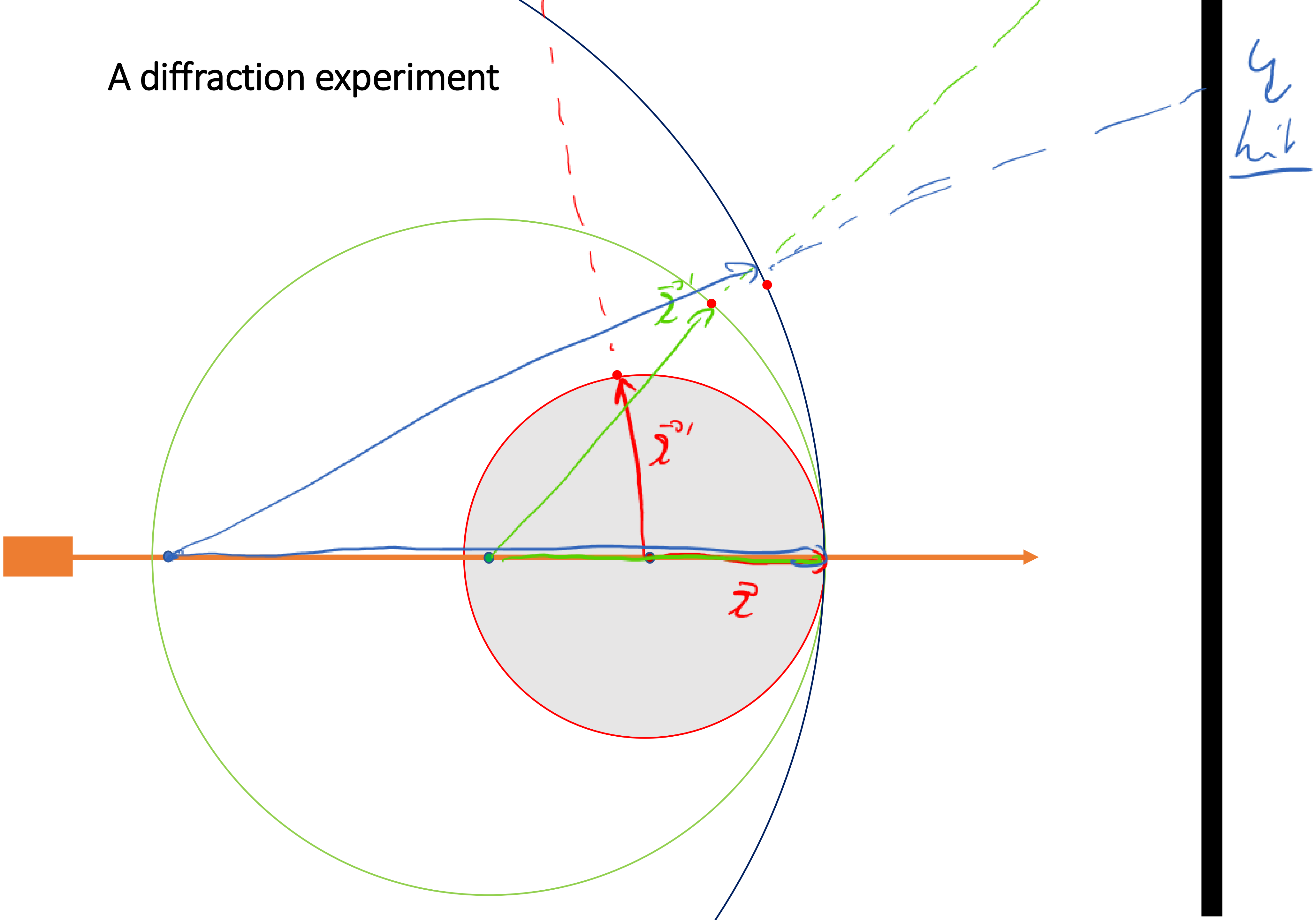
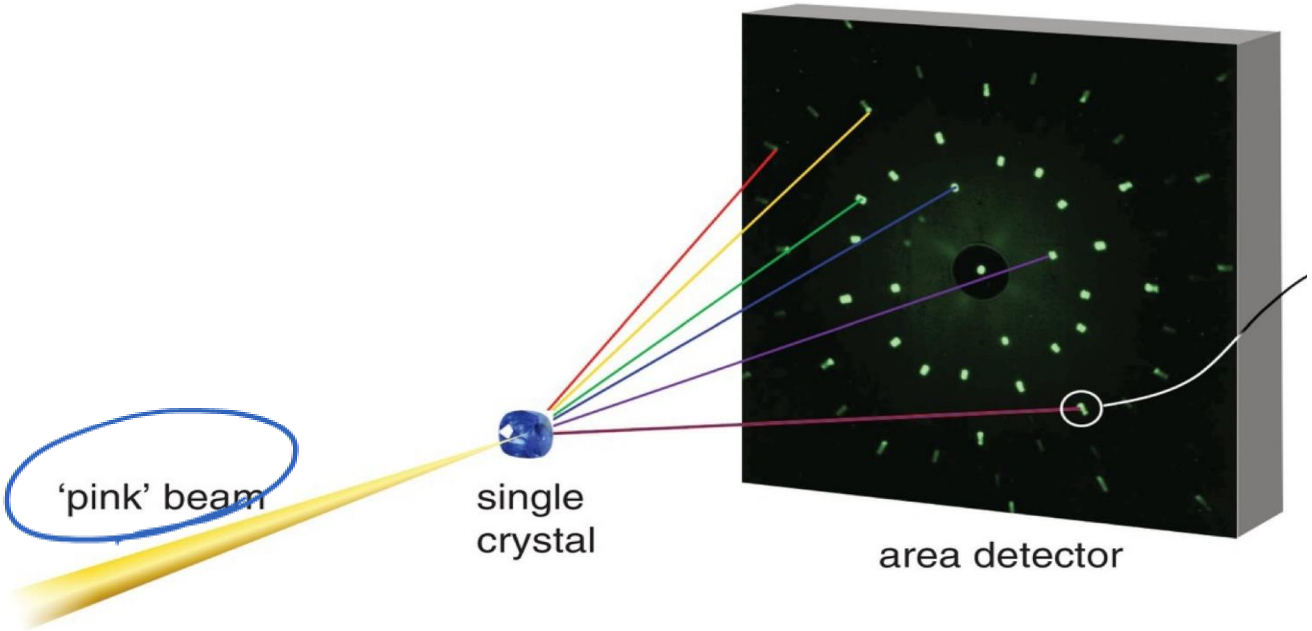
More accessible reflections for higher energies & higher resolution

A diffraction experiment

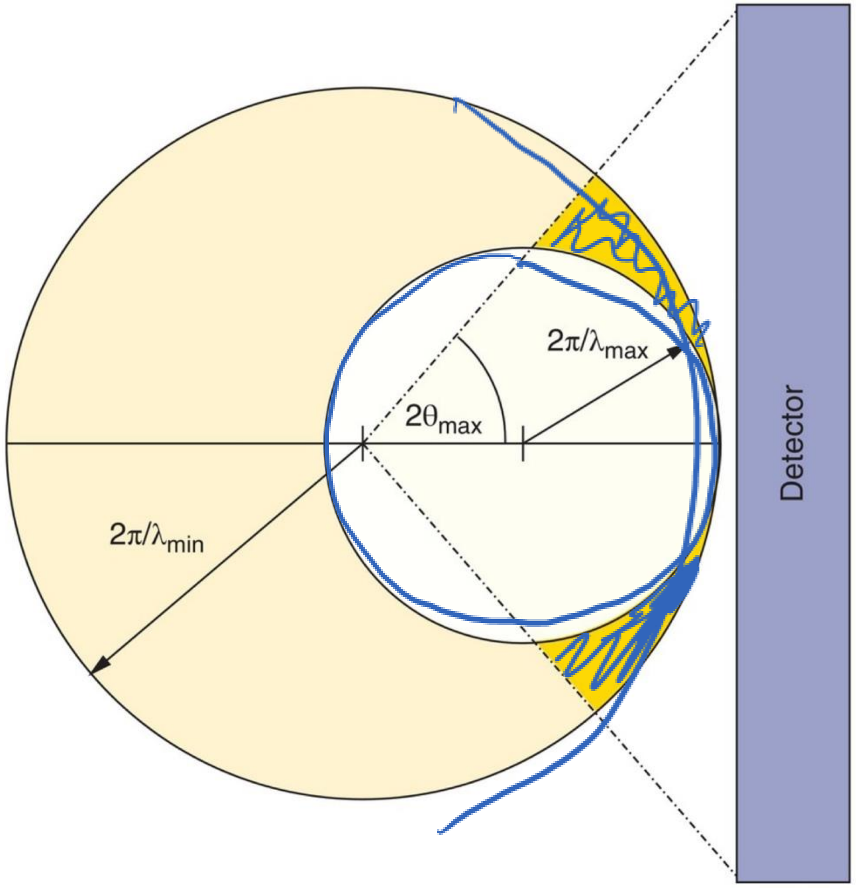


Laue method

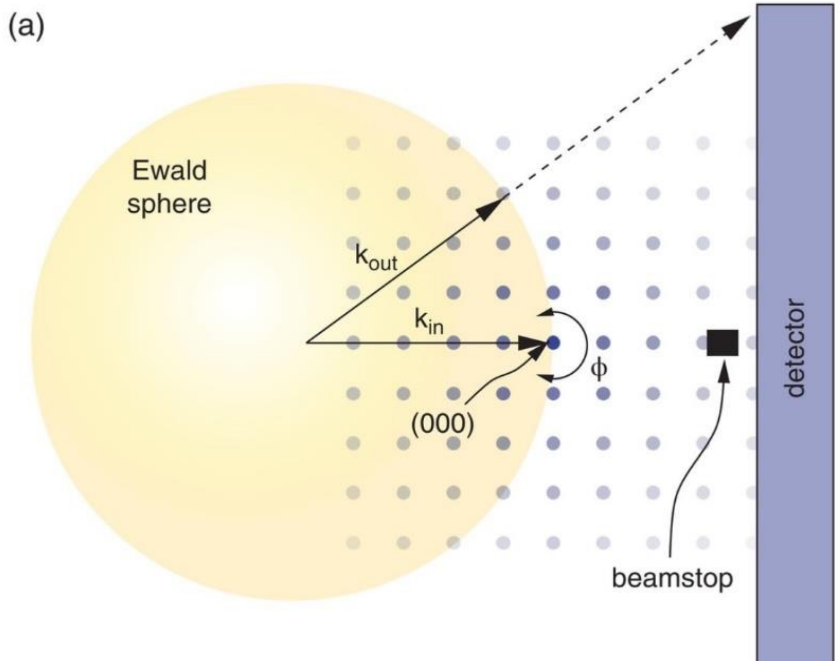
→ multiple colors
"pink beam" → broader bandwidth



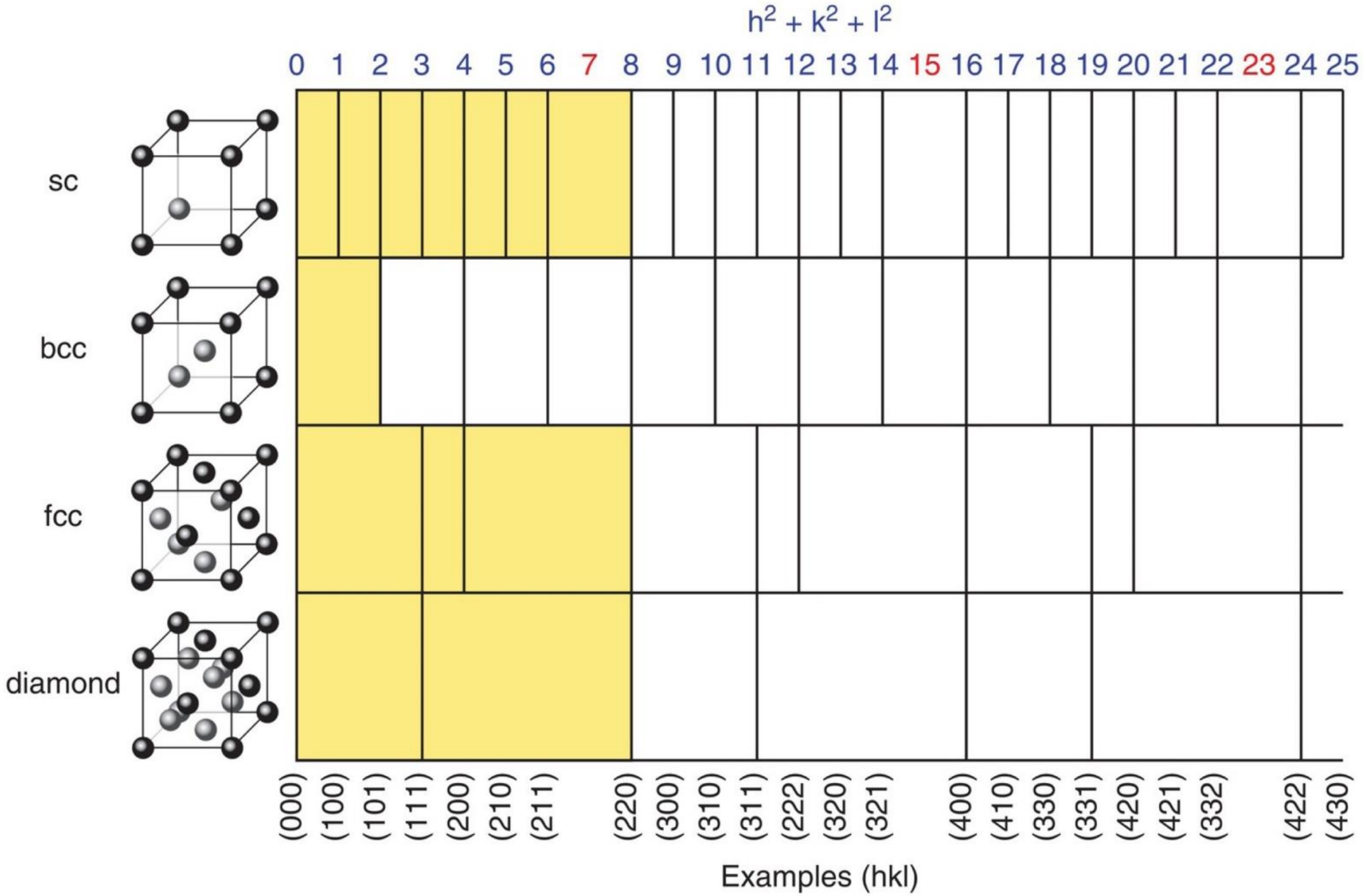
↓
all reflections
within bandwidth



A diffraction experiment

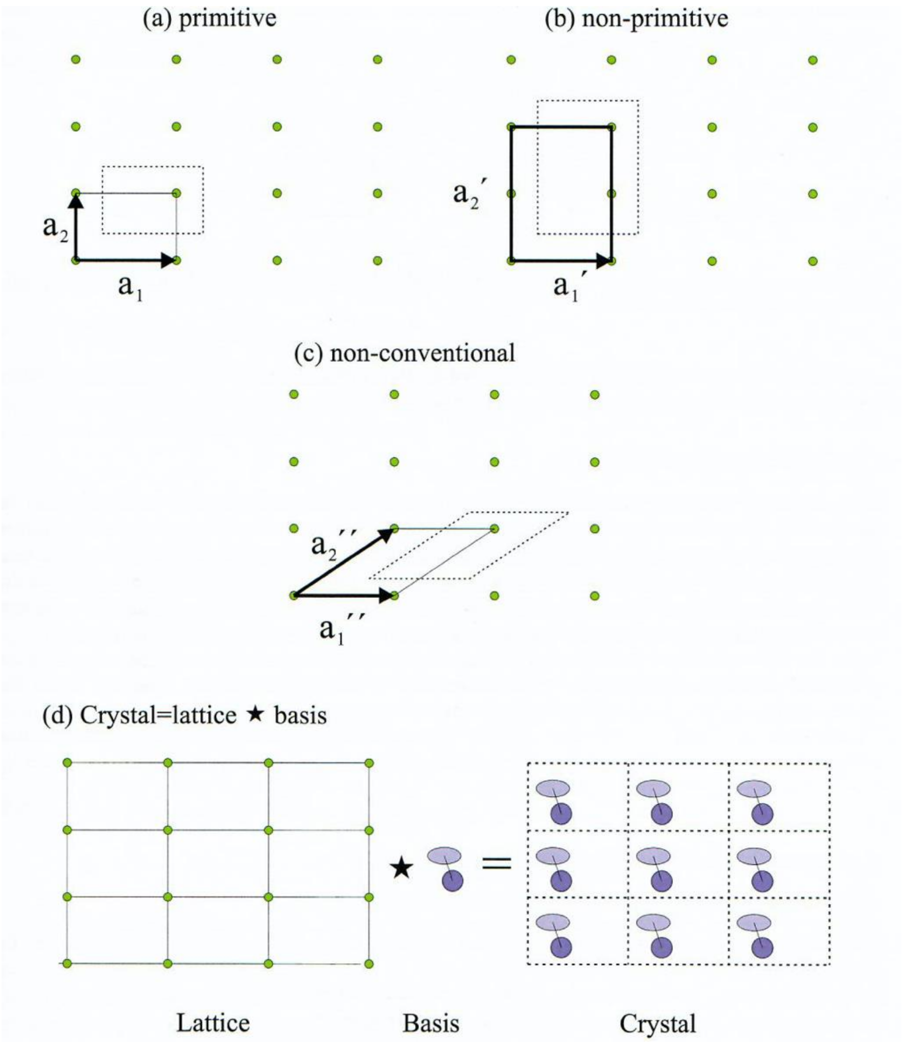


Allowed and forbidden reflections

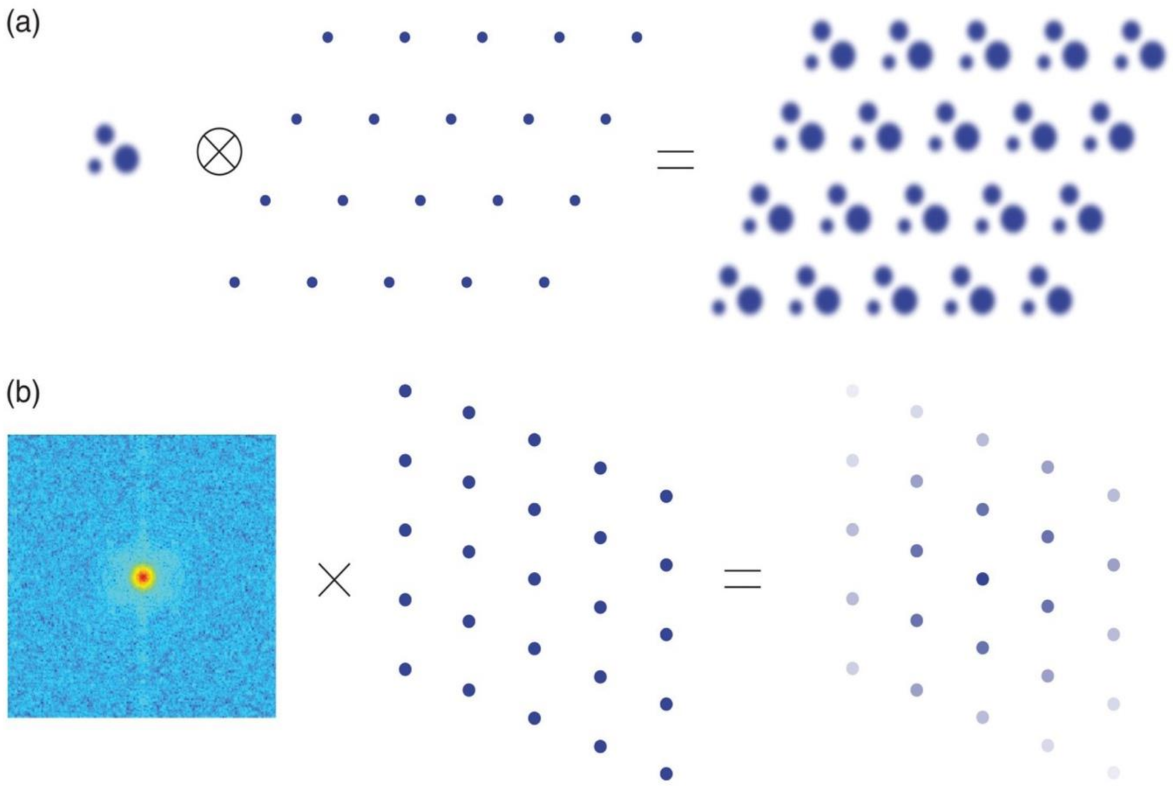


More on Bragg peaks

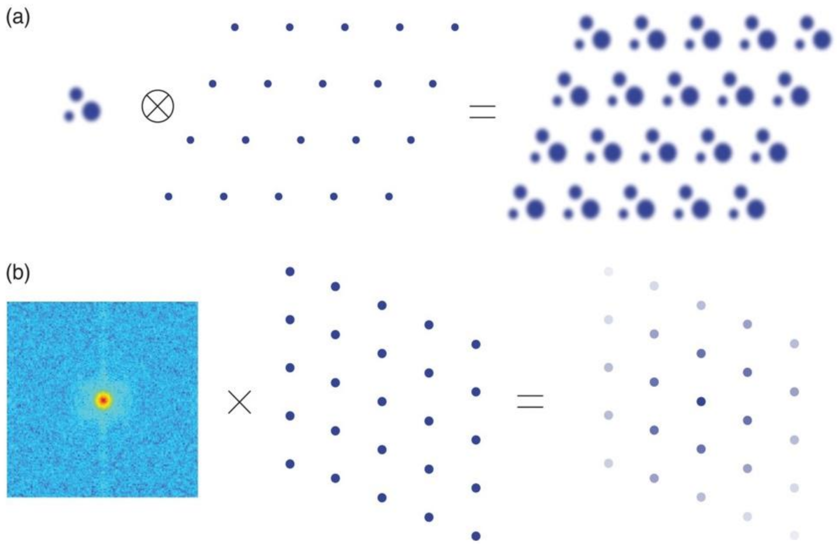
A crystal is defined by ist lattice and basis

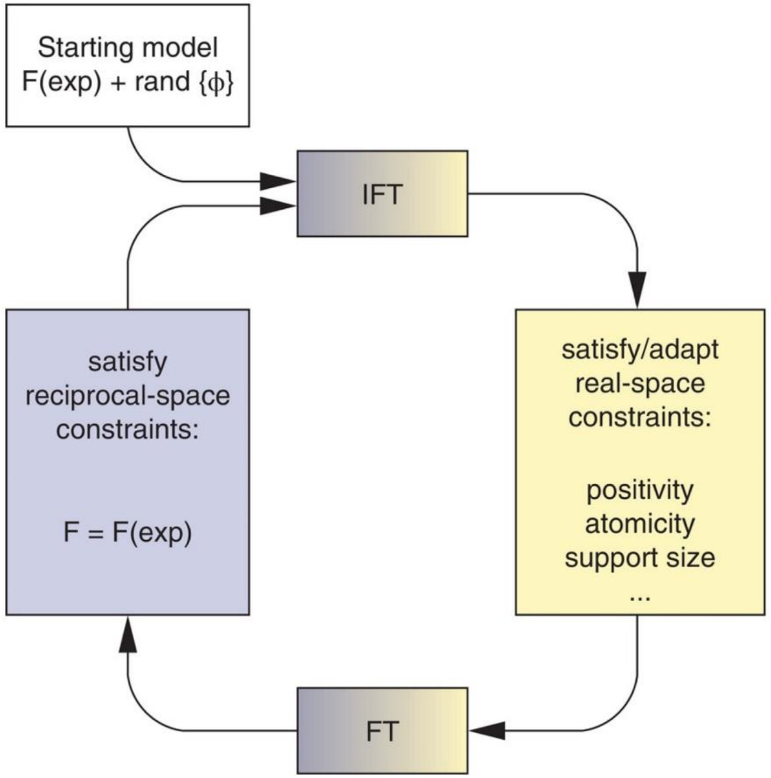


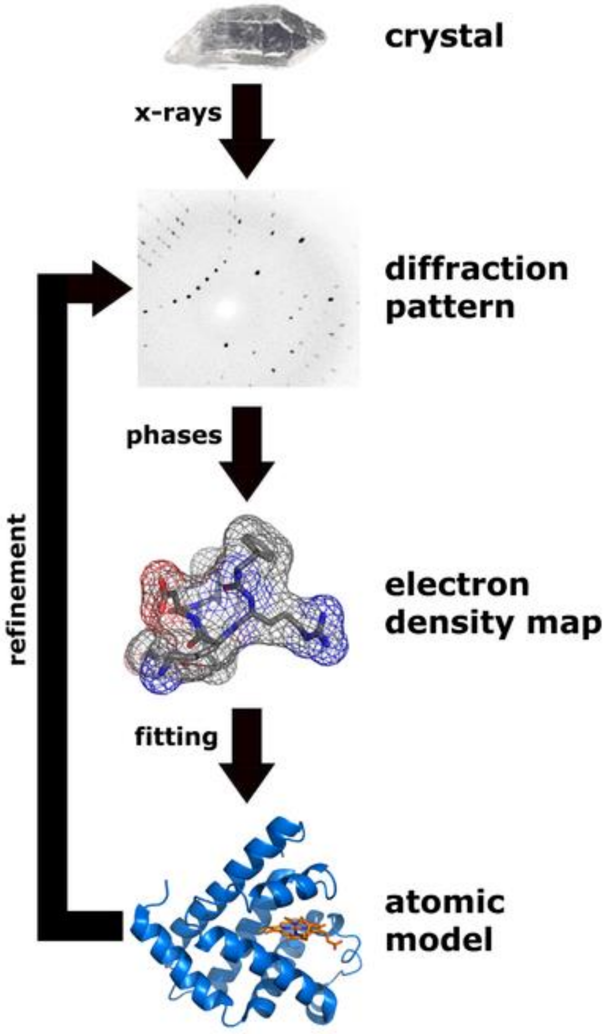
The structure factor



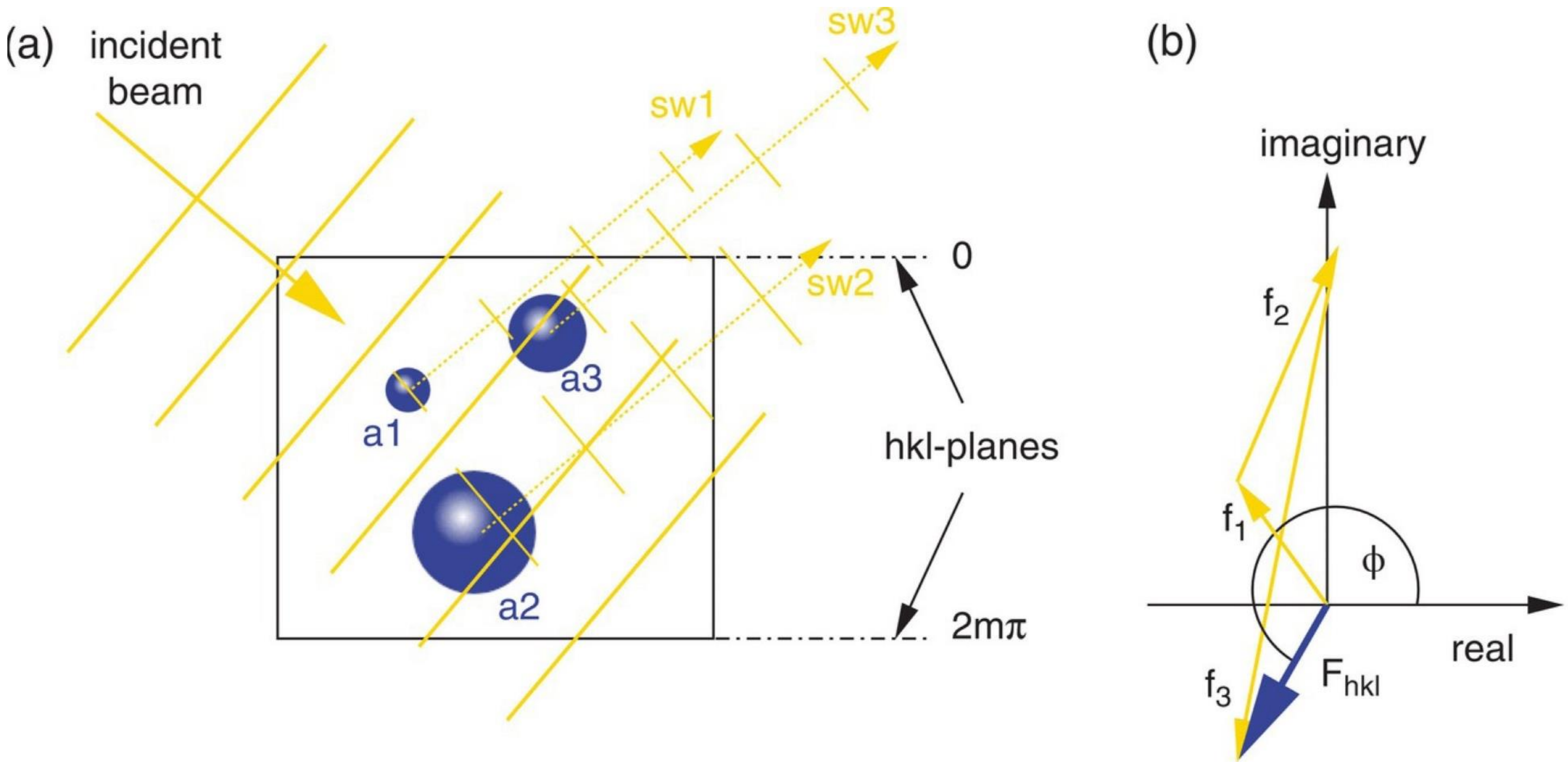
Solving a crystal structure



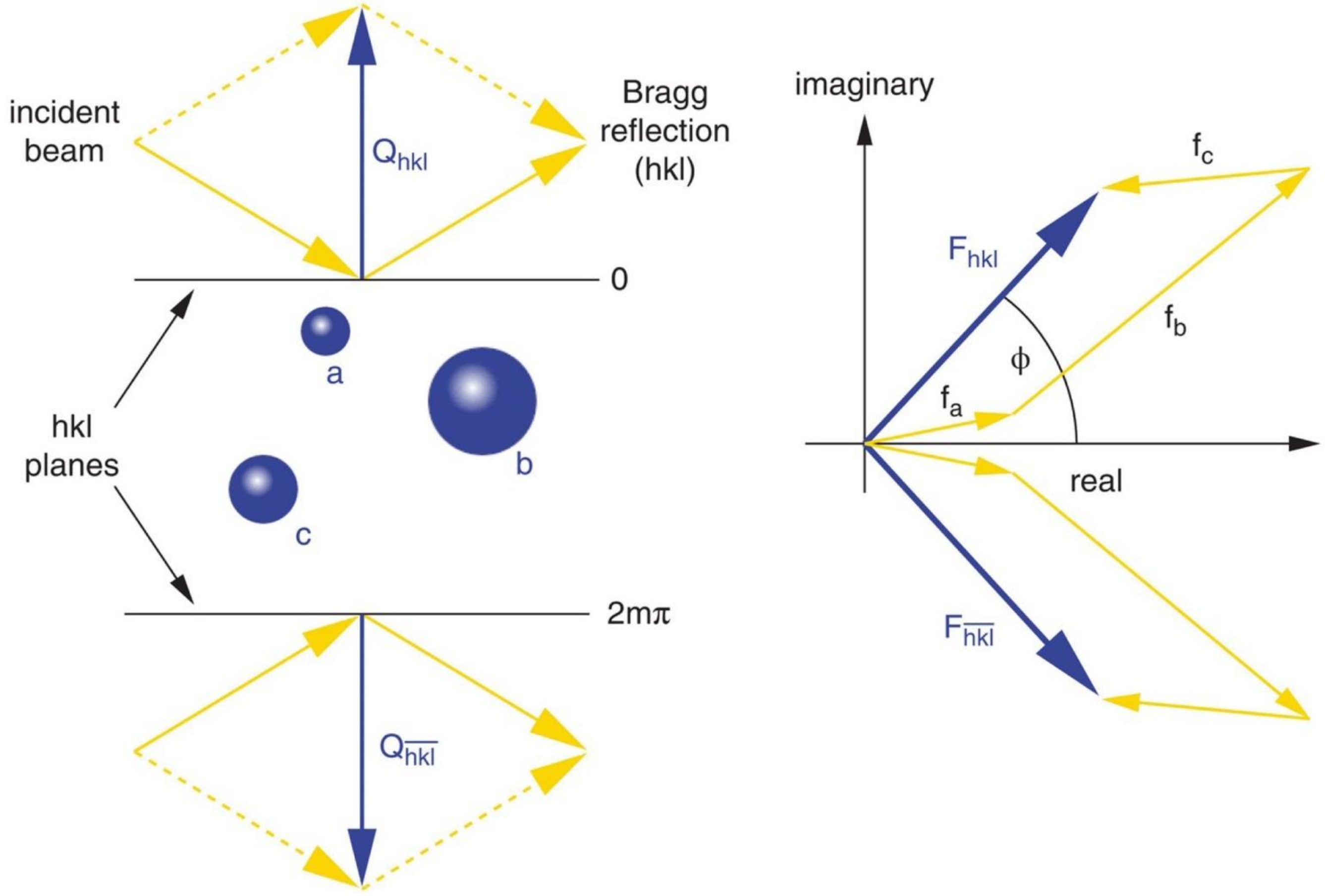




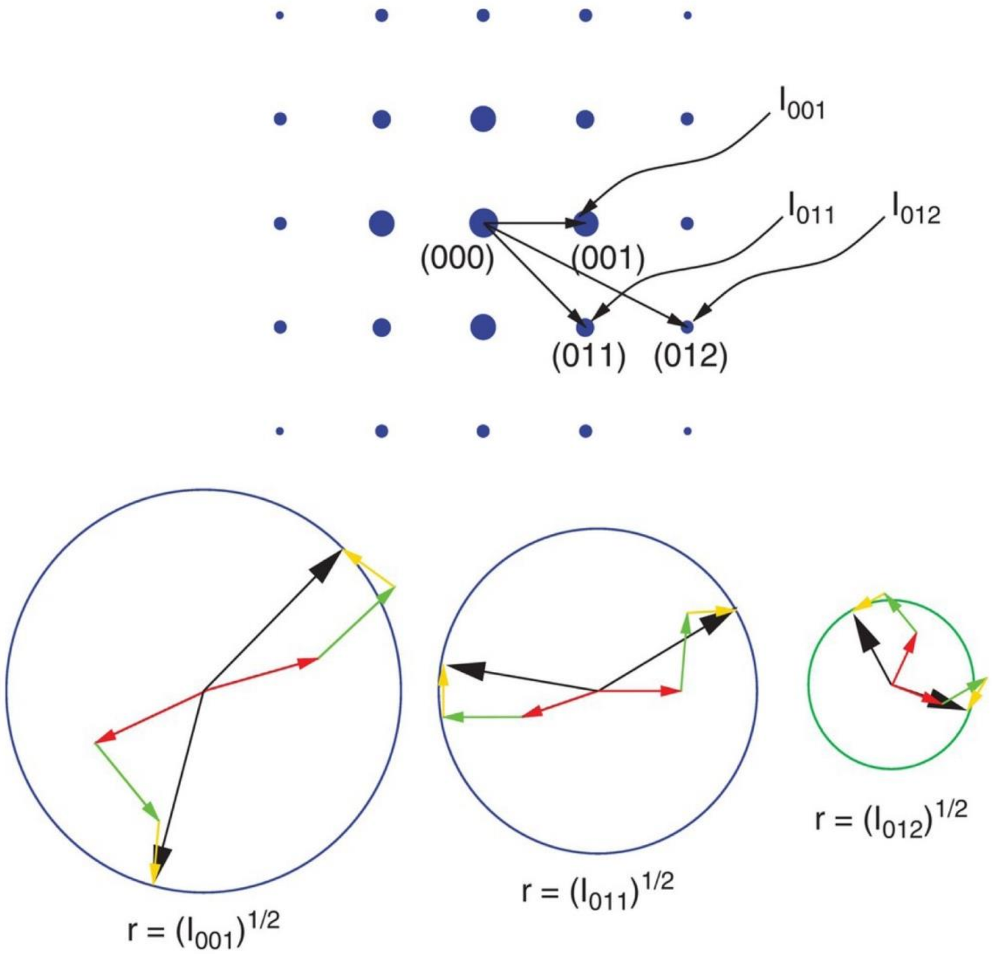
The structure factor



Friedels law



The phase problem



The end