Structural Analysis
Part III - X-ray tools

Session 3

X-ray scattering and diffraction

Intermezzo: Fourier Transform

~~Alternative~~ Remember 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

Relationships

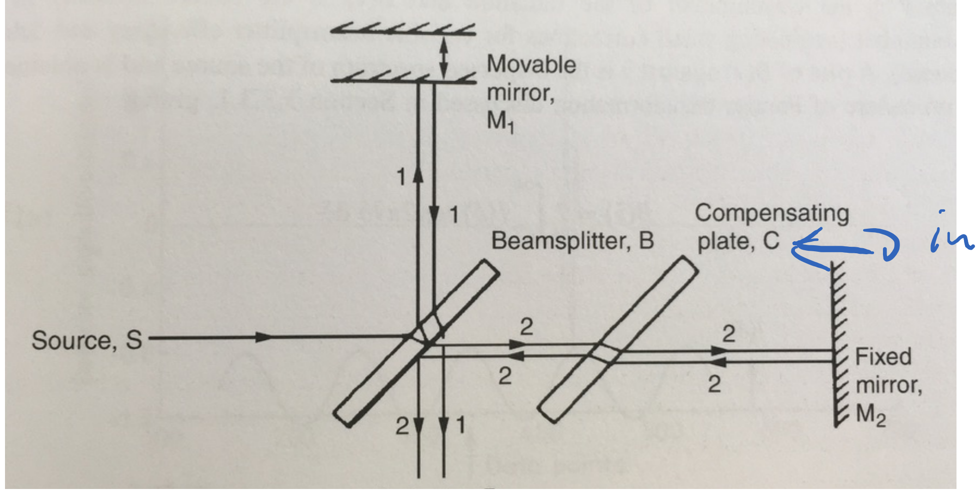
$\sim cm \sim \frac{1}{cm}$

real $\sim$ inverse

space

Measuring an interferogram

Fourier transform → relationship between frequency & real space



in x

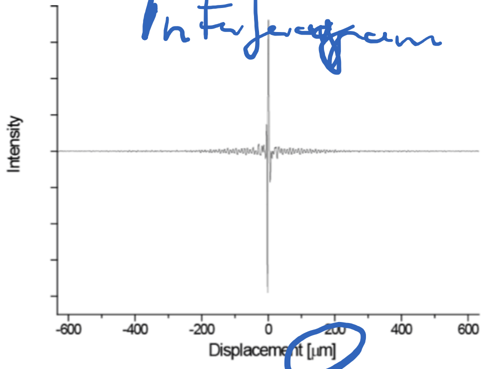
Sample

Detector

Computer $\xrightarrow{FT}$ Spectra in $\frac{1}{x}$ [frequency] space

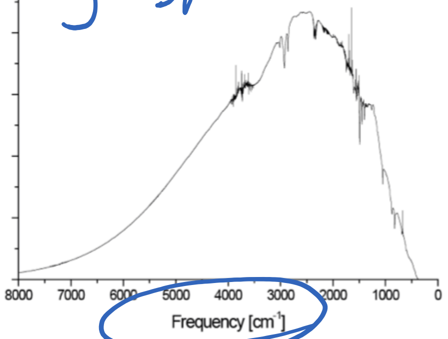
Energy

Interferogram

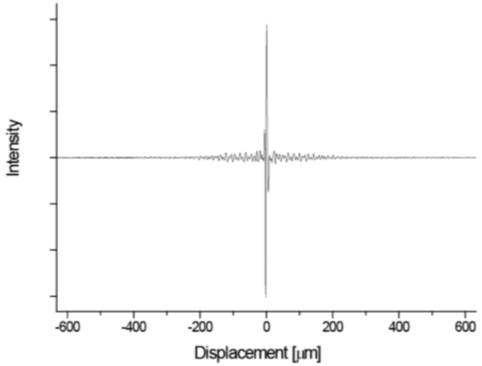


Empty Cell
FT

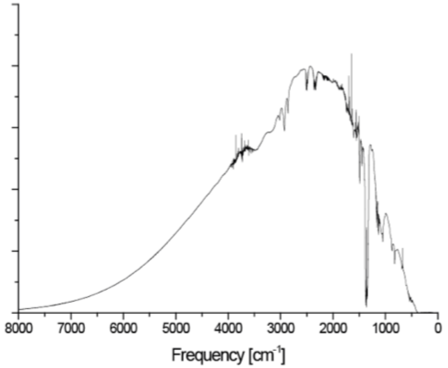
Spectra



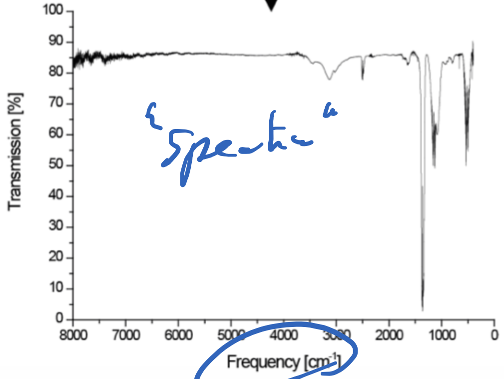
maths



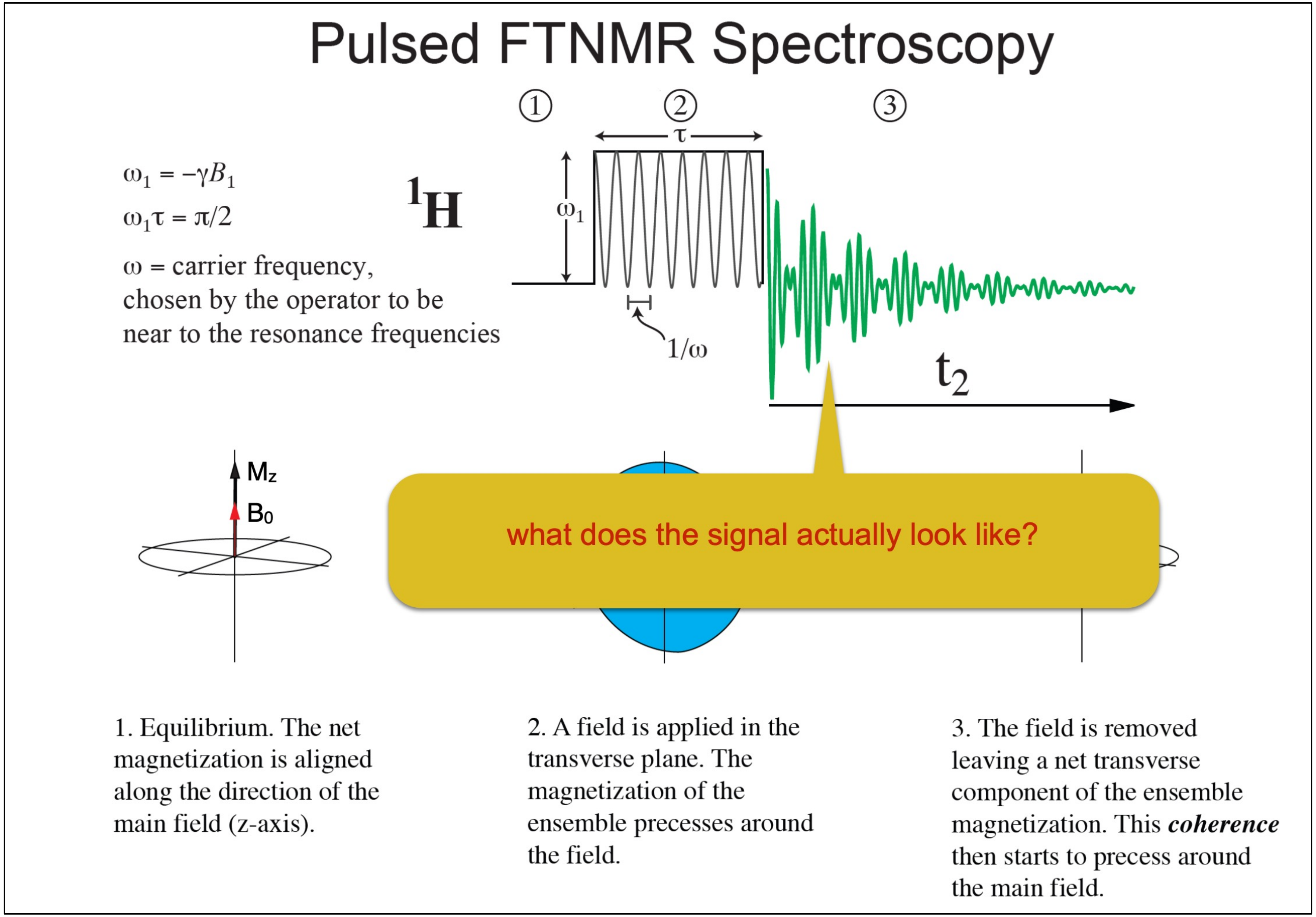
Filled Cell
FT



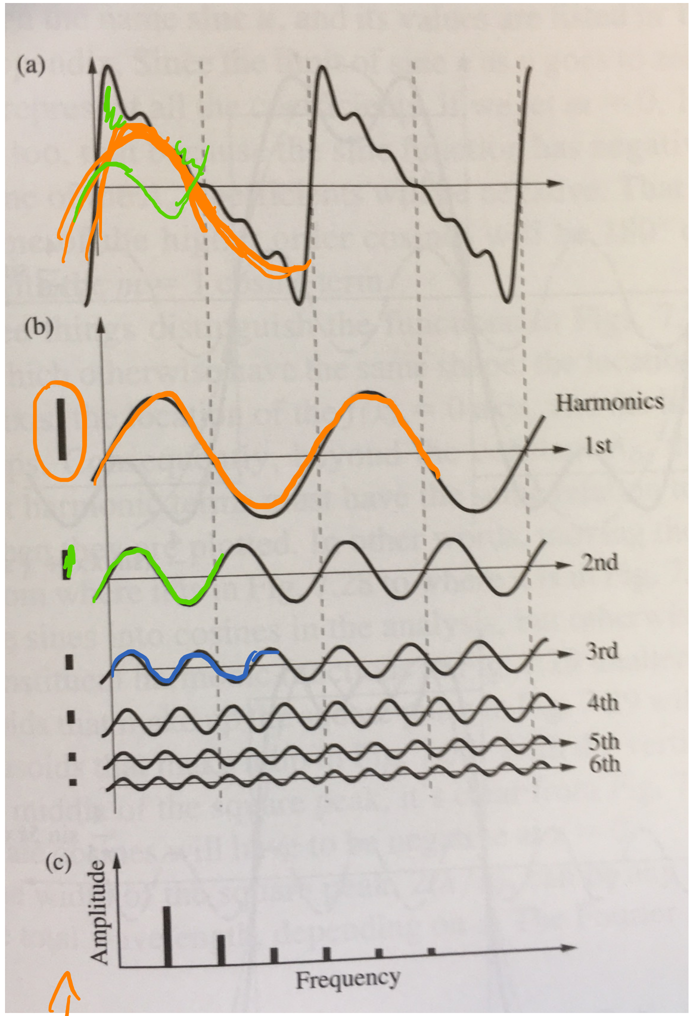
Divide



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



Principle idea



Amplitude

Fourier Series

Fourier series →
infinite sum of harmonic functions that can describe any / another function

Use Σ of harmonic fcts
to approximate any function

use different amplitudes for each harmonic fct
(→ frequencies)

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.

Fourier transform

Thus we can write

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

frequencies

harmonic fct

provided that

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

Fourier transform is the "rule how amplitudes & frequencies come together"

Note Computers do Fourier Transforms really well

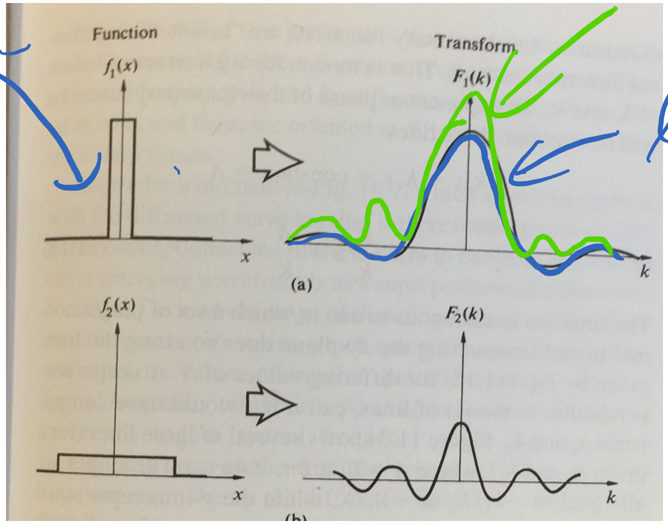
$\Rightarrow$ FFT $\longleftrightarrow$ GPU

Hecht chapter 11

Examples → selected FT

Square functions

Could be transmission from slit



Intensity $|A|^2$

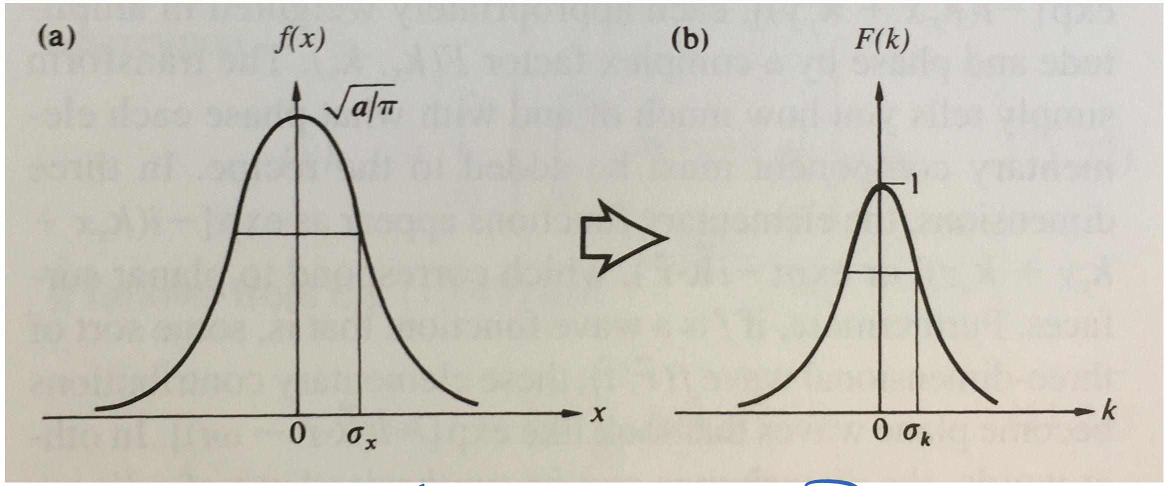
↕

looks like interference pattern

↓

Remember in experiment we do not measure waves but but intensity $I = |A|^2$

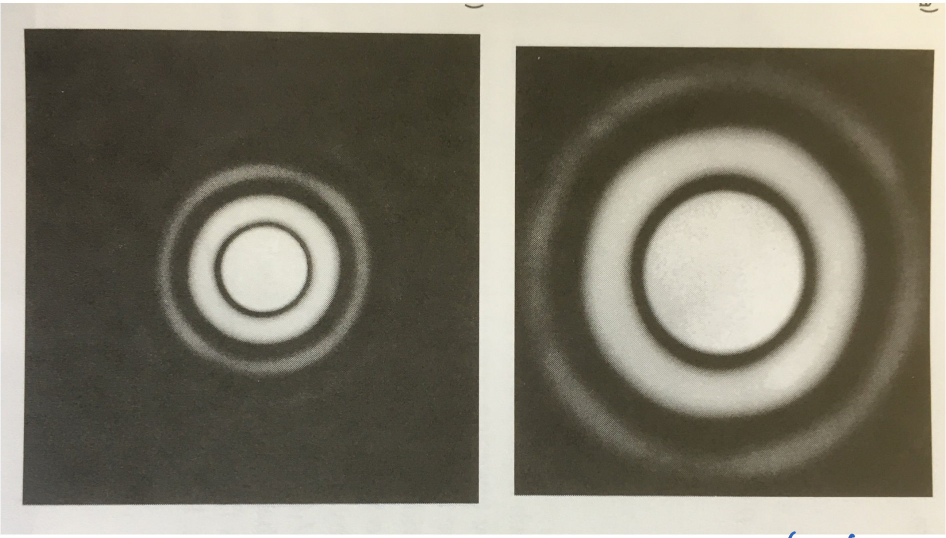
Gauss function



FT "Gaussian" → "Gaussian"

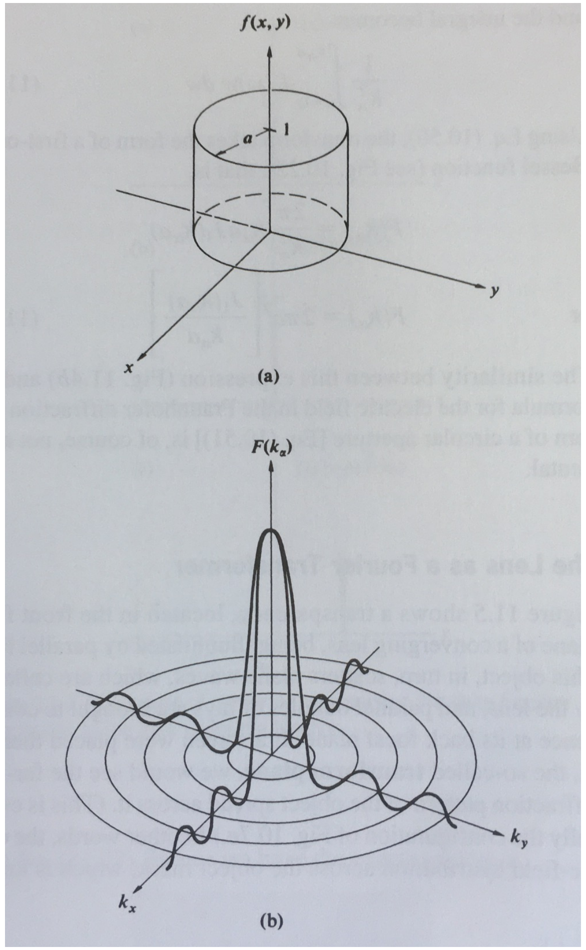
Fourier transform of round aperture and airy pattern

Experiment: Diffraction pattern of circular aperture, Airy pattern



↳ Bessel fct

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



General

The diffraction pattern of an object is described by its Fourier transform

Diffraction as Fourier transform: → Convolution theorem

FT of a convoluted fct → point product of their FT

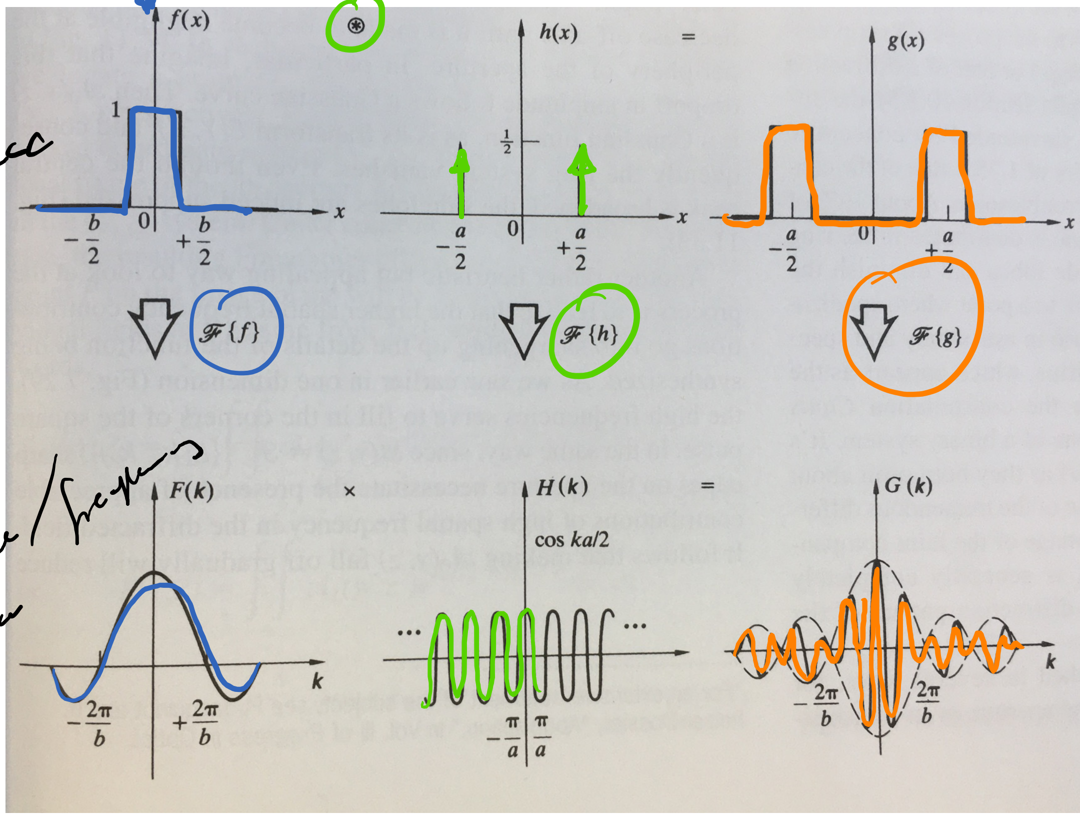
From maths

$$FT(f \otimes g) = FT(f) \cdot FT(g)$$

Single slit

δ-fct

Real space



inverse/frequency space

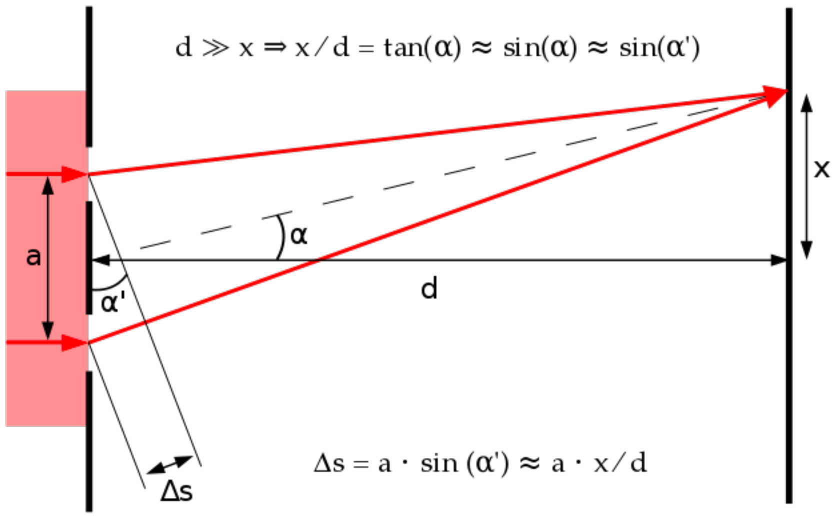
sinc fct

slit with width

⇒ Reconstructed the double slit experiment

<u>Note</u> measure $\underbrace{I = |A|^2}_{\text{double slit}}$

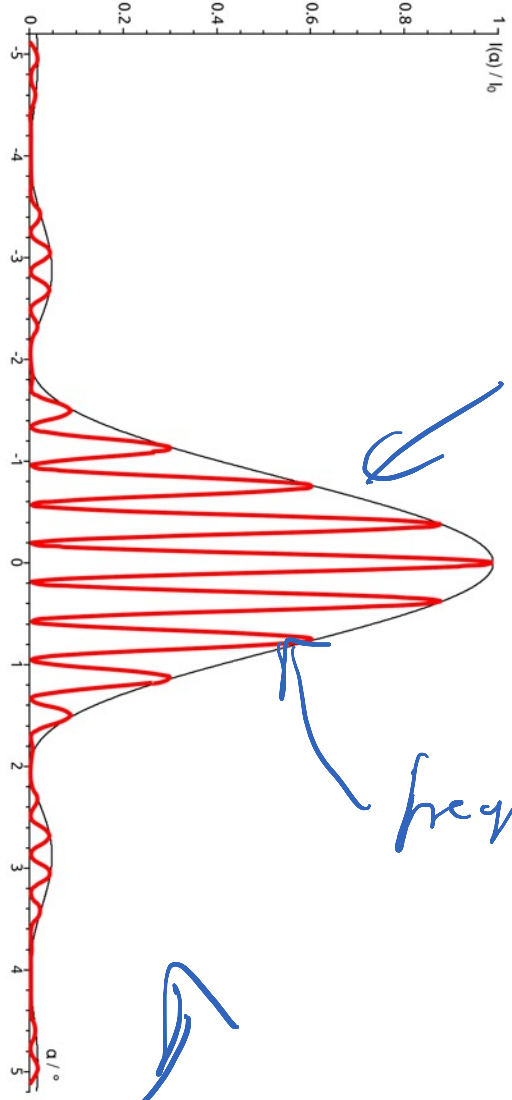
The double slit



double slit

↳ Convolution theorem

$F(f \ast g) = F(f) \cdot F(g)$



envelope

"from single slit"

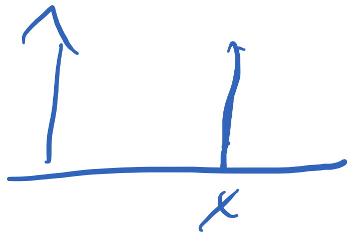
frequencies from distance

"δ fct"

Image source: wikipedia

Fourier relationships – some examples

Relationship between time & frequency domain
real & inverted

$\sin(x)$  $\longrightarrow$ $\delta(x)$ 

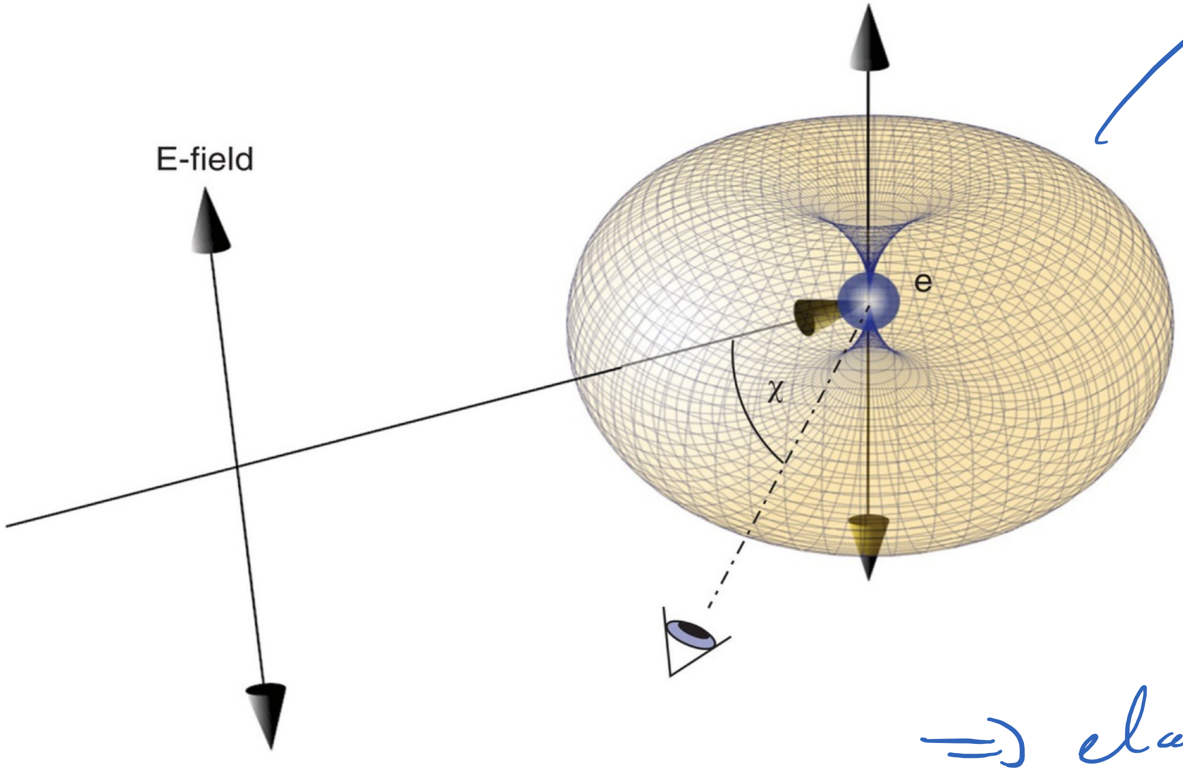
Note

- diffraction pattern is FT of object
- lens is a FT → information in focus is FT(object)

(→ Opt Methods in Chem)

From Session 1

Thomson scattering from a single electron



learned x-ray scattering of electrons

↳ Thomson scattering

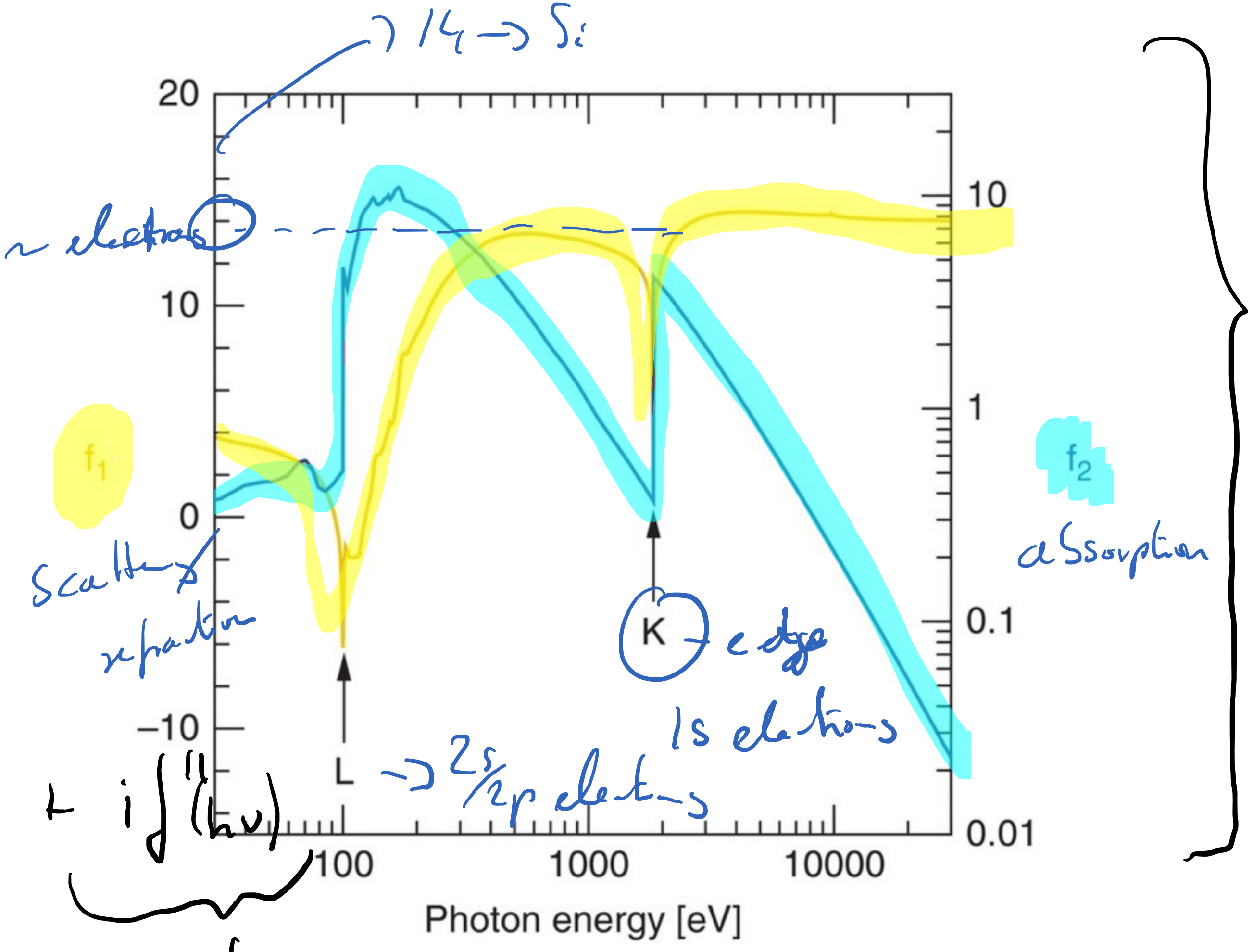
↳ classical analog is dipole radiation

⇒ an incoming plane x-ray wave is converted to spherical wave

⇒ elastic ⇒ no energy change only directional change

⇒ can employ principles & ideas from optical regime

Atomic scattering factors and refractive index



$$f(h\nu) = \underbrace{f_0 + f'(h\nu)}_{f_1} + i\,\underbrace{f''(h\nu)}_{f_2}$$

↑ # electrons ↑ correction

f_2 ← absorption

↳ x-ray analogue to "refractive index"

importance
↓
absorption
↓
electronic levels

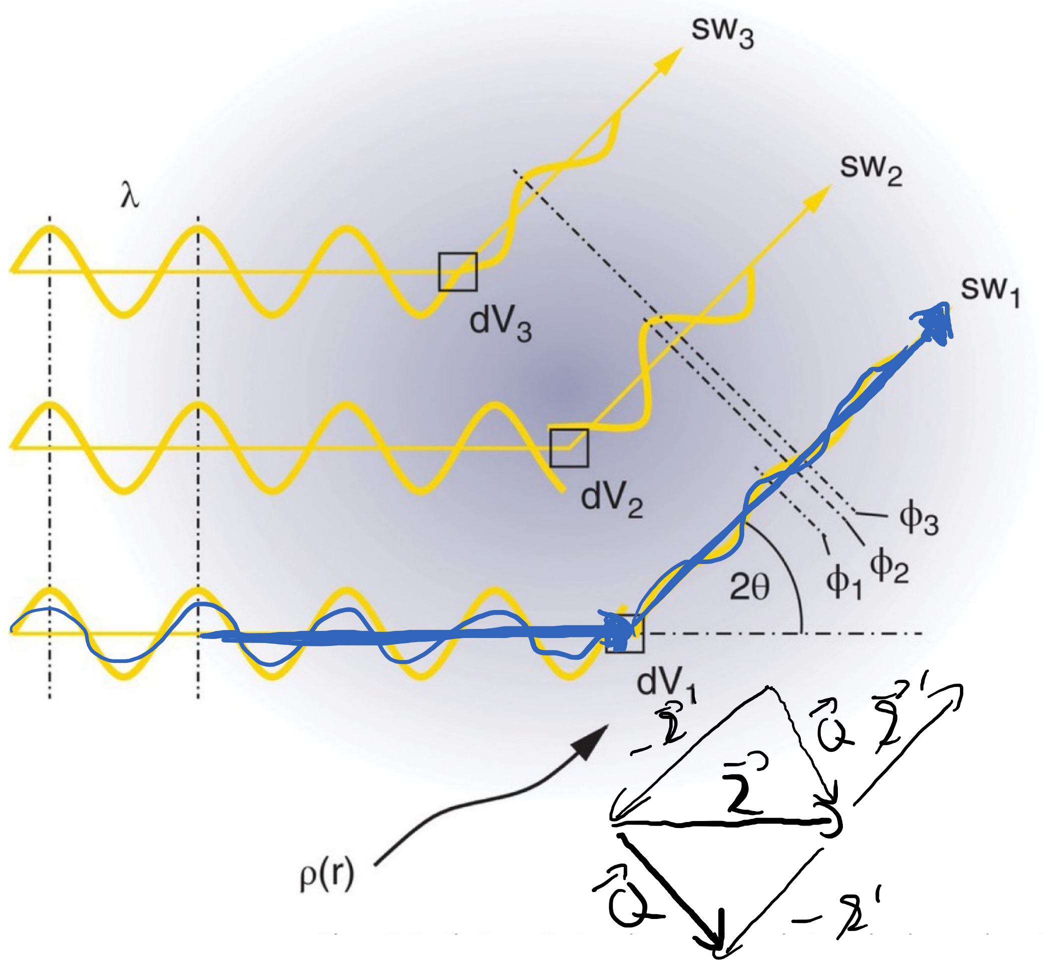
---

scattering
↓
electronic information

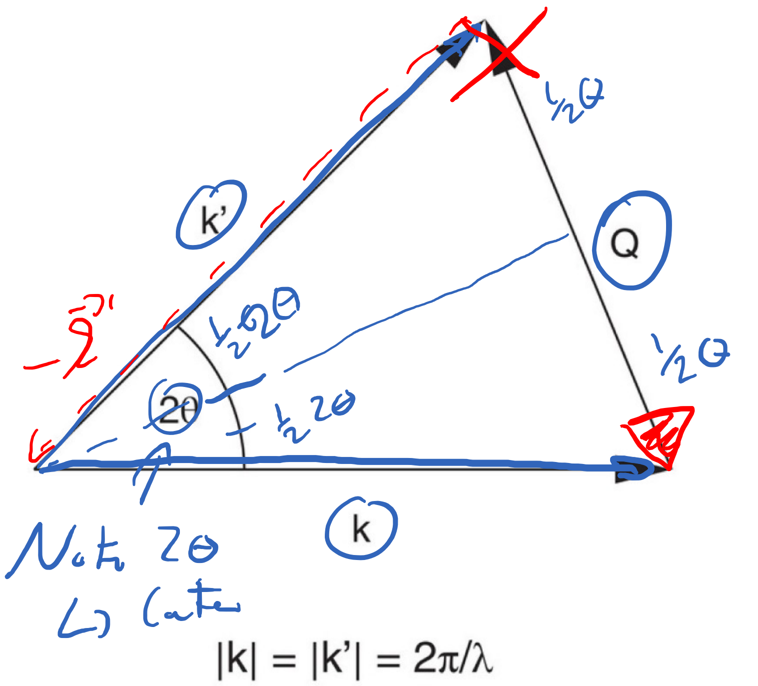
Definition of the scattering vector $\vec{Q}$ $\longrightarrow$ vectorial difference between incident & elastically scattered wave vector $\vec{k}, \vec{k}'$

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

(a)



(b)

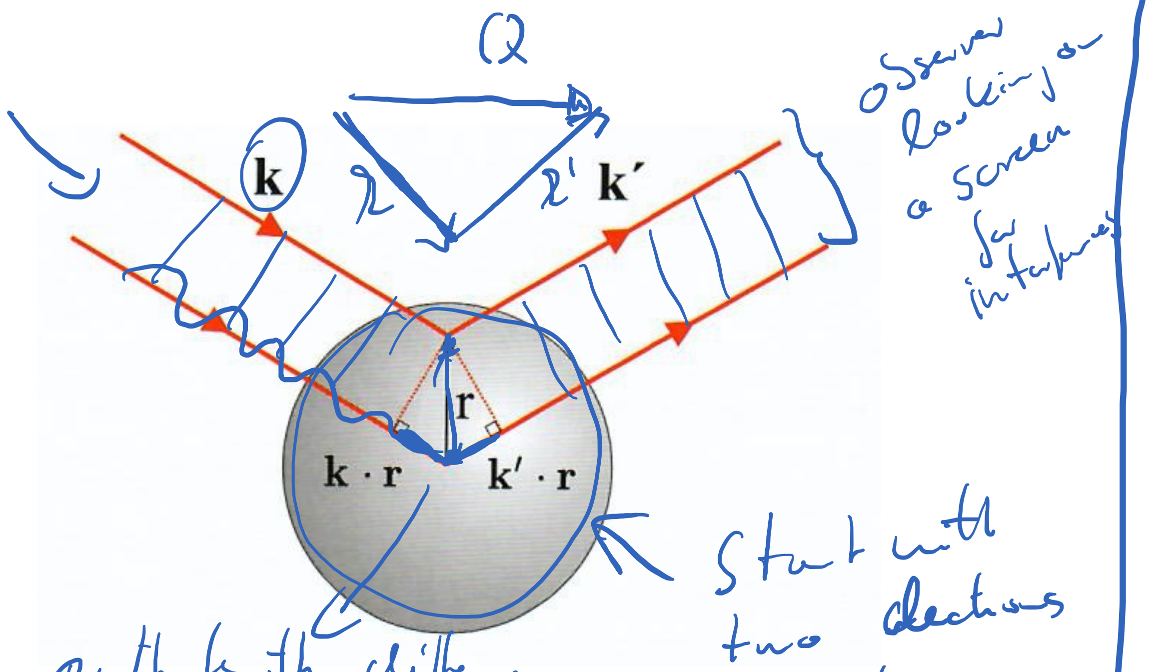


$\frac{1}{2} \frac{Q}{k} = \sin\theta$

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

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

Scattering from an electron cloud



path length difference
λ → constructive interference
→ equivalent of saying 2π difference

→ cloud density $\rho(r)$

→ constructive interference for phase difference 2π

→ $\vec{k}\cdot\vec{r}$ ~ "phase"
(look at projections of $\vec{k}, \vec{r}$)

⇒ At observer the difference

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

⇒ elastic $|\vec{k}| = |\vec{k}'|$

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

⇒ Lets look at volume dr at r

~ $r_0\,\rho(r)\,dr$ with $e^{\vec{Q}\vec{r}}$

↑ volume element, ↑ phase factor $e^{i\phi}$

Now full cross section / atomic scattering factors

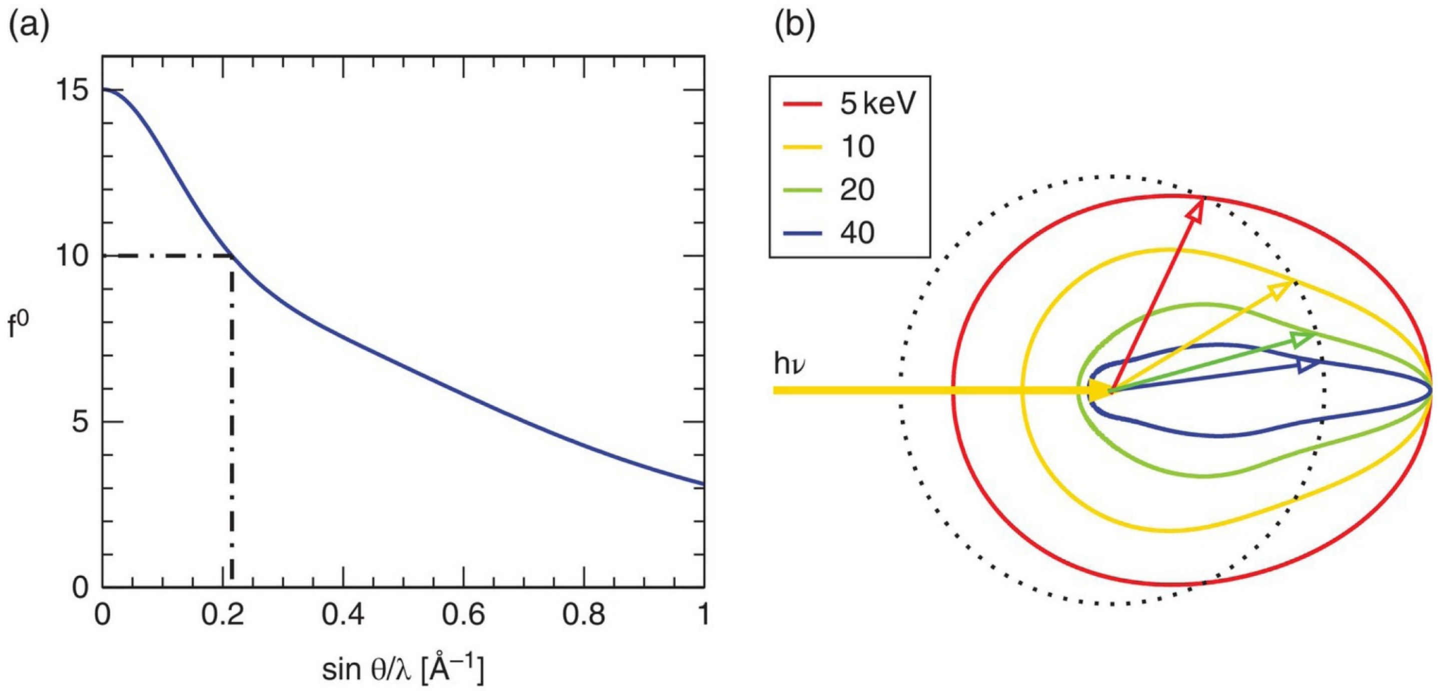
$-r_0 \rho(r) dr$ with e^{iQr}

$-r_0 f^0(Q) = r_0 \int \rho(r) e^{iQr} dr$

For $Q \to 0 \Rightarrow Z$

FT of electron distribution

"form factor"

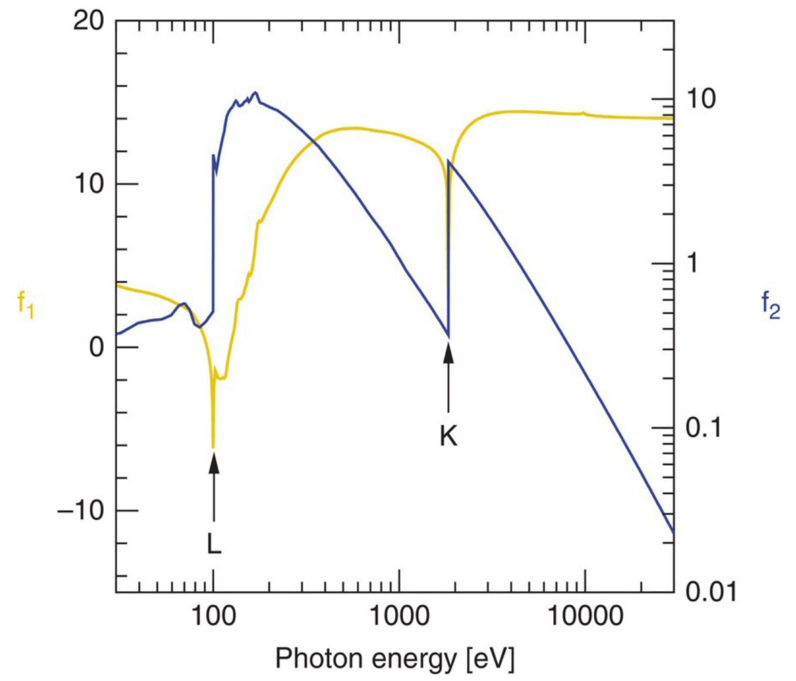


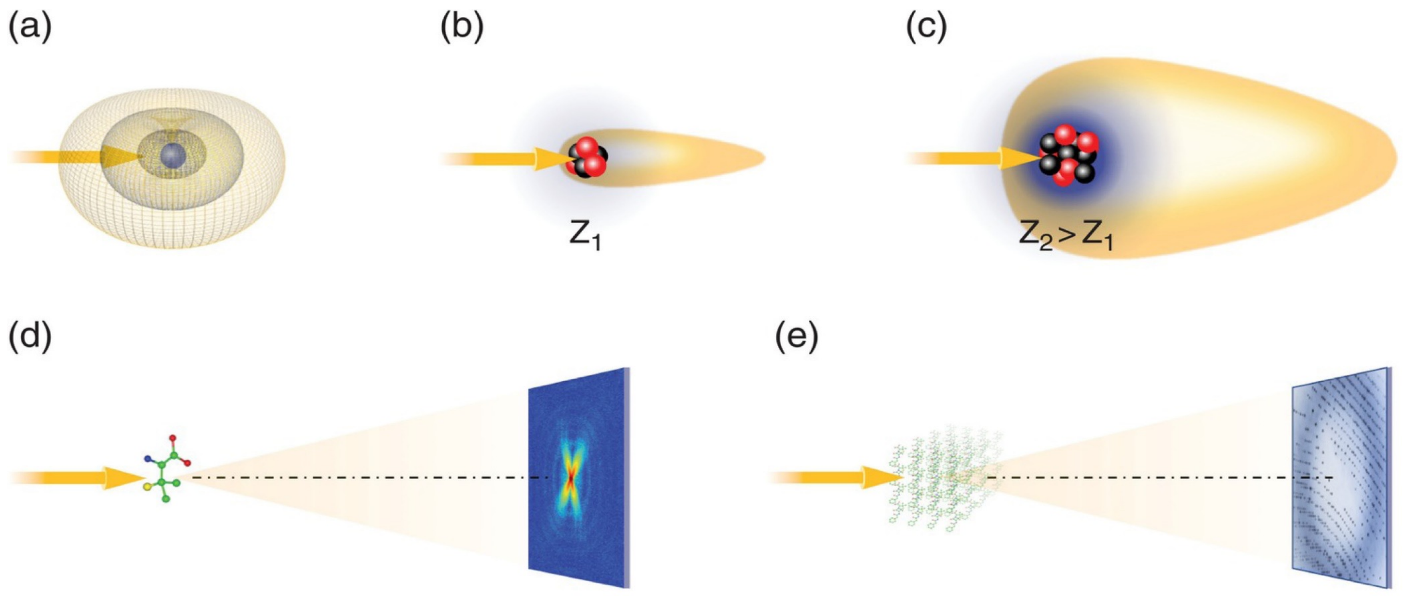
f^0 → is form factor of atoms
→ Z in forward direction
→ decreases with increasing scattering angles
⇒ tabulated

If Q increases, volume elements get out of phase

⇒ f^0 is a fct of Q

Atomic scattering factors again





now fct of Q

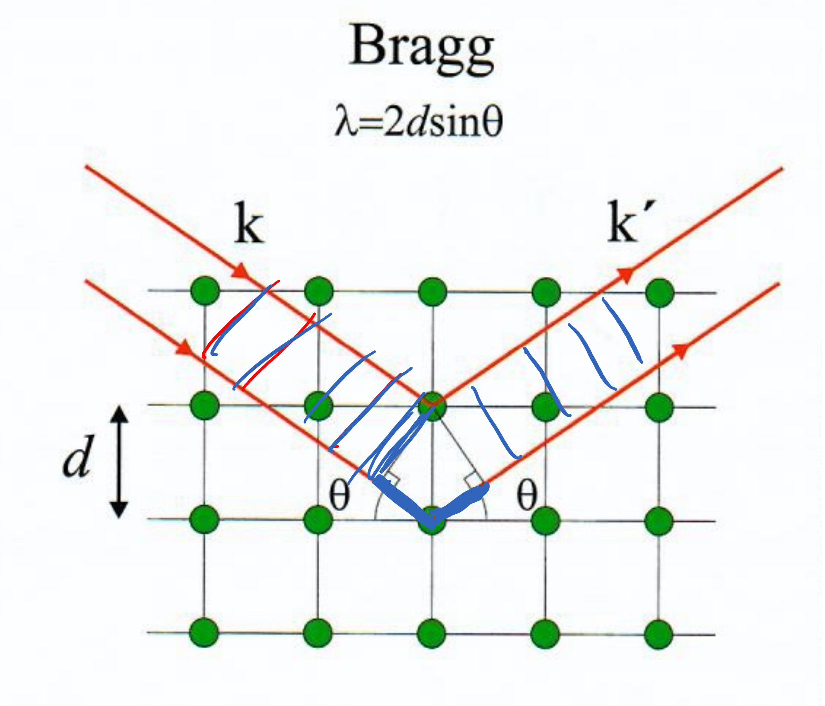
Z for $Q=0$

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

From Session 2

The Nobel Prize in Physics 1915

Bragg scattering



$\rightarrow \sin\theta = \dfrac{n\lambda}{2d} \Rightarrow 2d\sin\theta = n\lambda$

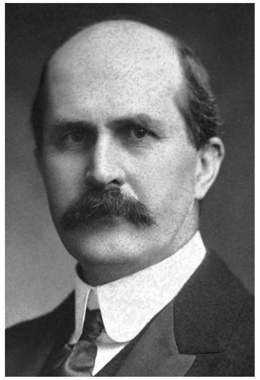


Photo from the Nobel Foundation archive.

Sir William Henry Bragg

Prize share: 1/2

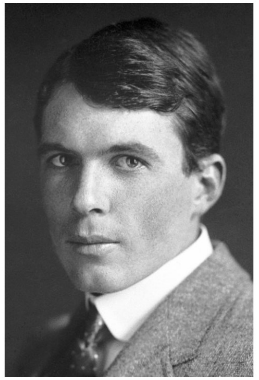
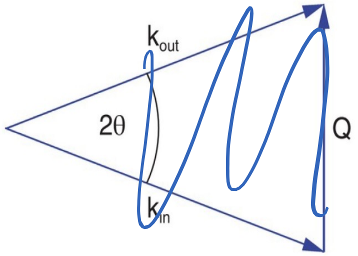
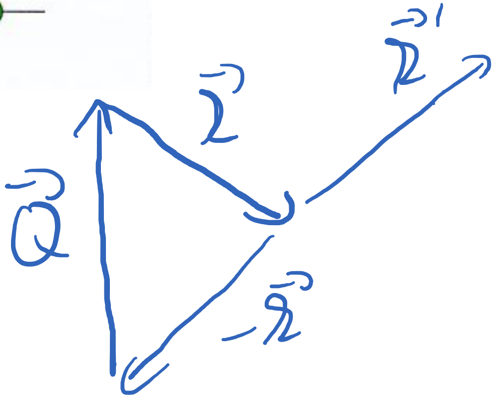


Photo from the Nobel Foundation archive.

William Lawrence Bragg

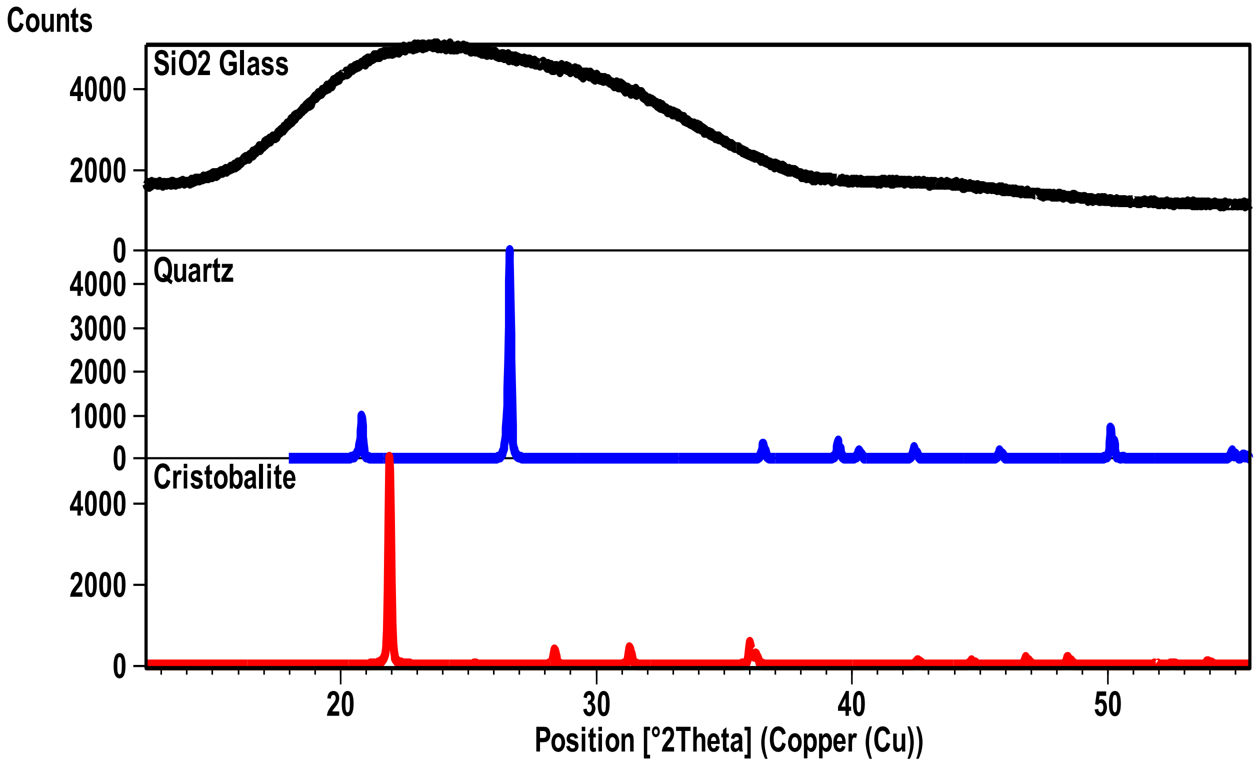
Prize share: 1/2

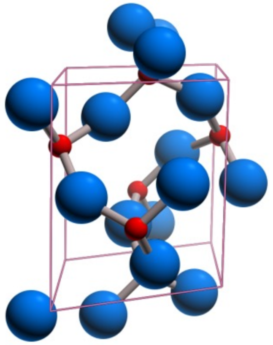


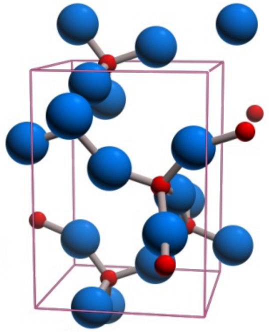


Note $\vec{Q}$ is normal to the lattice planes

Characteristic signals from different – chemically identical – samples

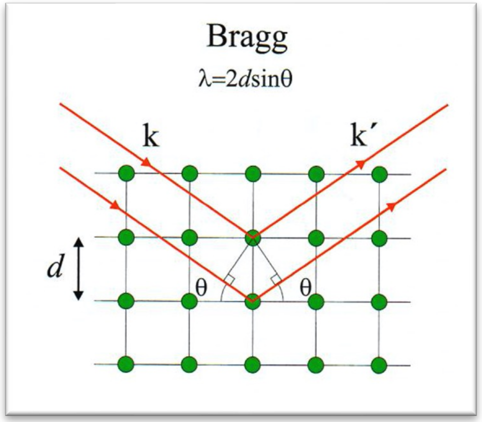


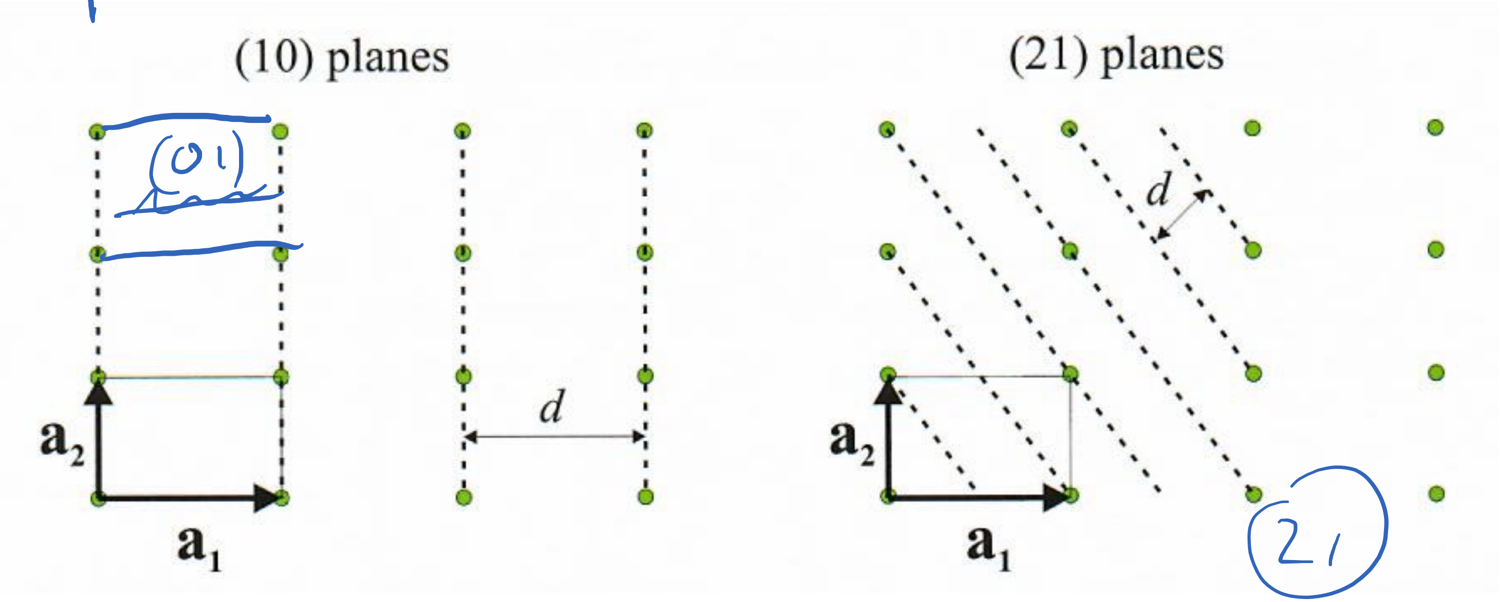




Lattice planes

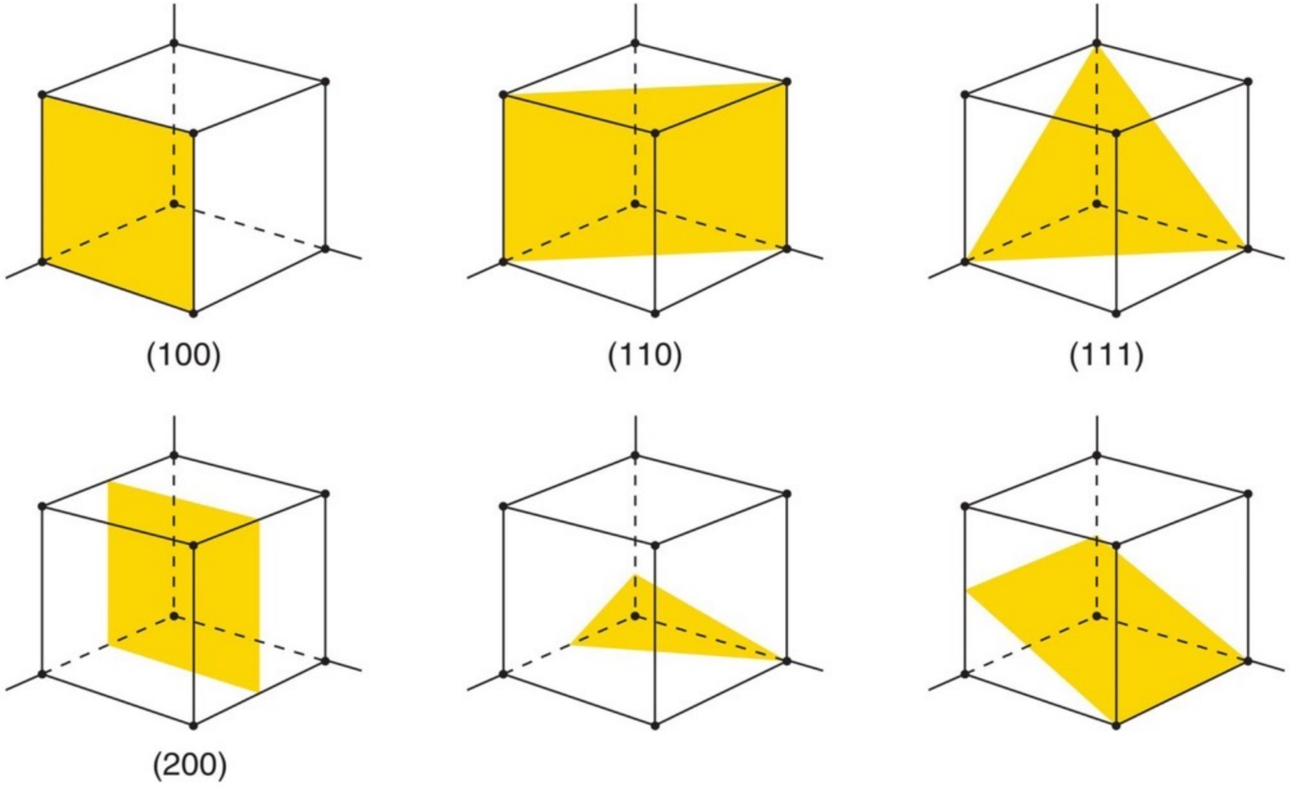
(10)

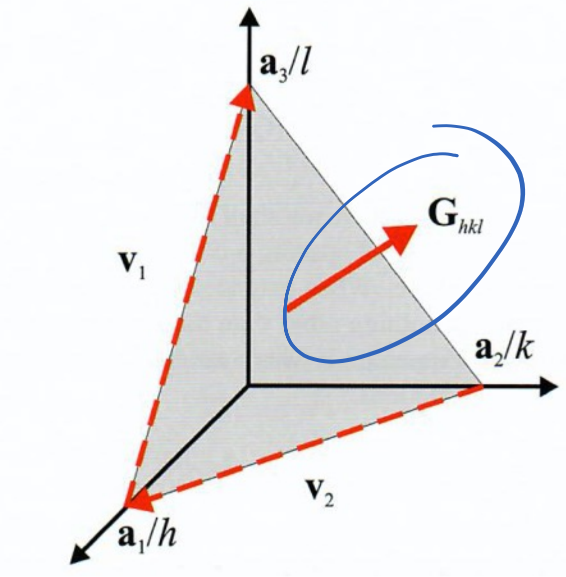




- Find the intercepts of the plane with the respective crystal axis
- Take the reciprocal of these numbers, reduce to smallest integer

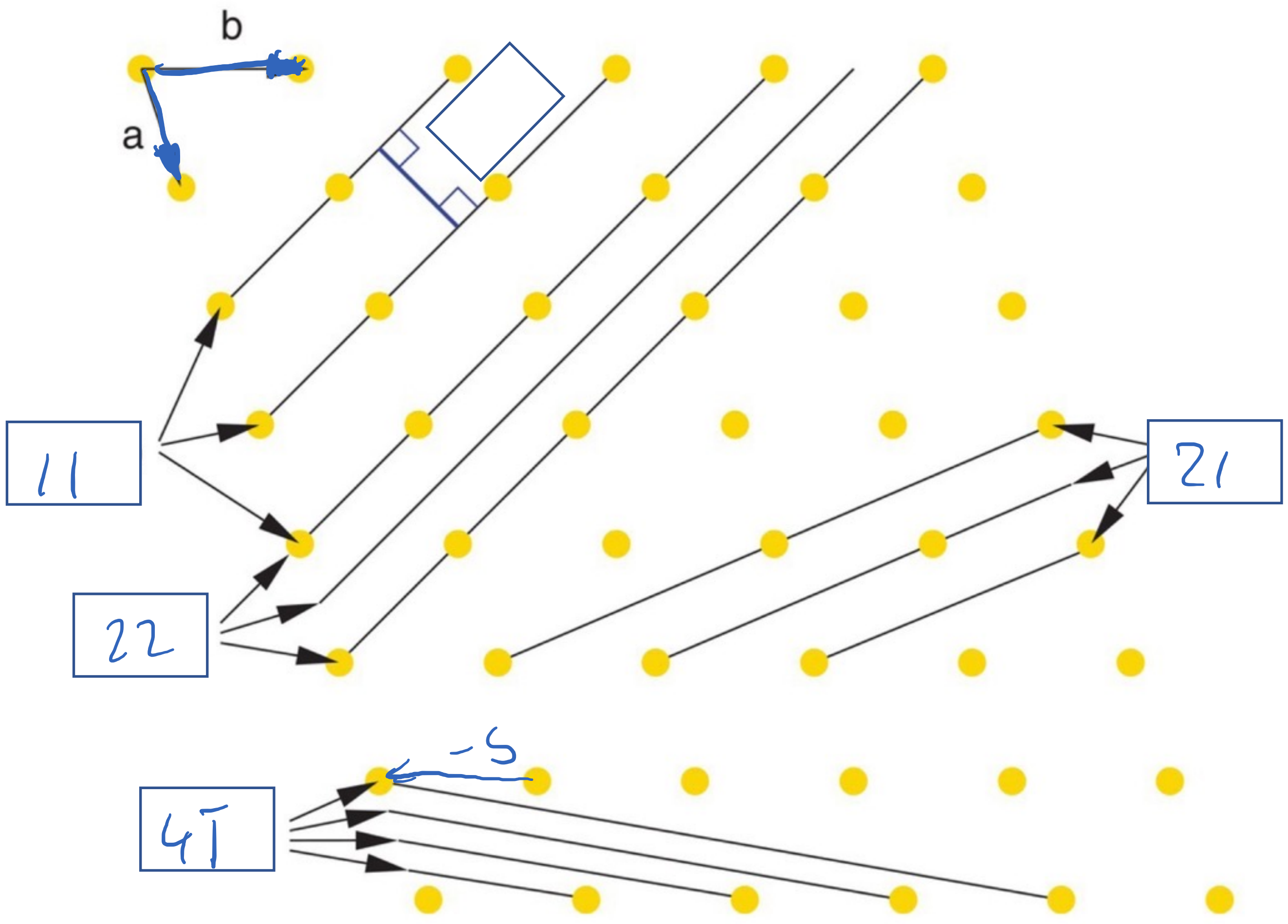
Miller indices





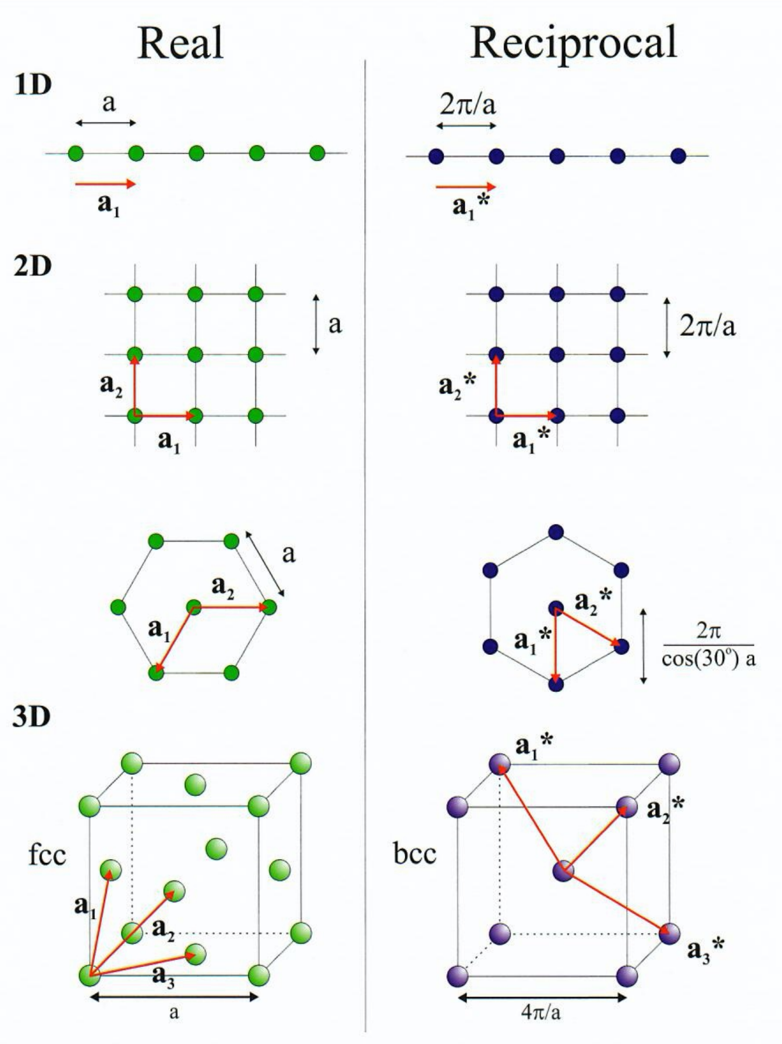
- Find the intercepts of the plane with the respective crystal axis
- Take the reciprocal of these numbers, reduce to smallest integer

Exercise: Identify lattice planes



More on diffraction of single crystals

For each lattice a reciprocal lattice can be defined



→ For each lattice there exists a so-called reciprocal lattice

→ Reciprocal lattice is the Fourier transform of the direct lattice

→ Reciprocal lattice is defined by

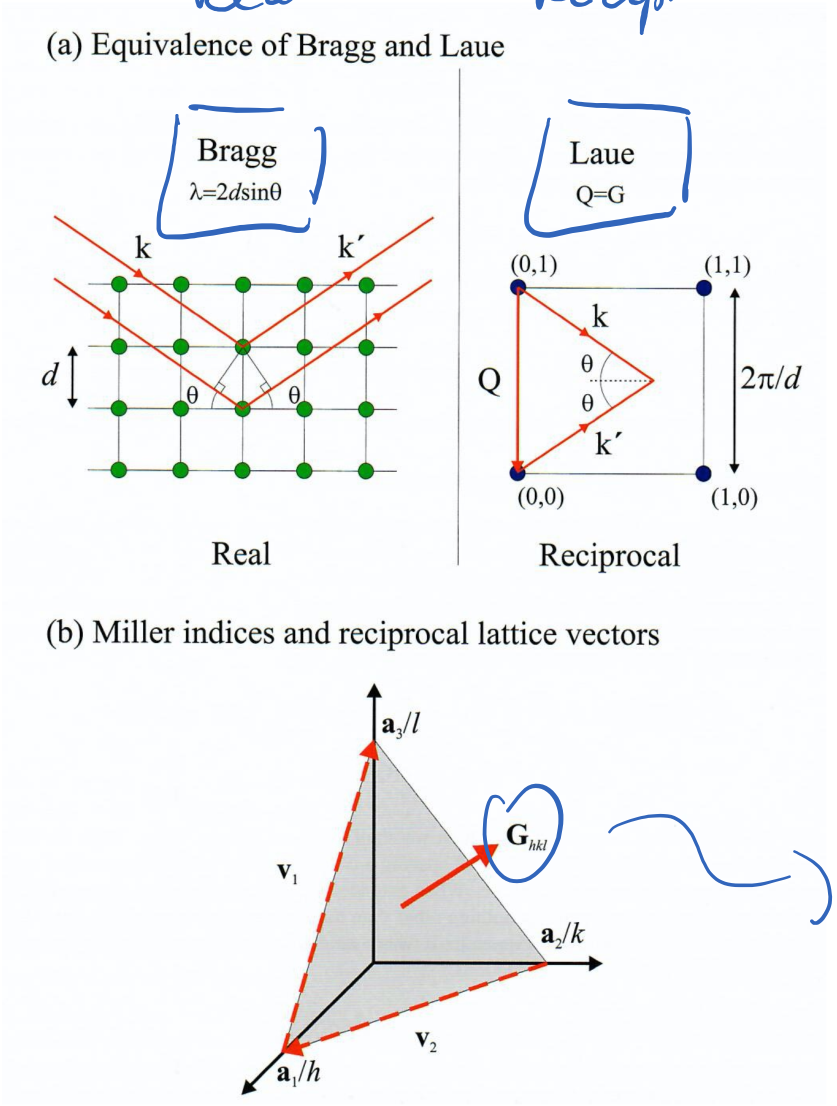
$$\vec{G} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$

perpendicular on planes $h\,k\,l$

$$|G_{hkl}| = \frac{2\pi}{d_{hkl}}$$ → lattice planes

Bargg and Laue conditions

Real Reciprocal



In reciprocal space one can show that constructive interference is observed for

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

Photo from the Nobel Foundation archive.

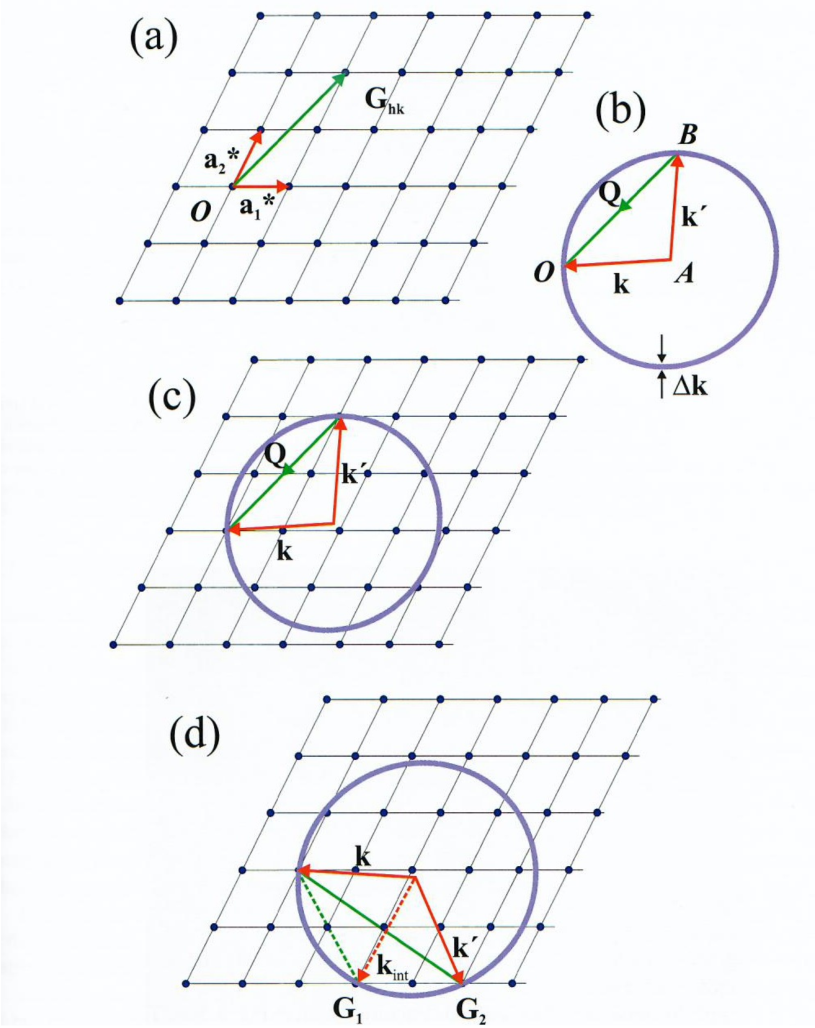
Max von Laue

Prize share: 1/1

$\vec{G} \rightarrow$ perpendicular to the lattice planes with Miller indices hkl

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

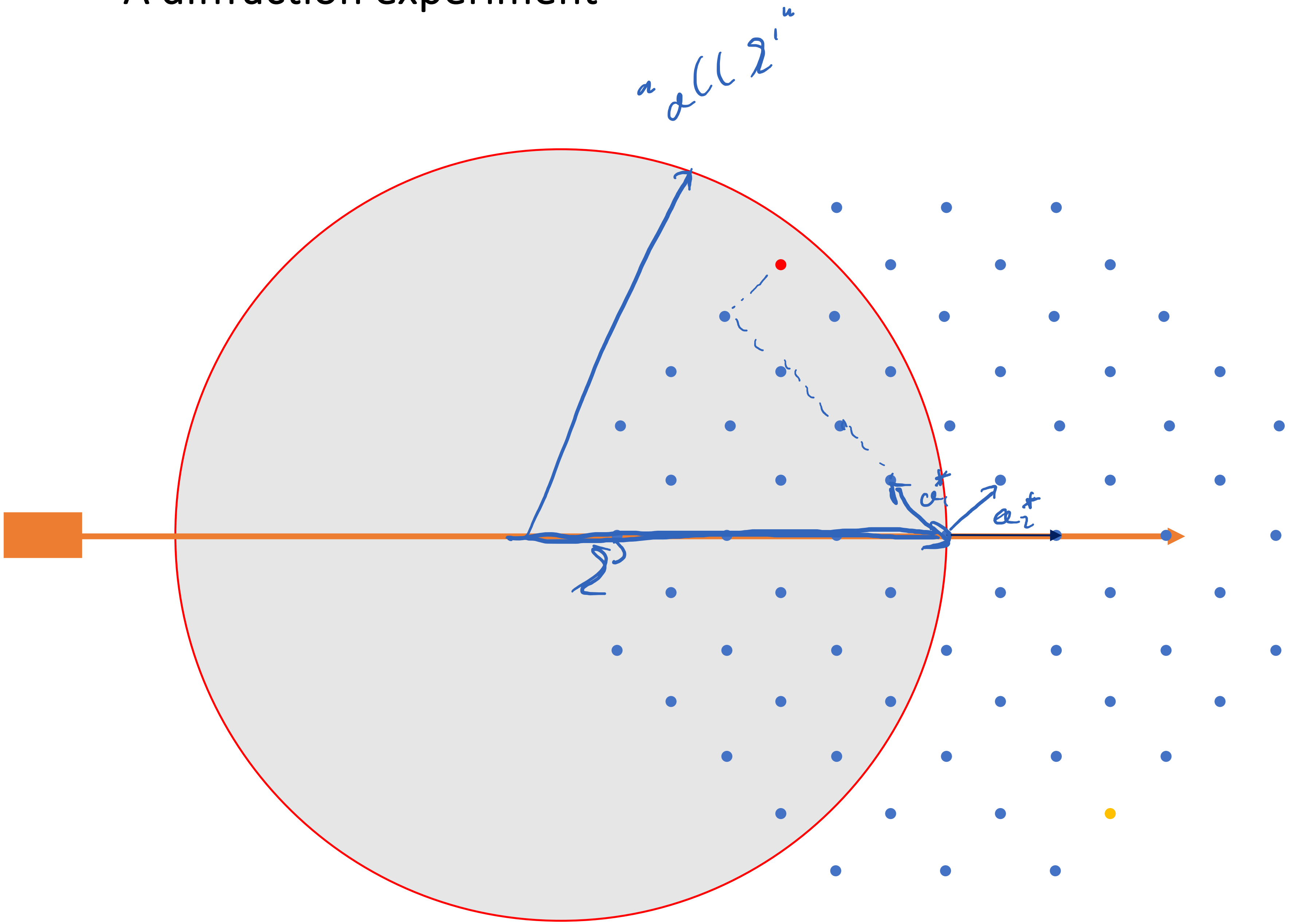
The Ewald Sphere



- Elegant geometric construction of the relationships
  - → wave vector $\vec{k}$
  - → diffraction angle
  - → in the ~~reciprocal~~ reciprocal lattice
- Laue condition $\vec{Q} = \vec{G}_{hkl}$
- Create sphere (circle) with radius $|\vec{k}|$
- 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



reciprocal lattice fixed with respect to real lattice

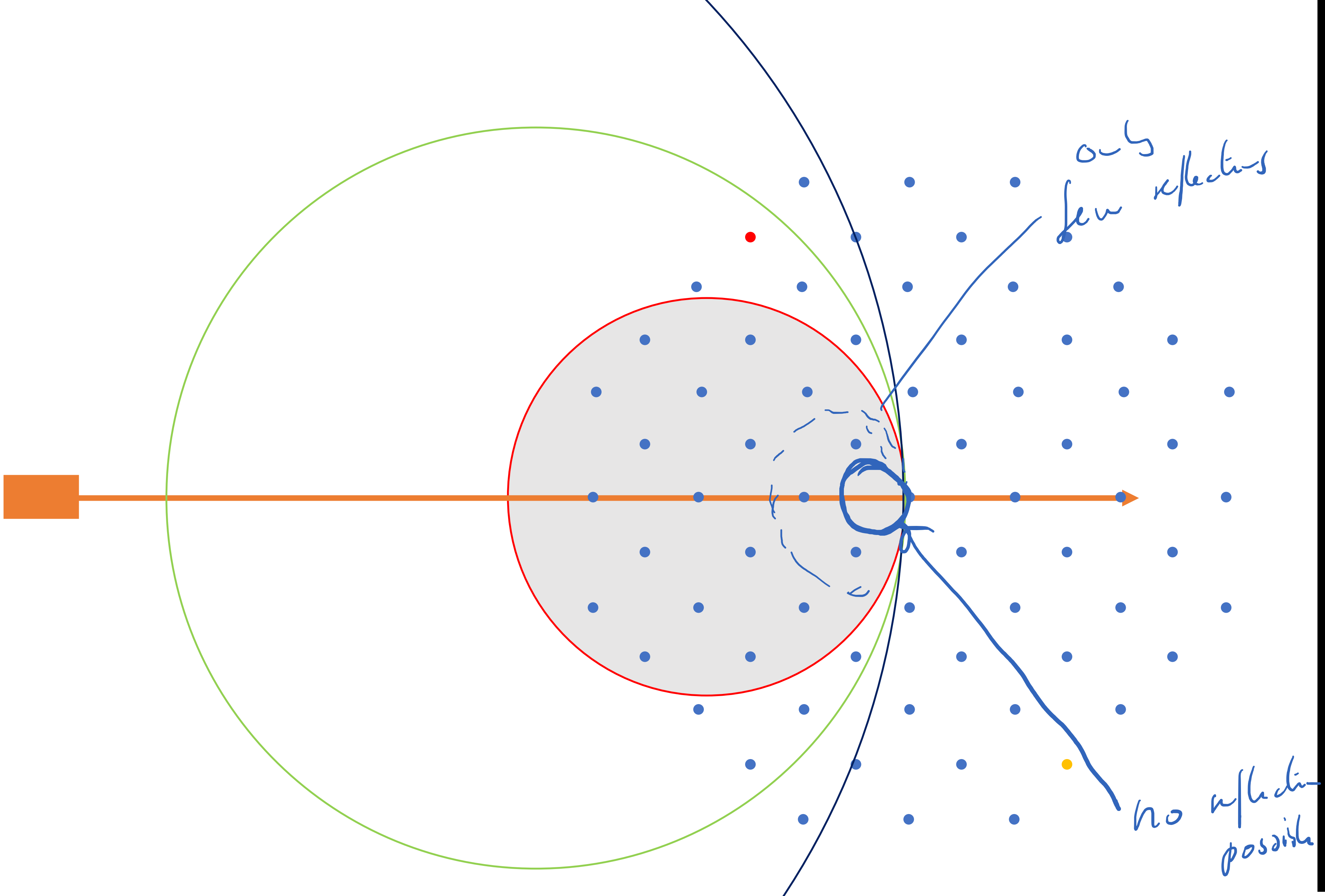
↓

rotate crystal until we see reflection

↓

Reflection angles from respective points

A diffraction experiment

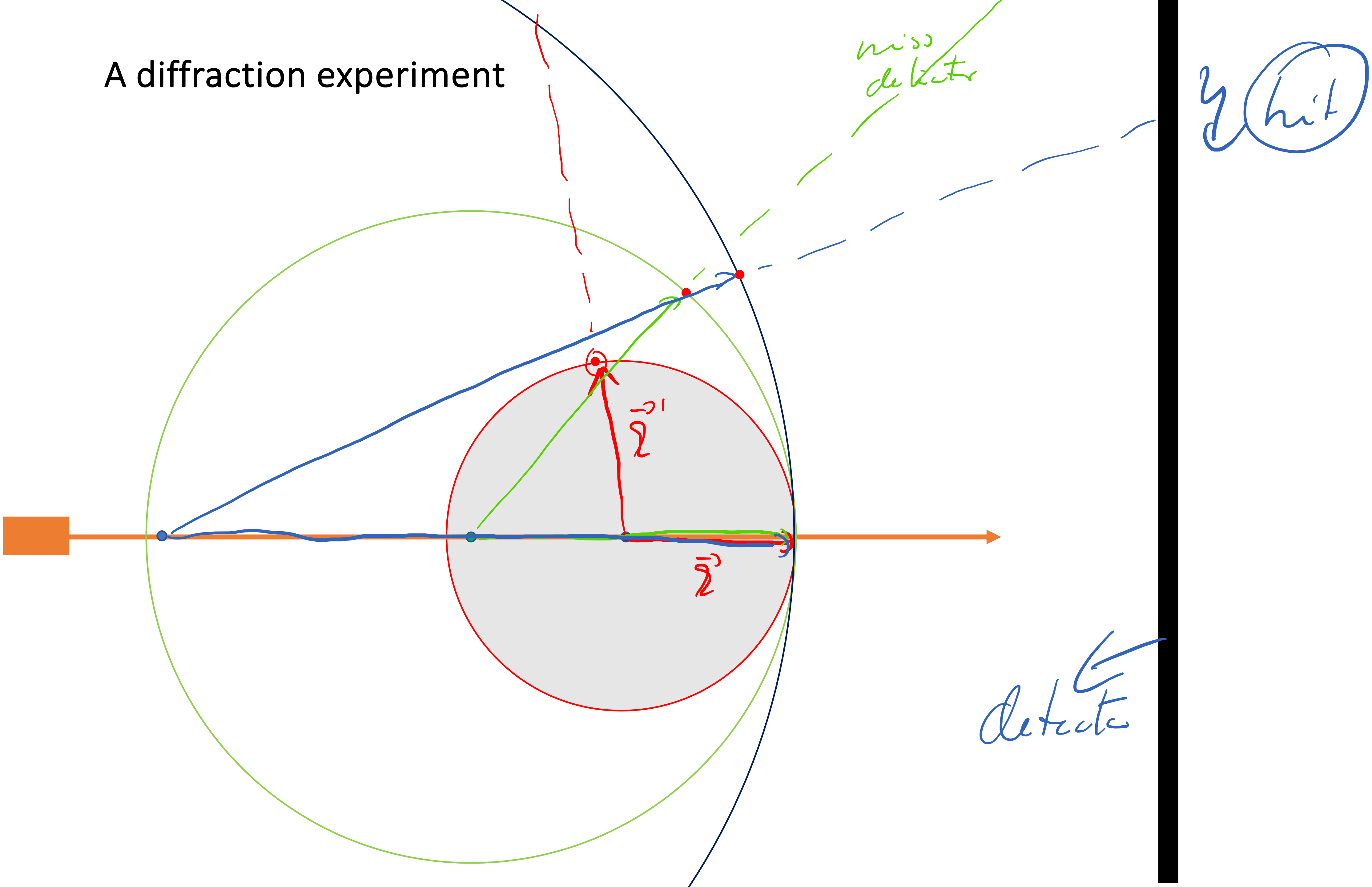


See dependence of reflections as fct of $\vec{k}$, i.e. energy

Radius of sphere $\sim |\vec{k}|$ $\sim h\nu$

More accessible reflections for higher energies
$\Downarrow$
higher resolution

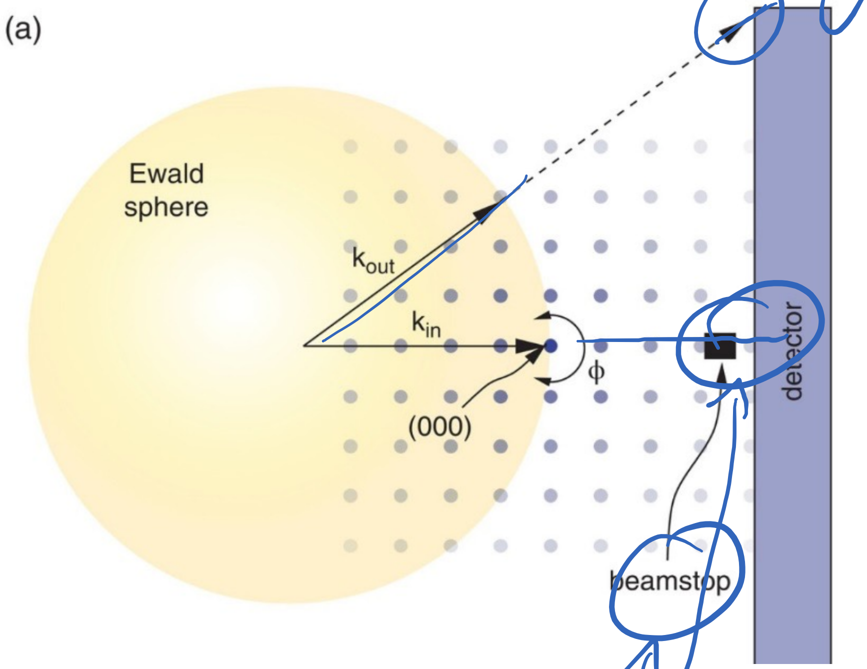
A diffraction experiment



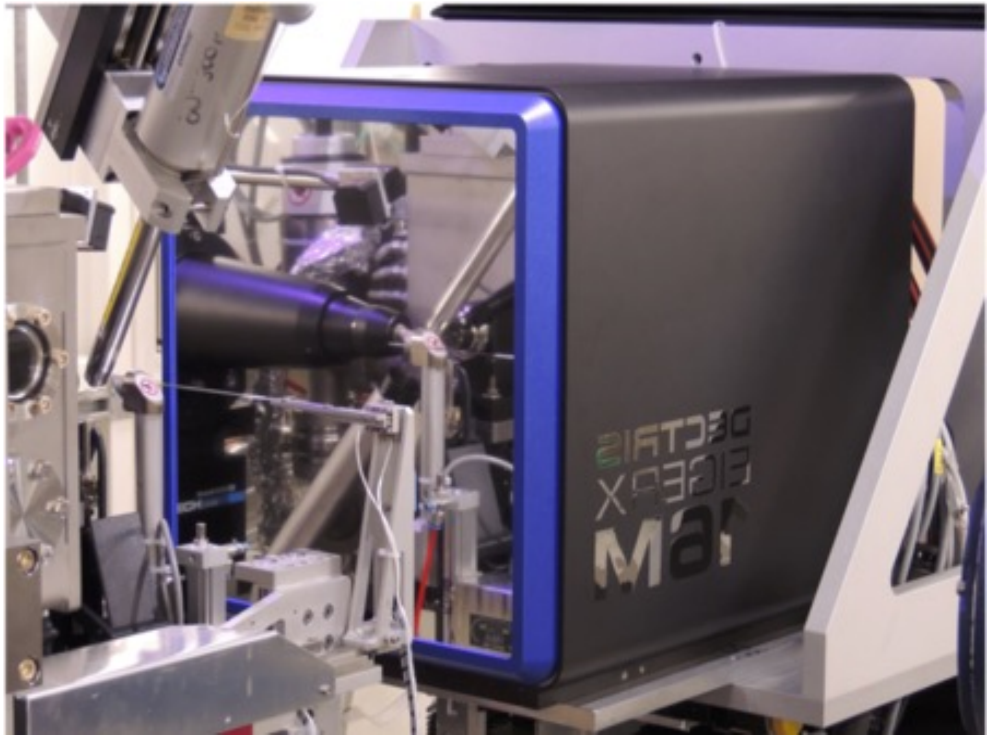
A diffraction experiment

In lab: weak source & small detector and sample
→ quite inefficient

↳ signal

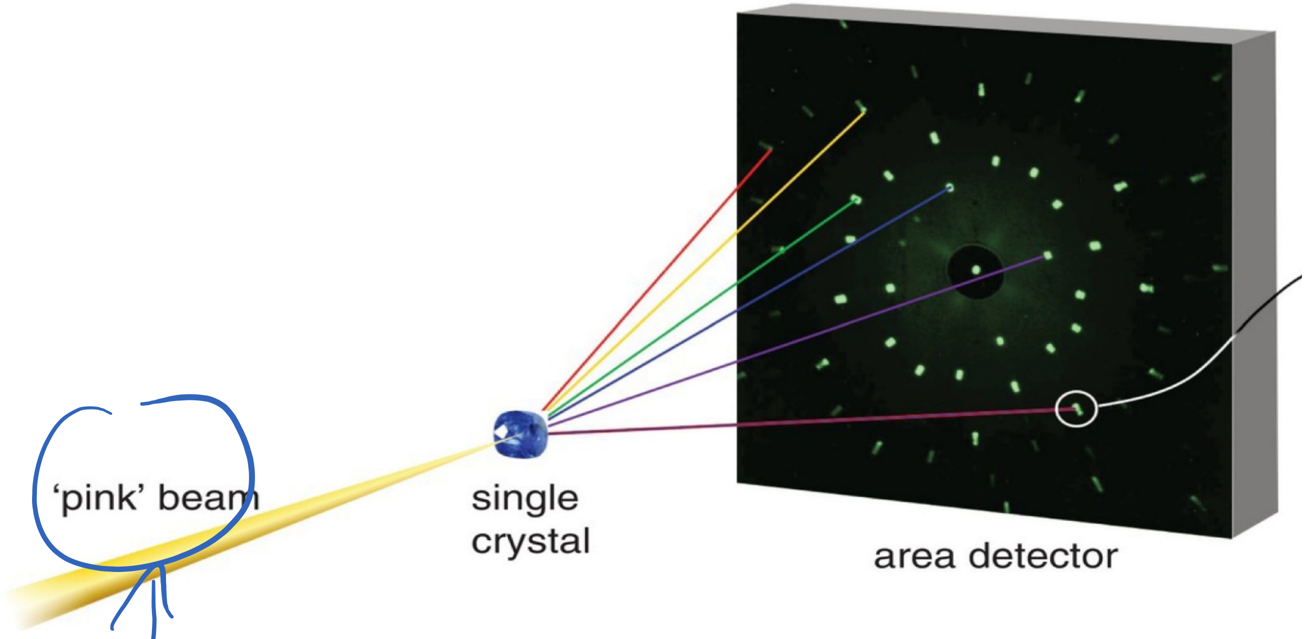


important so that you don't kill detector



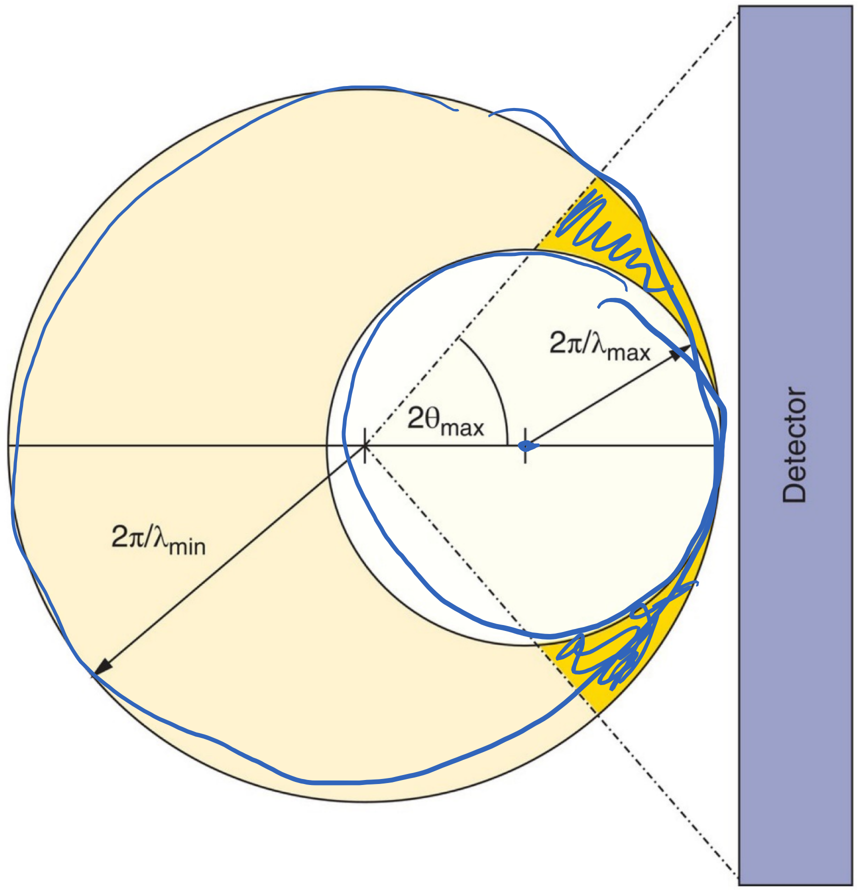
At S.R. facilities → rotate sample
use area detectors
⇒ efficient

Laue method



"bandwidth"

pink beam
⇓
all reflections within bandwidth are visible



The end