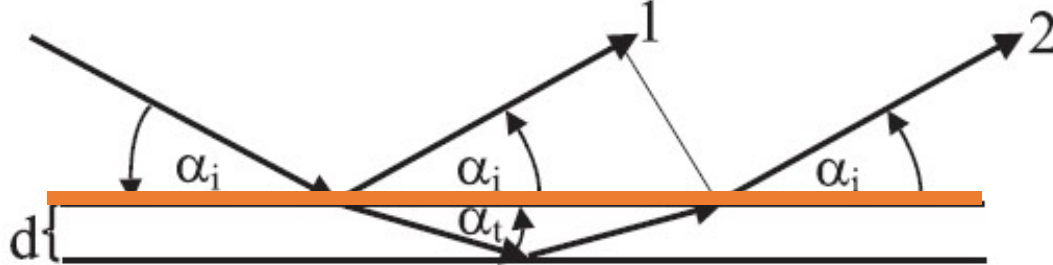# X-ray reflectivity from a thin film

ΔQ between two oscillations correlates to film thickness D=2π/ΔQ
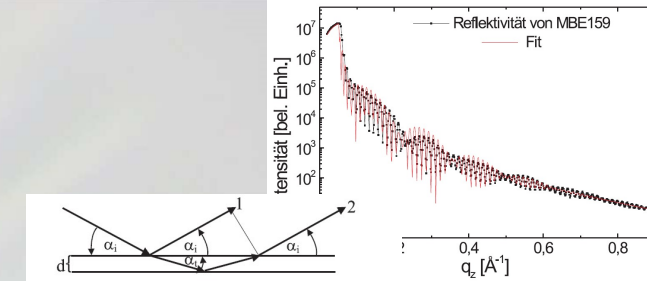
Second, much longer periodicity must correspond to a second very thin layer
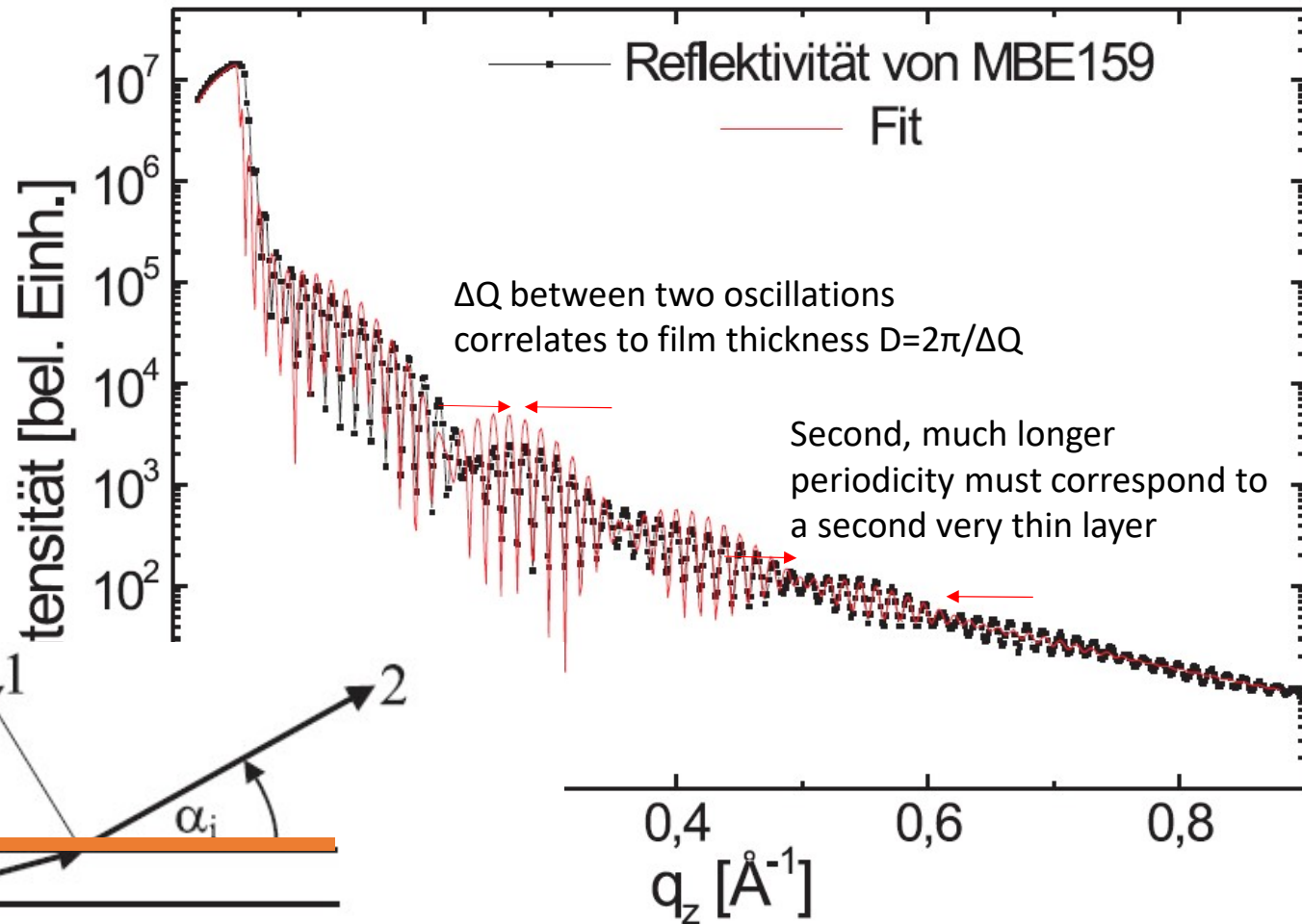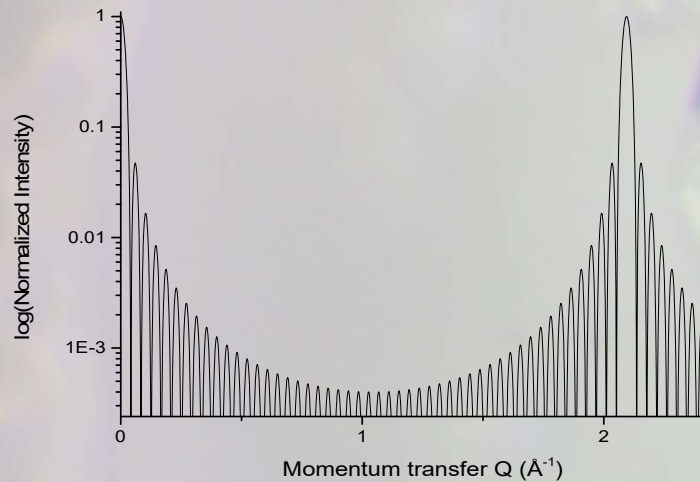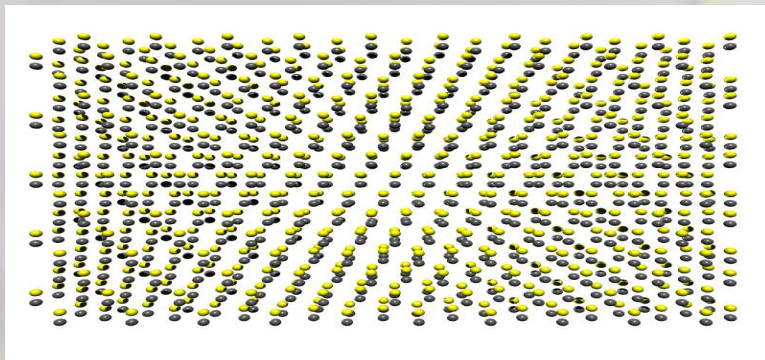
From Reflectivity to diffraction

Reflectivity: Continuum description of Material is enough.

Reality: "granular" description of a point lattice is required (otherwise there may well be reflectivity but no Bragg peaks)

If we look only at momentum transfers along z ("The specular path"), we can look at the scattered amplitude of light from a linear chain of atoms along z with a well defined truncation on top and bottom of the film.

Diffraction Amplitude from a linear chain

$1*a$

a

$2*a$

$3*a$ f_a

z

N_a*a
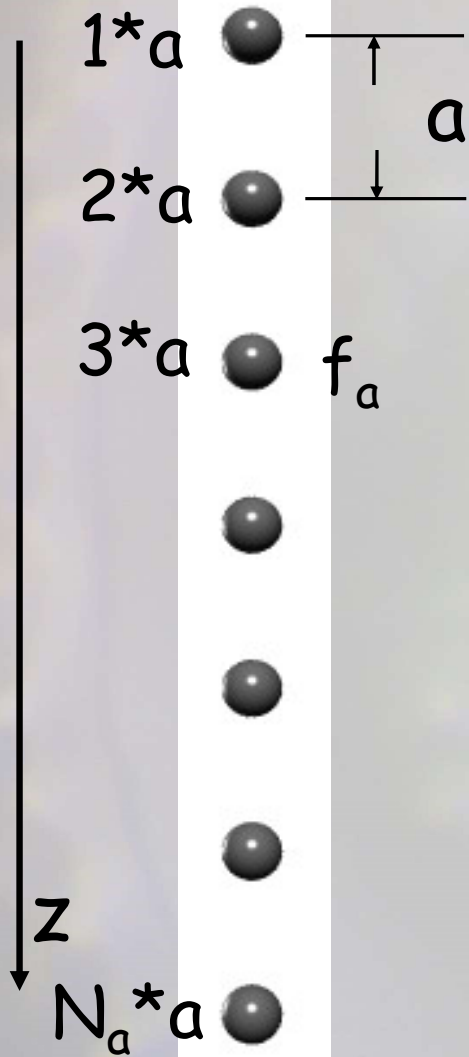
$$A(q) = f_a \sum_{n=1}^{N_a} \exp(i*q*n*a)$$

$$= f_a * \frac{\exp(i*q*N_a*a)-1}{\exp(i*q*a)-1}$$

$$A*A^* = f_a^2 \left[\frac{\sin(\frac{1}{2}*q*N_a*a)}{\sin(\frac{1}{2}*q*a)} \right]^2$$

Diffraction amplitude from a linear chain as model for a thin crystalline film

PhDthesis

(contains an analytical treatment of diffraction from crystalline perfect thin films on pp42-56 and on pp 123-130)

$$I(Q) = AA^* =$$

$$2\left[f_{a_1}^2 + f_{a_2}^2 + 2f_{a_1}f_{a_2}\cos\left(\phi_{a_1} - \phi_{a_2} - \frac{1}{2}aQ\right)\right]\left(\frac{\sin\left(\frac{1}{2}aN_aQ\right)}{\sin\left(\frac{1}{2}aQ\right)}\right)^2$$

$$+ \; 2\left[f_{b_1}^2 + f_{b_2}^2 + 2f_{b_1}f_{b_2}\cos\left(\phi_{b_1} - \phi_{b_2} - \frac{1}{2}bQ\right)\right]\left(\frac{\sin\left(\frac{1}{2}bN_bQ\right)}{\sin\left(\frac{1}{2}bQ\right)}\right)^2$$

$$+ \; 2\left[f_{a_1}f_{b_1}\cos\left(\phi_{a_1} - \phi_{b_1} - aQ - \frac{1}{2}aN_aQ - \frac{1}{2}bN_bQ\right)\right.$$

$$+ \; f_{a_1}f_{b_2}\cos\left(\phi_{a_1} - \phi_{b_2} - aQ - \frac{1}{2}aN_aQ - \frac{1}{2}bN_bQ - \frac{1}{2}bQ\right)$$

$$+ \; f_{a_2}f_{b_1}\cos\left(\phi_{a_2} - \phi_{b_1} - \frac{1}{2}aQ - \frac{1}{2}aN_aQ - \frac{1}{2}bN_bQ\right)$$

$$+ \; \left.f_{a_2}f_{b_2}\cos\left(\phi_{a_2} - \phi_{b_2} - \frac{1}{2}aQ - \frac{1}{2}aN_aQ - \frac{1}{2}bN_bQ - \frac{1}{2}bQ\right)\right]$$

$$* \; \frac{\sin\left(\frac{1}{2}an_aQ\right)\sin\left(\frac{1}{2}bN_bQ\right)}{\sin\left(\frac{1}{2}aQ\right)\sin\left(\frac{1}{2}bQ\right)}$$

From thin films to normal crystals

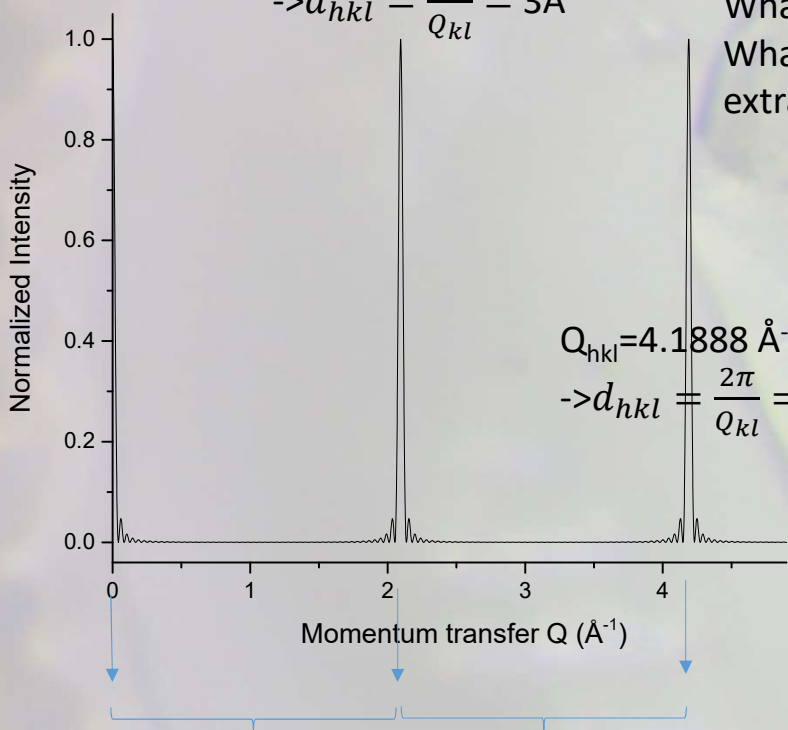$$A * A^* = f_a{}^2 \left[\frac{\sin(\tfrac{1}{2} * q * N_a * a)}{\sin(\tfrac{1}{2} * q * a)} \right]^2$$
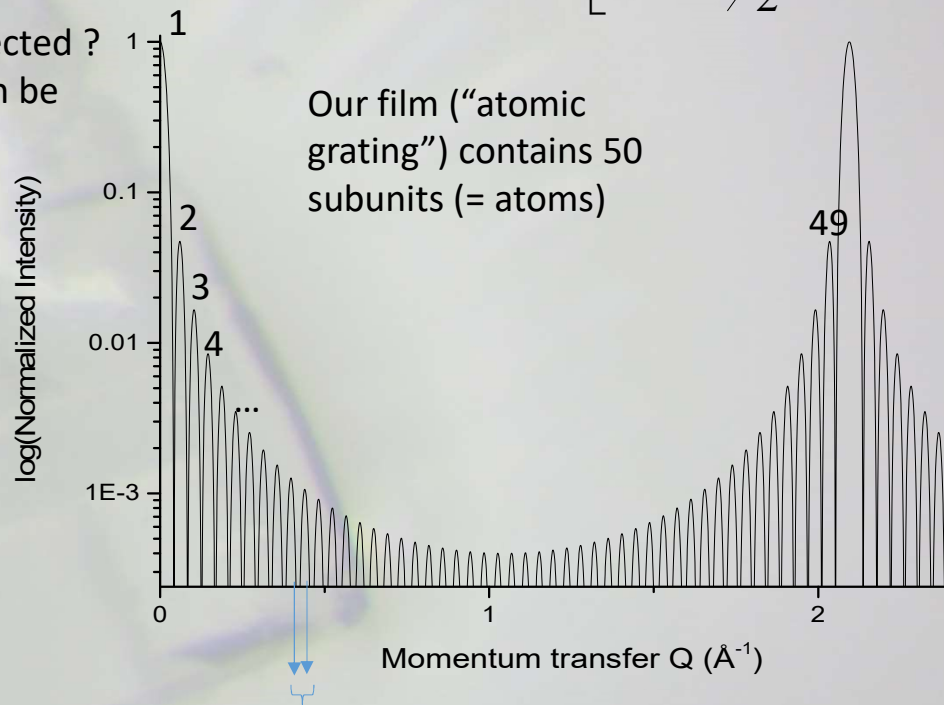
Q_{hkl}=2.0944 Å^{-1},
-> $d_{hkl} = \frac{2\pi}{Q_{kl}} = 3$Å

Ideal thin film:
What has been neglected ?
What parameters can be extracted ?

Q_{hkl}=4.1888 Å^{-1},
-> $d_{hkl} = \frac{2\pi}{Q_{kl}} = 1.5$Å

Our film ("atomic grating") contains 50 subunits (= atoms)

Normalized Intensity

Momentum transfer Q (Å^{-1})

log(Normalized Intensity)

Momentum transfer Q (Å^{-1})

Periodicity in reciprocal space
2π(periodicity in real space)$^{-1}$

Periodicity in reciprocal space ΔQ=0.0419 Å^{-1}
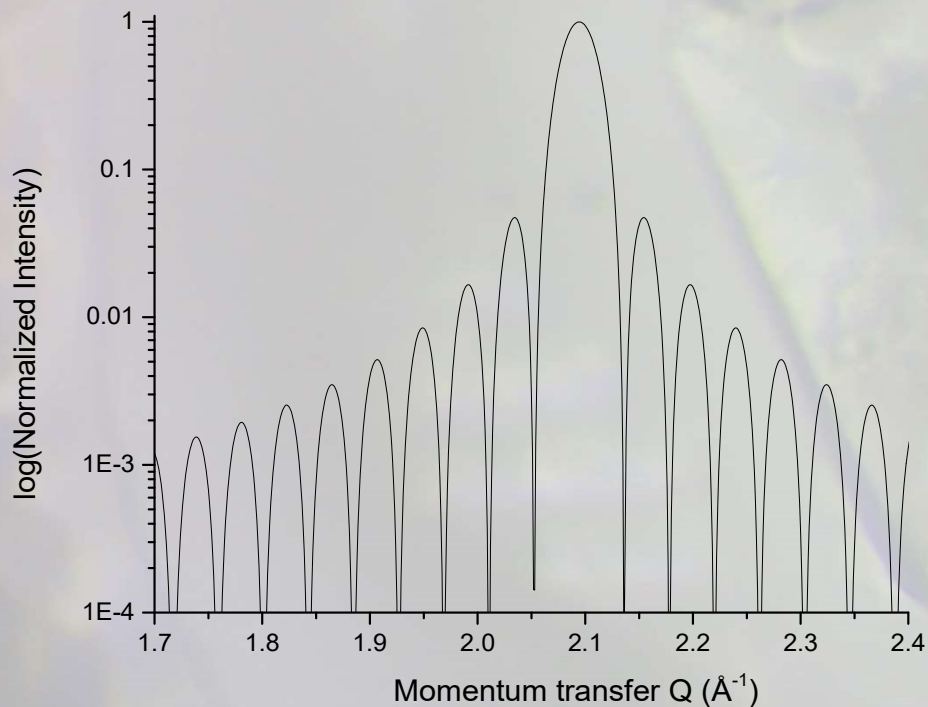= 2π(size in real space)$^{-1}$=150Å film thickness

The use of reciprocal space (=Fourier space) becomes practical when we look at periodic objects or well truncated objects
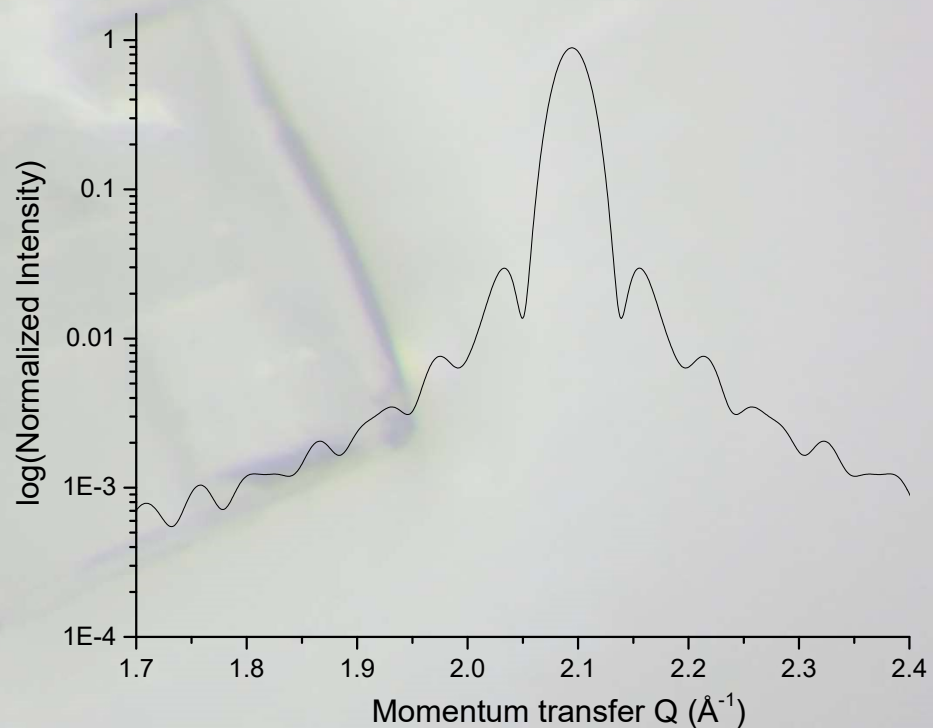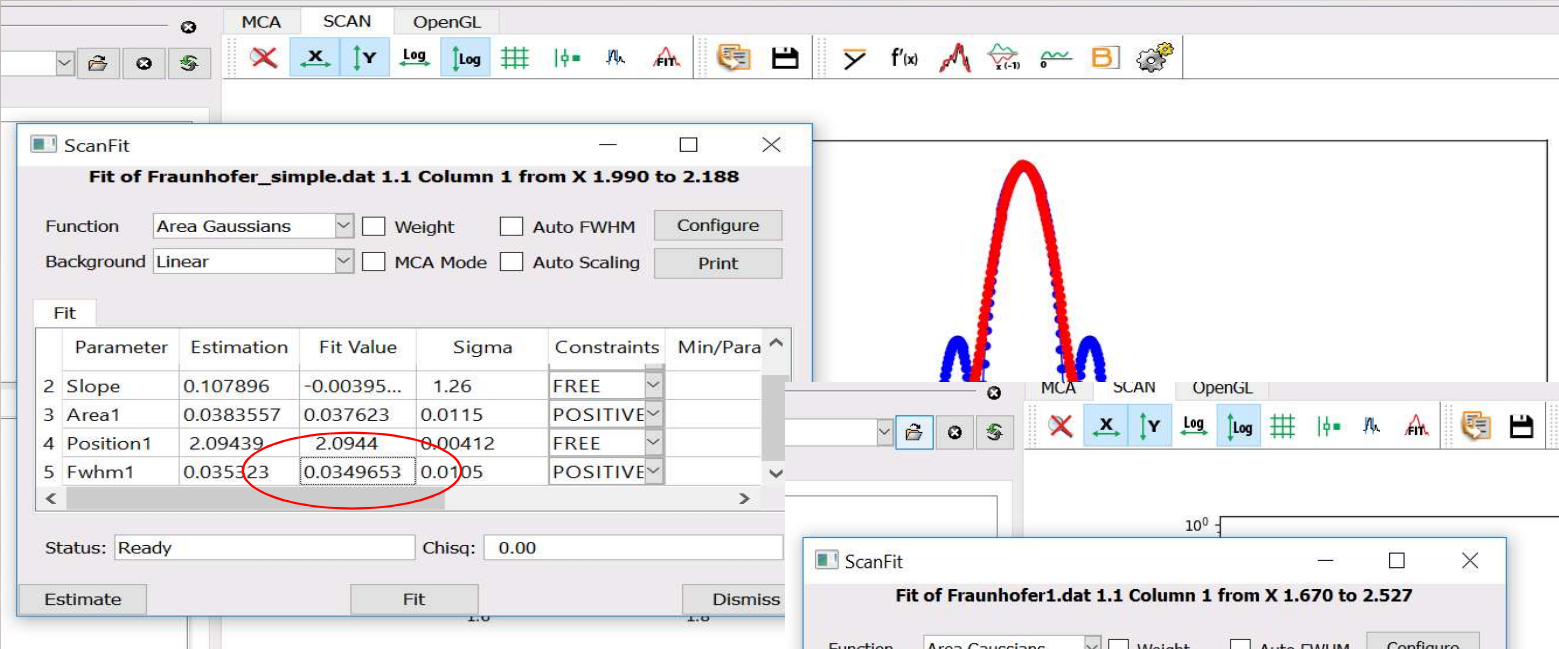
From thin films to normal crystals
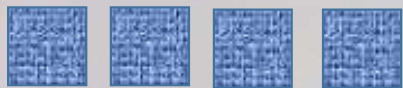
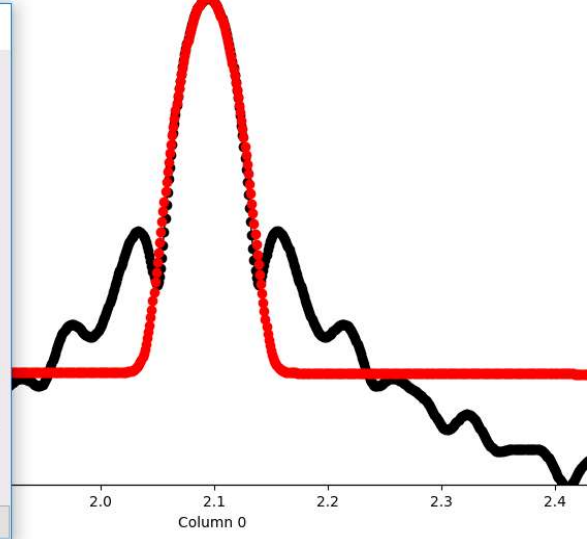Thin film or crystals with identical sizes (50 atoms in size)
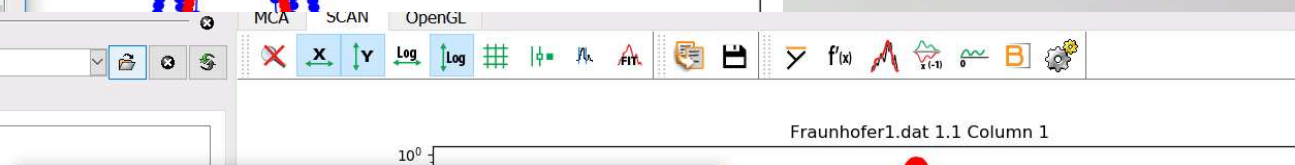
9 different sizes between 40 and 60 atoms

Effect of size distribution on Full Width at Half Maximum of Bragg Peak

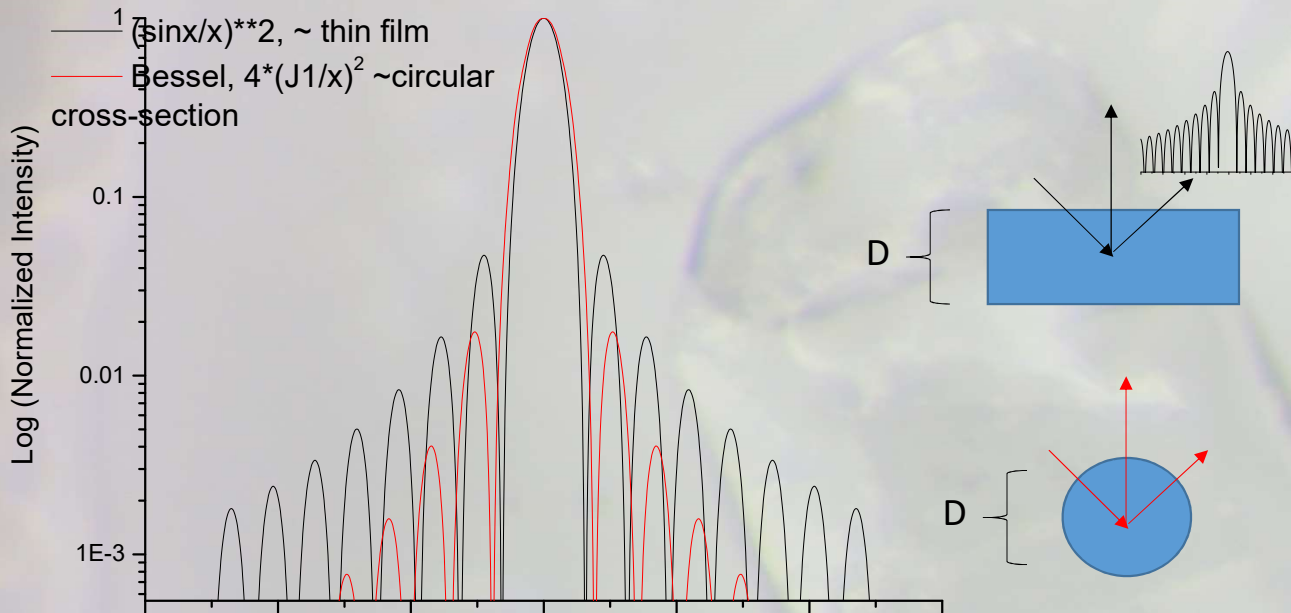FWHM~ 0.035 Å^{-1} ->
mean size= $\dfrac{2\pi}{0.036 \text{ Å}^{-1}}$ =170 Å
A more detailed consideration leads to the

Size distribution only washes out finite size oscillations and modifies eventually the shape of the central maximum.
The FWHM for the central maximum corresponds however very well to the average crystallite size. It is a very powerful tool for the evaluation of this parameter

Differently shaped particles

Legend (on plot):
- (sinx/x)**2, ~ thin film
- Bessel, 4*(J1/x)^2 ~circular cross-section

Y-axis: Log (Normalized Intensity)

Again, the width on the central maximum depends only poorly on the particle shape, it is a very good reference to its average size D. This size is derived in a first approximation from the with ΔQ of the Bragg peak in reciprocal space:

$$D = \frac{2\pi}{\Delta Q} \text{ or } D * \Delta Q = 2\pi$$

Philosophically looking at sharp Bragg peaks means determining the momentum of a photon with great precision. This is why a small ΔQ (narrow width) must be related to an uncertainty of the crystals size it has been interacting with

Heisenberg:

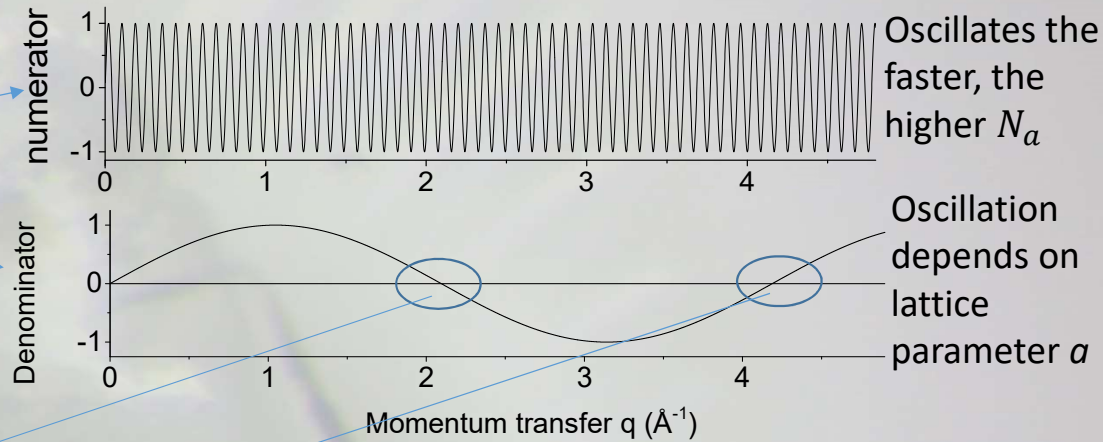$$\Delta x \Delta p \geq \frac{h}{2\pi} \quad (1)$$

h: Planck's constant

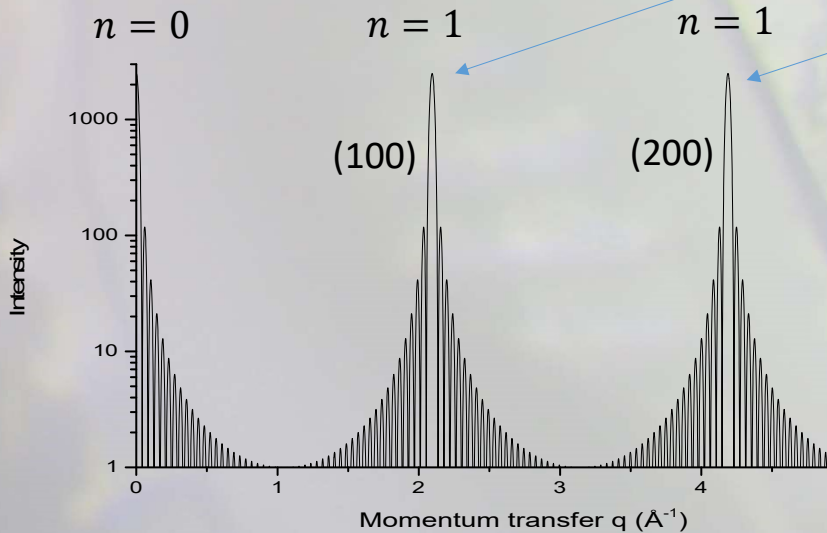$$FWHM_{BraggPeak} \sim 1/(Crystal\ size\ D)$$

Further quantification of peak properties: height and area

Bragg intensity from a perfect small crystal $N_a = 50$ atoms in size grown along axis a:

$$A * A^* = f_a^{\ 2} \left[\frac{\sin(\frac{1}{2} * q * N_a * a)}{\sin(\frac{1}{2} * q * a)} \right]^2$$

This oscillatory term leads to strong peaks whenever $\frac{1}{2} * q * N_a * a$ is an integer multiple of π, thus whenever $q * a = n * 2\pi$


Oscillates the faster, the higher N_a

Oscillation depends on lattice parameter a

Momentum transfer q (Å^{-1})

$n = 0$ $n = 1$ $n = 1$

(100)   (200)

Intensity

Momentum transfer q (Å^{-1})

$$A * A^* = f_a^{\ 2} \left[\frac{\sin(\frac{1}{2} * q * N_a * a)}{\sin(\frac{1}{2} * q * a)} \right]^2$$

We know that FWHM$_{BraggPeak} \sim 1/N_a$
What is the influence of N_a on the peak height ?

Further quantification of peak properties: height and area

We know that $FWHM_{BraggPeak} \sim 1/N_a$
What is the influence of N_a on the peak height ?

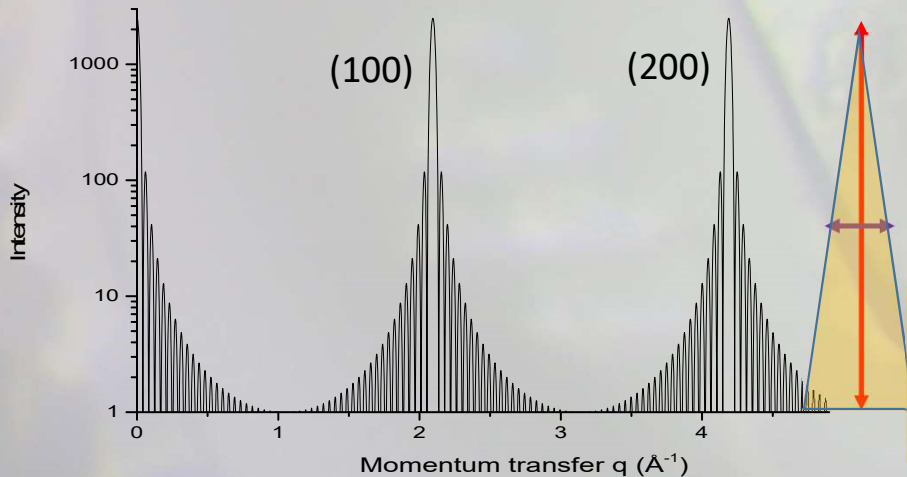$$A * A^* = f_a{}^2 \left[\frac{\sin(\frac{1}{2} * q * N_a * a)}{\sin(\frac{1}{2} * q * a)} \right]^2$$

For $x \approx 0, sinx \approx x$
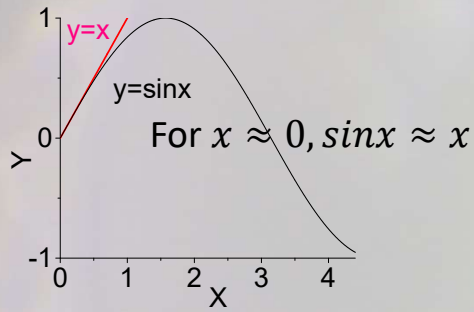
If $\frac{1}{2} * q * N_a * a \approx 0$
and $\frac{1}{2} * q * a \approx 0$

$$A * A^* = f_a^2 \left[\frac{\frac{1}{2}*q*N_a*a}{\frac{1}{2}*q*a} \right]^2 = f_a^2 * N_a{}^2$$

$y=x$

$y=sinx$

(100)   (200)

The Peak Intensity I_P (height) is thus proportional to $N_a{}^2$

The Peak Width **FWHM** is proportional to $1/N_a$

The peak Area, the *integrated intensity* of the Bragg Peak is thus proportional to I_P * FWHM and thus proportional to N_a , *i.e. the number of atoms in the crystal*

This is the basis of all structure resolution and refinement using XRD !!!

Further quantification of peak properties: height and area

$$A * A^* = f_a{}^2 \left[\frac{\sin(\tfrac{1}{2} * q * N_a * a)}{\sin(\tfrac{1}{2} * q * a)} \right]^2$$

Leads to an integrated intensity $\sim N_a$

It is obviously proportional to f_a^2, with f_a being the atomic scattering factor. Being the Fourier transform of the electron distribution of one atom, f_a depends itself on momentum transfer q (neglected on the previous pages)
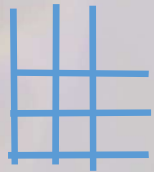
$$f_a \sim Z \text{ (number of electrons)}$$
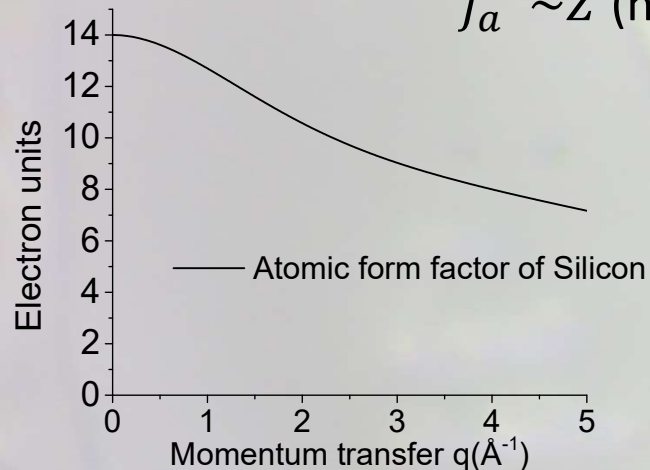
We conclude that the peak intensity (Both, height and integrated one) are proportional to Z^2 for the example of the monoatomic simple lattice considered here. For a more complex structure (anything that is not simple cubic elemental crystal, hence almost everything) this term must not be the atomic scattering factor, but the Fourier transform of the smallest periodic unit that builts up the crystal: the unit cell. The Fourier transform of the unit cell is called the structure factor F_{hkl}. It logically changes for every Bragg reflection, making the integrated Bragg diffraction intensities sensible to the structure of the unit cell.

(Graph: vertical axis "Electron units" from 0 to 14; horizontal axis "Momentum transfer q(Å⁻¹)" from 0 to 5; curve labeled "Atomic form factor of Silicon")

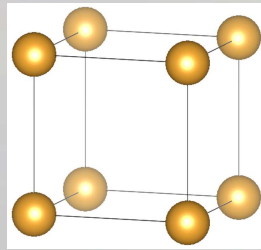$$A * A^* = F_{hkl}^2(q) \left[\frac{\sin(\tfrac{1}{2} * q * N_a * a)}{\sin(\tfrac{1}{2} * q * a)} \right]^2$$

Diffraction from crystals,
reflections about reciprocal space distribution of intensity

Grating

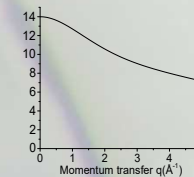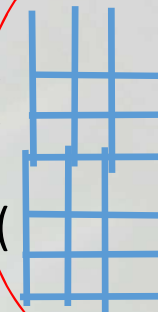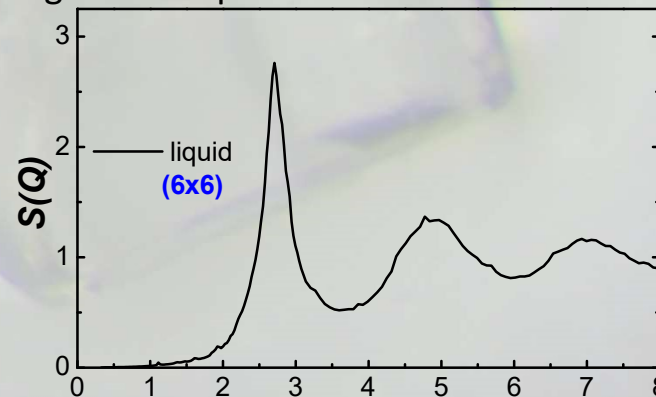Unit cell

$\bigotimes$

Convol.

= Crystal:

Fourier Transform= FT(   )*FT(   )

Or in the simplest case = FT(   )*FT(   )

14
12
10
8
6
4
2
0
0   1   2   3   4   5
Momentum transfer q(Å^{-1})
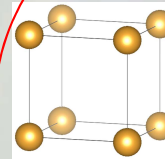
Scattering from a liquid = some local order

$S(Q)$

3

2

1

0

0   1   2   3   4   5   6   7   8

liquid
(6x6)

The separation of "periodicity" and "building blocks" is a Christmas present of Fourier space !!

Diffraction from a 3D crystal with a 3D unit cell

Grating

$\bigotimes$
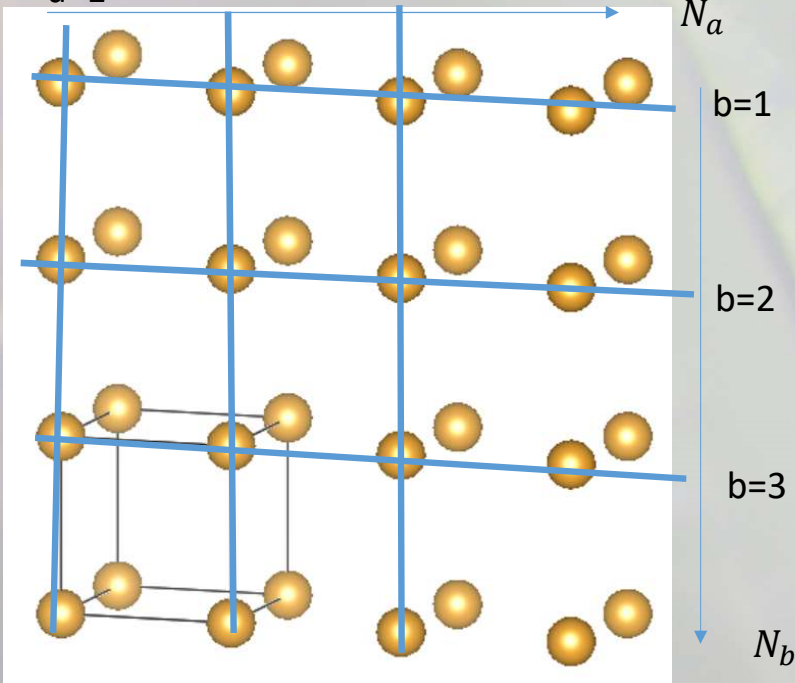*Convol.*

Unit cell

= Crystal:

a=1   a=2   a=3

N_a

b=1

b=2

b=3

N_b

(FT of unit cell) * (FT of grating)

$$A * A^* =$$
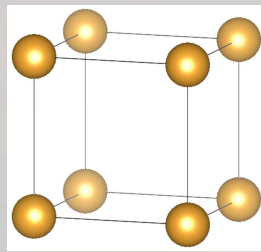
$$F_{hkl}^2(q)\left[\frac{\sin(^1/_2 * q_a * N_a * a)}{\sin(^1/_2 * q_a * a)} * \frac{\sin(^1/_2 * q_b * N_b * b)}{\sin(^1/_2 * q_b * b)}\right.$$

$$\left. * \frac{\sin(^1/_2 * q_c * N_c * c)}{\sin(^1/_2 * q_c * c)}\right]^2$$

Remember: This oscillatory term leads to strong peaks whenever $^1/_2 * q * N_a * a$ is an integer multiple of π, thus whenever $q * a = n * 2\pi$

$$\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} * \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = a * q_x = n * 2\pi$$
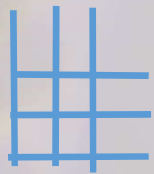
Or for a 3-dimensional crystal each of the products :

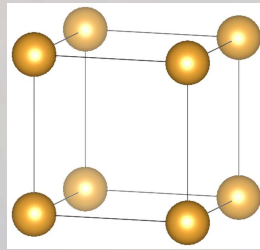$$a * q_x, b * q_y, c * q_z = n * 2\pi$$

(Powder) Diffraction from a 3D crystal with a 3D unit cell
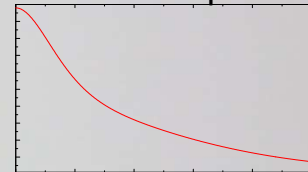
Grating

Unit cell: crystal system: cubic (simple)

I(powder)=M*(FT of unit cell) * (FT of grating)
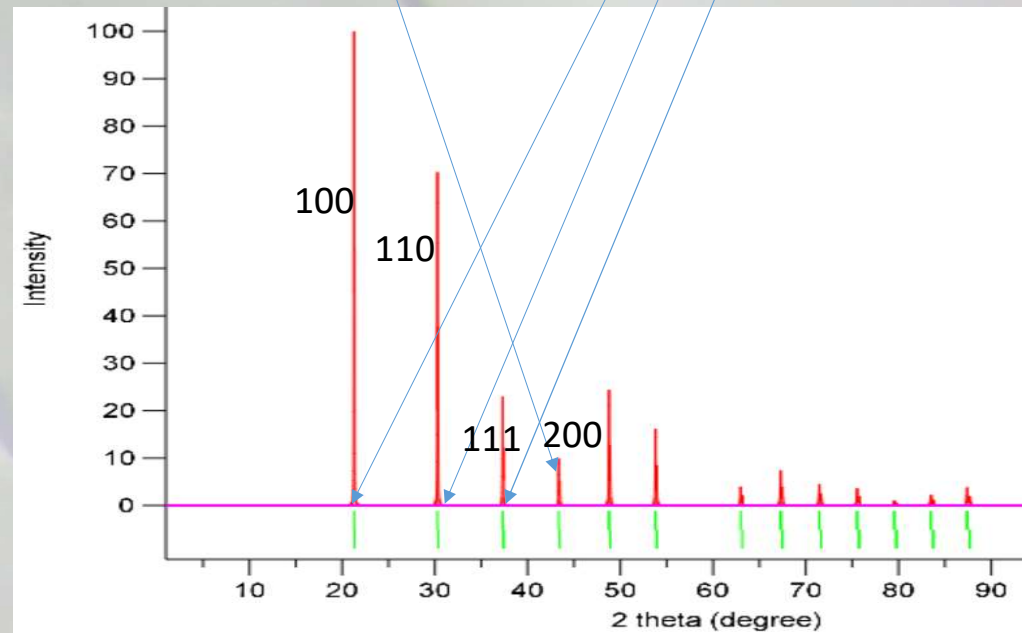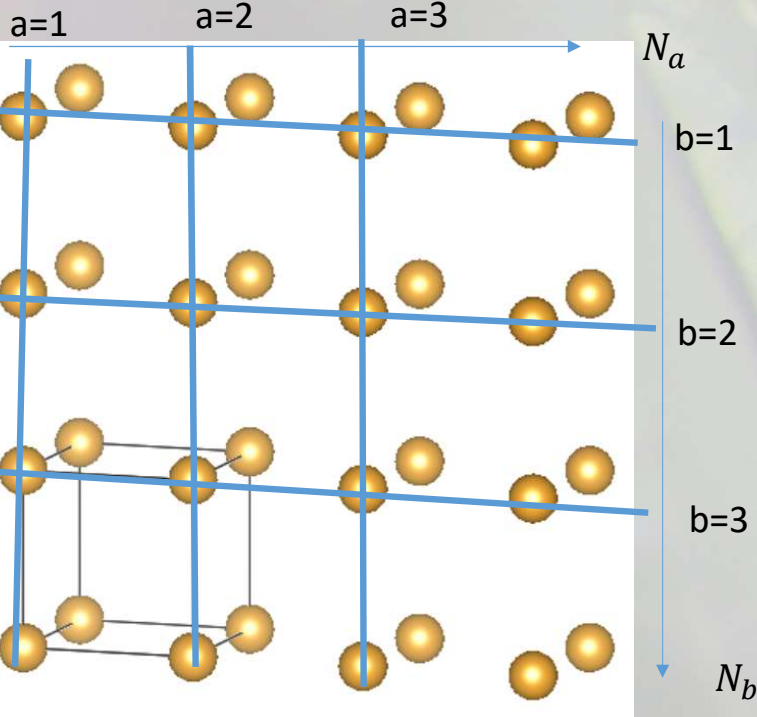
$\bigotimes$

Convol.

Simple cubic structure: 1 Atom in unit cell, no symmetry operations ("simple")

= Crystal:

FT of one atom, should give a "smooth" envelope
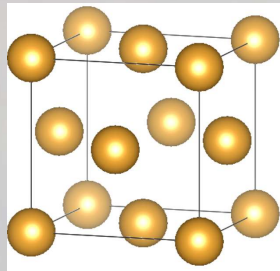
Multiplicity M, changes the intensities

a=1   a=2   a=3

N_a

b=1

b=2

b=3

N_b

(Powder) Diffraction from a 3D crystal with a 3D unit cell

Grating

$\bigotimes$ *Convol.*

Unit cell: crystal system: cubic (fcc)

= Crystal:

a=1   a=2   a=3

N_a

b=1

b=2

b=3

N_b

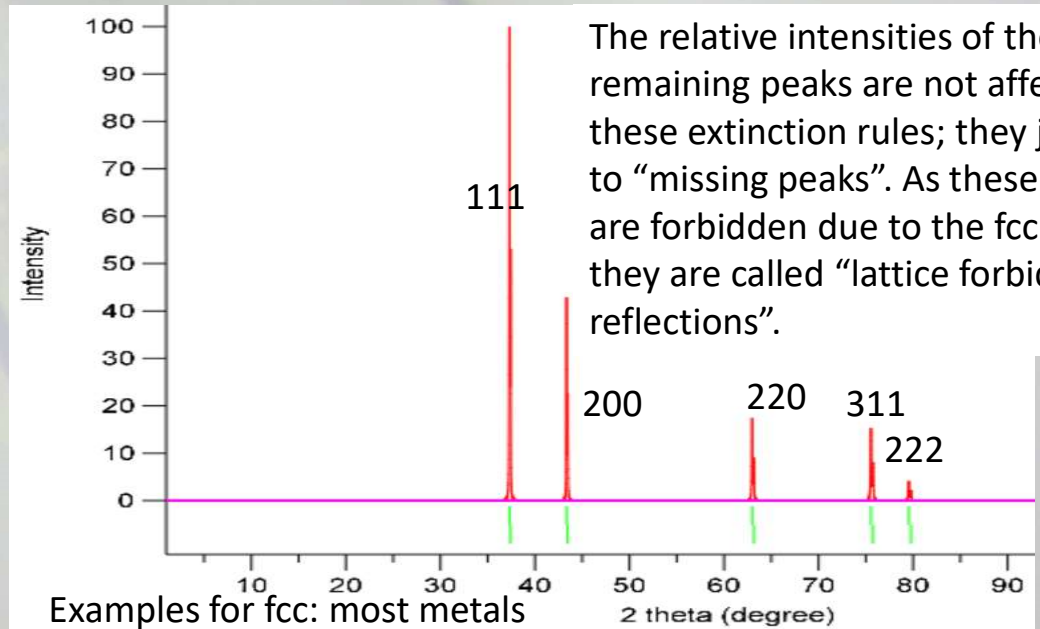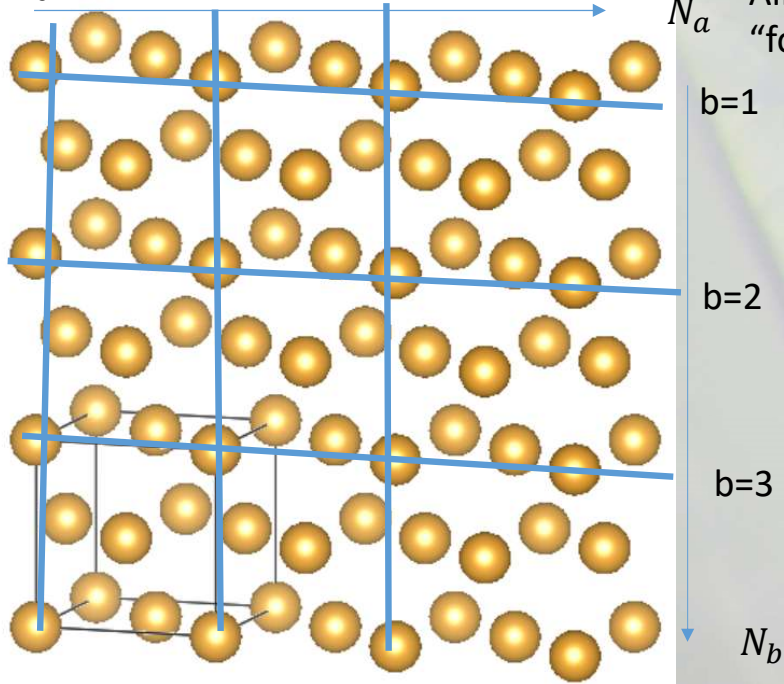I(powder)=M*(FT of unit cell) * (FT of grating)

Face centered cubic structure (fcc): 2 symmetry equivalent Atoms in unit cell

Still only one Atom, but on two symmetry equivalent sites: Many peaks are extinguished due to destructive interference between the two sites: This leads to "selection rules" specific to the fcc lattice:

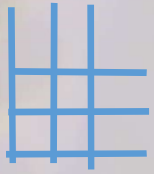All peaks with h,k,l all even or all odd are allowed, h,k,l mixed are "forbidden"= extinct

The relative intensities of the remaining peaks are not affected by these extinction rules; they just lead to "missing peaks". As these peaks are forbidden due to the fcc lattice they are called "lattice forbidden reflections".

100
90
80
70
60
50
40
30
20
10
0

Intensity

111

200   220   311
              222

10 20 30 40 50 60 70 80 90
2 theta (degree)

Examples for fcc: most metals

(Powder) Diffraction from a 3D crystal with a 3D unit cell

Grating

$\bigotimes$

Convol.

Unit cell : crystal system: cubic (fcc)+basis (more atoms in unit cell)
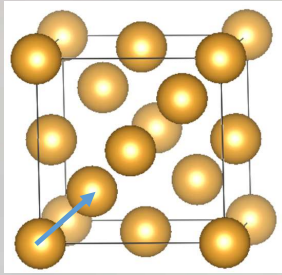
I(powder)=M*(FT of unit cell) * (FT of grating)

Face centered cubic structure (fcc): 2 symmetry equivalent Atoms in unit cell, Basis contains only one atom that is reproduced on the corners and faces (fcc...) Here: Basis contains a second atom at position 0.25, .25, .25. All other fcc atoms are just "doubled" to sit on equivalent positions -> two interpenetrating fcc lattices.
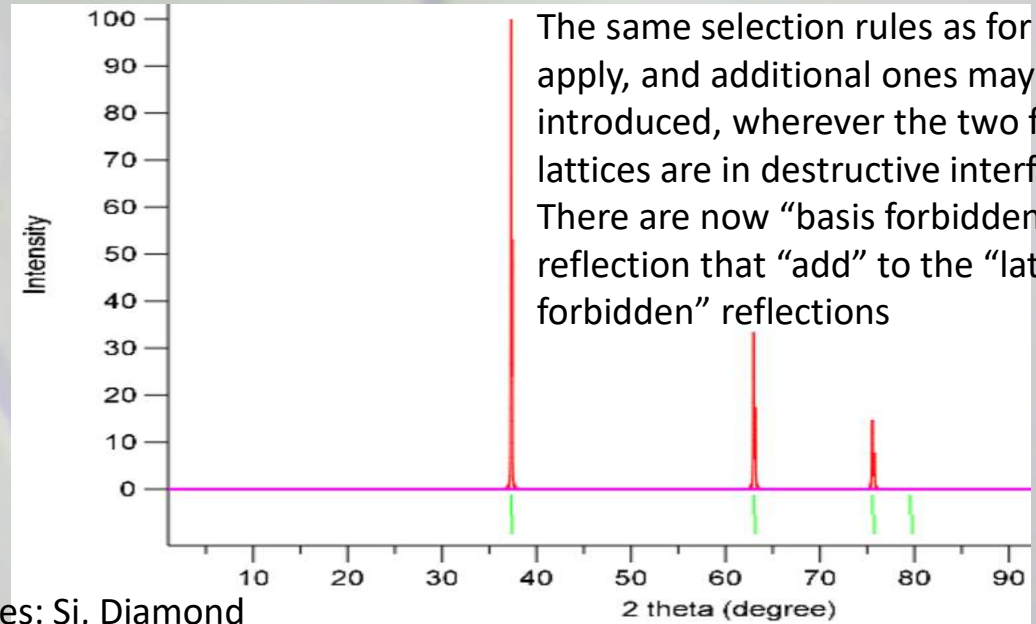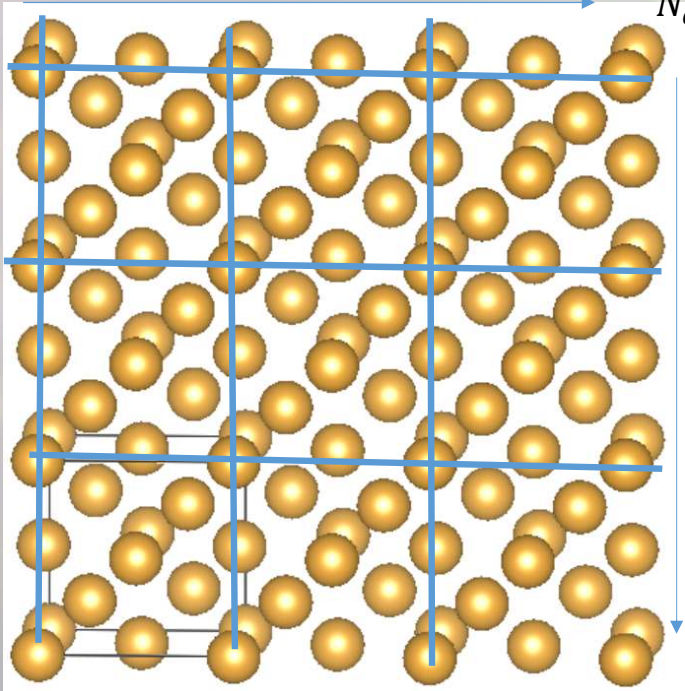
= Crystal:

a=1   a=2   a=3

N_a

b=1

b=2

b=3

N_b

The same selection rules as for fcc apply, and additional ones maybe introduced, wherever the two fcc lattices are in destructive interference. There are now "basis forbidden" reflection that "add" to the "lattice forbidden" reflections

Examples: Si, Diamond

Examples for typical crystals and limits of these considerations for peak shapes

As a start, we clearly have to differentiate between

1.)Powders

2.) (perfect) monocrystals

3.) Ideal imperfect crystals ("real" monocrystals) and perfect thin films

We have looked at 3.) with the example of a thin film or a "small crystal" goal: understanding peak *Intensities.*

What about 2.) ?

Intensity/ peak shape from "Bigger" Crystals

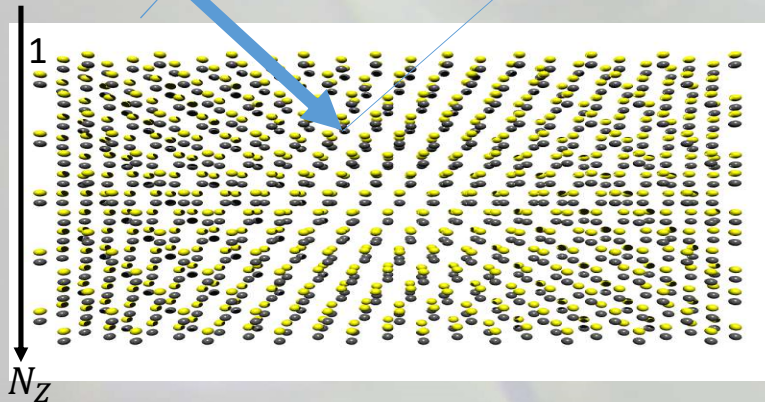$$A = A_o \, e^{i(\omega t + \vec{k}\vec{r})}$$

Incoming plane wave

(hkl) Bragg reflection:
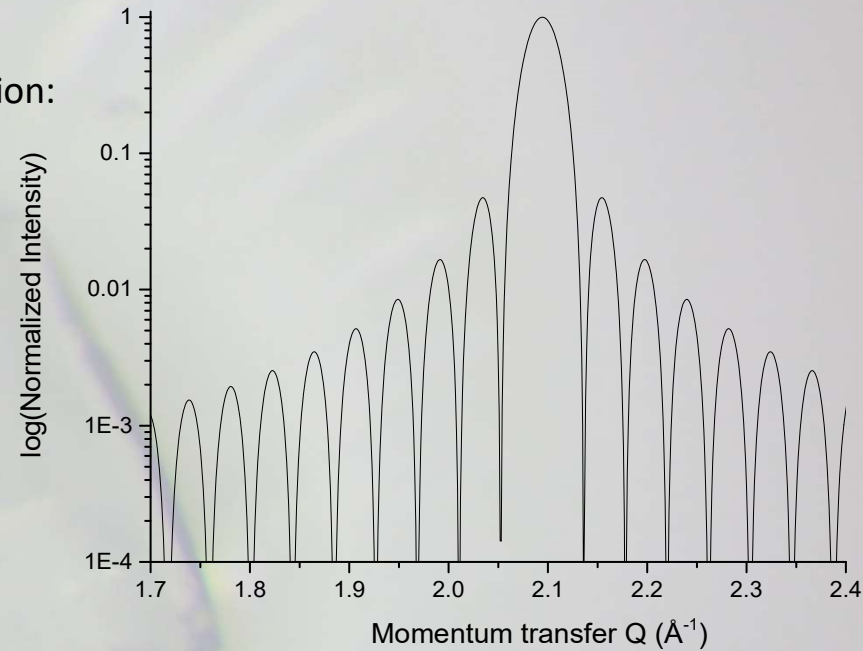
$$I_{hkl} = |A_{hkl}|^2$$

$$I_0 = |A|_t{}^2$$

Represented by "thickness"

$$A_{hkl} = \sum_{1}^{N_Z} F_{hkl} e^{i\vec{q}\vec{r}}$$

$$= \sum_{1}^{N_Z} F_{hkl} e^{iq_z z}$$

1

N_Z

Fraunhofer diffraction

log(Normalized Intensity)

Momentum transfer Q (Å⁻¹)
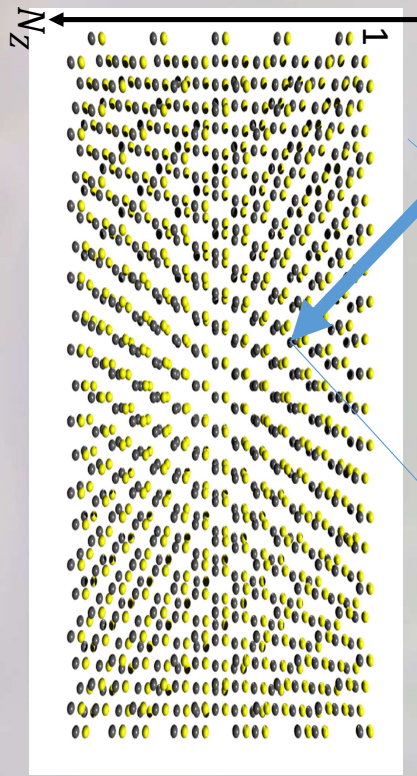
From before we know that $I_{hkl}(\text{Peak}) \sim I_0 * N_Z{}^2$ and $I_{hkl}(\text{Integrated}) \sim I_0 * N_Z$, if N_x, N_y=const.

But, for reasons of Energy conservation $I_{hkl}(\text{Peak}) < I_0$

X-ray absorption and peak shapes:

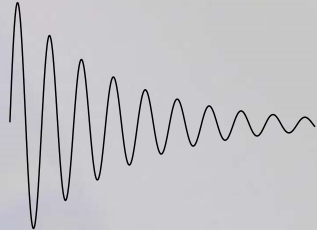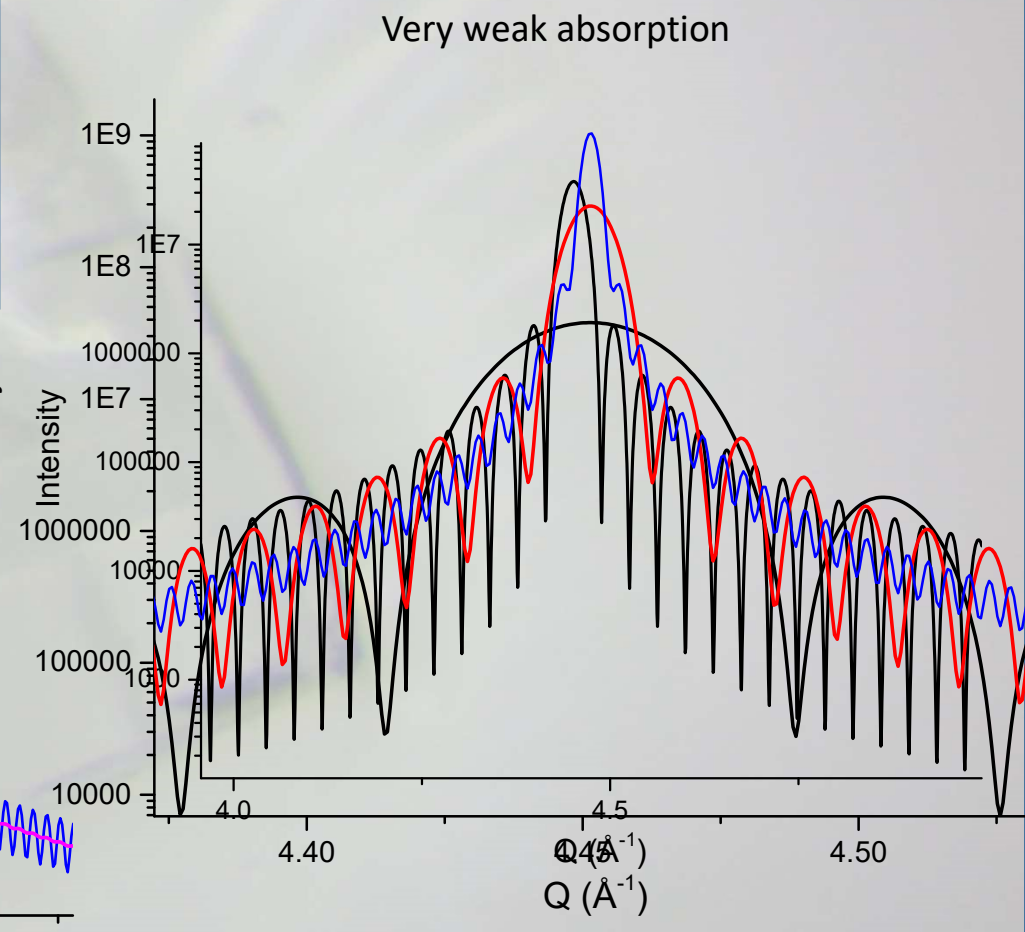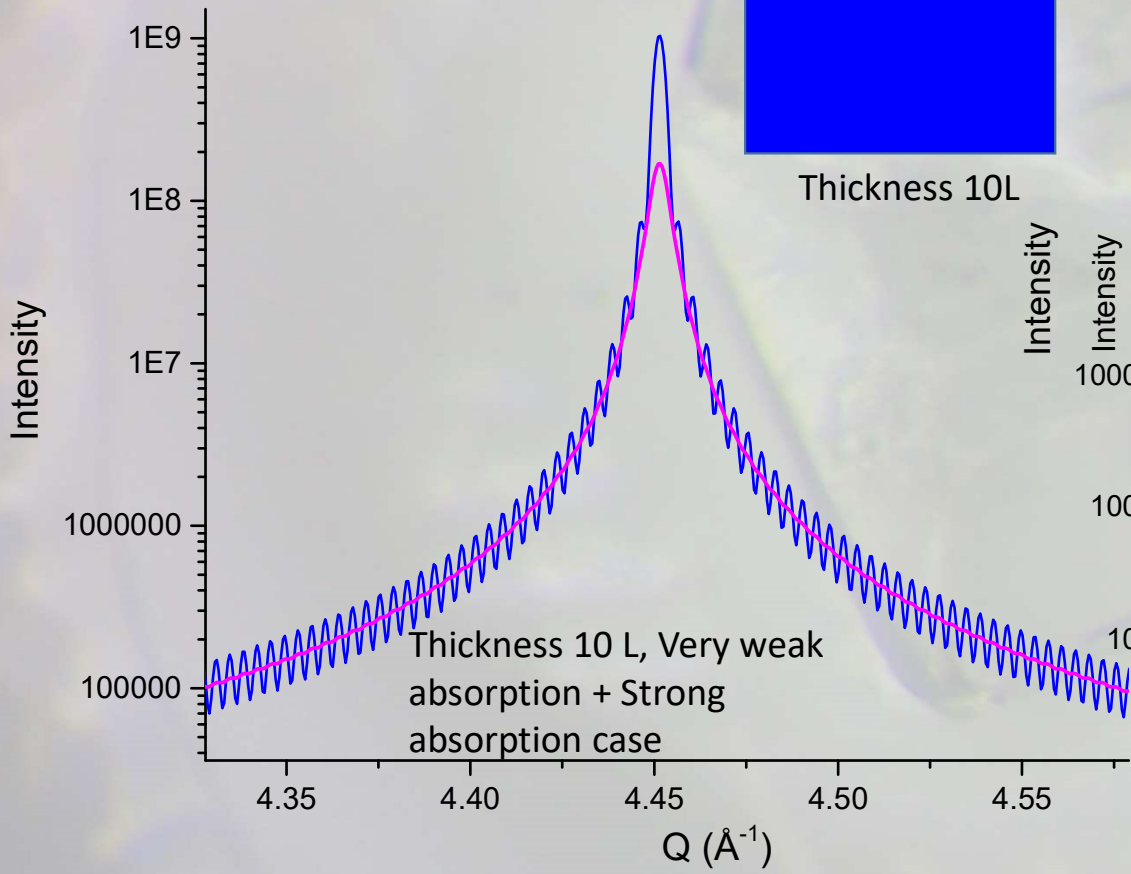$$A = A_o\, e^{i(\omega t + \vec{k}\vec{r})}$$

Incoming plane wave

(hkl) Bragg reflection:
$$I_{hkl} = |A_{hkl}|^2$$

$$I_0 = |A|_t{}^2$$

$$A_{hkl} = \sum_{1}^{N_Z} F_{hkl}\, e^{iq_z z} * e^{-\mu z}$$

X-ray absorption and peak shapes: Ge-film (001) oriented

Real peak shapes of real perfect crystals

Under Bragg conditions in perfect crystals,
Absorption does not limit the penetration depth…

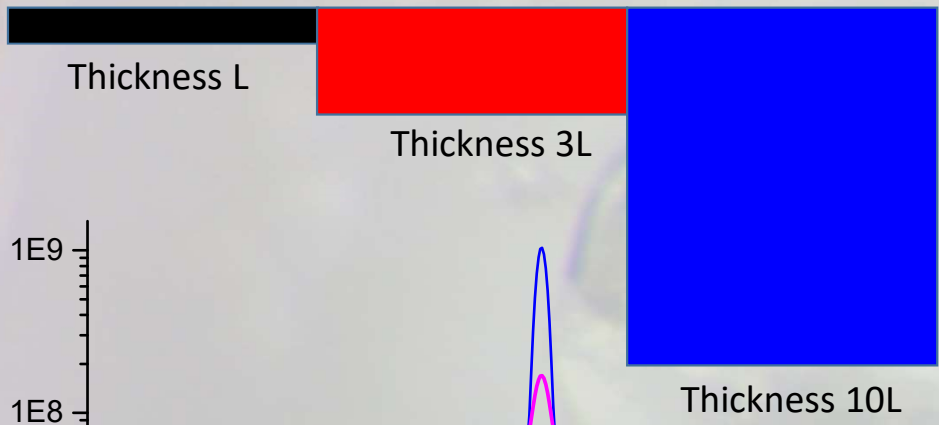$$A = A_o \, e^{i(\omega t + \vec{k}\vec{r})}$$
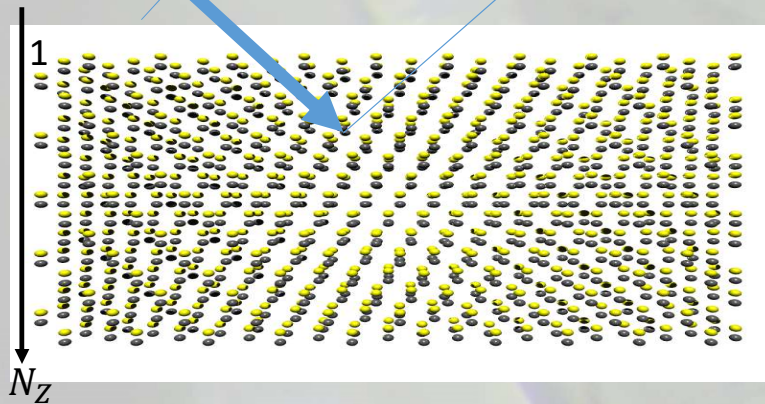
Incoming plane wave

(hkl) Bragg reflection:

$$I_{hkl} = |A_{hkl}|^2$$

$$I_0 = |A|_t^{\,2}$$
Represented by "thickness"

$$A_{hkl} =$$

$$\sum_{1}^{N_z} F_{hkl} e^{i\vec{q}\vec{r}}$$

$$= \sum_{1}^{N_z} F_{hkl} e^{iq_z z}$$

…but a process called "extinction", i.e. the weakening of the electric field by scattering,

This is requires a complete treatment of the interaction between a plane wave with a lattice, including the presence of multiple scattering events. All derivations above and structure analysis as a whole depend on what is called the "kinematic scattering theory."
The strength of X-ray (and neutrons), as compared to electrons is that in general this assumption is valid

Resolving (finding…, guessing…) Structures by X-ray diffraction

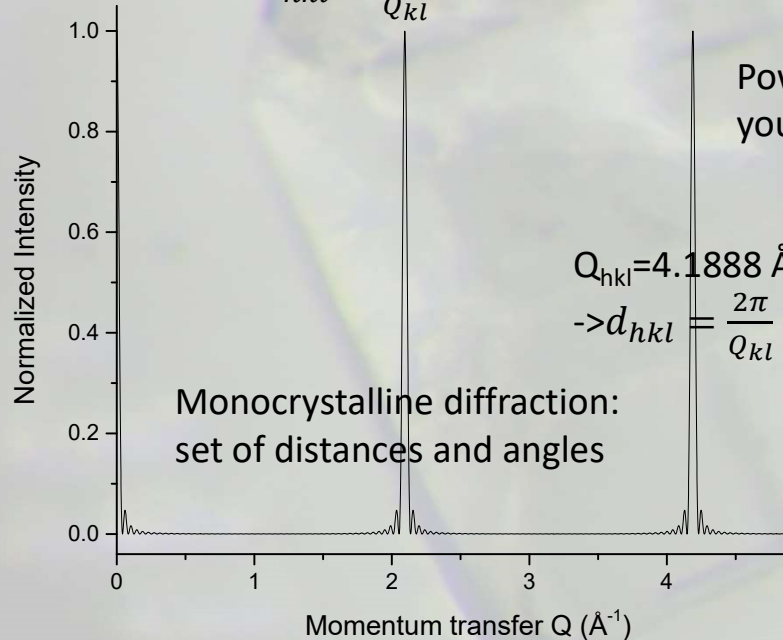Distances, angles and "structure factors" make up the decisive information

Depending on the type of radiation and the characteristics of our sample they can be measured (or not)

Q_{hkl}=2.0944 Å^{-1},

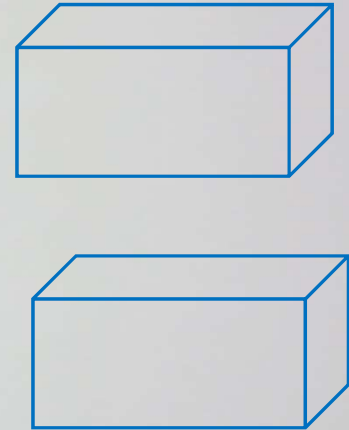->$d_{hkl} = \frac{2\pi}{Q_{kl}} = 3$Å

Distances: "easy"

Powder: "set of distances"+
your imagination=

Angles: +- difficult

Q_{hkl}=4.1888 Å^{-1},

->$d_{hkl} = \frac{2\pi}{Q_{kl}} = 1.5$Å

Monocrystalline diffraction:
set of distances and angles

Structure factors: +- difficult, depends a bit on "how good is good":

Integrated Bragg Intensity=F_{hkl}*(crystallite size)*(Incoming flux)*(other factors….)