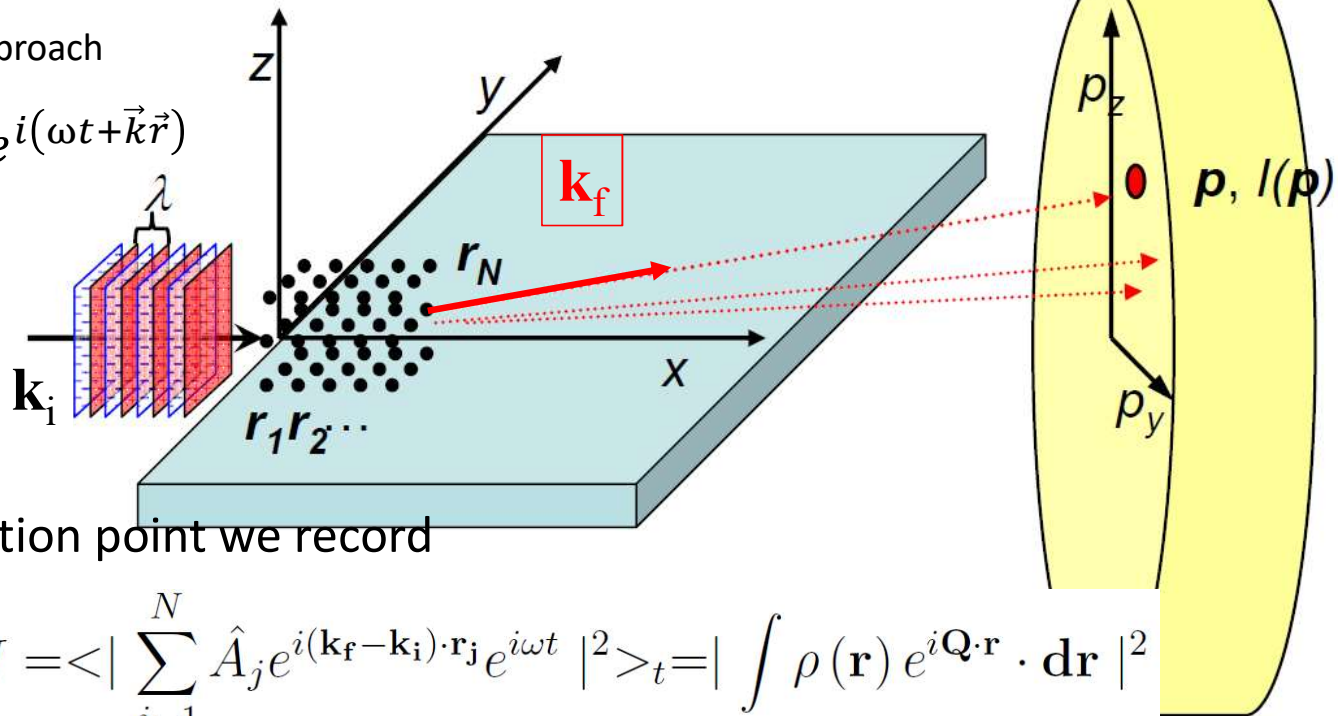


A scattering experiment – wave picture

Plane wave approach

$$A(\vec{r}, t) = A_0 e^{i(\omega t + \vec{k}\vec{r})}$$



At the observation point we record

$$I = \left\langle \left| \sum_{j=1}^N \hat{A}_j e^{i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_j} e^{i\omega t} \right|^2 \right\rangle_t = \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \cdot d\mathbf{r} \right|^2$$

Fourier Transform (complex) from space \mathbf{r} to space \mathbf{Q}

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as

$$\rho(\mathbf{r}) = \sum_{j=1}^N \hat{A}_j \delta(\mathbf{r}_j)$$

Fourier transform: useful relations

$$I = \langle \left| \sum_{j=1}^N \hat{A}_j e^{i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}_j} e^{i\omega t} \right|^2 \rangle_t = \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \cdot d\mathbf{r} \right|^2$$

1. **Linearity:** The FT of $\rho(\vec{r}) = f(\vec{r}) + g(\vec{r})$ is

$$FT[f(\vec{r}) + g(\vec{r})] = FT[f(\vec{r})] + FT[g(\vec{r})]$$

2. **Convolution:**

$$\rho(\vec{r}) = \int f(\vec{\xi}) g(\vec{r} - \vec{\xi}) d\vec{\xi}$$

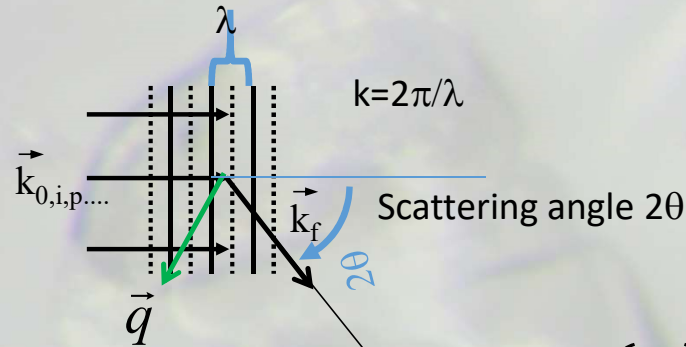
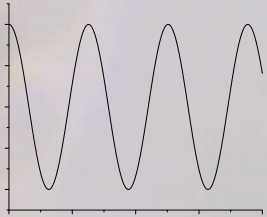
$$FT[f(\vec{r}) * g(\vec{r})] = FT[f(\vec{r})] \bullet FT[g(\vec{r})]$$

FT “converts” a convolution in a product and vice versa

Fourier
Transform of the
charge density
distribution ρ
from \mathbf{R} space to-
 \mathbf{Q} space

Scattering of x-rays by electrons and crystals

A few definitions

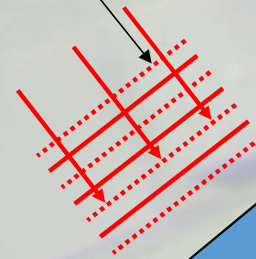


$$I(k) = \left(\int \rho(r) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \right)^2$$

Momentum transfer q , unit: $1/\text{m}$.
Is the best defined measurable quantity
in an experiment.

**The scattering angle is useless without
information on the wavelength.**

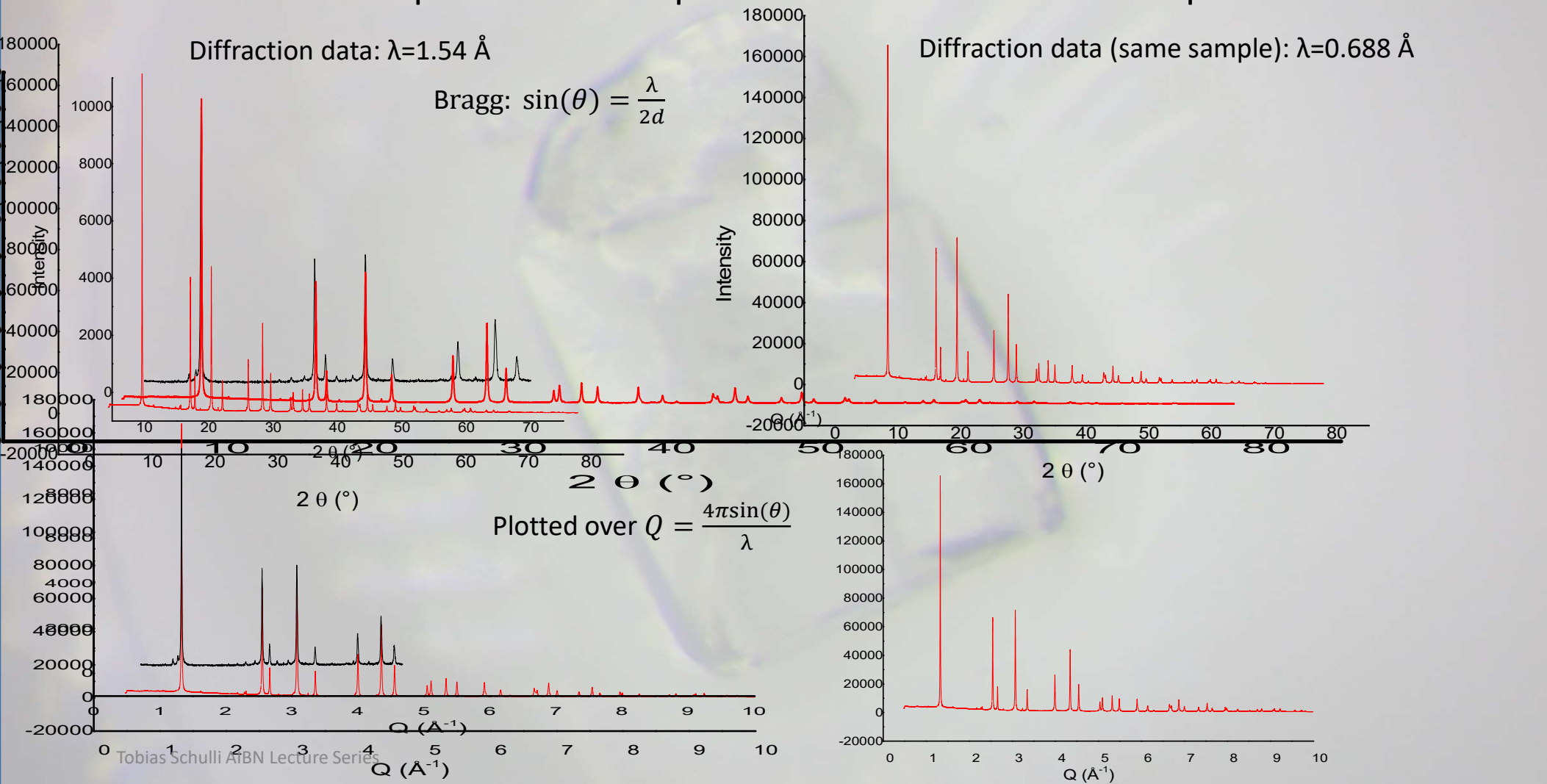
**An adapted choice for a reciprocal
orientation space will be very useful to
understand scattering experiments**



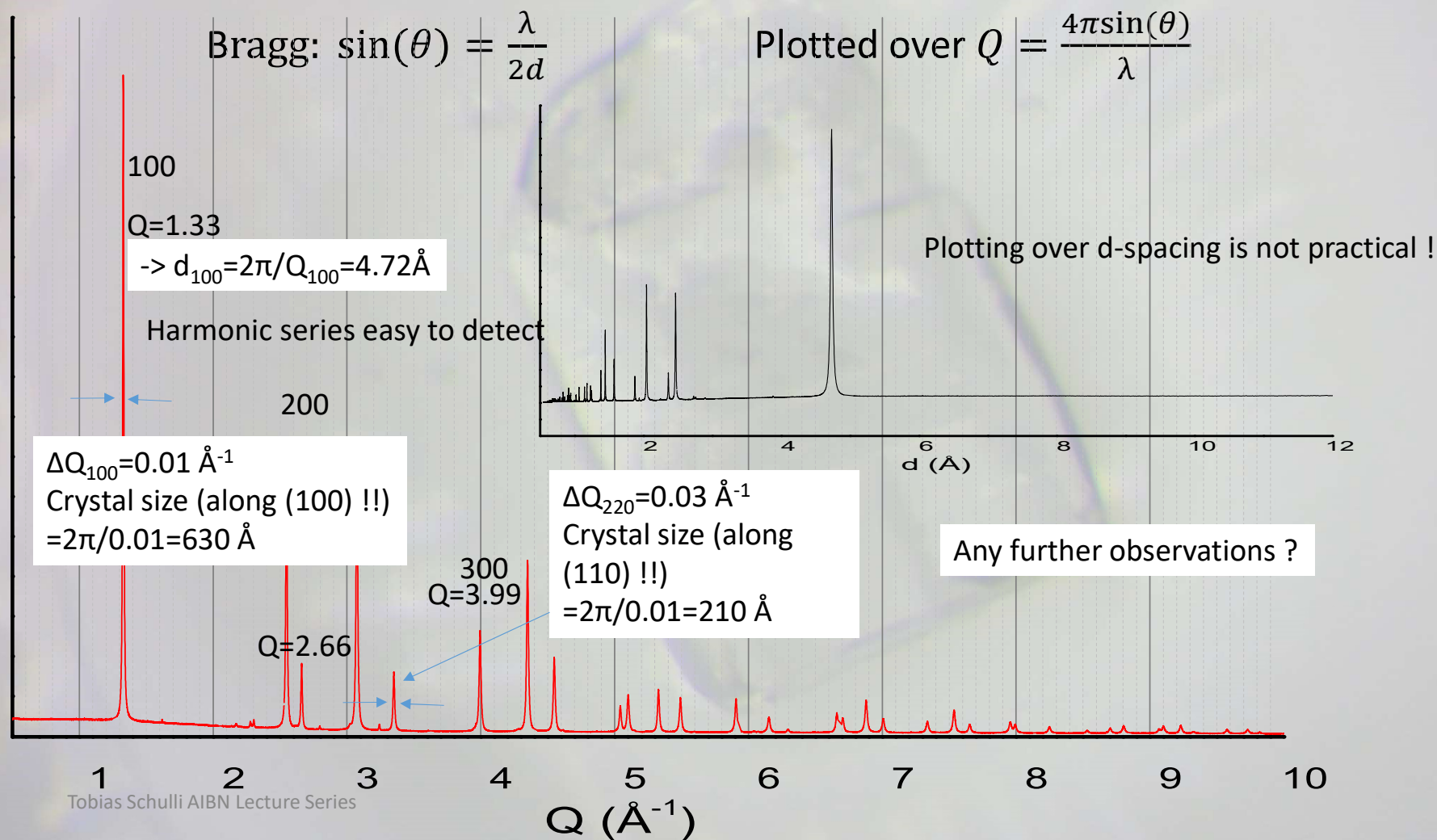
We measure the Fourier transform of
the distribution of electrons in space r
to space q

$$\vec{q} \text{ or } \vec{Q} = (\vec{k}_f - \vec{k}_i); \quad |q| = q = \frac{4\pi \sin \theta}{\lambda}$$

Intermezzo: few practical aspects of momentum space



Intermezzo: few practical aspects of momentum space



Concept of reciprocal space and practicality in experiments

- Makes it easy to compare different scattering experiments (*this point is essential as Cu K-alpha wavelength is less and less a "world standard"*)
- Quick interpretation possible, peak width of harmonic peaks (110 220 330 etc.) can be extracted and interpreted (angular space is useless for peak width analysis)
- Quantity of Momentum Transfer best suited and most widely used is \AA^{-1} , in diffraction, the SAXS community tends to use nm^{-1} . With the convenient definition of the wave-vector $k=2\pi/\lambda$, the momentum transfer Q results in $Q=4\pi\sin\theta/\lambda$.
- This leads to the relation $Q_{hkl}=2\pi/d_{hkl}$ linking momentum transfer to d-spacing of a certain reflection.
- When moving beyond structure determination (most cases you may work on), any high resolution analysis of a Bragg peak makes much more sense in reciprocal space than in angular space

Size broadening and strain gradient broadening

Strain may lead to lattice parameter gradients within one crystal. The resulting distribution Δd lattice parameter and its impact on the peak width ΔQ in reciprocal space Q can be obtained by looking at the first derivative of Q assuming a d -spacing change Δd :

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

$$\frac{\Delta Q}{\Delta d} = -\frac{2\pi}{d^2}$$

Strain broadening

$$\Delta Q(\Delta d) =$$

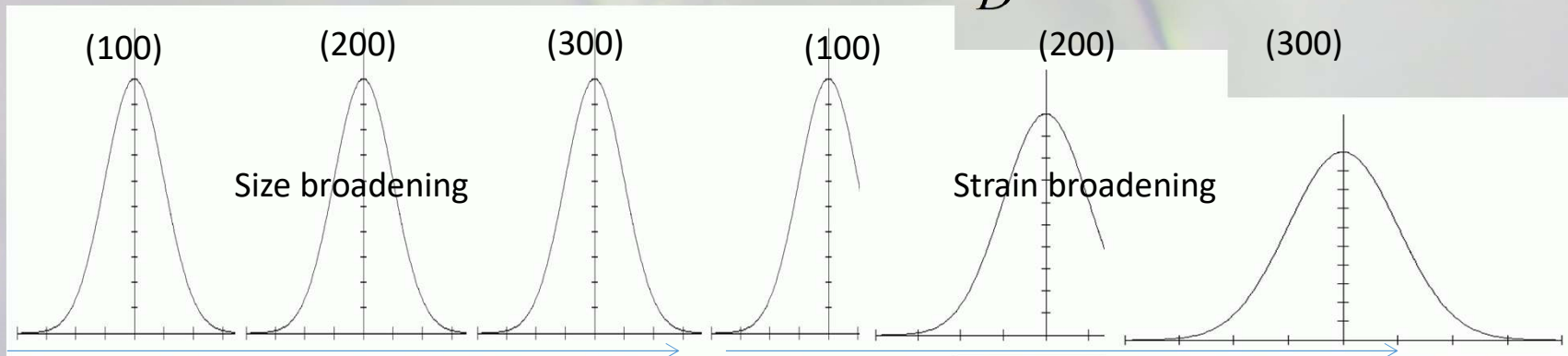
$$-\frac{\Delta d}{d} \frac{2\pi}{d} = -\frac{\Delta d}{d} Q$$

Depends on Q itself

Particle size (D) broadening:

$$\Delta Q(D) = \frac{2\pi}{D}$$

No Q -dependence



Strain broadening is a constant value (here for harmonic peaks, as in case of anisotropy this may not be true). Strain broadening increases in Q

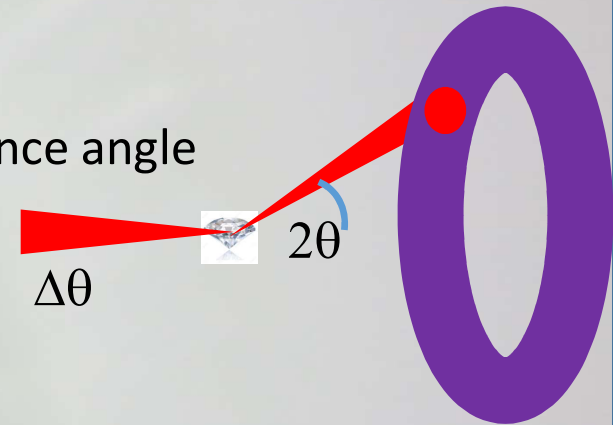
Instrumental influences for peak broadening (examples)

Peak Broadening by spectral bandwidth $\Delta\lambda$

$$Q = \frac{4\pi s}{\lambda}, \rightarrow \frac{\Delta Q}{\Delta\lambda} = -\frac{4\pi \sin\theta}{\lambda^2} \rightarrow \Delta Q(\Delta\lambda) = \frac{4\pi \sin\theta}{\lambda^2} \Delta\lambda = Q * \frac{\Delta\lambda}{\lambda},$$

"equivalent" to strain broadening

$\Delta\theta$: convergence angle



Peak Broadening by beam divergence $\Delta\theta$:

$$Q = \frac{4\pi s \sin\theta}{\lambda}, \rightarrow \frac{\Delta Q}{\Delta\theta} = \frac{4\pi s \cos\theta}{\lambda} \rightarrow$$

$$\Delta Q(\Delta\theta) = \Delta\theta \frac{4\pi s \cos\theta}{\lambda} = \Delta\theta \frac{Q}{\tan\theta}$$

(“Peak Broadening”) as a function of Beam divergence $\Delta\theta$

Peak broadening, how to deal with

- it contains information that should be exploited
- It teaches us to look at integrated intensities (Peak areas), rather than peak “heights”

Divergence: $\Delta Q(\Delta\theta) = \Delta\theta \frac{Q}{\tan\theta}$

All these contributions mix... in the form of convolutions

Bandpass: $\Delta Q(\Delta\lambda) = Q * \frac{\Delta\lambda}{\lambda}$

Strain: $\Delta Q(\Delta d) = \frac{\Delta d}{d} Q$

Size D : $\Delta Q(D) = \frac{2\pi}{D}$

FWHM (result)=

FWHM (curve1) + FWHM(curve2)..... $\sqrt{FWHM(curve1) + FWHM(curve2)}$

The truth is in general somewhere in between..... depends on the shape of the peaks

Peak broadening, how to deal with

- it contains information that should be exploited
- It teaches us to look at integrated intensities (Peak areas), rather than peak “heights”

$$\text{Divergence: } \Delta Q(\Delta\theta) = \Delta\theta \frac{Q}{\tan\theta}$$

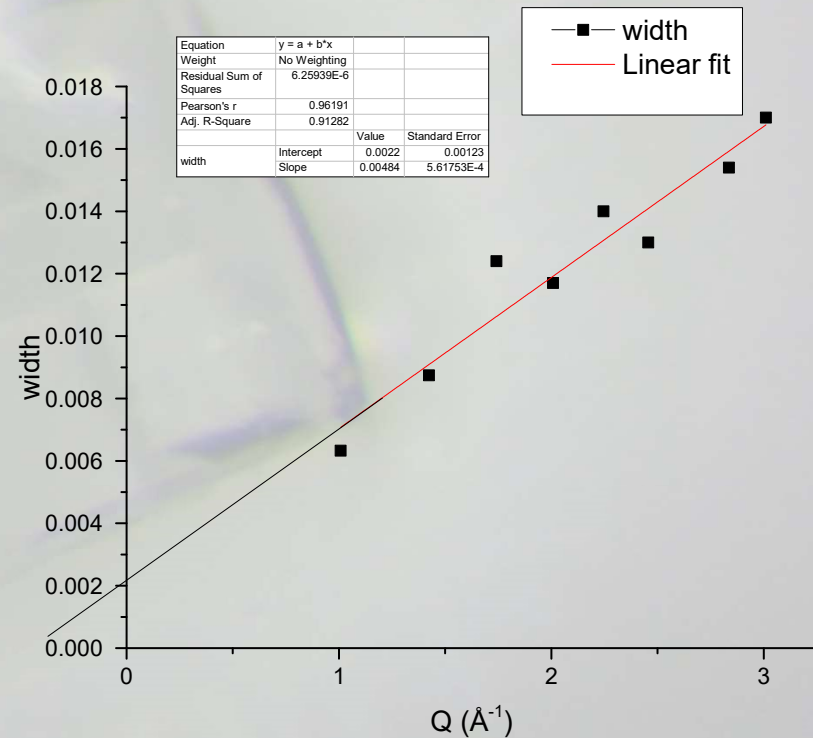
$$\text{Bandpass: } \Delta Q(\Delta\lambda) = Q * \frac{\Delta\lambda}{\lambda}$$

$$\text{Strain: } \Delta Q(\Delta d) = \frac{\Delta d}{d} Q$$

$$\text{Size } D : \Delta Q(D) = \frac{2\pi}{D}$$

For $Q=0$ only divergence and size contributions \rightarrow the minimum crystallite size can be estimated to be $D >$

$$\frac{2\pi}{0.002} \sim 3000 \text{ \AA} \text{ (300 nm)}$$



A bit more about Crystallite size D

Particle size (D) broadening: $\Delta Q(D) = \frac{2\pi}{D}$ No Q - dependence

If no other broadening effects are involved the size D can be extracted from any Bragg peak

A similar formula often cited is the Scherrer formula:

Hi...

In my today's tutorial, I will show you how to calculate crystallites size and average crystallites size from XRD data using Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where,

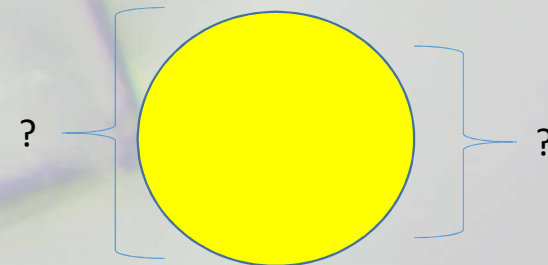
D = crystallites size (nm) β =FW in rad

K = 0.9 (Scherrer constant)

λ = 0.15406 nm (wavelength of the x-ray sources)

General remark:

Be careful about what result you expect from particle size



What ever you extract, call it rather 200 nm instead of 218.67 nm
However, if you stick to one method and compare different samples, relative differences may well be tracked down to few %

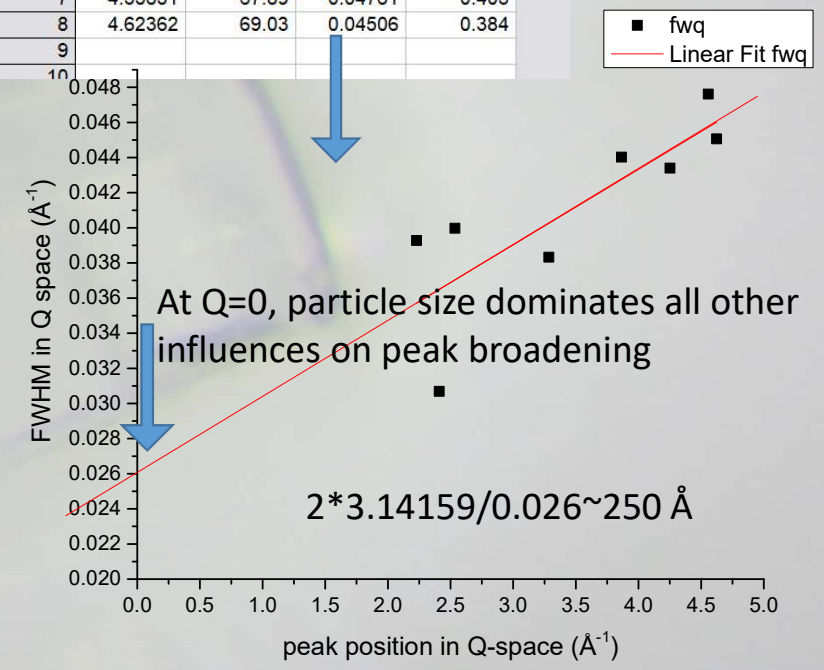
A bit more about Crystallite size D



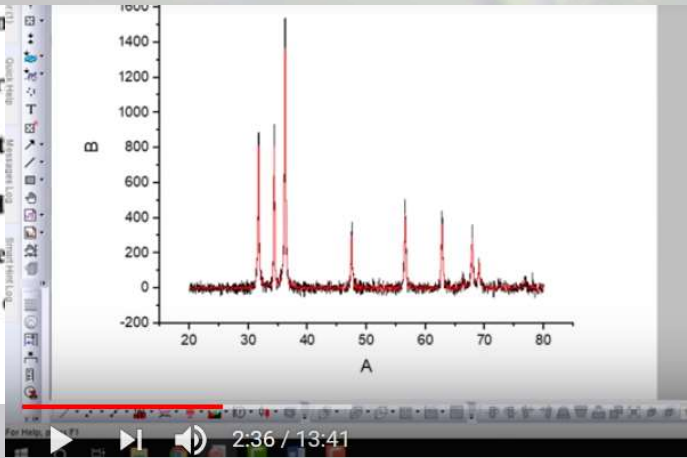
Peak position (2 Theta)	FWHM	Crystallite Size D (nm)	D nm (Average)
31.70868	0.28673	28.80216877	28.00516633
34.36301	0.22556	36.86545833	
36.19607	0.29529	28.30362871	
47.47974	0.29426	29.49314718	
56.54624	0.35102	25.69776413	
62.80407	0.35766	26.02344011	
67.8968	0.40304	23.76124067	
69.03285	0.38421	25.09448275	

	pposQ(X)	ppos(Y)	fwq(Y)	fw(Y)
Long Name				
Units				
Comments				
F(x)	$b((ppos)^*pi/180/2)/1$		$(ppos)^*pi/180/2)/1$	
1	2.22865	31.7	0.03928	0.2867
2	2.41025	34.36	0.03069	0.22556
3	2.53511	36.2	0.03997	0.29529
4	3.2851	47.48	0.03833	0.294
5	3.86479	56.54	0.04403	0.351
6	4.25143	62.8	0.0434	0.357
7	4.55651	67.89	0.04761	0.403
8	4.62362	69.03	0.04506	0.384
9				
10				

In Q-space things are linear that weren't linear before



$\lambda = 0.15406 \text{ nm}$
 $\beta = \text{FWHM (radians)}$
 $\theta = \text{Peak position}$
 First, we need XRD data the calculation of
 Lets' start...



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

As a start, we clearly have to differentiate between

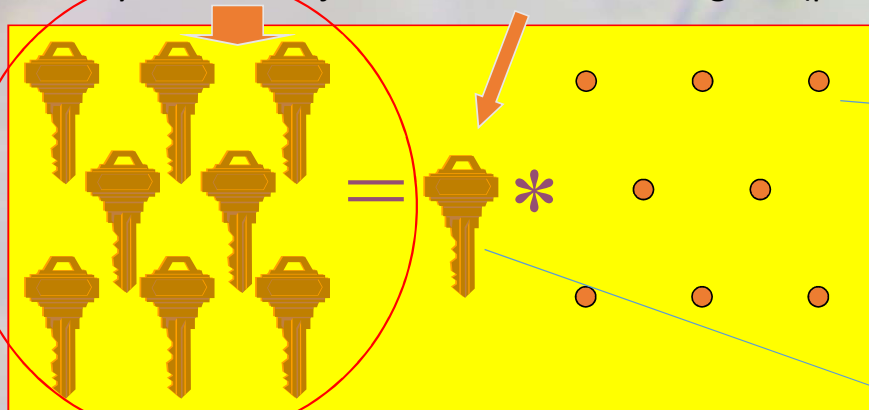
- 1.) Powders
- 2.) (perfect) monocrystals
- 3.) Ideal imperfect crystals (“real” monocrystals) and perfect thin films

2.) Sounds easy but is the worst, so let's start with 3.) and the example of a thin film: goal: understanding peak *Intensities*

“Crystallography” = study of periodic objects

But in the end, what we are interested in may well be “the object”

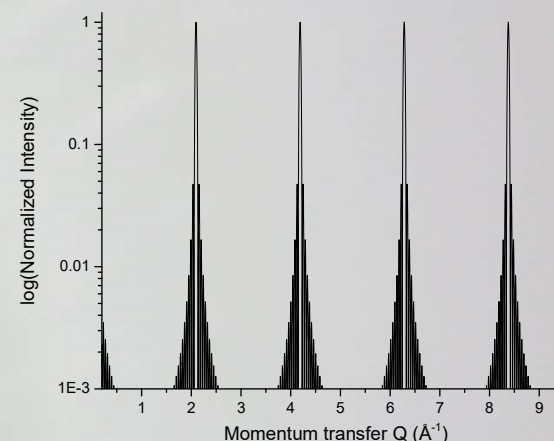
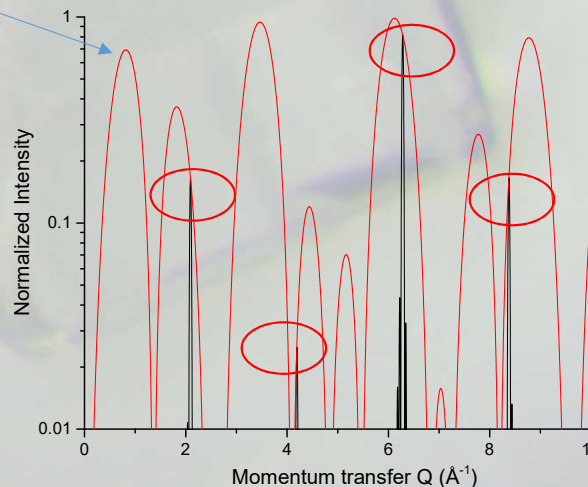
A Crystal is an object associated with a regular (periodic or non-periodic) grating, defining its repetition



“Object” leads to a structure that determines the height of the peaks

Crystallography: We can only sample the read curve in distinct points, but a precise knowledge of the red curve is required to resolve an image of the “object”

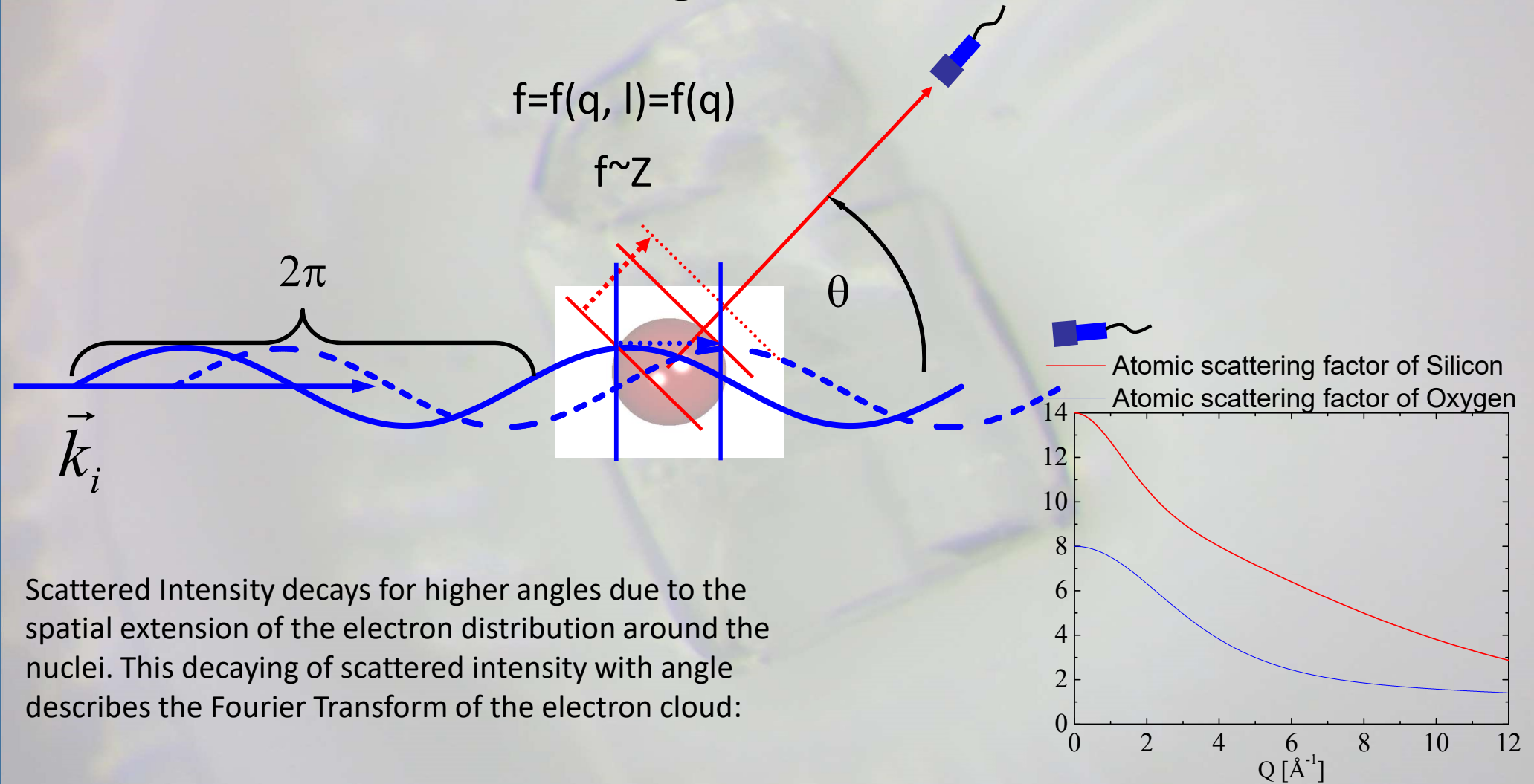
Grating Leads to regular “Bragg” peaks



Scattering f from an Atom

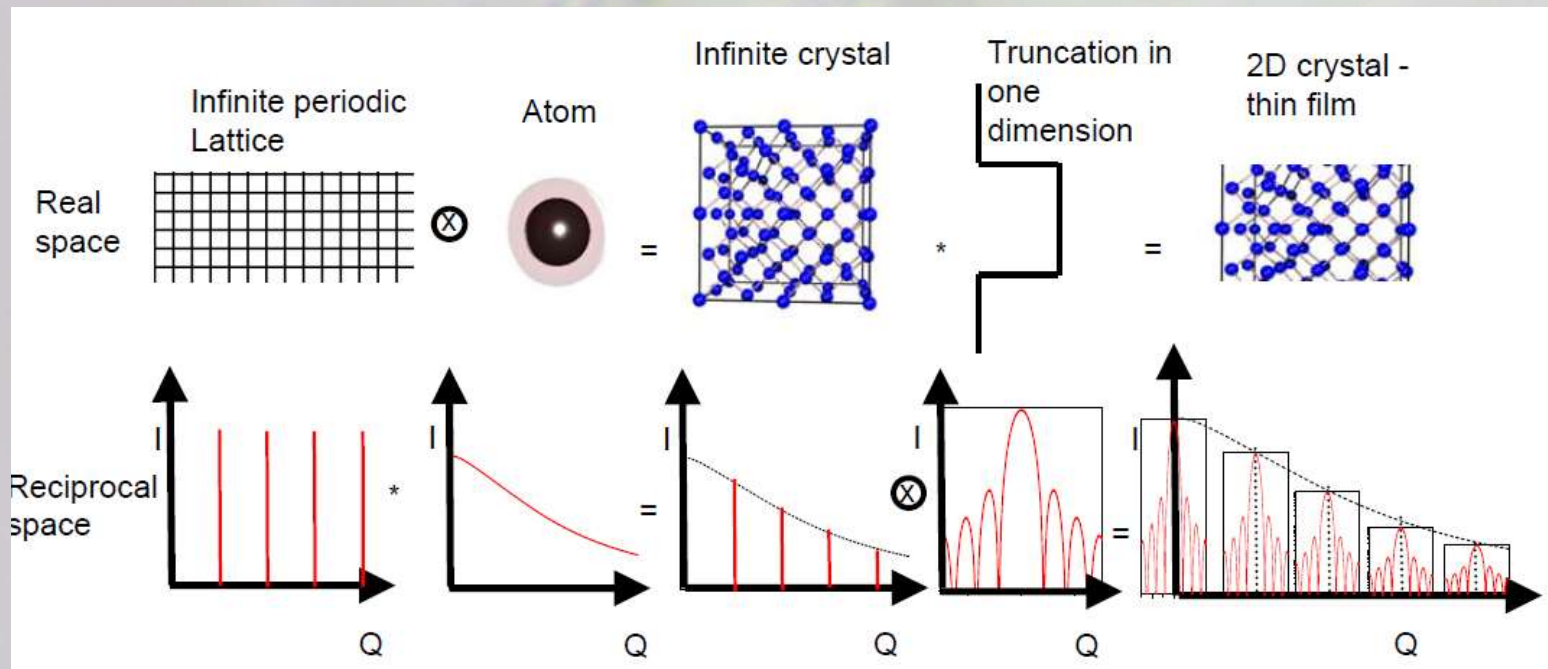
$$f=f(q, l)=f(q)$$

$$f \sim Z$$



Scattering from an Crystalline thin block

Being a periodic arrangement of atoms a crystal can be “built” using a periodic arrangement of delta-functions convoluted with one atom (or a unit cell). A convolution in real space becomes a product in reciprocal space



Big crystals: sharp peaks, small crystals: narrow peaks. Peak intensities depend on the structure factor.

Diffraction from a thin film, simplified approach

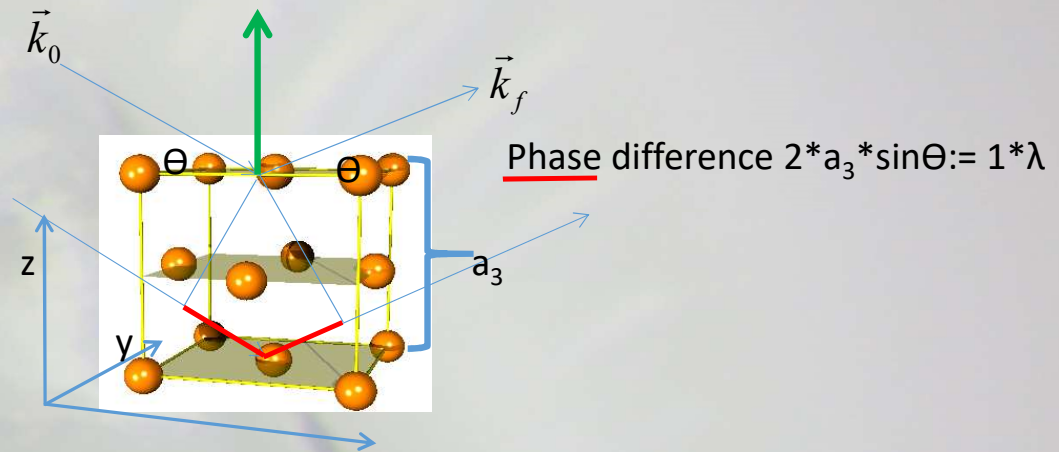
We recall: The function describing intensity distribution in reciprocal space is related to the Fourier Transform of the distribution of scatterers in real space.

If we try to understand the building blocks of materials we can eventually treat their Fourier Transforms separately and use then these building blocks to built up reciprocal space.

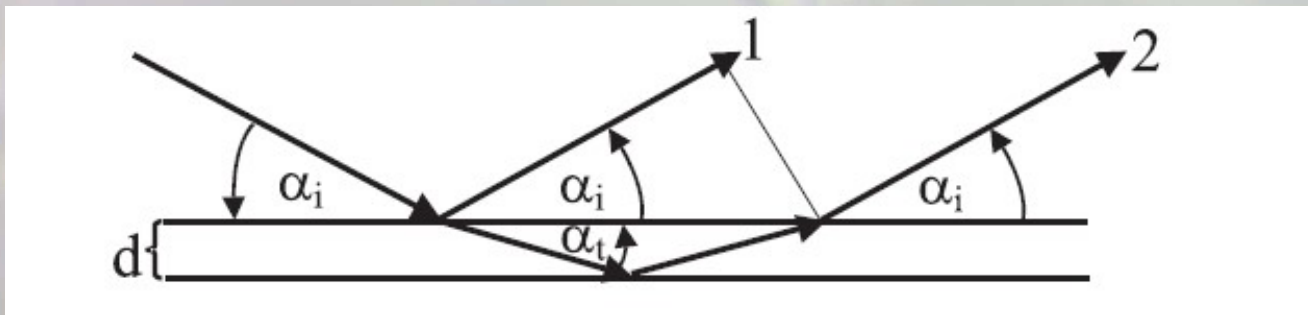
What we are looking for is a set of lego pieces that we can decompose and recompose freely when moving from reciprocal space to real space

Diffraction from a thin film

Reciprocal space consideration in a wider sense....



With reflection of X-ray light from the top and the bottom of a thin film there must also be a “Bragg-condition”, but at very low angles of incidence, as the film thickness is “much thicker” than the spacing between atoms. Of course the path difference here as well can be 1,2, 3, ...,n, times λ . Leading to a series of tightly spaced peaks



At much lower angles than Bragg diffraction, there must be a “Bragg’s law” for constructive interference from the top and the bottom of the thin film

[1] H. Kiessig (1931)

„Interferenz von Röntgenstrahlen an dünnen Schichten“. Annalen der Physik 10, 769-87.

X-ray reflectivity from a thin film

