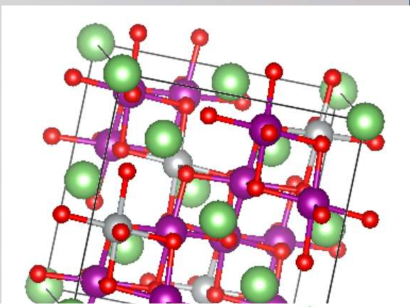
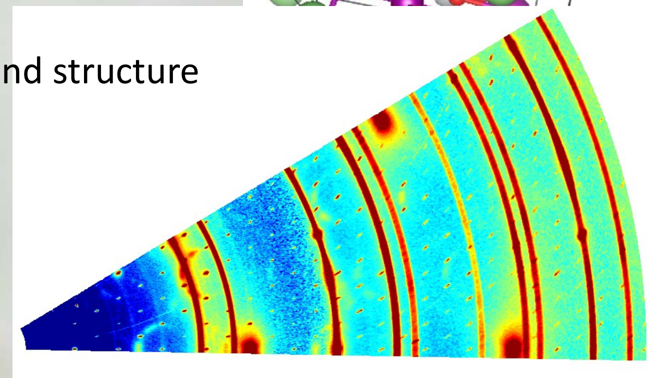
… to be continued (from week of July 22nd, 4 more lectures)

A closer look on F_{hkl} applications and examples of integrated intensities, graphical representation of the complex scattering factor

We will quickly discuss other factors affecting the intensity



Examples of scattering experiments and extraction of information beyond structure resolution & beyond average strutcures

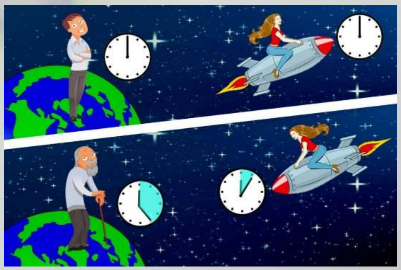


About x-ray sources/ optics and their influence on our data

Why are synchrotron sources so powerful ?

V_1=30 Km/h

V_2=30 Km/h

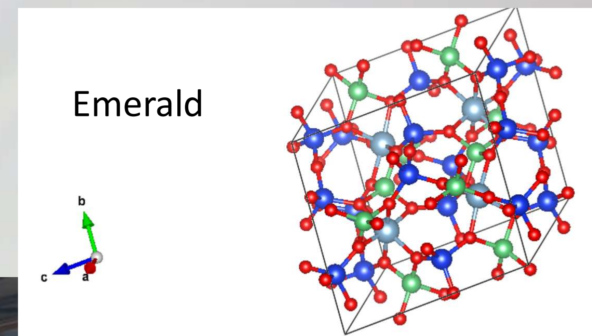


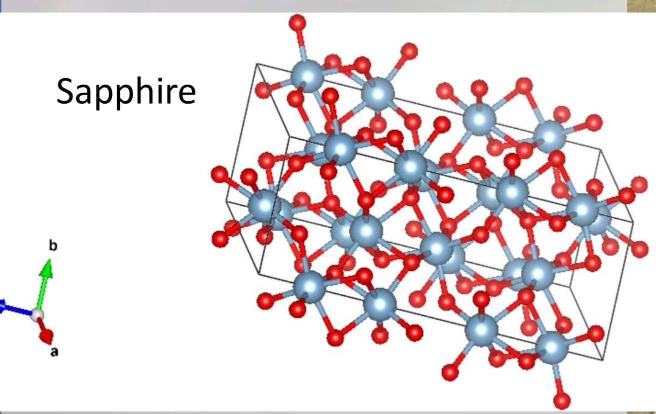
Twin paradox & contraction of space

$V_{relative}$=~~60 Km/h~~
=59.9999999999997916

This “error” makes Synchrotrons 1 Trillion (!) times more brilliant

Goal of today: The structure factor, and how to make use of it

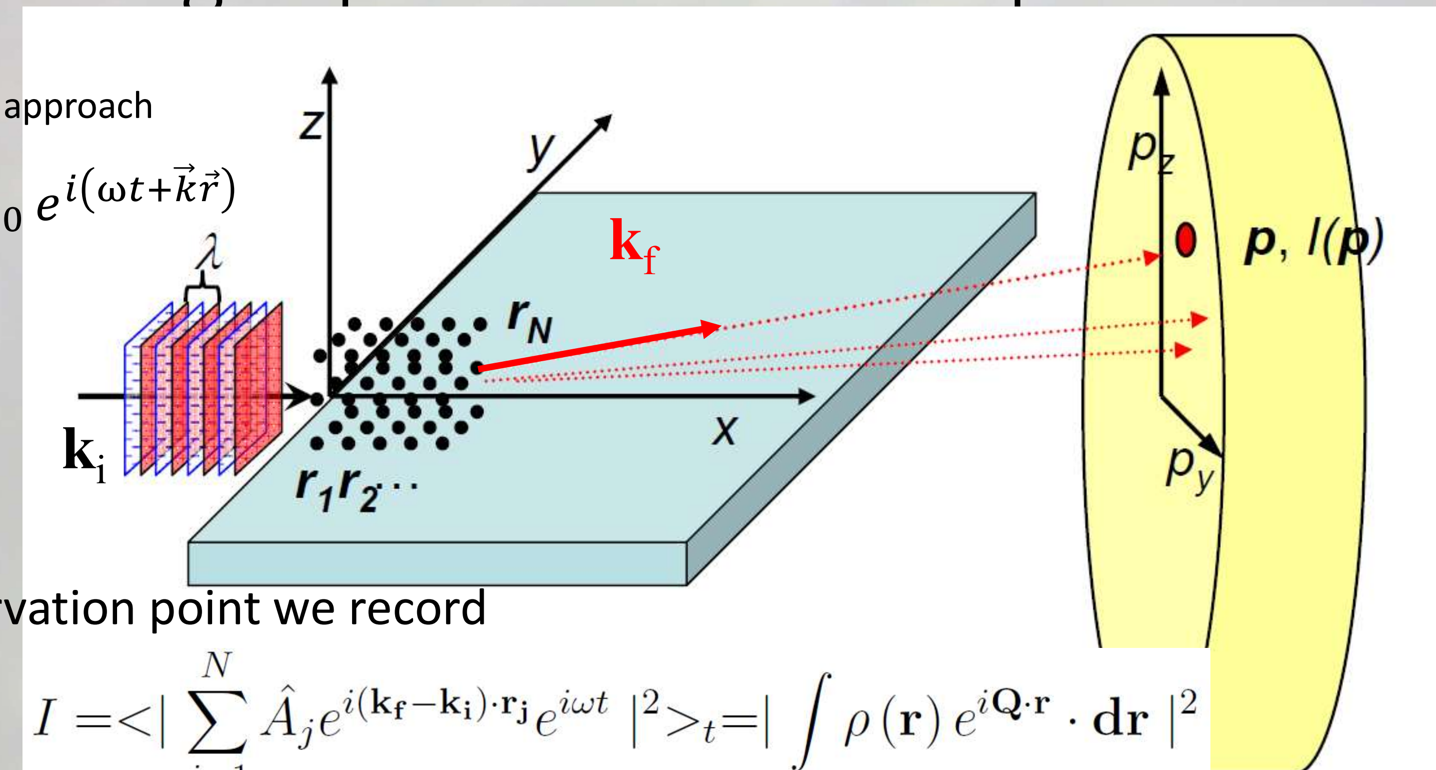




A scattering experiment – wave picture

Plane wave approach

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



At the observation point we record

$$I = <|\sum_{j=1}^{N} \hat{A}_j e^{i(\mathbf{k_f}-\mathbf{k_i})\cdot\mathbf{r_j}} e^{i\omega t}\ |^2>_t = |\int \rho\left(\mathbf{r}\right) e^{i\mathbf{Q}\cdot\mathbf{r}} \cdot \mathbf{dr}\ |^2$$

Fourier Transform (complex) from space ***r*** to space ***Q***

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as $\rho\left(\mathbf{r}\right) = \sum_{j=1}^{N} \hat{A}_j \delta\left(\mathbf{r_j}\right)$

This integration or summing up leads to the Fourier Transform from real space $\vec{r}$ to reciprocal space $\vec{q}$=($\vec{k}_f - \vec{k}_i$)

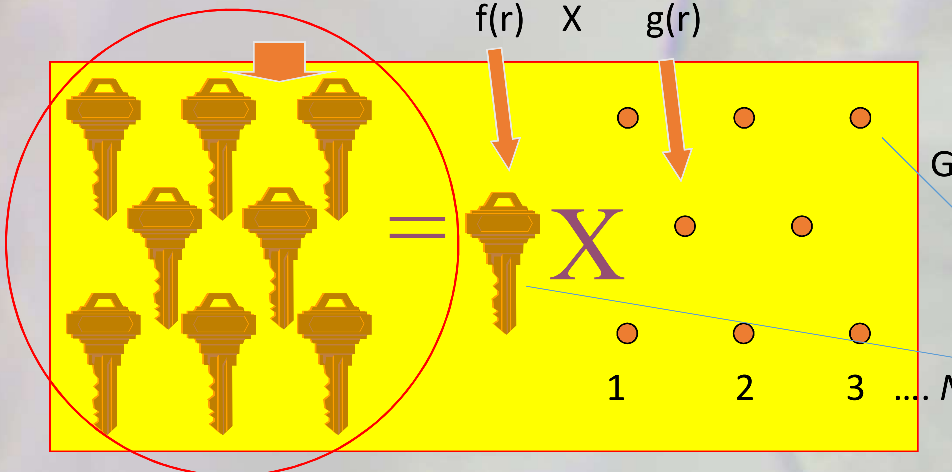
Fourier Transform – applied to crystals

We recall that convolutions lead to products in Fourier space and vice versa: f(r)Xg(r)=F(q)*G(q)

X: convolution; *: product f(r)*g(r)=F(q)XG(q)

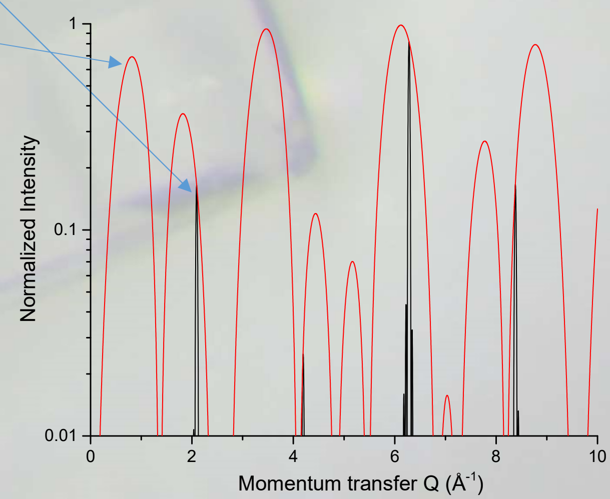
"Unit cell" "grating"

f(r) X g(r)



Grating Leads to regular "Bragg" peaks

Becomes F(q)*G(q)

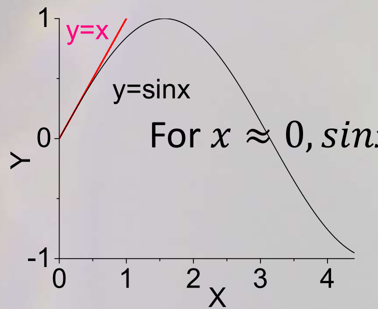


"Object" leads to a structure that determines the intensity of the peaks

The separation of lattice and its internal structure is the powerful basis of structure resolution in Fourier space

Recall: Quantification of ***lattice*** peak properties: height and area

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

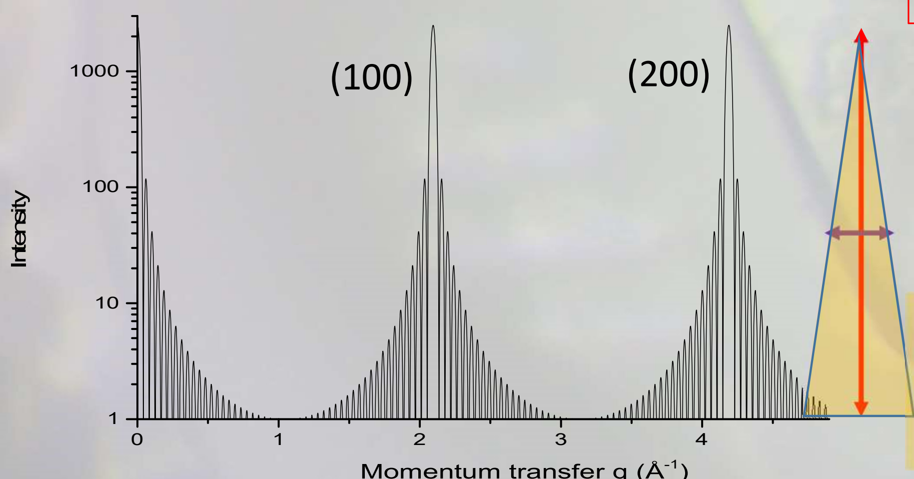


For $x \approx 0, sinx \approx x$

If $^1/_2 * \mathrm{q} * N_a * a \approx 0$
and $^1/_2 * \mathrm{q} * a \approx 0$

$$A * A^* \sim \left[\frac{^1/_2 * q * N_a * a}{^1/_2 * q * a}\right]^2 \sim {N_a}^2$$

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



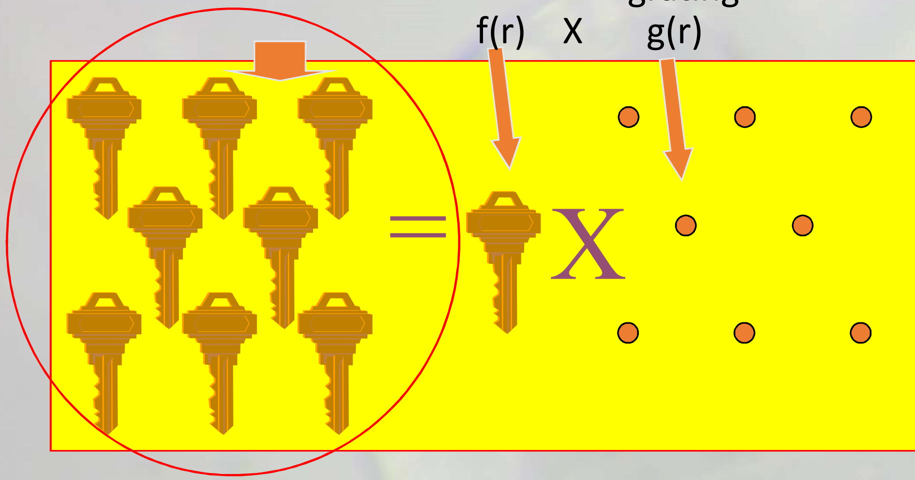
The Peak Width FWHM is proportional to $1/N_a$

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*

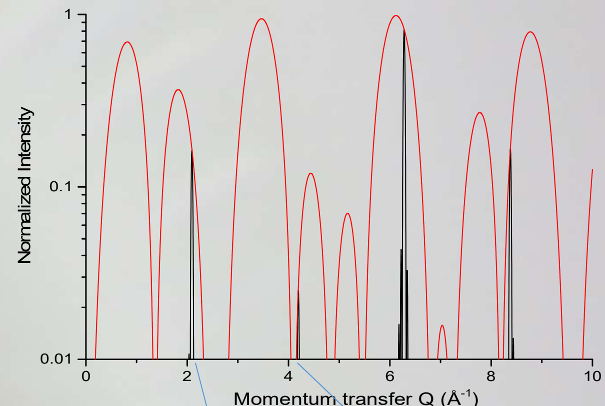
This is the basis of all structure resolution and refinement using XRD !!!

Fourier Transform – lattice and structure factor

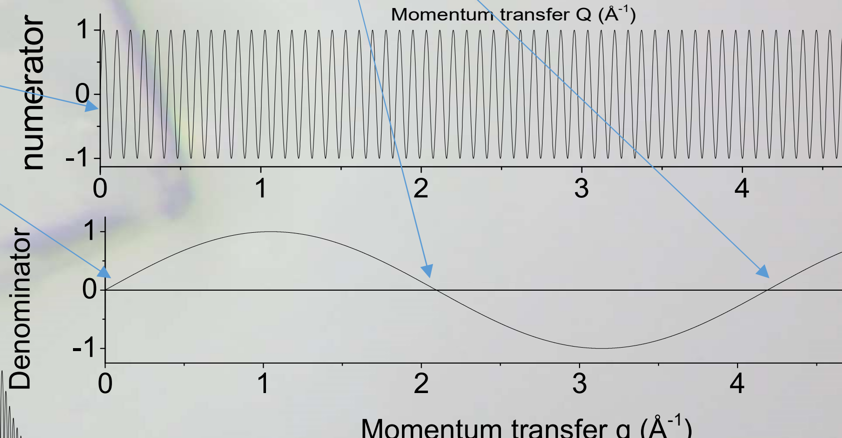
“Unit cell” “grating”
f(r) X g(r)



Becomes F(q)*G(q)

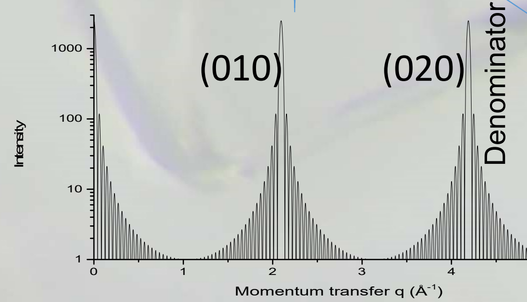


$$F_{hkl}^2(q)\left[\frac{\sin(^1/_2 * q_a * N_a * a)}{\sin(^1/_2 * q_a * a)} * \frac{\sin(^1/_2 * q_b * N_b * b)}{\sin(^1/_2 * q_b * b)} * \frac{\sin(^1/_2 * q_c * N_c * c)}{\sin(^1/_2 * q_c * c)}\right]^2$$

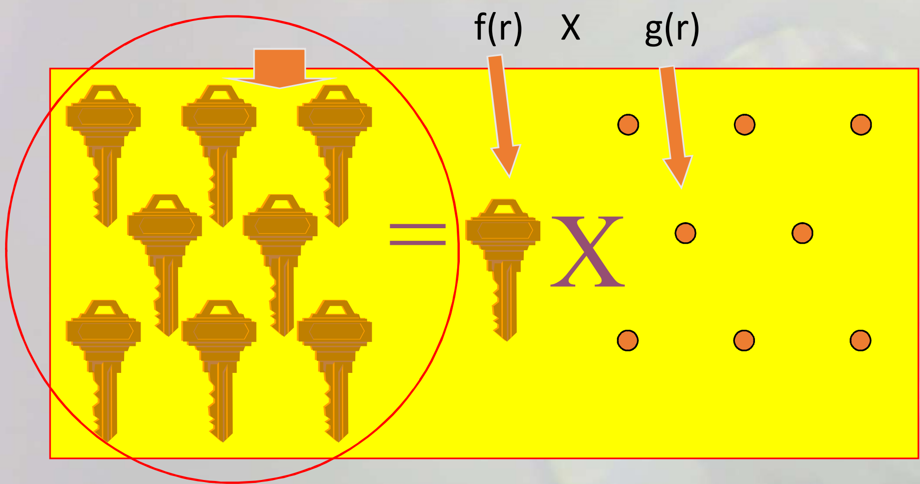


For a 3-dimensional crystal this leads to peaks whenever:

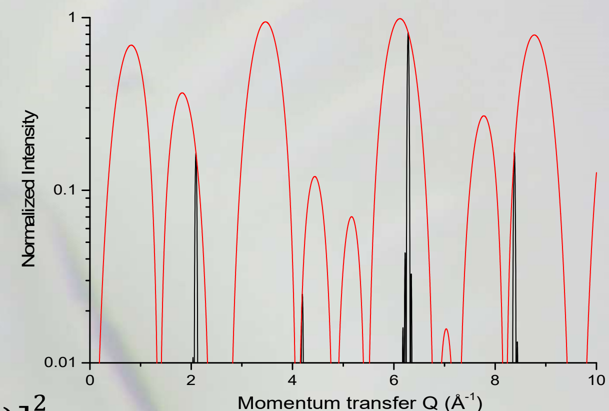
$$\frac{a * q_x}{2\pi} = \mathrm{h} \cap \frac{b * q_y}{2\pi} = \mathrm{k} \cap \frac{c * q_z}{2\pi} = \mathrm{l},$$



Fourier Transform – lattice and structure factor, a very full slide !!!



Becomes F(q)*G(q)



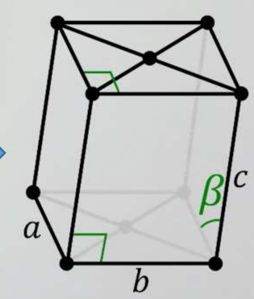
$$F_{hkl}^2(q)\left[\frac{\sin\left({}^1\!/_2 * q_a * N_a * a\right)}{\sin\left({}^1\!/_2 * q_a * a\right)} * \frac{\sin\left({}^1\!/_2 * q_b * N_b * b\right)}{\sin\left({}^1\!/_2 * q_b * b\right)} * \frac{\sin\left({}^1\!/_2 * q_c * N_c * c\right)}{\sin\left({}^1\!/_2 * q_c * c\right)}\right]^2 = F(\vec{q}) * G(\vec{q})$$

Or for a 3-dimensional crystal this leads to peaks whenever

$$\frac{\mathrm{a} * q_x}{2\pi} = \mathrm{h} \cap \frac{\mathrm{b} * q_y}{2\pi} = \mathrm{k} \cap \frac{\mathrm{c} * q_z}{2\pi} = \mathrm{l},$$

and h, k, l integers that we will use to "name" our peak ***positions***, these allow us to extract the basic periodicities

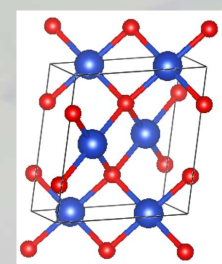
$G(\vec{q})$



Lattice

The ***intensity*** of this peak depends on……

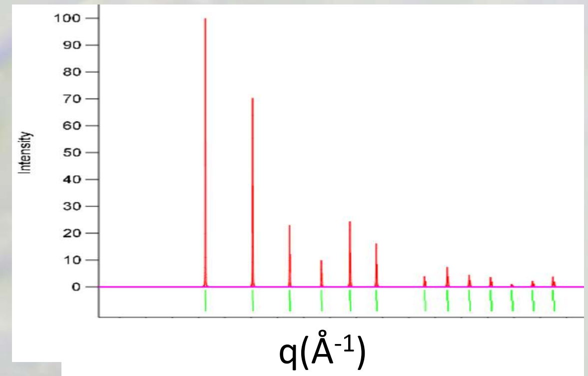
$F(\vec{q})$



Structure

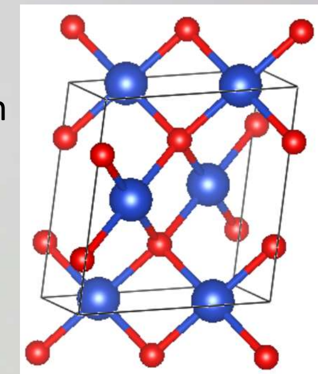
A closer look on $F(\vec{q})$

$F(\vec{q})$



Fourier Transform

$\rho(\vec{r})$



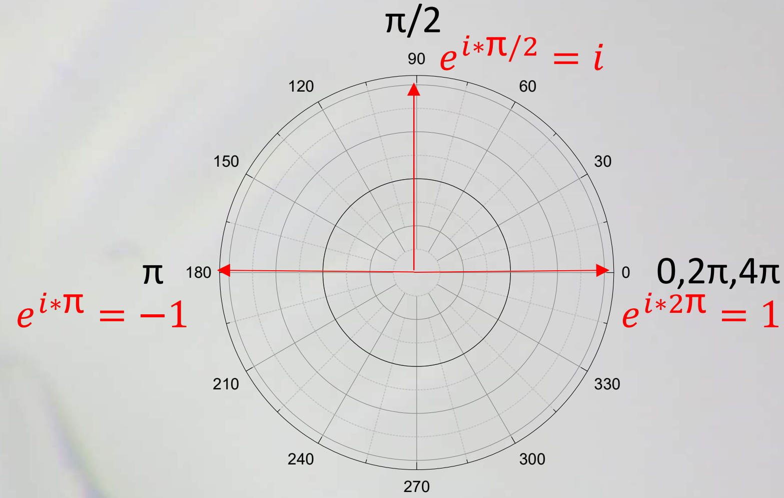
With the plane wave approach we obtained the scattering amplitude from an object to be its
Fourier Transform from $\vec{r}$-space into $\vec{q}$-Space, with $|q| = \frac{4\pi sin}{\lambda}$,
With the convolution theorem, we can separately look at the contributions from lattice and Structure Factor

$$F_{hkl}(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q}\vec{r}} \delta\vec{r} = \sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i\vec{q}\vec{r}_i} = \sum_{Ato\quad i=1}^{Atom\ i=N} f_i e^{i(q_x r_x + q_y r_y + q_z r_z)}$$

And we know that $F(\vec{q})$ is only measured at positions $F_{hkl}(\vec{q})$ with as $\frac{a*q_x}{2\pi} = \mathrm{h} \cap \frac{b*q_y}{2\pi} = \mathrm{k} \cap \frac{c*q_z}{2\pi} = \mathrm{l}$,

Or $$q_x = h\frac{2\pi}{a} \cap q_y = k\frac{2\pi}{b} \cap q_z = l\frac{2\pi}{c}$$

A closer look on $F(\vec{q})$

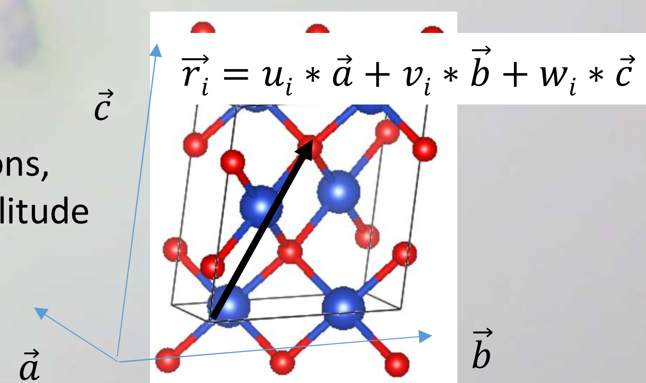


$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i\vec{q}\vec{r}_i}$$

And we know that $F(\vec{q})$ is only measured at positions $F_{hkl}(\vec{q})$ with as $q_x = h\frac{2\pi}{a} \cap q_y = k\frac{2\pi}{b} \cap q_z = l\frac{2\pi}{c}$

This leads us to

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+lw_i)}$$

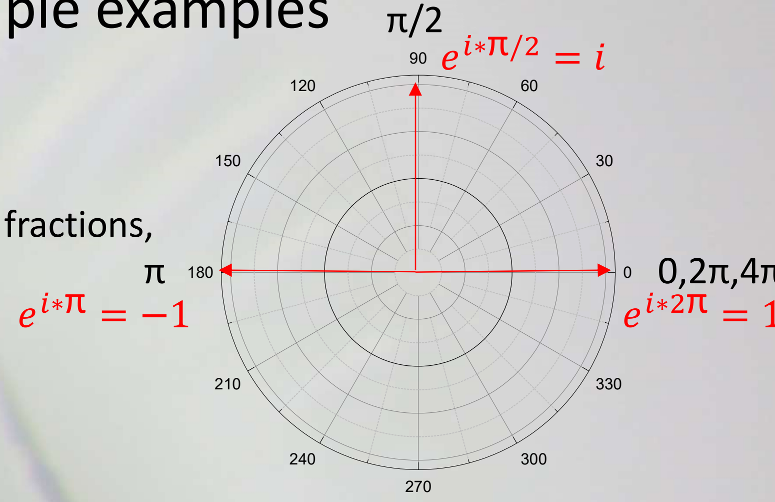


Where u_i v_i w_i are the real space coordinates expressed in unit cell parameter fractions,
f_i describes the atomic scattering factor (how strong an atom scatters)-> atomic amplitude

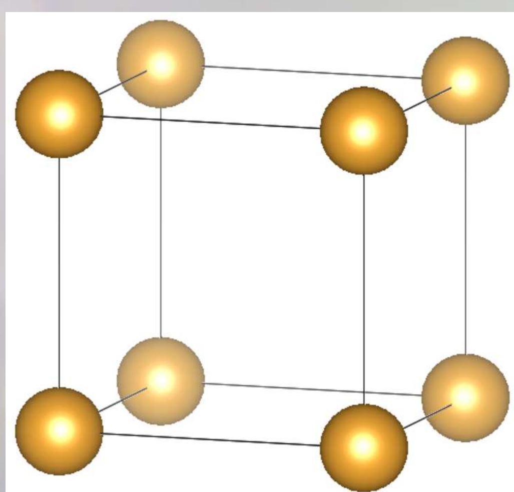
$e^{i2\pi(hui+kvi+lw_i)}$ can best be named the “atomic phase”

A closer look on- $F(\vec{q})$ - simple examples

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+lw_i)}$$



Where u_i v_i w_i are the real space coordinates expressed in unit cell parameter fractions,
f_i describes the atomic scattering factor (how strong an atom scatters)
$e^{i2\pi(hui+kvi+lw_i)}$ can best be named the “atomic phase”
The sum has to run over all atoms “ ***i*** ” inside the unit cell.
Per definition this means al atoms with coordinates $0 \leq u_i, v_i, w_i < 1$



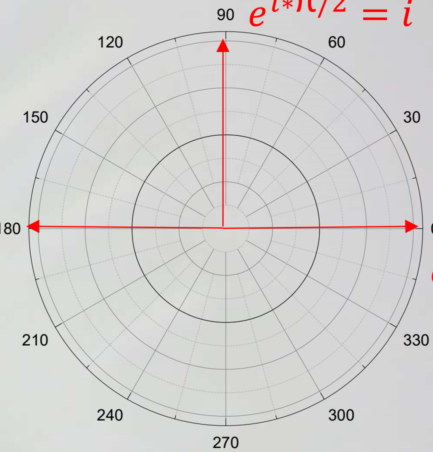
Simple cubic, how many atoms ?

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=1} f_{Po} \underbrace{e^{i2\pi(h*0+k*0+l*0)}}_{=1} = f_{Po}(\vec{q})$$

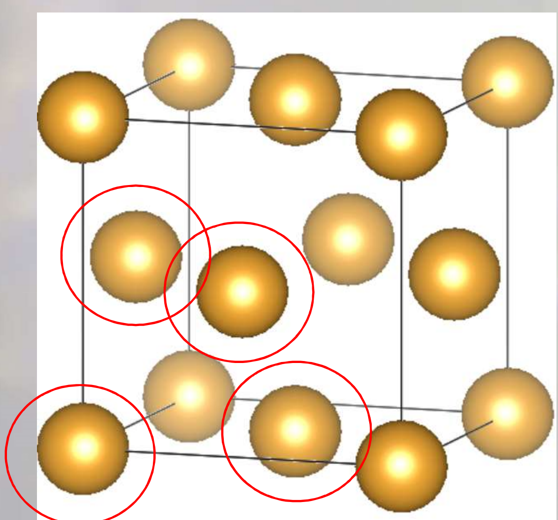
Same structure factor for every Bragg Peak !

A closer look on- $F(\vec{q})$ - simple examples

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+k\ \ _i+l\ \ _i)}$$



Where $u_i\ v_i\ w_i$ are the real space coordinates expressed in unit cell parameter fractions,
f_i describes the atomic scattering factor (how strong an atom scatters)
$e^{i2\pi(hui+kvi+l\ \ _i)}$ can best be named the "atomic phase"
The sum has to run over all atoms " ***i*** " inside the unit cell.
Per definition this means al atoms with coordinates $0 \leq u_i, v_i, w_i < 1$



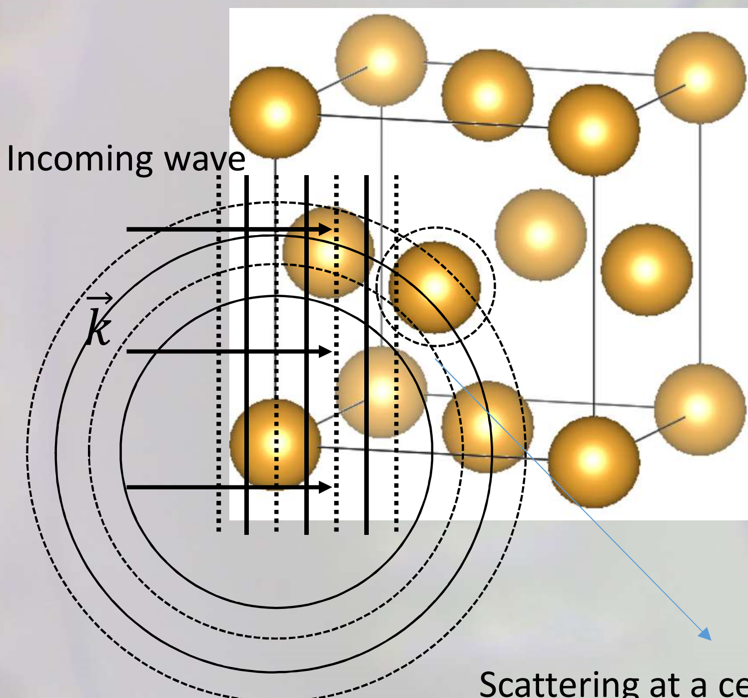
FCC, how many atoms ?

$$F_{hkl}(\vec{q})= f_{Au}(1+e^{i2\ \ (h*0+k*\frac{1}{2}+l*\frac{1}{2})} + e^{i2\ \ (h*\frac{1}{2}+k*0+l*\frac{1}{2})}+e^{i2\ \ (h*\frac{1}{2}+k*\frac{1}{2}+l*0)})$$

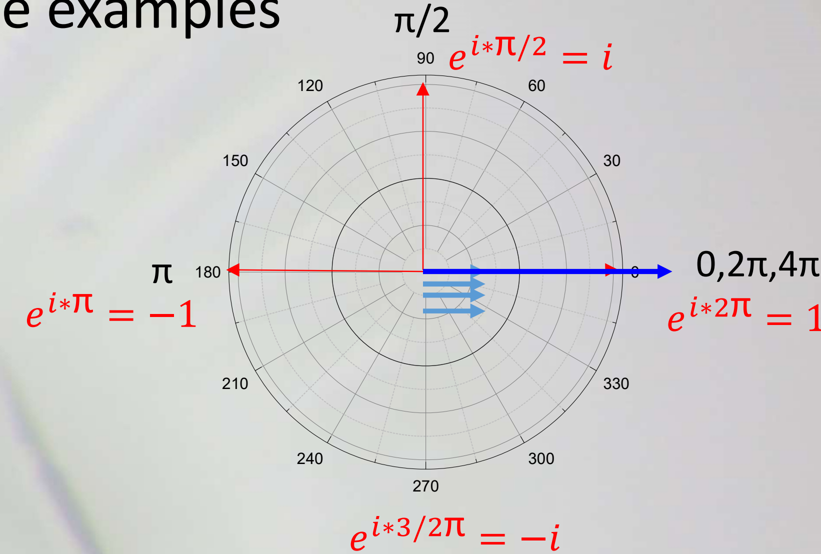
Leads to "selection rules" for monoatomic fcc (or fcc with monoatomic basis):
F_{hkl}=4f_{Au} for h,k,l = all even or all odd
F_{hkl}=0 for h,k,l= mixed

A closer look on- $F(\vec{q})$ - simple examples

$$F_{hkl}(\vec{q}) = \sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+k\ _i+l\ _i)}$$



Scattering at a certain momentum transfer (depends on observation point)



For h,k,l= 1,1,1:

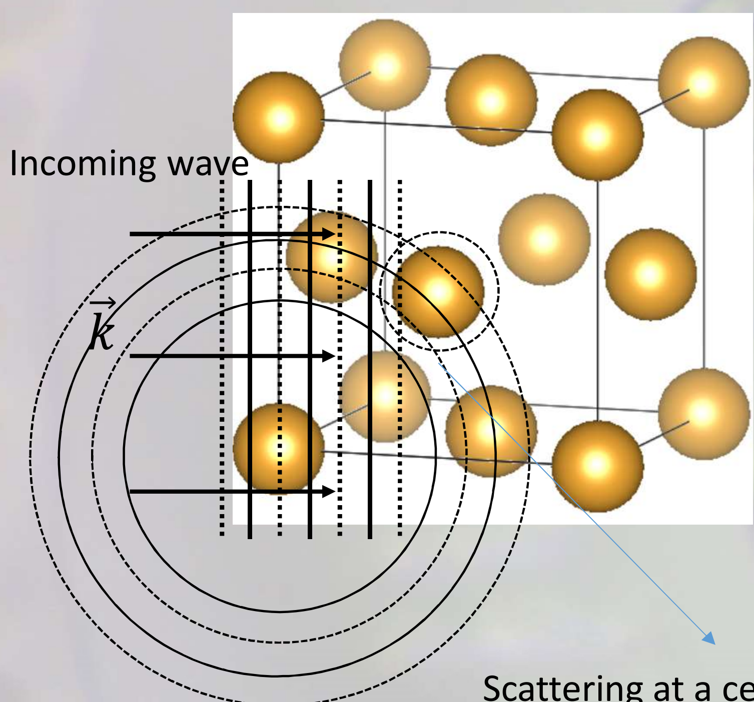
$$F_{hkl}(\vec{q}) = f_{Au}\left(1 + e^{i2\ (h*0+k*\frac{1}{2}+l*\frac{1}{2})} + e^{i2\pi(h*\frac{1}{2}+k*0+l*\frac{1}{2})} + e^{i2\pi(h*\frac{1}{2}+k*\frac{1}{2}+l*0)}\right)$$

$$= 4f_{Au}$$

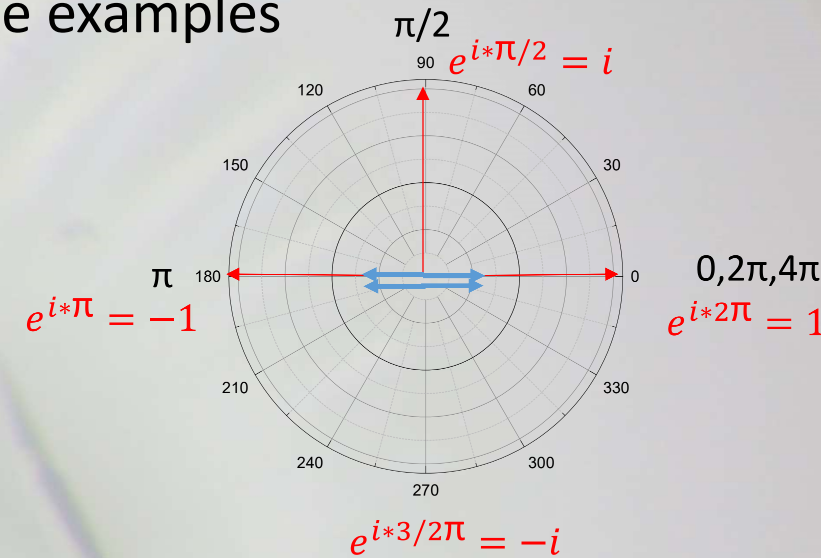
We measure $\mathrm{I} = |F_{hkl}(\vec{q})|^2$!!!

A closer look on- $F(\vec{q})$ - simple examples

$$F_{hkl}(\vec{q}) = \sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+lw_i)}$$



Scattering at a certain momentum transfer (depends on observation point)



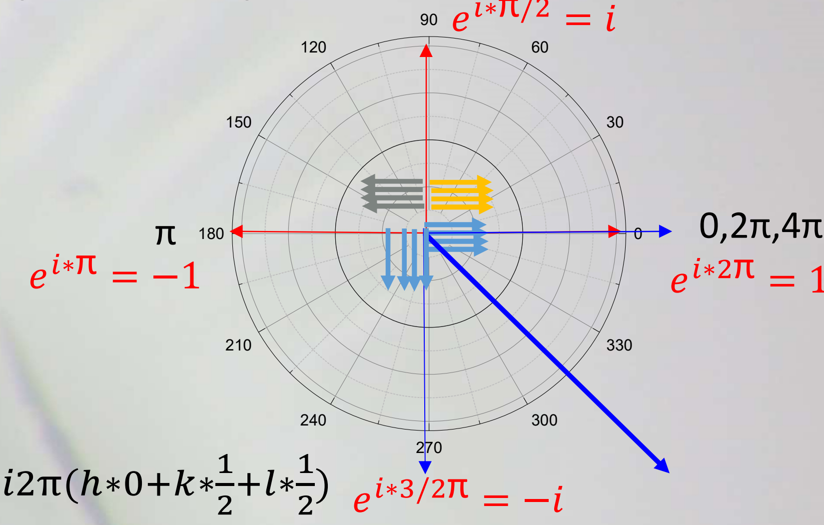
For h,k,l= 1,0,1:

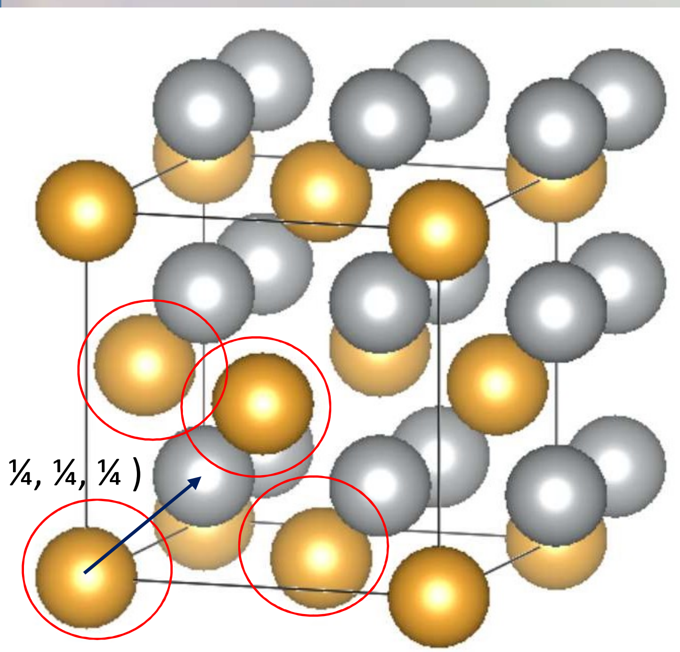
$$\underbrace{F_{hkl}(\vec{q})}_{=0} = f_{Au}\left(1 + e^{i2\pi(h*0+k*\frac{1}{2}+l*\frac{1}{2})} + e^{i2\ (h*\frac{1}{2}+k*0+l*\frac{1}{2})} + e^{i2\ (h*\frac{1}{2}+k*\frac{1}{2}+l*0)}\right)$$

A closer look on- $F(\vec{q})$ - simple examples

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+l\ \ _i)}$$

Silicon: FCC with two atomic basis, shifted by (¼, ¼, ¼)
-> 2x4=8 atoms in the unit cell





$$F_{hkl}(\vec{q})= \begin{array}{l} f_{Si}(1+e^{i2\pi(h*0+k*\frac{1}{2}+l*\frac{1}{2})} \\ +e^{i2\pi(h*\frac{1}{2}+k*0+l*\frac{1}{2})}+e^{i2\pi(h*\frac{1}{2}+k*\frac{1}{2}+l*0)}) \\ +f_{Si}(e^{i2\pi(h*\frac{1}{4}+k*\frac{1}{4}+l*\frac{1}{4})}+e^{i2\ \ (h*\frac{1}{4}+k*\frac{3}{4}+l*\frac{3}{4})} \\ +e^{i2\ \ (h*\frac{3}{4}+k*\frac{1}{4}+l*\frac{3}{4})}+e^{i2\pi(h*\frac{3}{4}+k*\frac{3}{4}+l*\frac{1}{4})}) \end{array}$$

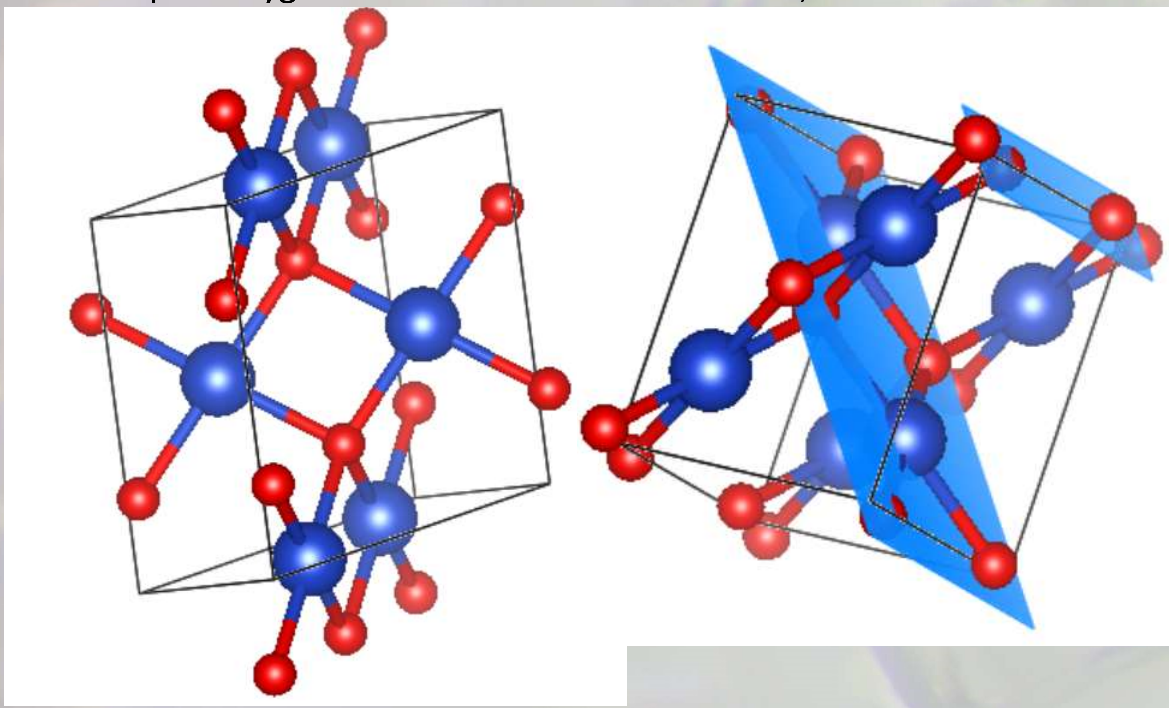
FCC selection rules will continue to exist:
F_{hkl}=0 for h,k,l= mixed ("lattice forbidden")
F_{hkl}=0 for h,k,l= 2n+2 ("basis forbidden") For example (2 0 0)
$else\ for\ F_{hkl}$=8f_{Si} for h,k,l all even
For h,k,l all odd ? For example (111) $F_{hkl}(\vec{q})=4\sqrt{2}f_{Si}$

In GaAs, InAs or ZnS, (Zincblende structure), These two fcc lattices are occupied by different atoms and F_{200}~f_{Ga}-f_{As}

Structural analysis as an approach to specific questions – Where to look in *F(q)*

$$F_{hkl}(\vec{q}) = \sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i + kv_i + lw_i)}$$

Example: Oxygen vacancies in monoclinic CuO,



Atomic positions are for Cu $(\frac{1}{4}, \frac{1}{4}, 0)$, $(\frac{3}{4}, \frac{3}{4}, 0)$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$

And for O $(0, 0.42, \frac{1}{4})$, $(\frac{1}{2}, 0.92, \frac{1}{4})$, $(\frac{1}{2}, 0.08, \frac{3}{4})$, $(0, 0.58, \frac{3}{4})$

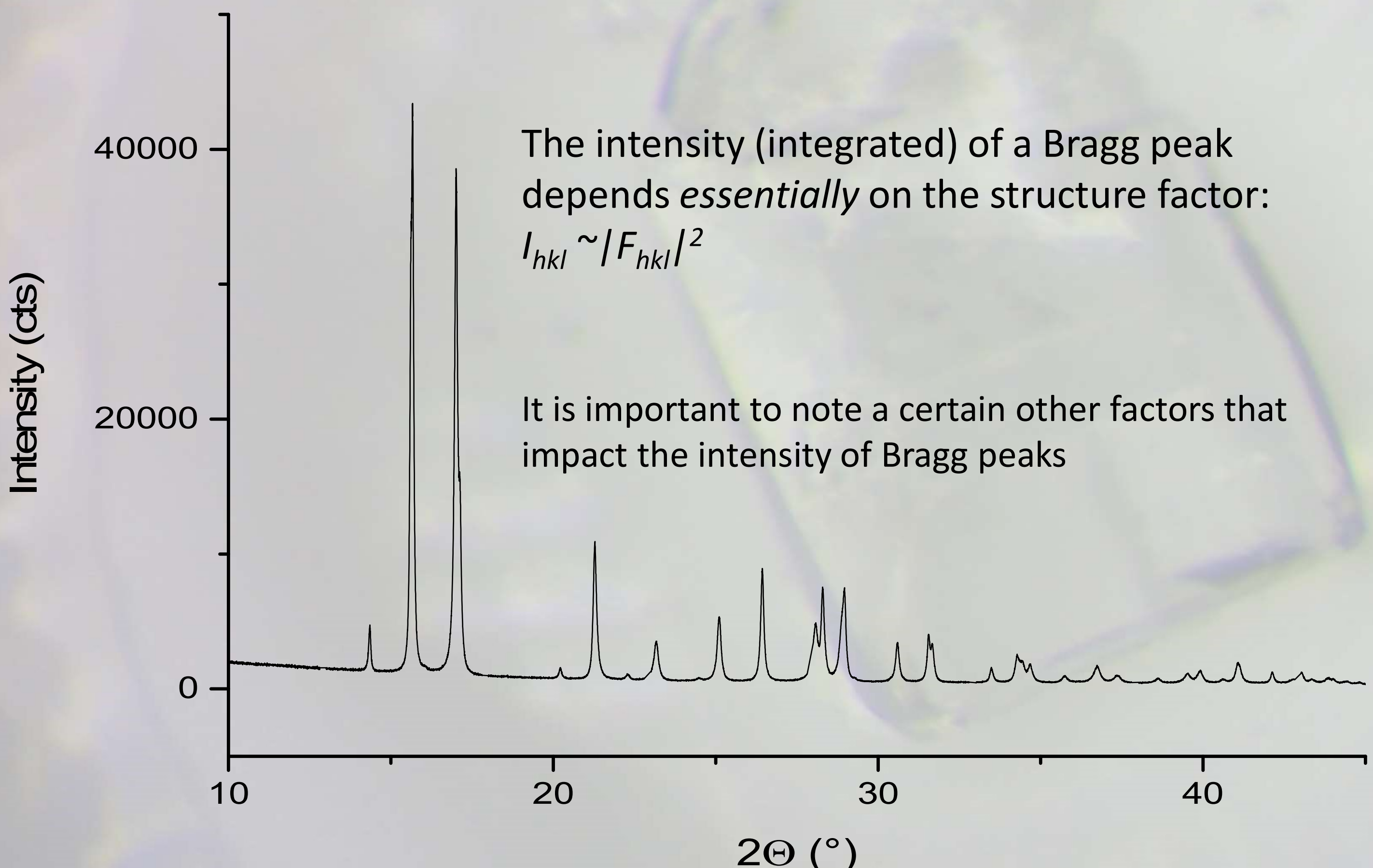
For (1 1 0): We obtain 4x the projected length, ->

$F_{110} = 4 * f_O * \cos[(1-0.84)\pi] = 3.505 * f_O$

110 planes contain Cu and O atoms, an intermediate plane contains only Cu atoms

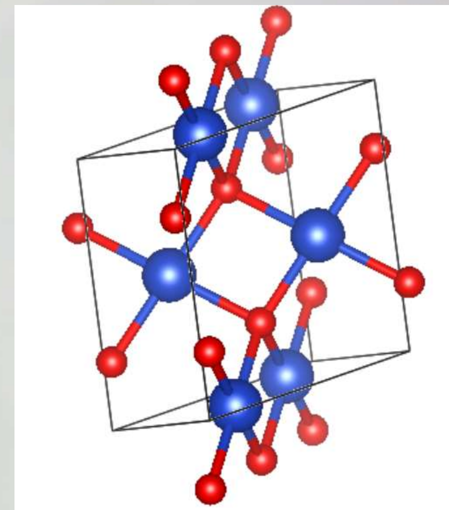
Structure resolution from a powder pattern

$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+k\ \ _i+lw_i)}$$

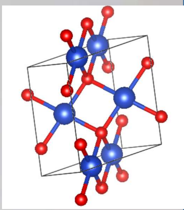


The intensity (integrated) of a Bragg peak depends *essentially* on the structure factor:
$I_{hkl} \sim |F_{hkl}|^2$

It is important to note a certain other factors that impact the intensity of Bragg peaks

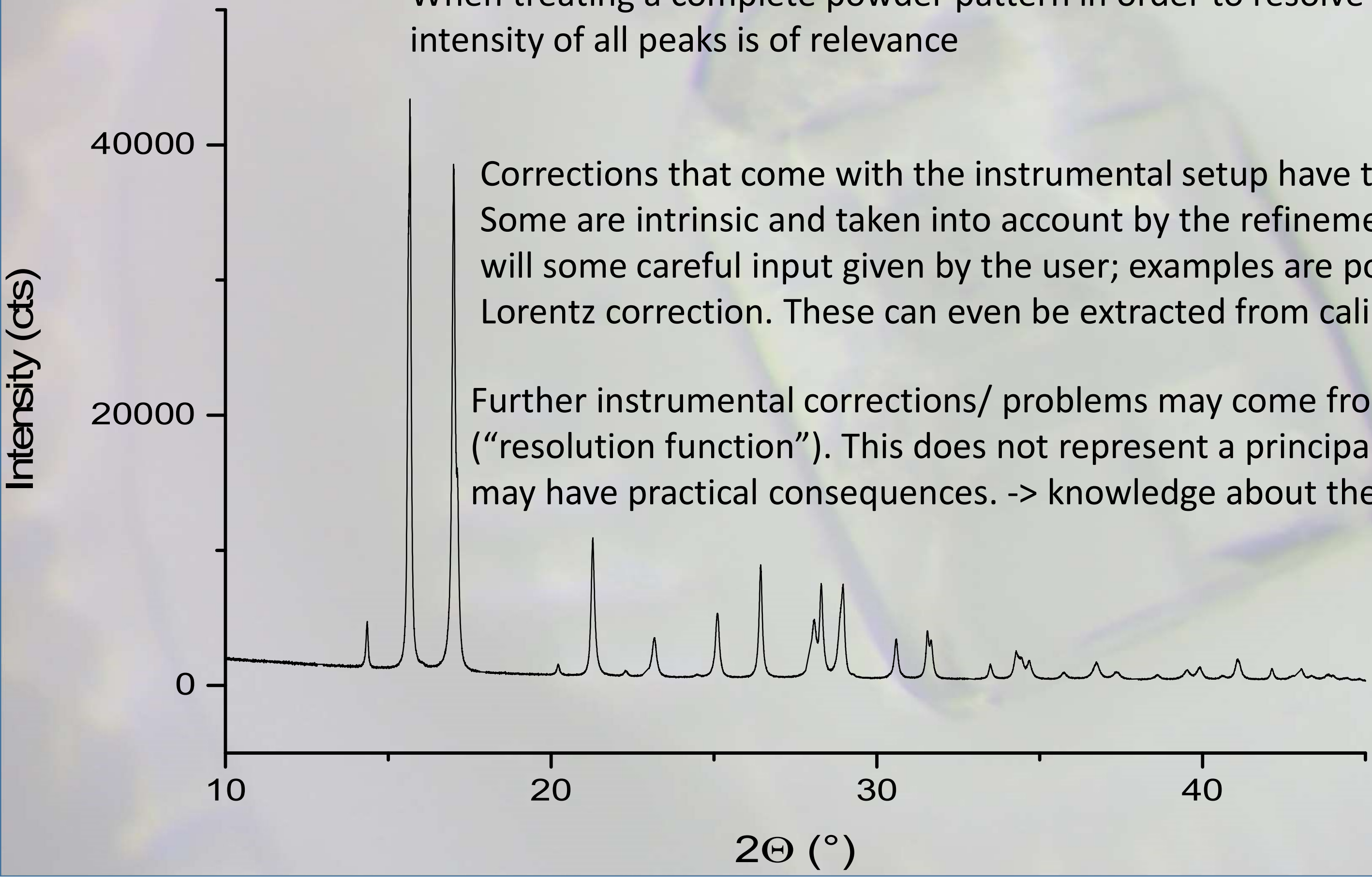


Intensity corrections , technical corrections



$$F_{hkl}(\vec{q}) = \sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i + kv_i + lw_i)}$$

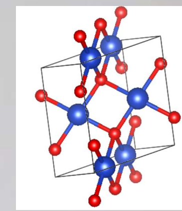
When treating a complete powder pattern in order to resolve a structure, the exact relative intensity of all peaks is of relevance



Corrections that come with the instrumental setup have thus to be taken into account. Some are intrinsic and taken into account by the refinement software. Nevertheless this will some careful input given by the user; examples are polarization correction and Lorentz correction. These can even be extracted from calibration standards.

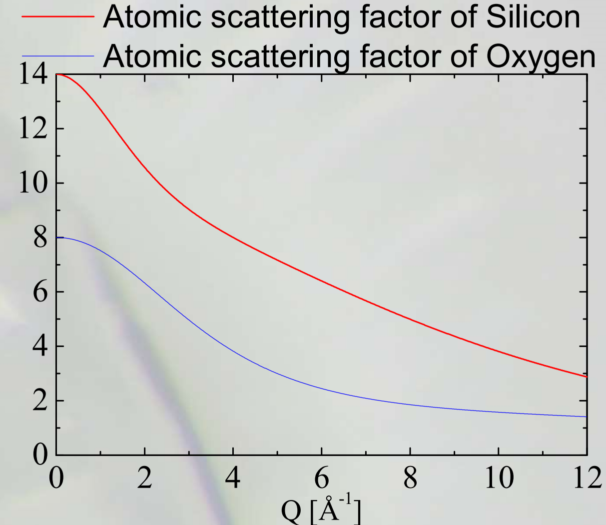
Further instrumental corrections/ problems may come from limited angular resolution ("resolution function"). This does not represent a principal problem for structure resolution but may have practical consequences. -> knowledge about the beam preparation can be useful

Intensity corrections , sample specific

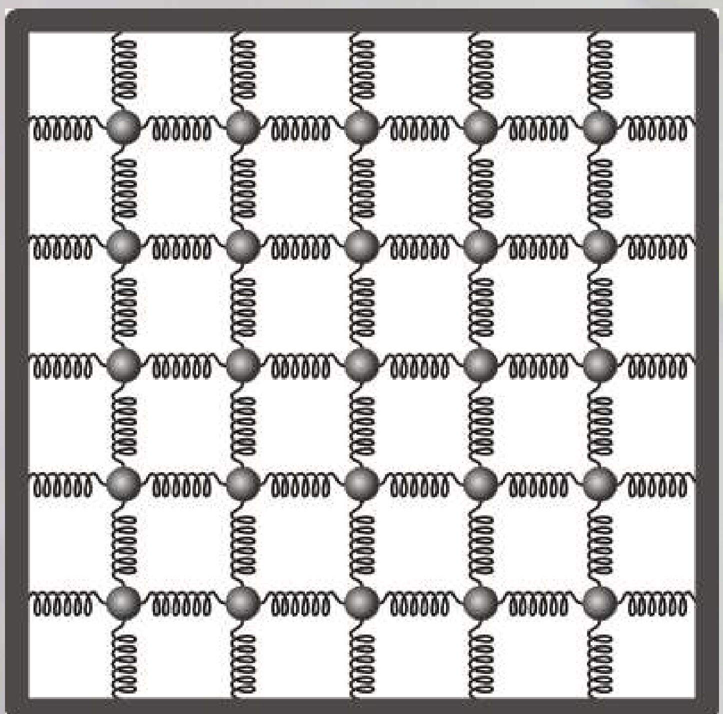


$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+l\ \ _i)}$$

We recall the atomic form factor:



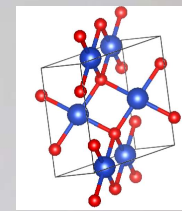
Thermal motion of atoms on the lattice.



Decreases in for higher momentum transfer as an atom is not point object but a “blurred” e-cloud.

Thermal motion blurs this even more
-> Bragg intensities decrease with increasing temperature
-> this effect is stongly q-dependent
-> this effect is likely to affect some atoms more than others
-> is likely to be anisotropic

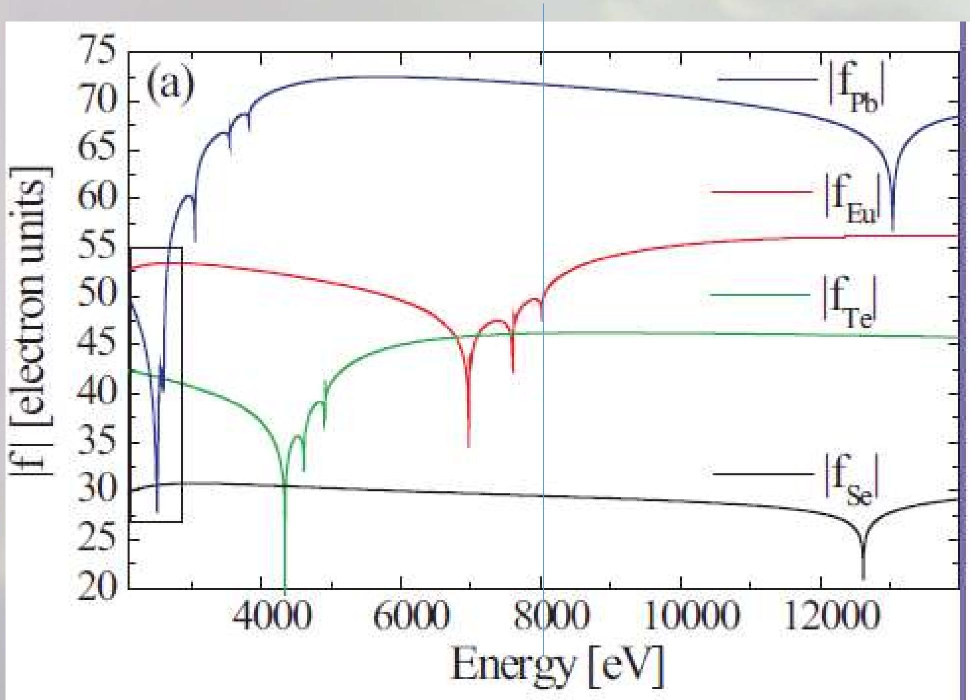
Intensity corrections , sample specific



$$F_{hkl}(\vec{q})=\sum_{Atom\ i=1}^{Atom\ i=N} f_i e^{i2\pi(hu_i+kv_i+lw_i)}$$

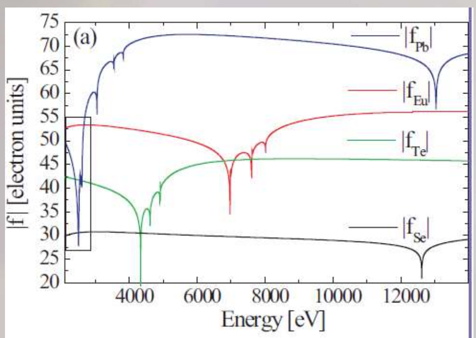
The atomic scattering factor is strictly speaking energy-dependent (and of course q-dependent)

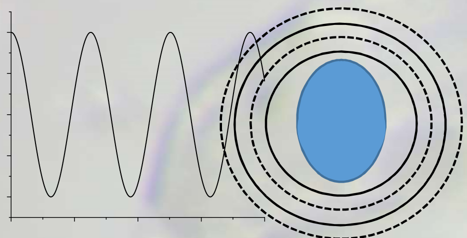
Cu K-alpha X-rays



The reason for this are resonant effects when the X-ray energy comes close to the binding energy of a specific electron. Varying the X-ray energy to exploit a change in contrast is often referred to as “anomalous scattering”, although “resonant scattering” would be better suited

Interaction of X-rays (or light) with materials





For a “free” oscillation the emission would be in the eigenfrequency.
Exposed to a monochromatic light wave one expects however elastic scattering from a driven oscillator

Polarized electron clouds=driven harmonic oscillators,
We recall from optics:

The refractive index is expressed as n $\approx \sqrt{1+\chi}$ χ=polarizability Polarization P=$\chi * E$

This can find a simple mechanical equivalent: the driven harmonic oscillator (a popular model….)

The dilemma of x-ray optics

The refractive index is expressed as n $\approx \sqrt{1+\chi}$ χ=polarizability

Polarized electron clouds=driven harmonic oscillators

Polarization P=$\chi * E$ ~ equiv. mechanical Amplitude

Amplitude

$$X_0 \cong P \propto \frac{\omega_0^2}{\sqrt{(\omega_0^2-\omega^2)^2+\phi^2\omega^2}}$$

For $\omega \ll \omega_0$: P=const. (does hardly vary with ω)

eyeglasses work for all colours,
In this regime, refraction is almost achromatic

For $\omega \gg \omega_0$: P~$1/\omega^2$, thus P-> 0

Refraction in the x-ray regime is very weak and highly chromatic!!,

n ≈0.99999..