



Basic aspects of X-Ray Diffraction

Outline:

- Properties of X-rays
- Diffraction methods
- Kinematic theory of scattering
- Scattering of amorphous materials
- Scattering of crystalline materials
- Bragg condition
- Atomic form factor
- Structure factor
- Experimental diffraction setups
- Methods for quantitative phase analysis



Properties of X-rays

- X-rays were discovered in 1895 by Wilhelm Conrad Röntgen.
- Electromagnetic radiation with very short wavelength, and very high energy.
- Wavelength: Gamma rays < X-rays < Ultraviolet rays.
- Energy: Ultraviolet rays < X-rays < Gamma rays.
- Wavelength: from 10^{-12} m (picometers) to 10^{-9} (nanometers).
- Energy: 124 eV to 124 keV ($E=hc/\lambda$).
- Useful in Materials Science, Restoration, Medicine, Security, Astronomy, Industry, etc.



Diffraction methods

Basic methods for determining the structure of materials.

The material is irradiated by a beam with smaller wavelength than the characteristic length (e.g. lattice constant).

The beam diffracts on the sample and the Fraunhofer-interference image (interference of parallel waves) is examined.

The image is the product of both scattering and interference.

The lattice constants typically fall in the $(0,4 - 0,6)$ nm interval therefore the applied wavelength is:

$$\lambda < 0,2 \text{ nm.}$$

X-ray, neutron and electron waves are used for the experiments.

The mechanism of scattering is different in the case of the three waves.

If we don't take into account the mechanism, but only the dependence on the geometrical factors, then a common model can describe the diffraction of the three waves.

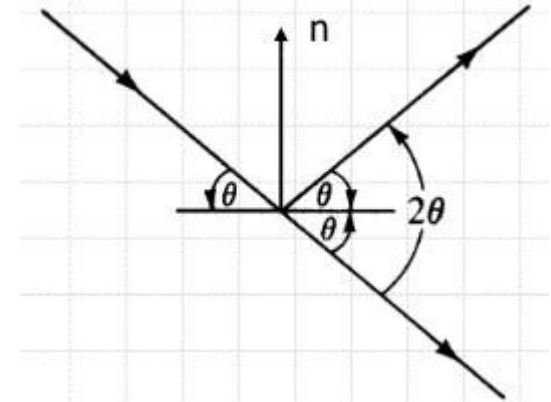
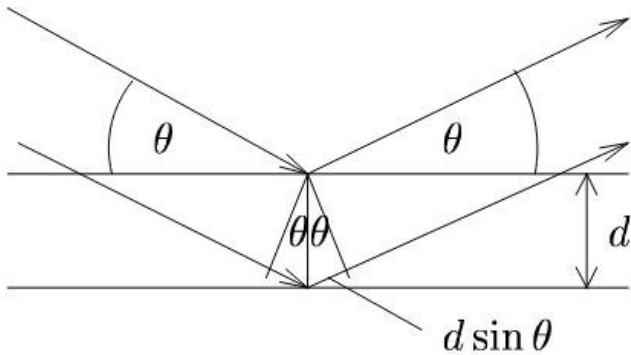


Kinematic scattering theory

The approximations in the assumptions of the kinematic scattering theory:

- The scattering is elastic: the energy of the scattered beam is unchanged, therefore the λ wavelength is constant during the process.
- The scattering is coherent: all of the scattering centers scatter in the same way (e.g. the phase shift between the incoming and scattered beam is constant).
- The scattering is weak. There are two consequences:
 - The intensity is not changed when the beam penetrates the deeper regions of the sample;
 - there is only first order scattering.

Scattering on crystal planes:



The difference of path of the two waves: $2d\sin\theta$.

If the difference of path $2d\sin\theta$ is a multiple of the x-ray wavelength λ , then two waves will give a constructive interference: this should be n (integer) times the λ wavelength. The diffracted waves interfere destructively if this equation is not satisfied.

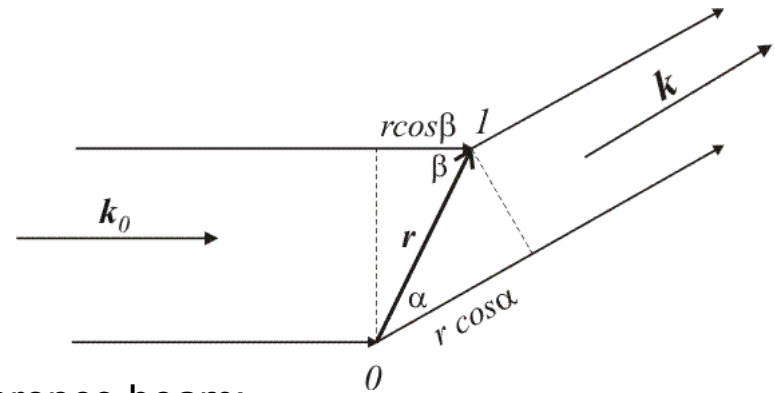
This is the Bragg equation and the angle θ is the Bragg angle and n is called the order of diffraction.

Basic geometrical background

Plane wave in the direction \mathbf{k}_0 :

$$A(\mathbf{k}_0) = a_0 e^{i(\omega t - \mathbf{k}_0 \cdot \mathbf{x} + \delta_0)}$$

$$\mathbf{k}_0 = \frac{2\pi}{\lambda} \mathbf{e}, \quad \omega = \frac{2\pi}{T}$$



The phase shift between the 1st beam and the reference beam:

$$\delta = \frac{2\pi}{\lambda} (r \cos \beta - r \cos \alpha) = \mathbf{k}_0 \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{r} = -\Delta \mathbf{k} \cdot \mathbf{r}, \quad \Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_0$$

The scattered beam from 1st center (expressed with the reference beam):

$$A(\mathbf{k}) = a_0 e^{i(\omega t - \mathbf{k} \cdot \mathbf{x} + \delta_0 + \delta)} = A_0 e^{i\delta} = A_0 e^{-i\Delta \mathbf{k} \cdot \mathbf{r}}$$

Since A_0 is constant, we can set $A_0 = 1$.

All of the beams scattered from all centers should be summed.

In the case of continuum material:

$$A(\mathbf{k}) = \int_V \rho(\mathbf{r}) e^{-i\Delta \mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{r}$$

The integrals should be calculated over the V illuminated volume, $\rho(\mathbf{r})$ is the density of the scattering centers.

In fact this is a Fourier-transform.

Amorphous materials

We measure the intensity:

$$I = |A(\mathbf{k})|^2 = A(\mathbf{k})A^*(\mathbf{k}) = \int_V \int_{V'} \rho(\mathbf{r})\rho(\mathbf{r}') e^{i\Delta\mathbf{k}\mathbf{r}} e^{-i\Delta\mathbf{k}\mathbf{r}'} d^3\mathbf{r} d^3\mathbf{r}'$$

Characterizing liquids and amorphous materials:

$$I = \int_{V_r} \int_{V_u} \rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{u}) e^{-i\Delta\mathbf{k}\mathbf{u}} d^3\mathbf{r} d^3\mathbf{u}. \quad \mathbf{r}' = \mathbf{r} + \mathbf{u}, \quad d^3\mathbf{r}' = d^3\mathbf{u},$$

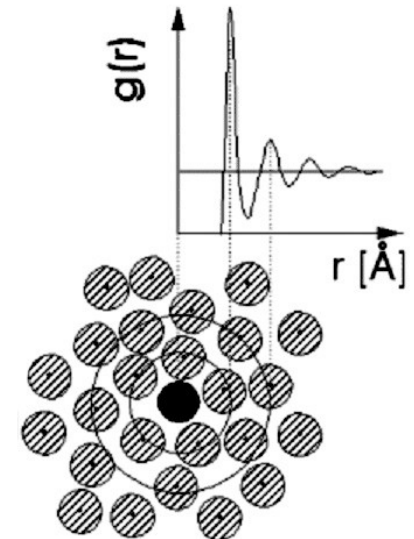
$$P(\mathbf{u}) = \int_V \rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{u}) d^3\mathbf{r} \quad \text{here we introduced the self correlation function}$$

$$I = \int_V P(\mathbf{u}) e^{-i\Delta\mathbf{k}\mathbf{u}} d^3\mathbf{u} \quad \text{The Fourier transform of the self correlation function.}$$

From this we obtain $P(\mathbf{u})$ by inverse Fourier transformation.

In the case of isotropic material it is enough to use the 1D projection of the self correlation function, which is called $g(r)$ radial distribution function.

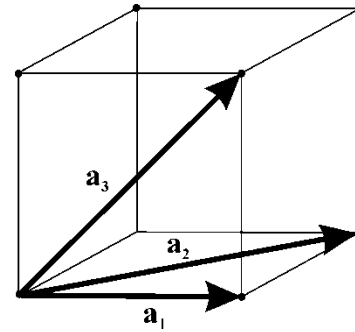
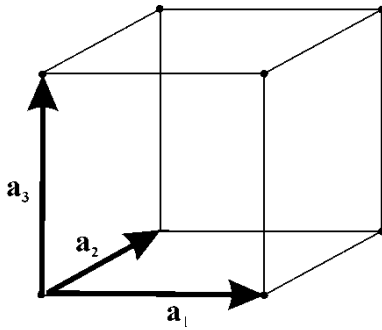
In the case of amorphous material, the radial distribution function shows the most likely distance of first, second, etc. neighbours.



Crystalline materials

Characterizing crystalline materials:

The cell is determined by the lattice vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 . They are not unique.



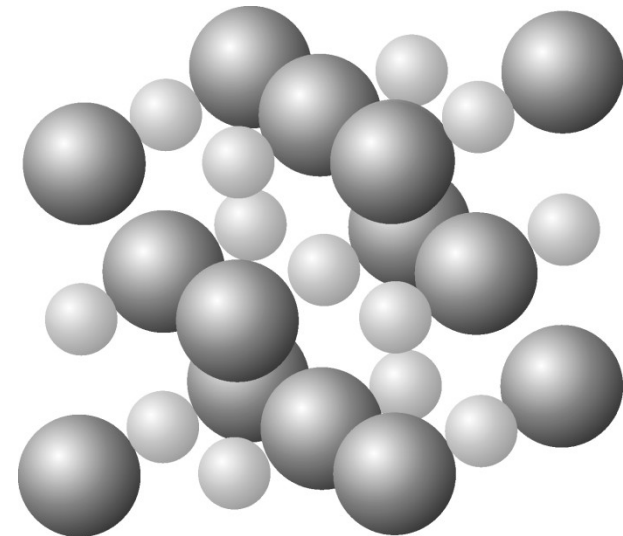
The points of the cell are given by the vector $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$).

If we use primitive unit cell vectors, then x , y , z integer numbers give the points of the lattice.

If the unit cell vectors are not primitive vectors, then x , y , z are not necessarily integer numbers.

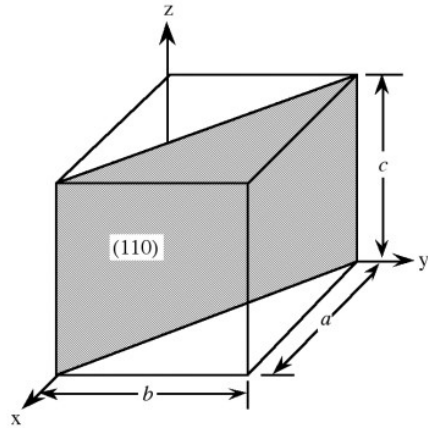
The Bravais-cells are not always unit cells!

The crystal structure is obtained by associating a base with the points of the lattice.



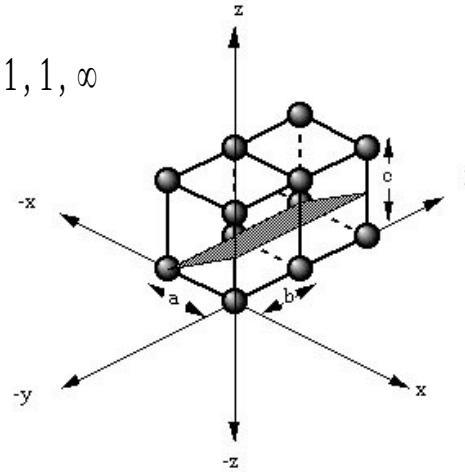
Crystalline materials

Characterizing crystal planes: Miller-indices



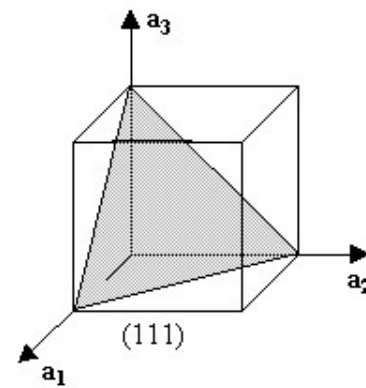
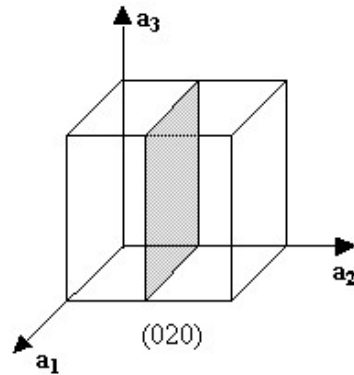
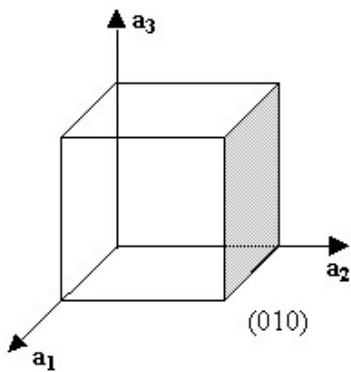
Coordinates of intersection: $1, 1, \infty$

$$(hkl) = \left(\frac{1}{1} \frac{1}{1} \frac{1}{\infty} \right) = (110)$$



$-1, \infty, \frac{1}{2}$

$$(hkl) = (\bar{1}02)$$





Reciprocal lattice

We can define the reciprocal lattice with base vectors:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 (\mathbf{a}_3 \times \mathbf{a}_1)} \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 (\mathbf{a}_1 \times \mathbf{a}_2)}$$

So $\mathbf{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is a reciprocal lattice vector, with dimension 1/length.

From the definition of the reciprocal lattice vectors $\mathbf{a}_i \mathbf{b}_j = 2\pi \delta_{ij}$ is satisfied.

The points of the reciprocal lattice are determined by the h, k, l integer numbers.

- The h, k, l integer numbers (Miller-indices) are also determining a crystal plane denoted by (hkl) .
- $\mathbf{g}(hkl)$ is perpendicular to the plane (hkl) .
- $\frac{2\pi}{|\mathbf{g}|} = d_{hkl}$ is the distance of the (hkl) planes.
- Because of the definition of the reciprocal lattice planes, the h, k, l numbers are not only determining the plane intersecting atoms, but also the planes with half-, third-, etc. distance.

Bragg - condition

Bragg - condition

We examine further the amplitude of the diffracted beam:
$$A(\mathbf{k}) = \int_V \rho(\mathbf{r}) e^{-i\Delta \mathbf{k} \mathbf{r}} d^3 \mathbf{r}$$

The crystal can be divided into cells,
and into the atoms contained by the cells.

Similarly we divide the integral too:

First we make the integration around the atoms,
then we are summing the contribution of the atoms of the cells
and finally we are summing the contribution of all cells.

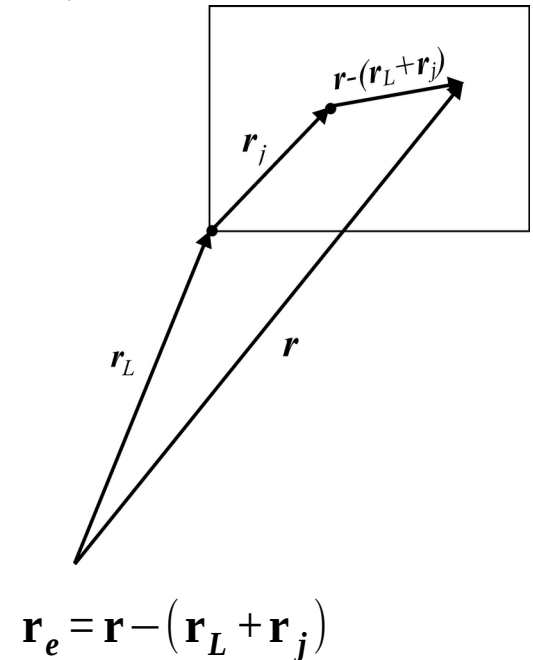
$$A(k) = \sum_{L=1}^N F_{hkl} e^{-i\Delta \mathbf{k} \mathbf{r}_L} = F_{hkl} \sum_{L=1}^N e^{-i\Delta \mathbf{k} \mathbf{r}_L}$$

Structure factor:

$$F_{hkl} = \sum_j f_j e^{-i\Delta \mathbf{k} \mathbf{r}_j}$$

Atomic form factor:

$$f_j(\mathbf{g}) = \int_V \rho_j(\mathbf{r}_e) e^{-i\Delta \mathbf{k} \mathbf{r}_e} d^3 \mathbf{r}_e = \int_V \rho_j(\mathbf{r}) e^{-i\Delta \mathbf{k} \mathbf{r}} d^3 \mathbf{r}$$

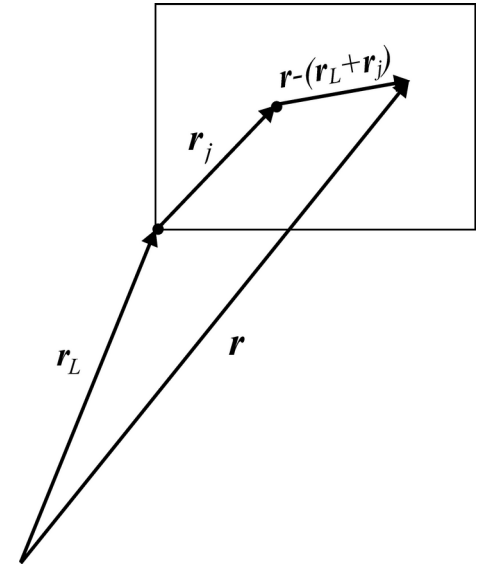


Bragg - condition

The contribution of all cells:

$$A(\mathbf{k}) = \sum_{L=1}^N F_{hkl} e^{-i\Delta\mathbf{k}\mathbf{r}_L} = F_{hkl} \sum_{L=1}^N e^{-i\Delta\mathbf{k}\mathbf{r}_L}$$

The second summation is over the lattice points.



In the case of ideal (infinitely large) lattice:

$$N = \infty.$$

This sum is only different to zero, if the phase in the exponential is $2\pi n$.

This condition is fulfilled if: $\Delta\mathbf{k} = \mathbf{g}_{hkl}$ This is the Bragg – condition.

In this case the value of the sum is N . In the case of ideal lattice this sum is composed of Dirac-delta functions.

By using the Bragg – condition we can rewrite:

Atomic form factor: $f_j(\mathbf{g}) = \int \rho_j(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} d^3\mathbf{r}$

Structure factor: $F_{hkl} = \sum_j^V f_j e^{-i\mathbf{g}\mathbf{r}_j}$

Diffracted amplitude: $A_g = N \sum_j^j F_{hkl}$

Bragg - condition

The other form of the Bragg-condition:

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

$$\sin \theta = \frac{|\mathbf{g}_{hkl}|}{2|\mathbf{k}_o|}$$

By using the following two expressions we obtain:

$$|\mathbf{g}_{hkl}| = \frac{2\pi}{d_{hkl}} \quad |\mathbf{k}_o| = \frac{2\pi}{\lambda}$$

$$2 d_{hkl} \sin \theta = \lambda$$

Because of the definition of the reciprocal lattice planes, the h, k, l numbers are not only determining the plane intersecting atoms, but also the planes with half-, third-, etc. distance, they also have the corresponding h', k', l' reciprocal lattice vectors.

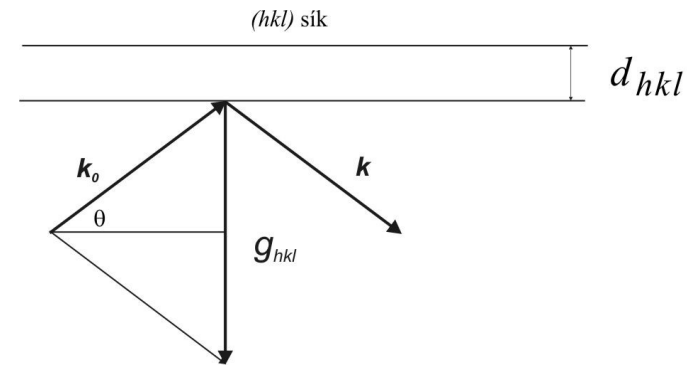
$$d_{hkl} = n d_{h'k'l'}$$

By applying the previous equation to the h', k', l' planes, we obtain for h, k, l :

$$2 d_{hkl} \sin \theta = n\lambda \quad \text{This is the other form of the Bragg-equation.}$$

There is another important equation (see the figure):

$$|\mathbf{g}| = \frac{4\pi \sin \theta}{\lambda}$$





Atomic form factor

$$f_j(\mathbf{g}) = \int_V \rho_j(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} d^3\mathbf{r}$$

This form already contains the Bragg – condition

The ρ_j density of scattering centers:

- In the case of X-ray photons ρ_j is the density of the electrons of the j -th atom (dimension: 1/volume).
- The electrons are scattered on the Coulomb-potential of the nuclei and electrons, so the density of scattering centers has two terms which are proportional to the Coulomb-potential of electrons and nuclei.
- The neutrons are mainly scattered by the nuclei, therefore ρ_j is proportional to the density of nuclei, which is in fact a Dirac – delta function located at the position of the j -th nucleus.

Properties of X-ray atomic form factor

The atomic form factor: $f_j(\mathbf{g}) = \int_V \rho_j(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} d^3\mathbf{r}$

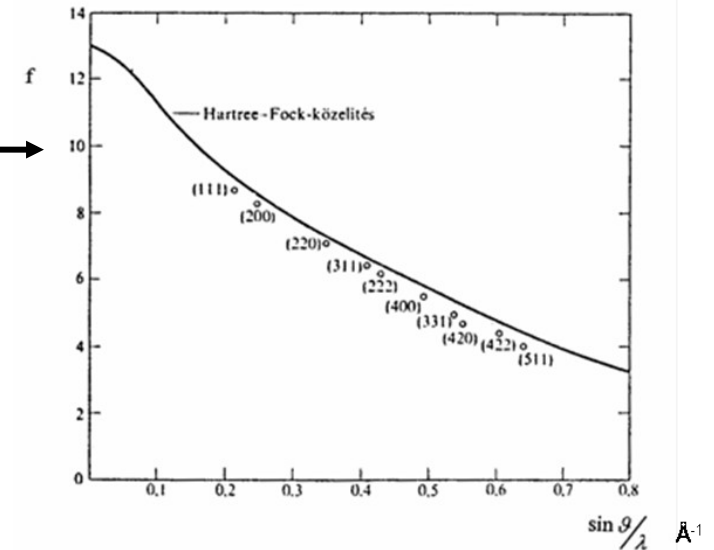
In the case of X-rays, the atomic form factor as a function of:

$$|\mathbf{g}| = \frac{4\pi \sin \theta}{\lambda} \quad |\mathbf{g}| \propto \frac{\sin \theta}{\lambda}$$

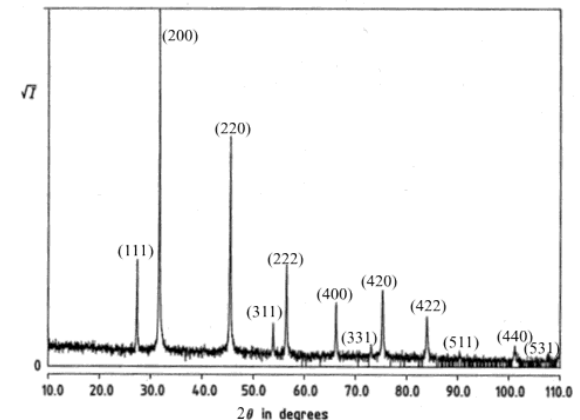
The value of the function for X-ray photons at $g = 0$ is equal to the number of electrons of the atom.

In the case of elastic X-ray scattering there is a strong angular dependence, because the size of the electron density function ($\sim 0,1 \text{ nm}$) has the same order of magnitude as the wavelength of the scattered wave (X-ray photons).

The angular dependence can be well observed by the shape of X-ray patterns.



The form factor of Al. Theoretical curve and experimental values.



The X-ray diffraction pattern of NaCl



Properties of X-ray atomic form factor

The **X-ray** measurements have a **disadvantage**, the elements with low **charge number** can barely be examined, because the atomic form factor is small due to the low number of electrons.

In such cases, the **neutron diffraction** experiments can be used instead of X-rays.



The properties of neutron diffraction

Wavelength: $\lambda = \frac{h}{p}$, $E = \frac{3}{2} kT = \frac{p^2}{2m_n}$,

$$\lambda = \frac{h}{\sqrt{3kTm_n}}$$

The wavelength corresponding to 300 K is: $\lambda = 0,145 \text{ nm}$.

Energy:

$$E = \frac{3}{2} kT$$

The energy of the beam with temperature $T = 300 \text{ K}$: $E = 0,039 \text{ eV}$.
Compared for example to the line $\text{Cu } K_\alpha$

$$\lambda_{\text{Cu}K_\alpha} = 0,154 \text{ nm} \quad E \approx 8 \text{ keV}$$

The wavelengths have the same order of magnitude, however the **energies are very different**.

The neutron energy falls to the phonon and magnon thermic energies, therefore the inelastic scattering of neutrons is well suitable to measure the dispersion relations of phonon and magnon excitations.



The properties of neutron diffraction

The atomic form factor of neutron scattering is independent of the scattering angle.

Explanation:

The wavelength of the neutrons used in the diffraction experiments is about $0,1 \text{ nm}$.

If the neutrons are scattered by the **atomic nuclei**:

The size of the nucleus is about: $1 \text{ fm} = 10^{-15} \text{ m} = 10^{-6} \text{ nm}$.

So the size of the nucleus is smaller by 5 orders of magnitude than the wavelength of the neutrons.

Therefore the difference in path (or phase) is negligible between the waves scattered from different points of the nucleus.

Neutron sources: fission reactors, spallation neutron sources.

The moderator is used to adjust the wavelength of neutrons.

The temperature corresponding to the top of the Maxwell-Boltzmann distribution is adjusted.

The properties of neutron diffraction

The particular properties of neutron diffraction:

- The neutron **absorption and scattering cross sections** are usually **smaller** by several orders of magnitude than in the case of X-rays.

Therefore the **sample sizes** are **much larger**, than in the case of X-rays. The typical sample volume is about cm^3

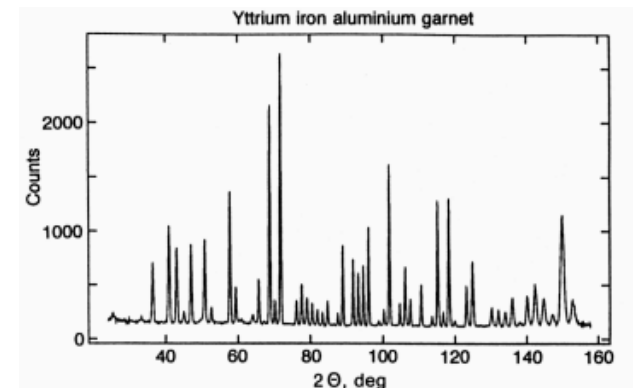
- The scattering angle independent **form factor** is called: **scattering length**. It is usually denoted by b . The structure factor expressed with this:

$$F_{hkl,nuc} = \sum_j b_j e^{-igr_j}$$

The typical value of the scattering length is about: $10^{-12} cm = 1 \text{ barn}$.

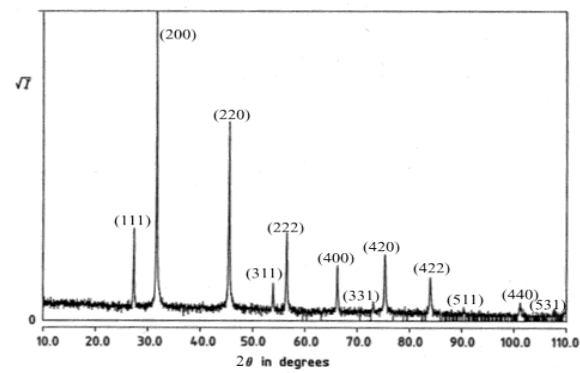
- The neutron beam scattered by the nucleus have **π phase shift** compared to the incoming beam.
- The neutron diffraction patterns contains peaks at **higher angles** too, because of the diffraction angle independent form factor.

This is important in the determination of crystal structure.





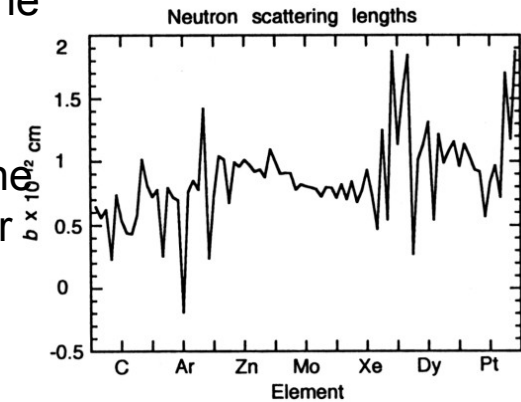
The properties of neutron diffraction



The properties of neutron diffraction

- The scattering length is changing „randomly” as a function of the atomic number (this is completely different in the case of X-rays).

In many cases the scattering length of neighbour elements of the periodic table is significantly different, which is an advantage for structure determination, compared to X-ray diffraction where it is hard to make difference between neighbour elements.



For example in the case of *Fe*, *Mn* alloys:

$$b_{Fe} = 0,96 \cdot 10^{12} \text{ cm} \quad b_{Mn} = -0,38 \cdot 10^{12} \text{ cm}$$

- The X-ray analysis of elements with low electron number is hard, because their atomic form factor is small.

For example in the investigation of organic materials the hydrogen analysis is important, but the X-ray scattering of hydrogen is weak.

On the other hand, the neutron scattering length of hydrogen is sufficiently large.

A problem is that the inelastic scattering of hydrogen is large, However, in the case of deuterium it is small, therefore by replacing hydrogen with deuterium, the H positions can also be determined during the structure analysis.

The properties of neutron diffraction

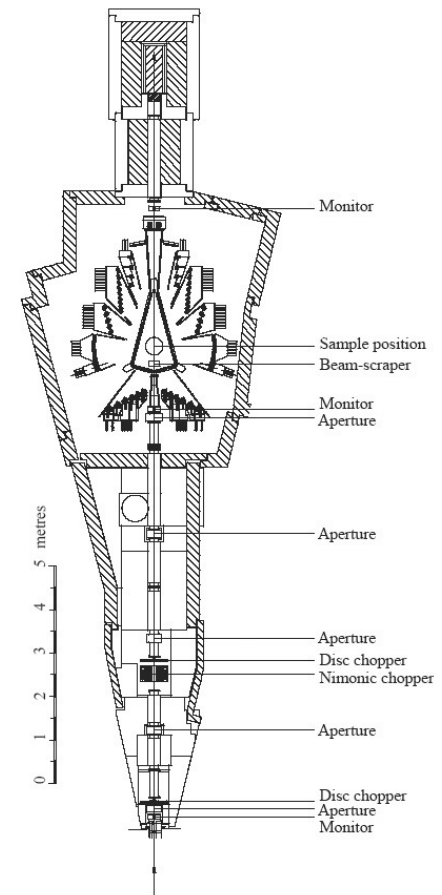
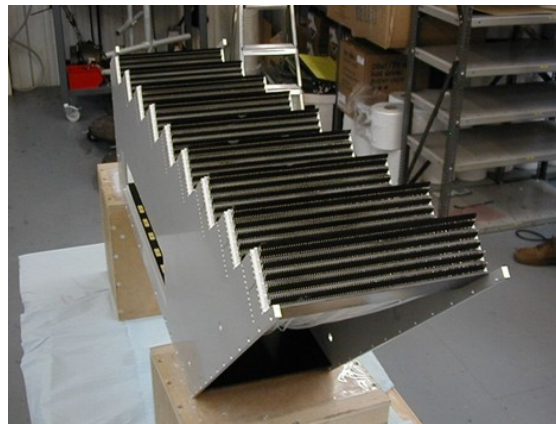
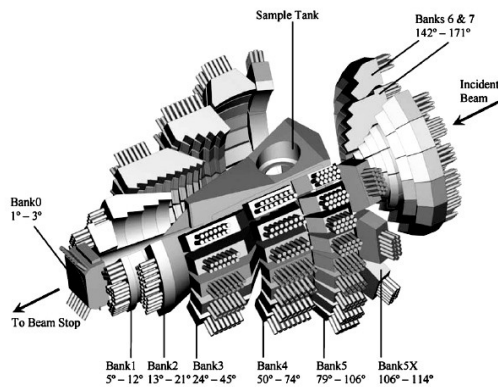
- The **neutrons** are scattered not only by the nuclei, but by the **electrons too**.

Since the neutrons have spin momentum, their spin interact with the spins of the electron system.

Therefore the neutron diffraction is also important in the investigation of magnetic properties of materials.

- The instrumental setup and methods of neutron diffraction is similar to the setup and methods of X-ray diffraction.

However, while in the case of X-ray diffraction, the experimental devices can be placed on a normal sized desk, in the case of neutron diffraction, the goniometers and detectors can be much larger, e.g. their size can be several meters.





The properties of electron diffraction

The diffraction properties of electrons are mainly used in the Transmission Electron Microscope. One of the functions of the *TEM* is to view the diffraction image.

In the case of modern electron microscopes, the energy of electrons is $E = 200 - 300 \text{ keV}$.

The wavelength:
$$\lambda (\text{nm}) = \frac{h}{\sqrt{2m_e E}} = \frac{1,2}{\sqrt{E (\text{eV})}}$$

In the case of $E = 300 \text{ keV}$: $\lambda = 2,2 \cdot 10^{-3} \text{ nm}$

This is smaller by two orders of magnitude, than in the case of thermal neutrons, or the usual X-ray wavelengths.

The properties of electron diffraction

Consequences:

1. Since the wavelength is smaller by two orders of magnitude compared to the lattice constant, the radius of the Ewald sphere in the reciprocal space is larger by two orders of magnitude than the base vectors of the reciprocal lattice.

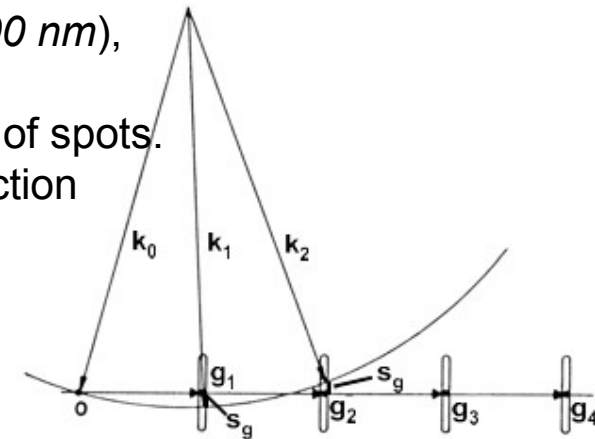
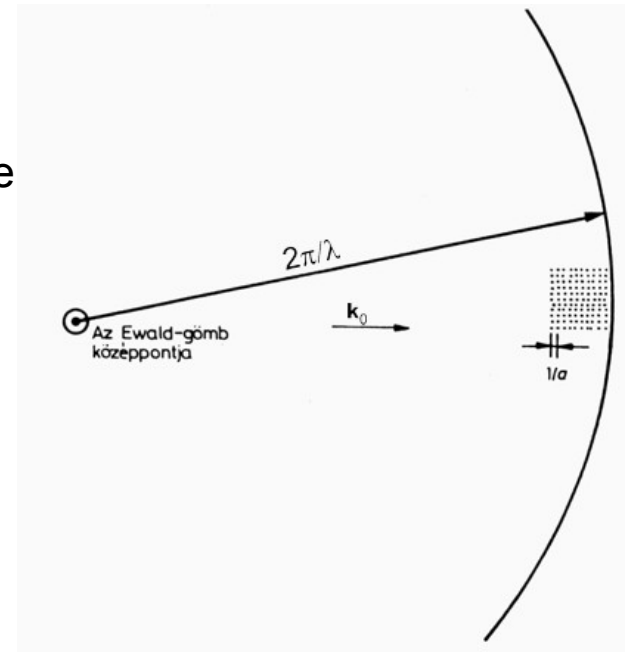
Therefore the **Bragg-angle is small** ($2\theta < (1-2)^\circ$).

2. In the position of the reciprocal lattice, the surface of the Ewald-sphere can be treated as plane, therefore the Bragg-condition is fulfilled simultaneously for several reciprocal lattice points. In the electron diffraction images

we always see the a **plane intersection of the reciprocal lattice**.

3. Since the sample prepared for electron diffraction is thin ($t < 100 \text{ nm}$), the **diffraction spots are broadened in the perpendicular direction to the sample**, and can be imagined as bars instead of spots.

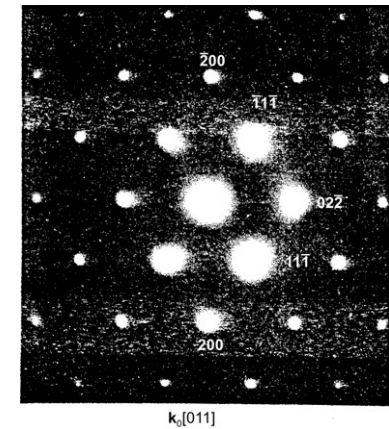
This way several points of the reciprocal lattice can be in diffraction position.



The properties of electron diffraction

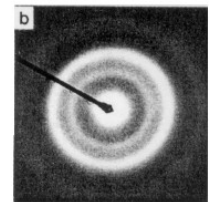
Examples:

Electron diffraction image of (011) plane of an fcc crystal

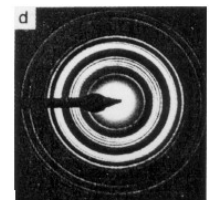


The diffraction image and TEM microscopic image of the same sample:

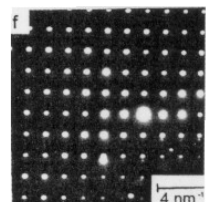
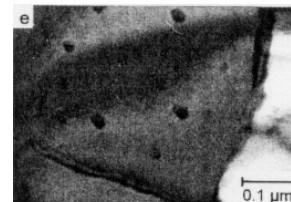
amorphous



polycrystalline



quasi single crystal

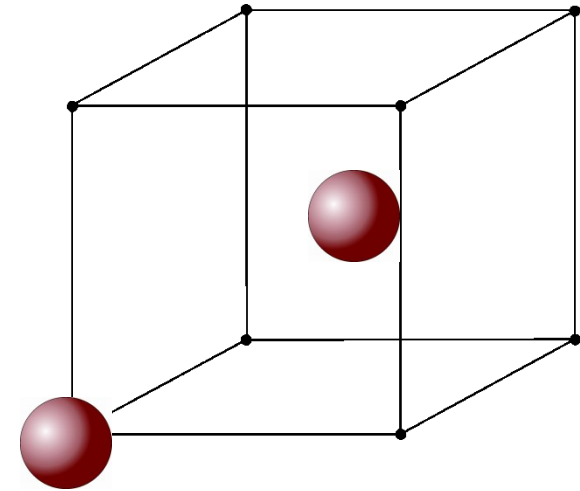


Structure factor

The structure factor calculated in practice:

$$F_{hkl} = \sum_j f_j e^{-i\mathbf{g}\mathbf{r}_j} = \sum_j f_j \exp\{-i2\pi(hx_j + ky_j + lz_j)\}$$

Example for body centred cubic = *bcc*
unit cell: the Bravais-cell contains 2 identical atoms located at the lattice points with $x_1=y_1=z_1=0$ and $x_2=y_2=z_2=1/2$ coordinates.



The structure factor:

$$F_{hkl} = f \left(e^{-2\pi i(0+0+0)} + e^{-\pi i(h+k+l)} \right) = f \left(1 + (-1)^{h+k+l} \right)$$

It can be seen that:

$$F=2f \quad \text{if } h+k+l \text{ is even}$$

$$F=0 \quad \text{if } h+k+l \text{ is odd.}$$

This is the so-called systematic extinction.

In the case of body centered cubic lattice for example the (100) , (111) etc. lines are missing. Elements with such lattice: *Li*, *Na*, *Fe*, *Mo* etc.



Structure factor

In other type cells, other lines are missing because of the systematic extinctions.

It can be seen, that the crystal structure can be identified based on the missing lines.

$$K^2 = g^2 = \frac{4\pi^2}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{N}{a^2}$$

N	<i>hkl</i>	Simple cubic	Body centered cubic	Face centered cubic	Diamond
1	<i>100</i>	x			
2	<i>110</i>	x	x		
3	<i>111</i>	x		x	x
4	<i>200</i>	x	x	x	
5	<i>210</i>	x			
6	<i>211</i>	x	x		
(7)					
8	<i>220</i>	x	x	x	x
9	<i>300, 221</i>	x			
10	<i>310</i>	x	x		
11	<i>311</i>	x		x	x
12	<i>222</i>	x	x	x	
13	<i>320</i>	x			
14	<i>321</i>	x	x		
(15)					
16	<i>400</i>	x	x	x	x
17	<i>410, 322</i>	x			
18	<i>411, 330</i>	x	x		
19	<i>331</i>	x		x	x
20	<i>420</i>	x	x	x	
21	<i>421</i>	x			
22	<i>332</i>	x	x		
(23)					
24	<i>422</i>	x	x	x	x



Structure factor

In the general case, when the atomic positions in the unit cell are not so regular than in the case of *bcc* or *fcc* cell, the structure factor has imaginary part too. This means that the phase is non-zero.

However, the information about phase cannot be extracted from the measurement, since we do not measure the amplitude, but its square of absolute value, the intensity.

During the measurement, the information about phase is lost.

The phase is needed for determining the structure, however we cannot get this information from the measurement. This is called phase-problem.

$$A(\mathbf{k}) = NF_{hkl} = \int_V \rho(\mathbf{r}) e^{-i\mathbf{g}\mathbf{r}} d^3\mathbf{r}$$

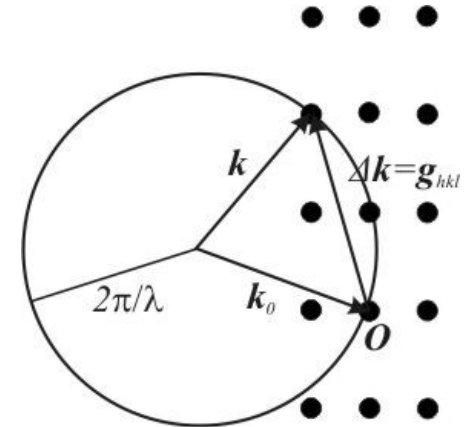
Ewald - construction

Ewald - construction

The geometrical representation of the $\Delta\mathbf{k} = \mathbf{g}$ Bragg – condition is the Ewald-construction.

- The vector $|\mathbf{k}_0| = \frac{2\pi}{\lambda}$ is pointed to the origin of the reciprocal lattice
- We construct a sphere with this radius.

By using the $|\mathbf{k}| = |\mathbf{k}_0|$ condition of the elastic scattering, the possible \mathbf{k} vectors are the radii of the sphere.



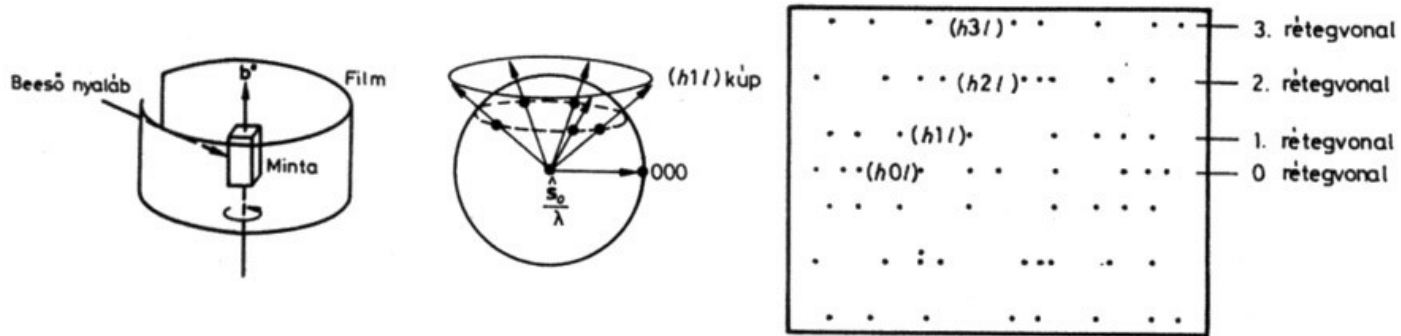
The Bragg condition is not always fulfilled.

The main point of the different experimental methods is to create the geometrical setup where the Bragg condition is fulfilled.

Single crystal diffraction

Rotating crystal diffraction

We use a monochromatic beam

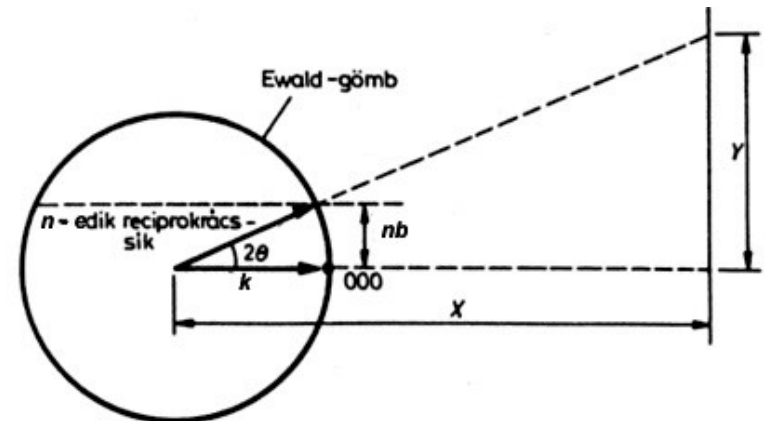


We measure diffraction spots in the directions where a point of the reciprocal lattice intersects the Ewald sphere during the rotation.

If we rotate the crystal around a reciprocal lattice vector, then the obtained diffraction image is composed by diffraction spots forming horizontal (layer) lines.

The length of the reciprocal lattice vector in the direction of the rotation axis can be determined from the distance of the lines by using simple geometrical equations:

$$\frac{nb}{k} = \frac{Y}{\sqrt{X^2 + Y^2}}$$



Single crystal diffraction

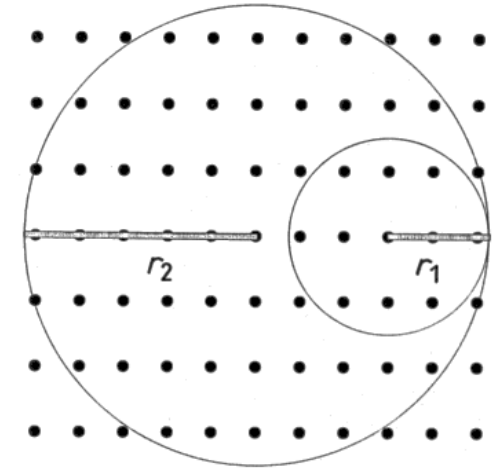
Laue method

A polichromatic X-ray beam is used.

Reciprocal space geometry of the setup.

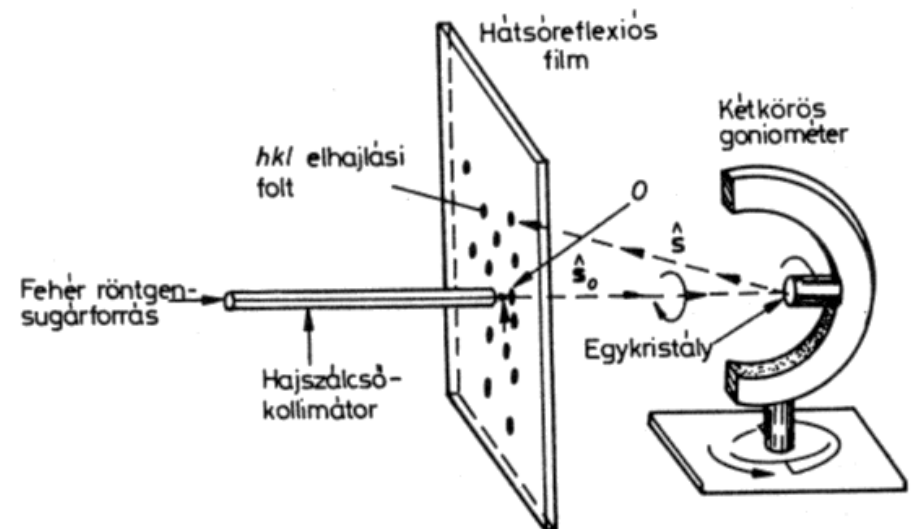
The figure shows the Ewald spheres corresponding to the largest and smallest wavelength of the polichromatic beam.

We obtain diffraction image from the reciprocal lattice points falling between the two spheres.



Backscattering setup in real space.

The method can be used to measure or automatically setup the crystal orientation.

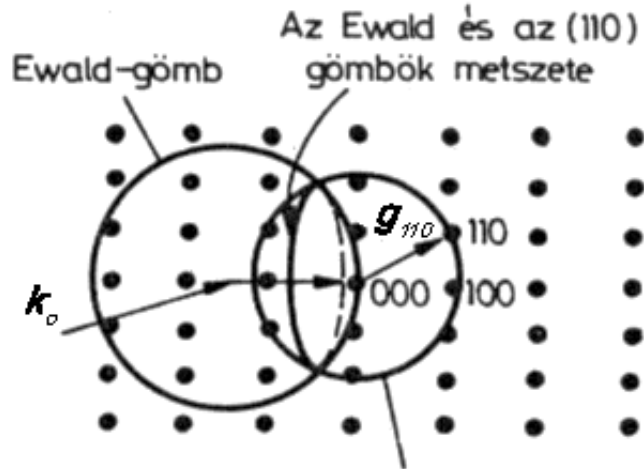


Policrystal diffraction

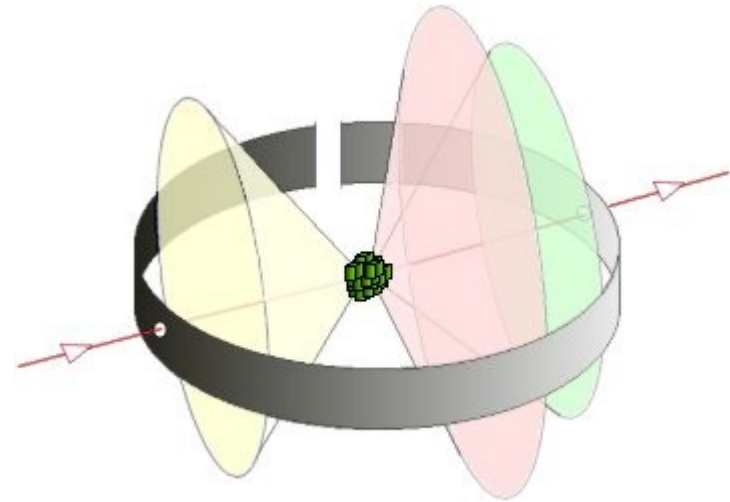
Policrystal diffraction (powder method)

The sample is either a powder of a polycrystal composed by small crystallites.

The beam is monochromatic.



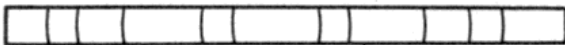
The reflection cone in the reciprocal lattice.



The experimental setup in the real space.

The intersection of the Ewald-sphere and the sphere corresponding to a reciprocal lattice point is a circle.

The cones corresponding to the reciprocal lattice points are intersecting the film in arcs. The angle of the cone is: 4ϑ



We obtain the d_{hkl} distances from the angles by using the Bragg-equation.

The film can be substituted by a detector moving on the same circle (Debye-Scherrer principle).

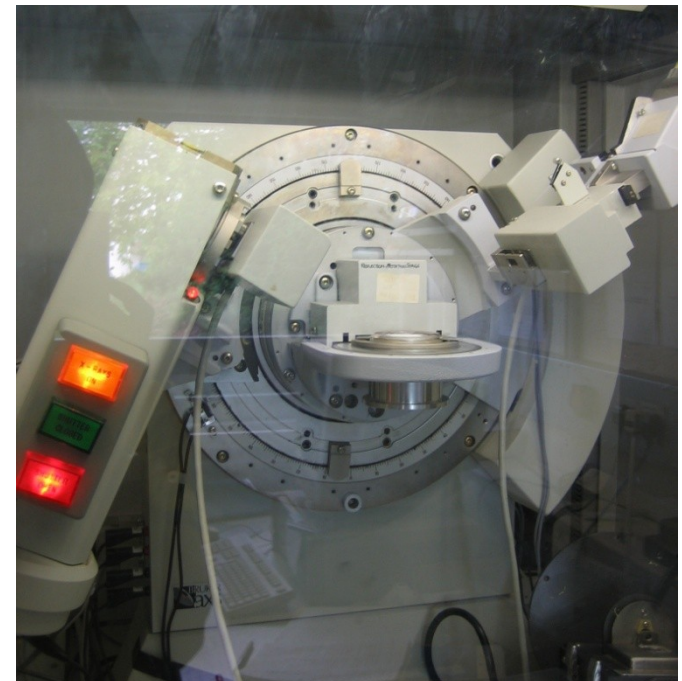
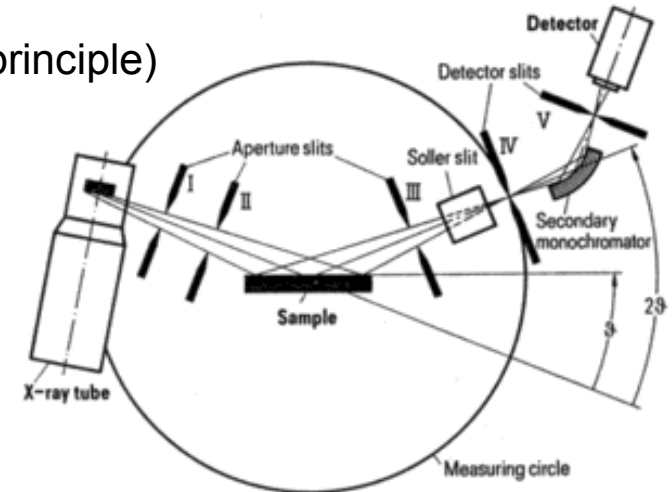
X-ray diffractometers

Bragg–Brentano setup (not based on Debye–Scherrer principle)

- The angle between the surface of the sample and the incoming and diffracted is the same.
- The sample is rotated by angle θ , while the detector is rotated by angle 2θ .
- We always measure the diffracted beam corresponding to a set of planes parallel to the surface of the sample.

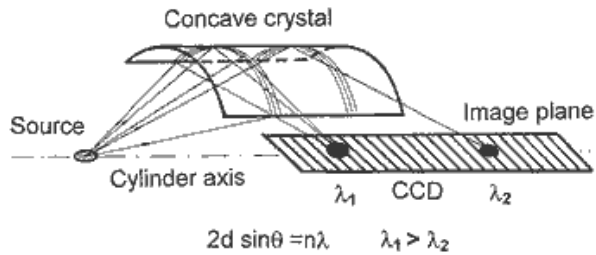
Components:

- X-ray tube
- Soller-slit
- monochromator
- detector

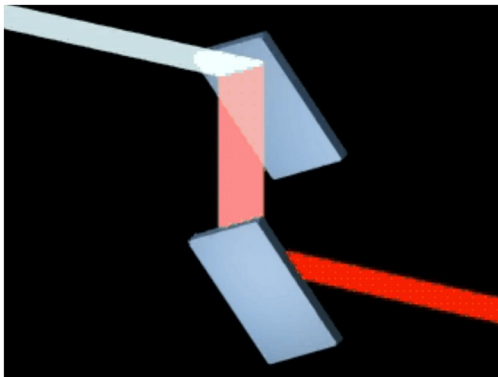


X-ray diffractometers

We can use **monochromators** to select the monochromatic waves which is needed by the experiment.



HOPG=highly oriented pyrolytic graphite



Single crystal (Ge) monochromator



Measuring/creating 1D X-ray patterns

Most of the theory is developed for 1D line profiles, so we need to generate 1D patterns.

X-ray peaks are always 3D (intensity distribution around the reciprocal lattice points).

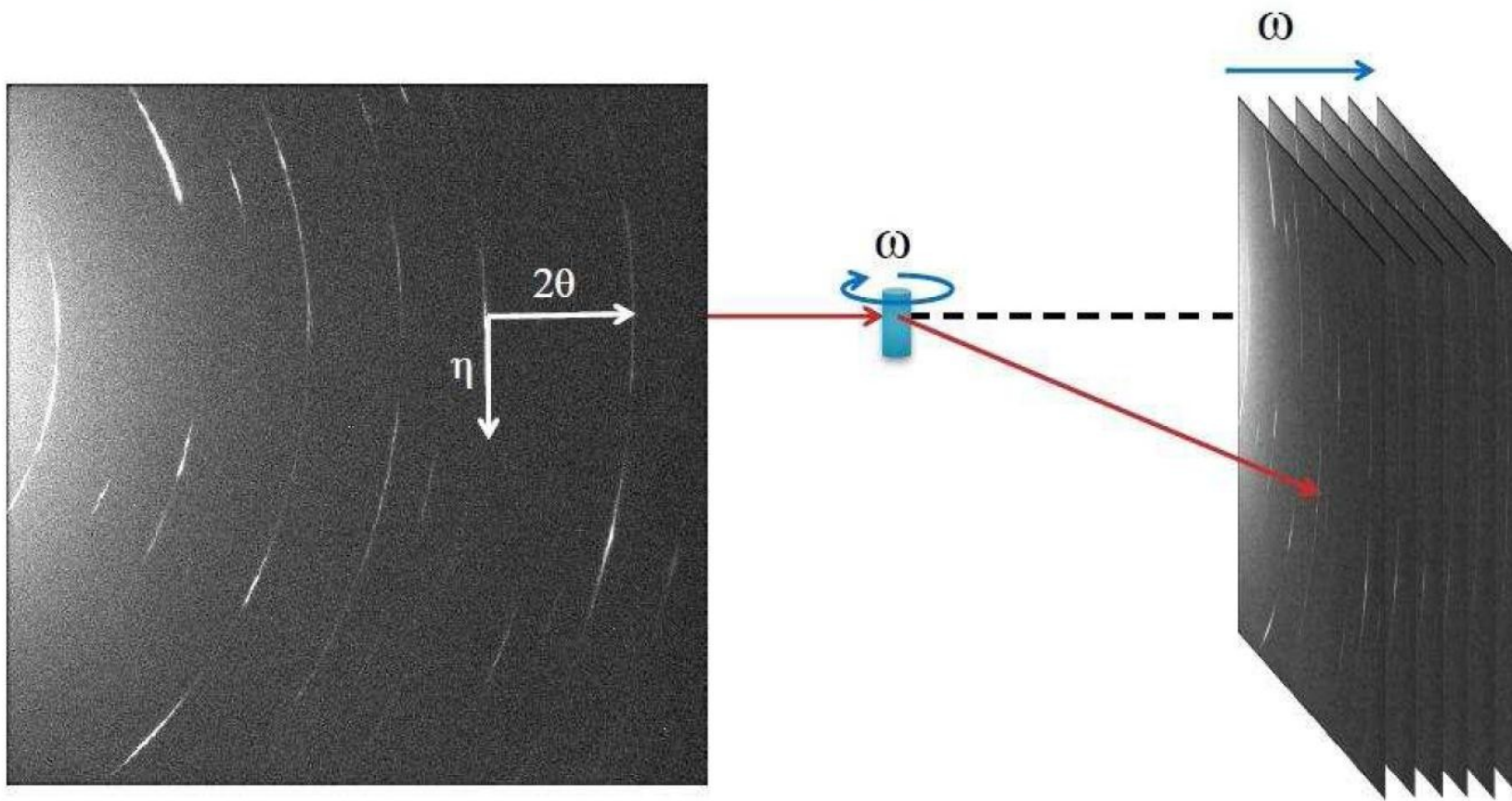
In a powder diffractometer, we are using a point detector which moves around a circle and we are measuring a 1D diffraction pattern.

We can also use a 1D (position sensitive) line detector.

In other cases we are using 2D detectors (solid state detectors, e.g. CCD). If we are also rotating the sample, we can also measure 3D profiles. In order to compare these measurements to the theory, we have to integrate these profiles to 1D.

Measuring/creating 1D X-ray patterns

3D intensity profile ($2\theta, \eta, \omega$) $\xrightarrow{\text{Integration}}$ 1D line profile (2θ)





The position and intensity of the peaks

Based on the Bragg condition, a powder diffraction peak would be a set of Dirac delta functions at the exact Bragg positions.

The position of the peaks is determined by:

- The crystal structure (the crystal symmetry group, the value of lattice constants and the position and type of the unit cell's atoms)
- The crystal defects (causing internal stresses) and external stress can cause lattice parameter change, so line positions can be shifted.

The intensity of the peaks is affected by:

- Basically it depends on the structure factor: $I_g = N^2 F_{hkl}^2$
- The **temperature** of the crystal

The oscillations of the phonons do not broaden the lines, but the intensity becomes lower.

$$I_{hkl} = I_o e^{-\frac{1}{3} \langle u^2 \rangle g^2}$$

$$\frac{1}{3} \langle u^2 \rangle g^2 = 2W$$

The e^{-2W} factor is called **Debye–Waller factor**.

u is the amplitude of the quantum oscillator

Example: in the case of Ni at room temperature and for the (111) reflection $e^{-2W} = 0,88$, in the case of Pb for the (111) reflection $e^{-2W} = 0,52$.

- The multiplicity of the peaks and the Lorentz polarization factor are also affecting the intensity. In the case of **texture** (presence of preferred orientations), intensity is also changed.



Phase identification using databases

The positions and the relative intensities of diffraction peaks in the powder pattern for a randomly orientated polycrystalline material are determined by the crystal structure.

The diffraction pattern is a fingerprint of the crystalline phase.

There are several databases for phase determination. One of the most important databases is the Powder Diffraction Files (ICDD-PDF) which was made by the International Centre for Diffraction Data (ICDD). The PDF-4+ issue released in 2015 contains diffraction data for more than 365,000 crystalline materials.

There are special softwares for phase identification based on these databases.

The most important search criterion is based on the d_{hkl} values of the three strongest peaks in the pattern.

Software for Rigaku SmartLab diffractometer: PDXL (for quantitative phase analysis). It has two main operating modes:

- Reference Intensity Ratio (RIR) method: based on the position and intensities of lines
- Whole Powder Pattern Fitting (WPPF) method: it's a full profile fitting Rietveld method



The Rietveld method

Model based intensity pattern:

$$y(2\theta_i)_{\text{calc}} = B(2\theta_i) + \sum_j I_j P(2\theta_i)_j$$

Squared Residuals:

$$D = \sum_i^N w_i [y(2\theta_i)_{\text{obs}} - y(2\theta_i)_{\text{calc}}]^2$$

Goodness of fit:

$$R_p = \frac{\sum_i^N |y(2\theta_i)_{\text{obs}} - y(2\theta_i)_{\text{calc}}|}{\sum_i^N y(2\theta_i)_{\text{obs}}}$$

$$R_{wp} = \left\{ \frac{\sum_i^N w_i [y(2\theta_i)_{\text{obs}} - y(2\theta_i)_{\text{calc}}]^2}{\sum_i^N w_i y(2\theta_i)_{\text{obs}}^2} \right\}^{1/2}$$

The Rietveld method

Analytical functions used for fitting: Gaussian, Lorentzian, Pearson-VII, Pseudo-Voigt, etc.

Example: split-type Pseudo-Voigt function:

$$P(2\theta)_{p-v} = \frac{(1+A) [\eta_h + (1-\eta_h)\sqrt{\pi \ln 2}]}{\eta_l + (1-\eta_l)\sqrt{\pi \ln 2} + A [\eta_h + (1-\eta_h)\sqrt{\pi \ln 2}]}$$
$$\times \left\{ \eta_l \frac{2}{\pi W} \left[1 + \left(\frac{1+A}{A} \right)^2 \left(\frac{2\theta - T}{W} \right)^2 \right]^{-1} + (1-\eta_l) \frac{2}{W} \sqrt{\frac{\ln 2}{\pi}} \exp \left[- \left(\frac{1+A}{A} \right)^2 \ln 2 \left(\frac{2\theta - T}{W} \right)^2 \right] \right\}$$

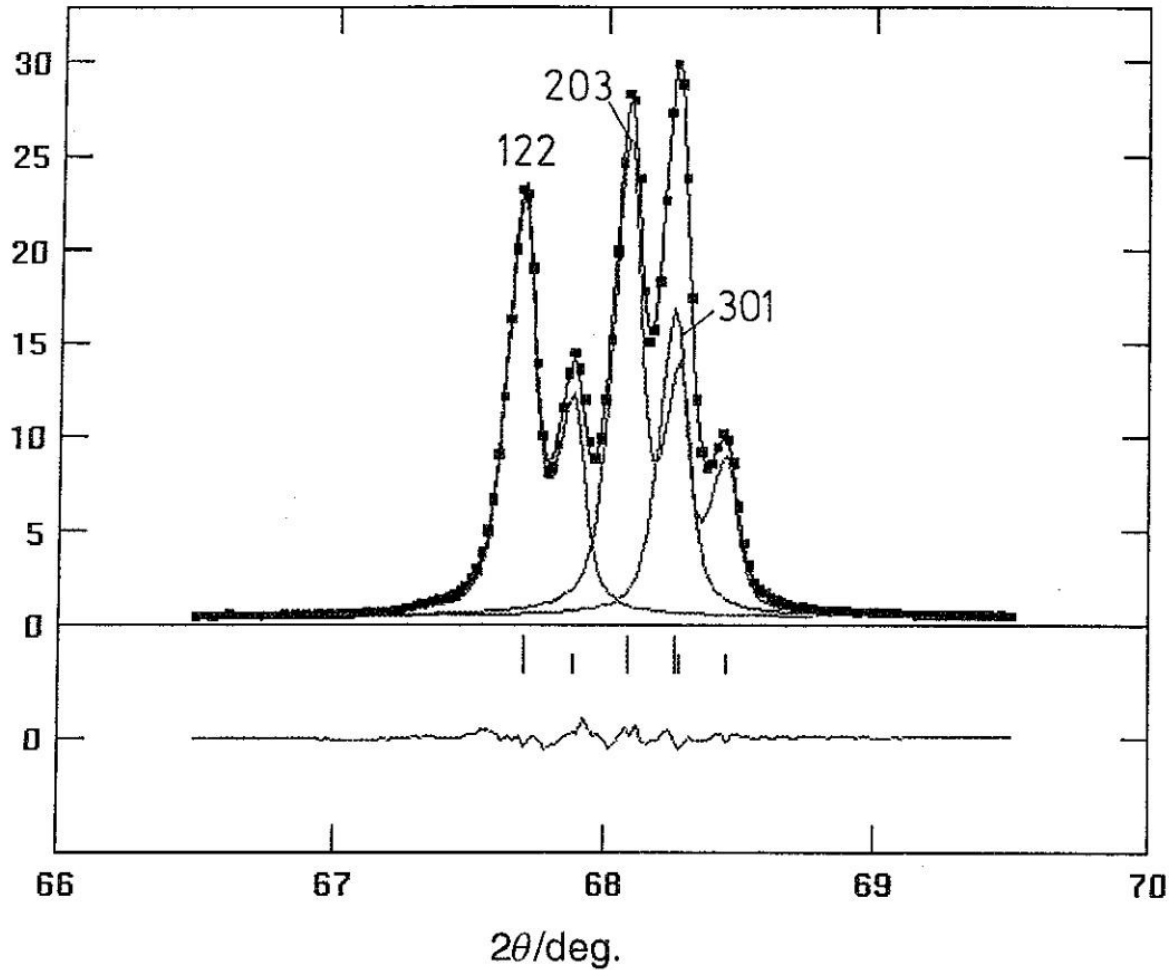
Polynomial function used for background fitting:

$$B(2\theta) = b_1 + b_2 2\theta + b_3 (2\theta)^2$$

The Rietveld method

Example for overlapping peak fitting using analytical functions:

Intensity/ 10^3 counts





The Rietveld method

List of least-squares parameters in WPPF

Global parameters

$b_1, b_2, b_3, b_4, b_5, b_6$	Background level
K	Intensity ratio of $K\alpha_1$ to $K\alpha_2$
e	Correction of the difference $\lambda_2 - \lambda_1$ (Å)
t_1, t_2, t_3	Peak shift correction (2θ)

Parameters for each component

I_j	Integrated intensity of the j th peak (counts)
$a, b, c, \alpha, \beta, \gamma$	Unit-cell parameters
w_1, w_2, w_3	Full width at half-maximum (FWHM) (2θ)
a_1, a_2, a_3	Peak asymmetry
$r_{l1}, r_{l2}, r_{l3};$ η_{l1}, η_{l2}	Decay rate of profile intensity at the low angle side; or η parameter at the low angle side
$r_{h1}, r_{h2}, r_{h3};$ η_{h1}, η_{h2}	Decay rate of profile intensity at the high angle side; or η parameter at the high angle side



The broadening of the peaks

Based on the Bragg condition, a powder diffraction peak would be a Dirac delta function.

The width and shape of the line profiles is affected by:

- **Natural** line width
- Diffraction on the slits of the **machine**
- The line broadening effect of **detectors**

- The sample **size**
- $$\Delta\theta = \frac{\lambda}{L \cos \vartheta}$$

This equation is valid between $\sim 10 \text{ nm} - 1 \mu\text{m}$

- The **crystal defects**

The lattice distortions caused by crystal defects are also present in the reciprocal lattice, this means that the reciprocal lattice points will be broadened and the condition of diffraction is satisfied in a finite volume near the ideal reciprocal lattice points.