



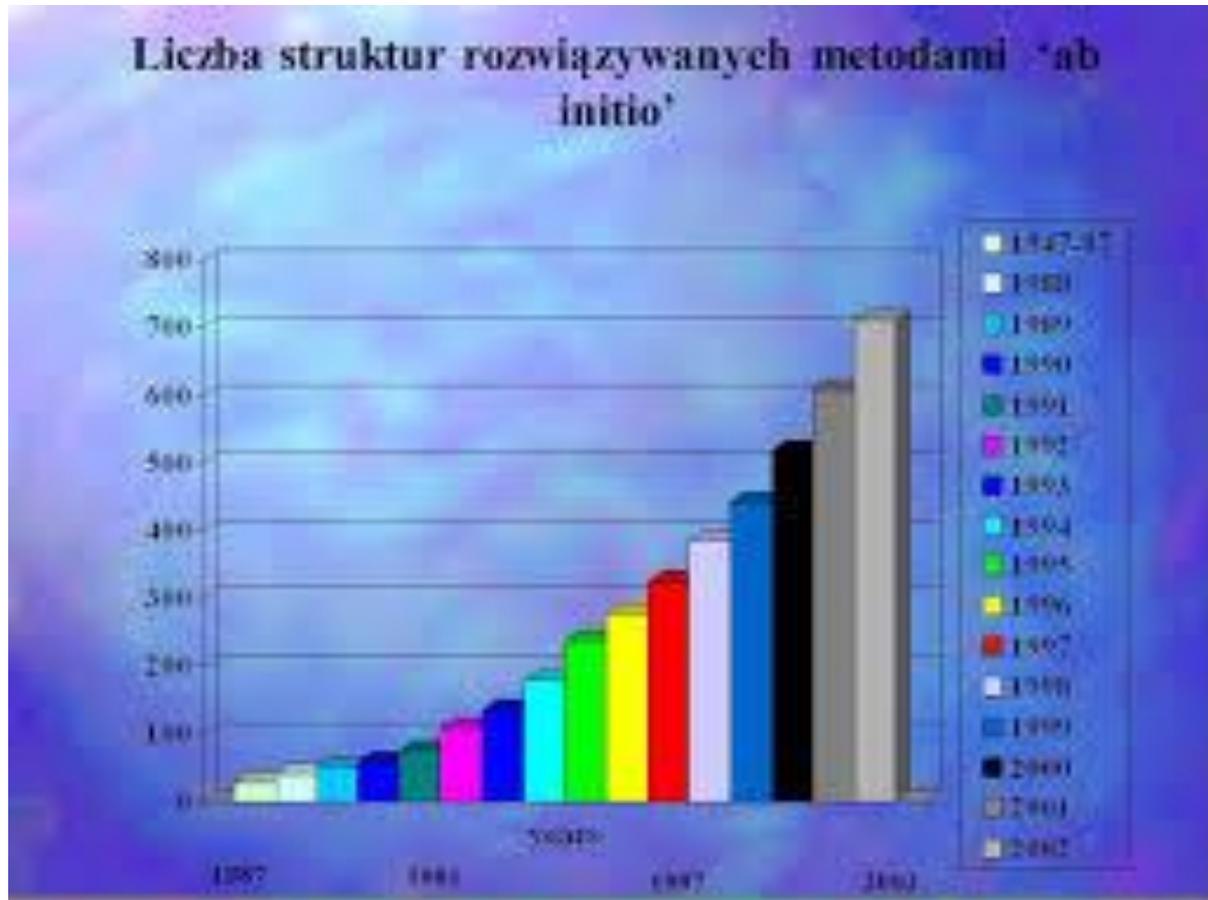
Characteristics of materials structure by the X-ray diffraction XII Powder diffraction

The intensive development of solid state chemistry and material engineering necessitates structural analysis based on single crystal diffraction. In the case of many solid materials, crystal breeding is not easy or sometimes impossible. In this case, and also in cases where the defects of the crystalline structure cannot be removed, the crystallographic description of the phases was often omitted. However, advances in diffraction powder techniques and computer techniques have significantly improved the situation in this area. Rietveld's work was of key importance here.

Undoubtedly, it is important to study solids that do not form large crystals, but also all the materials developed with the help of new technologies - thin layers, nanomaterials, natural materials such as clays, rocks, etc. - in order to find out more about them.



Since the introduction of Rietveld's method, tens of thousands of structures have been solved ab-initio based on diffraction data from powder samples.



Limitations on powder methods

Materials with specific properties (functional materials) are often developed from low symmetrical phases, which are therefore anisotropic. Optimization of their properties depends on the development of processes that maintain microscopic anisotropy at the macroscopic level. Optimisation techniques are complex - complex deformation patterns, magnetic or electric fields, thermal gradients, etc.

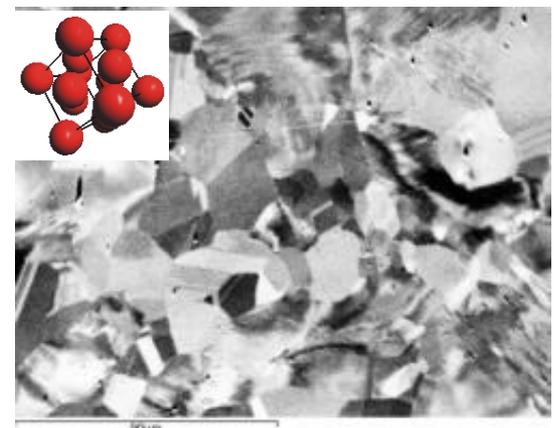
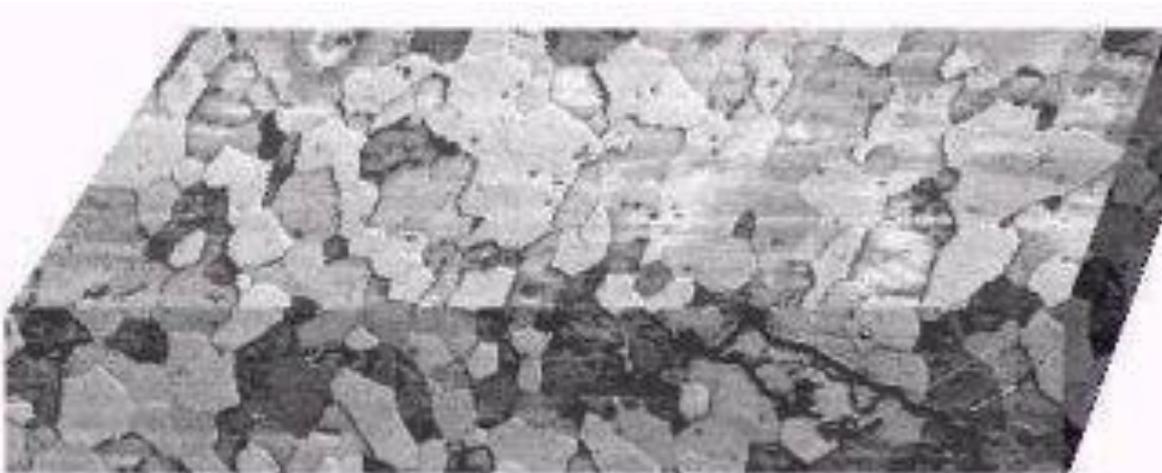
Preparing a sample is difficult and time-consuming. Non-destructive characterisation is often required. And the technique of characterization (like Rietveld's method) requires the powdering of samples. This is often unacceptable, for the reasons described above and for rare samples such as fossils, meteorites and others.

In all the above cases it becomes necessary to combine the different types of analysis.

Crystalline, grain, polycrystalline and powder

A polycrystalline material is a solid divided into very small homogeneous elementary particles (monocrystals) called crystallites. Crystallites are three-dimensional domains that propagate incident X-rays (electron or neutron) in a consistent (coherent) manner.

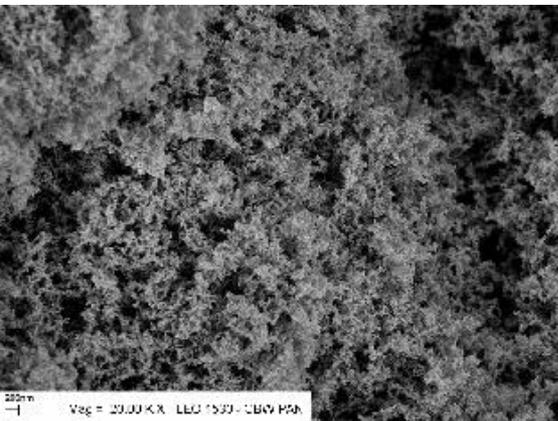
Crystallites are sometimes called in crystallization "coherent domains". Grains (such as those observable under the microscope, for example) may consist of one or more crystallites. A single crystal (monocrystal) consists of only one crystal and a polycrystal consists of a group of crystals.





Powder is a aggregation of crystallites (metal, ceramics, polymers or other materials) of different quantity, shape, size and crystalline state. So it is a polycrystal.

The ideal powder or 'standard powder' for diffraction testing consists of a large number (tens of thousands at least) of crystallites in an excellent crystalline state (without faults in the crystalline lattice) which exhibit a very narrow range of variations in size and shape. In addition, "standard powder" crystallites are randomly oriented (without crystallographic texture). Under these conditions, regardless of the angle at which the beam of radiation falls, there is always the same proportion of volume of crystallites oriented in such a way that they comply with the Bragg's law.



A spongy microstructure of nanocrystalline SiC obtained by decomposition of organosilicon compounds and annealing.

Monochromator

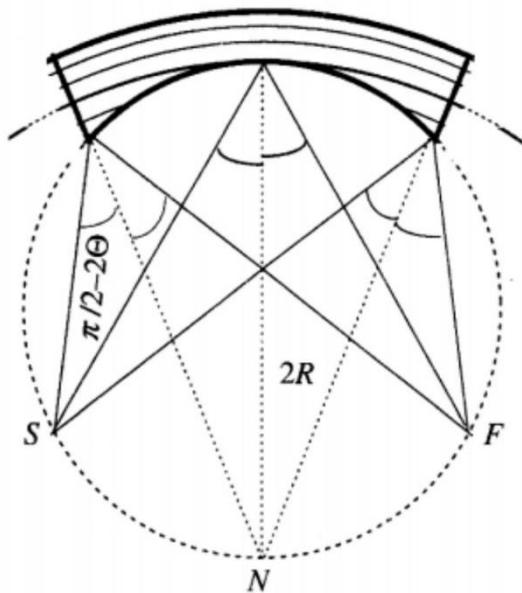
The direct application of Bragg's law allows you to select a stream of photons with a specific (discrete) wavelength from among the components of the polychromatic radiation source of radiation. **It can be shown that a monocrystal with defined interplanar distances d_{hkl} at which polychromatic radiation is emitted at an angle of θ 'emits a beam deflected (at an angle of 2θ to the incident beam) which will consist only of photons with a wavelength of λ for which Bragg's right is fulfilled.**

Such a crystal is a monochromator. Of course, the resolution of the monochromator depends on the quality of the crystal. In practice, the acceptable wavelength range $\Delta\lambda$ is selected to allow the use of a monochromator in measurements.



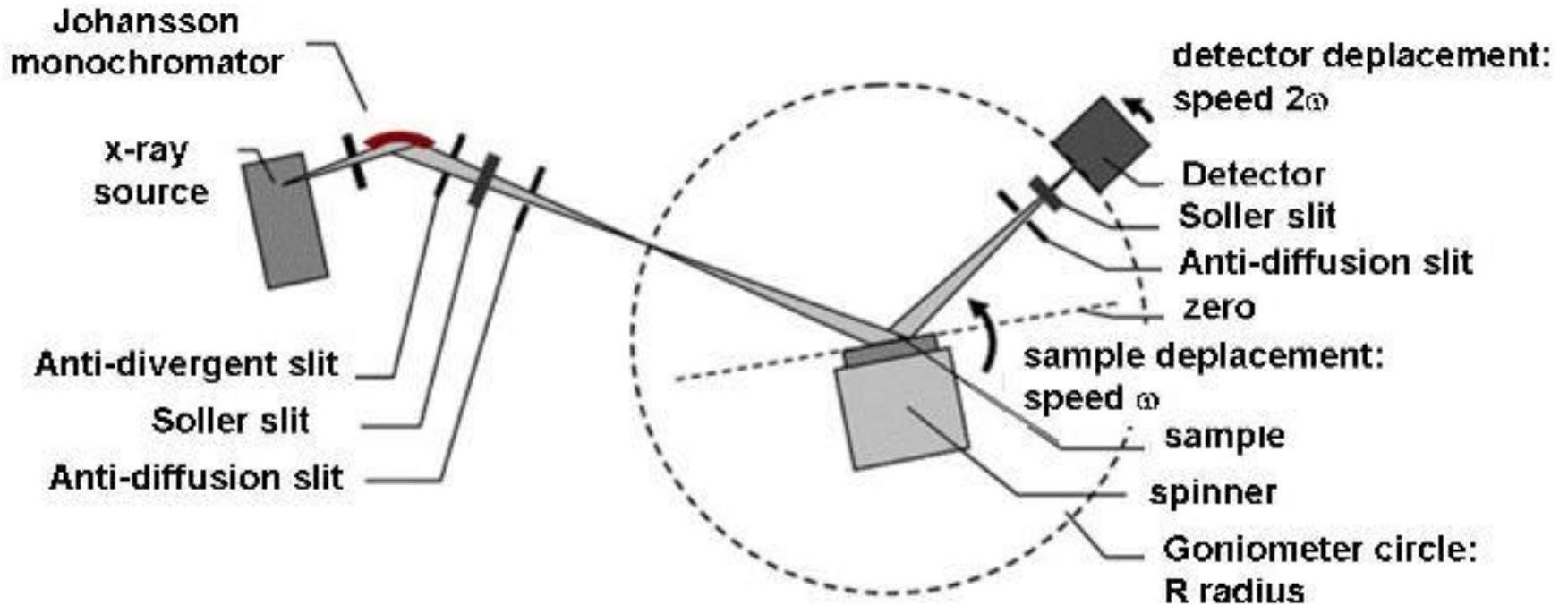
Monochromator

Johansson Geometry



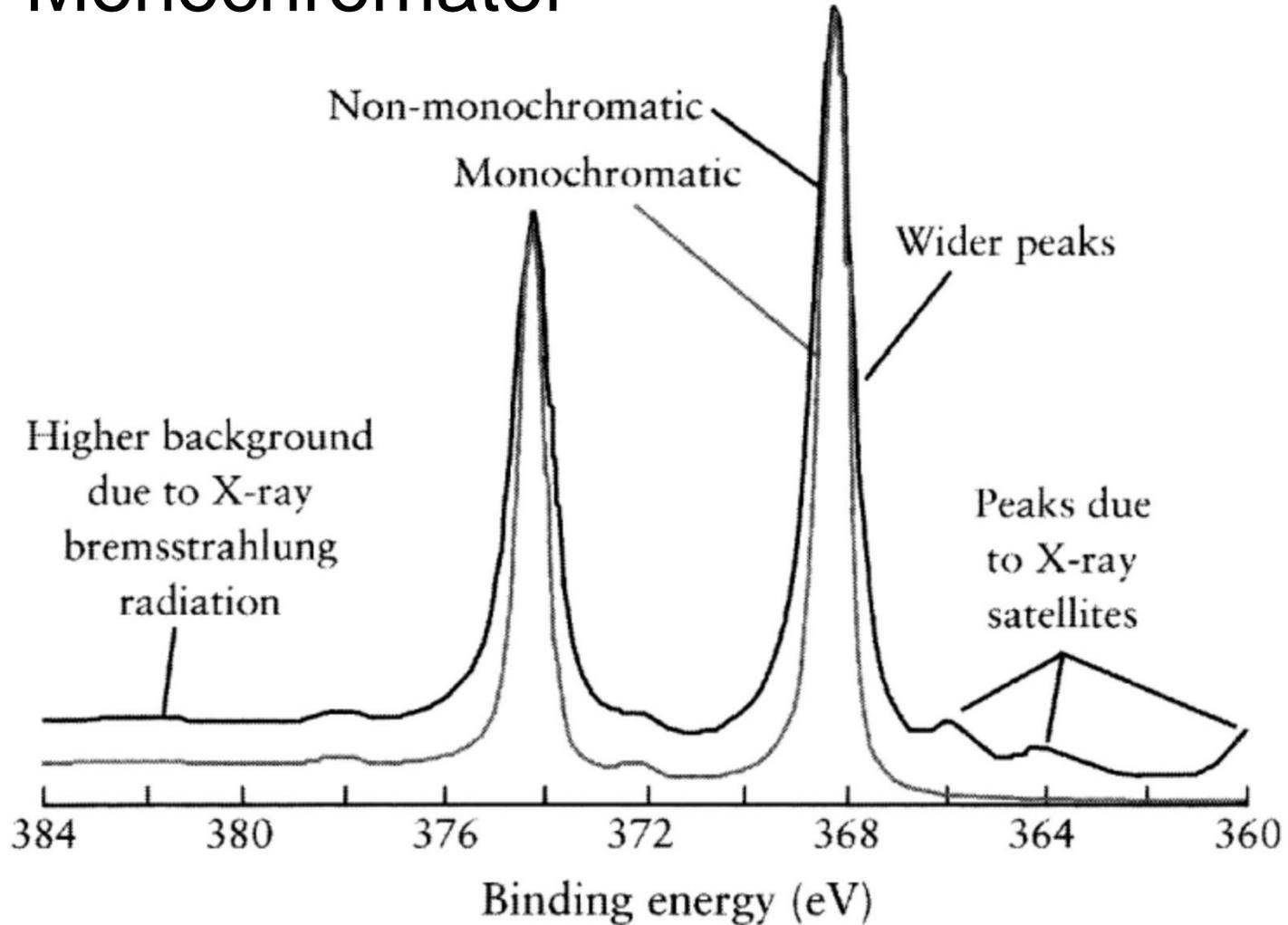
- Source, crystal and sample on a Rowland sphere
- Bending radius $R_B = 2R_R$
- Grounding radius $R_G = R_R$
- Focusing on sample

A design for bent crystal monochromators in which spacing is constant along any circular arc terminating at the two foci and with equally spaced Bragg planes curved about only one axis.





Monochromator



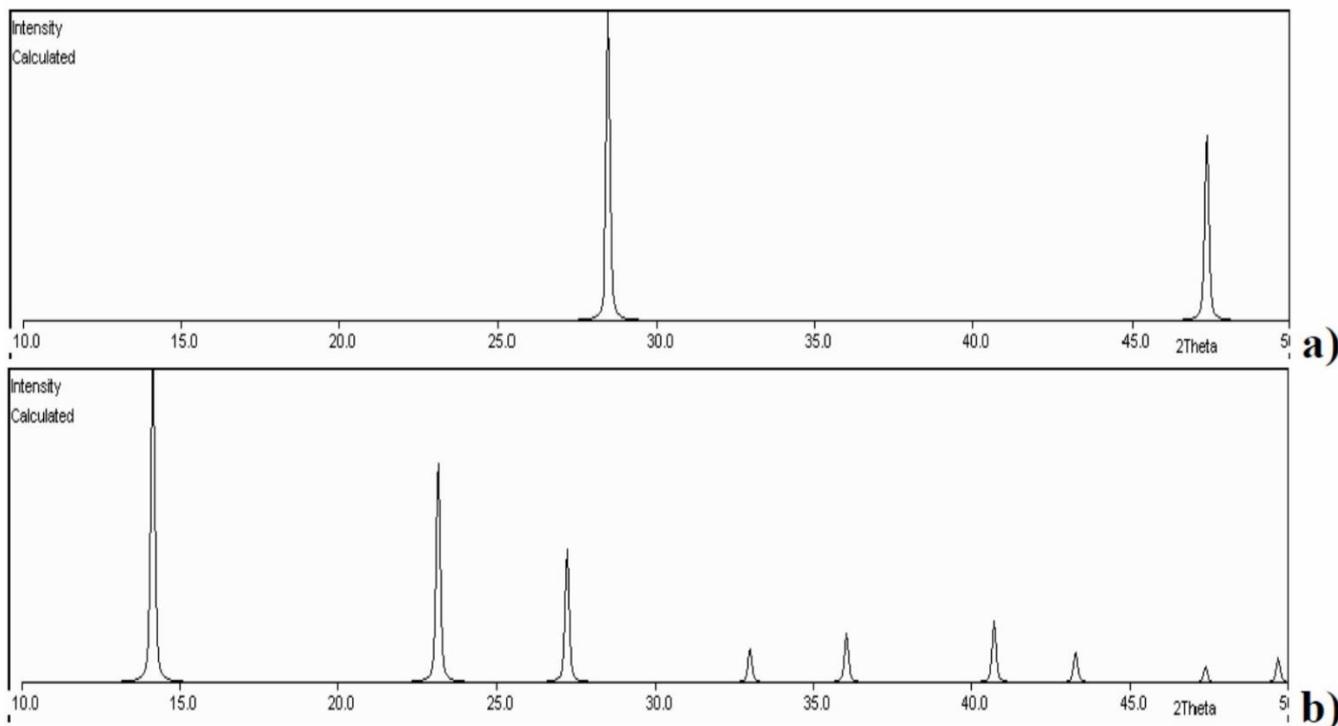
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Harmonic radiation components

Even for a perfect monocrystal, the monochromator can select different radiation components, which nevertheless fulfil the Bragg equation. Because any λ/n radiation will also comply with Bragg's law. These radiation components of $\lambda/2$, $\lambda/3$... wavelength are called harmonics.



Simulated diffraction diagrams $\lambda/2$ for silicon powder, within a range of $10^\circ \leq 2\theta \leq 50^\circ$. The diagram with the nominal wavelength (1,5406 Å) contains only the lines of 111 and 220, and for $\lambda/2$ (0,7703 Å) all 11 lines are shown (i.e. 111, 220, 311, 222, 400, 331, 422, 511, 333, 440, 531).

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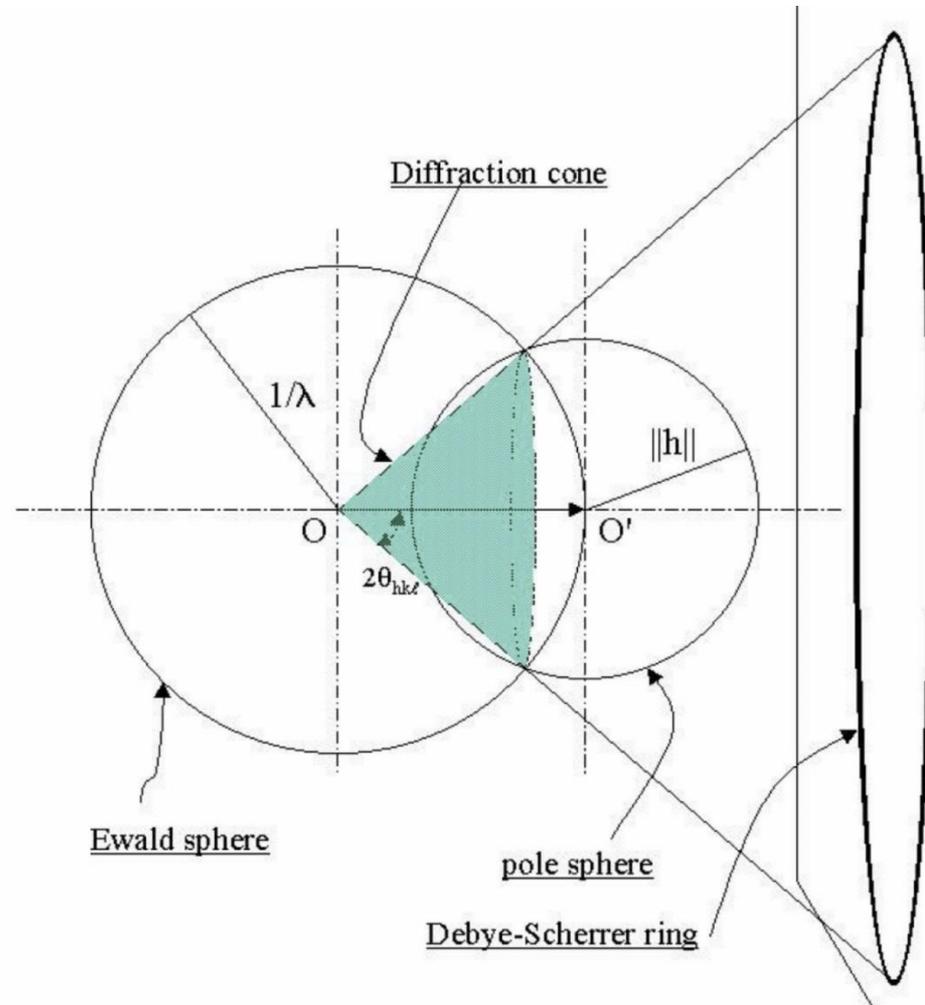


Using a classic X-ray generator, there is a strong emission of discrete transition metal lines (e.g. Cu $K\alpha$ line), for which a monochromator is justified. Harmonic e.g. $\lambda/2$ corresponds to a relatively low "bremstralung", which makes their intensity weak compared to the main selected radiation. However, in some cases, such as thin layers deposited on single crystalline substrates, the harmonic diffraction lines are sometimes larger than the peaks on the layer. Translated with www.DeepL.com/Translator

When using synchrotron X-rays or thermal neutrons, the incident spectrum is continuous and the harmonic effect may be negligible.

In the practice of powder diffraction, the harmonic lines are barely visible. In the case of large monocrystals only lines from $\lambda/2$ are detected.

Geometric conditions of diffraction, Ewald sphere





Imperfections of the powder method

Interpretation of diffractive images based only on their geometry is usually too simplistic to describe the phenomenon correctly. This would require three objectives to be met:

- (a) the dimensions of crystals may be considered infinite in comparison with typical distances between diffuser planes,
- (b) perfect three-dimensional arrangement of the powder sample space,
- (c) the point source provides monochromatic radiation of λ wavelength, the dimensions of the sample are insignificant and the experimental configuration shows no aberration.

When these three conditions are met, the intensities deflected in the planes (hkl) can be represented by Dirac distributions in $2\theta_{hkl}$ positions.

In fact, condition (c) is never fulfilled and conditions (a) and (b) may not be fulfilled in case of imperfections of the sample crystals.

Therefore, there is a widening of diffraction lines because of this:

Condition (a) is not met as soon as the crystallite sizes are small enough (typically less than 300 nm for typical laboratory resolutions). The boundaries of 'coherent domains' are always related to network defects (superficial, alignment errors, relocations, twins, etc.). **Scherrer showed that the size of the crystals is inversely proportional to the width of the reflex.**

Condition (b) is no longer met when the crystalline samples have crystalline lattice defects such as micro deformations inducing internal micro-strains, stoichiometric heterogeneities, dislocations, surface and point defects, alignment errors...

Condition (c) is never fulfilled, because each device has its own characteristics (and imperfections). These have an impact on the shape, width and position of the diffraction lines. The resulting peak extension is represented by either the $g(x)$ function or the "instrument resolution function", x being the variable appropriate for the measurement type.



Diffraction line profile

Uncoordinated powder diffraction consists of a combination of intensities measured at multiple angles within a specified range. The first task of the experimenter is to reduce the data to sets that can be analysed using the knowledge available on the diffraction and crystallographic parameters (parameters of the elementary cell, distances and angles, crystalline sizes, phase fractions, ...). This analysis is not possible without a prior knowledge of the participation of each of the above mentioned effects in the $h(x)$ profile. $h(x)$ depends on two relationships, defined by the sample as $f(x)$ for conditions (a) and (b) and $g(x)$ specified by the apparatus, condition (c).

The components of the sample and apparatus are convoluted in the observed profile $h(x)$, [Jones 1938]:

$$h(x) = f(x) \otimes g(x) = \int_{-\infty}^{+\infty} f(y)g(x - y)dy$$

where x and y - the variables defining the angular position of each measured profile point, having the same dimensions as 2θ or as reciprocal lattice variables.



Genesis $g(x)$

The imperfections of the apparatus depend on the technique used (Bragg-Brentano, Guinier, ...). The resolution function - $g(x)$ - of the instrument is the result of a convolution of various imperfections that "contribute" to the measured profile, including purely geometric (beam divergence, optical misalignment, deviation from the point of source, width of the slot collimator, ...) or physical imperfections such as the width of the emitted spectrum and the distribution of incident radiation [Alexander].

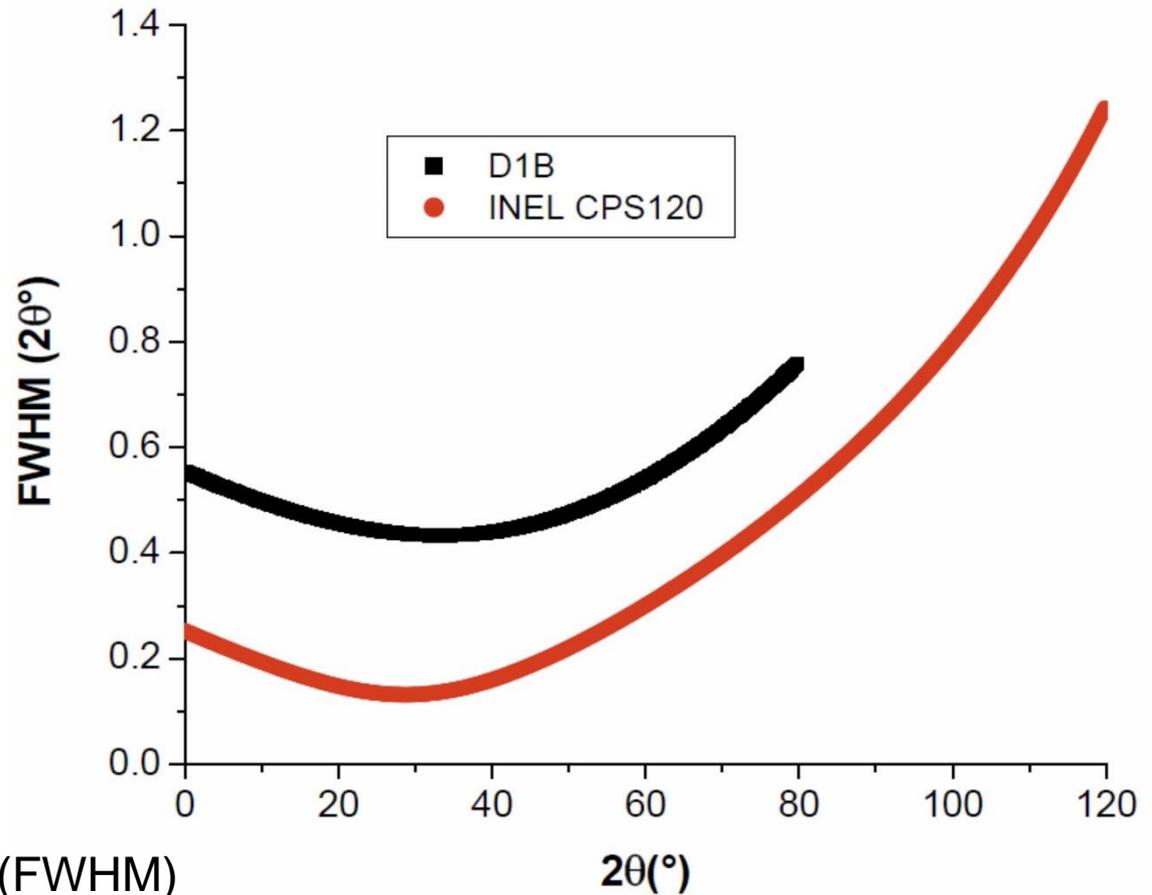
It is interesting that $g(x)$ is dependent on the variable used in the experiment (Bragg's angle - radiation energy versus wavelength).

Compare also: Energy dispersion spectrometer (EDS) with wavelength spectrometer (WDS)



The function of $g(x)$ can be determined experimentally by measuring standard powder samples. An example of the camera resolution function is shown on the instrument D1B (neutron diffraction) and on the INEL CPS120 (X-ray diffraction).

Camera resolution curves for neutrons (D1B calcite rostrum sample) and for X-rays (INEL CPS120 standard LaB6 powder sample)



Full-width at half-maximum H (FWHM)

Genesis $f(x)$

Using a high-resolution diffractometer, a deviation of $h(x)$ from $g(x)$ can be observed due to the microstructure of the sample.

The broadening of diffraction lines comes essentially from the following two effects:

(1) Enlargement by finite size of crystals. Small crystallites participate in diffraction lines which are no longer Dirac's character but have widths and shapes depending on the size and shape of the crystallites in the direction of h . Simple analysis of this extension was given by Scherrer:

$$\Delta(2\theta) = \frac{K\lambda}{T \cos \theta}$$

where T is the mean thickness of the diffracting crystals in the direction h , determined by an angle θ , and K is the dimensionless Scherrer constant, close to unity, which depends on the shape of the crystals.

Genesis $f(x)$

2) broadening of diffraction lines due to microcrystalline lattice distortions. Such an broadening is caused by heterogeneous changes in the distance between the planes of crystals d_{hkl} , which may be produced by external stresses, defects of the crystal lattice (e.g. dislocations) or local variations in composition.

It can be shown that:

$$\Delta(2\theta) = 4 \varepsilon \tan\theta$$

where ε is the relative lattice deflection: $\varepsilon = \Delta d_{hkl} / d_{hkl}$.

Diffraction profile parameters

Parameters used to determine peak profiles:

- (i) the positions of the different peaks,
- (ii) angular or energetic dispersion (FWHM),
- (iii) the area beneath the profile (intensity),
- (iiii) shape.

Sometimes, a parameter is also used to determine the centre of gravity of the diffraction profile.

Modelling of diffraction peaks

The main problem to be solved for powder diffraction is the overlapping of the peaks [Smith, Wagner]. An increase in the density of the diffraction peaks with an increase of 2θ results in their strong superimposition, in particular for low symmetry of the crystal and low instrumental resolutions. This causes information to be 'jammed' for large values of 2θ , and the diagram becomes unusable. A limit value of 2θ above which a diagram becomes useless is never strictly defined.

The problem of peak superposition requires appropriate optimisation of the equipment as well as the development of "mathematical/computer" skills.

Modelling of powder diffraction

Depending on the information and a priori knowledge of the material you are looking for, you can use one of two methods.

Method I

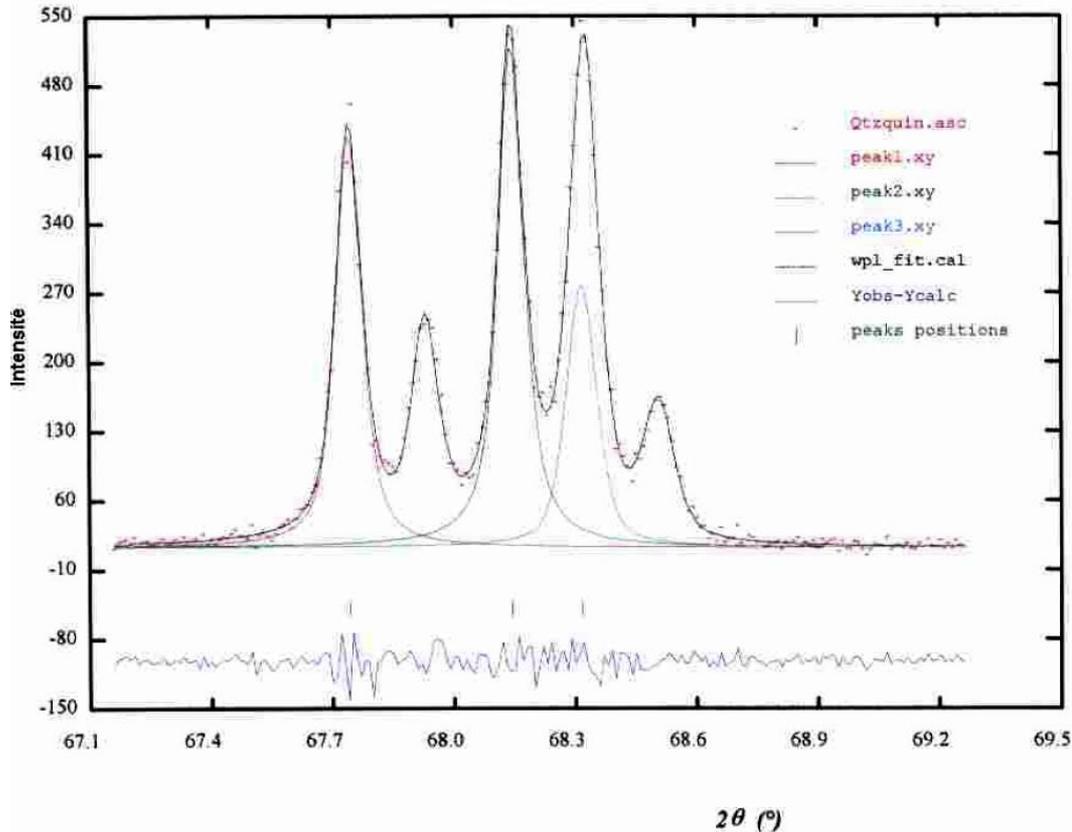
The principle of this method, called direct integration, is to adapt the analytical function to each peak, unless the individual components overlap too much. This method is used when information of a crystallographic nature is required, which can be obtained from the position of a limited number of peaks - we do not need the whole diagram for the analysis. In this approach, the diagram can be divided into several individually treated parts. The approximate peak positions and widths are first read visually from the graphical interface and then adjusted by the method of least squares by minimising M:

$$M = \sum_i \frac{1}{y_{ic}} (y_{io} - y_{ic})^2$$

where y_{io} and y_{ic} are appropriately measured and calculated intensities at the point i , which describe the peak.

This method is limited by the choice of the mathematical function used to describe individual profiles. There is a set of functions that can be used to describe peak profiles. The simplest are the Gauss and Lorentz functions [Snyder, Suorti].

It is important to give physical meaning to the parameters of the function. The effectiveness of the method is limited by the rapid overlapping of neighbouring peaks.



Application of the least squares method
for quartz powder

2θ (°)



Functions describing the peak shape

Gauss function:

$$G(2\theta_i) = \frac{2I_0 \sqrt{\ln 2}}{H_k \sqrt{\pi}} \exp\left(\frac{-4 \ln 2 (2\theta_i - 2\theta_k)^2}{H_k^2}\right)$$

Where:

$$H_k = \sqrt{U \tan^2 \theta_k + V \tan \theta_k + W + P / \cos^2 \theta_k}$$

where: I_0 is the integrated peak rate, 2θ is the angular value of each point of the I-profile, $2\theta_k$ is the angular value expected for each reflex k , H_k is the FWHM for each k -reflex. U , V , W and P are the function parameters of the diffractometer's resolution and are subject to adjustment.



Lorentz function

$$L(2\theta_i) = \frac{I_0 \sqrt{C}}{\pi H_k} \left(\frac{1}{1 + C \left(\frac{2\theta_i - 2\theta_k}{H_k} \right)^2} \right)^m$$

with $C = 4(2^{1/m} - 1)$

m changes from 0 to infinity.

m = 1 gives a "pure" Lorentzian function.

m = 1.5 gives the "indirect" Lorentz function [Malmros et Thomas].

m = 2.0 gives the "modified" Lorentz function [Sonneveld et Visser].

Fitting parameters: U, V, W, P, m



Thank you