X-Ray Analytical Methods

The use of X-ray methods in the field of materials analysis covers many techniques based on the scatter, emission and absorption properties of X-radiation, the two most common are X-ray fluorescence (XRF) spectrometry and X-ray powder diffractometry (XRD).

X-ray fluorescence spectrometers/ spectrographs(XRFS)-

When a sample of material is bombarded with energetic radiation (X-rays, γ-rays, electrons, protons, etc.) vacancies may arise from the removal of inner orbital electrons. One of the processes by which the atom regains stability is by transference of electrons from outer to inner electron shells. Each of these transitions is accompanied by the emission of an X-ray photon having an energy equal to the energy difference between the two states. The X-ray emission wavelengths are characteristic of the atom in question and there is a simple relationship (Moseley's law) between the wavelength of the emission line and the atomic number of the atom. Thus when a sample is made up of many different types of atoms, each atom will produce a series of wavelengths, and all of the contributions add up to become the total X-ray emission from the sample.

Thus XRF is a technique which utilizes the diffracting power of a single crystal, or the proportional characteristics of a photon detector, to separate the polychromatic beam of radiation from the sample into separate wavelengths, thus allowing qualitative and quantitative elemental measurements to be made.

Powder X-Ray Diffractometer

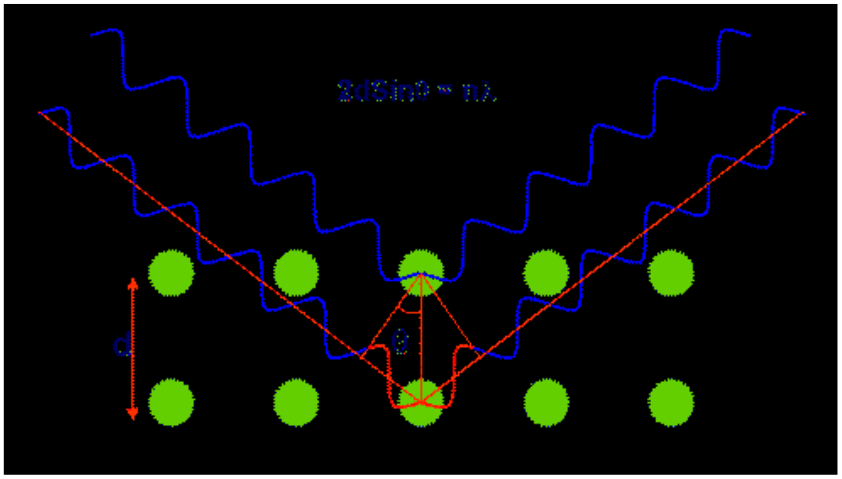
A beam of monochromatic radiation may also be scattered when X-ray photons collide with atomic electrons. Where the scattered wavelengths interfere with one another diffraction of X-rays occurs. All substances are built up of individual atoms and nearly all substances have some degree of order of periodicity in the arrangement of these atoms. It is the scattering from these periodic arrays that leads to the diffraction effect, and there is a simple relationship (Bragg's law) between the scattering angle, the wavelength of the radiation and the spacing between the planes of atoms.

Since the distances between the atomic planes are dependent on the size and distribution of atoms – i.e. the structure of the material, X-Ray Diffraction (XRD) can be used for qualitative and quantitative phase identification.

Bragg's Law

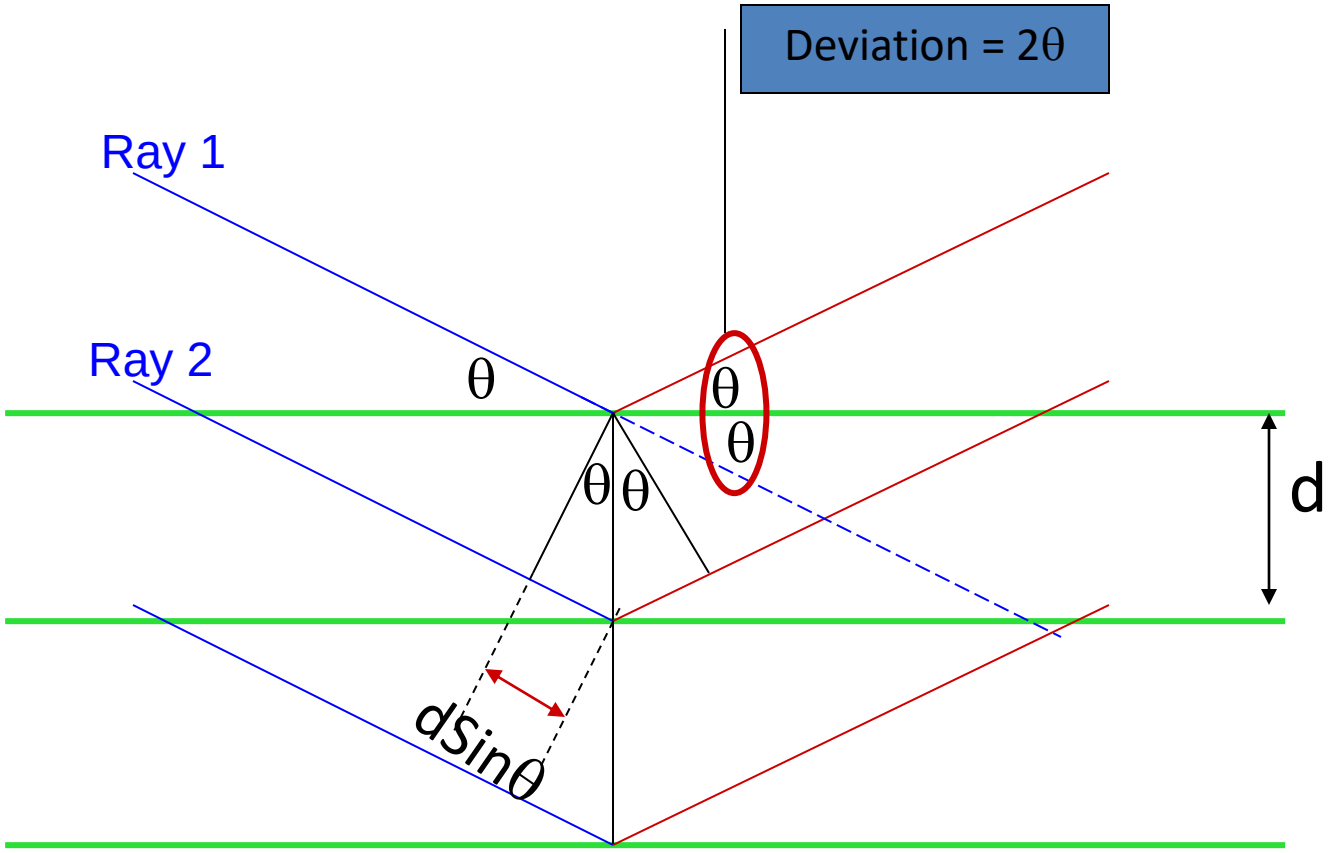
Sir William Henry Bragg (1862-1942)

William Lawrence Bragg (1890-1971)



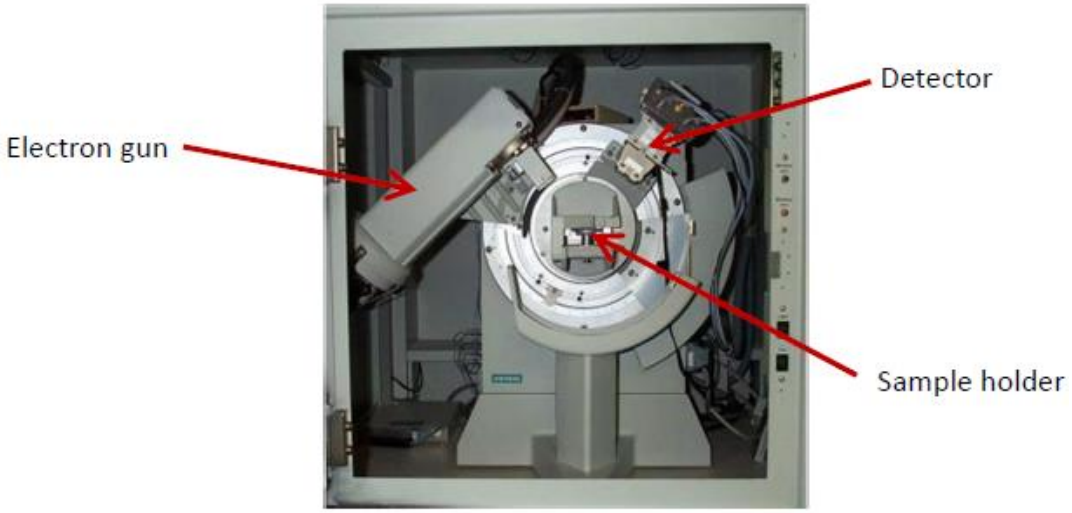
- The father and son team of Sir William Henry and William Lawrence Bragg were awarded the Nobel prize for physics *"for their services in the analysis of crystal structure by means of Xrays" in 1915.*
- Bragg's law was an extremely important discovery and formed the basis for the whole of what is now known as crystallography. This technique is one of the most widely used structural analysis techniques and plays a major role in fields as diverse as structural biology and materials science.

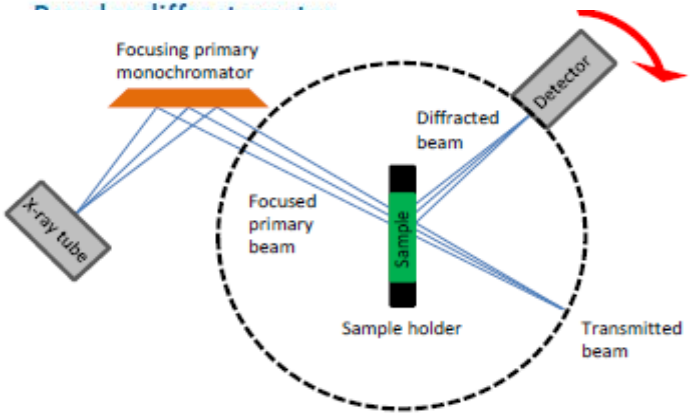
BRAGG's EQUATION/LAW

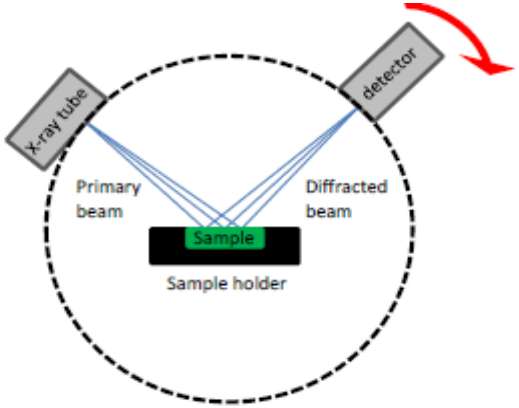


- The path difference between ray 1 and ray 2 = 2d Sinθ
- For constructive interference: nλ = 2d Sinθ

How do we measure the X-rav diffraction pattern of a solid?







Classic **transmission** geometry

(**Debye-Scherrer** geometry)

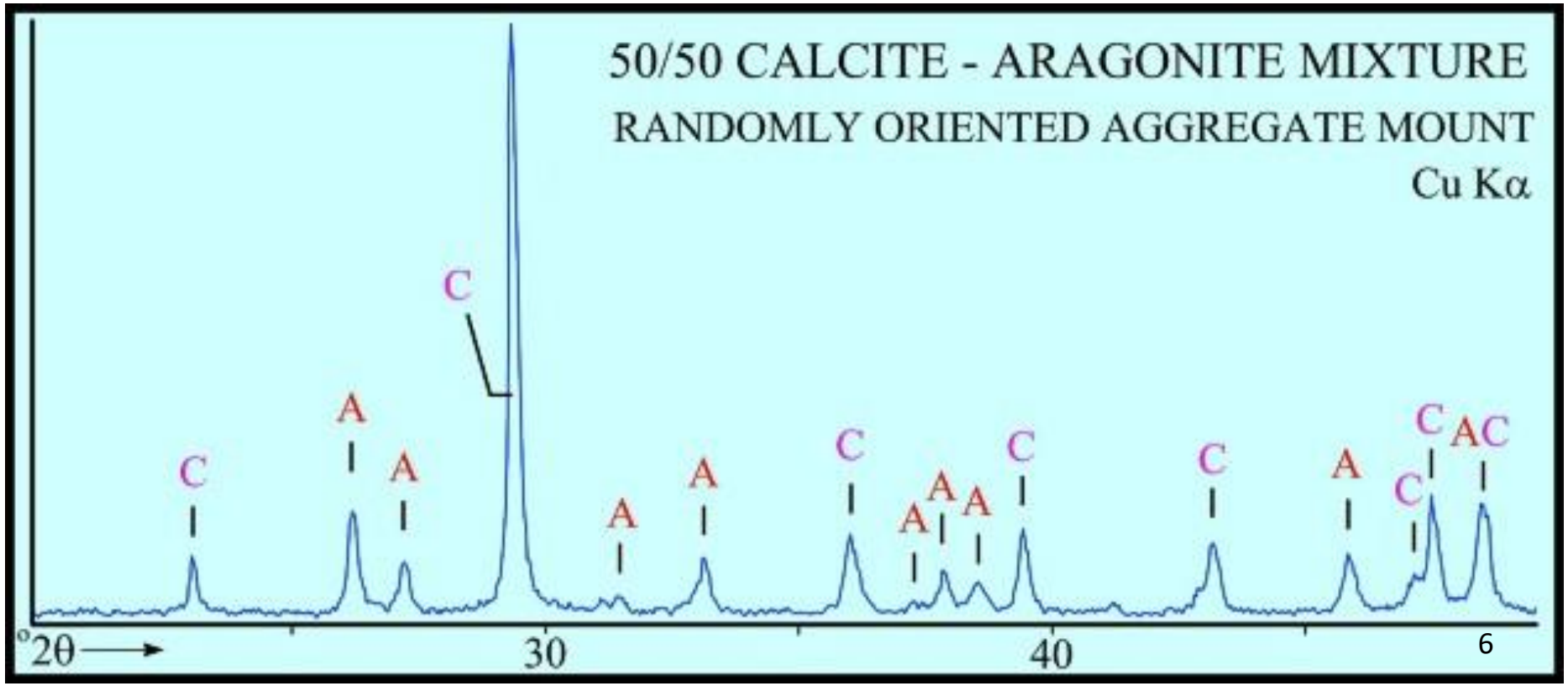
- Best for samples with low absorption.
- Capillaries can be used as sample holders (measurement of air sensitive samples / suspensions).

Classic **reflection** geometry

(**Bragg-Brentano** geometry).

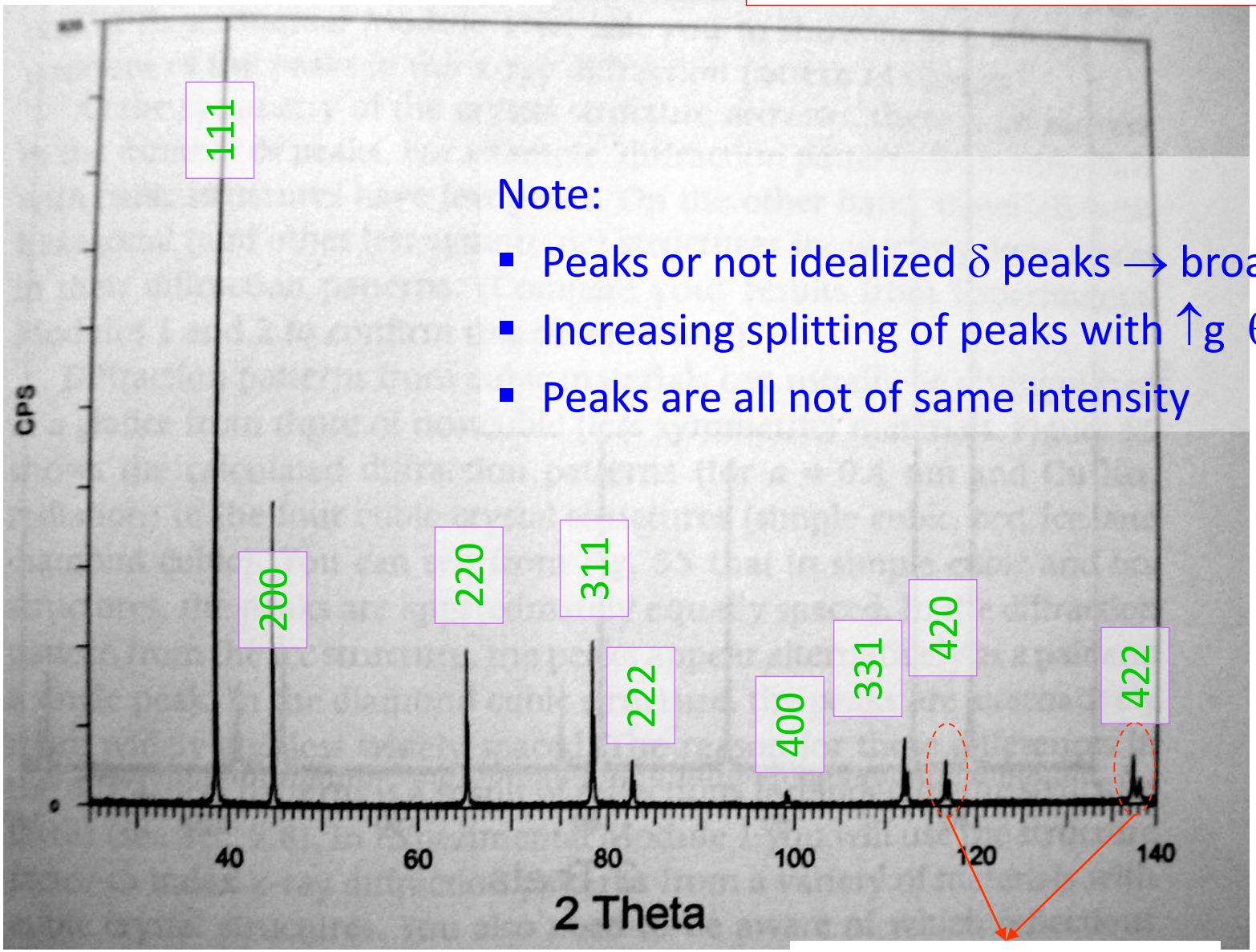
- Best for strongly absorbing samples.
- Requires flat sample surface.
- Easily adapted for *in situ* investigations.

X-ray Powder Diffraction Patterns are used to identify crystalline materials and to determine the amount of each phase in a mixture



Powder diffraction pattern from Al

Radiation: Cu Kα, λ = 1.54056 Å



Note:

- Peaks or not idealized δ peaks $\rightarrow$ broadened
- Increasing splitting of peaks with $\uparrow$g θ
- Peaks are all not of same intensity

α_1 & α_2 peaks resolved

X-Ray Diffraction: A Practical Approach, C. Suryanarayana & M. Grant Norton, Plenum Press, New York (1998)

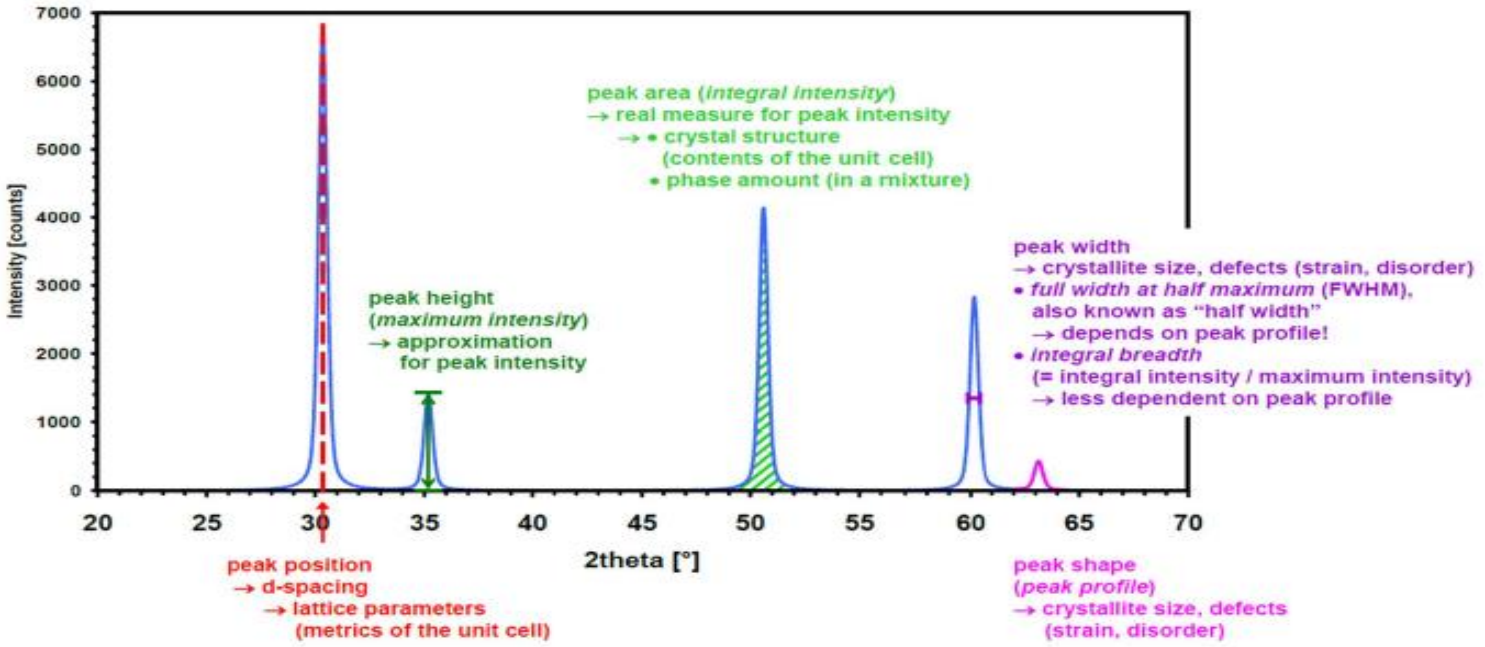
How do we present X-ray diffraction data?

- The intensity of the diffraction signal is usually plotted against the diffraction angle 2θ [°], but d [nm] or 1/d [nm^{-1}] may also be used.

- A 2θ plot is pointless if the wavelength used is not stated because the diffraction angle for a given d-spacing is dependent on the wavelength. The most common wavelength used in PXRD is 1.54 Å (Cu Kα).

- The "signals" in a diffractogram are called (Bragg or diffraction) peaks, lines, or reflections.

"Anatomy" of the XRD pattern



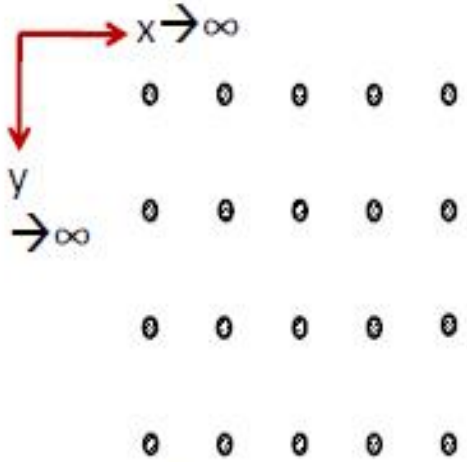
Information content of an idealized diffraction pattern.

How precisely can we analyze an X-ray diffraction pattern?

Differences between theory and reality :

- Models based on ideal systems (Sample and X-rays).

→ Reliant on several key assumptions.



'Infinite' lattice

All crystallite orientations present

Instrumental factors?

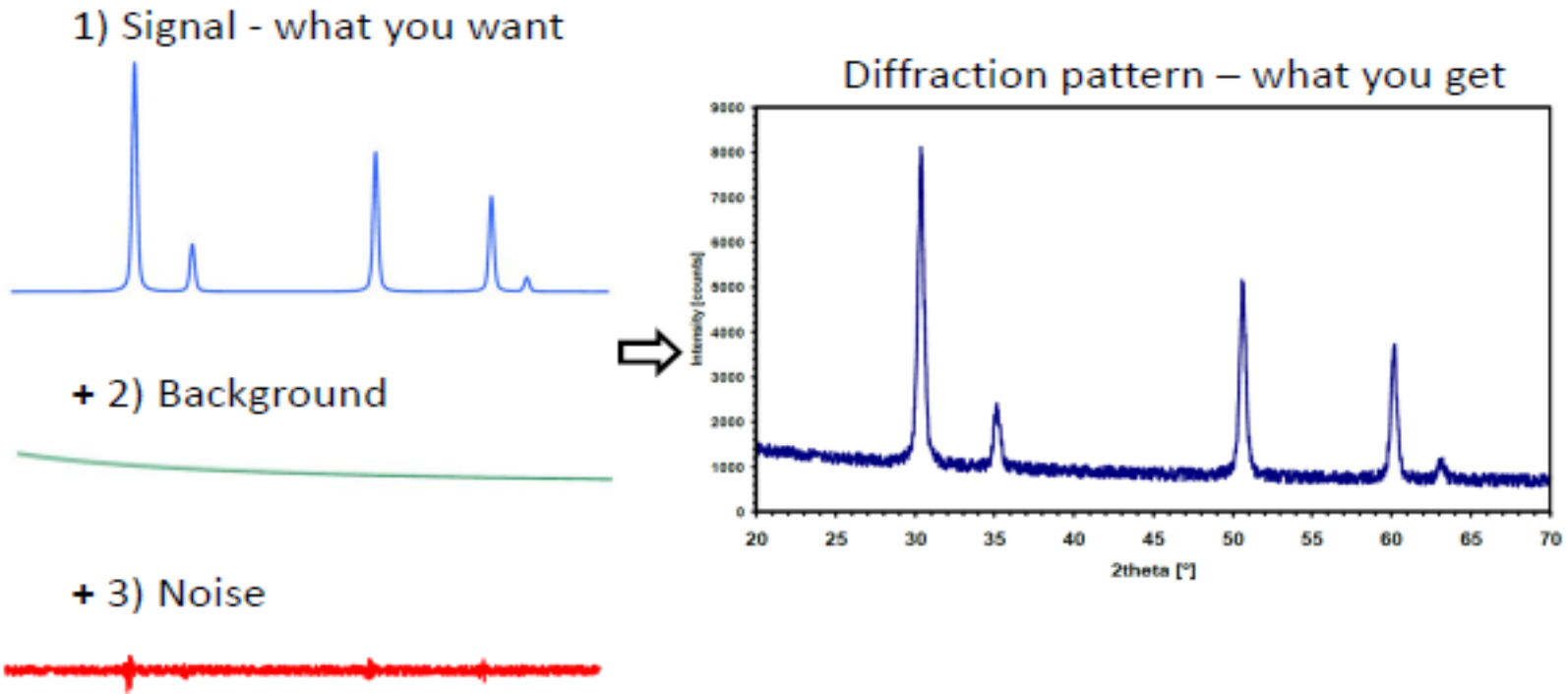
For monochromatic XRD
Single , constant, λ

What impact do these assumptions have for real experiment?

Why we do X-Ray Diffraction XRD?

- **Measure the average spacings between layers or rows of atoms**
- **Determine the orientation of a single crystal or grain**
- **Find the crystal structure of an unknown material**
- **Measure the size, shape and internal stress of small crystalline regions**

Experimentally recorded diffraction pattern:



Can we improve accuracy of analysis?

Precise analysis of XRD data requires separation of the sample signal from the background and noise.

Strategies to improve signal/noise ratio:

- Increasing intensity of incoming beam (synchrotron source).
- Shorter wavelength (less absorption).
- Increasing amount of sample beam (illuminated area)
- Increasing the counting time (square-root law!)

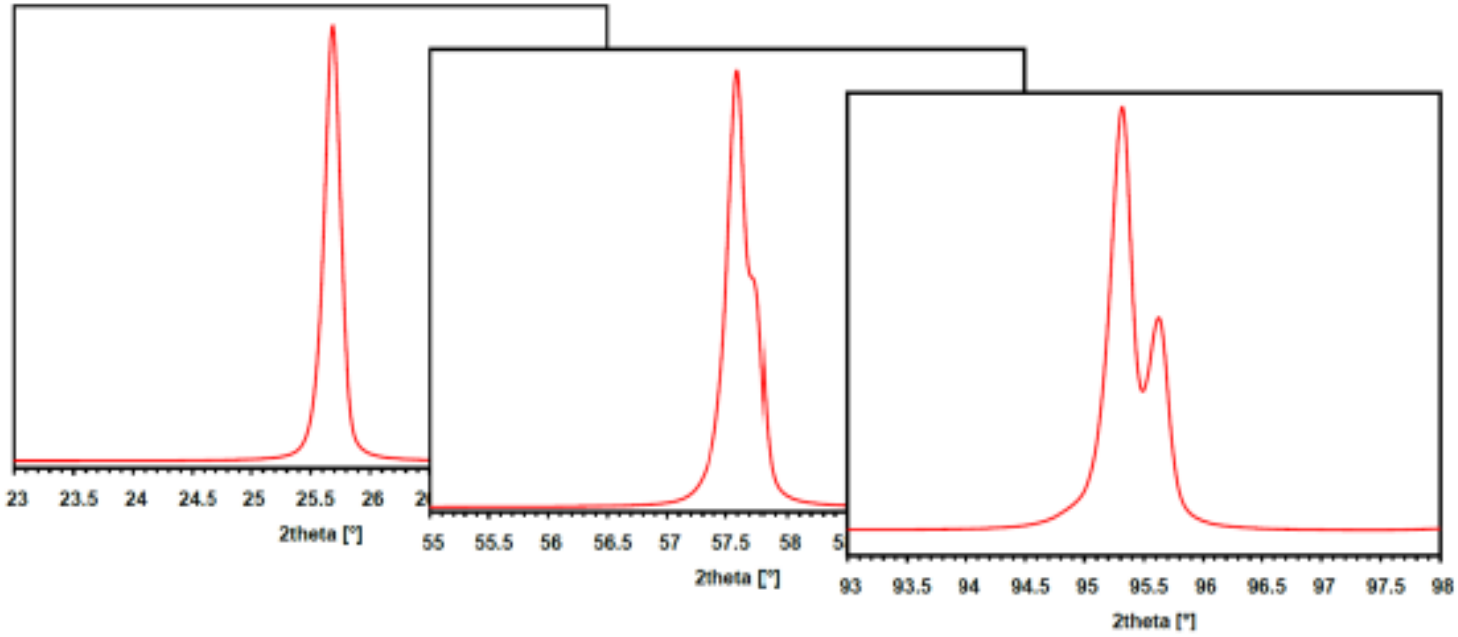
Separation of signal and background:

- Not trivial – Iterative refinement better than background subtraction.
- Normally should only be used for to aid data visualization and not during data analysis.

X-ray wavelength: Effect of Kα1+2 radiation

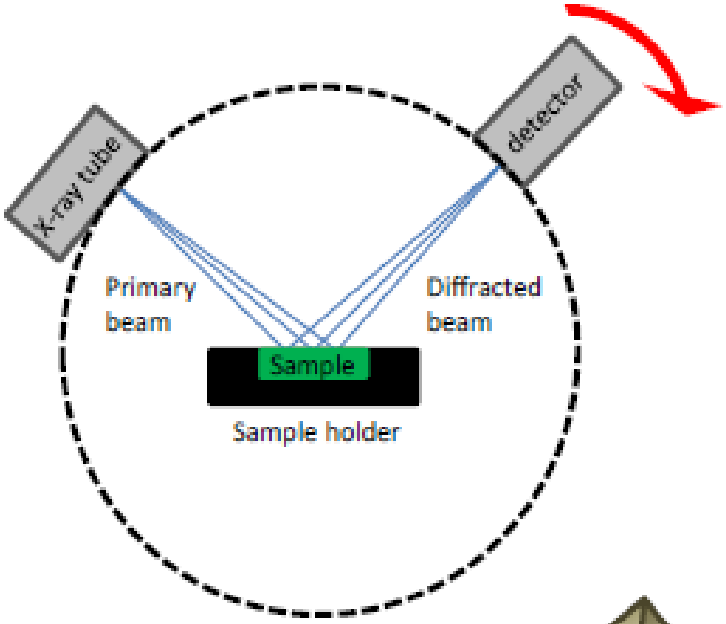
Majority of monochromators used in laboratory XRD unable to separate $K\alpha_1$ and $K\alpha_2$ radiation.

Thus, each Bragg reflection will occur trice with slightly different diffraction angles.



- The $K\alpha_2$ line lies to the right and has about 1/2 of the intensity of the corresponding $K\alpha_1$ line.
- The separation between the two peaks increases with increasing diffraction angle.
- How well the two peaks are resolved also depends on the FWHM of the peaks.

Are all crystallite orientations present?



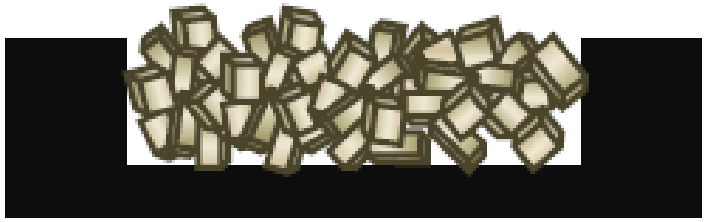
Certain crystal shapes favour stacking in a particular way (*e.g.* needles or plate-like).

➔ Not all crystal orientations present

➔ Intensity distribution different from expected.

This effect is known as :

'preferred orientation'.

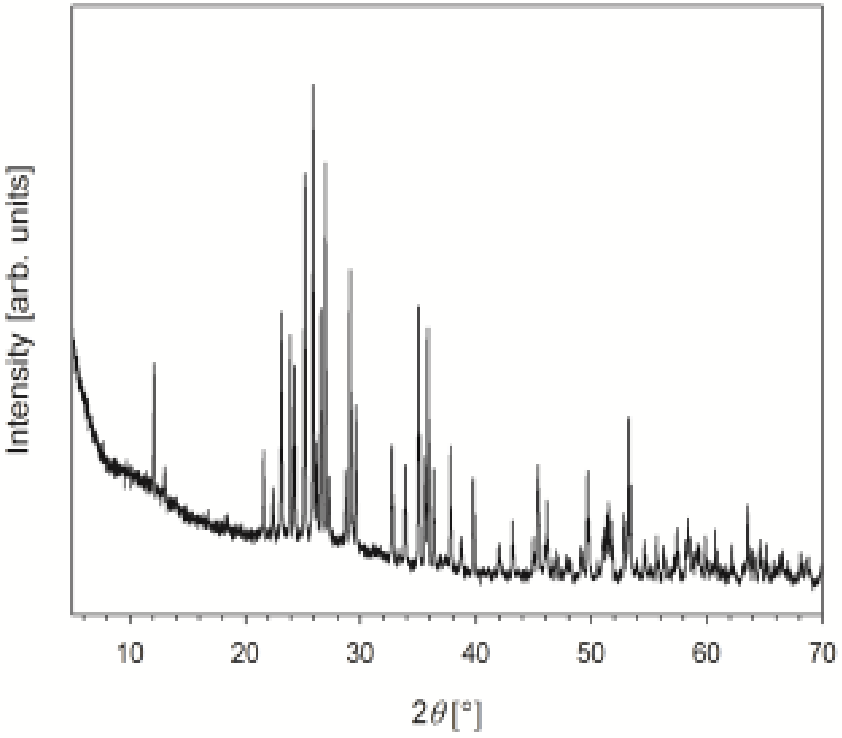


Preferred orientation on flat sample mount

So what can we determine from XRD data?

1) **Phase determination**

➔ Identification of crystalline phases.



2) **Quantitative phase analysis**

➔ Relative composition of mixed phases.

3) **Calculation of lattice parameters**

➔ Structural variations under different conditions.

4) **Analysis of crystallite size and strain**

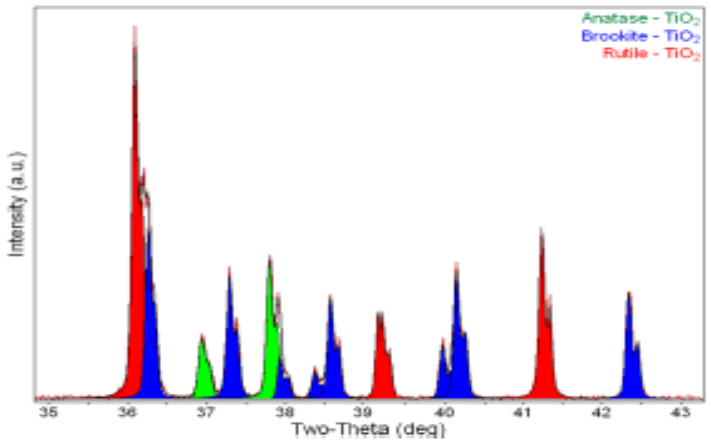
➔ Estimation of size of crystalline domain and disorder.

5) **Structure solution**

➔ Complete structure refinement of unknown phases.

1) Phase determination (Qualitative)

• Most common use in heterogeneous catalysis is for phase identification. Each different crystalline solid has a unique X-ray diffraction pattern which acts like a "fingerprint".



e.g. TiO_2

• Three commonly occurring structures.

• Phases with same chemical composition have different XRD patterns.

• XRD enables rapid determination of form.

Needs: Peak positions and approximate relative intensities.

Tools: Crystal structure databases. Possible to simulate the PXRD pattern of known crystal structures from the reported crystal information file (.cif) using several available software.

1) Phase determination

Method: Match diffraction pattern against reference data.

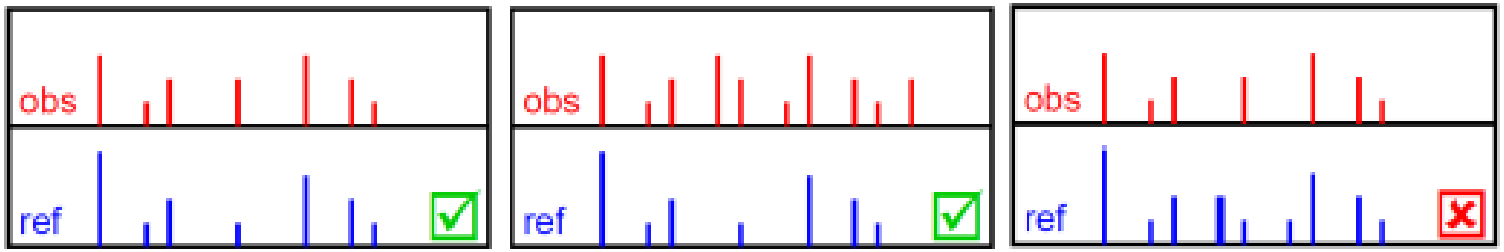
• This could be the diffraction pattern or the corresponding peak list (positions and intensities).

• The reference could be an experimentally collected (*e.g.* from known material), or simulated diffraction pattern.

• The matching process: Manual or automated.

1) Phase determination: FAQ

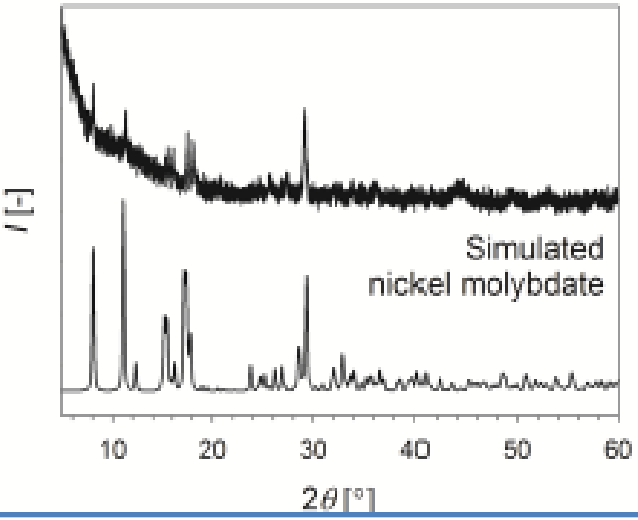
Q: How many peaks must match between a reference PDF pattern and a measured diffractogram?



A: Generally, **all expected reflections** should be seen in the diffractogram, otherwise it is not a valid match.

Exceptions?

- Low **signal to noise** ratio. → Weak reflections not visible.
- Strong **preferred orientation** effect. → Different relative intensities with a systematic dependence on *hkl*.
- **Anisotropic disorder.** → FWHM of the peaks show a systematic dependence on *hkl*



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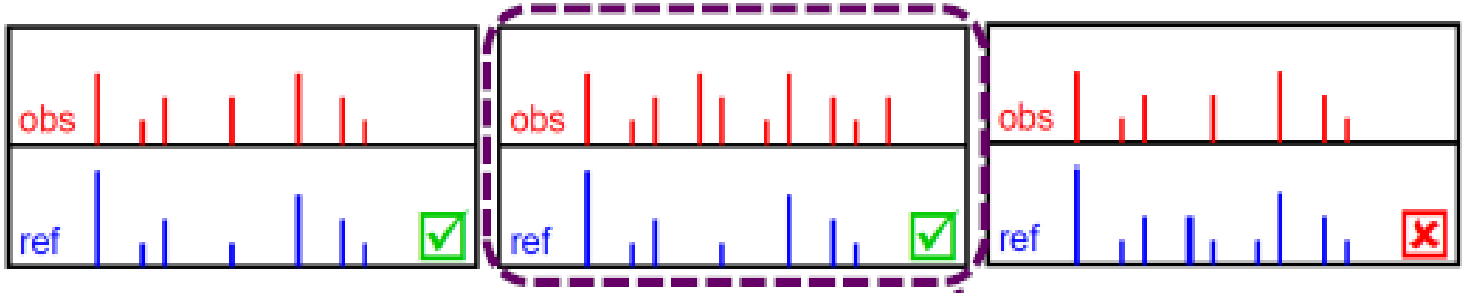
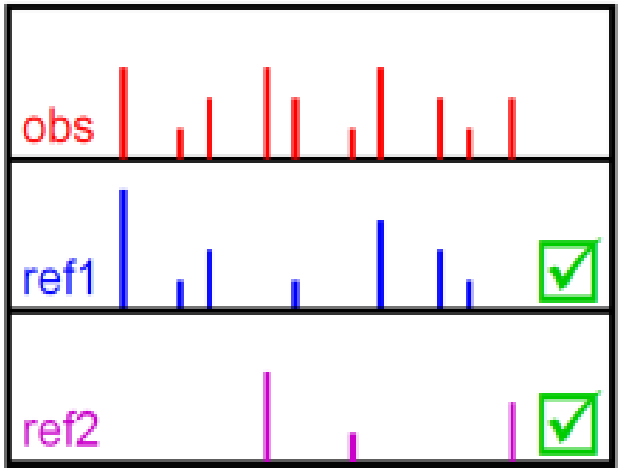


A: Generally, **all** expected reflections should be seen in the diffractogram, otherwise it is not a valid match.

Q: What if the measured pattern contains more reflections than the reference?

A: More than one phase present.

→ Keep the reference pattern, continue searching for references to explain the additional peaks. Proceed until all peaks accounted for.



1) Phase determination: FAQ

Deviations in relative intensities

- Preferred orientation effects. → The deviation of intensities should be systematic with hkl.

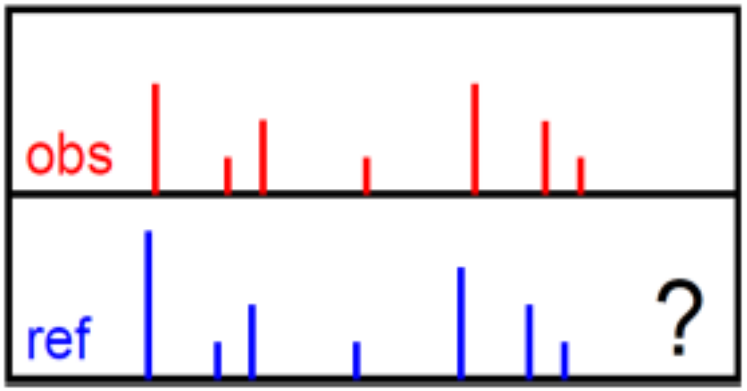
→ Check by applying a Rietveld fit including a preferred orientation model.

- Incorrect identification (Not likely).
- Isostructural phase. Presence of substitutional impurities of similar atomic size but differing Z may give rise to deviation in intensity. → Verify sample composition

Deviations in peak positions

- Thermal expansion
- Isostructural phase. Presence of substitutional impurities of similar Z but differing atomic size.

→ Verify sample composition.

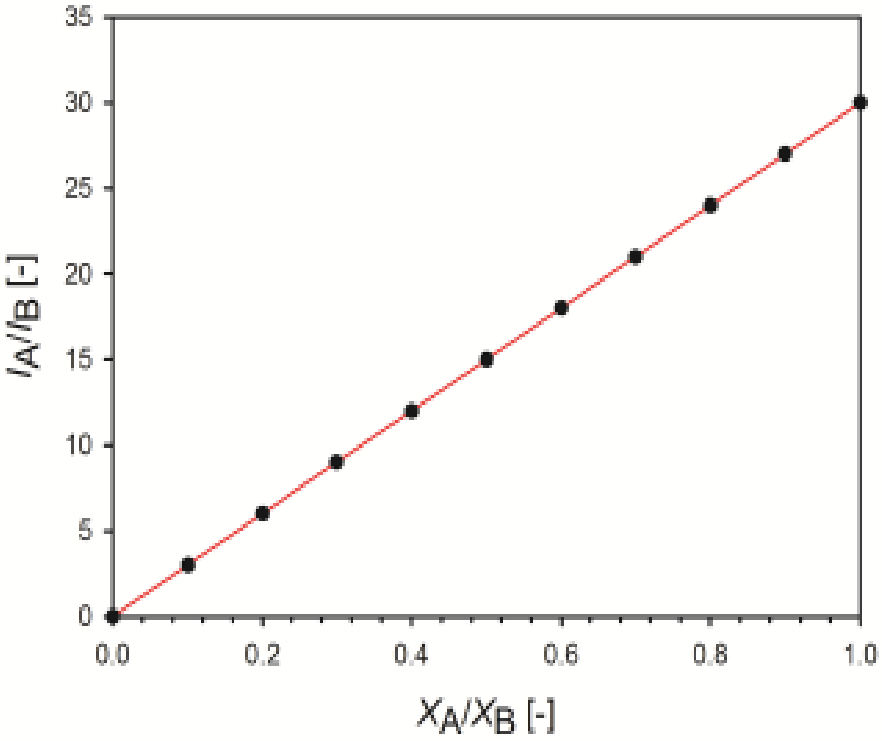


Isomorphism: Instead of AO_2, you may have $A_{1-x}B_xO_2$, BO_2, AO_{2-x},...

2) Quantitative phase analysis

Determining the relative proportions of crystalline phase present in an unknown sample.

• Ratio of peak intensities varies linearly as a function of weight fractions for any two phases (*e.g.* A and B) in a mixture.



This can crudely be estimated by free-hand scaling of XRD patterns.

Needs: I_A/I_B value for all phases involved.

Tools: Calibration with mixtures of known quantities.

➔ Fast and gives semi-quantitative results.

b) Quantification by whole pattern fitting using **Rietveld** method is more accurate but more complicated approach.

2) Quantitative phase analysis: Seeing the invisible, is my product really single phase?

Determination of amorphous content of a sample containing crystalline phase A.

➔ Use internal standard of known crystallinity (spiking/ reference intensity ratio)

Needs: Appropriate XRD standard B.

- No overlap of reflections of standard with phase to be determined.
- High crystallinity, uniform particle size.
- Careful sample preparation

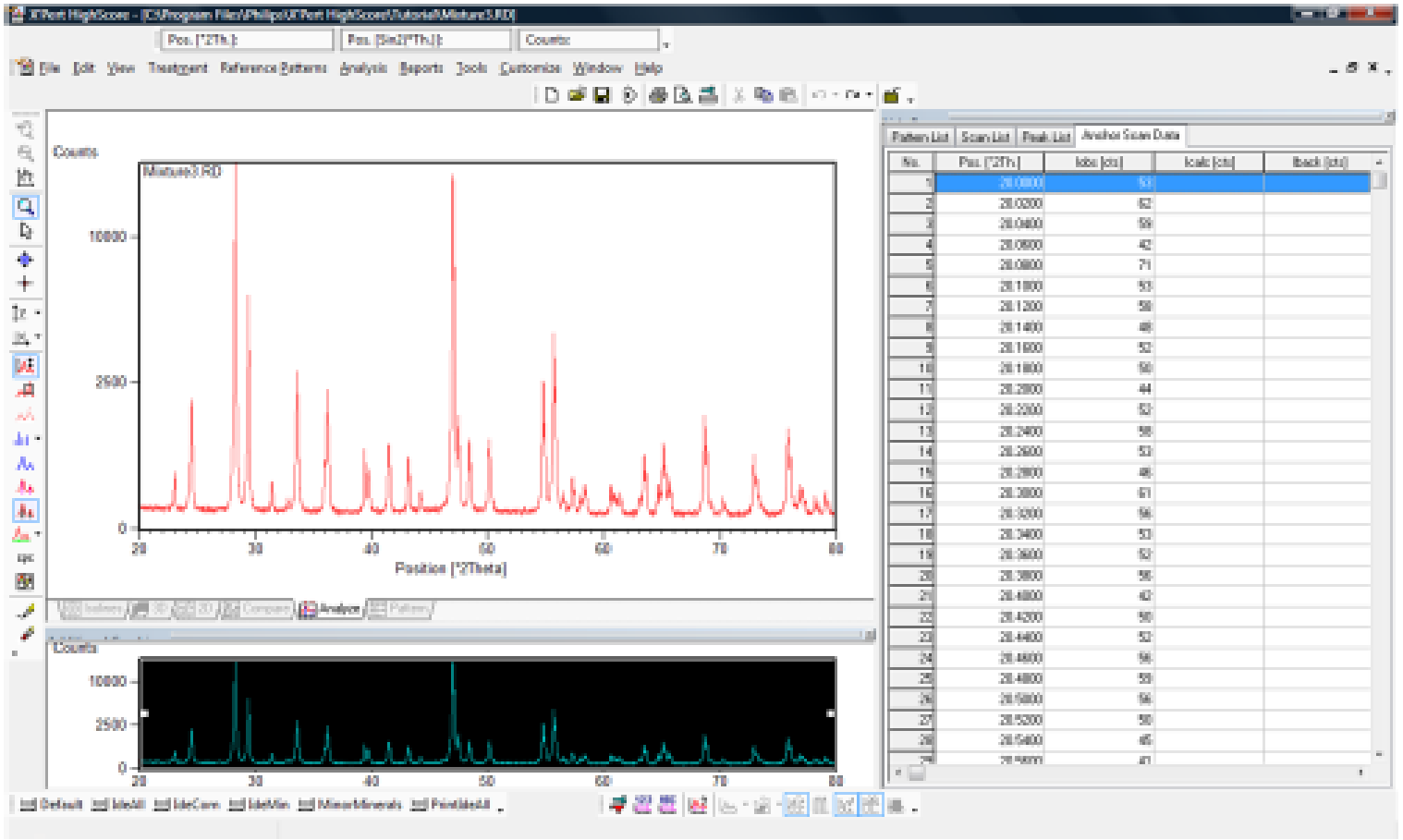
Al_2O_3 (Corundum)
SiO_2 (Quartz)
ZnO

Method: Known amount standard B is added to specimen containing phase A.

$$\frac{I_{(hkl)A}}{I_{(hkl)B}} = k \frac{X_A}{X_B}$$

3) Calculation of lattice parameters

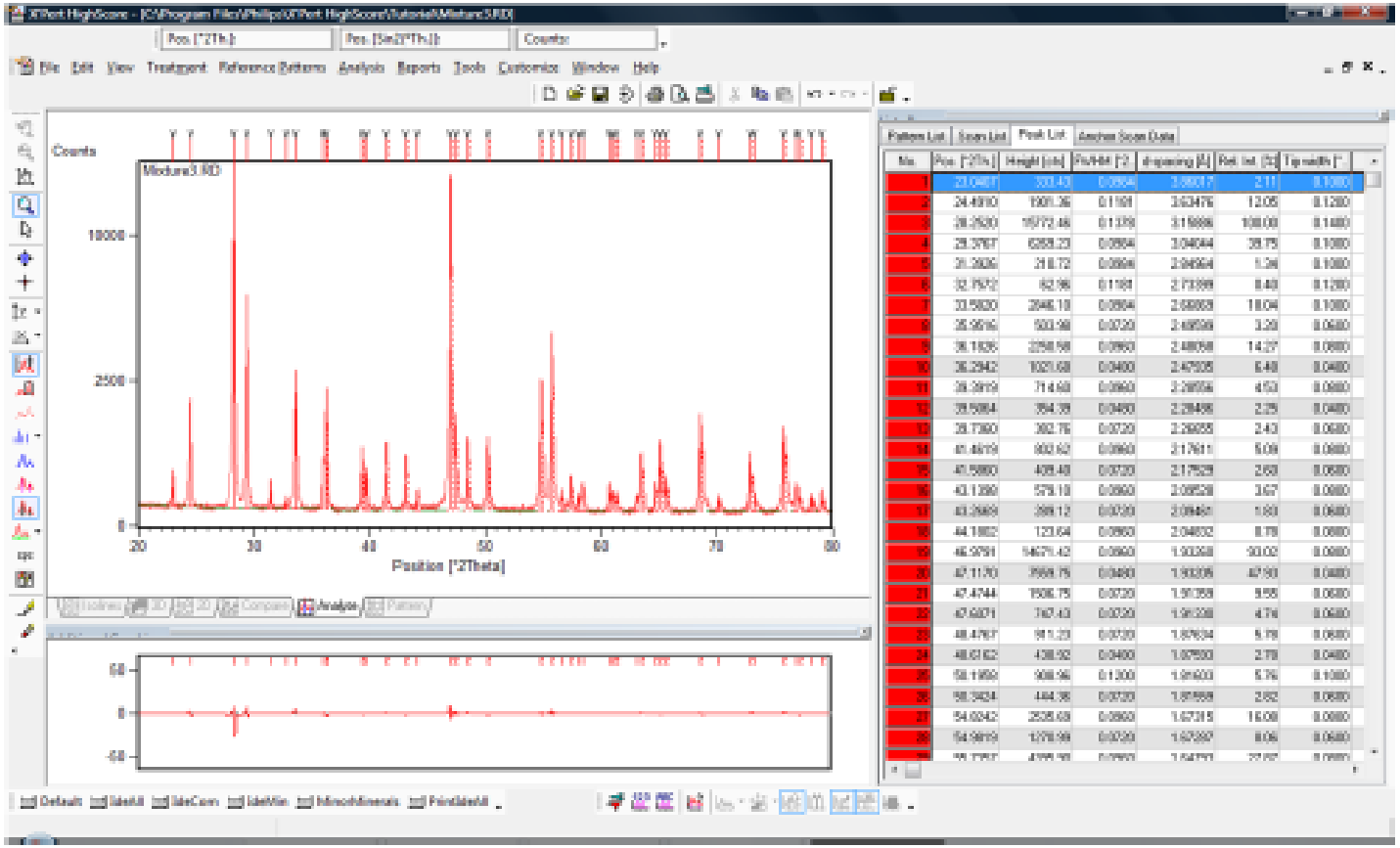
- Diffraction angle related to d-spacing via Bragg equation.



Step 1: Identify peaks in diffraction pattern

3) Calculation of lattice parameters

- Diffraction angle related to d-spacing via Bragg equation.



Step 2: Calculate corresponding d-spacings.

3) Calculation of lattice parameters

Step 3: Index the PXRD pattern

- Easiest if crystal system known and for higher symmetry *e.g.* Cubic.
- Iterative process.
- Once *hkl* determined can calculate lattice parameters *a,b,c etc.*

Bragg's law

$$\lambda = 2d\sin\theta \qquad \sin^2\theta = \frac{\lambda^2}{4d^2}$$

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

+

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2}$$

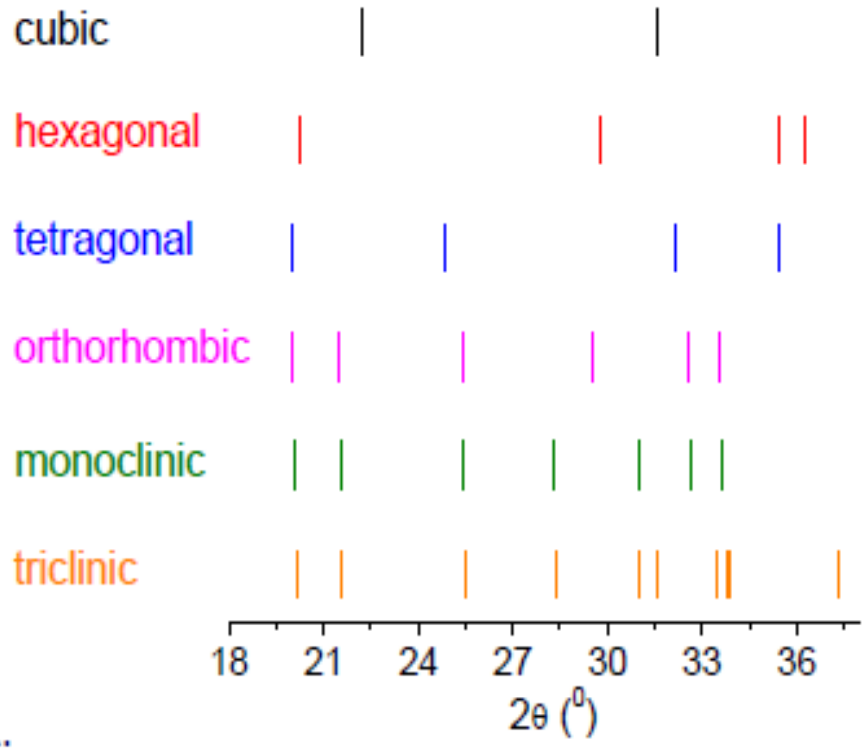
$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)\left(h^2+k^2+l^2\right) \qquad \left(\frac{\lambda^2}{4a^2}\right) = \text{constant}$$

Reflection	2θ	$\sin^2\theta$	$\sin^2\theta/\sin^2\theta_{min}$	$n\cdot(\sin^2\theta/\sin^2\theta_{min})$	$h^2+k^2+l^2$	*hkl*
1	38.43					
2	44.67					
3	65.02					
4	78.13					

Relating lattice planes to crystal symmetry

- Increasing symmetry ➔ decrease in number of reflections observed.
- With certain symmetries reflections from different lattice planes cancel out ➔ **Systematic absences.**

Predicted Bragg positions for primitive cells with $\lambda = 1.54$ Å.

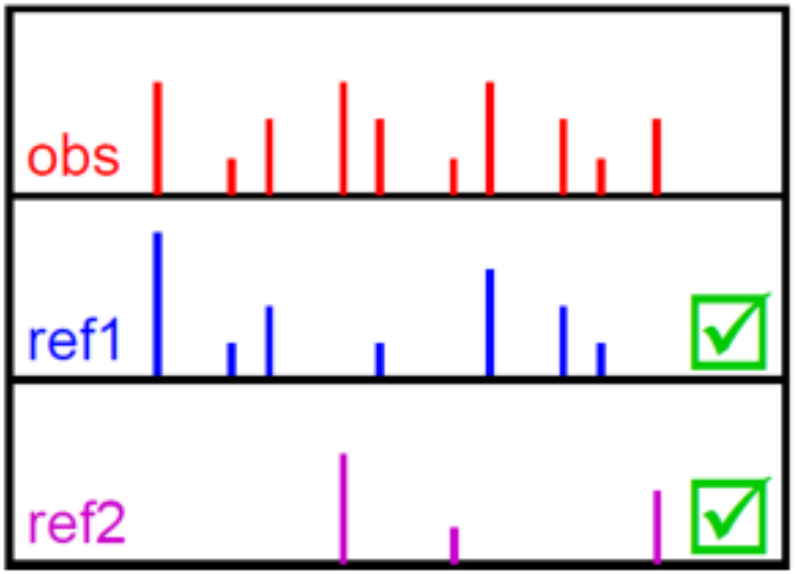


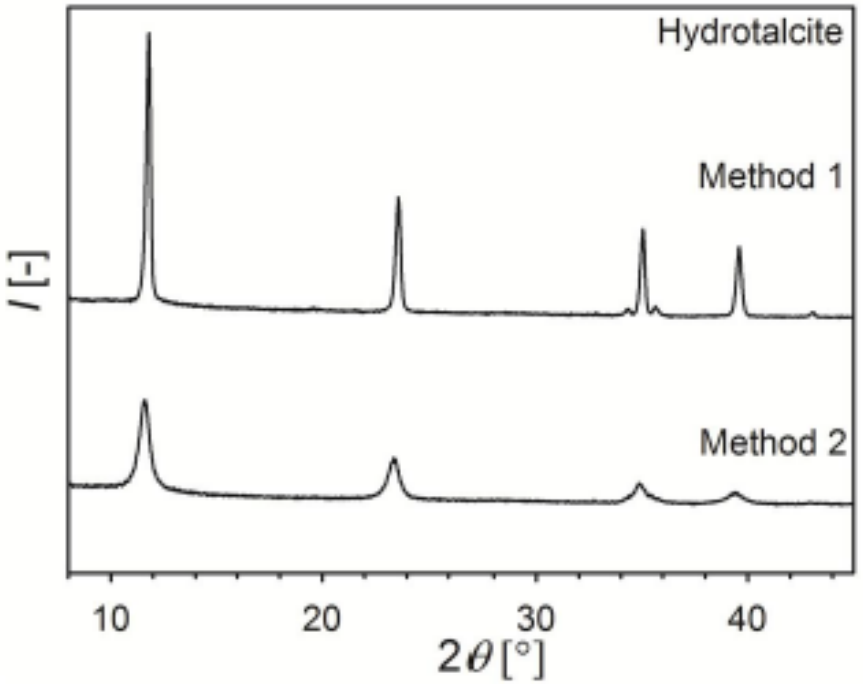
Peak multiplicities decrease from cubic to triclinic:

e.g. cubic $d_{(100)} = d_{(-100)} = d_{(010)} = d_{(0-10)} = d_{(001)} = d_{(00-1)}$

orthorhombic $d_{(100)} = d_{(-100)} \neq d_{(010)} = d_{(0-10)} \neq d_{(001)} = d_{(00-1)}$

4) Analysis of crystallite size and strain





Ideal sample and diffractometer

➔ Zero width diffraction lines

Real measurement

➔ Diffraction lines have finite width.

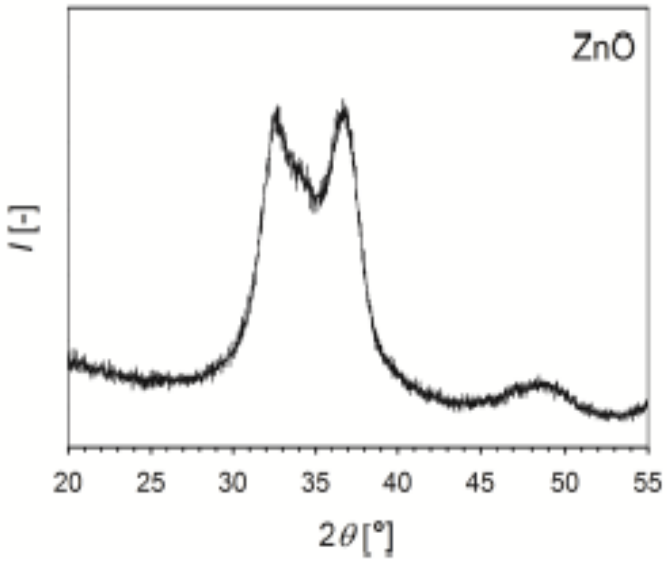
➔ Peak profile.

- What factors determine the peak profile?
- Can we gain useful information?

4) Analysis of crystallite size and strain

What factors determine the peak profile?

- XRD peak profile shape and width are the result of imperfections in both the experimental setup and the sample.



→ Instrumental broadening

- Dependent on experimental set up (*e.g.* sample size, slit widths, goniometer radius).
- Function of 2θ.
- Determined by measurement of a suitable reference.

→ Sample broadening

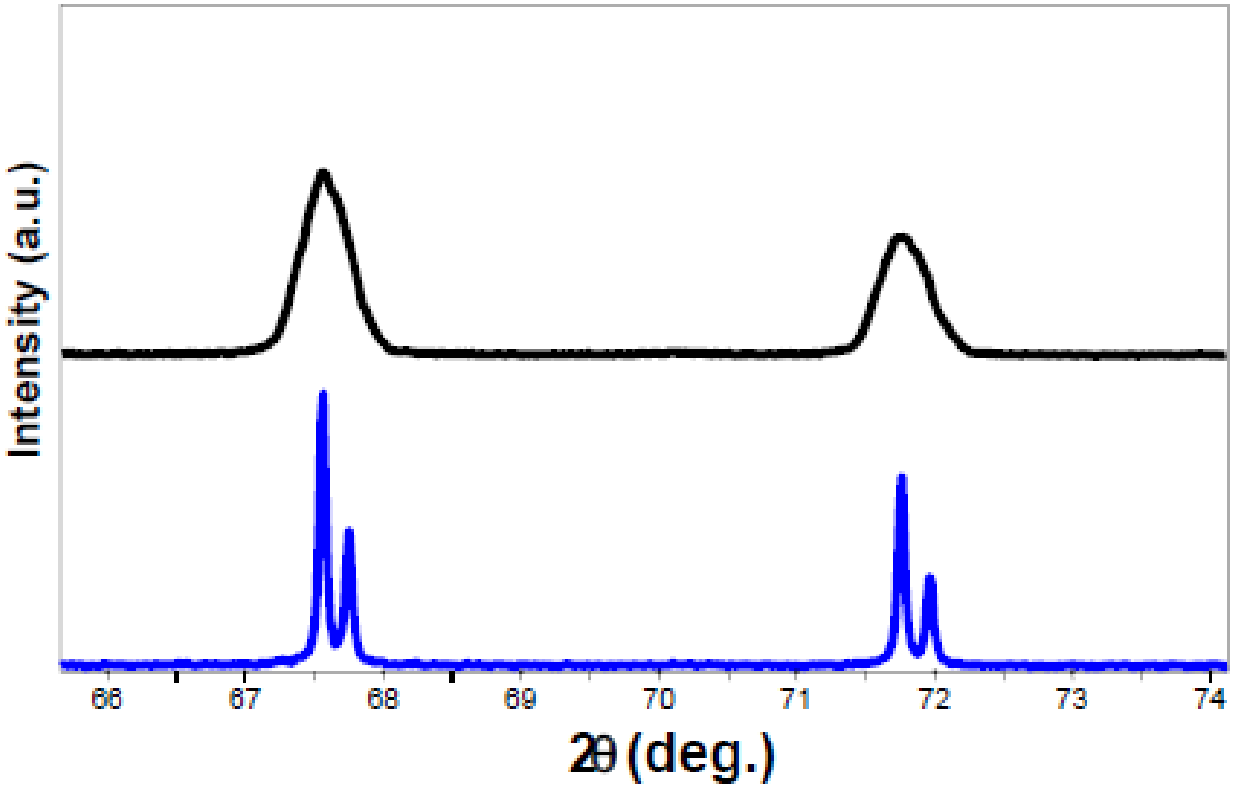
- Periodicity in crystals is not infinite as crystals have:

Finite size → **size broadening**. Most apparent in crystals smaller than *ca* 100 nm.

Lattice imperfections (*e.g.* dislocations, vacancies, substitutional) → **strain broadening**.

4) Analysis of crystallite size and strain

Which of these diffraction patterns comes from a nanocrystalline material?



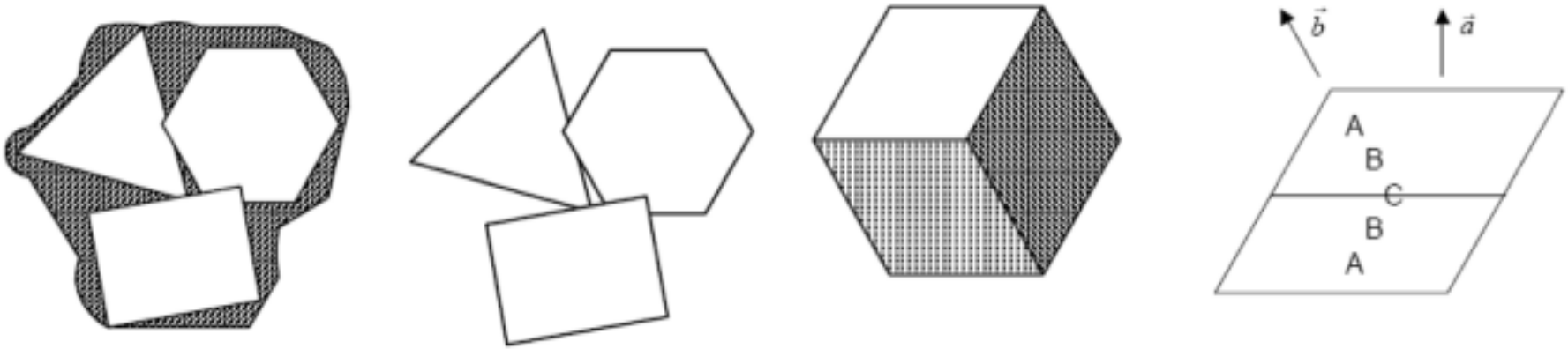
Exact same sample!

Measured using different diffractometers, with different optical configurations.

➔ Instrumental contribution must be known to determine sample broadening.

4) Analysis of crystallite size and strain

The term "size" needs to be carefully defined:



particle* or *grain size ≥ ***crystal size*** ≥ ***crystallite size*** ≥ ***domain size***

Methods:
light microscopy, SEM, laser size analysis, sieving, ...

Problems:
agglomeration

Methods:
XRD, HRTEM

Problems:
XRD only indirect!

4) Analysis of crystallite size: The Scherrer equation

Published by Scherrer in 1918

$$B_{size}(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Relates peak width to crystalline domain size

B is the FWHM of the peak profile (corrected for instrumental broadening)

L Volume average of crystal thickness in direction normal to reflecting planes.

K is constant of proportionality.

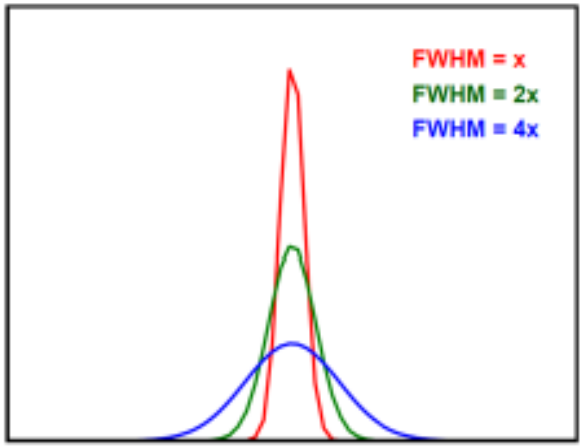
θ Diffraction angle of the reflection.

λ is the wavelength.

Assume: Crystals uniform size and shape.

Scherrer constant, K: Dependent on crystal shape

0.94 for spherical crystals with cubic symmetry.



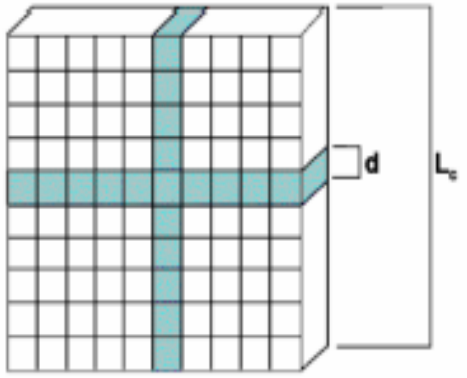
Change of peak height with FWHM (peak shape and area constant)

4) Analysis of crystallite size: How does the size broadening effect translate to crystal size?

Influence of crystallite shape, domain structure, size distribution *etc.*

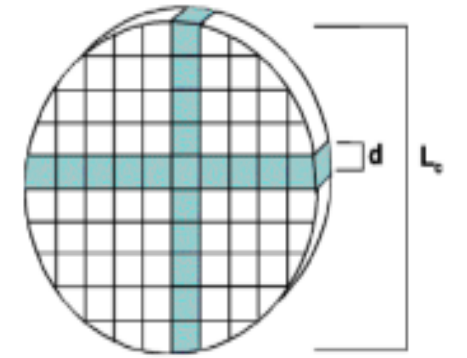
Significance of apparent crystal thickness L

•Volume averaged crystal thickness, L, dependent on crystal shape. Examples:



a) Cubic crystallite **$L = L_c$** = crystallite edge length

(for reflections of lattice planes parallel to the cube faces)

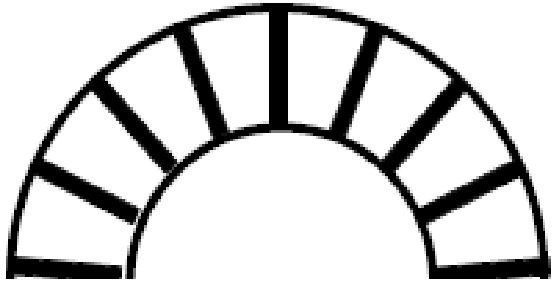


b) Spherical crystallite **$L \leq L_c$** = crystallite diameter

$L_{Vol} = 3/4\ L_c$ (for all reflections)

4) Analysis of microstrain broadening

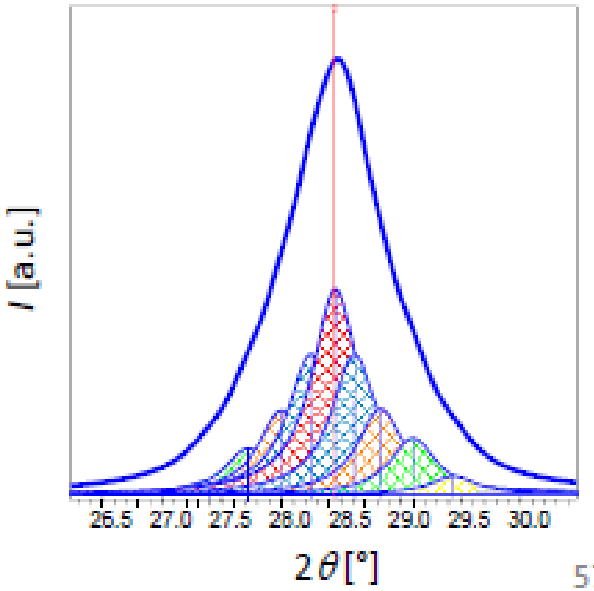
- Lattice strain (microstrain) arises from displacements of the unit cells about their normal positions.
- Often caused by dislocations, surface restructuring, lattice vacancies, interstitials, substitutionals, *etc.*
- Very common in nanocrystalline materials.



➔ Strain is usually quantified as $\varepsilon_0 = \Delta d/d$, with d the idealized d-spacing and Δd the most extreme deviation from d.

➔ The peak broadening due to strain is assumed vary as:

$$B_{strain}(2\theta) = 4\varepsilon_0 \tan\theta$$



4) Size/strain analysis: peak broadening summary

Several factors contribute to the observed peak broadening, B_{obs} :

$$B_{obs} = B_{instr} + B_{sample} = B_{instr} + B_{size} + B_{strain}$$

- The instrumental broadening B_{instr} can be determined experimentally with a diffraction standard or calculated with the fundamental parameters approach.
- The separation of the size and the strain effect on the sample broadening, however, is more complicated and depends on the method used.

Most methods consider the following angular dependencies:

$$B_{size} \propto 1/\cos\theta$$

$$B_{strain} \propto \tan\theta$$

Note: Broadening may alter FWHM or the integral breadth of the peak (peak shape).

5) Crystal structure determination (Rietveld analysis)

Rietveld refinement is an automated procedure which simulates the XRD patterns of model systems (theoretical or known) and calculates the difference of fit with measured data.

What can Rietveld refinement tell us?

- Lattice parameters
- Quantitative phase analysis
- Atomic positions
- Crystallinity
- Atomic occupancy
- Phase transitions
- Structure factors
- Grain size

What do we need?

Model crystal structure of each crystalline component.

Good quality data.

Information from peak intensity?

- Absolute intensities vary depending on both experimental and instrumental parameters.

$I \propto |F|^2$ ➔ $I = kL(\theta)p(\theta)A(\theta)m|F_{hkl}|^2$

Where **I** is the intensity of the reflection (hkl) and **F** is the amplitude of the diffracted X-ray beam (the structure factor).

k = constant for a given sample

L(θ) = Lorentz correction: Geometric correction to all reflections

p(θ) = polarization correction: X-ray waves are polarised

A(θ) = absorption correction: Some X-rays will be absorbed by the sample

m = multiplicity correction. All lattice planes which have the same Bragg angle superimposed.

➔ Very difficult to deconvolve intensities of individual reflections.

➔ 'Relative' reflection intensities of more use than absolute intensity.

What determines the intensity of the diffraction peak?

Electron density

- X-rays scattered by electrons

➔ Greater the atomic number, Z, the higher the scattering factor of a given element (directly proportional).

➔ Intensity proportional to sum of the scattering factors of atoms in a given lattice plane. $I \propto |F|^2$

Multiplicity

- For Powder samples all planes with equivalent d-spacing overlap.

➔ Intensity dependent on number of overlapping planes.