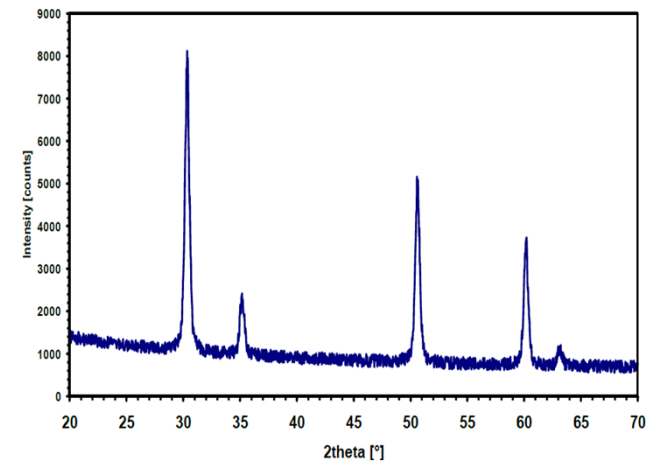
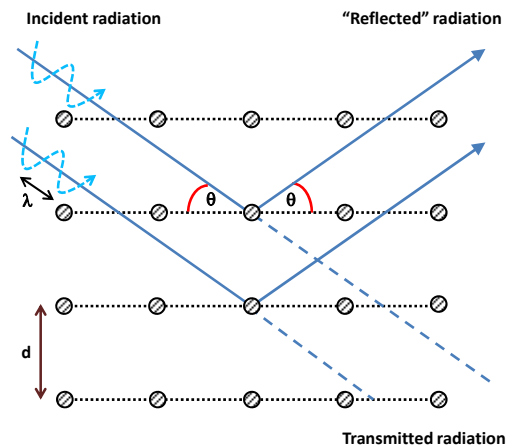


X-ray diffraction



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Three hours of input: Practically oriented guide to powder XRD in catalysis, only the basic theoretical concepts will be covered.

Lectures 1 and 2 (3 hours):

- Key crystallographic concepts and basics of diffraction
- Practical aspects of XRD
- Analysis of XRD diffraction data
- *In situ* studies and complementary techniques

Lecture 3 (1 hour):

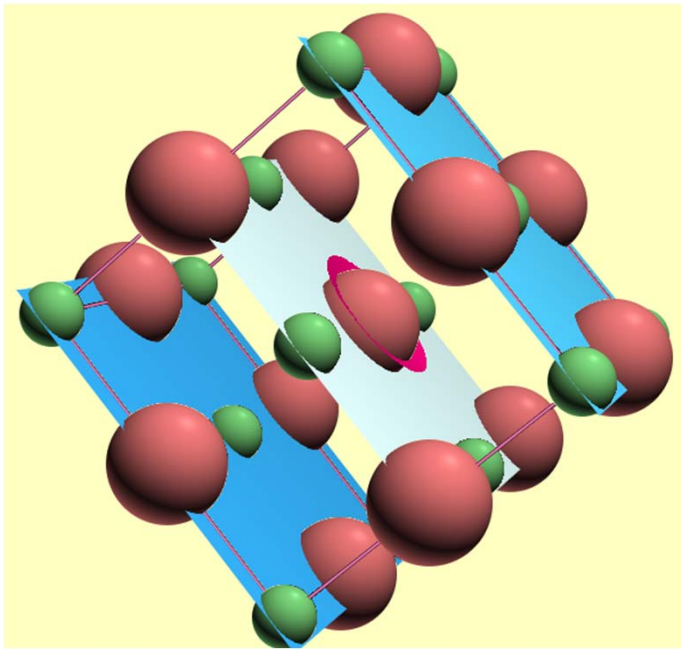
- Worked examples

Refer to standard textbooks for further details:

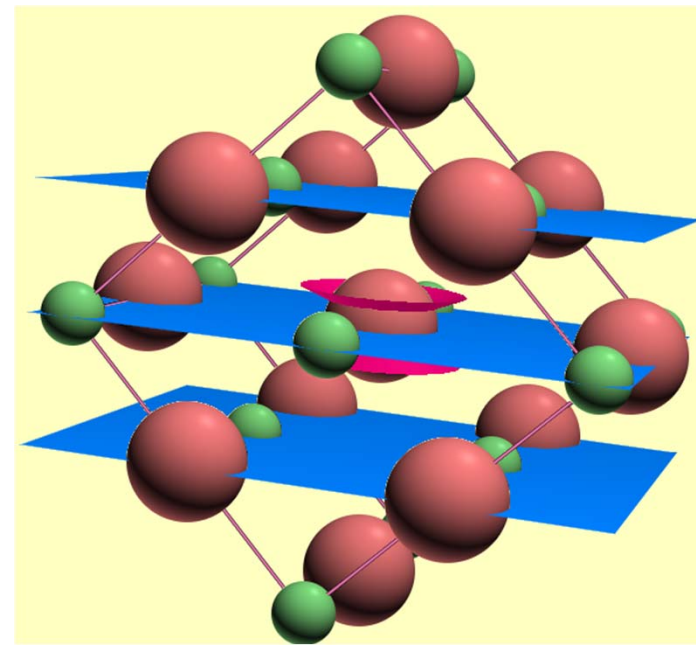
C. Suryanarayana, M.G. Norton. "X-ray Diffraction, A Practical Approach", 1998, pp. 207-221.

C. Hammond. "The basics of crystallography and diffraction", 2nd ed. OUP, 2001.

Key crystallographic concepts

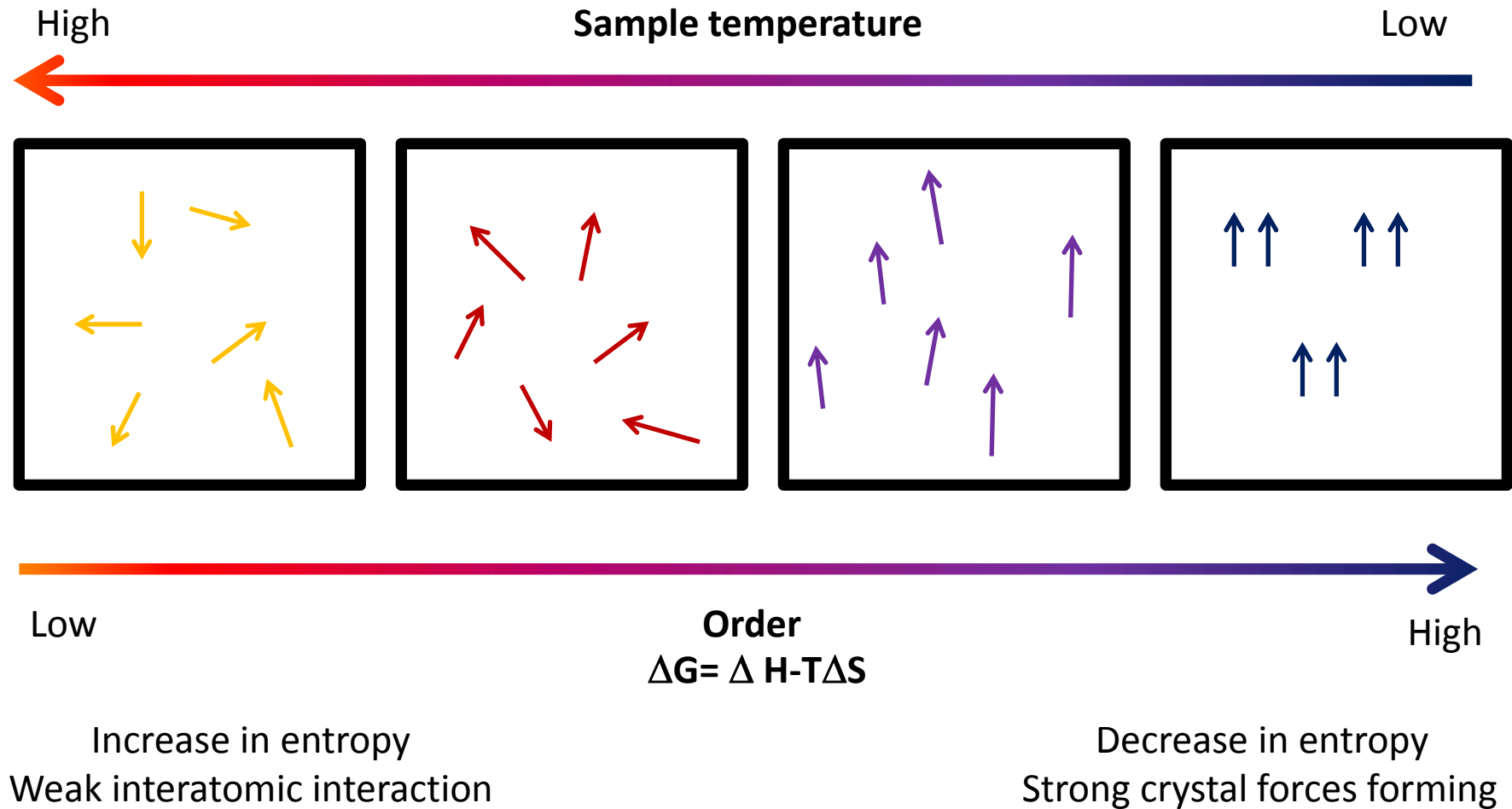


The (200) planes
of atoms in NaCl



The (220) planes
of atoms in NaCl

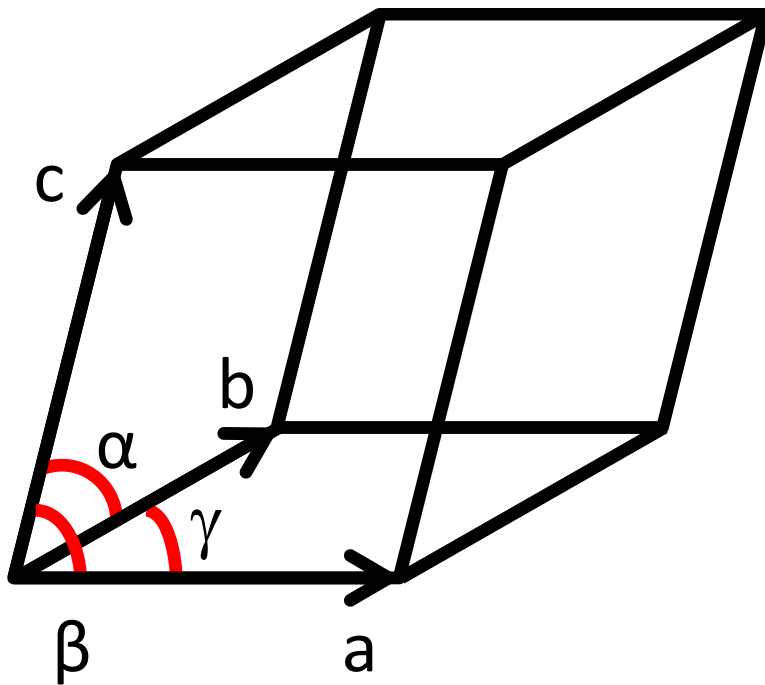
Arrangements of atoms/molecules in solids



Crystalline solids → Ordered three-dimensional array of atoms.
"Infinite" repetition required for diffraction.

Key crystallographic concepts

Conventions of lattice description

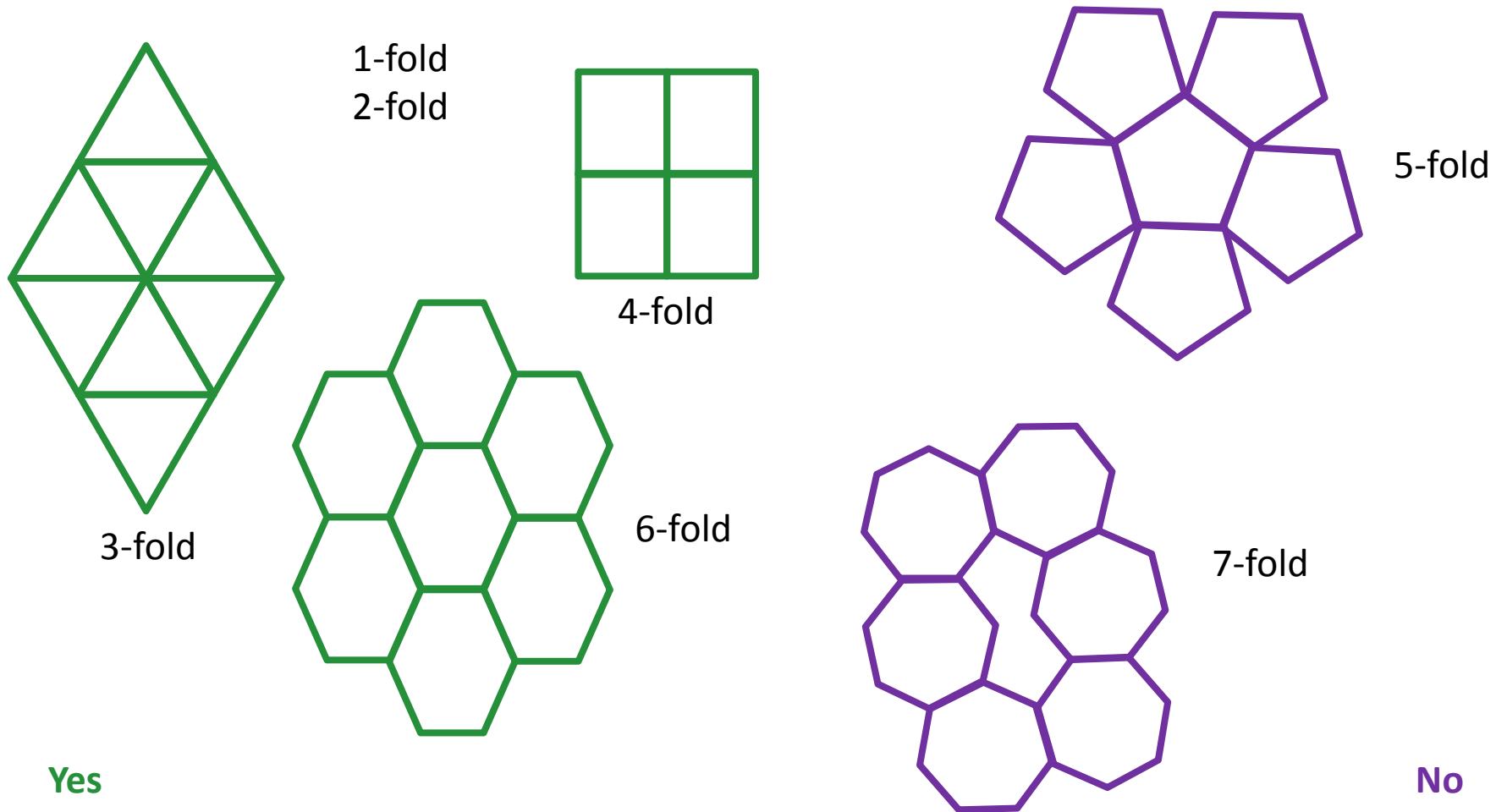


The **unit cell**: An infinitely repeating box

- The unit cell must be infinitely stackable using only translation.
- The three smallest non-coplanar vectors **a**, **b**, and **c** describe the unit cell, with inter-edge angles of α , β , and γ .

Key crystallographic concepts

Requirement for infinite stackability: Are all rotational symmetries infinitely stackable?



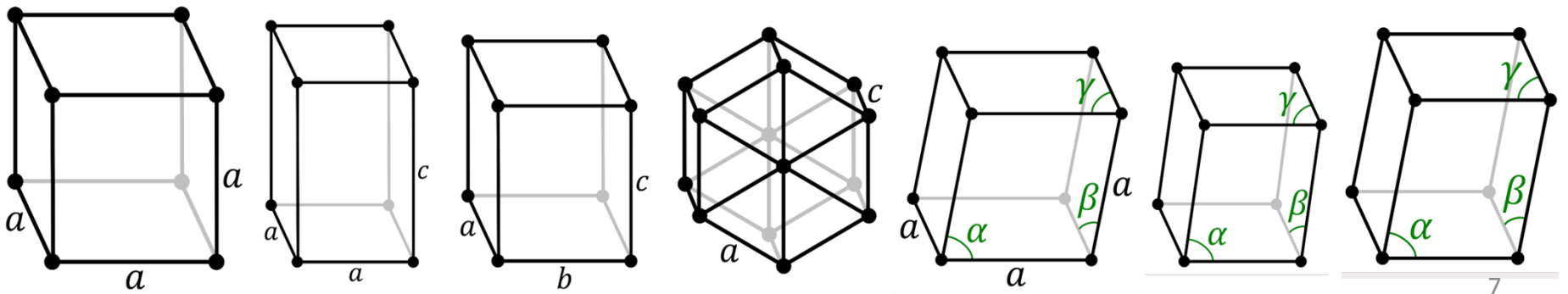
Key crystallographic concepts

Crystal systems: Only certain rotational symmetries (1, 2, 3, 4, 6) are allowed

→ 7 types of crystal systems:

Crystal system	Cell lengths	Cell angles
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$
Tetragonal	$a=b, c$	$\alpha=\beta=\gamma=90^\circ$
Orthorhombic	a, b, c	$\alpha=\beta=\gamma=90^\circ$
Hexagonal	$a=b, c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma$
Monoclinic	a, b, c	$\alpha, \beta=\gamma=90^\circ$
Triclinic	a, b, c	α, β, γ

Decreasing
symmetry



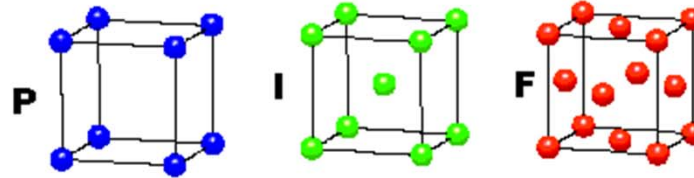
Key crystallographic concepts

What's in the box? Adding atoms to the unit cell

CUBIC

$$a = b = c$$

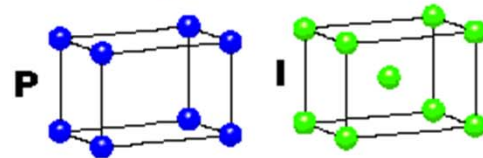
$$\alpha = \beta = \gamma = 90^\circ$$



TETRAGONAL

$$a = b \neq c$$

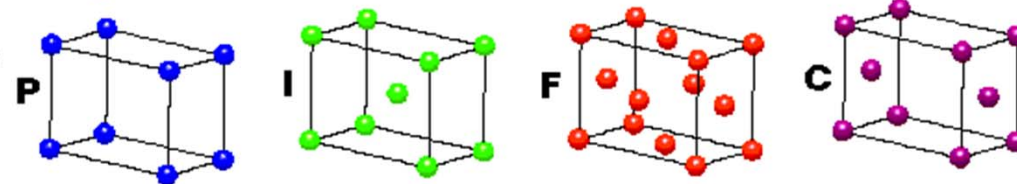
$$\alpha = \beta = \gamma = 90^\circ$$



ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

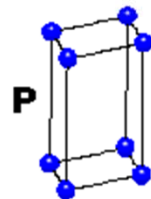


HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

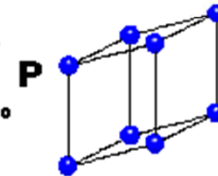
$$\gamma = 120^\circ$$



TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

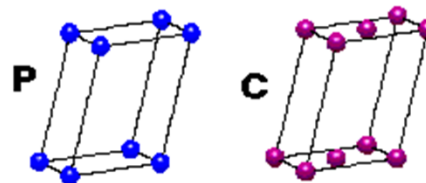


MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

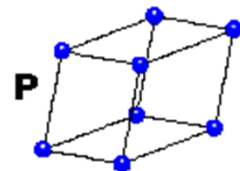
$$\beta \neq 120^\circ$$



TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

Key crystallographic concepts

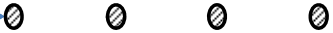
a)



b



a



c)



b)

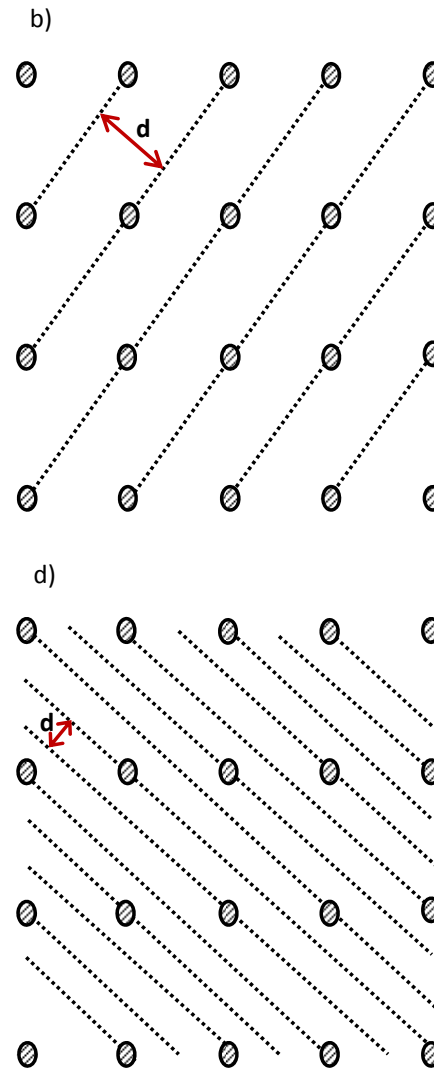
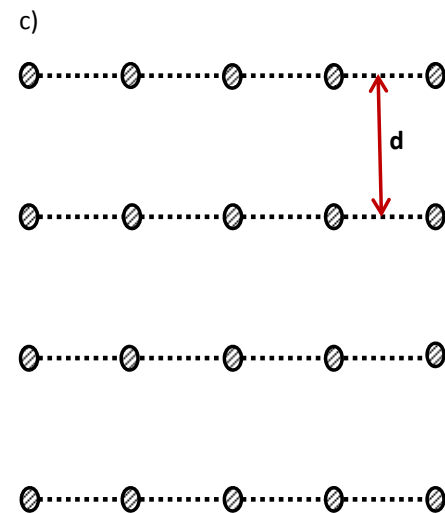
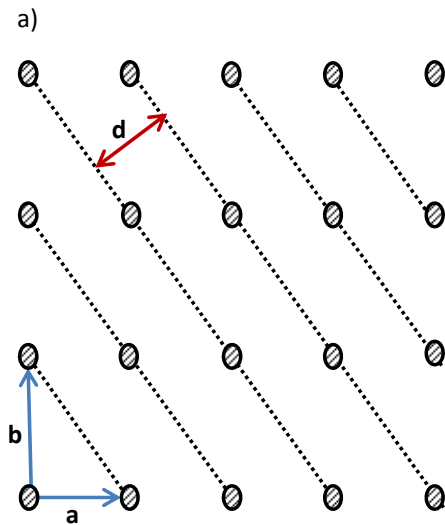


d)



How many periodic distances are there within a lattice?

Key crystallographic concepts

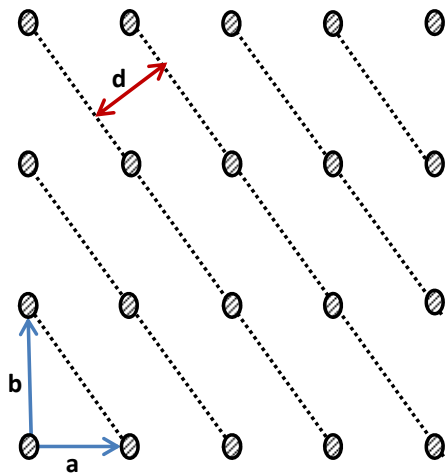


How many periodic distances are there within a lattice?

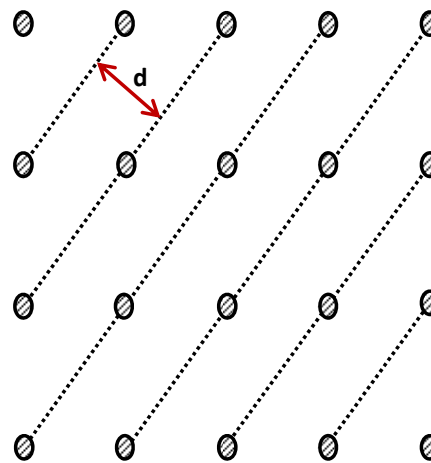
- A **lattice plane** is a plane which intersects atoms of a unit cell across the whole three-dimensional lattice.
- There are many ways of constructing lattice planes through a lattice.
- The perpendicular separation between each plane is called the **d-spacing**.

Key crystallographic concepts

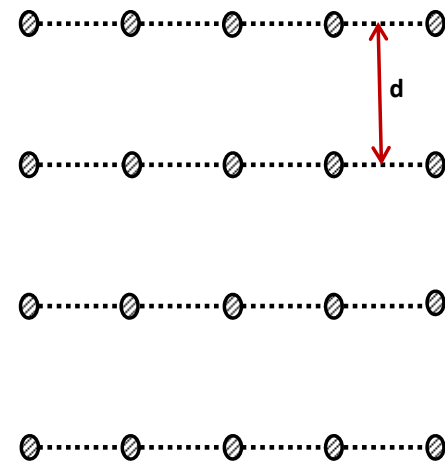
a) (110)



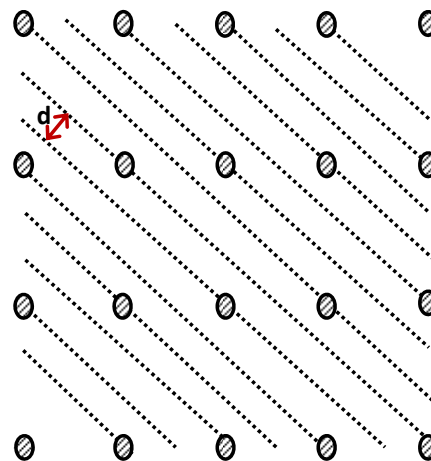
b) $(\bar{1}10)$



c) (010)



d) (230)



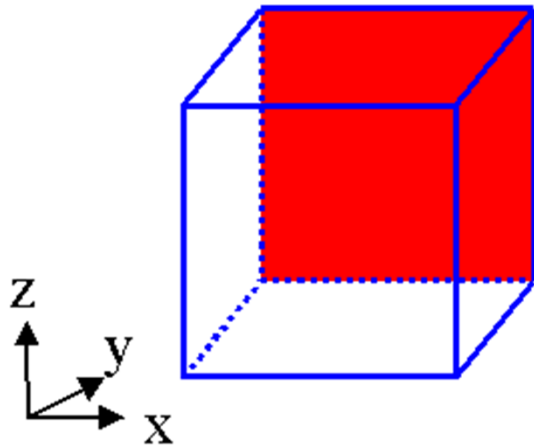
How do we describe lattice planes?

- Each plane intersects the lattice at a/h , b/k , and c/l .
- h , k , and l , are known as the **Miller indices** (hkl) and are used to identify each lattice plane.

Key crystallographic concepts

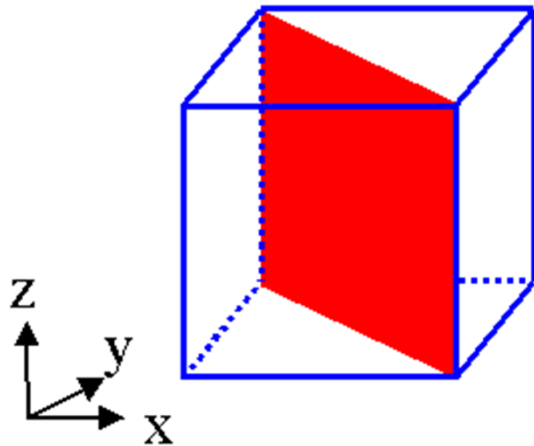
And in three dimensions:

How do we describe lattice planes?



Plane perpendicular to y cuts at $\infty, 1, \infty$

→ (010) plane



This diagonal plane cuts at 1, 1, ∞

→ (110) plane

Relationship between d-spacing and lattice constants

System

Cubic

$$\left[\frac{1}{a^2}(h^2 + k^2 + l^2) \right]^{-1/2}$$

Tetragonal

$$\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$$

Orthorhombic

$$\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]^{-1/2}$$

Hexagonal

$$\left[\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \right]^{-1/2}$$

Rhombohedral

$$\left[\frac{1}{a^2} \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{1 - 2 \cos^3 \alpha + 3 \cos^2 \alpha} \right]^{-1/2}$$

Monoclinic

$$\left[\frac{\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac}}{\sin^2 \beta} + \frac{k^2}{b^2} \right]^{-1/2}$$

Triclinic

$$\left[\frac{\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2hk}{ab}(\cos \alpha \cos \beta - \cos \gamma) + \frac{2kl}{bc}(\cos \beta \cos \gamma - \cos \alpha) + \frac{2lh}{ca}(\cos \gamma \cos \alpha - \cos \beta)}{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \right]^{-1/2}$$

d_{hkl}

→ Simplest for orthogonal crystal systems

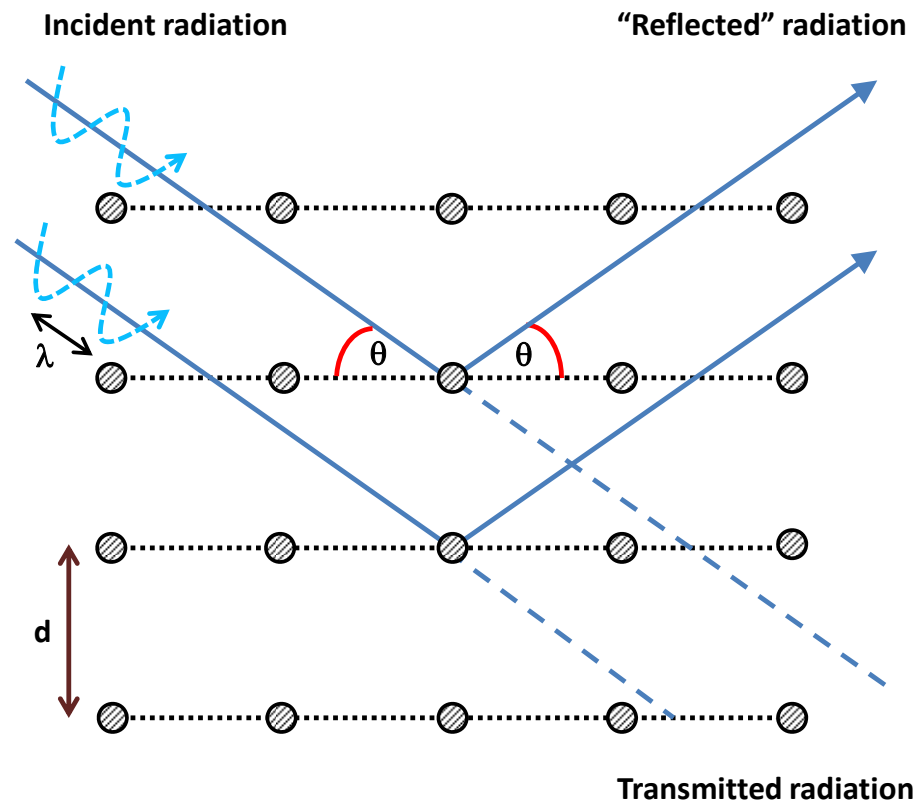
→ Increasingly complex with decreasing symmetry.

Key crystallographic concepts

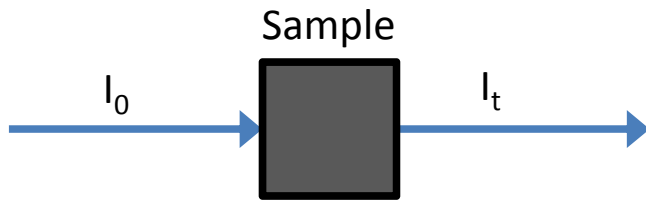
Summary:

- Ordering in materials gives rise to structural **periodicity** which can be described in terms of **translational**, **rotational** and other symmetry relationships.
- Crystalline materials composed of “**infinite**” array of identical **lattice** points.
- The **unit cell** is the smallest three dimensional box which can be stacked to describe the 3D lattice of a solid. The edges (**a**, **b**, and **c**) and inter-edge angles (**α** , **β** , and **γ**) of the unit cell are known as the **lattice parameters** of a crystalline solid.
- Relationship between unit cell, **crystal systems**, and **Bravais lattices**.
- **Lattice planes** are two dimensional planes which intersect the three dimensional lattice in a periodic way, with a fixed perpendicular separation known as the **d-spacing**.
- **Miller indices** define the orientation of the plane within the unit cell.

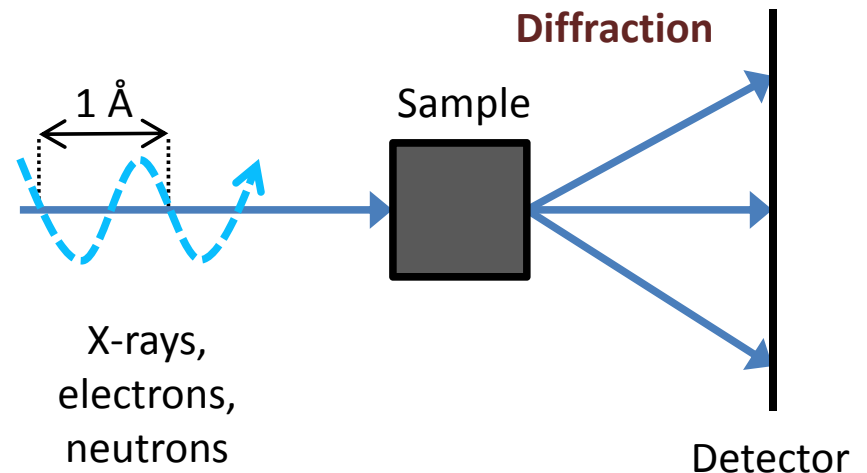
Basic theory of (X-ray) diffraction



When will diffraction occur?



$I_0 = I_t \rightarrow$ transmittance
 $I_0 \neq I_t \rightarrow$ diffraction and/or absorbance



- The periodic lattice found in crystalline structures may act as a diffraction grating for wave-particles or electromagnetic radiation with wavelengths of a similar order of magnitude ($10^{-10} \text{ m} / 1 \text{ \AA}$).
- For solids there are three particles/waves with wavelengths equivalent to interatomic distances and hence which will interact with a specimen as they pass through it: **X-rays**, **electrons**, and **neutrons**.

XRD basic theory

- In materials with a crystalline structure, X-rays scattered by ordered features will be scattered **coherently** “in-phase” in certain directions meeting the criteria for constructive interference → signal amplification.
- The conditions required for **constructive interference** are determined by Bragg's law.

Bragg's Law

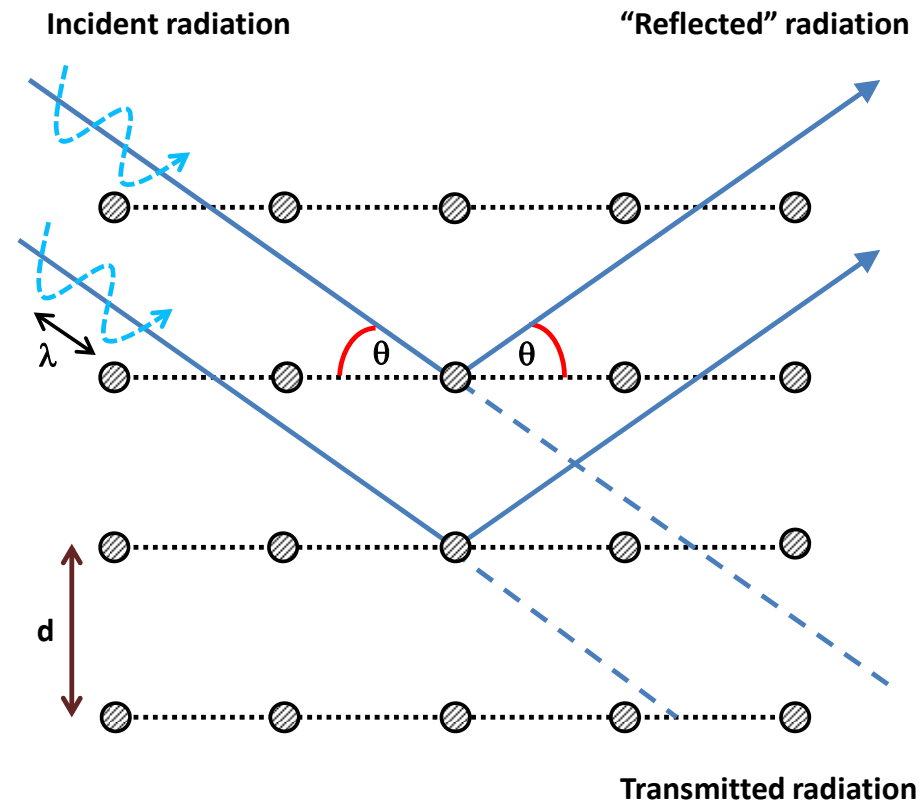
$$n \lambda = 2d \sin\theta$$

λ = X-ray wavelength

d = distance between lattice planes

θ = angle of incidence with lattice plane

n = integer



What type of materials can we study?

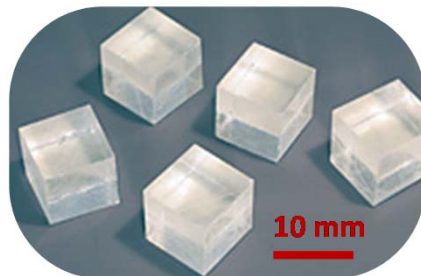
Gas: No structural order – see nothing.

Liquid/Amorphous solids: Order over a few angstroms – broad diffraction peaks

Ordered solids: Extensive structural order – sharp diffraction peaks.

Two types of ordered solids:

1) Single crystals

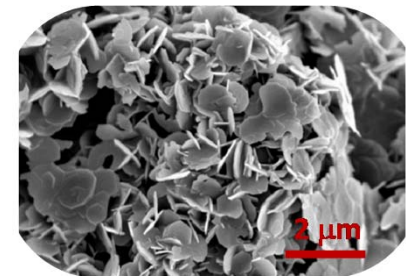


Large crystal required.

Crystal orientation known.

- Each lattice plane only present in one orientation.
- No overlap of reflections.
- Reflection intensities may be accurately measured.

2) Polycrystalline powders



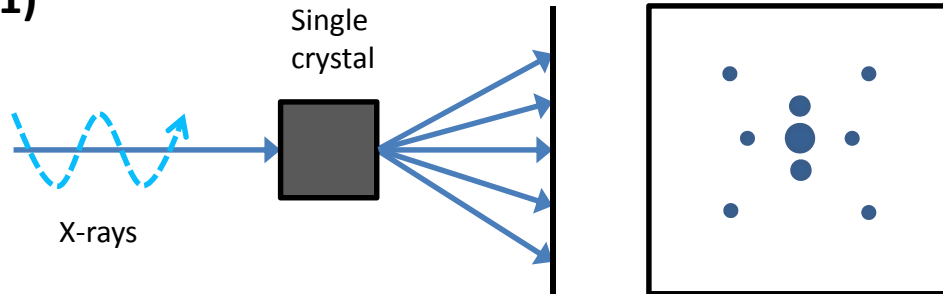
Most common in heterogeneous catalysis

Assume all crystal orientations present.

- Each lattice plane present at all orientations.
- Many overlapping peaks.
- Reflection intensities difficult to determine.

What do we observe?

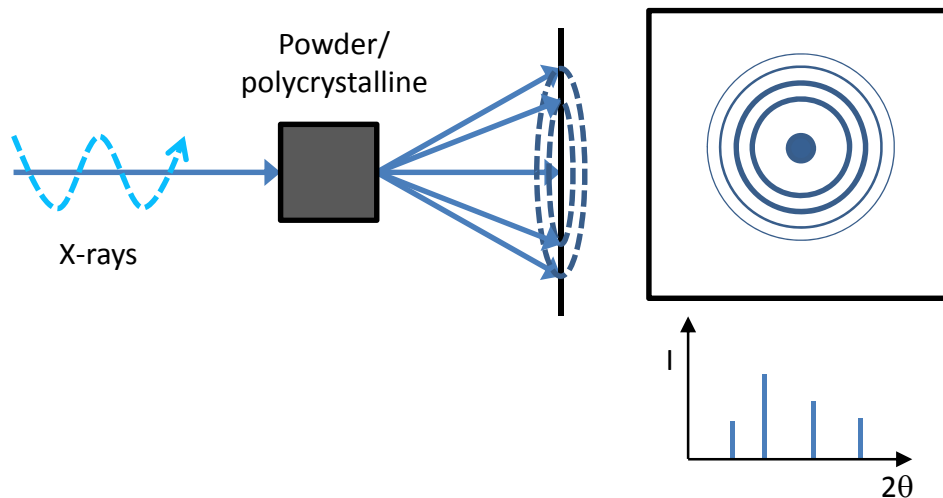
1)



Single crystals

- X-rays diffracted from a single crystal produce a series of spots in a sphere around the crystal. (**Ewald** sphere)
- Each diffraction peak uniquely resolved.

2)



Powders

- All orientations present → Continuous '**debye**' rings.
- Linear diffraction pattern with discrete "**reflections**" obtained by scanning through arc that intersects each debye cone at a single point.

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.

How can we satisfy the Bragg equation?

$$\text{Bragg's Law: } \lambda = 2d \sin \theta$$

- To observe diffraction from a given lattice plane, Bragg's law may be satisfied by varying either the wavelength, λ , or the Bragg angle, θ .

Monochromatic diffraction:

→ Vary θ

→ Bragg condition met once at a time.

- With a fixed wavelength (laboratory source) data is collected as a function of increasing diffraction angle up to a given value of d (resolution dependent).

Laue diffraction:

→ Vary λ .

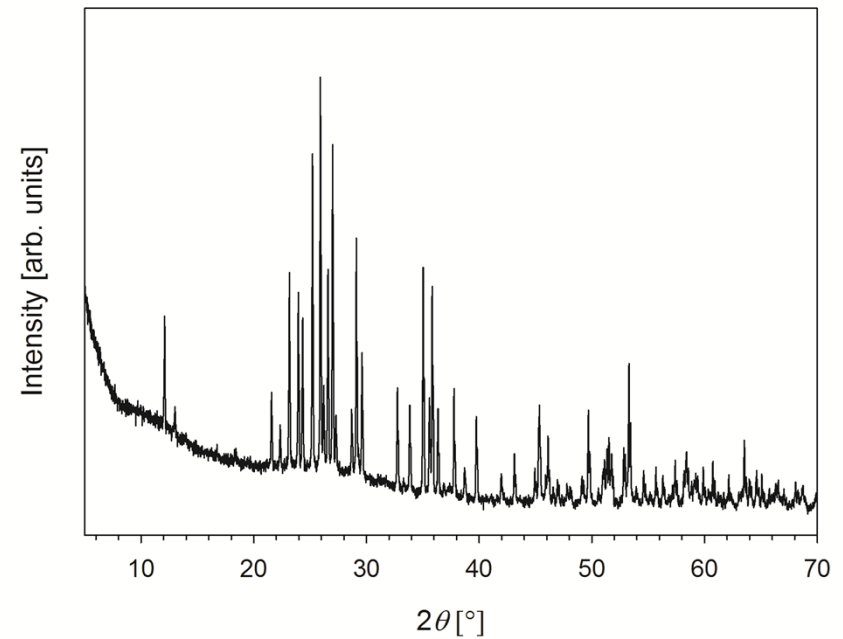
→ Bragg condition met many times simultaneously.

→ Faster but greater complexity in data analysis.

→ Requires synchrotron which is expensive.

X-ray diffraction

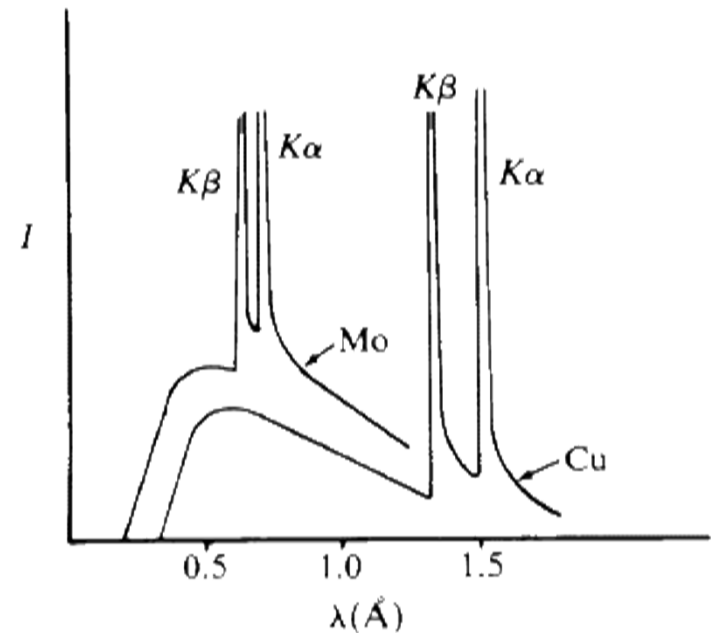
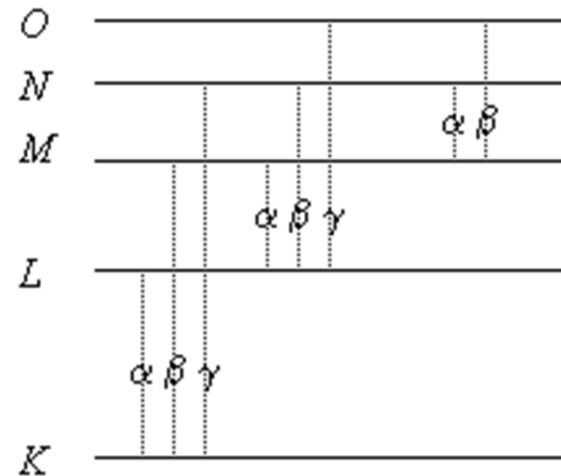
Measurement and data analysis



XRD practical aspects

Where do X-rays come from?

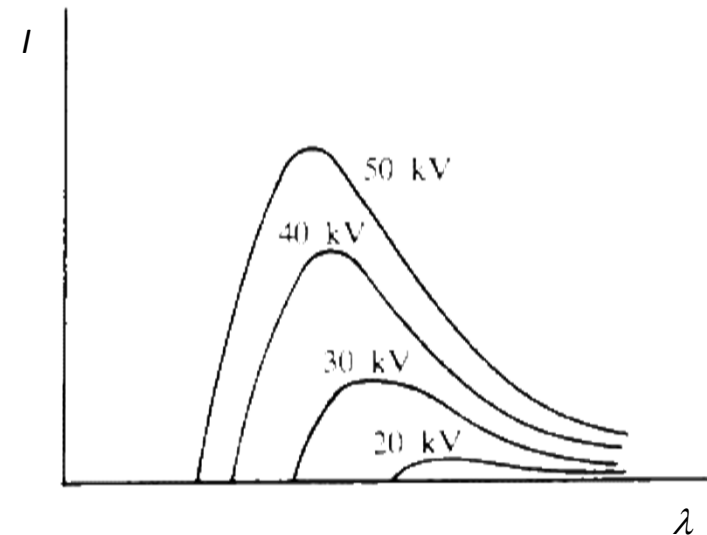
- Two principal methods for X-ray generation:
 - 1) Fire beam of electrons at metal target.
 - Ionization of inner shell electrons results in formation of an 'electron hole'.
 - Relaxation of electrons from upper shells. The energy difference ΔE ($\approx 10^{-10}$ m) is released in the form of X-rays of specific wavelengths.
- Commonly used metals are Cu K_{α} ($\lambda = 1.5418 \text{ \AA}$) and Mo K_{α} ($\lambda = 0.71073 \text{ \AA}$).
- Very Inefficient. Most energy dissipated at heat (requires permanent cooling).



XRD practical aspects

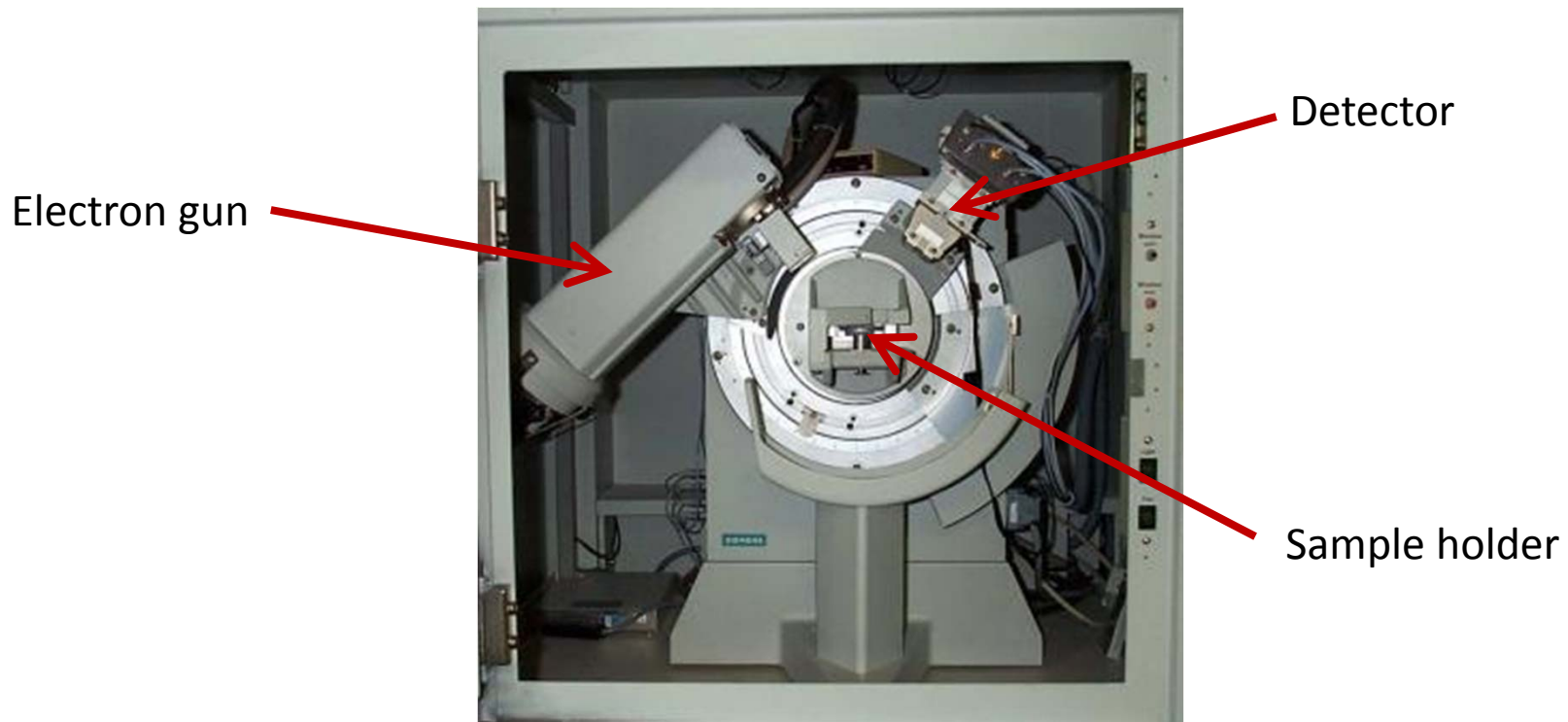
Where do X-rays come from?

- Two principal methods for X-ray generation:
 - 1) Accelerate electrons in a vacuum tube (X-ray tube).
 - 2) Accelerate electrons in a particle accelerator (synchrotron source). Electrons accelerated at relativistic velocities in circular orbits. As velocities approach the speed of light they emit electromagnetic radiation in the X-ray region.
- The X-rays produced have a range of wavelengths (white radiation or *Bremsstrahlung*).
- Results in high flux of X-rays.
- Laue experiment



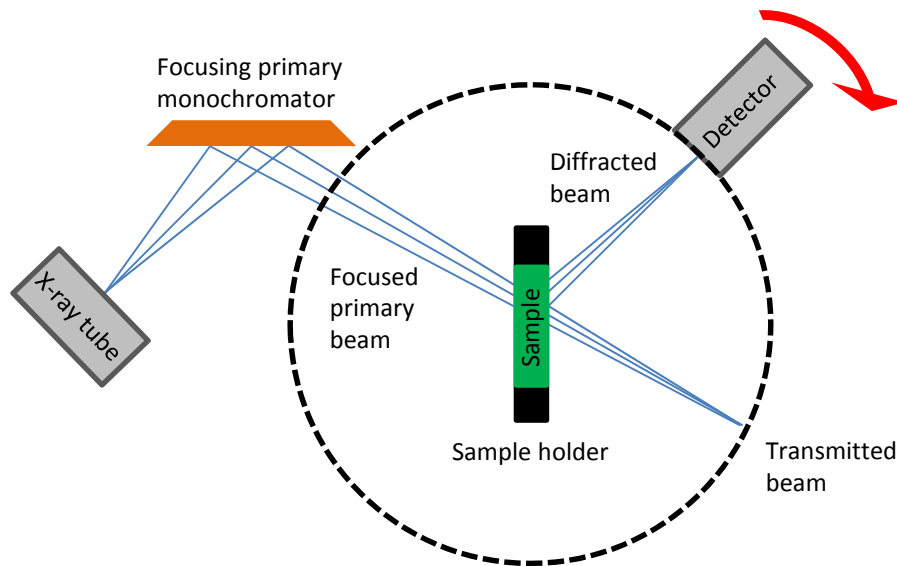
Minimum and maximum λ determined by initial kinetic energy

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



Powder diffractometer

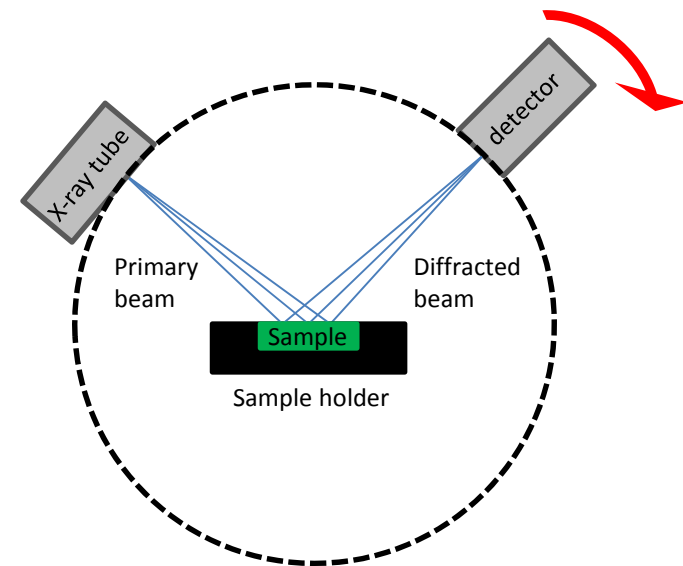
Diffractometer geometries:



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

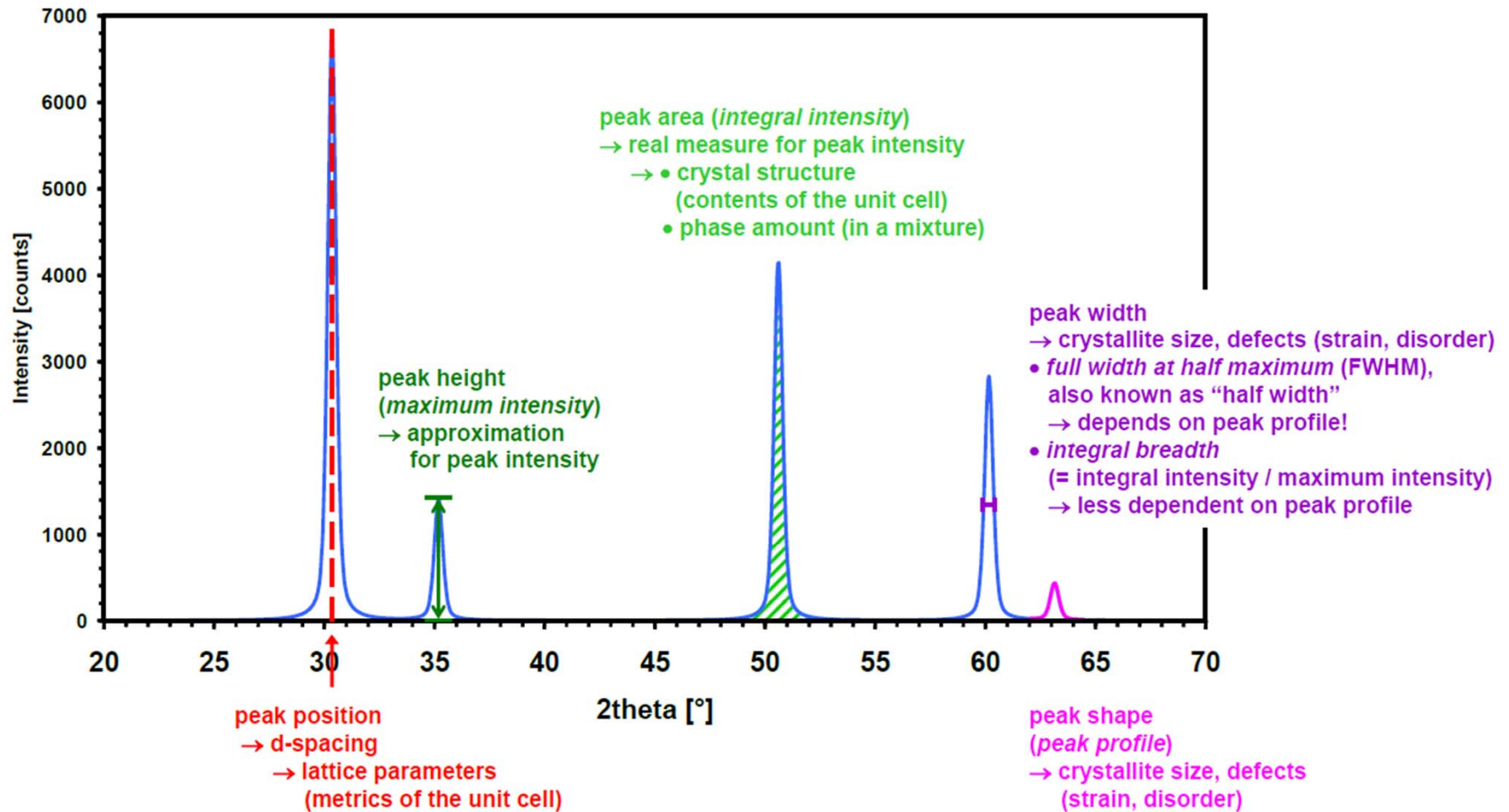
(**Bragg-Brentano** geometry).

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

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 K α).
- The “signals” in a diffractogram are called (Bragg or diffraction) peaks, lines, or reflections.

“Anatomy” of the XRD pattern

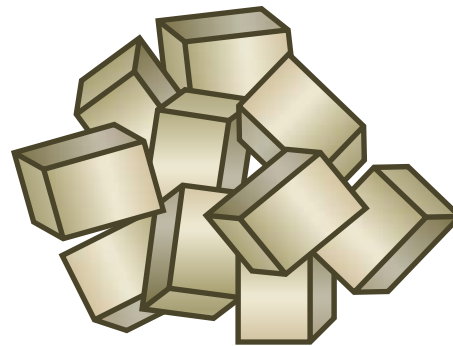
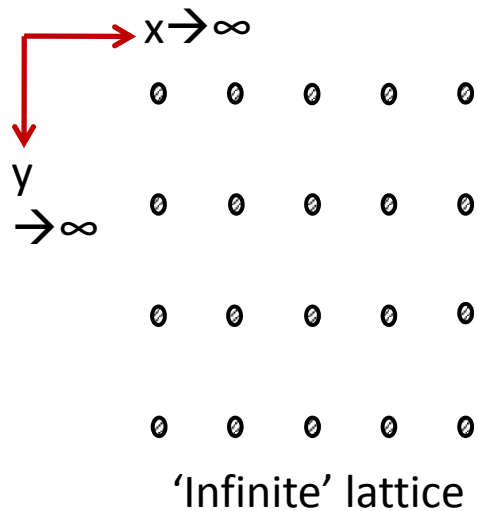


Information content of an idealized diffraction pattern.

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

Differences between theory and reality :

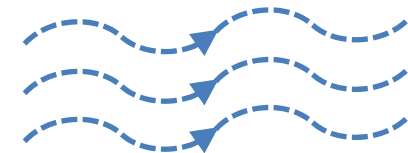
- Models based on ideal systems (Sample and X-rays).
- Reliant on several key assumptions.



All crystallite orientations present



Instrumental factors?

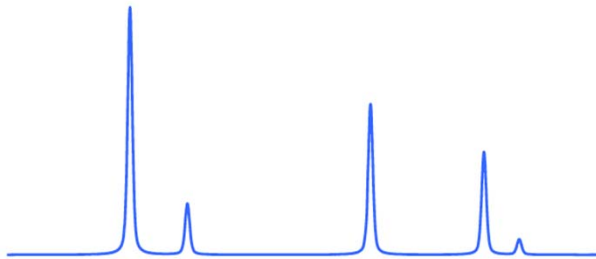


For monochromatic XRD
Single, constant, λ

What impact do these assumptions have for real experiment?

Experimentally recorded diffraction pattern:

1) Signal - what you want



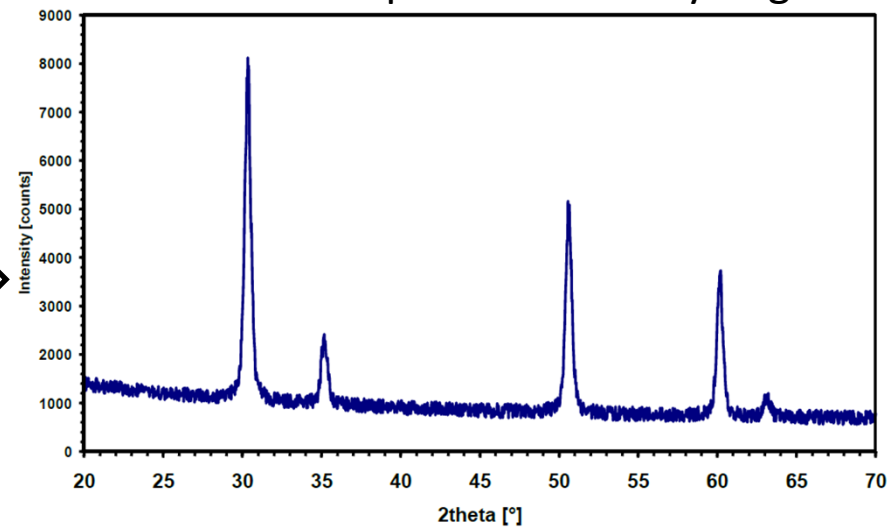
+ 2) Background



+ 3) Noise



Diffraction pattern – what you get



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:

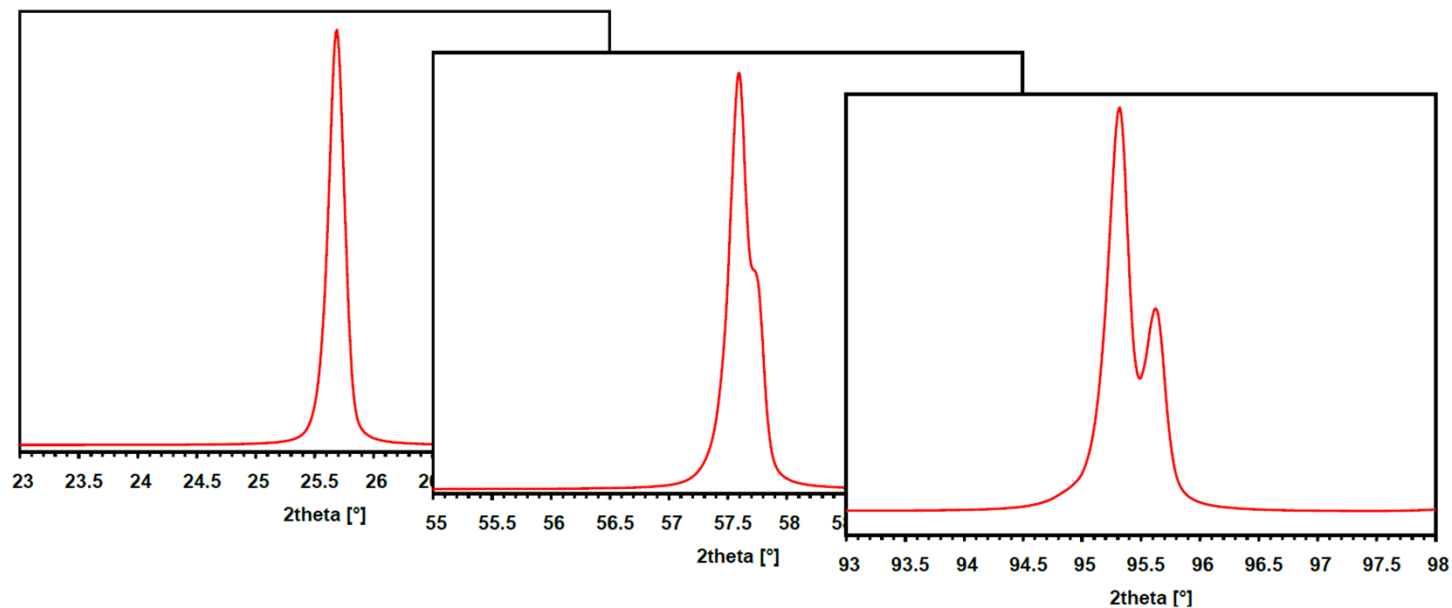
- Increasing intensity of incoming beam (synchrotron source).
- Shorter wavelength (less absorption).
- Increasing amount of sample beam (illuminated area)
- Increasing the counting time (square-root law!)

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 $K\alpha_{1+2}$ 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 twice 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.

Information from peak intensity?

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

$$I \propto |\mathbf{F}|^2$$



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

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

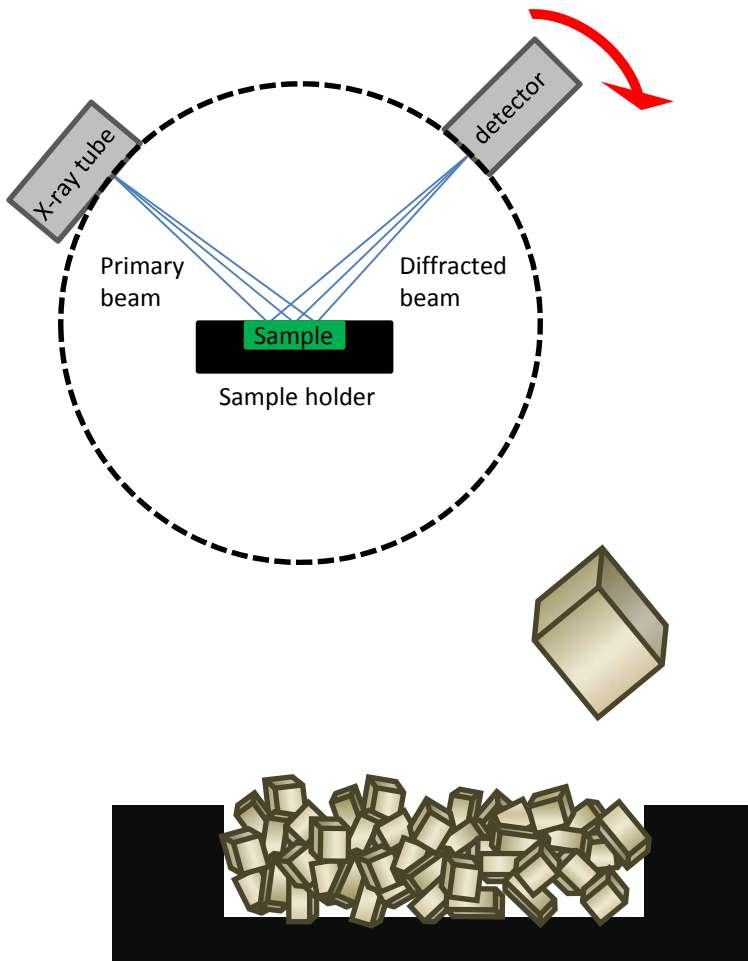
A(θ) = absorption correction: Some X-rays will be absorbed by the sample

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.

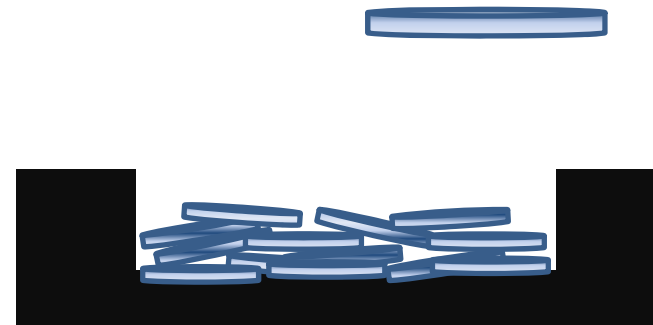
Are all crystallite orientations present?



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

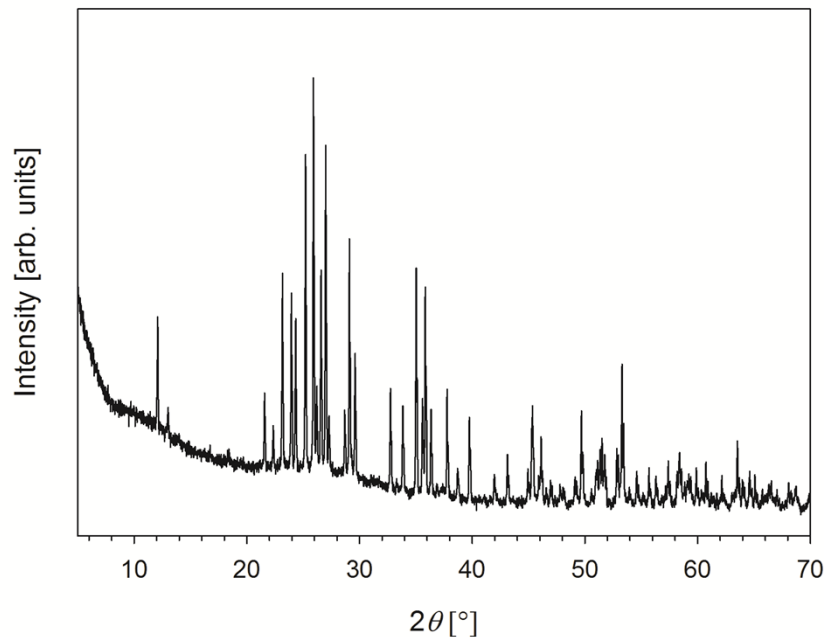
So what can we determine from XRD data?

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

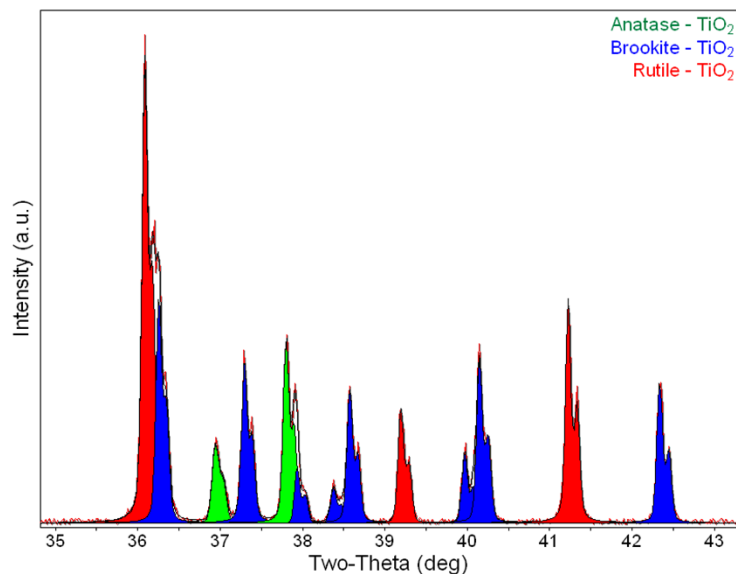
→ Estimation of size of crystalline domain and disorder.

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. TiO₂

- 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.

Simulating XRD data: For known crystal structures.

- Search for previously reported structures in database.
- Find suitable .cif file and open with viewing program such as Mercury, Materials Studio *etc.*
- Calculate powder diffraction pattern using suitable parameters.

1) Phase determination: Finding reference structures

The screenshot shows the ICSD (Inorganic Crystal Structure Database) web interface in a Mozilla Firefox browser. The page is titled "ICSD" and includes a navigation menu on the left with options like "Basic search & retrieve", "Advanced search & retrieve", "Bibliography", "Cell", "Chemistry", "Symmetry", "Crystal Chemistry", "Structure Type", "Experimental Information", "DB Info", "Query Management", "Load/Modify Queries", "Save Queries", and "Delete Queries". The main content area is titled "Basic Search" and contains several search criteria sections: "Bibliography" (Authors, Title of Journal, Year of Publication, Volume, Page), "Cell & Symmetry" (Cell Parameters, Cell Volume, Space Group, Symbol Number, Crystal class, Tolerance, Crystal System, Pearson Symbol), "Chemistry" (Composition: Ti O, Number of Elements: 2, ANX Formula, Cryst. Comp., AB Formula, Chem. Comp.), and "Exp. Info & Ref. Data" (New Data Only, Collection Code, PDF Number, Release Tag, Temperature, Pressure). There are buttons for "Clear Basic Search" and "Count Basic Search". A "Search Action" panel on the right has buttons for "Run Query", "Save Query", and "Clear Query". Below it, a "Search Summary" shows "Basic Search: 0" and a "Query History" table with one entry: "2010-09-27T09:31 BASIC 253". The footer includes "Legal Notices | Privacy Policy | Disclaimer | Copyright © FIZ Karlsruhe 2010" and "Version 1.2.1 (build 20100705-0515)".

Search terms:

- Literature reference
- Crystal structure
- Chemical name
- Composition
- Experimental data

Search

1) Phase determination: Finding reference structures

The screenshot shows the ICSD database search results page. The search criteria are: Coll. Code: P 42/m n m, HMS: Ti O2, Struct. Form.: TiO2, Struct. Type: TiO2(P6). The results table is as follows:

Coll. Code	HMS	Struct. Form.	Struct. Type	Title	Authors	Reference
23697	P 42/m n m	Ti O2	TiO2(P6)	Gutle: Normal probability plot analysis and accurate measurement of crystal structure	Abrahams, S.C.; Bernstein, J.L.	Journal of Chemical Physics (1971) 55, p3206-p3211
26492	C 1 2/m 1	Ti3 O5	Ti3O5	Crystal structure studies on trititanium pentoxide, Ti3 O5	Asbrink, S.; Magneé, A.	Acta Crystallographica (1,1948-23,1967) (1959) 12, p575-p581
29246	B 1 1 2/m	Ti O0.997		Vacancy - strain coupling in ordered Ti O	Terauchi, H.; Cohen, J.B.; Reed, T.B.	Acta Crystallographica A (24,1968-38,1982) (1976) 34, p556-p561
33837	P 42/m n m	Ti O2	TiO2(P6)	The crystal structure of rutile as a function of temperature up to 1600 degrees C	Sugiyama, K.; Takeuchi, Y.	Zeitschrift fuer Kristallographie (149,1979-) (1991) 194, p305-p313
34372	P 42/m n m	Ti O2	TiO2(P6)	Atomabstaende und Bindungswinkel im Rutil	Baur, W.H.	Naturwissenschaften (1955) 42, p295-p296
35121	I-1	Ti6 O11		Structural chemistry of the Magneli phases Tin O(2n-1), 4n=9	le Page, Y.; Strobel, P.	Journal of Solid State Chemistry (1982) 44, p273-p281
35122	I-1	Ti7 O13		Structural chemistry of the Magneli phases Tin O(2n-1), 4n=9	le Page, Y.; Strobel, P.	Journal of Solid State Chemistry (1982) 44, p273-p281
35123	I-1	Ti8 O15		Structural chemistry of the Magneli phases Tin O(2n-1), 4n=9	le Page, Y.; Strobel, P.	Journal of Solid State Chemistry (1982) 44, p273-p281
35124	I-1	Ti9 O17		Structural chemistry of the Magneli phases Tin O(2n-1), 4n=9	le Page, Y.; Strobel, P.	Journal of Solid State Chemistry (1982) 44, p273-p281
35148	I 1 2/c 1	Ti3 O5		The structure of gamma-Ti3 O5 at 297 K	Hong, S.H.; Asbrink, S.	Acta Crystallographica B (24,1968-38,1982) (1982) 38, p2570-p2576

Useful information:

Generates list of reported structures.

- Can select high quality data only.
- ➔ Data in which all experimental parameters are reported.

In general more recent data is higher quality (Improvements in diffractometers).

Results

1) Phase determination: Finding reference structures

The screenshot shows the ICSD database interface for collection code 33837. The 'Summary' section contains the following data:

Summary		Collection Code 33837	
Struct. formula	TiO ₂	Author	Sugiyama, K.; Takeuchi, Y.
Space Group	P 42/m n m (136)	Title of Article	The crystal structure of rutile as a function of temperature up to 1600 degrees C
Unit Cell	4.5924(2) 4.5924(2) 2.9575(2) 90 90 90	Reference	Zeitschrift fuer Kristallographie (149,1979-) (1991) 194, p305-p313
Cell Volume	62.37 Å ³	Formula Units per Cell	2
Temperature	298.00 K	Pressure	0.101325 MPa (default)
PDF-numbers	01-076-0317 21-1276	R-value	0.0269
Remark		Warnings & Comments	0 Warnings / 2 Comments

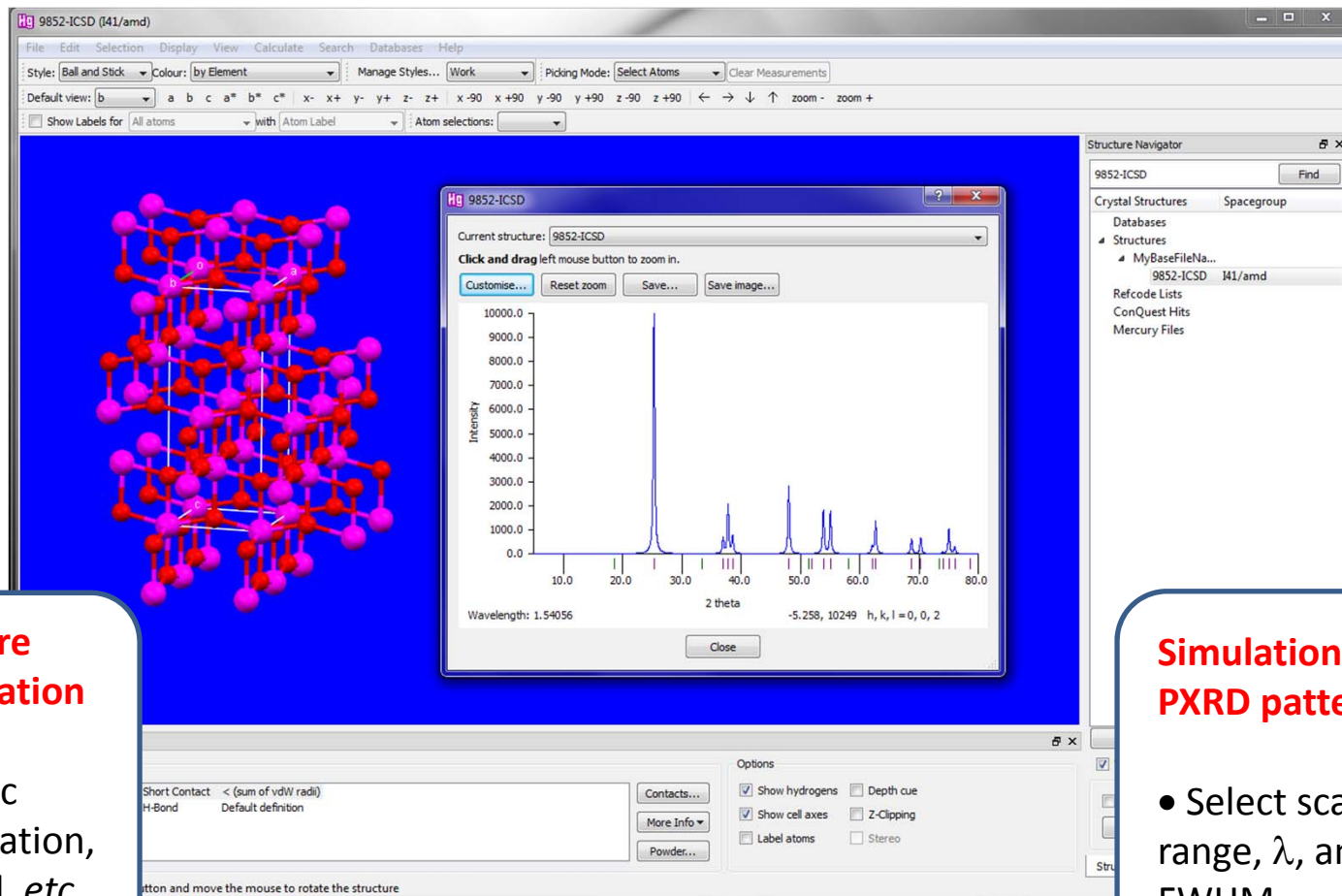
Below the summary, there is an 'Export CIF File' button with a red arrow pointing to it. The 'Details' section is expanded to show various categories like Visualization, Chemistry, and Experimental Information.

Useful information:

- Cell parameters
Useful for comparative purposes
- Bibliographic reference.
Preparation and experimental details.
- Temperature of data collection
Thermal expansion
→ Changes in lattice parameters
→ Changes in peak positions.
- R-Value
Indication of data quality

Download .cif file

1) Phase determination: Simulating the PXRD pattern of a reference structure



Structure visualization

- Atomic coordination, unit cell, *etc.*

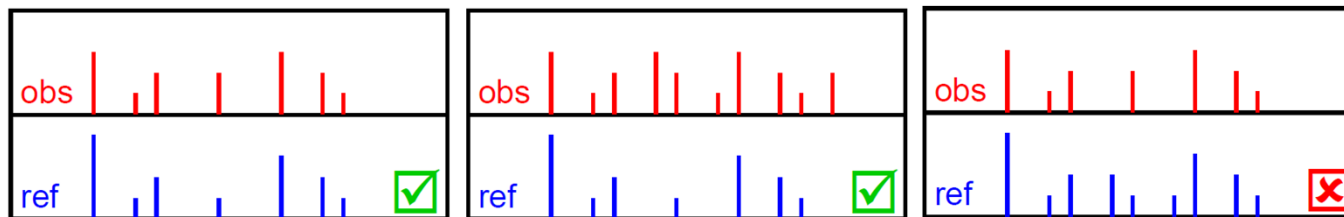
Simulation of PXRD pattern

- Select scan range, λ , and FWHM.

➔ Compare simulated patterns with measured data

1) Phase determination: FAQ

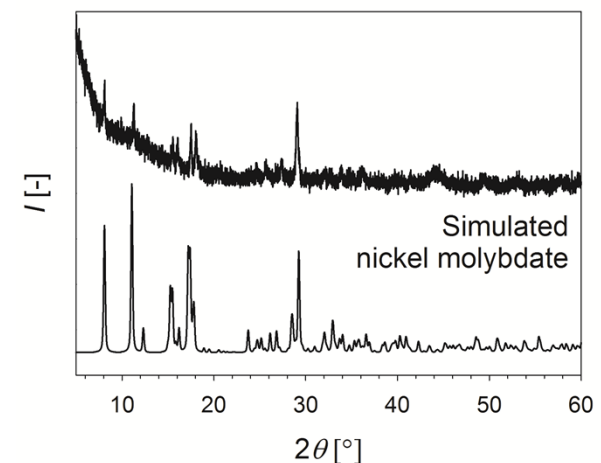
Q: How many peaks must match between a reference PDF pattern and a measured diffractogram?



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

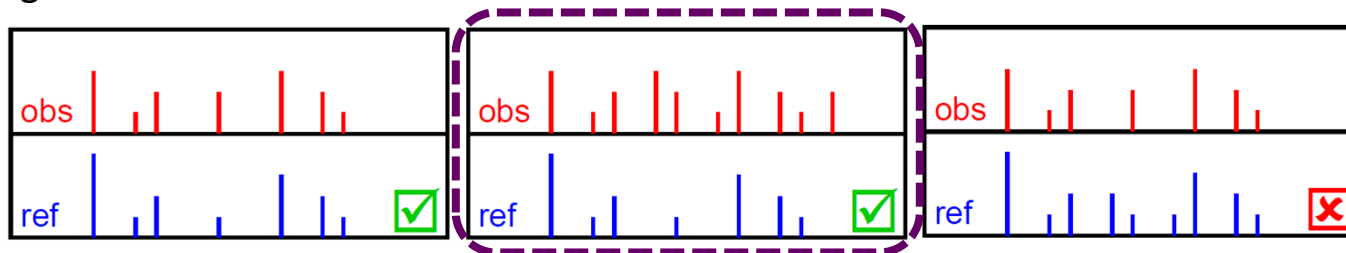
Exceptions?

- 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



1) Phase determination: FAQ

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

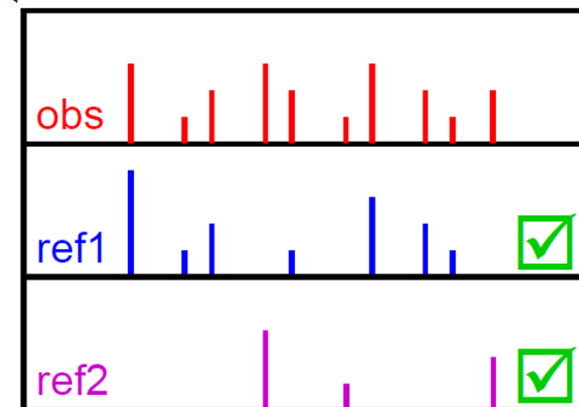


A: Generally, **all** expected reflections should be seen in the diffractogram, otherwise it is not a valid match.

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.



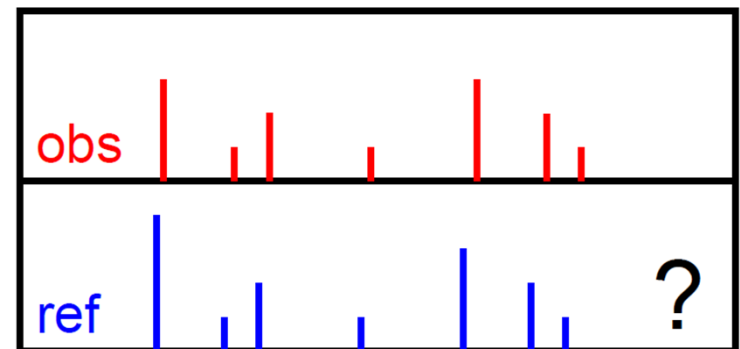
1) Phase determination: FAQ

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 $\text{A}_{1-x}\text{B}_x\text{O}_2$, BO_2 , AO_{2-x} ,...

2) Quantitative phase analysis

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

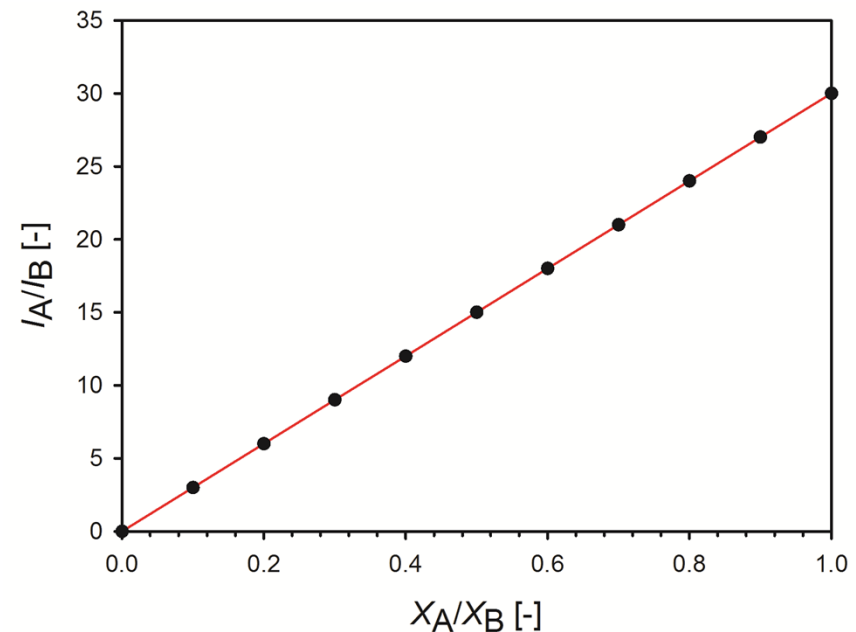
- Ratio of peak intensities varies linearly as a function of weight fractions for any two phases (*e.g.* A and B) in a mixture.

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

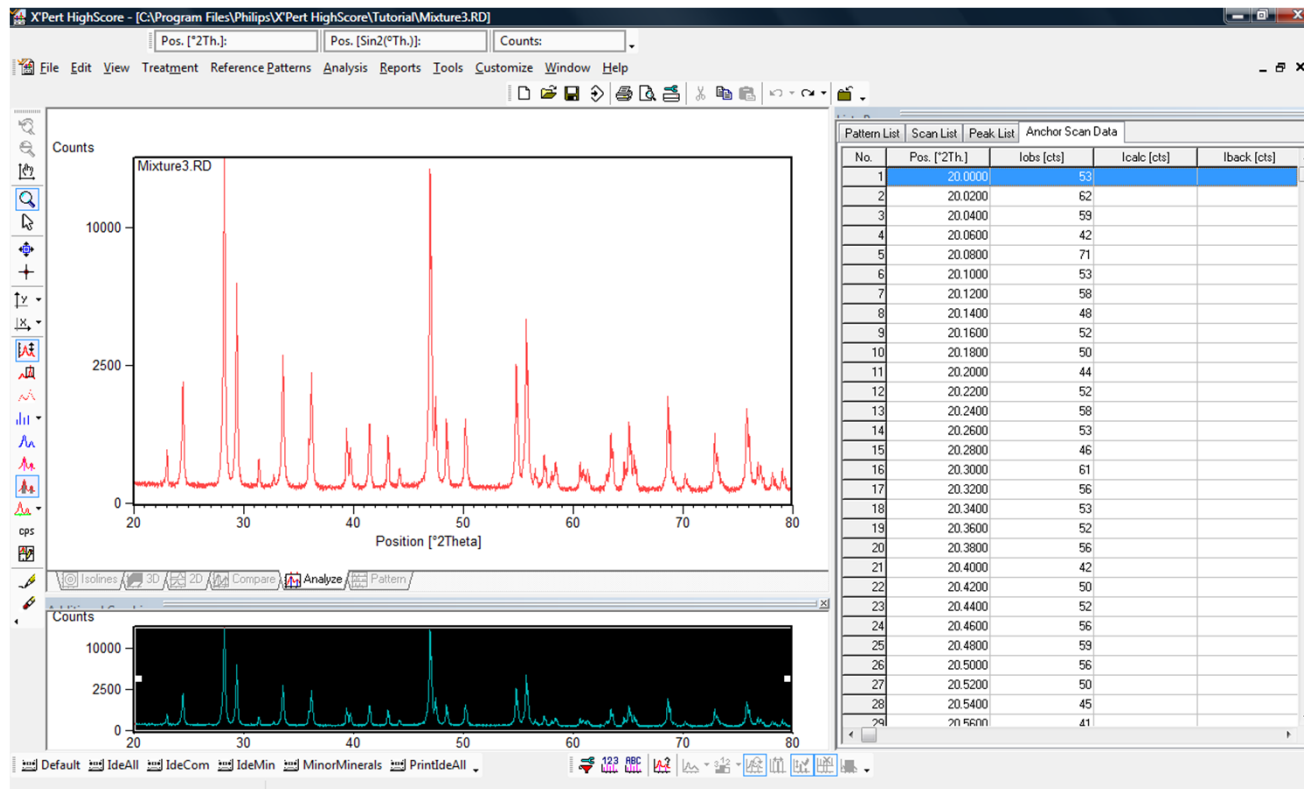
Al₂O₃ (Corundum)
SiO₂ (Quartz)
ZnO

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

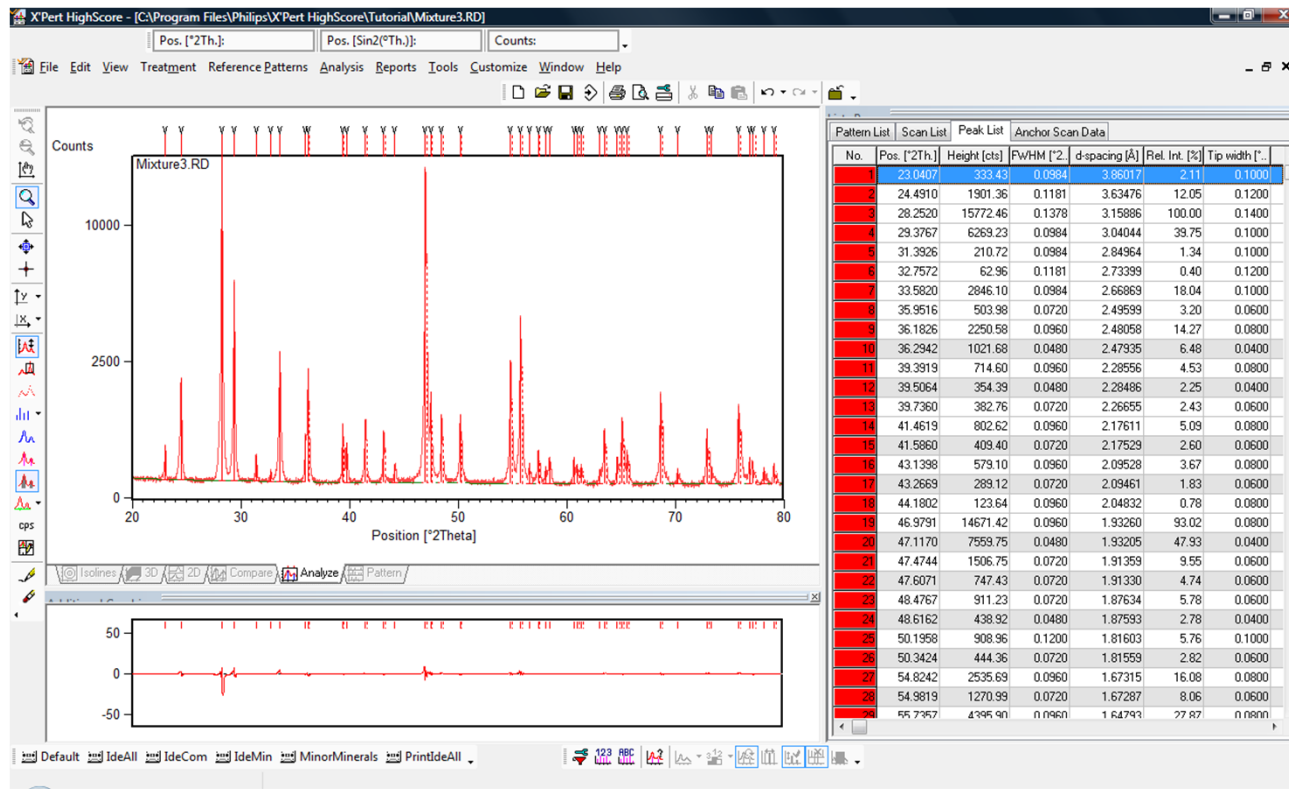
- Diffraction angle related to d-spacing via Bragg equation.



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

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

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

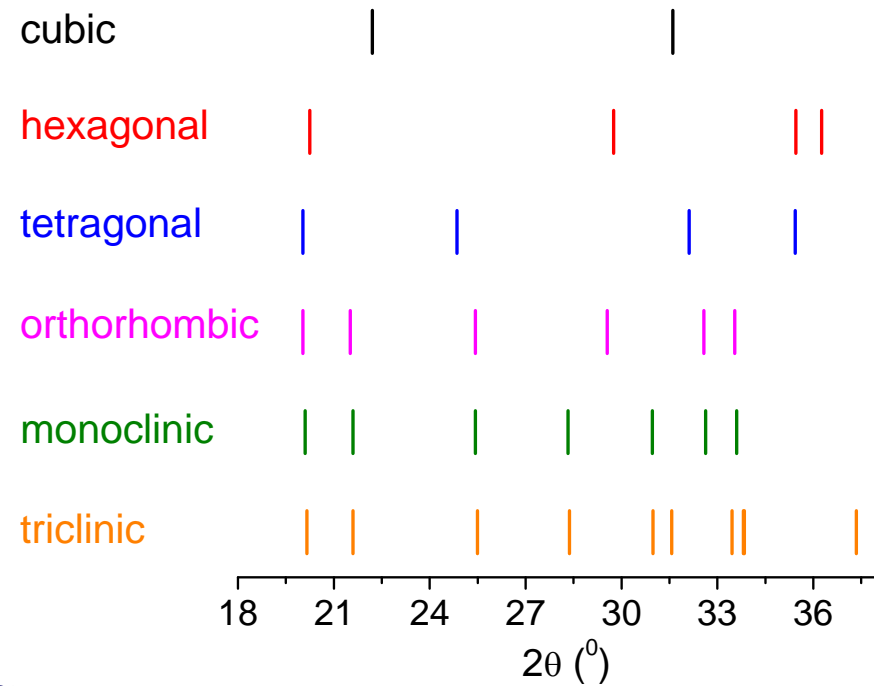
$$\sin^2 \theta = \left(\frac{\lambda^2}{4a^2} \right) (h^2 + k^2 + l^2) \quad \left(\frac{\lambda^2}{4a^2} \right) = \text{constant}$$

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 $\lambda = 1.54 \text{ \AA}$.

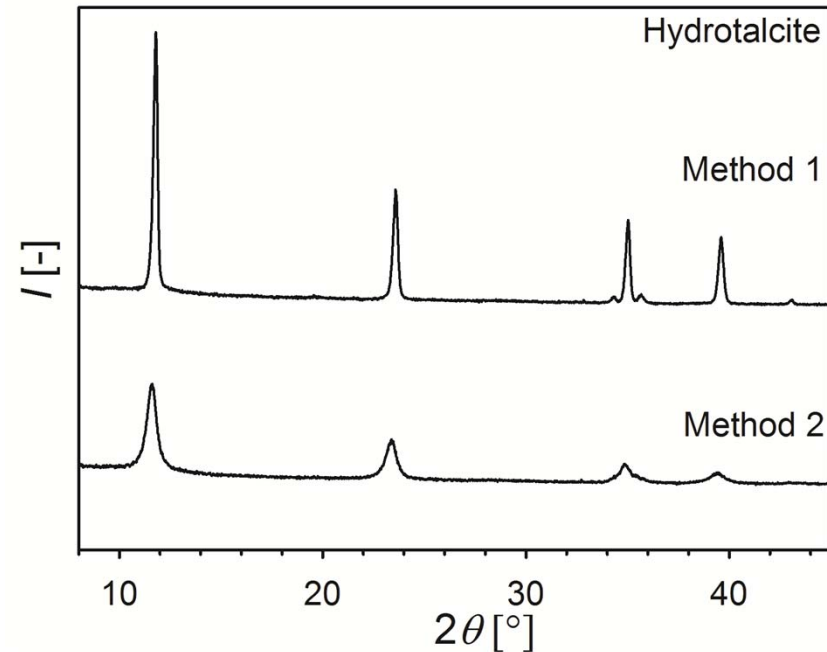
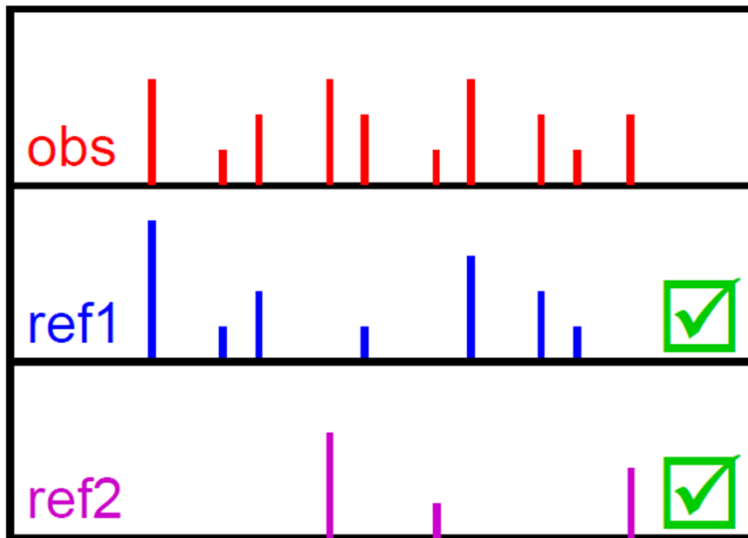


Peak multiplicities decrease from cubic to triclinic:

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

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

Real measurement

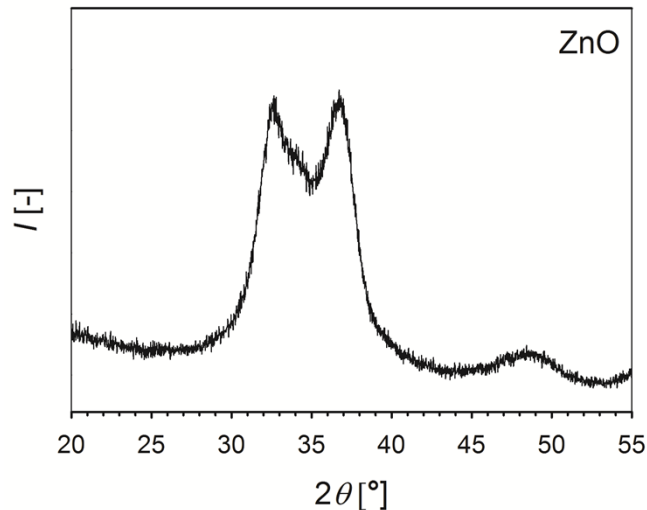
→ Diffraction lines have finite width.

→ Peak profile.

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

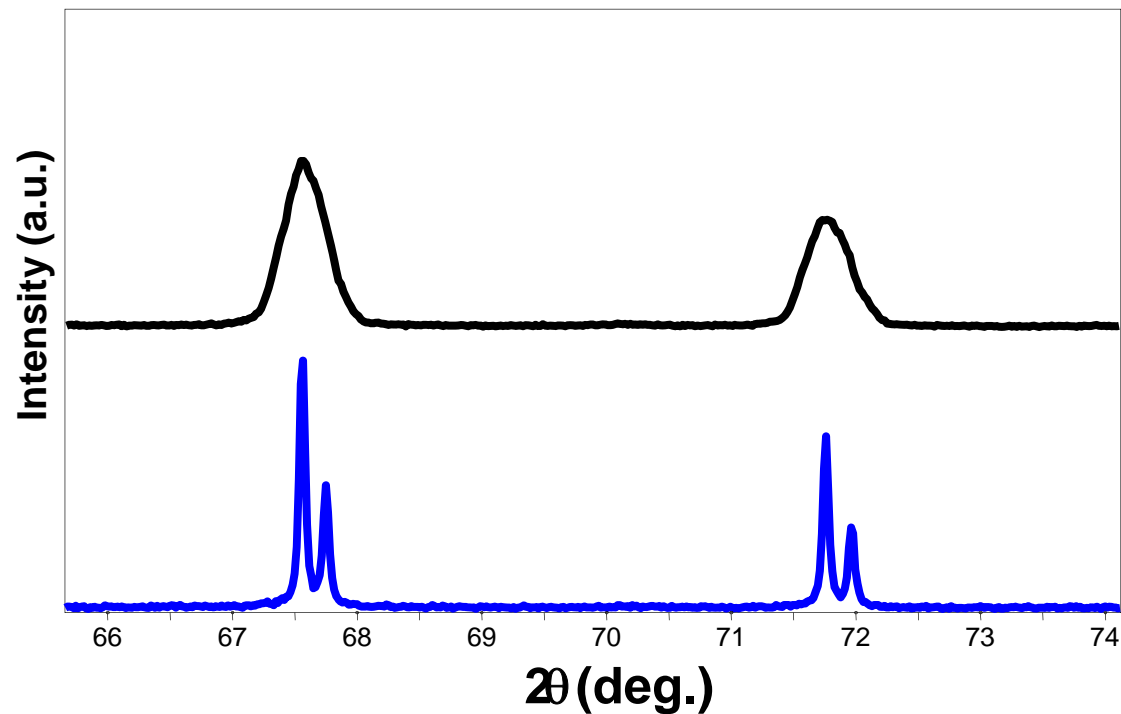
- Periodicity in crystals is not infinite as crystals have:

Finite size → **size broadening**. Most apparent in crystals smaller than ≈ 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?



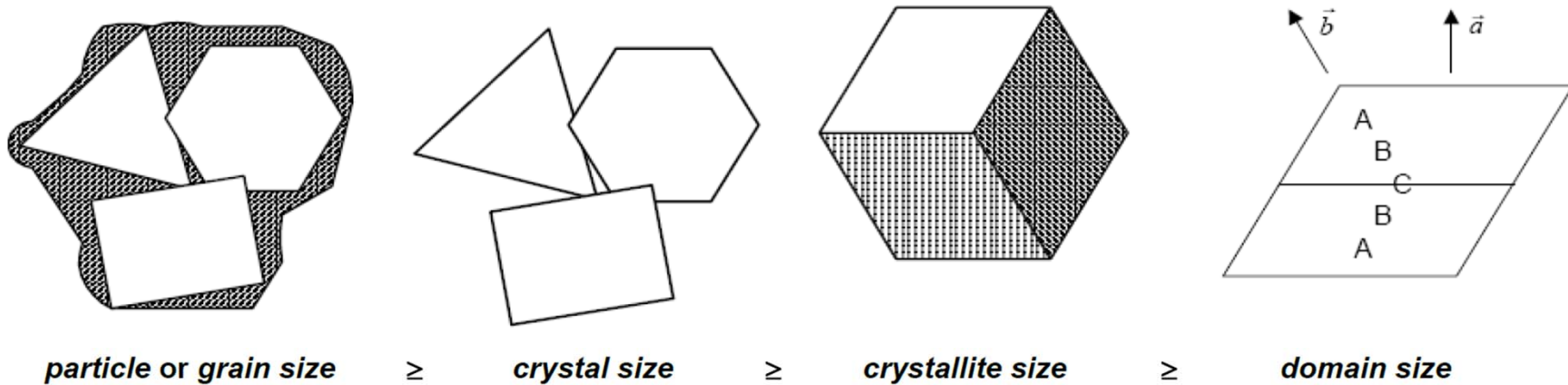
Exact same sample!

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:



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.

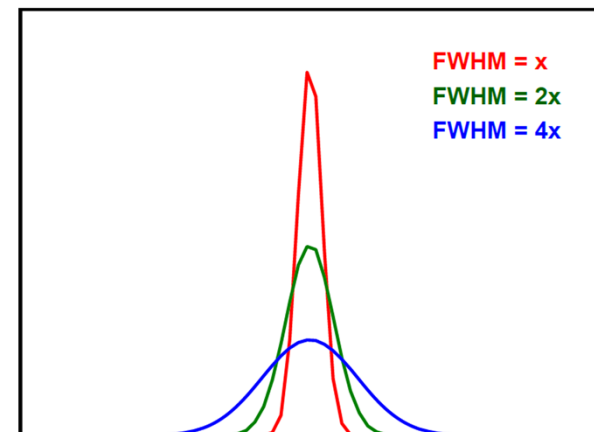
θ Diffraction angle of the reflection.

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)

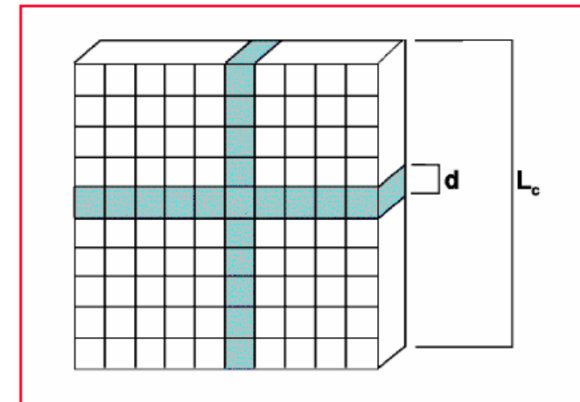
4) Analysis of crystallite size: How does the size broadening effect translate to crystal size?

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

Significance of apparent crystal thickness L

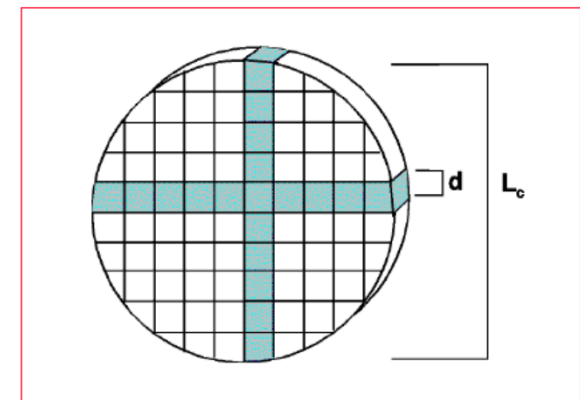
• Volume averaged crystal thickness, L , dependent on crystal shape. Examples:

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)



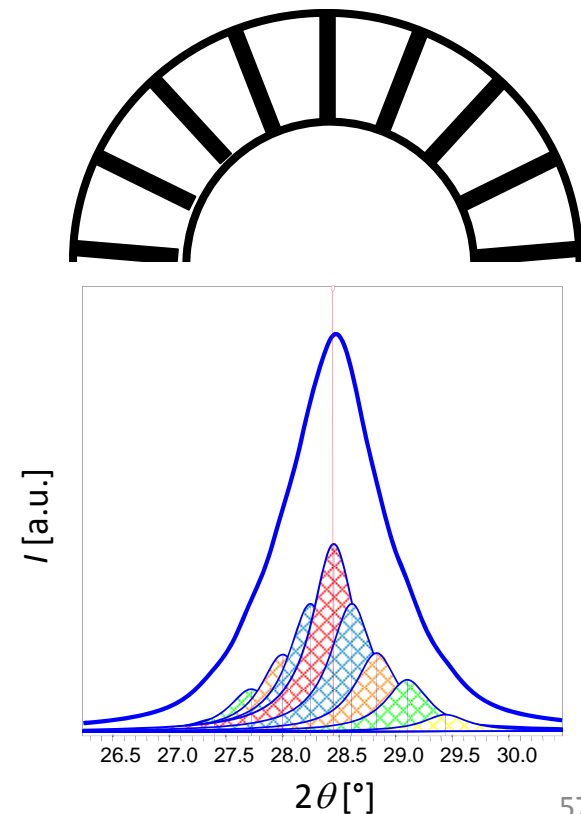
4) Analysis of microstrain broadening

- 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 $\epsilon_0 = \Delta d/d$, with d the idealized d -spacing and Δd the most extreme deviation from d .

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

$$B_{strain}(2\theta) = 4\epsilon_0 \tan \theta$$



4) Size/strain analysis: peak broadening summary

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

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

- 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:

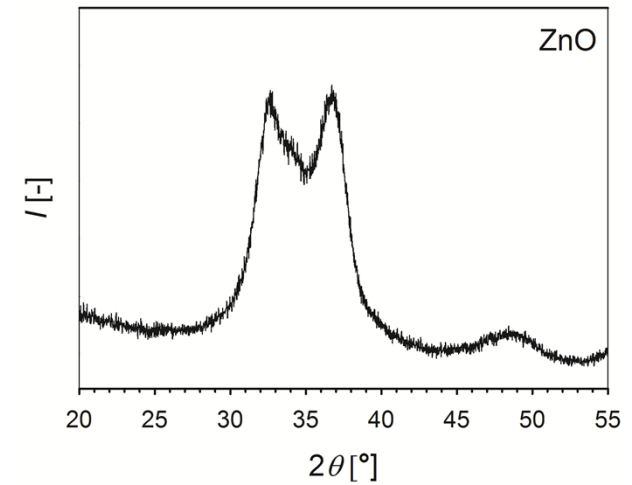
$$B_{\text{size}} \propto 1/\cos\theta$$

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

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

4) Practical aspects of size/strain analysis: Conclusions

- Do not trust the results in terms of **absolute values**.
- Use a constant procedure for a series of samples .
- Rely on **relative trends**.
- Do not seriously compare results from different sources.
- Don't be surprised if other analytical methods (*e.g.* TEM) yield different results.
- Publish results with detailed description of determination procedure



Warning: Unfortunately, people tend to believe in numbers. Uncertainties which do not appear as “error bars” are easily forgotten. Thus, if you give results from an XRD size/strain analysis to other people (*e.g.* as a table in your thesis), be aware that they will probably be taken more serious than they should...

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.

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.



How do we obtain an initial structural model? Trial and error

- Solid solutions usually adopt similar structure types as their parent compounds;
e.g. $\text{NaSr}_{4-x}\text{Ba}_x\text{B}_3\text{O}_9$ ($0 \leq x \leq 4$)
- Compounds with similar chemical formula may have similar structures *e.g.* $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{NdBa}_2\text{Cu}_3\text{O}_7$

Note: 100 % fit corresponds to all phases modeled which may not be 100 % sample (amorphous material/unknown phases *etc.*).

5) Rietveld analysis: Calculation of spectrum

Principles

To minimize the residual function :

$$WSS = \sum_i w_i (I_i^{exp} - I_i^{calc})^2, w_i = \frac{1}{I_i^{exp}}$$

where:

$$I_i^{calc} = S_F \sum_k L_K |F_k|^2 S(2\theta_i - 2\theta_k) P_k A + bkg_i$$

- F_k = Structure factor.
- P_k = Preferred orientation factor

$$P_k = \left(r^2 \cos^2 \alpha + \frac{\sin^2 \alpha}{r} \right)^{-\frac{3}{2}}$$

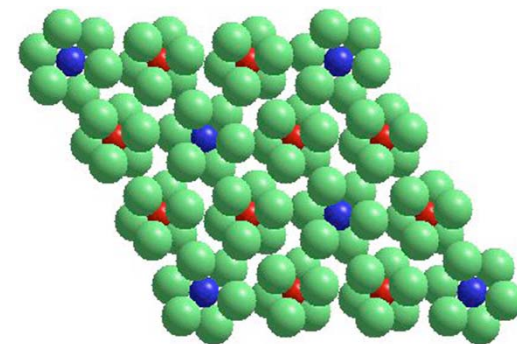
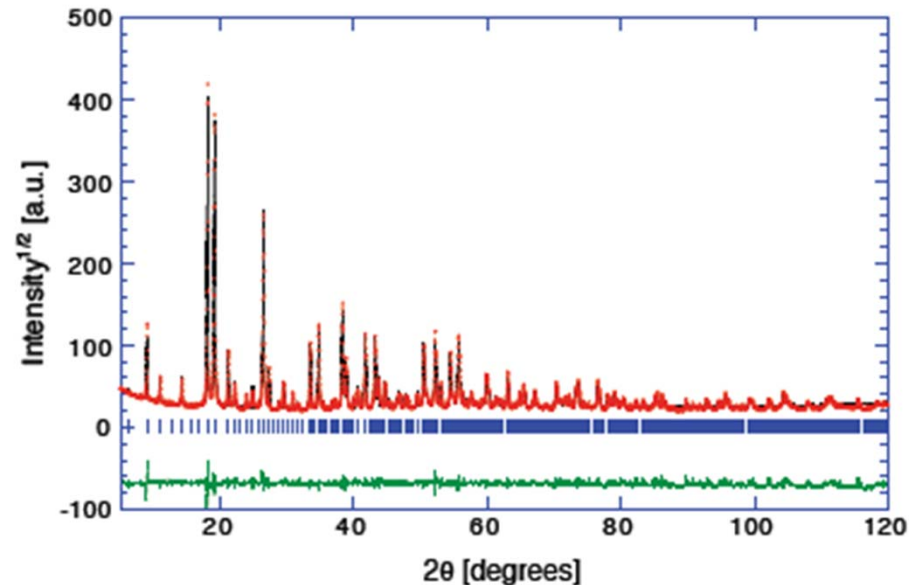
→ Accounts for intensity variation.

- $S(2\theta_i - 2\theta_k)$ = Profile shape factor (Pseudo Voigt)

$$FWHM^2 = U \tan^2 \theta + V \tan \theta + W$$

→ Accounts for line broadening.

- bkg_i = Accounts for background contribution.



Rietveld, Acta Cryst. 22, 151, 1967.

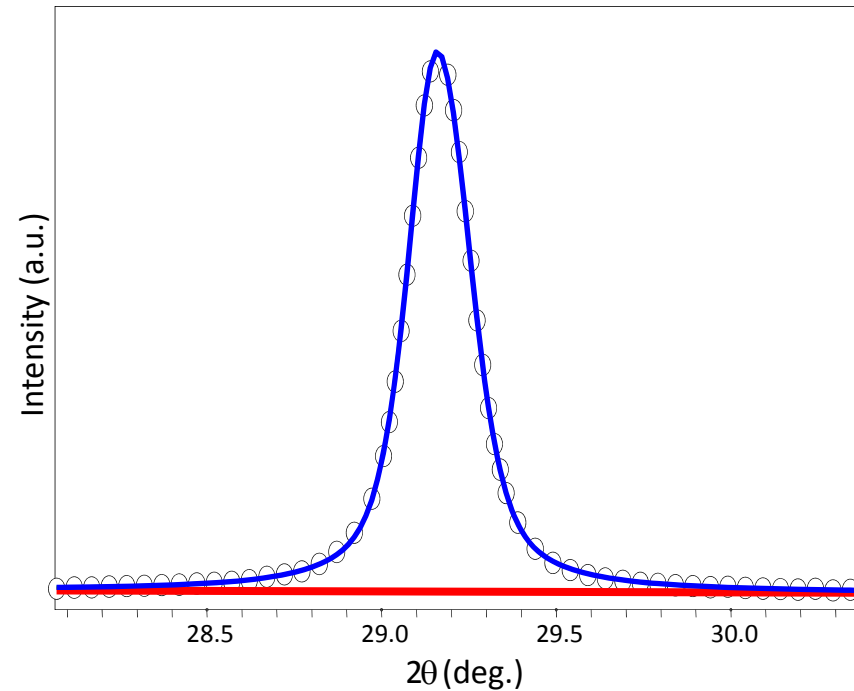
Profile fitting

- Empirically fit experimental data with a series of equations.

Methods:

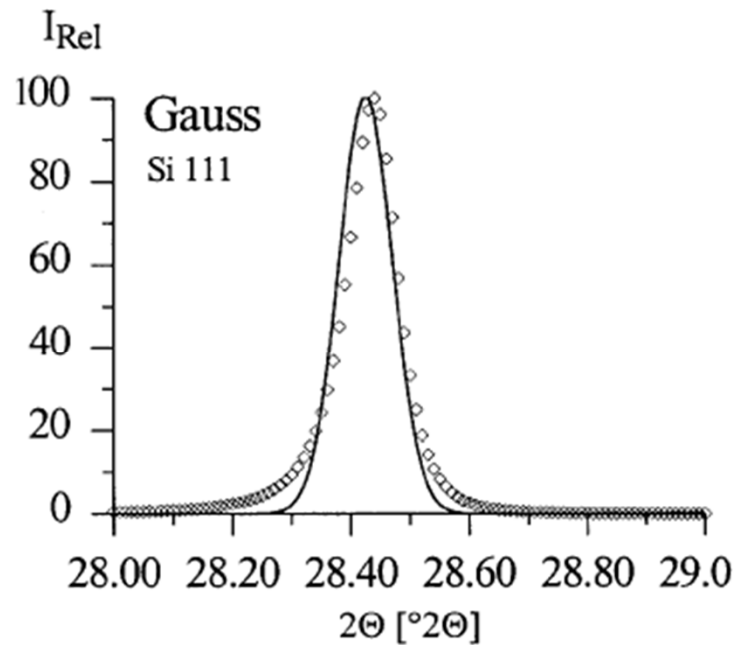
- Single Peak
- Whole pattern
(complicated if more than one phase).
- Rietveld (calculated structure).

Background typically assumed to be linear.

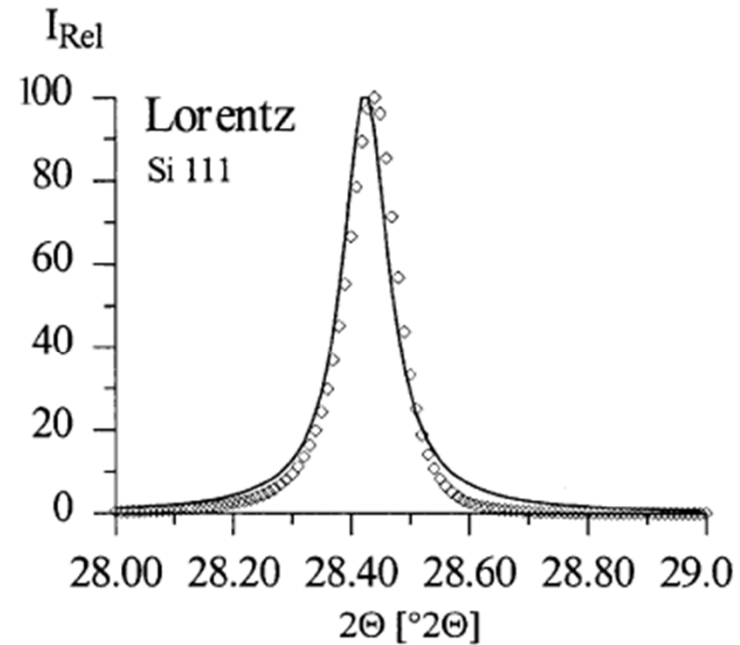


Peak fitting → precise peak parameters (position, intensity, FWHM, shape).

Profile fitting



a)



b)

- Diffraction peaks usually contain both Gaussian and Lorentzian contributions.

Difficult to deconvolve

➔ Most data fitted with a profile function combining both Gaussian and Lorentzian components:

- pseudo-Voigt (linear combination)

- Pearson VII (exponential mixing)

In situ XRD

XRD under “**Non-ambient**” conditions:

- Elevated or reduced temperature.
- Elevated or reduced pressure.
- Vacuum.
- Defined gas atmosphere.



Why is this important?

Knowledge of structure useless if the structure changes “under catalytic reaction conditions”.

→ “*in operando*” XRD.

What can we learn?

- Temperature or pressure induced phase transitions
- Solid/gas reactions
- Time resolved measurements → reaction kinetics
- Solid/solid reactions
- Formation of reaction intermediates

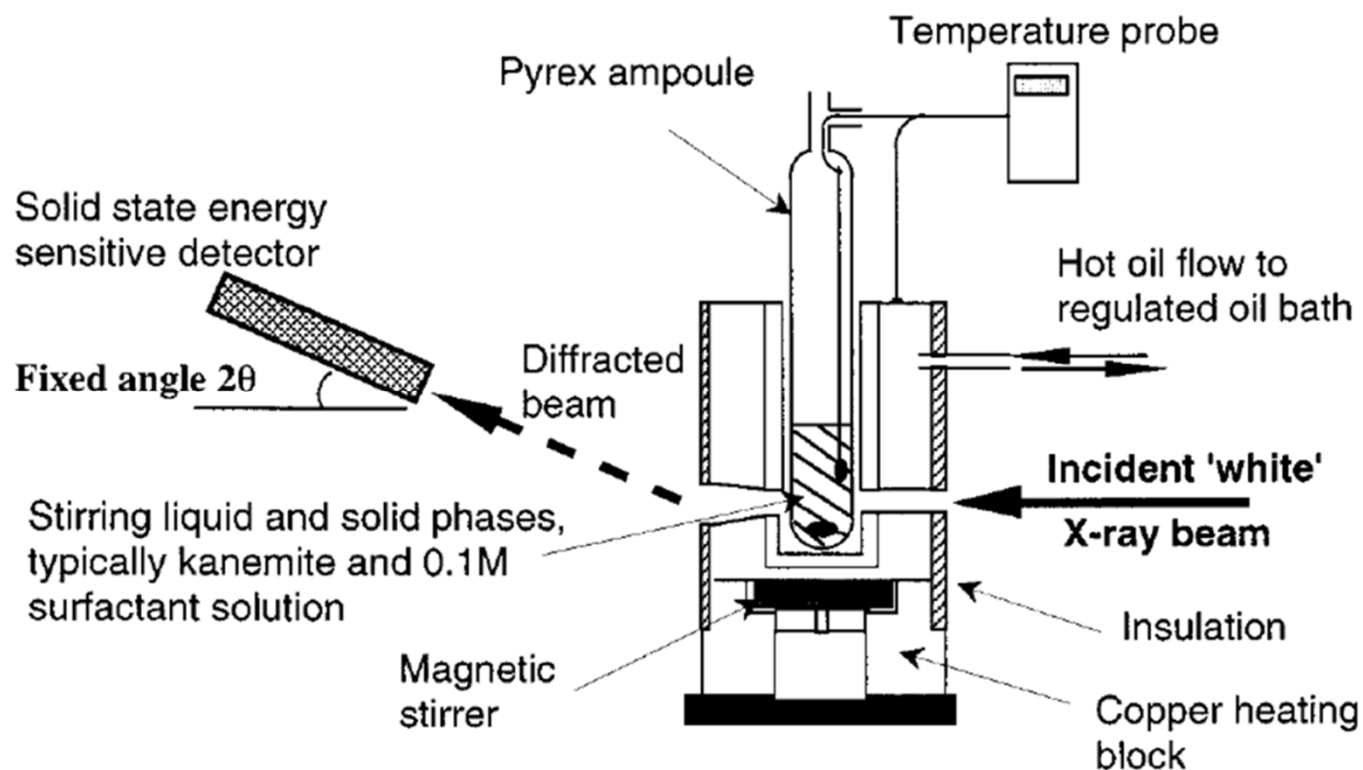
In situ XRD

In the context of catalysis, the application of *in situ* XRD may help with:

- Characterization of the active catalyst
 - Activation/deactivation behavior of the catalyst
 - Characterization of catalyst precursor materials
 - Investigation of some catalyst preparation steps
(*e.g. in situ* calcination)
 - Investigation of catalyst material reactivity
(oxidation, reduction, decomposition reactions)
- Clues for understanding activity/mechanisms
-
- Structure activity correlations
- Preparation/structure correlations.
(chemical memory)
- Knowledge based catalysis design

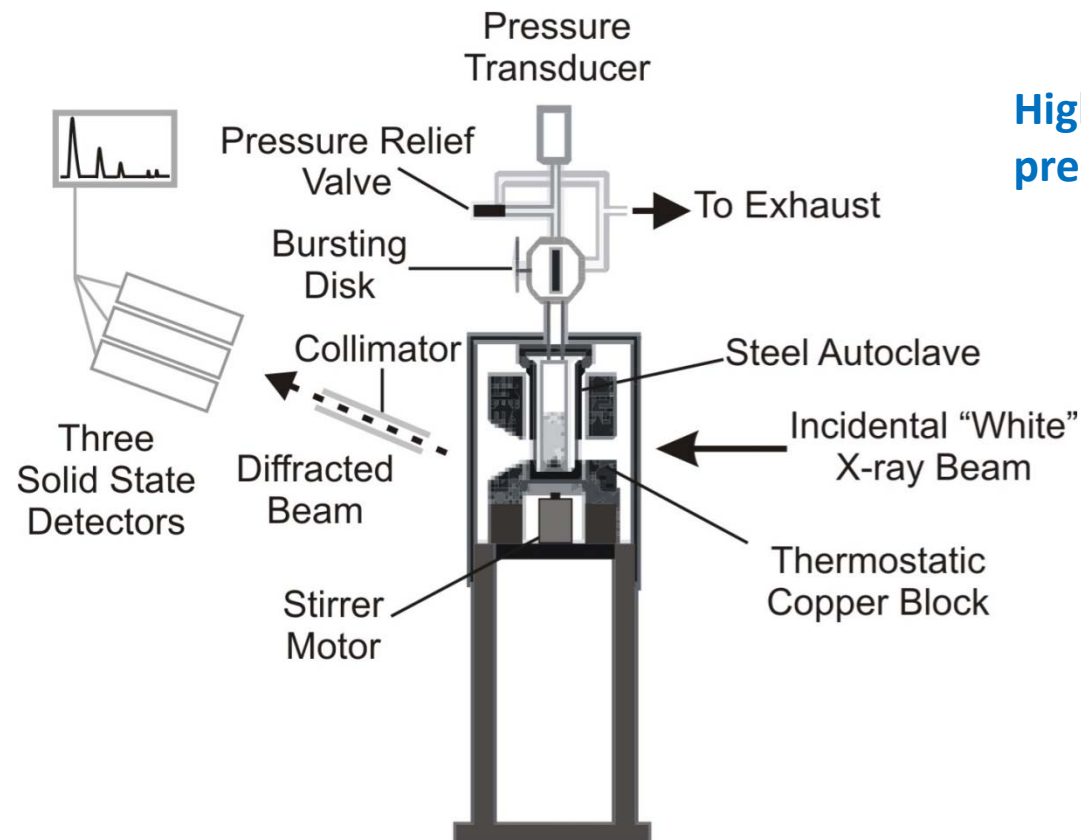
Example: If the onset temperatures of reduction and catalytic activity coincide, we may suspect that lattice oxygen is involved in the catalytic reaction mechanism.

In situ XRD: Synchrotron studies



- Higher flux → Rapid data acquisition
- Higher intensity → Greater penetration.
- Permits study of liquid phase reactions (also relevant to catalyst synthesis).

In situ XRD: Synchrotron studies



High temperature /
pressure studies

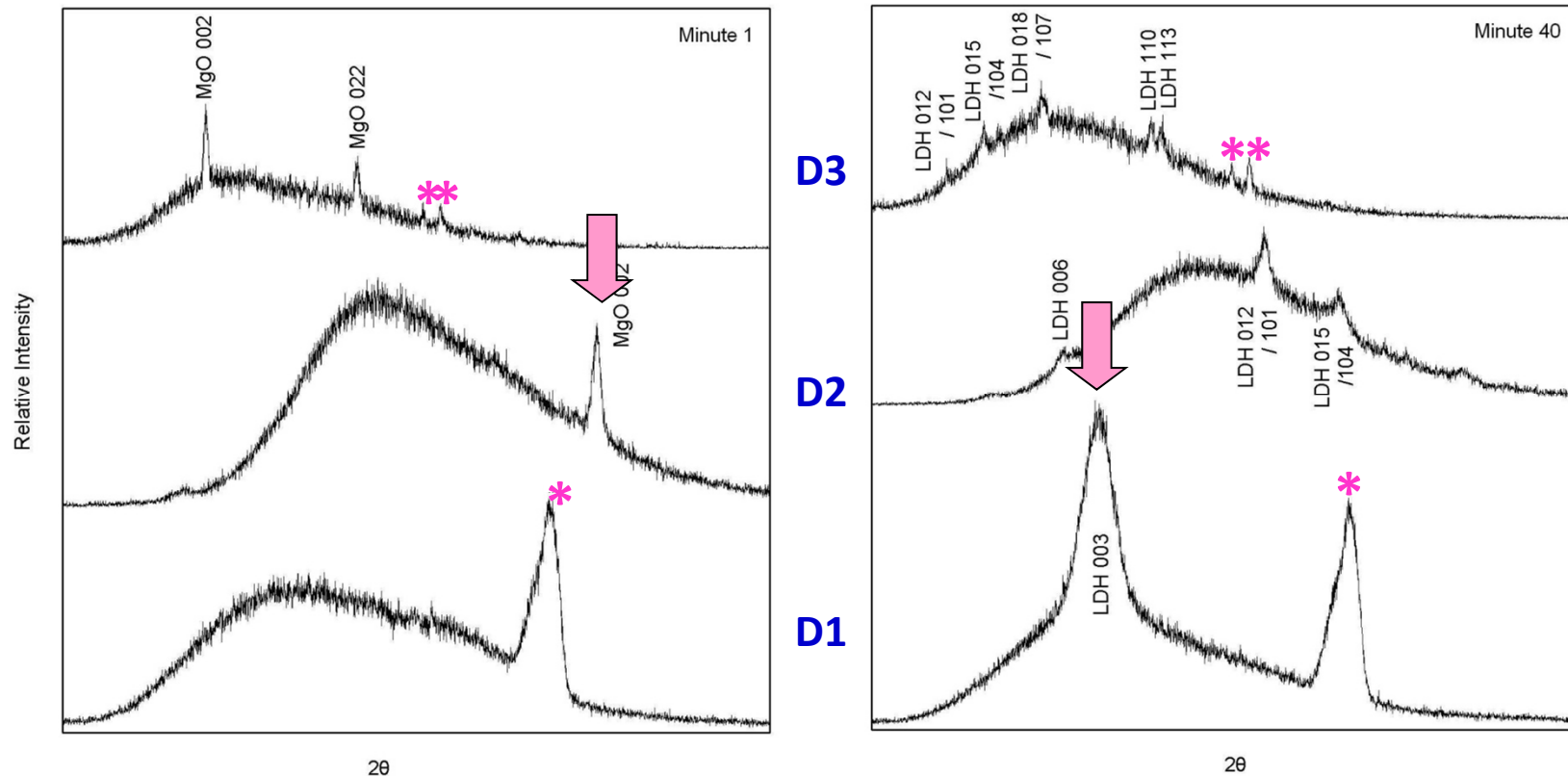
- Higher flux → Rapid data acquisition
- Higher intensity → Greater penetration.
- Permits study of liquid phase reactions (also relevant to catalyst synthesis).

In situ XRD: Synchrotron studies – Example



Precursor for
spinel base
catalysts

Diffraction patterns recorded at 150 °C

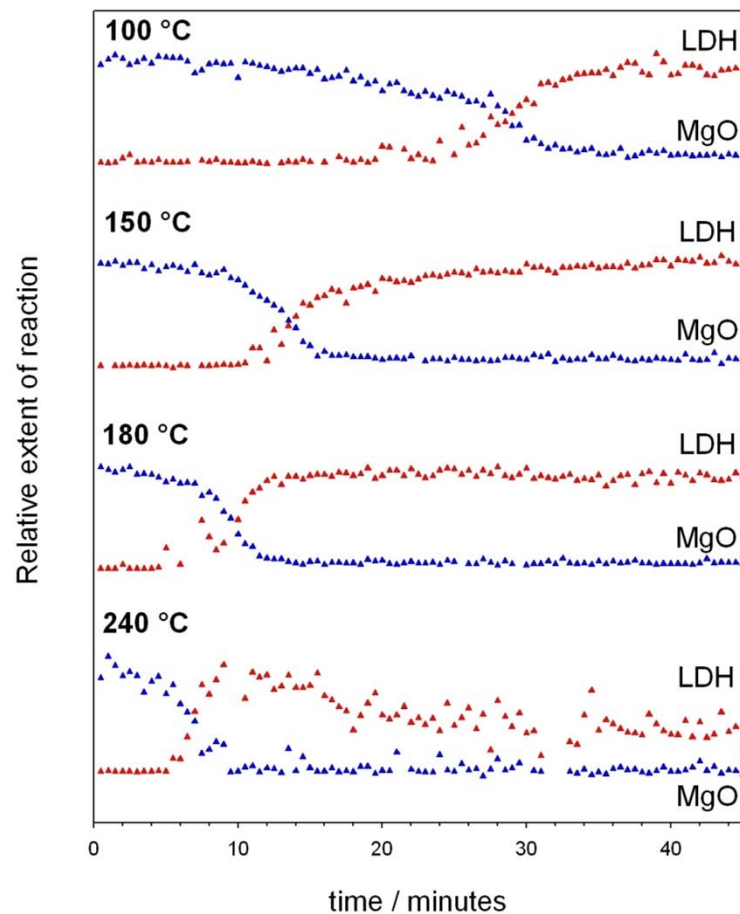


2θ D1 = 6 - 18.5 °, D2 = 18 - 50 °, D3 = 28 - 100 °

In situ XRD: Synchrotron studies – Example



Precursor for
spinel base
catalysts

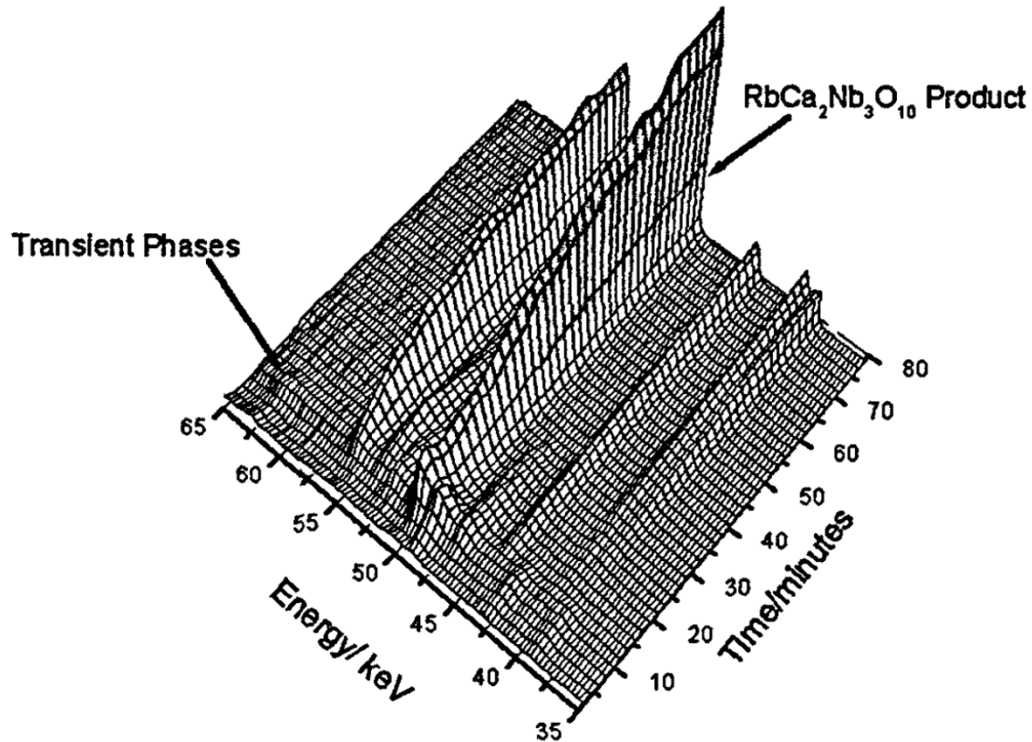


Obtainment of time resolved data:

- Kinetics of consumption and growth of crystalline phases.
- Reaction rate increases with temperature in agreement with **Arrhenius kinetics**.

In situ XRD: Synchrotron studies

Preparation of a layered Perovskite by molten salt route at 800 °C.



Obtainment of time resolved data:

→ Kinetics of consumption and growth of crystalline phases.

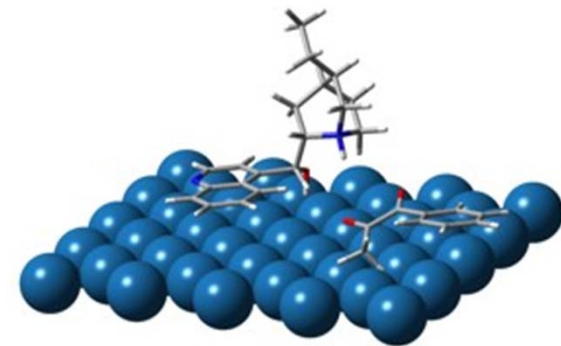
→ Detection of at least two transient phases.

Note: Data is presented as intensity versus energy (λ).

In operando XRD

To take full advantage of *in situ* investigations on catalysts under operation conditions, the **catalytic activity** must be monitored simultaneously.

➔ Provides common scale to correlate the results of different *in situ* methods.



On-line monitoring of the gas phase by:

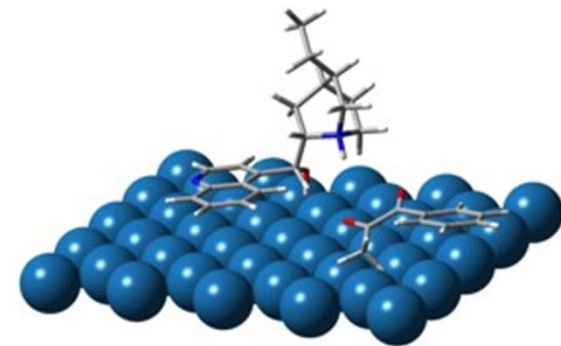
- mass spectrometry (high time resolution, but often only semi-quantitative),
- gas chromatography (lower time resolution (minutes scale), but better quantification).

***In situ* XRD: Relevance for catalysis**

X-ray diffraction characterizes the *average bulk structure* of *crystalline* material.

Are the results obtained relevant for catalysis?

- Catalytic reactions usually occur at the *surface* of a heterogeneous catalyst.
- *Active sites* often differ from '*average*' structure.
- The catalytically active phase may be *XRD amorphous*.



Depends on system under investigation, XRD *may* give clues relevant for catalysis, since:

- There is no surface without bulk, and no bulk without surface. Modifications of the bulk structure will probably affect the surface structure!
- Careful analysis of XRD data may shed light on specific *defects* (like *disorder* or *strain*) which can be relevant for catalytic activity.

Complementary methods

- Like all other analytical methods, XRD has both strengths and limitations.
- It is generally a good idea to combine a number of characterization techniques in order to answer specific scientific questions.
- Some techniques are particularly well suited to complement XRD.

Complementary methods: X-ray diffraction and EXAFS (extended X-ray absorption fine structure)

XRD

Analysis of long range order.
Limited to crystalline materials.
Not element specific.
Distinguishes different crystallographic sites.
Averages over different elements on the same crystallographic site.
Distinguishes different (crystalline) phases.

EXAFS

Analysis of short range order.
Covers both crystalline and amorphous materials.
Element specific.
Averages over different sites (for the same element).
Distinguishes different elements on the same crystallographic site.
Averages over different phases (containing the same element).

EXAFS will be covered in more detail by Prof. van Bokhoven on the 17th and 22nd of November.

Complementary methods: X-ray and electron diffraction (transmission electron microscopy)

XRD

Averaging over the whole sample.
Limited to larger crystallites (reflection broadening).
Amorphous material invisible.
3D distribution of d-spacings.
Usually no beam damage.

TEM

Relatively local.
Limited to smaller crystallites ($> 30 \text{ \AA}$)
→ beam transparency required!
Amorphous material visible.
2D projection of d-spacings (but collapsed into 1D).
Beam damage quite possible.

→ Take care when comparing particle sizes estimated by TEM and PXRD.

Electron microscopy will be covered in more detail by Dr. Krumeich on the 1st and 6th of December.

Complementary methods: X-ray and neutron diffraction?

X-rays

- Electromagnetic wave
- No mass, spin 1, no magnetic dipole moment
- X-ray photons interact with the electrons
- Scattering power falls off with 2θ .

Neutrons

- Particle wave
- Mass, spin $\frac{1}{2}$, magnetic dipole moment.
- Neutrons interact with the nucleus.
- Scattering power independent of 2θ .

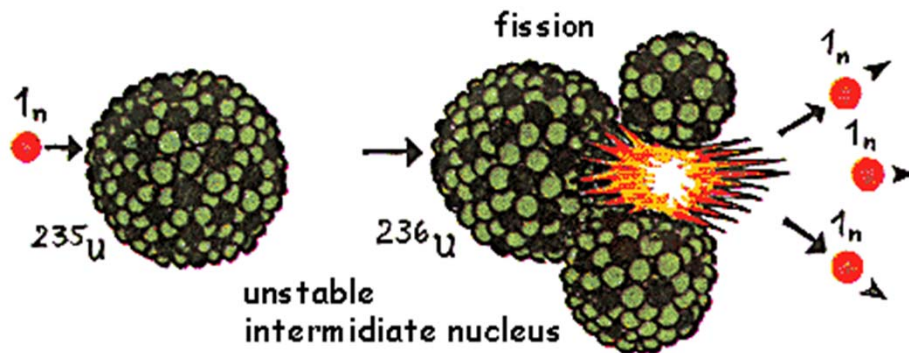
What are the consequences on diffraction?

Essentials of neutron diffraction

Neutrons generated from atomic nuclei.

Two methods:

1) Fission reactor



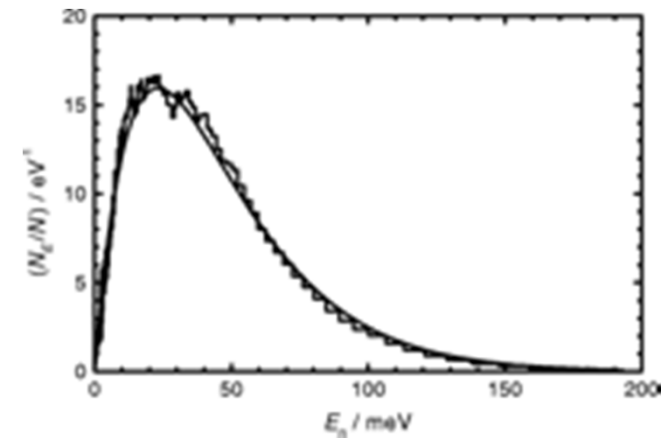
2) Spallation source: Proton

bombardment of lead nuclei, releasing spallation neutrons.

Wave-particle dualism

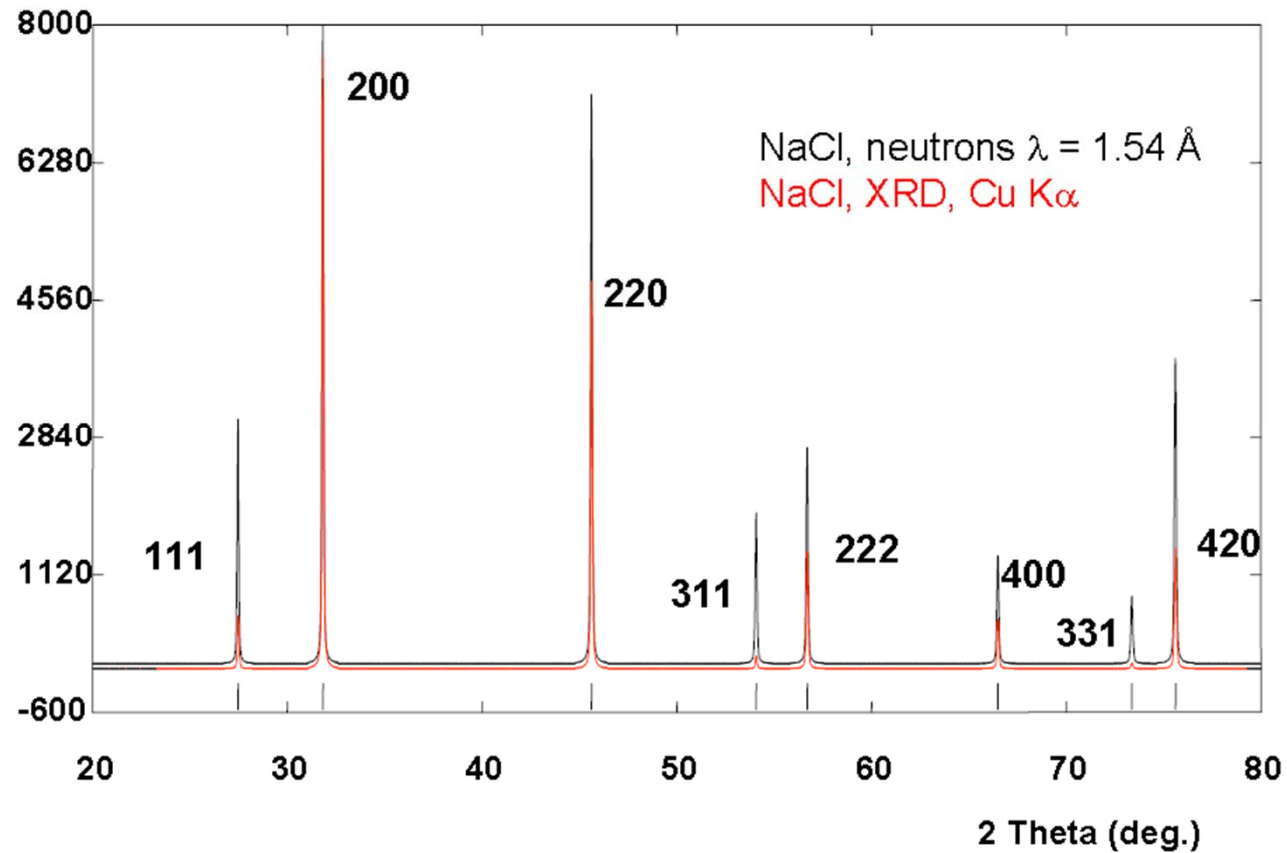
($\lambda = h/mv$, de Broglie).

- Similar λ and penetration to X-rays



Spectral distribution of neutrons from fission reactor. Neutron energies 1 MeV very high → slowed down for practical use.

Essentials of neutron diffraction



- ➔ Reflections in same position if neutrons and X-rays have the same wavelength.
- ➔ Different reflection intensities with X-ray/neutron diffraction.

Complementary methods: X-ray and neutron diffraction

XRD

Interaction with electron shell.

Atomic order only.

Scattering power depends on atomic number.

Cannot distinguish isotopes or neighboring elements in PSE.

Light elements hard to localize (hydrogen almost invisible).

Neutron diffraction

Interaction with nucleus.

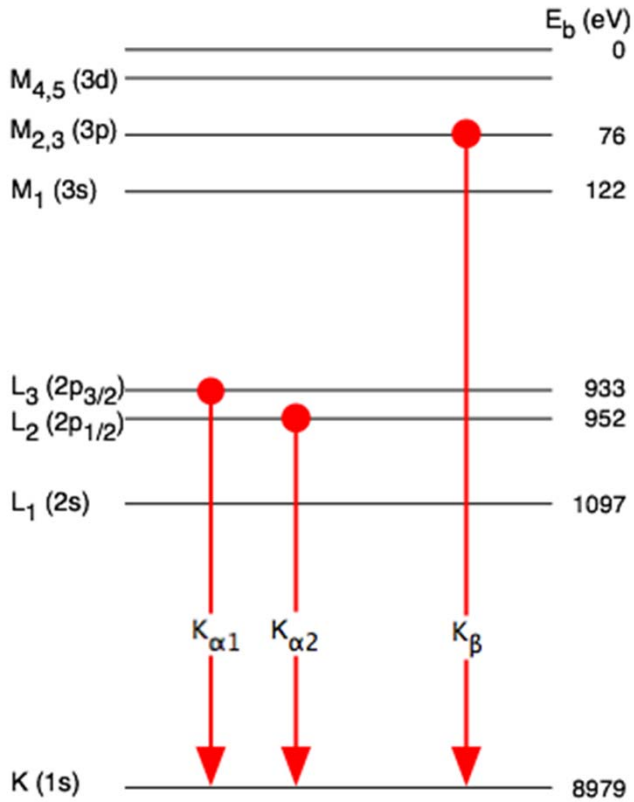
Atomic and magnetic order.

Scattering power depends on nucleus structure.

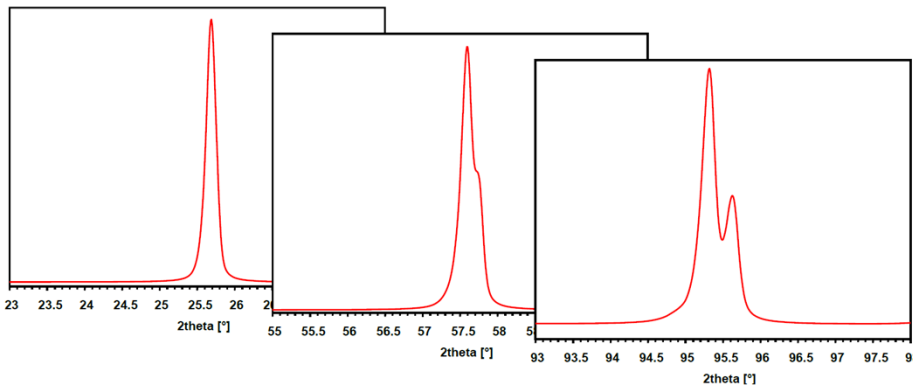
Distinguishes isotopes and neighboring elements in PSE.

No problem with light elements (vanadium almost invisible).

Clarification



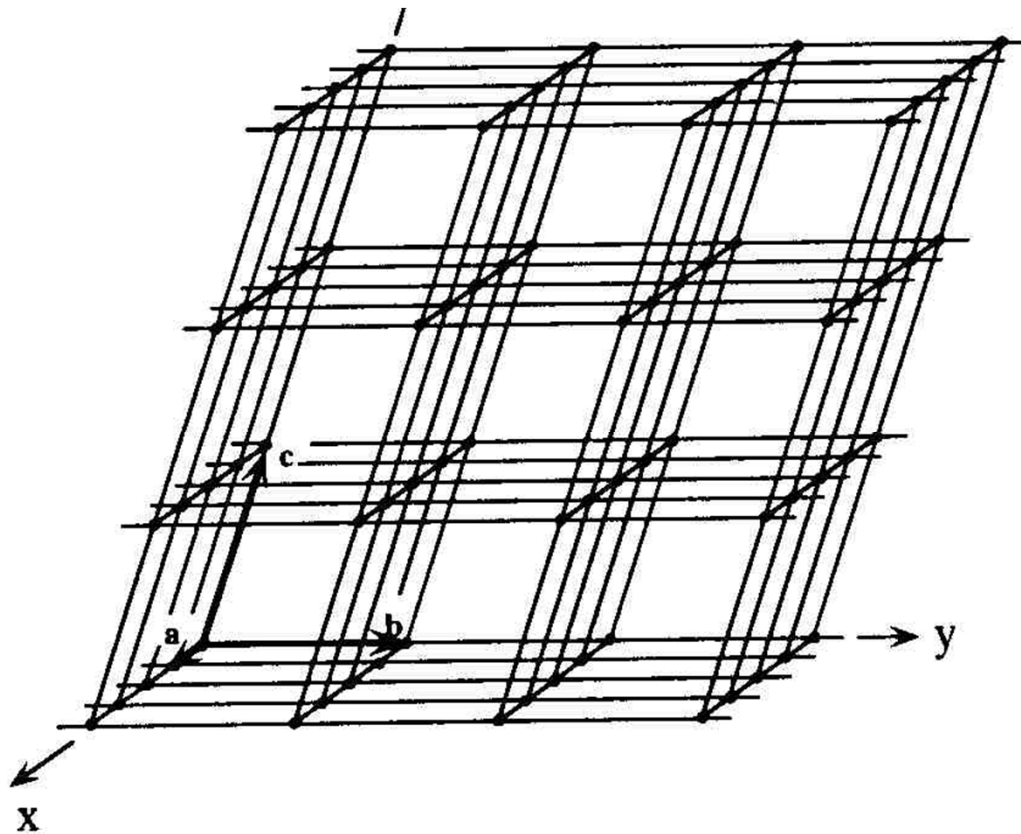
- Two X-ray emissions ($K_{\alpha 1}$ and $K_{\alpha 2}$) result from relaxation of electrons from second (L) to first (K) quantum shell.
- Both originate from 2p orbitals. The difference in energy arises from differences in the spin-orbit interaction (high/low spin state).
- Most monochromators can't separate these wavelengths → doublets in XRD pattern.
- Occurs at all diffraction angles but difference is more noticeable at higher 2θ due to greater multiplication (Bragg's law $n\lambda=2d\sin\theta$).



- Photo emission will be further studied in X-ray photoelectron spectroscopy (XPS) by Prof. van Bokhoven on 29th November.

Extension of basic crystallographic concepts

Symmetry = Patterned self-similarity e.g. through geometric **symmetry operators** such as translation, rotation, inversion *etc.*



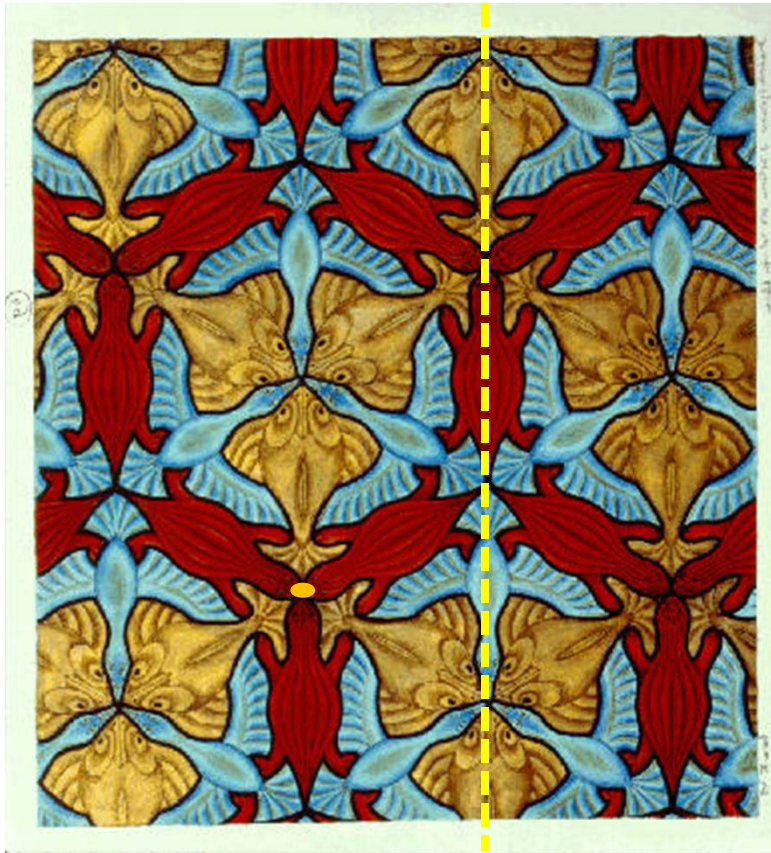
- Three dimensional crystal structure constructed by stacking of unit cell.

Crystal structures grouped according to the symmetry of their unit cell
→ 7 crystal systems.

Bravais demonstrated that for a three-dimensional lattice there are 14 possible lattice types based on translational symmetry.

Are other symmetries possible?

Extension of basic crystallographic concepts



Mirror symmetry
3-fold Rotational symmetry

Escher familiar to all crystallographers.

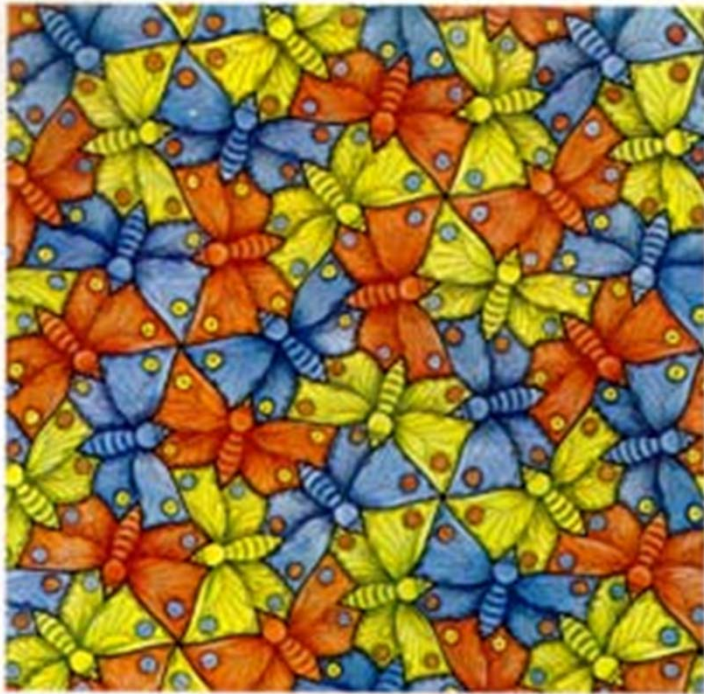
Explored symmetry operations such as reflection, rotation, inversion through art.

Point group symmetry describe symmetry operations which do not involve translation.

The combination of all available symmetry operators (32 point groups), with translational symmetry and the 14 available lattices → **230 Space Groups.**

Describe the only ways in which identical objects can be arranged in an infinite lattice.

Extension of basic crystallographic concepts



Certain space groups are immediately identifiable by the observation of systematic absences in the diffraction pattern.

Common systematic absences related to crystal structure

Symmetry Element

Absence conditions

A centered Lattice (A)

$$k+l = 2n+1$$

B centered Lattice (B)

$$h+l = 2n+1$$

C centered Lattice (C)

$$h+k = 2n+1$$

face-centered Lattice (F)

$$h+k = 2n+1$$

$$h+l = 2n+1$$

$$k+l = 2n+1$$

Body centered Lattice (I)

$$h+k+l = 2n+1$$

→ Helpful for crystal structure determination