Advanced Analytical Chemistry

Week 01

Crystal structural analysis

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How to obtain information of analyte ?

- To retrieve the desired information from the analyte, it is necessary to provide a stimulus, which is usually in the form of electromagnetic, electrical, mechanical, or nuclear energy

- The resulting information is contained in the phenomena that result from the interaction of the stimulus with the analyte.

- The stimulus elicits a response from the system under study whose nature and magnitude are governed by the fundamental laws of chemistry and physics.

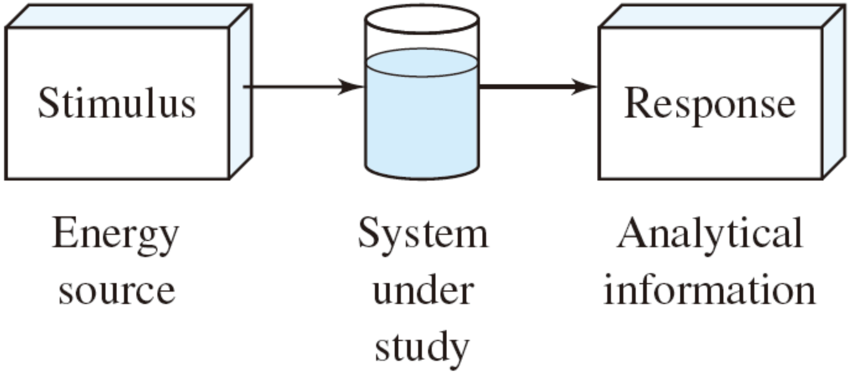
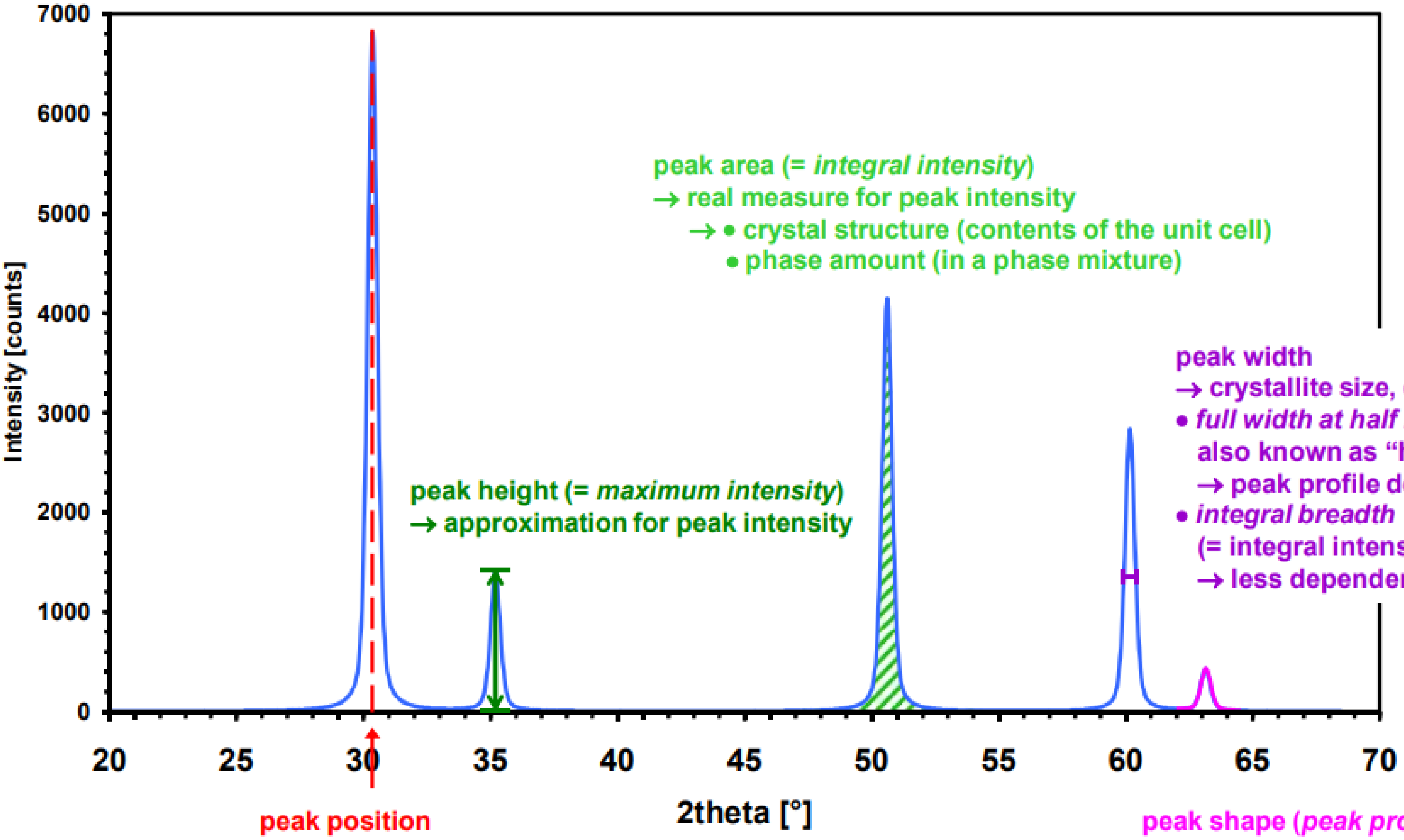


FIGURE 1-1 Block diagram showing the overall process of an instrumental measurement.

D. A. Skoog, Principles of Instrumental Analysis, 7th Ed., Cengage Learning, 2017, p. 3

X-ray powder diffraction analysis



peak area (= *integral intensity*)
→ real measure for peak intensity
→ • crystal structure (contents of the unit cell)
• phase amount (in a phase mixture)

peak height (= *maximum intensity*)
→ approximation for peak intensity

peak width
→ crystallite size, defects (strain, disorder)
- *full width at half maximum* (FWHM), also known as "half width"
  → peak profile dependent!
- *integral breadth* (= integral intensity / maximum intensity)
  → less dependent from peak profile

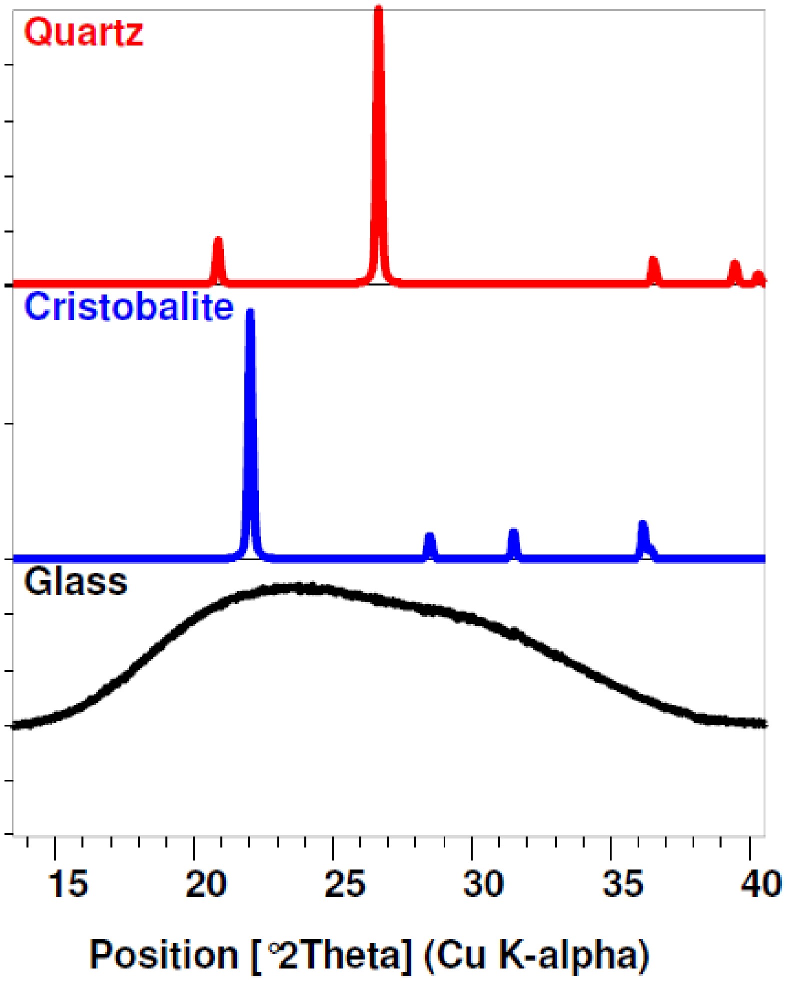
peak position
→ d-spacing
→ lattice parameters (metrics of the unit cell)

peak shape (*peak profile*)
→ crystallite size, defects (strain, disorder)

Frank Girgsdies, Electron Microscopy Group, Department of Inorganic Chemistry, Fritz-Haber-Institut der MPG, Berlin, Germany

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2015_2016/frank_girgsdies__peak_profile_fitting_in_xrd__151106.pdf (22.09.16)

Each “phase” produces a unique diffraction pattern



- A phase is a specific chemistry and atomic arrangement.
- Quartz, cristobalite, and glass are all different phases of SiO_2
  - They are chemically identical, but the atoms are arranged differently.
  - As shown, the X-ray diffraction pattern is distinct for each different phase.
  - Amorphous materials, like glass, do not produce sharp diffraction peaks.

The X-ray diffraction pattern is a fingerprint that lets you figure out what is in your sample.

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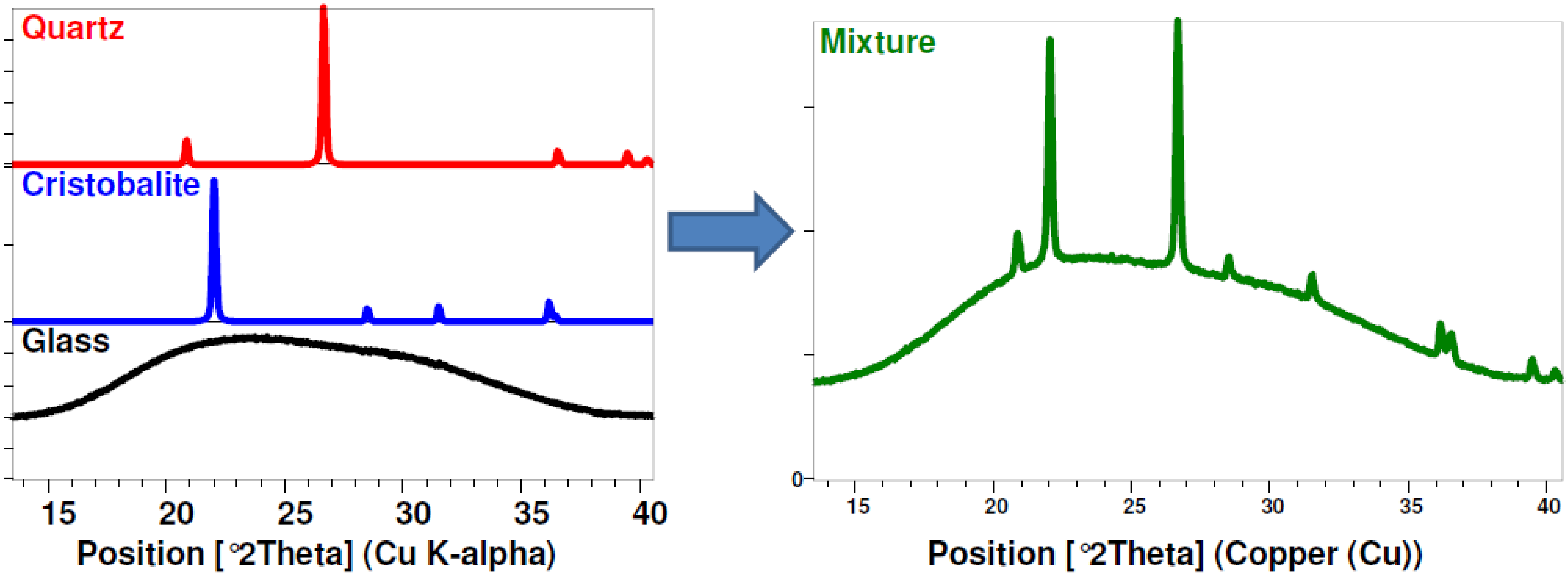
The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



- From the XRD pattern you can determine:
  - What crystalline phases are in a mixture
  - How much of each crystalline phase is in the mixture (quantitative phase analysis, QPA, is covered in another tutorial)
  - If any amorphous material is present in the mixture

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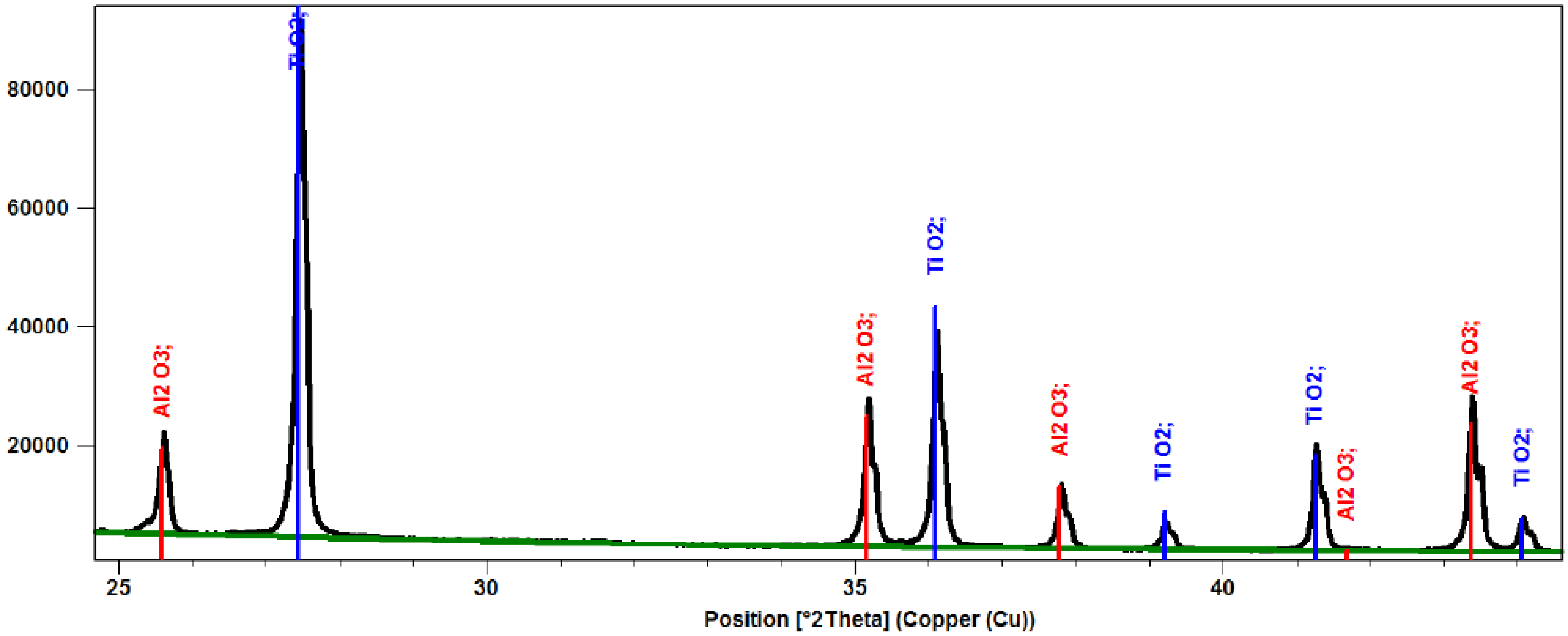
You cannot guess the relative amounts of phases based upon the relative intensities of the diffraction peaks



- The pattern shown above contains equal amounts of TiO_2 and Al_2O_3
- The TiO_2 pattern is more intense because TiO_2 diffracts X-rays more efficiently

With proper calibration, you can calculate the amount of each phase present in the sample

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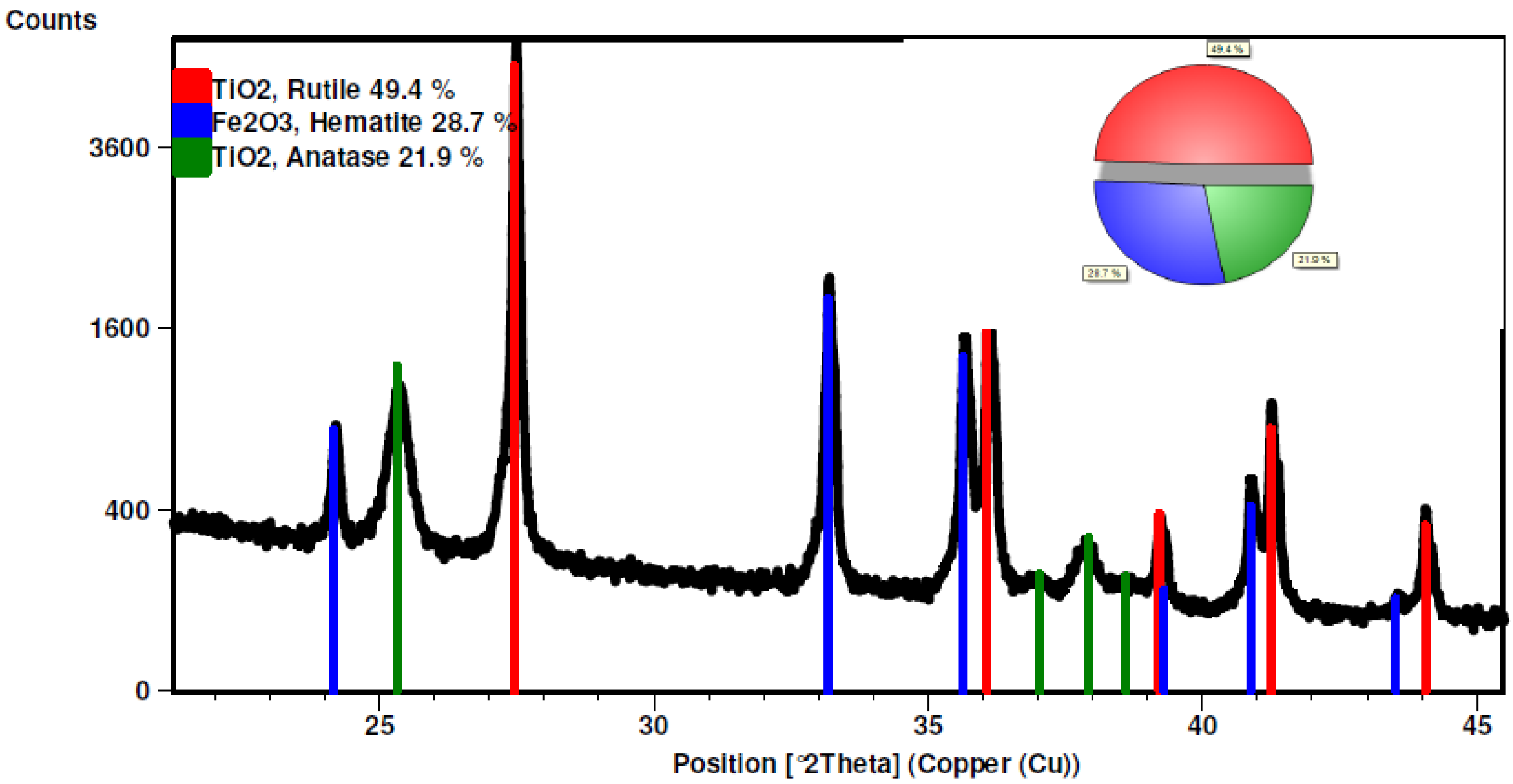
The weight fraction of each phase can be calculated if the calibration constant is known



- The calibration constants can be determined:
  - By empirical measurements from known standards
  - By calculating them from published reference intensity ratio (RIR) values
  - By calculating them with Rietveld refinement

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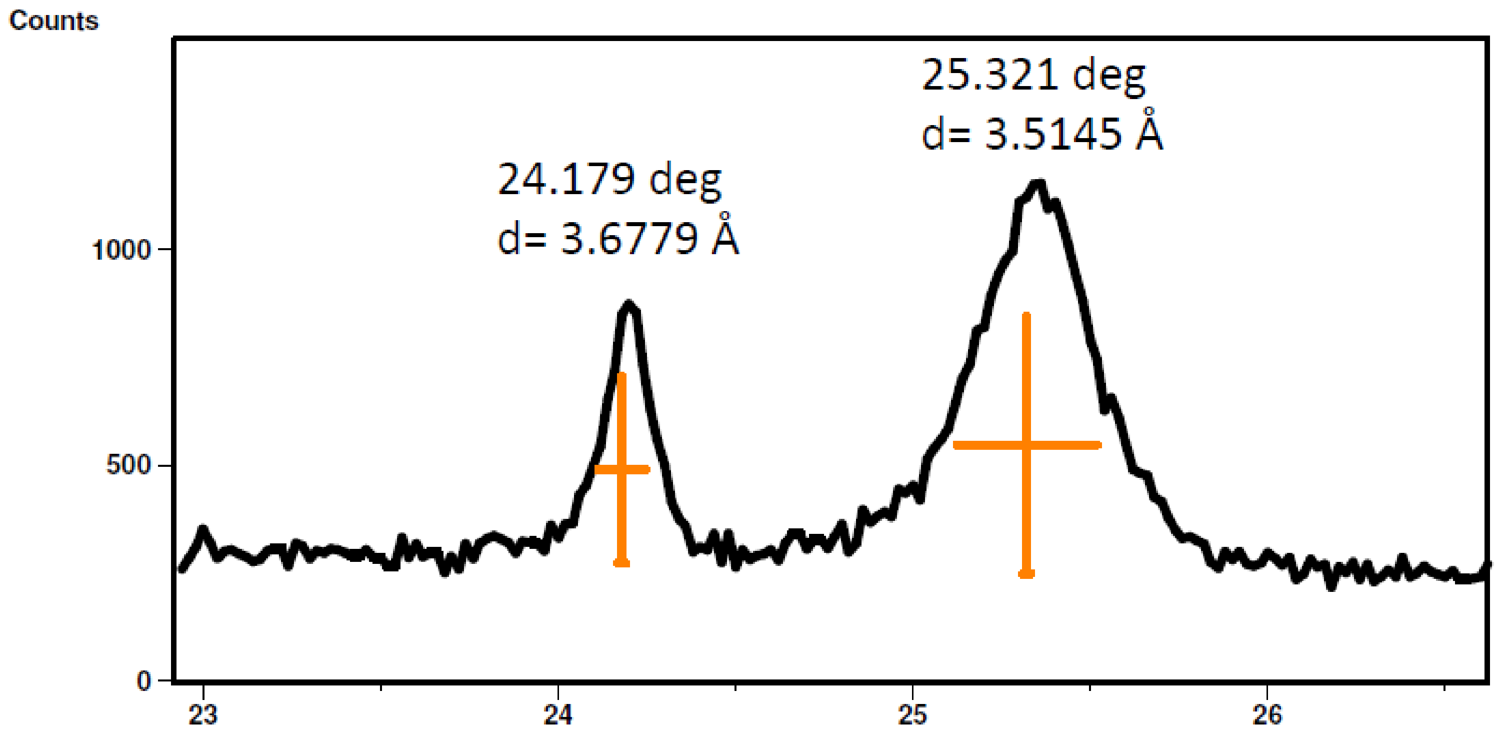
Diffraction peak positions can be used to calculated unit cell dimensions



- The unit cell dimensions can be correlated to interatomic distances
- Anything the changes interatomic distances- temperature, subsitutional doping, stress- will be reflected by a change in peak positions

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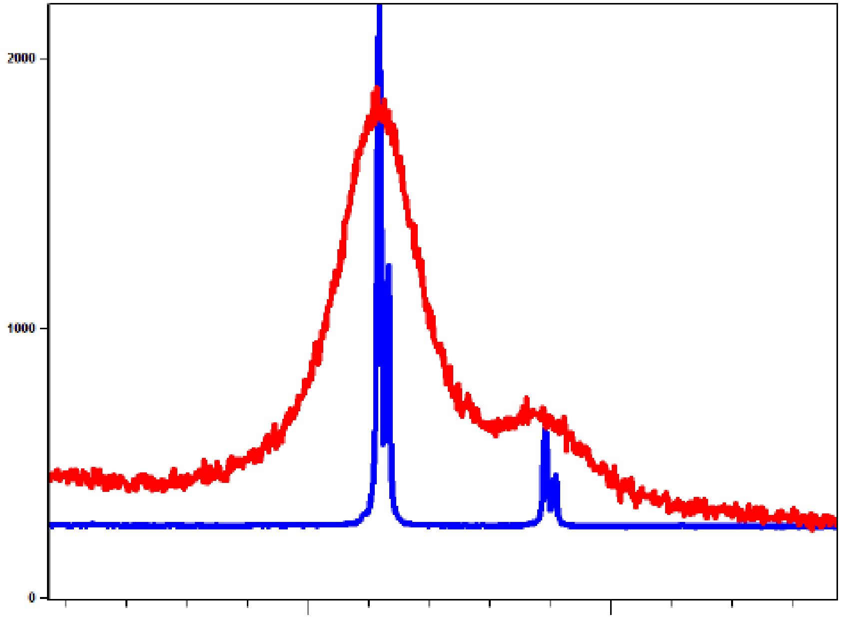
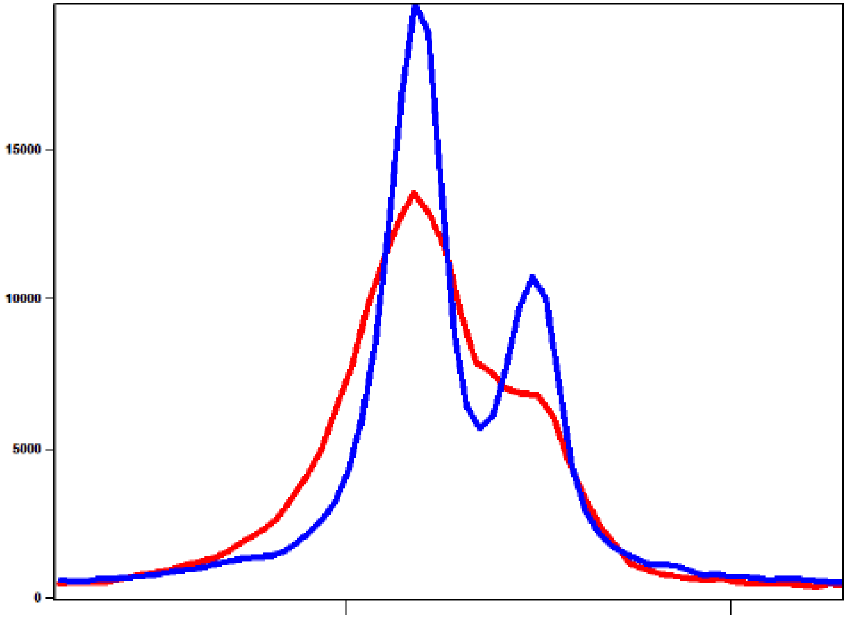
Diffraction peak broadening may contain information about the sample microstructure

- Peak broadening may indicate:
  - Smaller crystallite size in nanocrystalline materials
  - More stacking faults, microstrain, and other defects in the crystal structure
  - An inhomogeneous composition in a solid solution or alloy
- However, different instrument configurations can change the peak width, too



These patterns show the difference between bulk ceria (blue) and nanocrystalline ceria (red)



These patterns show the difference between the exact same sample run on two different instruments.

When evaluating peak broadening, the instrument profile must be considered.

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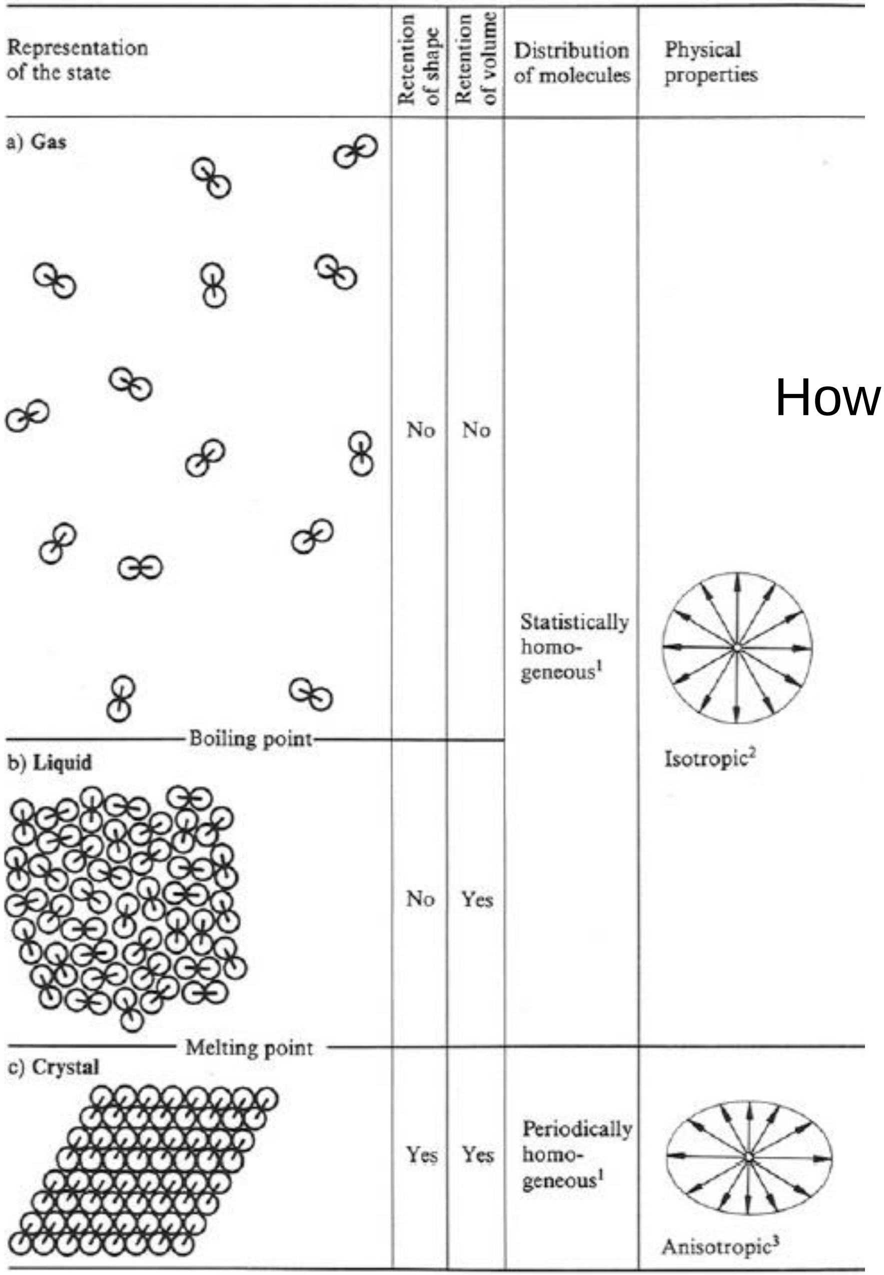
The states of matter



Representation of the state	Retention of shape	Retention of volume	Distribution of molecules	Physical properties
a) Gas	No	No	Statistically homogeneous[1]	Isotropic[2]
Boiling point				
b) Liquid	No	Yes		
Melting point				
c) Crystal	Yes	Yes	Periodically homogeneous[1]	Anisotropic[3]

How can we distinguish crystalline state ?

[1] Equal physical properties in parallel directions ⇉
[2] Equal physical properties in all directions
[3] Different physical properties in different directions

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 5

The states of matter

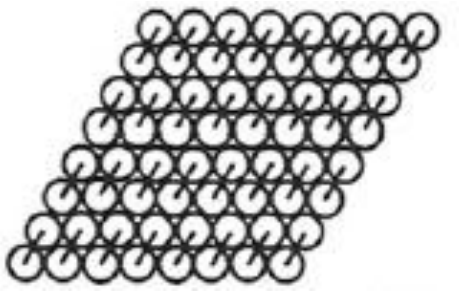
Crystal:

- When the temperature falls below the freezing point, the kinetic energy becomes so small that the molecules become permanently attached to one another.

- A three-dimensional framework of attractive interactions forms among the molecules and the array becomes solid – it crystallizes.

- The movement of molecules in the crystal now consists only of vibrations about a central position. A result of these permanent interactions is that the molecules have become regularly ordered.

“periodically homogeneous distribution”
“anisotropic physical properties”



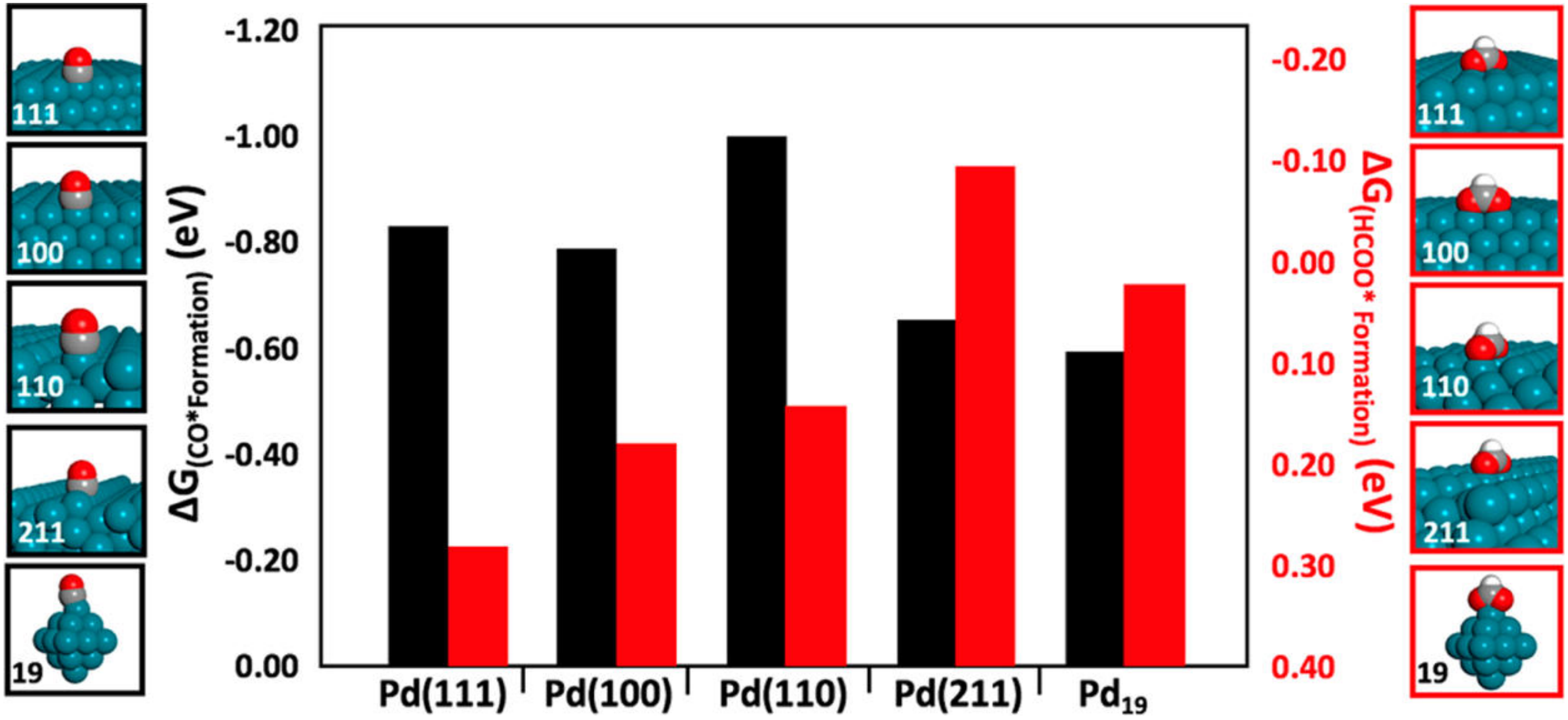
***A crystal** is an anisotropic, homogeneous body consisting of a three-dimensional periodic ordering of atoms, ions or molecules*.

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 5

Crystal structure analysis

Crystallography is the experimental science of determining the three-dimensional arrangement of atoms, ions and molecules in crystalline solids

Crystals play a role in many subjects, among them mineralogy, inorganic, organic and physical chemistry, physics, metallurgy, materials science, geology, geophysics, biology and medicine.



https://doi.org/10.1021/acscatal.6b01719 (22.09.16)

What is lattice?

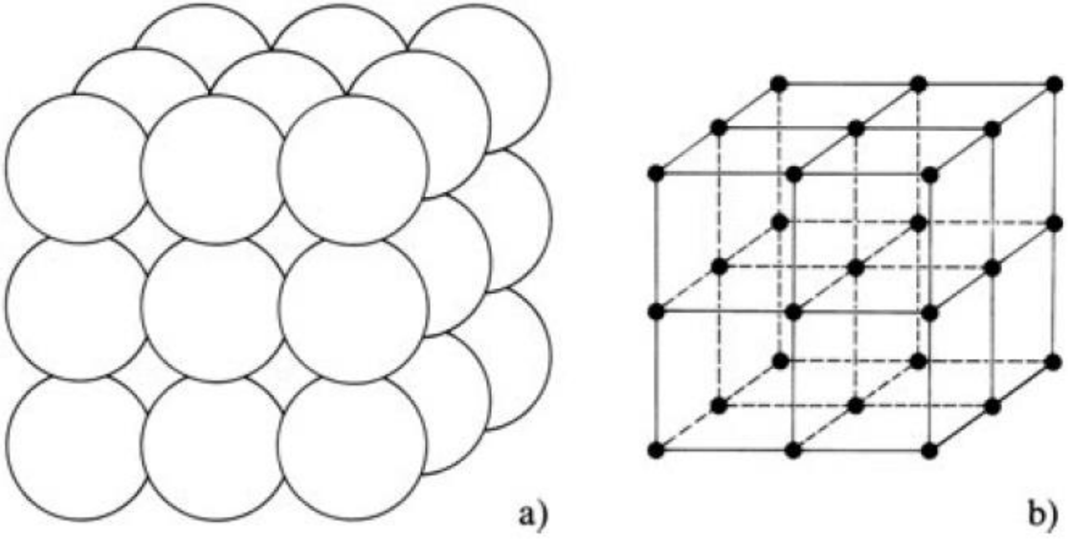
- **A space lattice** is a three-dimensional periodic arrangement of points, and is a pure mathematical concept.

- **basis:** the arrangement of atoms within a lattice cell.

- lattice + basis = crystal structure.

The concept of a lattice will now be developed from a lattice point via the line lattice and the plane lattice, finally to the space lattice.

Fig. 3.1a, b
Three-dimensional periodic arrangement of the atoms in a crystal of α-polonium (**a**) and the space lattice of the crystal (**b**)



Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 9

Line lattice, Plane lattice

- we may consider moving from the point 0 along the vector a to the point 1. By a similar movement of 2a, we will reach point 2, etc. By means of this operation, called a lattice translation, a line lattice has been generated.

- All points made by lattice translation are equivalent.
- $|\vec{a}| = a_0$ is called lattice parameter which defines the line lattice.

- If a lattice translation $\vec{b}$ is then allowed to operate on the line lattice, the result is the plane lattice. The plane lattice can be constructed from three lattice parameters, **a_0, b_0 and γ**.
- **unit cell** is the least volume being repeated in a solid

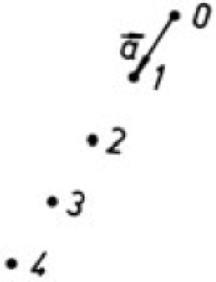


Fig. 3.2

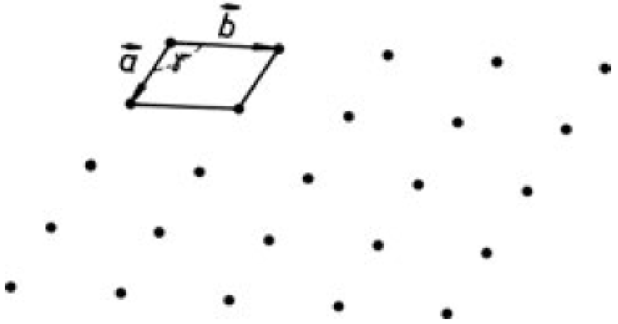


Fig. 3.3

Fig. 3.2 Line lattice with its lattice parameter $|\vec{a}| = a_0$

Fig. 3.3 Plane lattice with the unit mesh defined by the vectors $\vec{a}$ and $\vec{b}$

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 10

Space lattice

- If another lattice translation $\vec{c}$ is introduced, its action on the plane lattice generates the space lattice.

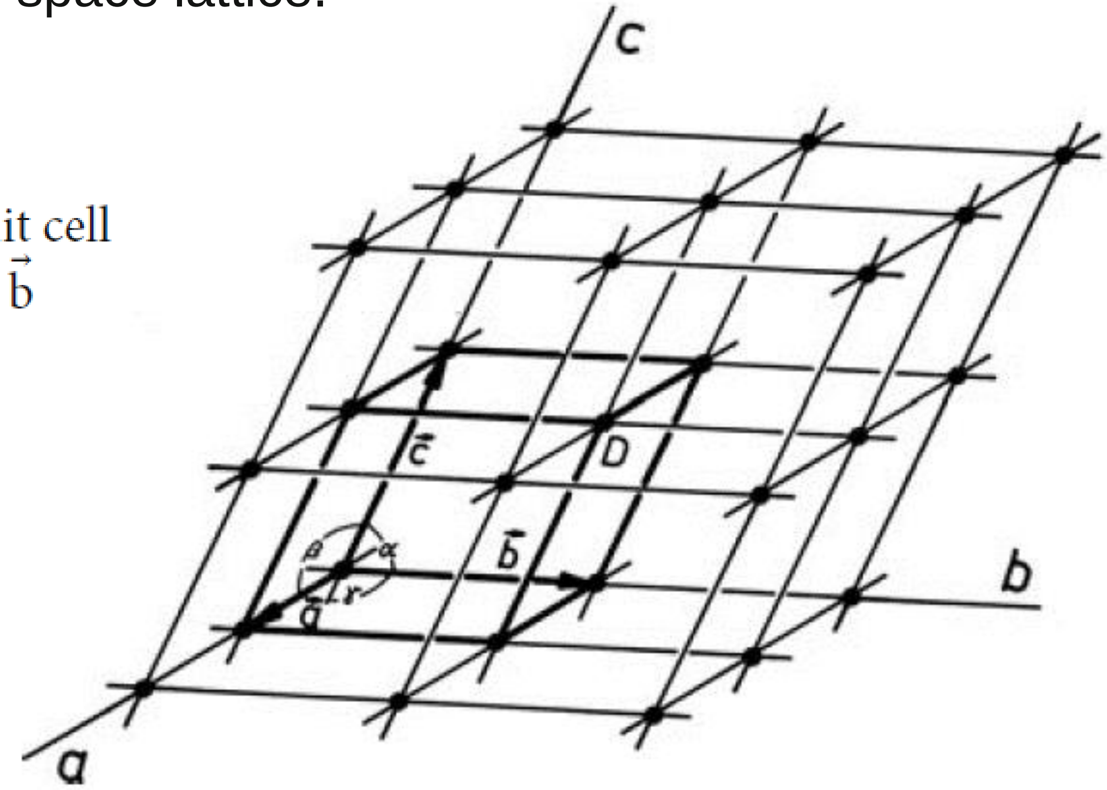


Fig. 3.4
Space lattice with the unit cell defined by the vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$

Table 3.1
Lattice constants of a unit cell

Length of lattice translation vectors	Interaxial lattice angles
$\lvert\vec{a}\rvert = a_0$	$\vec{a} \wedge \vec{b} = \gamma$
$\lvert\vec{b}\rvert = b_0$	$\vec{a} \wedge \vec{c} = \beta$
$\lvert\vec{c}\rvert = c_0$	$\vec{b} \wedge \vec{c} = \alpha$

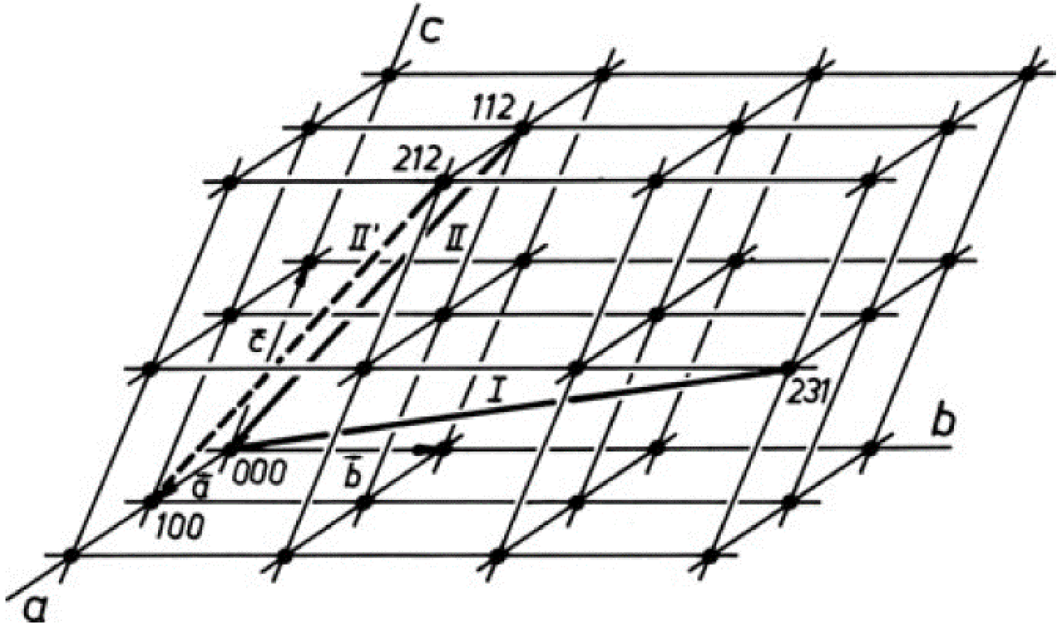
Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 11

Designation of points, lines and planes

- Every **lattice point** is uniquely defined with respect to the origin of the lattice by the vector $\vec{\boldsymbol{\tau}} = \boldsymbol{u}\vec{\boldsymbol{a}} + \boldsymbol{v}\vec{\boldsymbol{b}} + \boldsymbol{w}\vec{\boldsymbol{c}}$, and expressed as a "**uvw**".
- The vector $\vec{\tau}$ describes the point 231

- **lattice lines** are designated using the coordinates **[uvw]** that define the vector from the origin to the given point.

(Note that the [uvw] describes not only a lattice line through the origin and the point uvw, but also the infinite set of lattice lines which are parallel to it and have the same lattice parameter)



line I : [231]
line II : [112]
Line II' : [112]

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 12

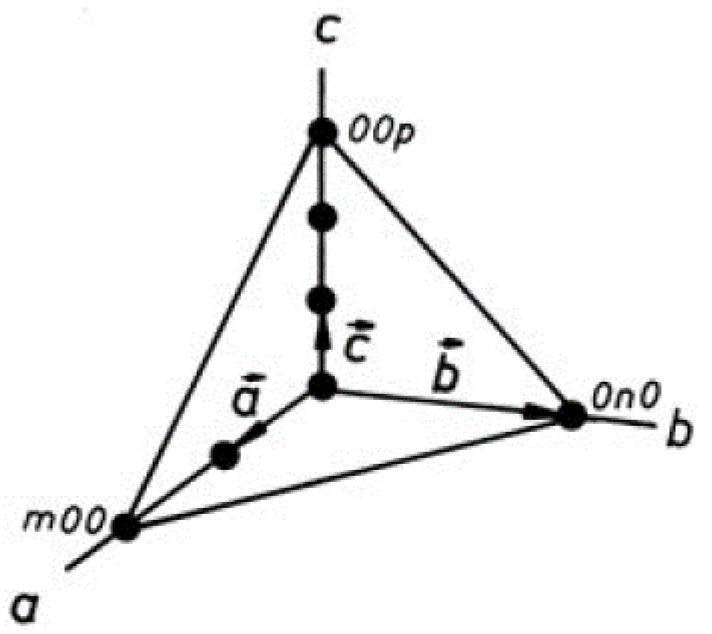
Designation of points, lines and planes

- Consider a plane in the lattice intersecting the axes a, b and c at the points m00, 0n0 and 00p. The coordinates of the three intercepts completely define the position of a lattice plane.

- however, the reciprocals of these coordinates are used rather than the coordinates themselves. **Miller indices, (hkl), are defined as the smallest integral multiples of the reciprocals of the plane intercepts on the axes.**

- The lattice plane has the intercepts **m | n | p = 2 | 1 | 3**.

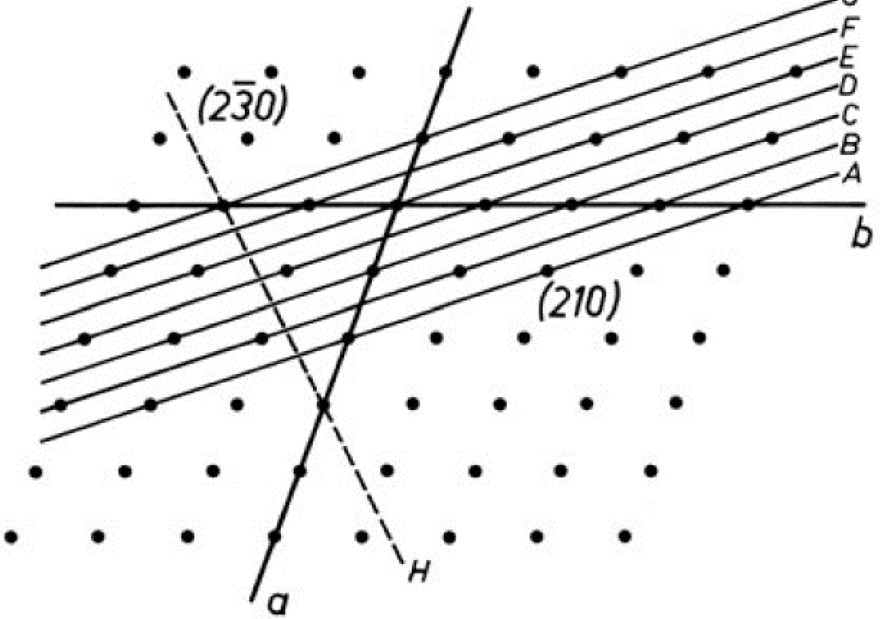
- The reciprocals of these are **1/2 | 1 | 1/3**, leading to the Miller indices **(362).**



Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 14

Designation of points, lines and planes

- Generally, **the triple (hkl) represents** not merely a single lattice plane, but **an infinite set of parallel planes** with a constant interplanar spacing.
- Note that (210) and $(\bar{2}\bar{1}0)$ define the same parallel set of planes.

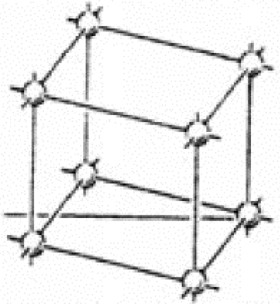
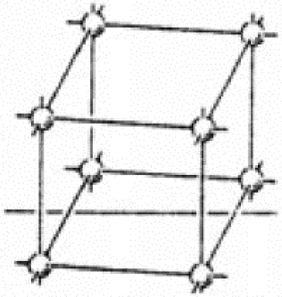
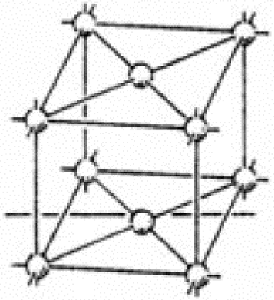
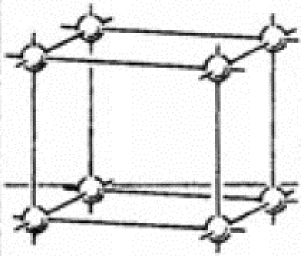
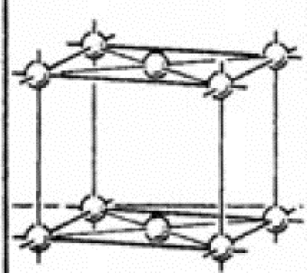
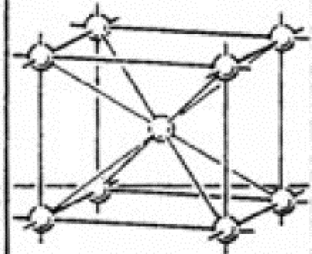
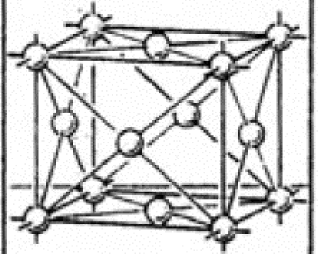


	m	n	p	$\frac{1}{m}$	$\frac{1}{n}$	$\frac{1}{p}$	(hkl)
A	2	4	∞	$\frac{1}{2}$	$\frac{1}{4}$	0	(210)
B	$\frac{3}{2}$	3	∞	$\frac{2}{3}$	$\frac{1}{3}$	0	(210)
C	1	2	∞	1	$\frac{1}{2}$	0	(210)
D	$\frac{1}{2}$	1	∞	2	1	0	(210)
E	–	–	–	–	–	–	
F	$\frac{\bar{1}}{2}$	$\bar{1}$	∞	$\bar{2}$	$\bar{1}$	0	$(\bar{2}\bar{1}0)$
G	$\bar{1}$	$\bar{2}$	∞	$\bar{1}$	$\frac{\bar{1}}{2}$	0	$(\bar{2}\bar{1}0)$
H	3	$\bar{2}$	∞	$\frac{1}{3}$	$\frac{\bar{1}}{2}$	0	$(2\bar{3}0)$

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 15

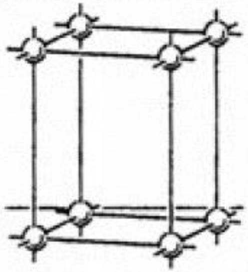
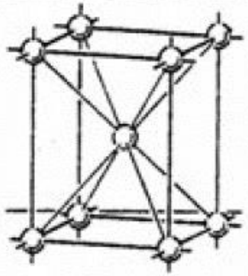
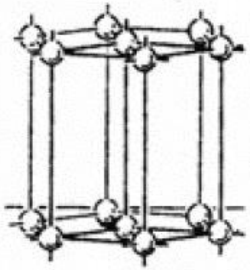
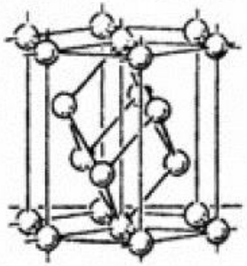
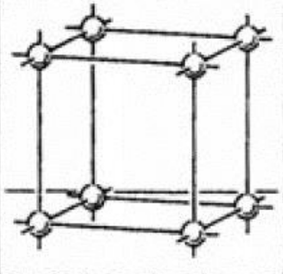
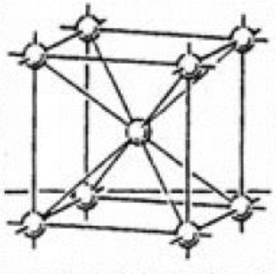
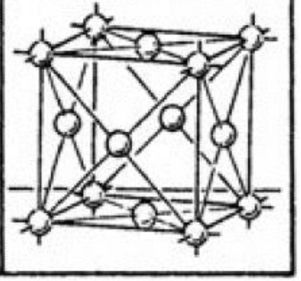
7 Crystal systems & 14 Bravais lattices

- **14 Bravais lattices:** the 14 and **only ways** in which it is possible **to fill space by a three-dimensional periodic array of points.**

Crystal system	primitive	base-centered	body-centered	face-centered
Triclinic $a_0 \neq b_0 \neq c_0$ $\alpha \neq \beta \neq \gamma$				
Monoclinic $a_0 \neq b_0 \neq c_0$ $\alpha = \gamma = 90°$ $\beta > 90°$				
Orthorhombic $a_0 \neq b_0 \neq c_0$ $\alpha = \beta = \gamma = 90°$				

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 94

7 Crystal systems & 14 Bravais lattices

	primitive	base-centered	body-centered	face-centered
Tetragonal $a_0 = b_0 \neq c_0$ $\alpha = \beta = \gamma = 90^\circ$				
Trigonal $a_0 = b_0 \neq c_0$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$				
Hexagonal $a_0 = b_0 \neq c_0$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$				
Cubic $a_0 = b_0 = c_0$ $\alpha = \beta = \gamma = 90^\circ$				

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 94

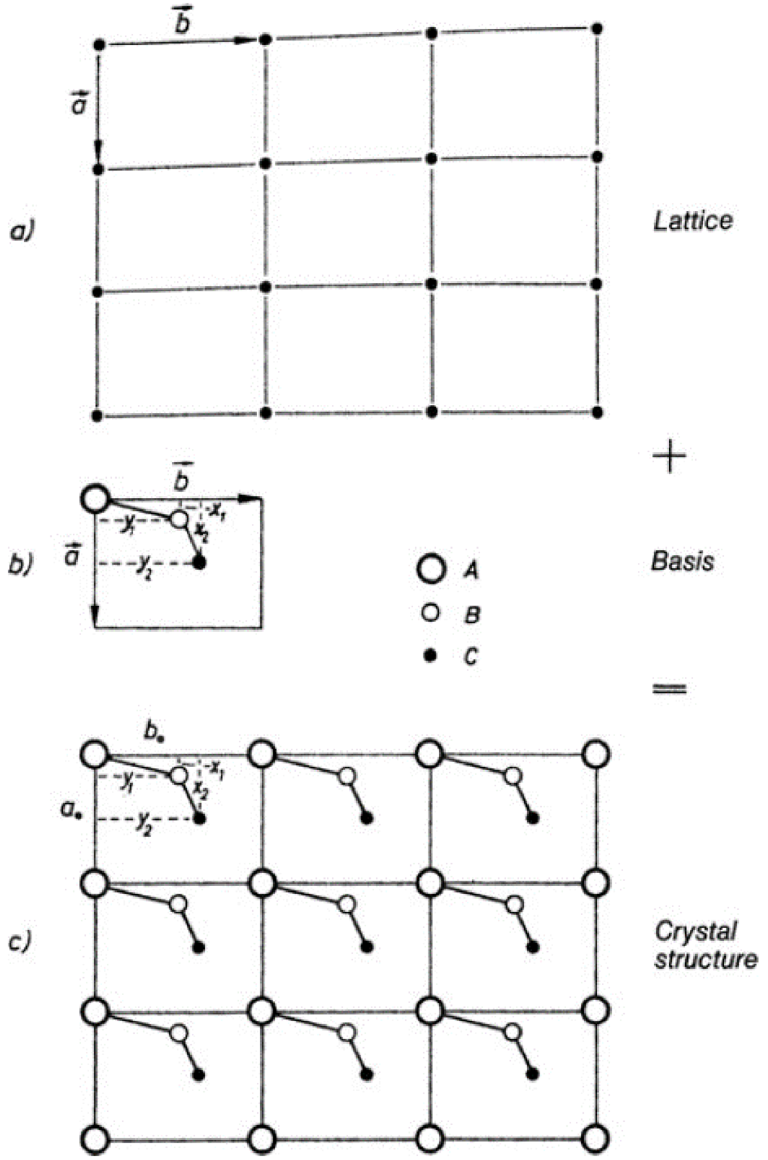
From a lattice to a crystal

- Crystal = lattice + basis
- **Basis:** the arrangement of atoms, ions and molecules

- **Lattice:** $a_0 = a_0, b_0 = b_0, \gamma = 90°$
- **Basis of molecule ABC:**
  A: 0,0,0; B: x_1, y_1, z_1; C: x_2, y_2, z_2

The position is described by a vector $\vec{\boldsymbol{r}}$ in terms of the lattice translations $\vec{\boldsymbol{a}}$, $\vec{\boldsymbol{b}}$, and $\vec{\boldsymbol{c}}$.

$$\vec{\boldsymbol{r}} = \boldsymbol{x}\,\vec{\boldsymbol{a}} + \boldsymbol{y}\,\vec{\boldsymbol{b}} + \boldsymbol{z}\,\vec{\boldsymbol{c}} \quad (0 \le x, y, z < 1)$$



Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 24

Describing the structure of CsI

- An example of a simple crystal structure is **CsI**
- **unit cell:** a cube with $a_0 = b_0 = c_0 = 4.57$ Å, $\alpha = \beta = \gamma = 90°$
- **basis:** I^-: 0,0,0; Cs^+: 1/2,1/2,1/2

$$m = \frac{Z \cdot M}{N_A} \quad \text{and}$$

$$\varrho = \frac{Z \cdot M}{N_A \cdot V} \text{ g cm}^{-3}$$

M : the mass of atoms in the unit cell
Z : the number of chemical formula units per unit cell
M : molar mass, Na: the Avogadro number
V : unit cell volume

$$\varrho_{\text{CsI}} = \frac{1 \cdot 259.81}{6.023 \cdot 10^{23} \cdot 4.57^3 \cdot 10^{-24}} = 4.52 \text{ g cm}^{-3}$$

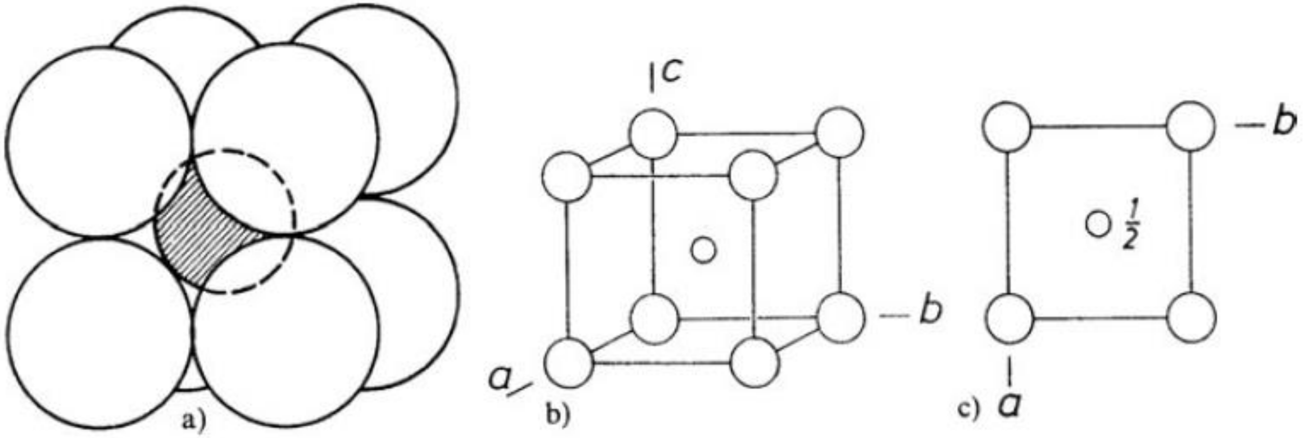
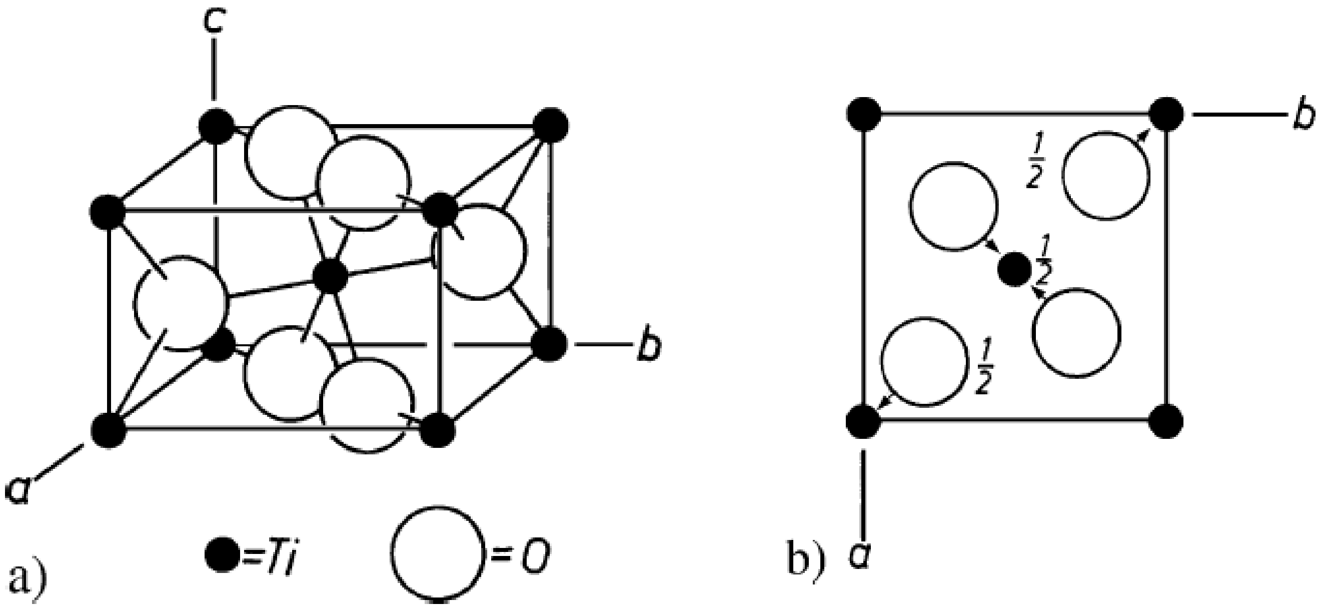


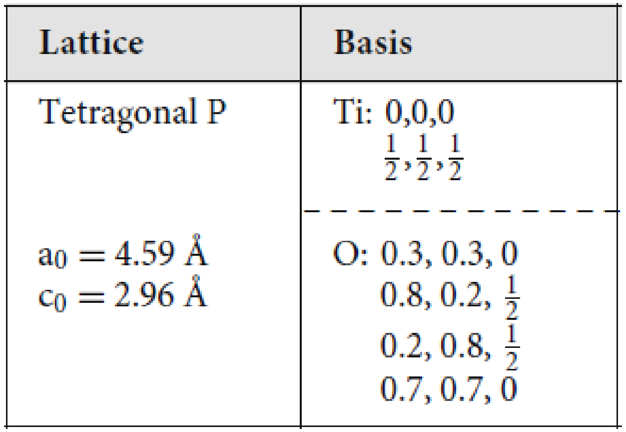
Fig. 4.4a–c The CsI structure shown in a perspective drawing taking account of the relative sizes of the ions (**a**), with ions reduced to their centers of gravity (**b**) and as a parallel projection on (001) (**c**)

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 25

Describing the structure of rutile TiO_2

- **Unit cell:** primitive tetragonal (a_0 = 4.59 Å, c_0 = 2.96 Å)
- **basis:** Ti: 0,0,0; 1/2,1/2,1/2
  O: 0.3,0.3,0.0; 0.8,0.2,0.5; 0.2,0.8,0.5; 0.7,0.7,0.0





Lattice	Basis
Tetragonal P	Ti: 0,0,0 $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
a_0 = 4.59 Å c_0 = 2.96 Å	O: 0.3, 0.3, 0 0.8, 0.2, $\frac{1}{2}$ 0.2, 0.8, $\frac{1}{2}$ 0.7, 0.7, 0

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 211

X-ray diffractometer

고분해능 X-선 회절장치

High Resolution X-Ray Diffractometer System

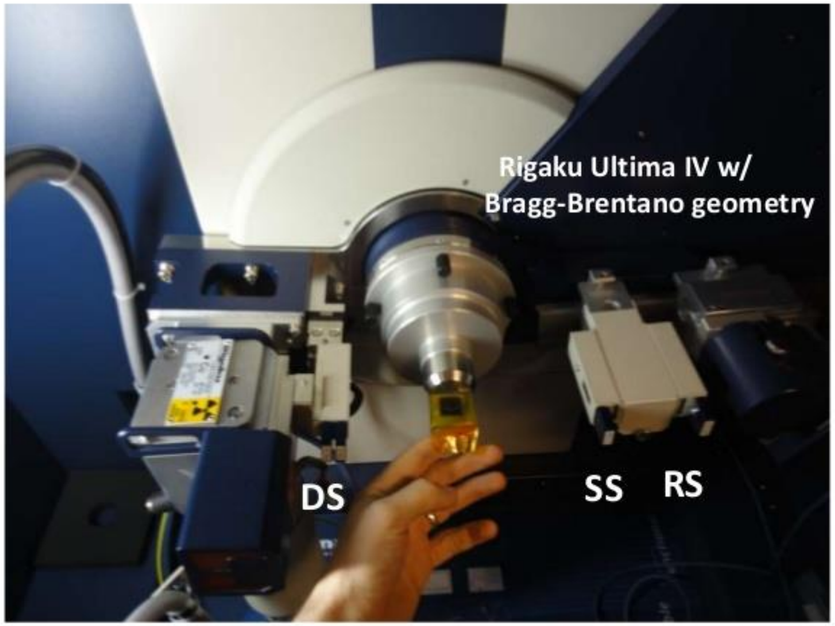
물품번호: YK2015-00396

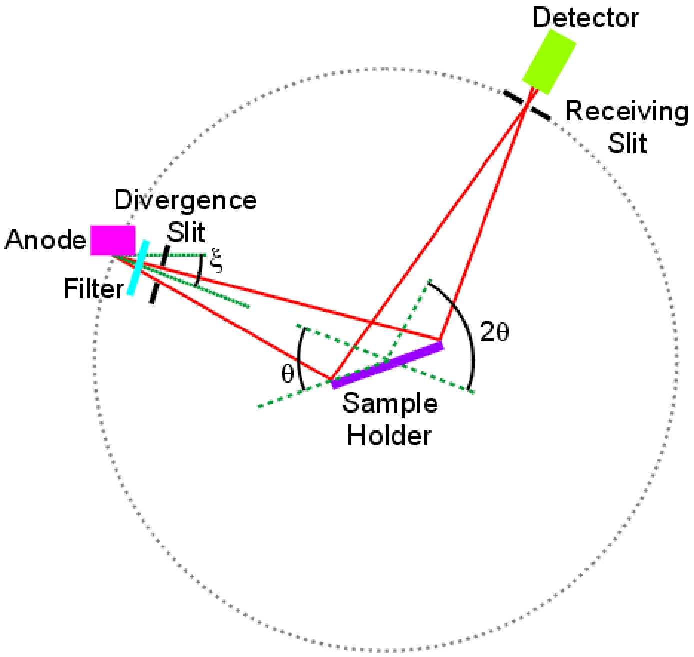
모델명: Ultima IV

제조국가: 일본

설치장소: 산학협력관 107호 XRD 실험실

연락처: 공동실험기기센터 02-910-4217



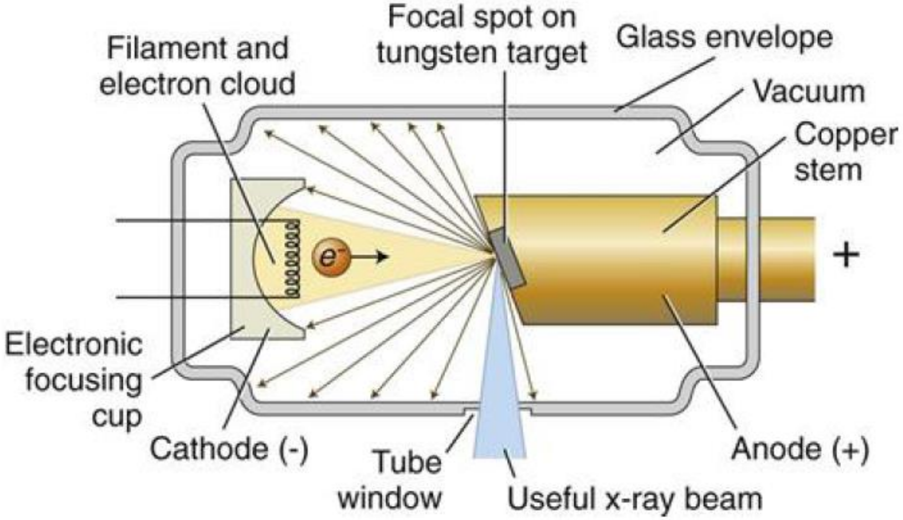


http://pd.chem.ucl.ac.uk/pdnn/inst1/optics1.htm (22.09.16)

Production of X-rays

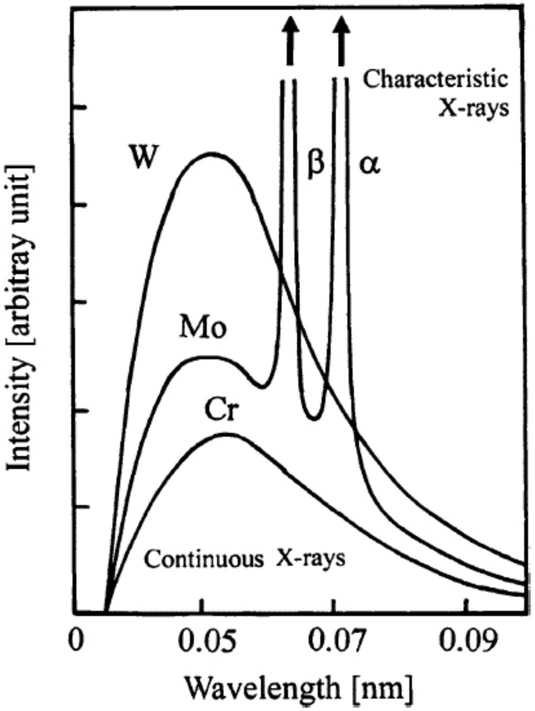
- When a **high voltage** is applied, high-speed **electrons collide with a target**
- Kinetic energy [eV] → **continuous X-ray** + **characteristic X-ray**

Sealed X-ray tube



Thesis "X-ray imaging using 100 μm thick Gas Electron Multipliers operating in Kr-CO$_2$ mixtures"

White X-ray spectrum



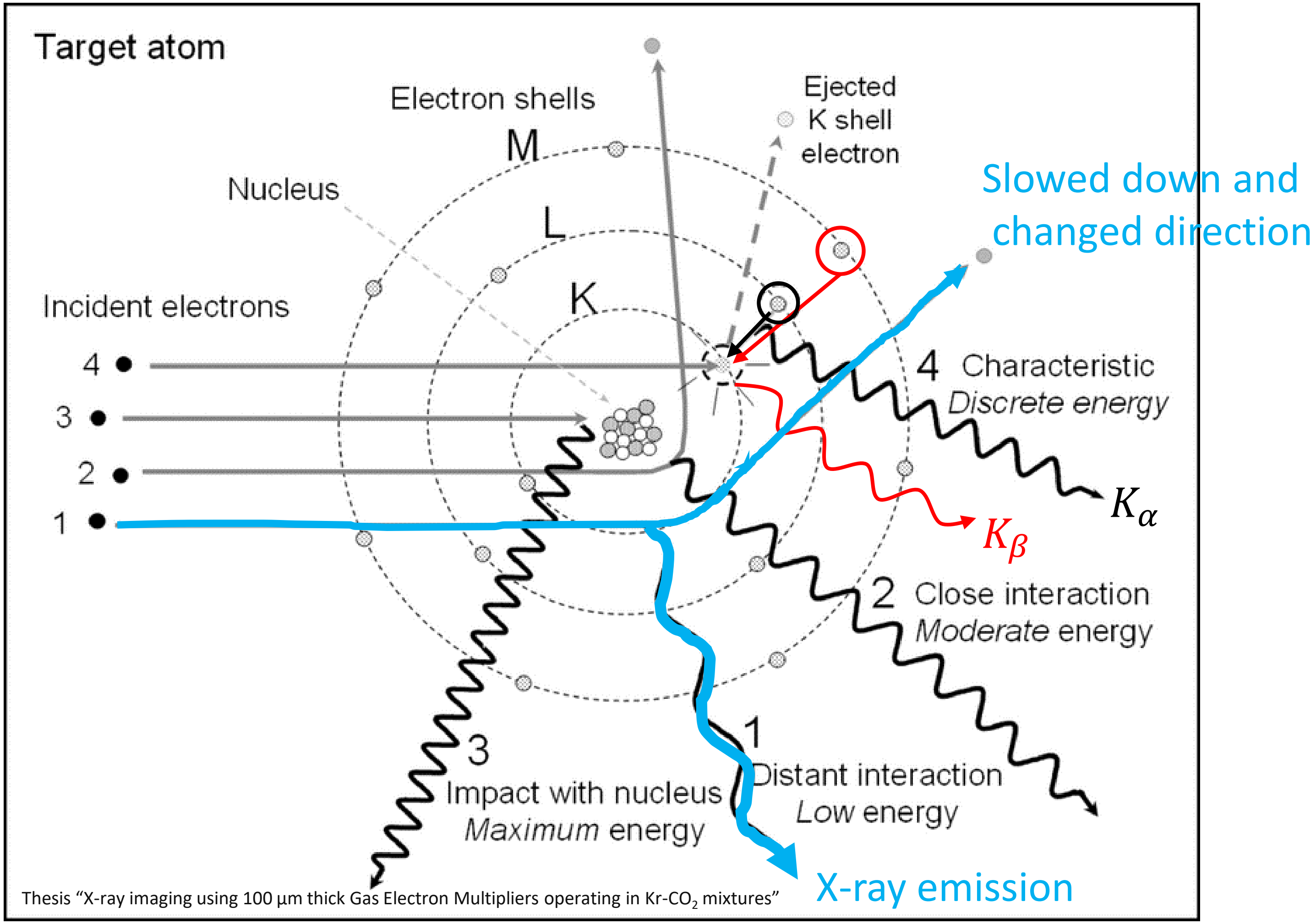
- Max energy and shortest λ_{SWL} of X-ray

$$E_{kinetic} = eV \qquad = E_{X-ray} = h\nu_{max} = h\frac{c}{\lambda_{SWL}}$$

Yoshio Waseda, X-ray Diffraction Crystallography, 1st Ed., Springer, 2011, p. 4

Rita Joana da Cruz Roque, X-ray imaging using 100 μm thick Gas Electron Multipliers operating in Kr-CO2 mixtures, University of Coimbra, 2018, p. 8

continuous & characteristic X-ray



Thesis "X-ray imaging using 100 μm thick Gas Electron Multipliers operating in Kr-CO$_2$ mixtures"

$$I_{\text{cont}} = AiZV^2$$

$$I_{\text{K}} = B_{\text{S}}i(V - V_{\text{K}})^{1.67}$$

I_{cont} =total intensity of white X-ray, i = tube current,
I_K = K_α intensity, Z = atomic number, V = voltage,
V_K = voltage to eject K-shell electron,
A, B_S = constant

Rita Joana da Cruz Roque, X-ray imaging using 100 μm thick Gas Electron Multipliers operating in Kr-CO2 mixtures, University of Coimbra, 2018, p. 8

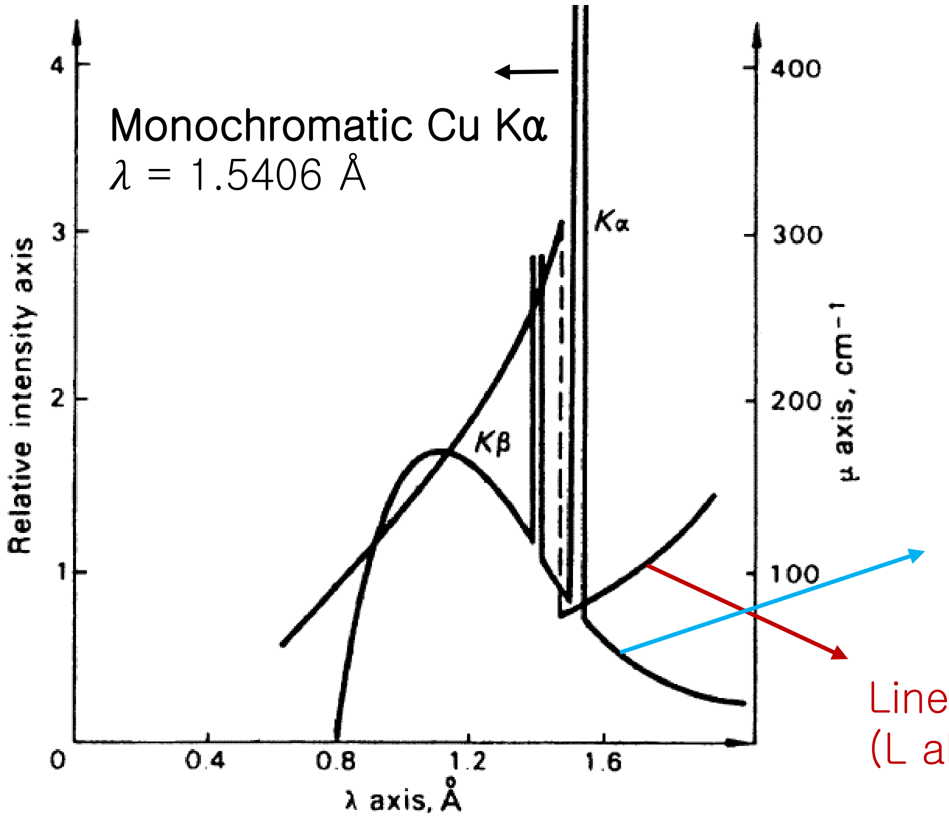
X-ray absorption and Ni filter

- X-rays which enter a sample are **scattered by electrons** around the nucleus of atoms → the reduction in intensity of X-rays

$$I = I_0 e^{-\mu x}$$

μ = linear absorption coefficient : the extent of absorption
I_0 = intensity of incident beam
x = the distance passed through

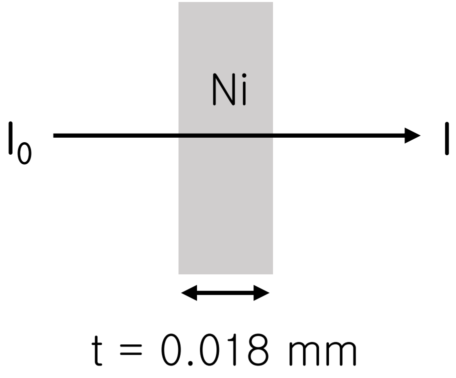
- μ depends on wavelength and absorbing material



Monochromatic Cu Kα
λ = 1.5406 Å

X-ray radiation of Cu target

Linear absorption coefficient for Ni
(L absorption edge = 1.4886 Å)



Interference on a set of lattice planes

- **X-ray diffraction**: a combined effect of **interference** and **scattering**

- Assume that a parallel, monochromatic beam of **X-rays** falls on a set of **lattice planes** with a spacing of **d**, making a glancing angle of **θ** with them.
- The waves I and II will be reflected at A_1 and B.
- At A_1, the path difference = $\Gamma = BA_1 - A_1B' = BA_3 - BC = CA_3 = 2d\sin\theta$
- An interference maximum will be observed when $\Gamma = \lambda$

correlation

Bragg equation: $\boldsymbol{\lambda = 2d\sin\theta}$, $n\lambda = 2(nd)\sin\theta$

(Cu Kα line, λ = 1.5406 Å)

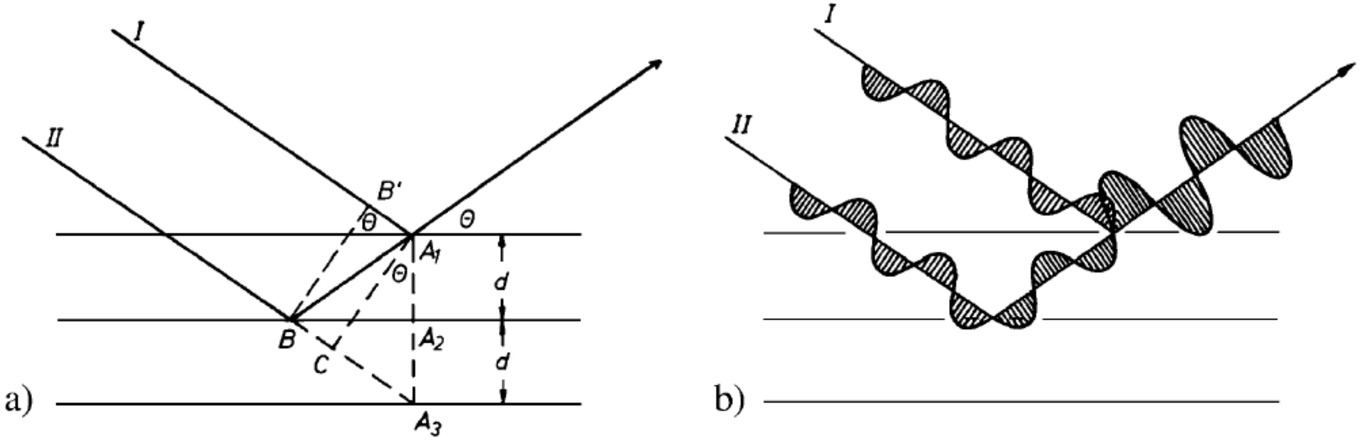


Fig. 13.1a Diffraction ("reflection") of an X-ray beam by a set of lattice planes. **b** Interference of waves reflected by a set of lattice planes ($\Gamma = 1\lambda$)

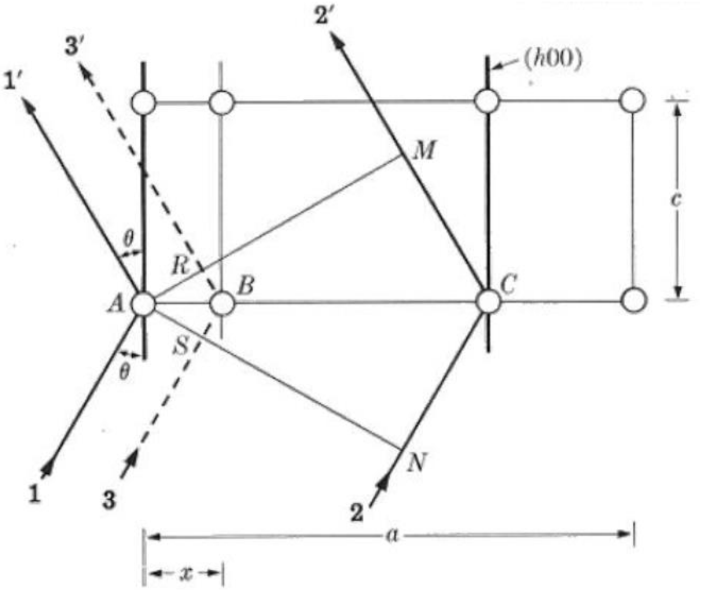
Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 278

Scattering by a unit cell

- **Structure factor:** sum of the scattered waves from (hkl) lattice planes by atoms in a unit cell

The diffraction intensity ∝ $|F_{hkl}|^2$.

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$



N = total number of atoms in a unit cell
f_j = atomic scattering factor of the *j* th atom
u_j, v_j, w_j = fractional coordinates of the *j* th atom
u = x/a, **v** = y/b, and **w** = z/c
a, b, c = lattice parameters
x, y, z = actual coordinates

1. Describes how atomic arrangement (*uvw*) influences the intensity of the scattered beam
2. It tells us which reflections (i.e., peaks, *hkl*) to be expected in a diffraction pattern

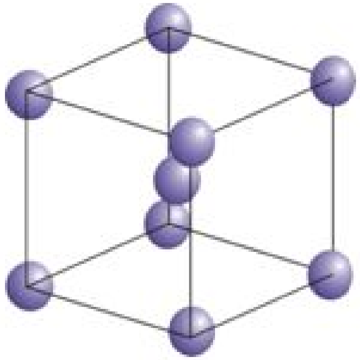
https://slideplayer.com/slide/9616887 (22.09.16)

Structure factor

ex) **body-centered cell** composed of the same element

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

$$uvw = 000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$$



$$F = f e^{2\pi i \times 0} + f e^{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)} = f[1 + e^{\pi i(h+k+l)}] = f[1 + (-1)^{h+k+l}]$$

When the number of $(h+k+l)$ is even: $F = 2f, F^2 = 4f^2$

When the number of $(h+k+l)$ is odd: $F = 0, F^2 = 0$

(cf) $e^{n\pi i} = (-1)^n$, $e^{n\pi i} = e^{-n\pi i}$

(110), (200), (211) reflections are possible
(111), (210), (300) are impossible

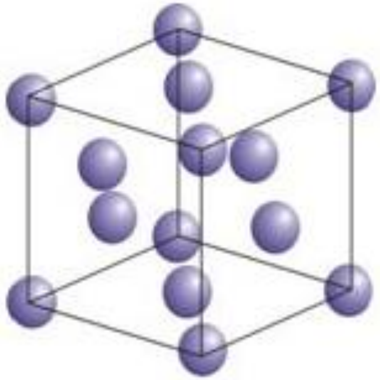
The **structure factor** is completely independent of the shape and size of the unit cell, and critically **depends on** the actual **atomic arrangement**

https://slideplayer.com/slide/5976269 (22.09.16)

Structure factor

ex) **face-centered cell** composed of the same element

$$F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$



$$uvw = 000\,, \frac{1}{2}\frac{1}{2}0\,, 0\frac{1}{2}\frac{1}{2}\,, \frac{1}{2}0\frac{1}{2}$$

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

$$F_{hkl} = f[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{h+l}]$$ (cf) $e^{n\pi i} = (-1)^n$, $e^{n\pi i} = e^{-n\pi i}$

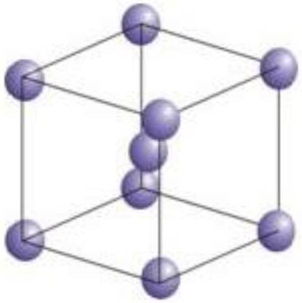
When h,k,l are all even or odd: $F = 4f$, $F^2 = 16f^2$
When h,k,l are mixed parity: $F = 0$, $F^2 = 0$

(111), (200), (220), (311), (222) reflections are possible

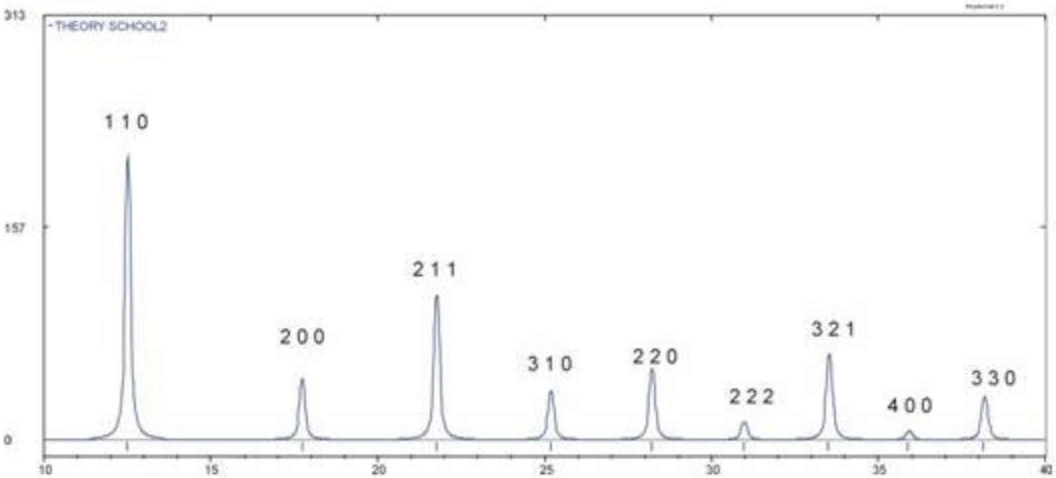
The **structure factor** is completely independent of the shape and size of the unit cell, and critically **depends on** the actual **atomic arrangement**

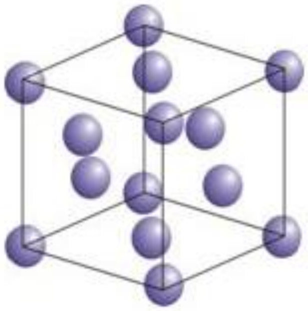
https://slideplayer.com/slide/5976269 (22.09.16)

Structure factor

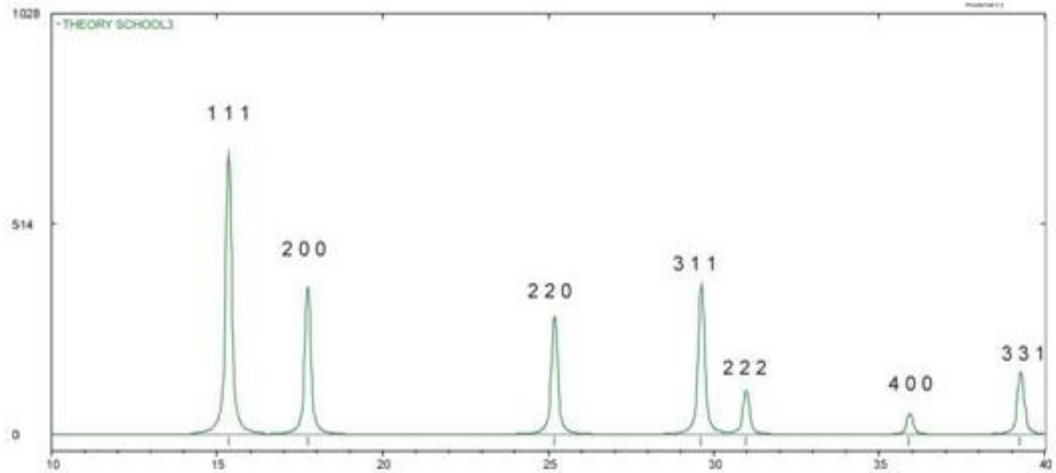


Body Centred Cubic





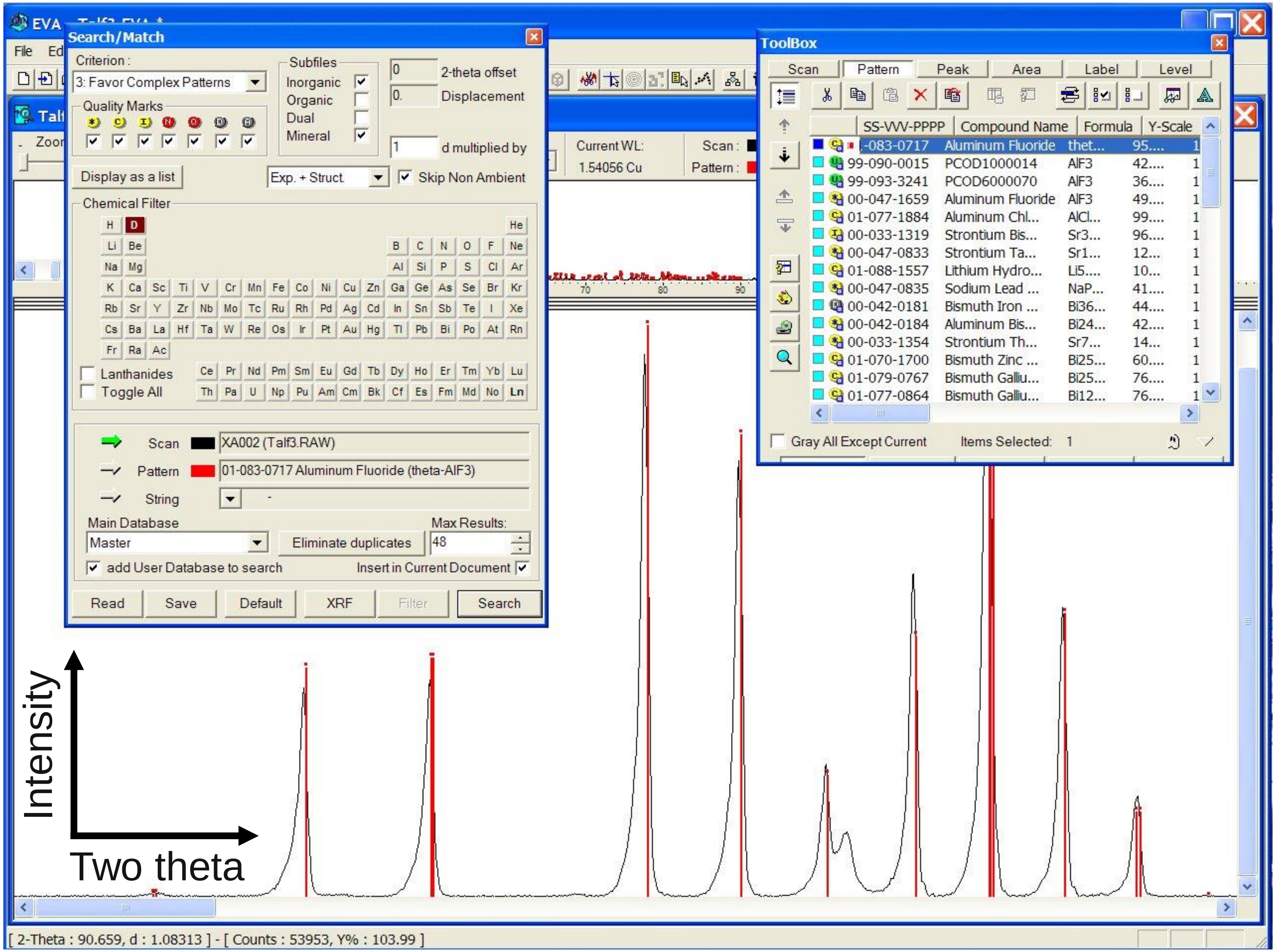
Face Centred Cubic



https://slideplayer.com/slide/5976269 (22.09.16)

XRD data analysis using software

Qualitative Identification of phase : *search and match !*



Criterion : 3: Favor Complex Patterns

Quality Marks ☑ ☑ ☑ ☑ ☑ ☑ ☑

Subfiles: Inorganic ☑ Organic ☐ Dual ☐ Mineral ☑

0 2-theta offset

0. Displacement

1 d multiplied by

Display as a list

Exp. + Struct.

☑ Skip Non Ambient

Chemical Filter: D

☐ Lanthanides

☐ Toggle All

Scan XA002 (Talf3.RAW)

Pattern 01-083-0717 Aluminum Fluoride (theta-AlF3)

String -

Main Database: Master

Eliminate duplicates

Max Results: 48

☑ add User Database to search

Insert in Current Document ☑

Current WL: 1.54056 Cu

SS-VVV-PPPP	Compound Name	Formula	Y-Scale	
-083-0717	Aluminum Fluoride	thet...	95....	1
99-090-0015	PCOD1000014	AlF3	42....	1
99-093-3241	PCOD6000070	AlF3	36....	1
00-047-1659	Aluminum Fluoride	AlF3	49....	1
01-077-1884	Aluminum Chl...	AlCl...	99....	1
00-033-1319	Strontium Bis...	Sr3...	96....	1
00-047-0833	Strontium Ta...	Sr1...	12....	1
01-088-1557	Lithium Hydro...	Li5....	10....	1
00-047-0835	Sodium Lead ...	NaP...	41....	1
00-042-0181	Bismuth Iron ...	Bi36...	44....	1
00-042-0184	Aluminum Bis...	Bi24...	42....	1
00-033-1354	Strontium Th...	Sr7...	14....	1
01-070-1700	Bismuth Zinc ...	Bi25...	60....	1
01-079-0767	Bismuth Galliu...	Bi25...	76....	1
01-077-0864	Bismuth Galliu...	Bi12...	76....	1

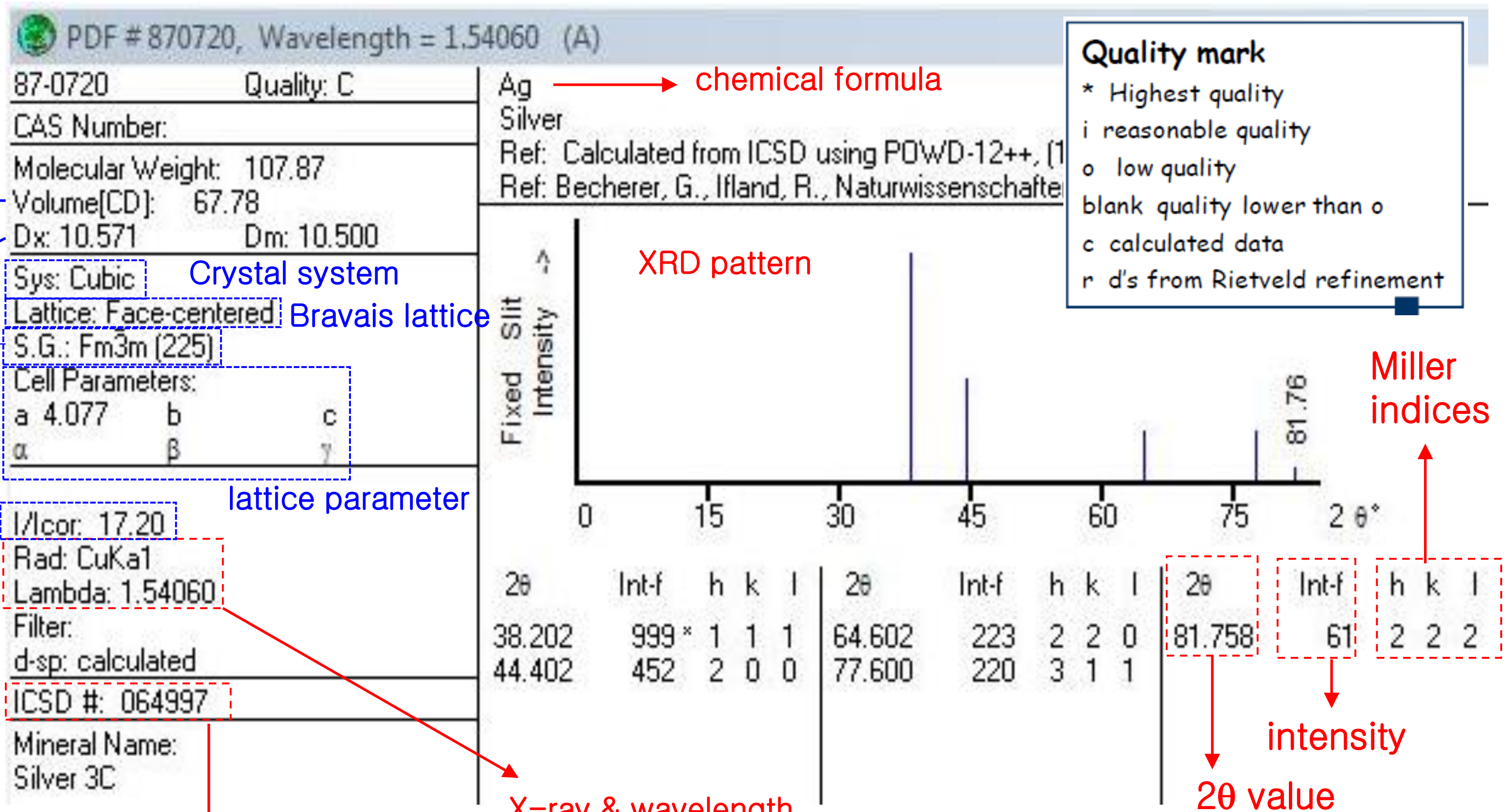
☐ Gray All Except Current   Items Selected: 1

[2-Theta : 90.659, d : 1.08313] - [Counts : 53953, Y% : 103.99]

http://www.crystallography.net/pcod/P2D2/EVA/index.html (22.09.16)

Database

- **ICDD(International Centre for Diffraction Data):** a scientific organization dedicated to collecting, editing, publishing, and distributing powder diffraction data for the identification of crystalline materials [Previously, JCPDS]
- **PDF (powder diffraction file):** a collection of single-phase X-ray powder diffraction patterns in the form of tables of characteristic interplanar spacings and corresponding relative intensities along with other pertinent physical and crystallographic properties



Space group: a group representing symmetries and atomic configuration in a unit cell

PDF # 870720, Wavelength = 1.54060 (A)

87-0720 Quality: C

CAS Number:

Molecular Weight: 107.87
Volume[CD]: 67.78
Dx: 10.571 Dm: 10.500

Sys: Cubic
Lattice: Face-centered
S.G.: Fm3m (225)
Cell Parameters:
a 4.077 b c
α β γ

I/Icor: 17.20
Rad: CuKa1
Lambda: 1.54060
Filter:
d-sp: calculated

ICSD #: 064997

Mineral Name:
Silver 3C

Ag
Silver
Ref: Calculated from ICSD using POWD-12++, (1
Ref: Becherer, G., Ifland, R., Naturwissenschafte

2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
38.202	999 *	1	1	1	64.602	223	2	2	0	81.758	61	2	2	2
44.402	452	2	0	0	77.600	220	3	1	1					

Quality mark
- * Highest quality
- i reasonable quality
- o low quality
- blank quality lower than o
- c calculated data
- r d's from Rietveld refinement

chemical formula

XRD pattern

Unit cell volume

Crystal system

Bravais lattice

Crystallographically Calculated density (D_m: measured density in g/cm^3)

lattice parameter

Miller indices

intensity

2θ value

X-ray & wavelength

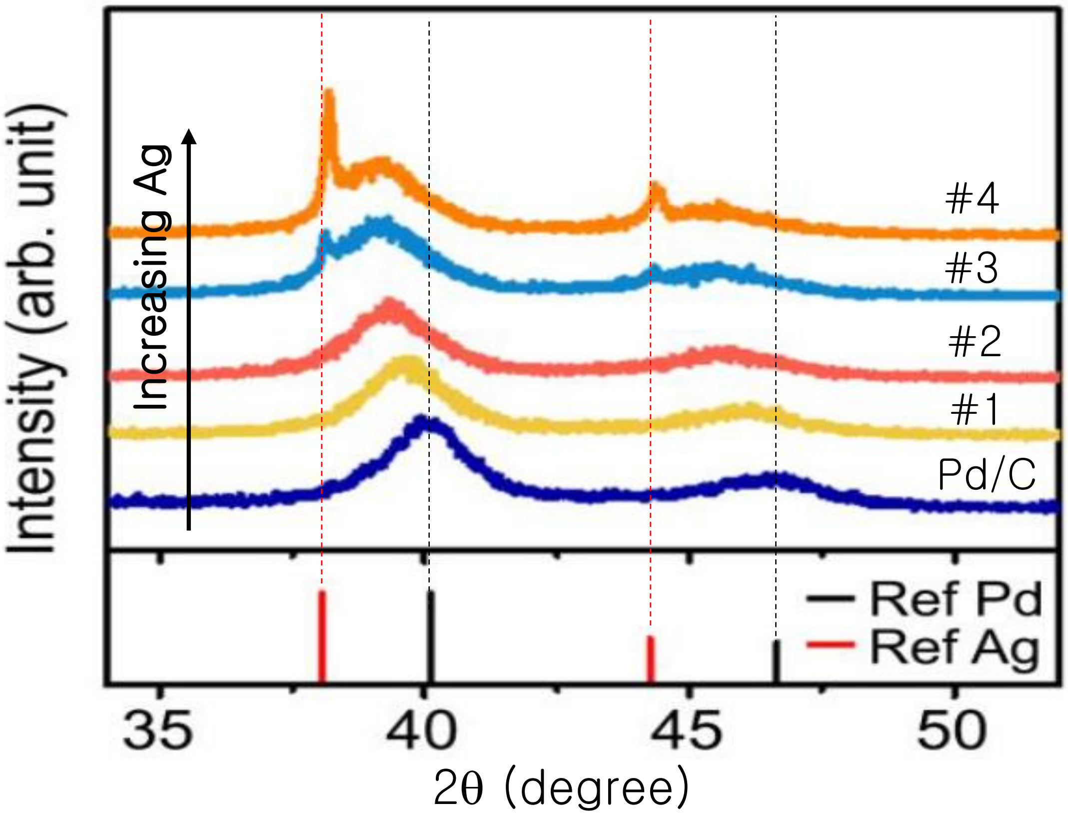
$$\frac{I_b}{I_a} = \frac{(I/I_c)_a}{(I/I_c)_b} \times \frac{X_a}{X_b}$$

I/I_{cor}: reference intensity ratio
Corumdum: a crystalline Al_2O_3

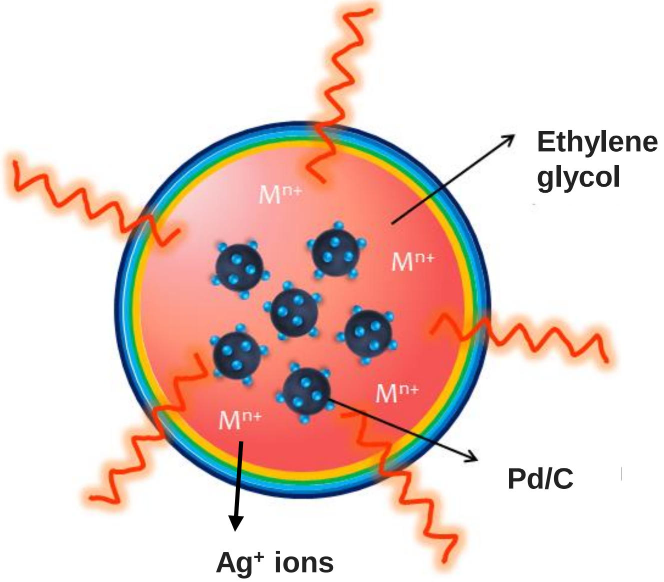
ICSD: inorganic crystal structure database

Example for XRD data analysis

XRD patterns of Pd-Ag alloy samples



Microwave-assisted Polyol method



1. What is the crystal structure and phase ?

→ Pd/C: Pd metal with face-centered cubic (FCC) crystal structure

→ #1 & #2: Pd-Ag alloy with unidentified composition

→ #3 & #4: the mixture of Pd-Ag alloy and pure Ag crystal

2. Why does the shift of 2θ values occur? → $\lambda = 2d\sin\theta$

3. How can we quantify the change of lattice parameters ?

https://doi.org/10.1038/s41467-019-11903-5 (22.09.16)

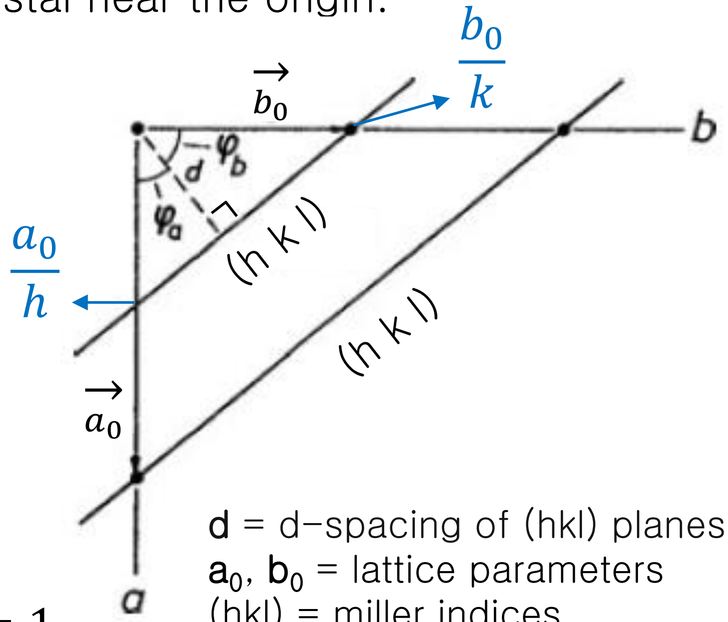
d-spacing & lattice parameter

Assume a set of planes (h k l) of orthorhombic crystal near the origin.

$$a_0 \times \frac{1}{h} \times cos\phi_a = d_{hkl}$$

$$b_0 \times \frac{1}{k} \times cos\phi_b = d_{hkl}$$

$$c_0 \times \frac{1}{l} \times cos\phi_c = d_{hkl}$$



d = d-spacing of (hkl) planes
a_0, b_0 = lattice parameters
(hkl) = miller indices

$$cos^2\phi_a + cos^2\phi_b + cos^2\phi_c = d_{hkl}^2\left(\frac{h^2}{a_0^2} + \frac{k^2}{b_0^2} + \frac{l^2}{c_0^2}\right) = 1$$

(orthorhombic system)

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a_0^2} + \frac{k^2}{b_0^2} + \frac{l^2}{c_0^2}}}$$

(cubic system, $a_0 = b_0 = c_0$)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

Relationship between the miller indices, d-spacings and lattice parameters

Walter Borchardt-Ott, Crystallography An Introduction, 3rd Ed., Springer, 2012, p. 279

Determination of lattice parameter

By substituting the equation for the d-spacing into the Bragg equation:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2+k^2+l^2}} \xrightarrow{\lambda = 2d\sin\theta} sin^2\theta = \frac{\lambda^2}{4a_0^2}(h^2+k^2+l^2) \quad \text{(Eq. 1)}$$

$$a_0^2 = \frac{\lambda^2}{4sin^2\theta}(h^2+k^2+l^2) \quad \text{(Eq. 2)}$$

- The **Eq. 1** suggests that the diffraction angle can be determined from the shape and size of the unit cell. "*principle of XRD measurement*"

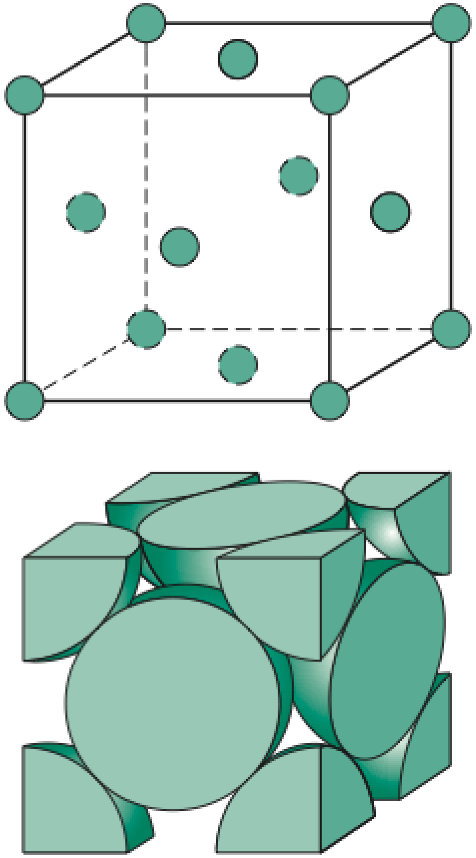
- One can determine lattice parameters by measuring diffraction angles from **Eq. 2**.

Sample	Plane	2θ (degree)	d-spacing, d_{hkl} (Å)	Lattice parameter (Å)
Pd/C	(111)	40.032	2.250	3.898
#1	(111)	39.674	2.270	3.932
#2	(111)	39.380	2.286	3.960

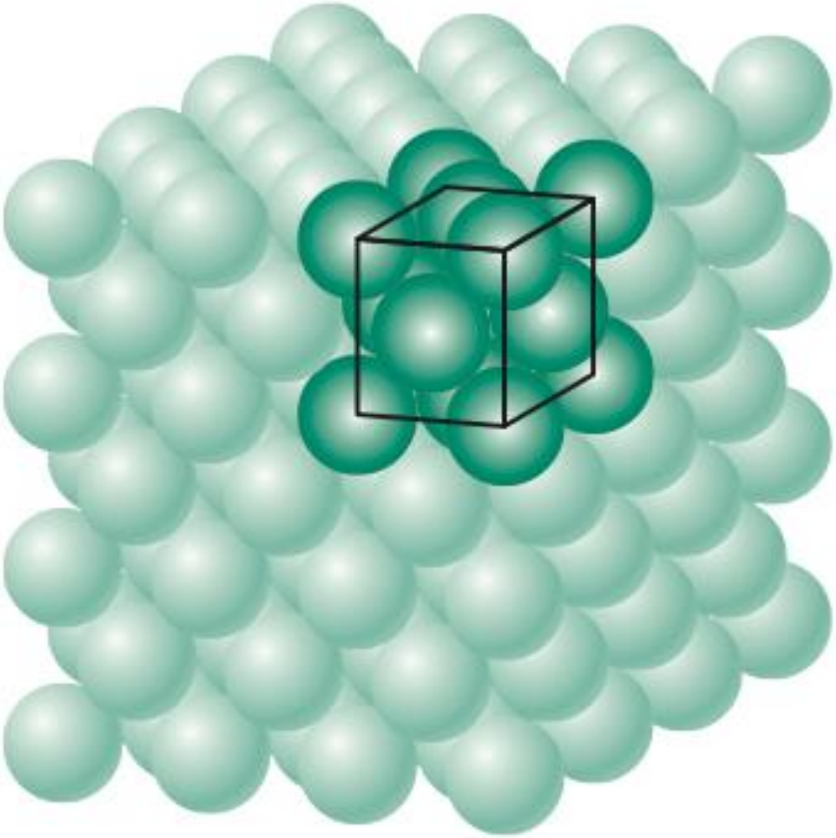
1.59% expansion

$$a_0 = \sqrt{\frac{\lambda^2}{4sin^2\theta}(h^2+k^2+l^2)} = \sqrt{\frac{(1.5406\ \text{Å})^2}{4 \times sin^2(20.016^\circ)}(1^2+1^2+1^2)} = 3.898\ \text{Å}$$

Lattice expansion



FCC crystal structure



DOI:10.13140/RG.2.2.27679.79522 (22.09.16)

d-spacing & lattice parameter

Table below provide the relationship between the **d-spacings** for specific **Miller indices** and the **lattice parameters** for each crystal system.

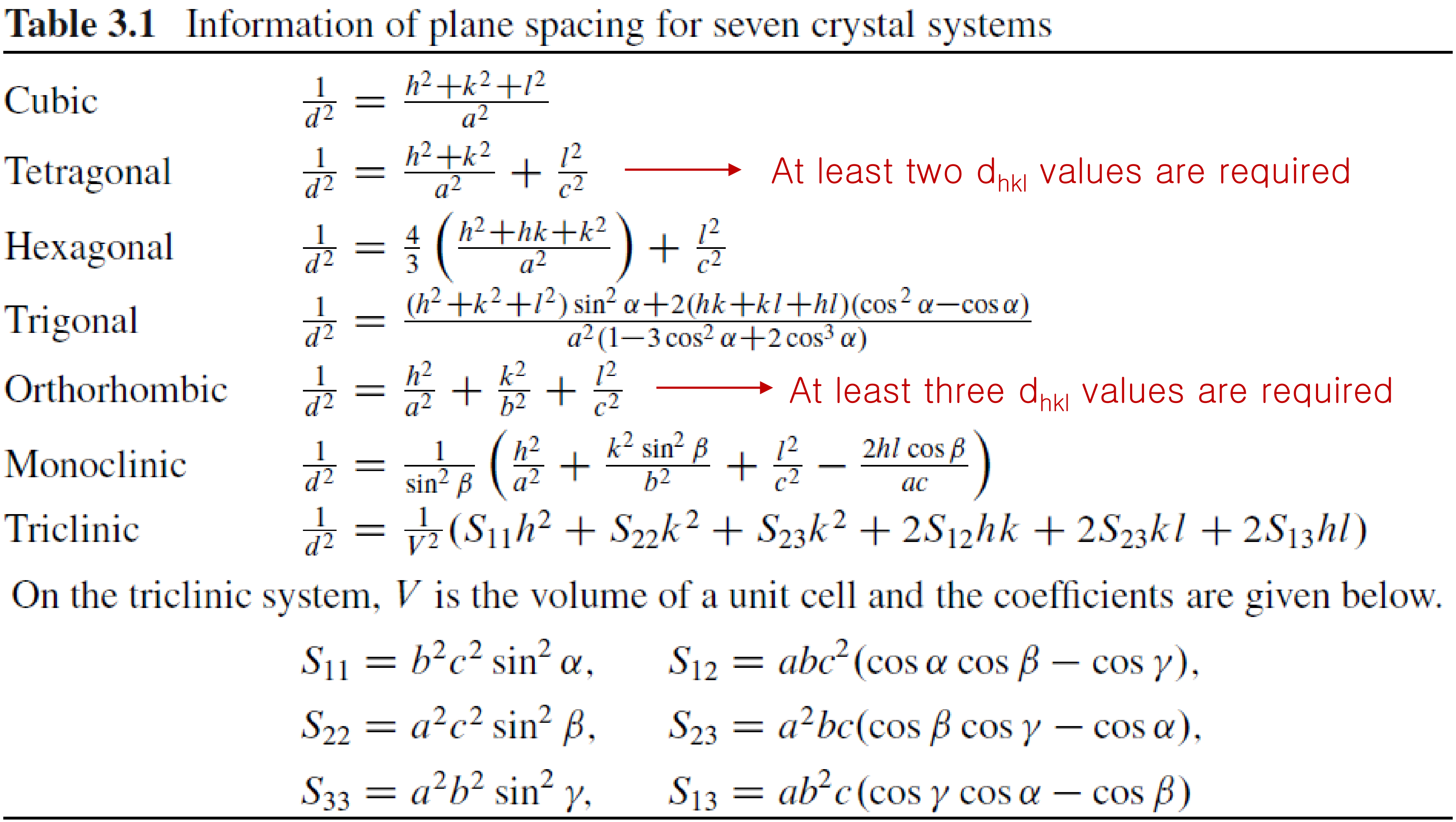


Table 3.1 Information of plane spacing for seven crystal systems

Cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$	
Tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$	→ At least two d_{hkl} values are required
Hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$	
Trigonal	$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+hl)(\cos^2\alpha-\cos\alpha)}{a^2(1-3\cos^2\alpha+2\cos^3\alpha)}$	
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$	→ At least three d_{hkl} values are required
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$	
Triclinic	$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{23}k^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$	

On the triclinic system, V is the volume of a unit cell and the coefficients are given below.

$$S_{11} = b^2c^2\sin^2\alpha, \qquad S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$

$$S_{22} = a^2c^2\sin^2\beta, \qquad S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$

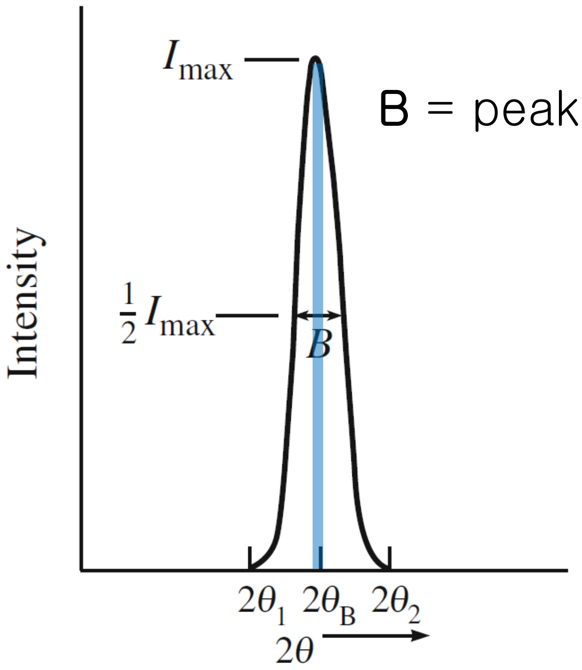
$$S_{33} = a^2b^2\sin^2\gamma, \qquad S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta)$$

Yoshio Waseda, X-ray Diffraction Crystallography, 1st Ed., Springer, 2011, p. 75

Line broadening

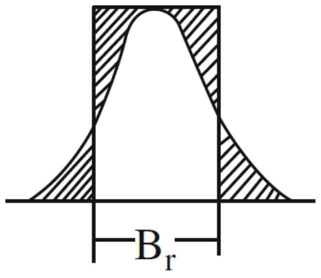
- Diffraction peak has the shape of distribution rather than a line (ideal case)
- Source: **instrumental** broadening + **size** broadening + **strain** broadening

Schematic diagram for X-ray diffraction peak profile of a fine crystalline sample

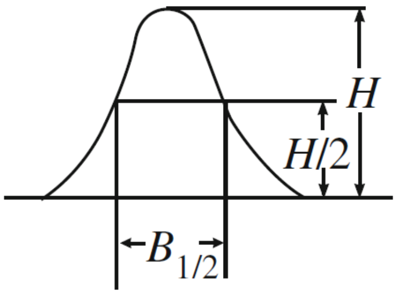


B = peak width

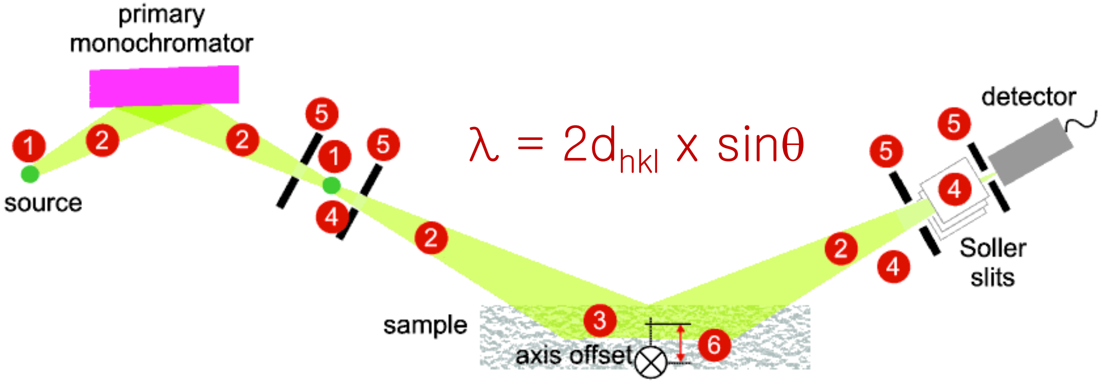
Integral breadth



FWHM



- **FWHM:** the full width at half maximum
- **Integral breadth:** the width of a rectangle having the same area and the same height as the peak



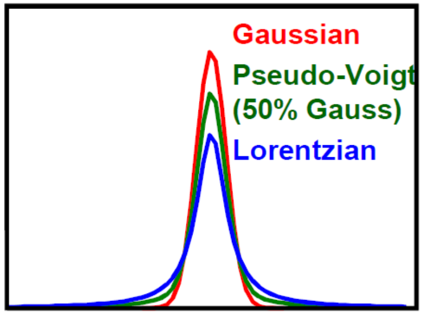
$\lambda = 2d_{hkl} \times \sin\theta$

Instrumental contributions:

(1) X-ray is not perfectly monochromatic. Superposition of $K\alpha_1$ and $K\alpha_2$ **(λ distribution)**
(2) Divergence issue of incident/reflected beams and slit width **(θ distribution)**

http://pd.chem.ucl.ac.uk/pdnn/peaks/broad.htm (22.09.16)

Line broadening



Depending on peak shape, different correction method

- Lorentzian: $\beta_{\text{observed}} = \beta_{\text{instrument}} + \beta_{\text{size}} + \beta_{\text{strain}}$
- Gaussian: $\beta^2_{\text{observed}} = \beta^2_{\text{instrument}} + \beta^2_{\text{size}} + \beta^2_{\text{strain}}$

the instrumental broadening can be determined using a standard material with very high crystallinity and large particle size

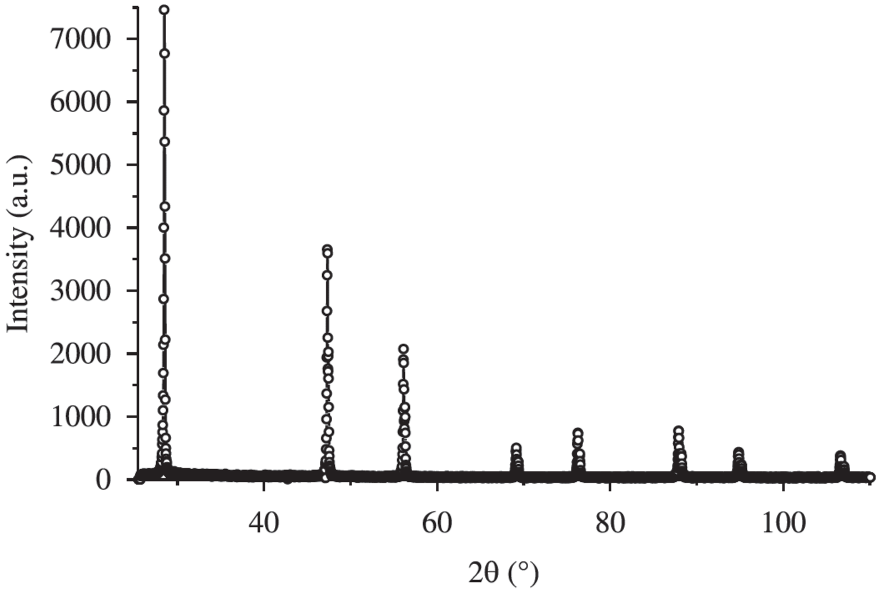


Figure 1. XRD pattern of standard silicon powder.

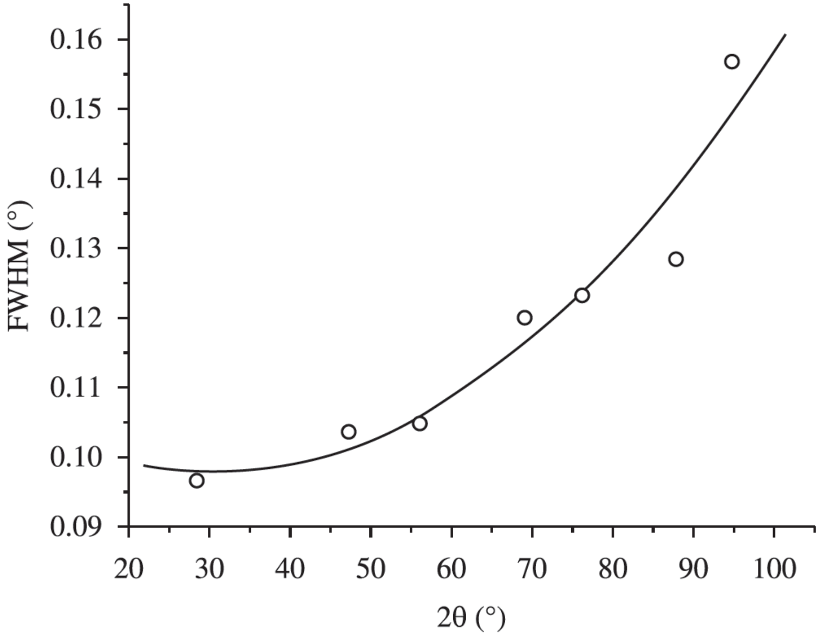


Figure 3. Instrumental broadening against 2θ for standard Silicon powder.

DOI:10.1590/S1516-14392011005000015 (22.09.16)

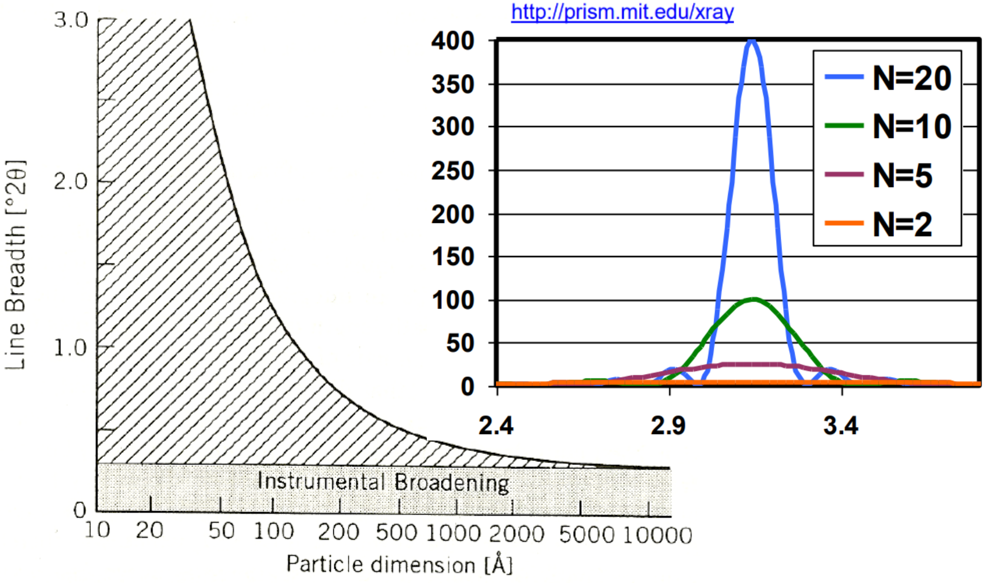
http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2015_2016/frank_girgsdies__peak_profile_fitting_in_xrd__151106.pdf (22.09.16)

Size broadening

(Effective in < c.a. 100 nm)

Scherrer equation:

$$B = \frac{K\lambda}{D\cos\theta_B}$$


http://prism.mit.edu/xray

λ : X-ray wavelength
θ_B : Bragg angle
K : Scherrer constant
(shape factor, 0.94 for FWHM of spherical crystals)
B : peak width in radians, corrected for instrumental broadening
D : a volume-weighted mean of crystallite sizes in the direction normal to the reflecting planes

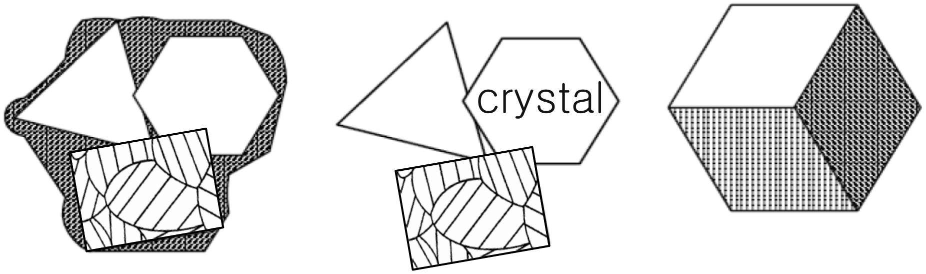
- Peak width (B) is inversely proportional to crystallite size (D)
  Infinite crystals means perfect periodicity and diffraction
  "The smaller the crystal, the smaller the number of periods, and thus the less perfect the Bragg diffraction"

- Peak width (B) is inversely proportional to $\cos\theta_B$
  "The size broadening is more pronounced at larger 2θ angles"

http://prism.mit.edu/xray (22.09.16)

What is crystallite size

[Figure taken from the TOPAS 3.0 Users Manual, Bruker AXS]

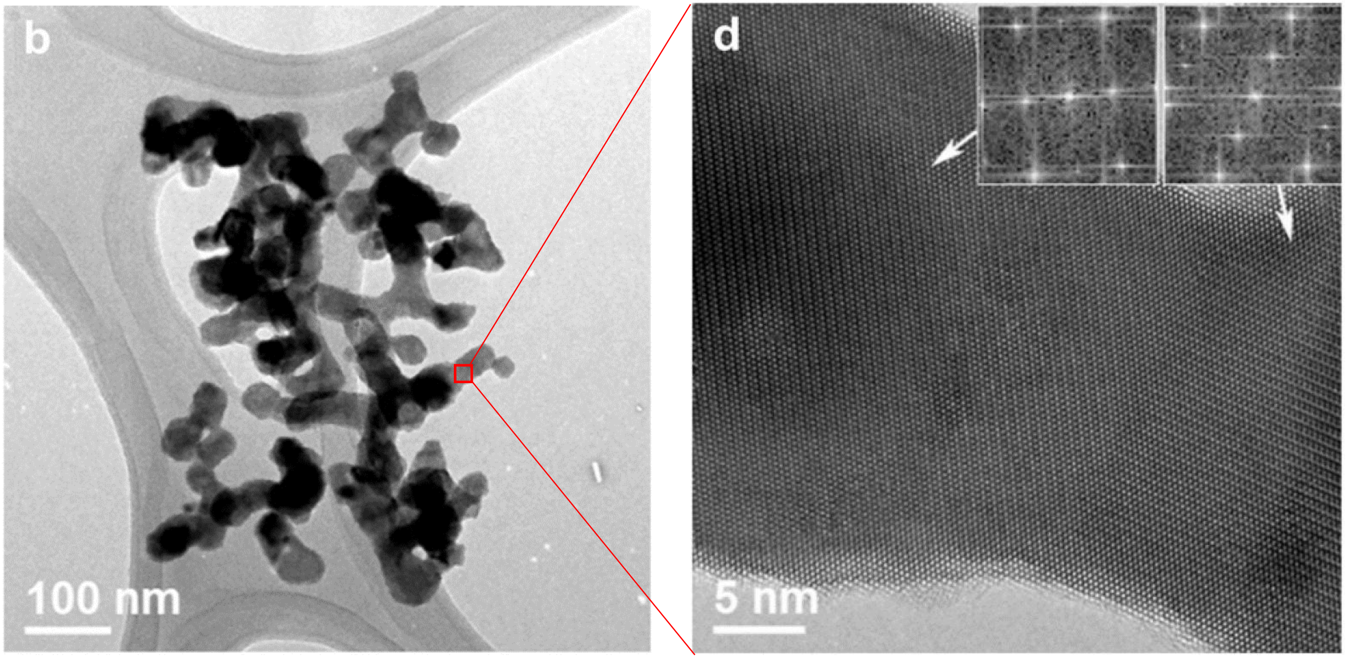


A particle

crystal

crystallite

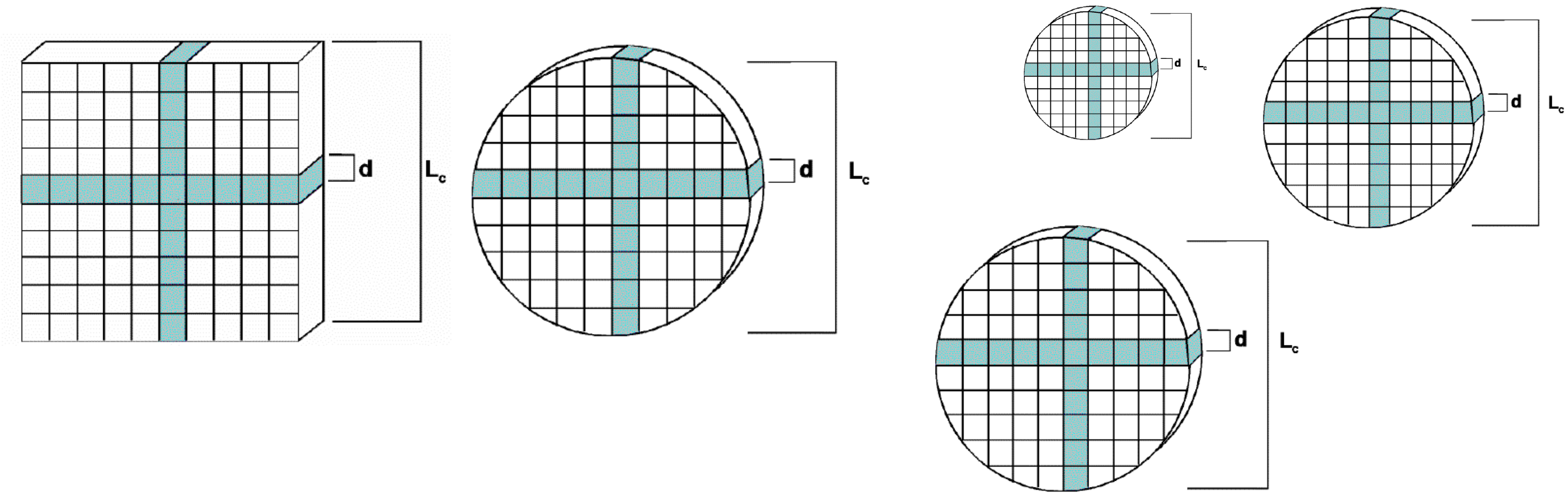
- **A particle** may consist of one or more crystals which are fused together
- **A crystal** may consist of several crystallites with different crystallographic orientations, which are fused by small angle boundaries
- **crystallite:** a small region of a solid with a single-crystalline property



https://doi.org/10.1016/j.ijhydene.2012.04.063 (22.09.16)

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2015_2016/frank_girgsdies__peak_profile_fitting_in_xrd__151106.pdf (22.09.16)

What is crystallite size



- The crystallite size will be different between crystallites
- Even in a single crystallite, various lengths of columns are present

→ we need to know the weighing scheme of crystallite sizes
→ X-ray diffraction is a volume effect. So, the derived size is a volume-weighted mean

(ex) Let us assume **two crystallites** (diameter = 1 for the 1st, and 2 for the 2nd)

- arithmetic mean size = $1 \times \frac{1}{2} + 2 \times \frac{1}{2} = 1.5$
- area weighted mean size = $1 \times \frac{1}{5} + 2 \times \frac{4}{5} = 1.8$
- volume weighted mean size = $1 \times \frac{1}{9} + 2 \times \frac{8}{9} = 1.89$

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2015_2016/frank_girgsdies__peak_profile_fitting_in_xrd__151106.pdf (22.09.16)

What is crystallite size

The crystallite size and the most common size are different

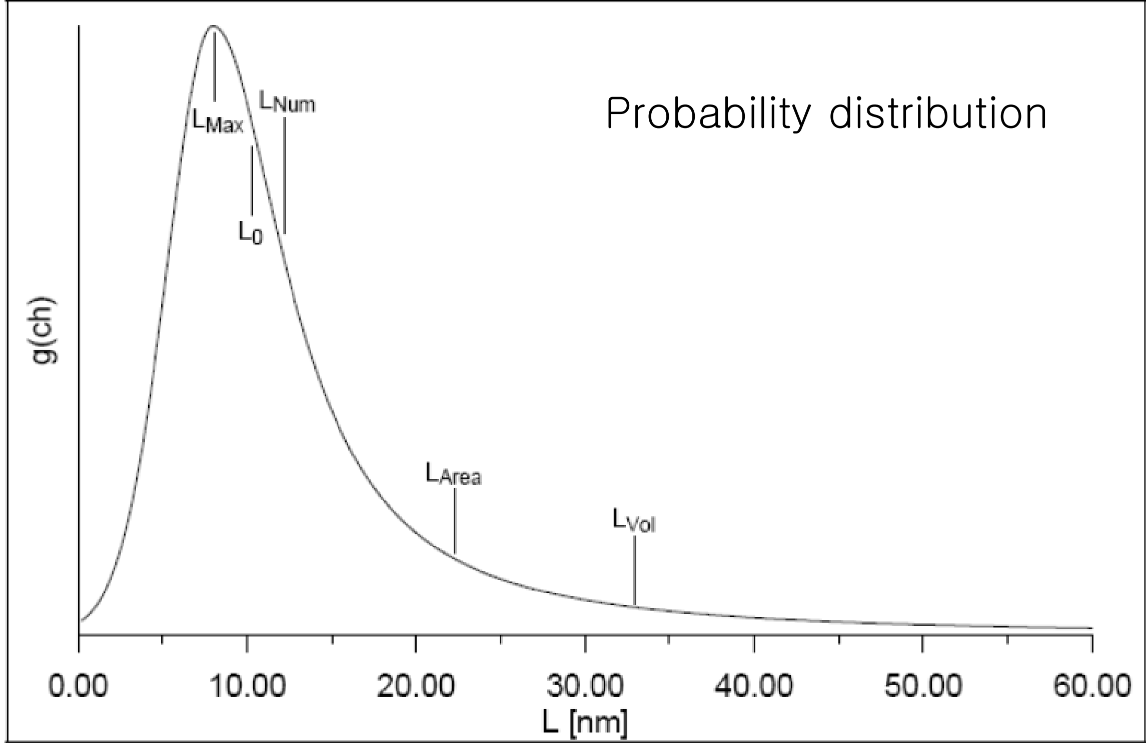


Fig. 3-20: Schematic representation of a column height distribution g(ch) showing the following characteristic points:

L_{Max} : most probable value
L_0 : median
L_{Num} : number weighted mean
L_{Area} : area weighted mean
L_{Vol} : volume weighted mean

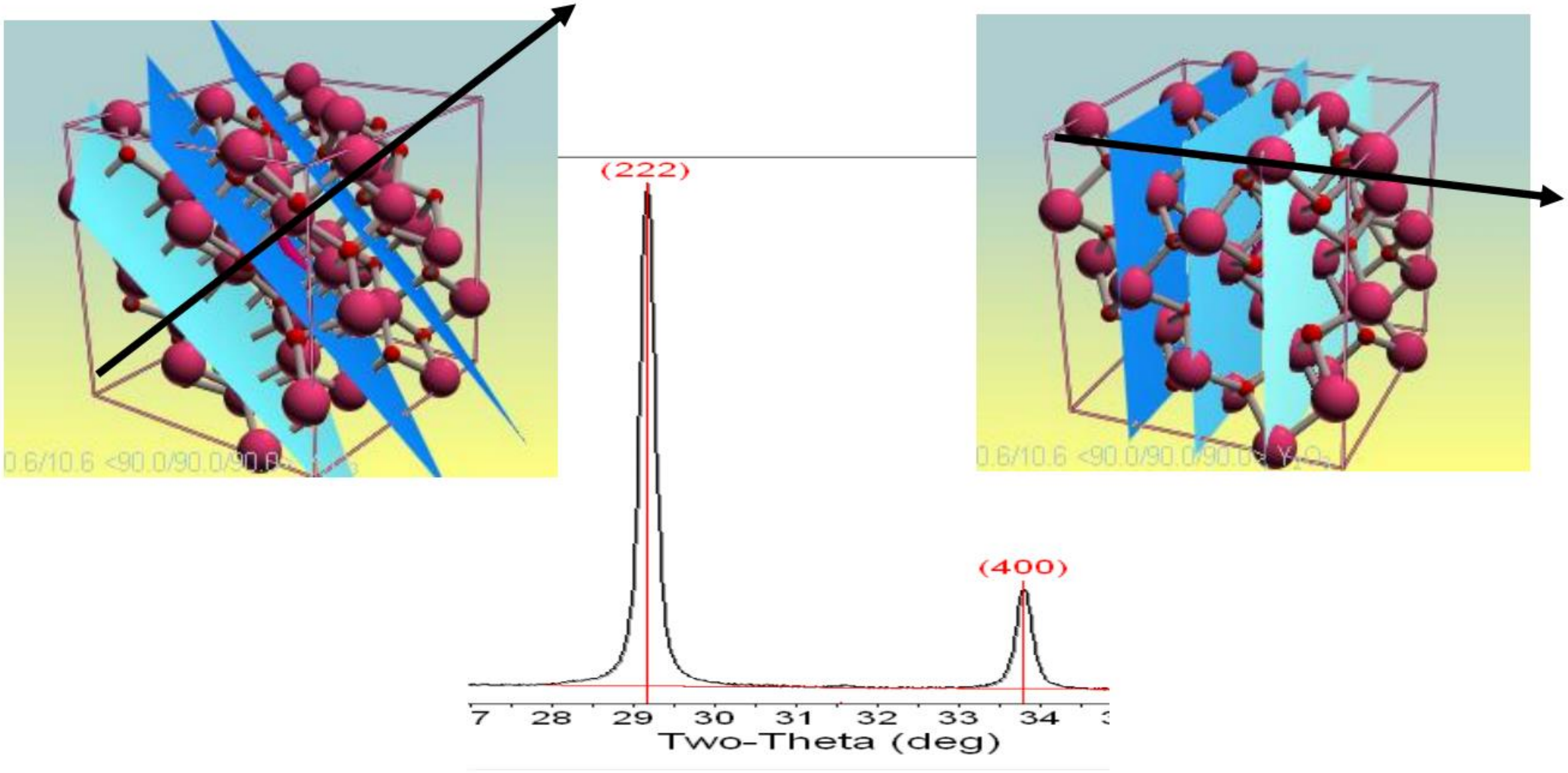
[Figure taken from the TOPAS 3.0 Users Manual, Bruker AXS]

L_{max} : most common value
L_0 : the value at which the integral of the curve is cut into two halves
L_{num} : number weighted mean (arithmetic mean)
L_{area} , L_{vol} : each value is given with a different weight according to the fraction that their area or volume contributes to the total area or volume.

http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2015_2016/frank_girgsdies__peak_profile_fitting_in_xrd__151106.pdf (22.09.16)

What is crystallite size

- The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak.



http://prism.mit.edu/xray (22.09.16)

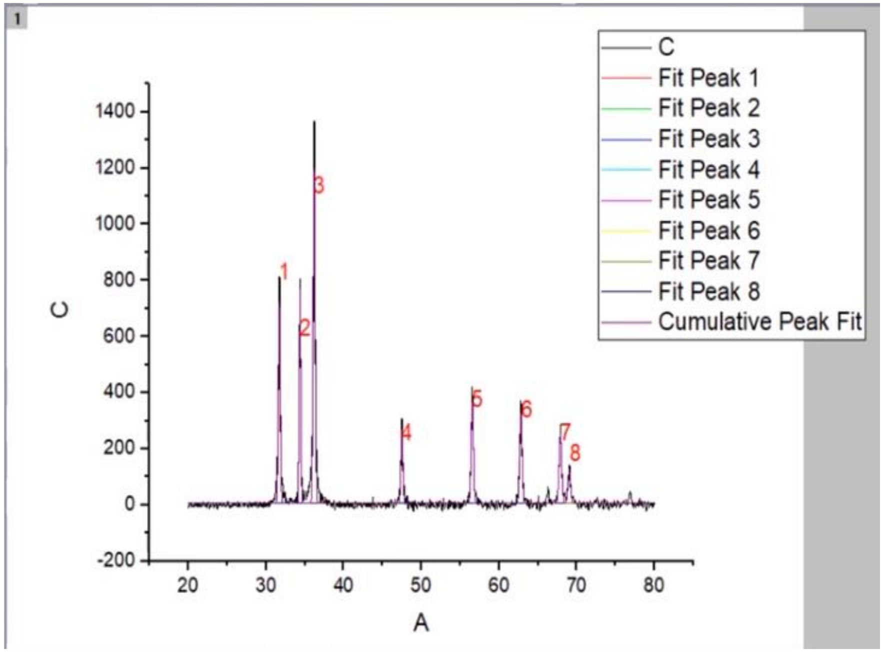
Example

(Effective in < c.a. 100 nm)

$$D = \frac{K\lambda}{B\cos\theta_B}$$

λ : 0.15406 (nm)
θ_B : peak position (radians)
K : 0.94 for FWHM of spherical crystals
B : FWHM (radians)
D : crystallite sizes in the direction normal to (hkl) (nm)

Procedure:
(1) XRD data; (2) Peak Fit; (3) θ_B, FWHM; (4) calculation



$$D = \frac{0.94 \times 0.15406\, nm}{(0.28673° * \frac{\pi\, rad}{180°})\cos(\frac{31.70868°}{2} * \frac{\pi\, rad}{180°})}$$

$$D = 30.08227\, nm$$

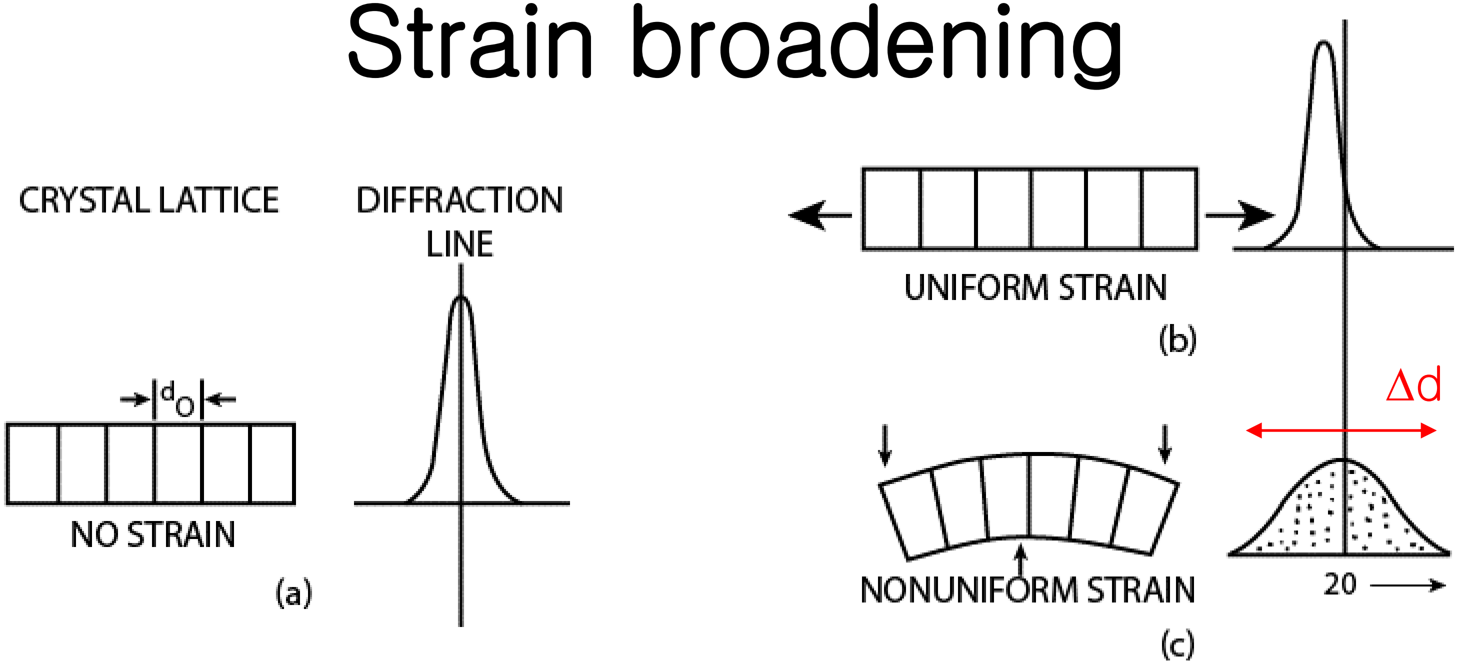
$D_{average}$ = 29.3 nm

peak position (2θ, °)	FWHM(°)	crystallite size D (nm)
31.70868	0.28673	30.08226516
34.36301	0.22556	38.50392314
36.19607	0.29529	29.56156776
47.47974	0.29426	30.80395372
56.54624	0.35102	26.83988698
62.80407	0.35766	27.18003745
67.8968	0.40304	24.81729582
69.03285	0.38421	26.20979309

The $D_{average}$ is not accurate due to the assumptions and instrumental effect, but gives comparable information .

https://www.youtube.com/watch?v=m8L-B4A75Ec (22.09.16)

Strain broadening



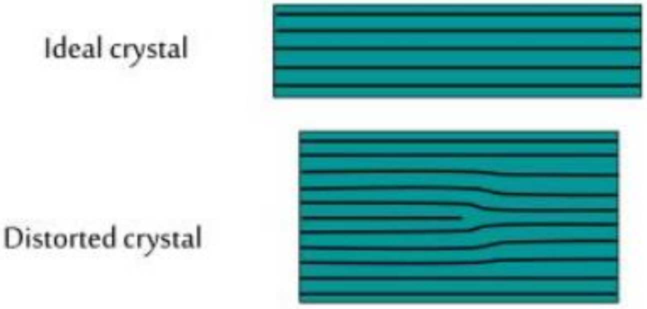
- When all crystallites receive a **uniform strain**, each d-spacing changes uniformly and then a **certain shift in the peak position** is observed.
- when applying a **non-uniform strain**, the different size of distortion depending on the place, the d-spacing show divergence at random with a certain width.

- **Lattice strain:** local devation of d-spacings from the average value where the forces of compression and expansion will be balanced

- Origins:
  - point defects like interstitial or missing or substitutional atoms
  - 1-D defects like screw dislocations
  - 2-D defects like twin boundaries
  - surface tensions in nanoparticles, morphological effect such as nanotubes

Strain broadening

$$B = 4\varepsilon \frac{sin\theta_B}{cos\theta_B} \qquad \varepsilon = \frac{\Delta d}{d} (\%)$$



$\boldsymbol{\varepsilon}$: a volume-weighted mean of lattice strain
θ_B : Bragg angle
B : peak width in radians

- Peak width (B) is proportional to strain (ε)
  "The larger the strain, the higher the broadening"

- Peak width (B) is proportional to $\tan\theta_B$
  "The strain broadening is more pronounced at larger 2θ angles"

Combined contribution

$$B_{obs} = B_{inst} + B_{size} + B_{strain} = B_{inst} + \frac{K\lambda}{Dcos\theta_B} + 4\varepsilon tan\theta_B$$

$$\mathrm{B}_{\mathrm{obs}}^2 = B_{\mathrm{inst}}^2 + B_{\mathrm{size}}^2 + B_{\mathrm{strain}}^2 = B_{\mathrm{inst}}^2 + \left(\frac{K\lambda}{Dcos\theta_B}\right)^2 + (4\varepsilon tan\theta_B)^2$$

https://slideplayer.com/amp/2355344 (22.09.16)

Williamson–Hall analysis

Williamson and Hall (1953) proposed a method for deconvoluting size and strain broadening. Assuming Lorentzian peak shape:

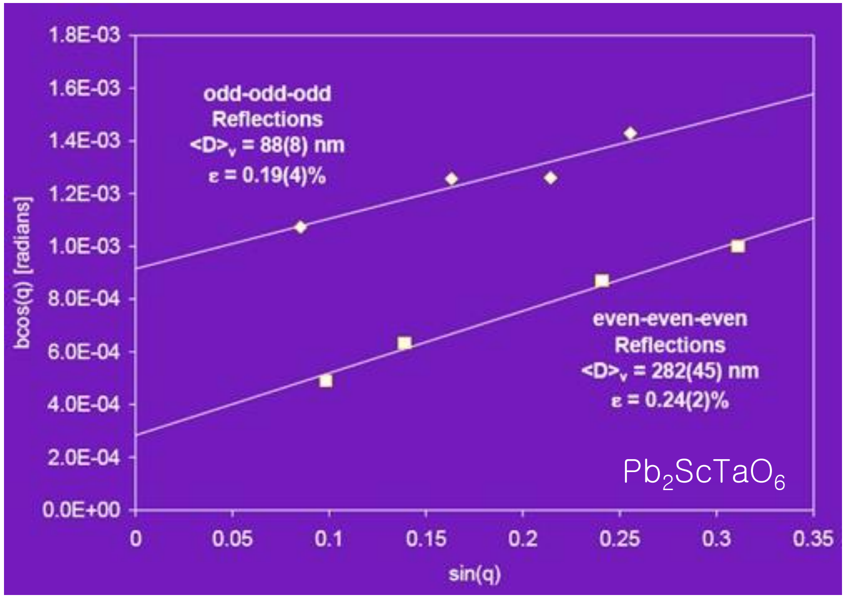
$$B_{obs} - B_{inst} = B_{size} + B_{strain} = \frac{K\lambda}{D cos\theta_B} + 4\varepsilon tan\theta_B$$

slope: strain

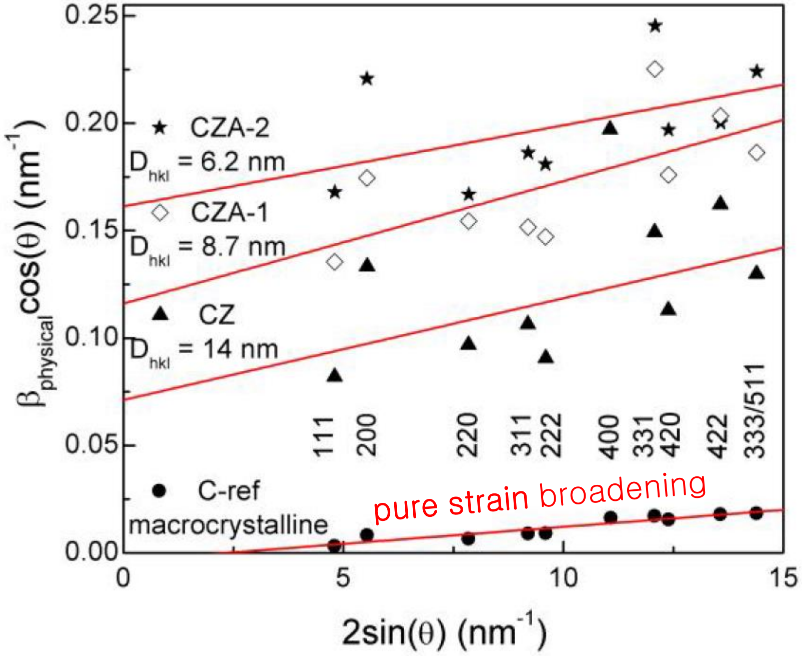
y-axis ← $(B_{obs} - B_{inst}) cos\theta_B = \frac{K\lambda}{D} + 4\varepsilon\, sin\theta_B$ → x-axis

y-axis intercept: size

Williamson–Hall plot



https://slideplayer.com/slide/4318558 (22.09.16)



DOI:10.1007/s11244-013-0175-2 (22.09.16)

RIR-based quantitative analysis

- **RIR (reference intensity ratio, I/I$_c$)**: the intensity of sample referenced to corundum.
- Experimentally, I/Ic can be determined by taking the ratio of the strongest line of the pattern to the intensity of the strongest line of corundum in a 50/50 wt% mixture.
- Or can be calculated theoretically from crystal structures

For analyte: $I_a = \dfrac{K_a\, X_a}{\rho_a\, \mu}$ For corundum: $I_c = \dfrac{K_c\, X_c}{\rho_c\, \mu}$

$$\frac{I_a}{I_c} = \frac{K_a\, \rho_c\, X_a}{K_c\, \rho_a\, X_c} = K\,\frac{X_a}{X_c} \xrightarrow[\text{50–50 mixture}]{X_a = X_c} \frac{I_a}{I_c} = K = \left[\frac{I}{I_c}\right]_a$$

- The intensity of a diffraction peak profile is a convolution of many factors including concentration. In the RIR method, we assume that the same phase has similar K_a and ρ_a values.

$$I_{ia} = \frac{K_{ia}\, X_a}{\rho_a\, \mu}$$

I_{ia} = intensity of reflection i of phase a (measured)
X_a = wt fraction of phase a (analyzed)
ρ_a = density of phase a
μ = linear attenuation coefficient
K_{ia} = contains structure, multiplicity, temperature, scale factors for reflection i of phase a

RIR-based quantitative analysis

- For any a + b mixture, the intensity ratio is related with their wt% composition.

Known values & constant

Measured

$$\frac{I_a}{I_b} = \frac{\frac{I_a}{I_c}}{\frac{I_b}{I_c}} = \frac{\frac{K_a\,\rho_c\,X_a}{K_c\,\rho_a\,X_c}}{\frac{K_b\,\rho_c\,X_b}{K_c\,\rho_b\,X_c}} = \frac{\frac{K_a\;X_a}{\rho_a}}{\frac{K_b\;X_b}{\rho_b}} = \frac{K_a}{\rho_a}\times\frac{\rho_b}{K_b}\times\frac{X_a}{X_b} = \frac{\left[\frac{I}{I_c}\right]_a}{\left[\frac{I}{I_c}\right]_b}\times\frac{X_a}{X_b}$$

Example:

Phase	I/I$_C$	Measured I
a	4.32	2415
b	3.90	5958

$$\left[\frac{I}{I_c}\right]_a = \frac{K_a\,\rho_c}{K_c\,\rho_a} \qquad \left[\frac{I}{I_c}\right]_b = \frac{K_b\,\rho_c}{K_c\,\rho_b}$$

$$\frac{X_a}{X_b} = \frac{1-X_b}{X_b} = \frac{I_a}{I_b}\times\frac{\left[\frac{I}{I_c}\right]_b}{\left[\frac{I}{I_c}\right]_a} = \frac{2415}{5958}\times\frac{3.90}{4.32} = 0.3659$$

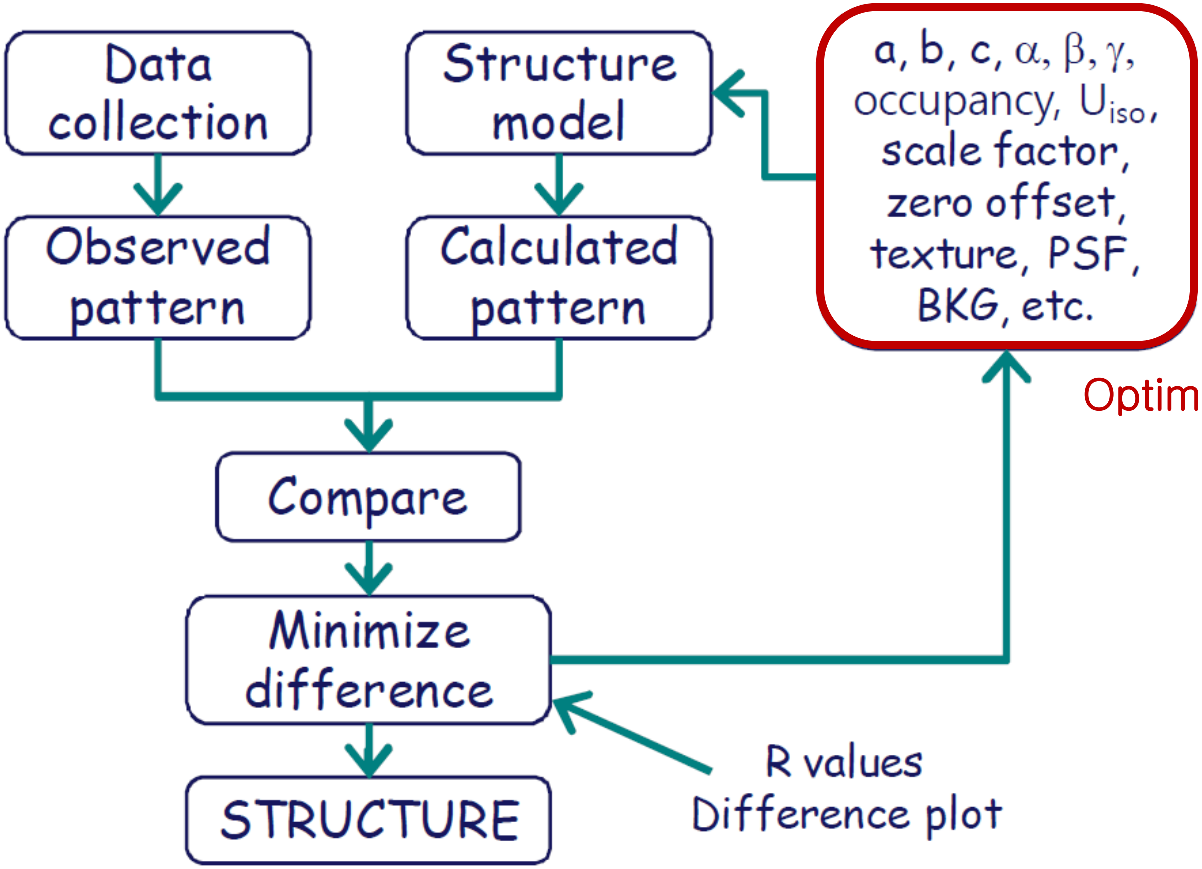
$$X_b = 73.2\%$$
$$X_a = 26.8\%$$

It should be noted that the presence of any unidentified or amorphous phases invalidates the use of this method. Also, the change of instrumental condition can affect the I/I$_C$ values.

Rietveld refinement

- **Rietveld Refinement** is to **fit** the entire diffraction pattern measured, optimizing the agreement between the **measured** and the **calculated**

- *What input is needed to carry out a Rietveld Refinement?*
  - Correct unit cell parameters, atomic positions, space group symmetry, etc.
  - For known materials, ***.cif file (a starting model)** include all information.



Data collection

Observed pattern

Structure model

Calculated pattern

a, b, c, α, β, γ, occupancy, U_{iso}, scale factor, zero offset, texture, PSF, BKG, etc.

Optimized parameters

Compare

Minimize difference

STRUCTURE

R values
Difference plot

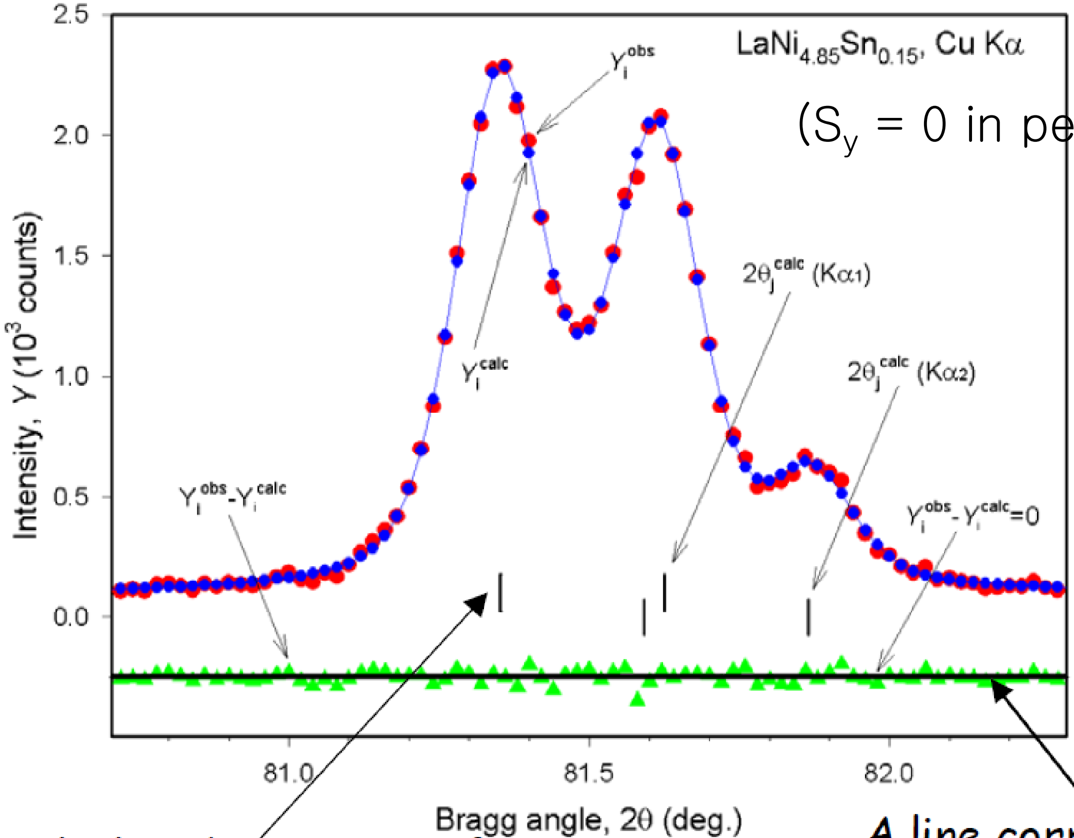
CHAN PARK

https://ocw.snu.ac.kr/sites/default/files/NOTE/2019-XSA-15-RIETVELD-04-15.pdf (22.09.16)

Rietveld refinement

$S_y = \Sigma\, w_i\, (Y_{o,i} - Y_{c,i})^2$ (S_y is the function that should be minimized)

w_i, weighting factor = $1 / \sigma^2[y_{o,i}]$
$Y_{o,i}$, $Y_{c,i}$ = Observed, Calculated intensity at the i th step
$\sigma[y_{o,i}]$: the standard deviation of $y_{o,i}$ "uncertainty"



(S_y = 0 in perfectly ideal case)

Observed I

Calculated I

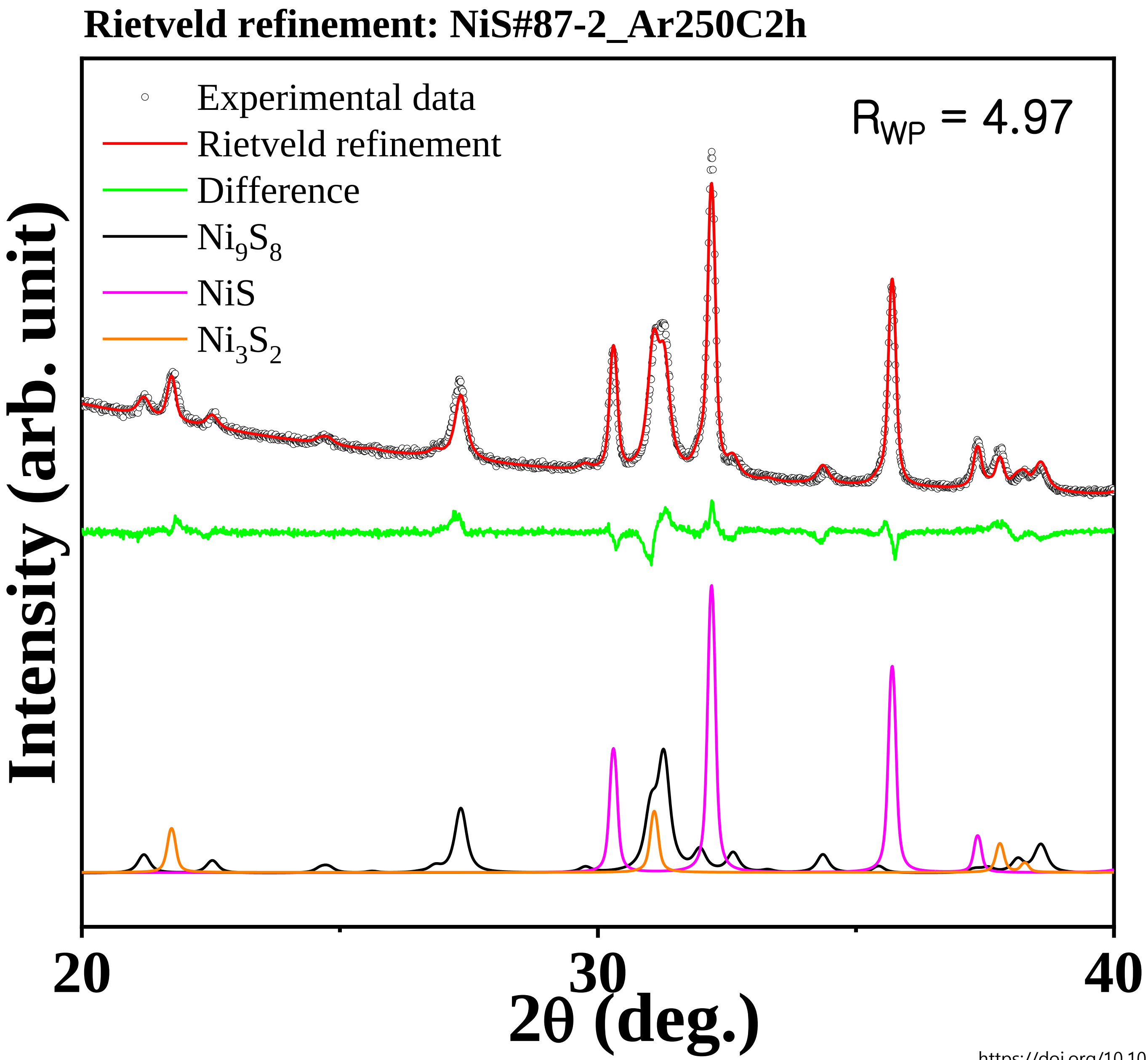
Difference between observed & calculated I

Calculated positions of Bragg peaks of each phase

A line corresponding to $Y_i^{obs} - Y_i^{calc} = 0$

https://ocw.snu.ac.kr/sites/default/files/NOTE/2019-XSA-15-RIETVELD-04-15.pdf (22.09.16)

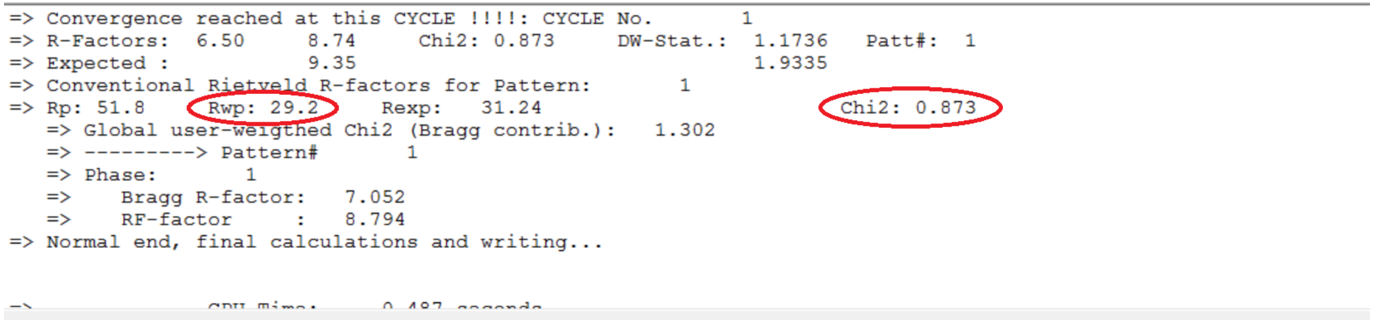
Rietveld refinement example



Phase	Wt%
Ni_9S_8	56.05
NiS	32.45
Ni_3S_2	11.5

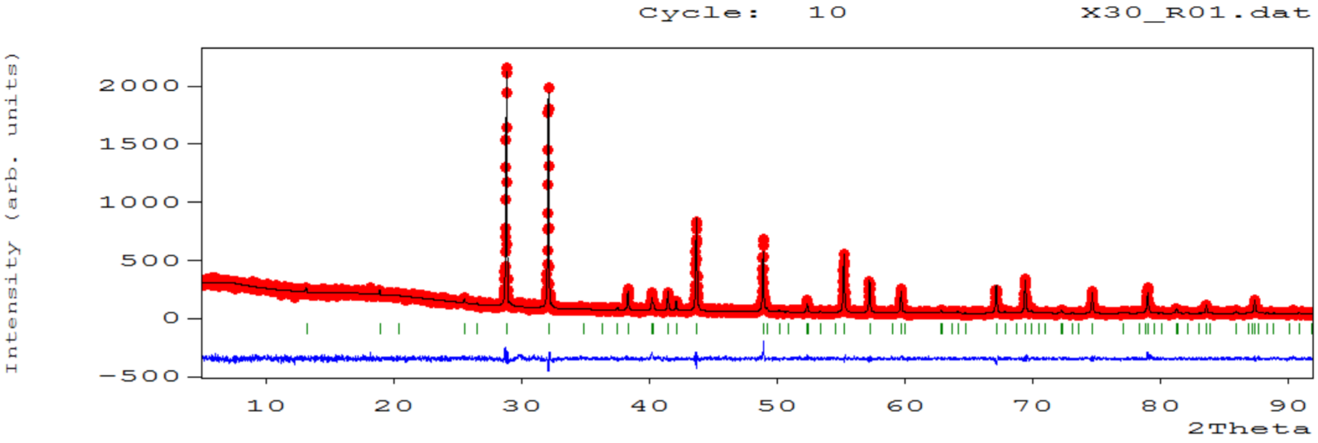
https://doi.org/10.1039/C4NR05942E (22.09.16)

Rietveld refinement example



```
=> Convergence reached at this CYCLE !!!!: CYCLE No.         1
=> R-Factors:  6.50     8.74     Chi2: 0.873      DW-Stat.:  1.1736   Patt#:  1
=> Expected :           9.35                                 1.9335
=> Conventional Rietveld R-factors for Pattern:        1
=> Rp: 51.8     Rwp: 29.2       Rexp:   31.24                 Chi2: 0.873
   => Global user-weigthed Chi2 (Bragg contrib.):   1.302
   => ---------> Pattern#        1
   => Phase:        1
   =>    Bragg R-factor:   7.052
   =>    RF-factor     :   8.794
=> Normal end, final calculations and writing...


=>              CPU Time:      0.487 seconds
```



Weighted profile residual:

$$R_{wp} = \sum_{i}^{n} \left(\frac{w_i (Y_i^{obs} - Y_i^{calc})^2}{\sum_i^n w_i (Y_i^{obs})^2} \right)^{\frac{1}{2}} \times 100\%$$

Goodness of fit:

$$X^2 = \sum_{i}^{n} \frac{(Y_i^{obs} - Y_i^{calc})^2}{n - p} = \left(\frac{R_{wp}}{R_{exp}} \right)^2$$

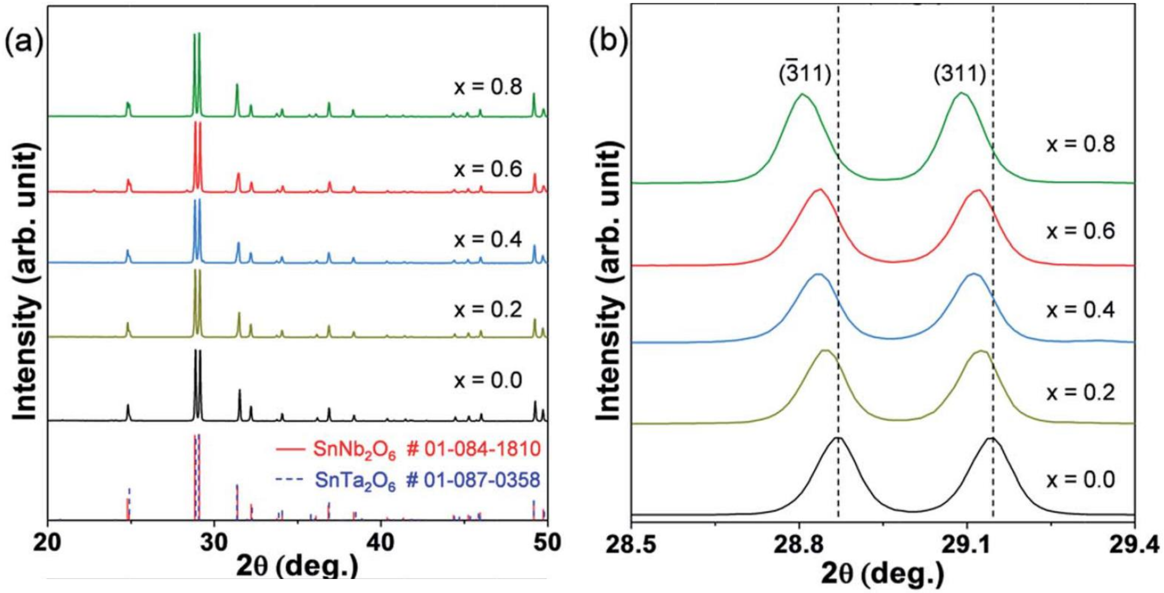
Normally, R_{WP} value less than 10 should be achieved

χ Value should be close to 1

https://www.researchgate.net/post/RIETVELD-REFINEMENT-Fullprof-What-causes-chi-square-to-be-smaller-than-one (22.09.16)

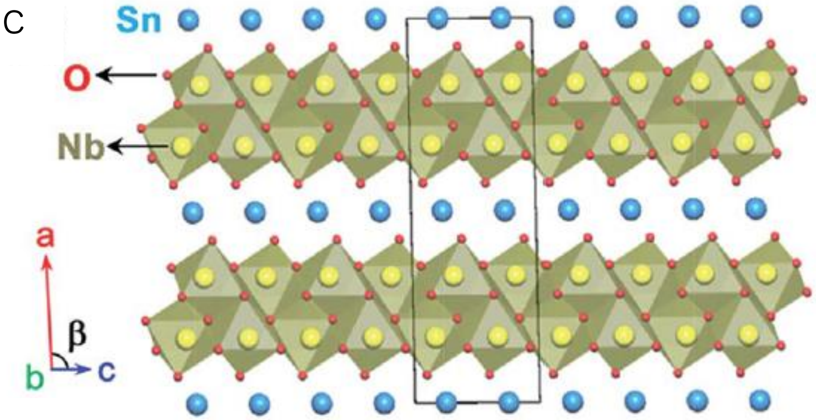
Rietveld refinement example

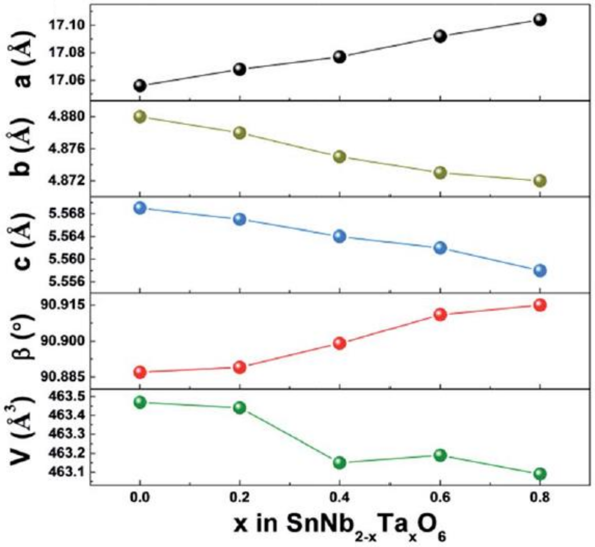
Solid-solution $SnNb_{2-x}Ta_xO_6$



Monoclinic

α 90
β 90.85
γ 90
a_0 17.093
b_0 4.877
c_0 5.558





https://doi.org/10.1039/C4TA05885B (22.09.16)

Rietveld refinement example

set

	Phase Name	SG	a (?	b (?	c (?	alpha(?	beta(?	gamma(?
1	Structure	C2/c	Refine	Refine	Refine		Refine	

Results

	Phase Name	SG	a (?	b (?	c (?	alpha(?	beta(?	gamma(?
1	Structure	C2/c	17.0683261	4.8783768	5.5674659		90.8891	

```
Number of independent parameters : 17
Number of hkls generated for C:₩Topas4-2₩sg₩c2oc.sg 68
 0  Time  1.84  Rwp  25.183   0.000 MC  0.00 0
 1  Time  1.88  Rwp  13.175 -12.009 MC  0.00 1
 2  Time  1.89  Rwp  12.399  -0.775 MC  0.00 1
 3  Time  1.91  Rwp  12.347  -0.052 MC  0.00 1
 4  Time  1.92  Rwp  12.343  -0.004 MC  0.00 1
 5  Time  1.94  Rwp  12.342  -0.000 MC  0.00 1
Refinement converged

*** Parameter(s) close to limit(s).
   Check for LIMIT_MIN and LIMIT_MAX in Grid/Text
```