Application of powder X-ray diffraction method for catalysts characterization

Marie Skłodowska-Curie Actions-Innovative Training Networks
H2020-MSCA-ITN-2018: BIKE 813748

Workshop: Preparation and Characterization of Catalysts for Hydrogen Production

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Why powder X-ray diffraction ?

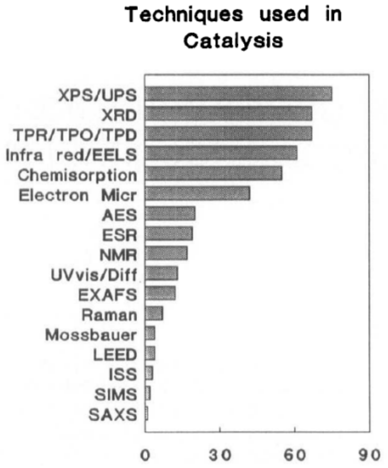
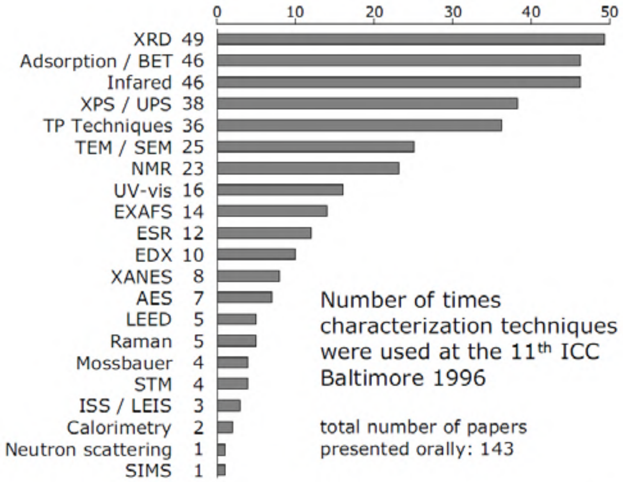

Techniques used in Catalysis

Fig. 10.1. Bar diagram showing how often certain techniques have been used in the papers at the Ninth International Congress on Catalysis [1].



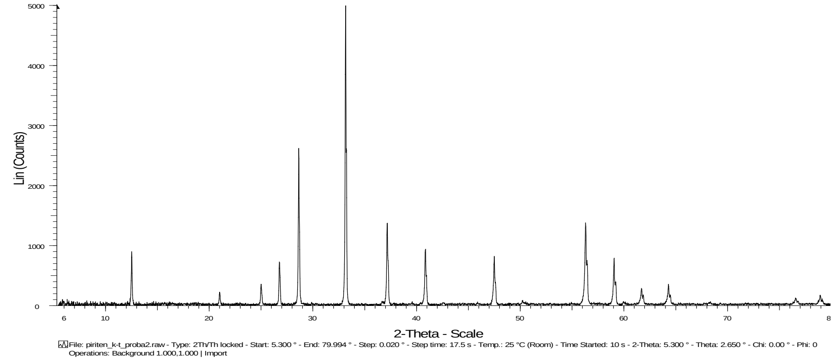
Number of times characterization techniques were used at the 11th ICC Baltimore 1996

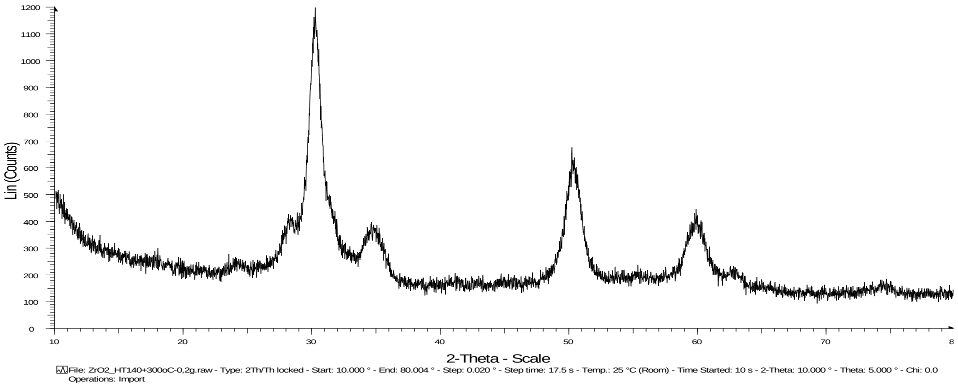
total number of papers presented orally: 143

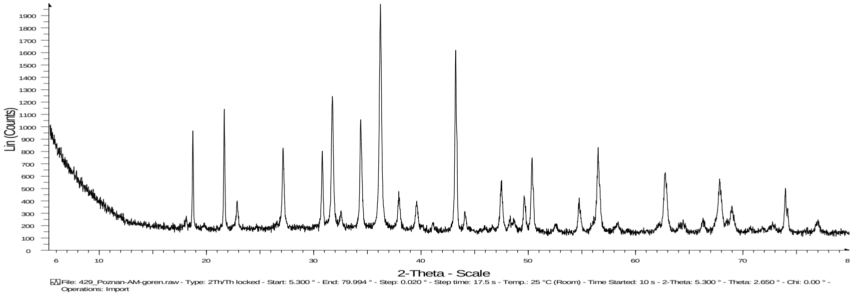
Figure 4.3. Number of studies in which the listed techniques were employed, out of a total of 143 papers presented orally at the 11th Baltimore, 1996 [Reproduced from J.W. Niemantsverdriet, *Spectroscopy in Catalysis, An Introduction* (2000), Wiley-VCH, Weinheim].

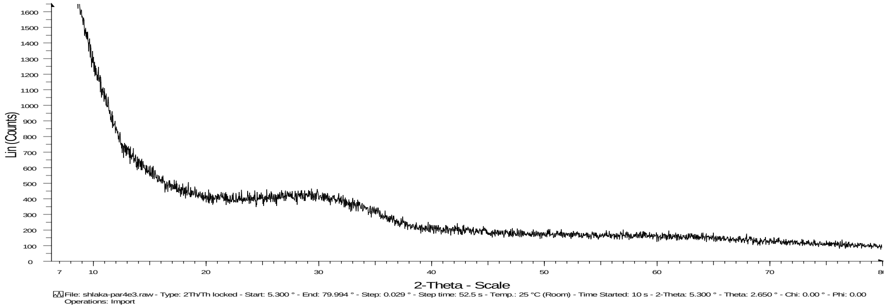
- Solids used for a catalytic reaction are in the form of powder
- Available (laboratory diffractometers)
- Strong interaction with the sample
- Small quantities
- Nondestructive

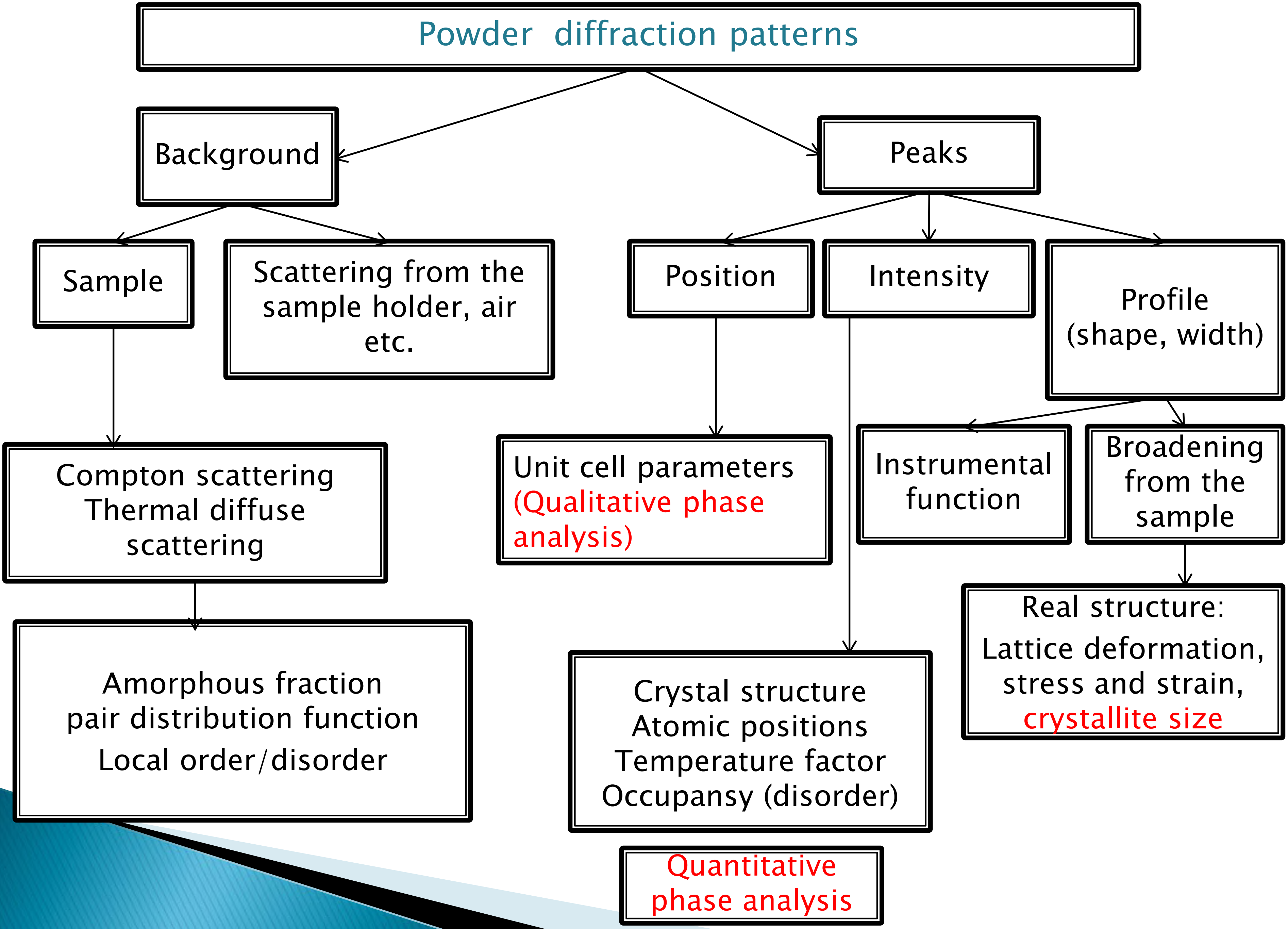
Powder diffraction patterns











Powder diffraction patterns

Background

Peaks

Sample

Scattering from the sample holder, air etc.

Position

Intensity

Profile (shape, width)

Compton scattering
Thermal diffuse scattering

Unit cell parameters (Qualitative phase analysis)

Instrumental function

Broadening from the sample

Amorphous fraction
pair distribution function
Local order/disorder

Crystal structure
Atomic positions
Temperature factor
Occupansy (disorder)

Real structure:
Lattice deformation, stress and strain, crystallite size

Quantitative phase analysis

Lecture plan:

•Crystal structure and lattice

•Lattice planes, Miller indices

•X-Rays

•Interaction of X-Rays with matter

•Bragg equation

•Powder diffraction pattern

-background

-peak positions - relation between d-spacings and unit cell parameters

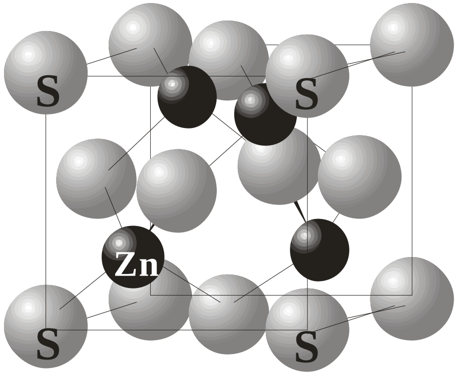
-peak intensities – relation between the structure factor and arrangement of the atoms in the unit cell

How to extract the information about the crystalline phases?

The possibility to obtain information about the crystal structure is based on the ability of X-rays with an appropriate wavelength to diffract from the crystalline material, the later can be regarded as a 3-dimentional diffraction grating for X-rays.

The **crystal structure** is a unique arrangement of atoms, ions or molecules in a crystalline solid or liquid. It describes a highly ordered structure, due to the intrinsic nature of its constituents to form symmetric patterns.

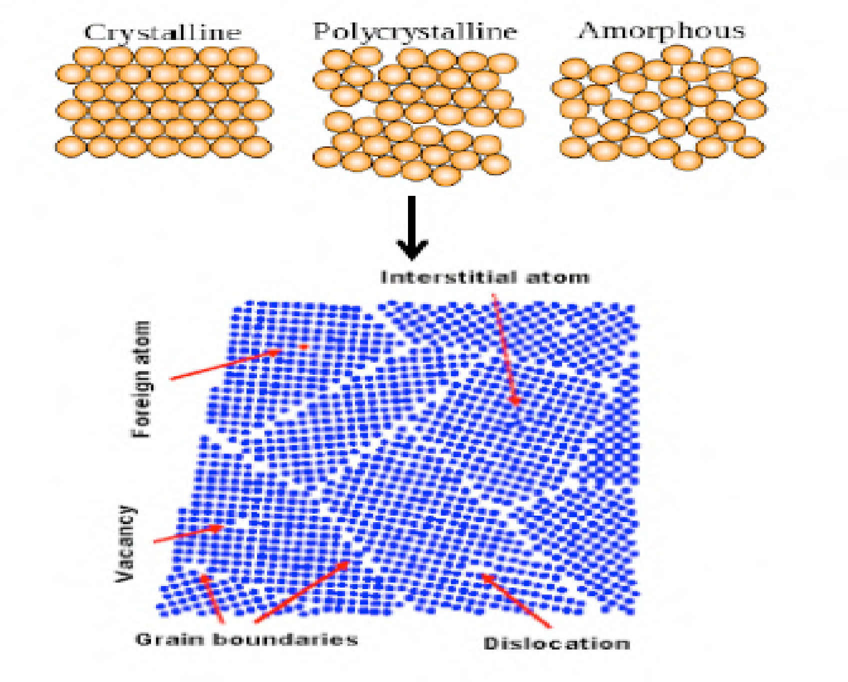
We know that a huge variety of structures exist in nature, each of them is formed as a result of many factors.

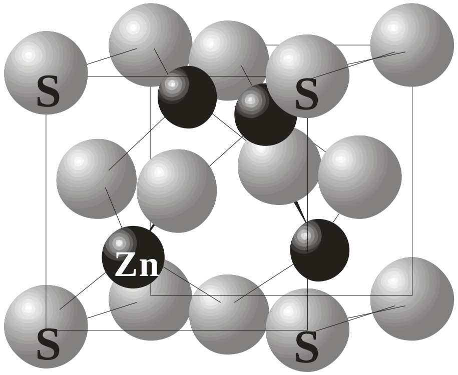


Various compounds crystallize sometimes in the same type of structure, or certain compound can have a number of structural modifications, depending on the external conditions.

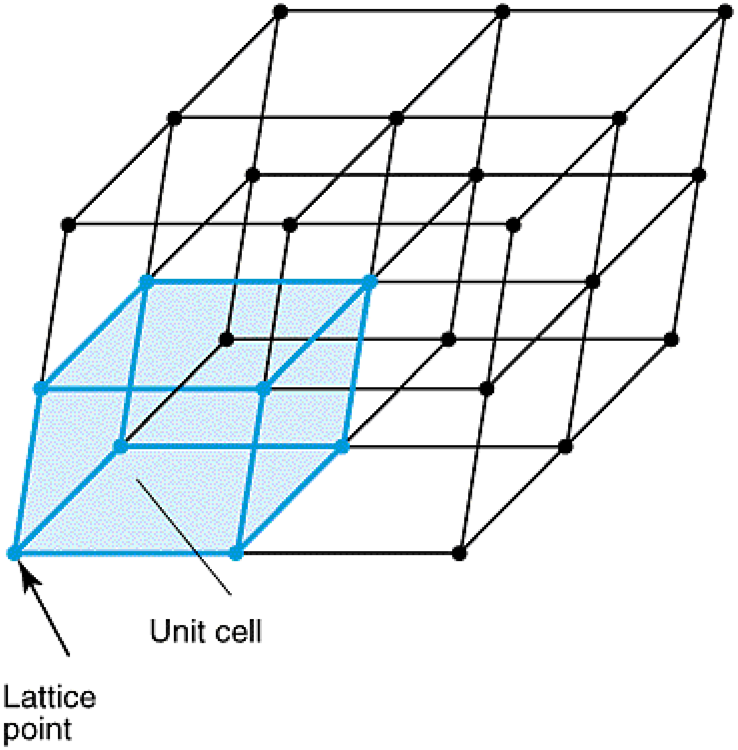
Various atoms and ions can be substituted in specific positions of a particular crystal structure and thereby alter the physical and chemical properties of crystalline materials.

Defects of the crystal structure of real crystals are also very important tool for modifying their properties.

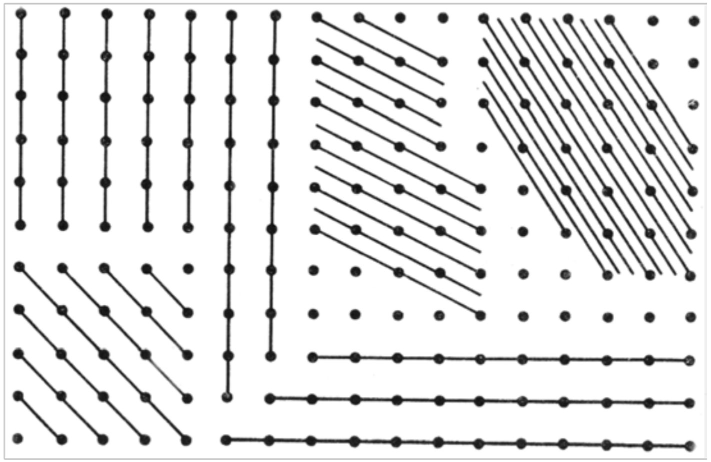




The crystal structure is a periodic arrangement of real material particles.



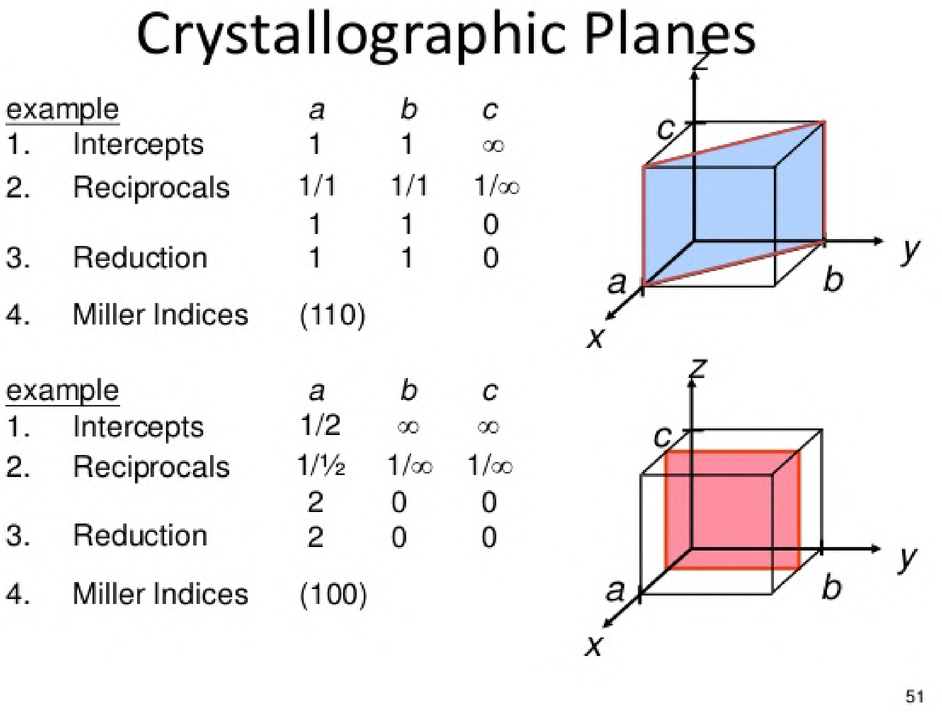
Crystal lattice is a way of presenting the periodic repetition in the space of different material particles or groups of particles and the gaps between them.



In each lattice system, there exist a big number of parallel planes with different interplanar distances. The values of these distances depend on the Miller indices of the planes, the type of the crystal system and the values of the unit cell parameters.

Some labels

(hkl) plane
[hkl] direction
<hkl> Family of symmetrically related directions
{hkl} Family of symmetrically connected planes

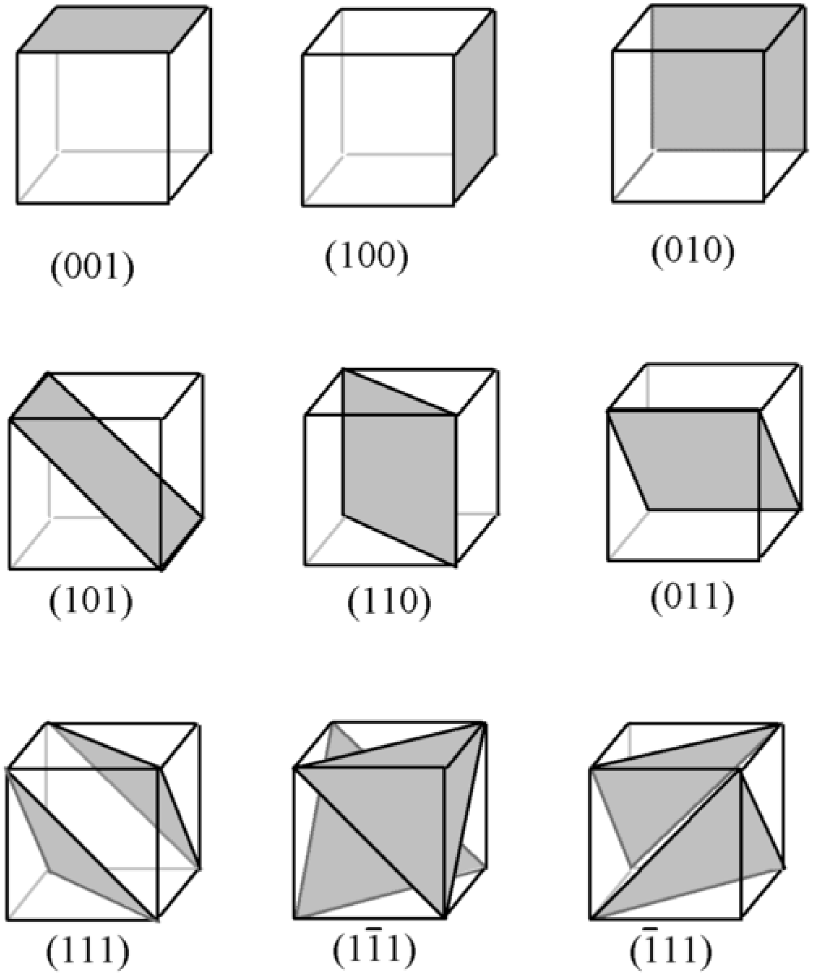


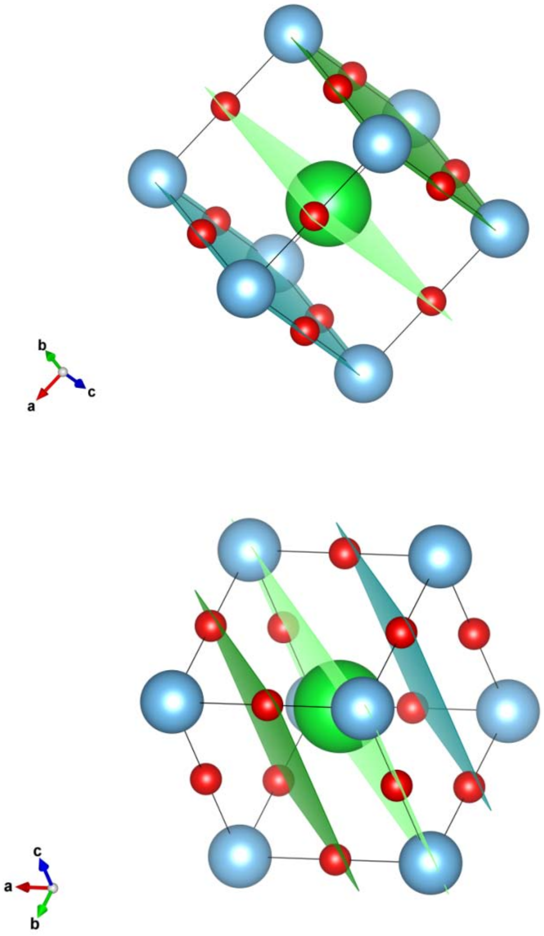
Crystallographic Planes

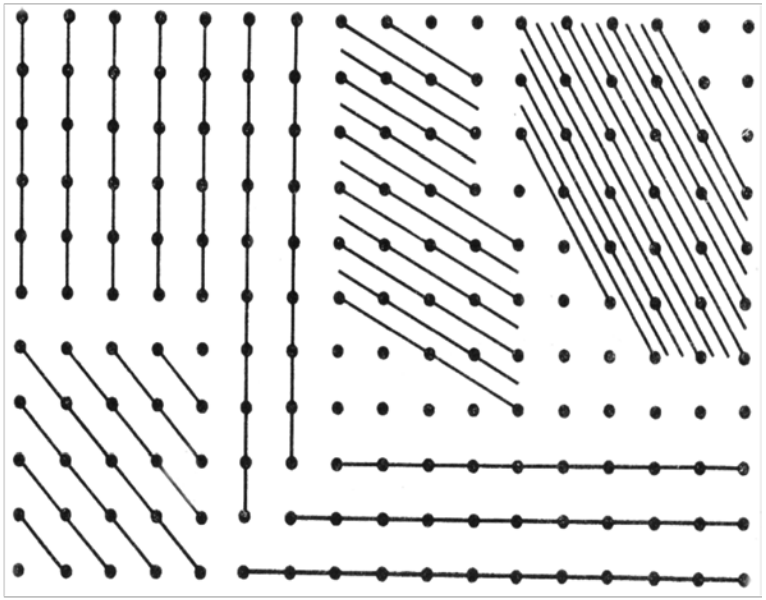
example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		

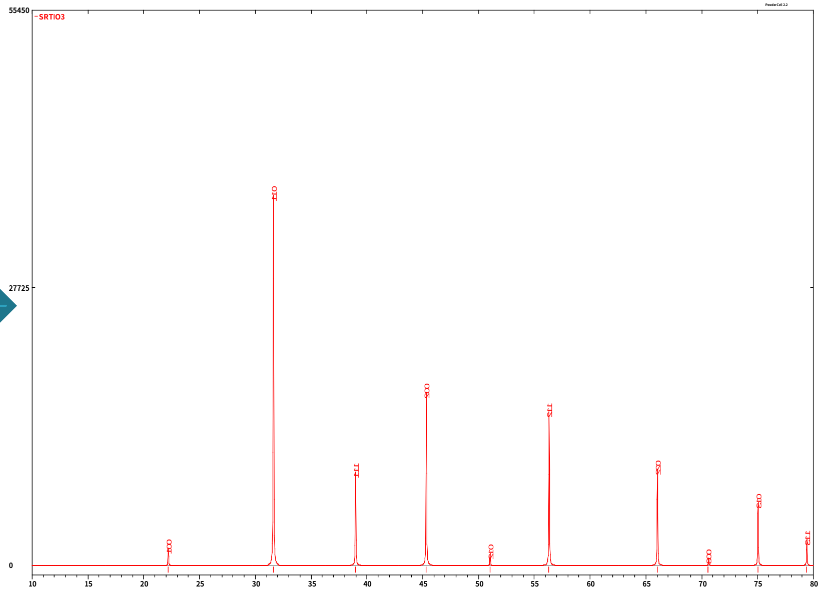
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		

51


(001)
(100)
(010)
(101)
(110)
(011)
(111)
$(1\bar{1}1)$
$(\bar{1}11)$


b
a
c
c
a
b



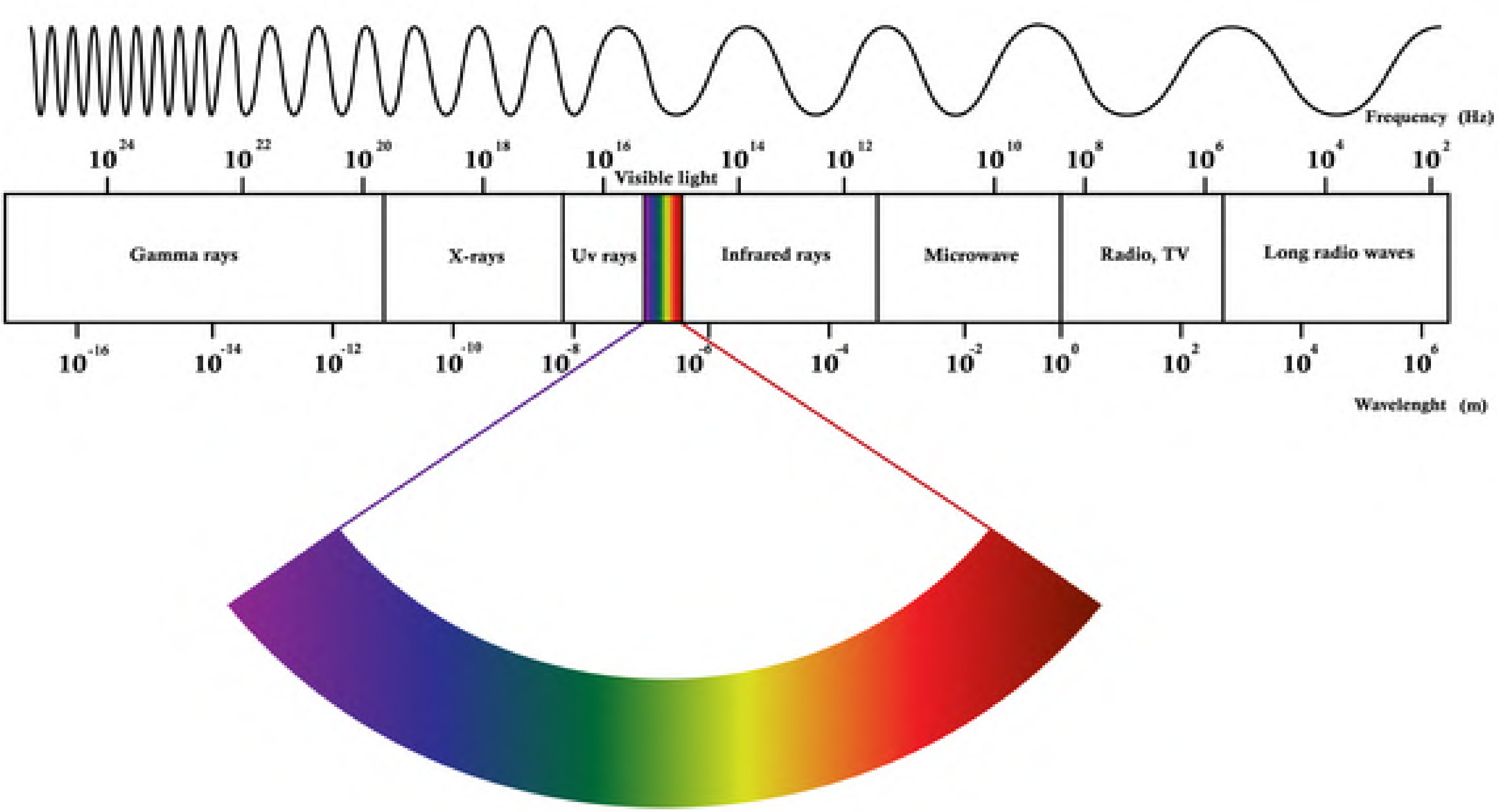

55450
27725
0
SRTIO3
PowderCell 2.2
001
011
111
002
012
112
022
003
013
113
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80

X-Rays were discovered in 1895 by Wilhelm Conrad Röntgen during the investigation of the effects of high tension electrical discharges in evacuated glass tubes.

Röntgen's original paper, "On A New Kind Of Rays" (Über eine neue Art von Strahlen), was published on 28 December 1895.

In 1901 he was awarded the very first Nobel Prize in Physics for this discovery.

Properties of X-Rays



X-rays are electromagnetic waves with a wavelength shorter than that of visible light.

Properties of X-Rays

X-rays are photons with:

- Charge = 0,
- Magnetic moment = 0
- Spin = 1

$E=h\nu$, $E=hc/\lambda$

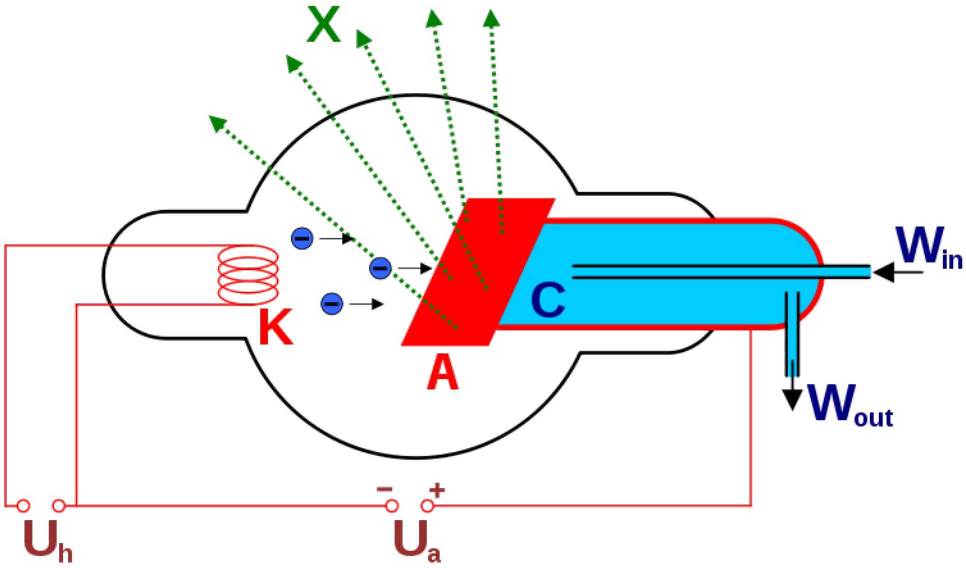
E (keV)	λ (Å)
0.8	15.0
8.0	1.5
40.0	0.3
100.0	0.125

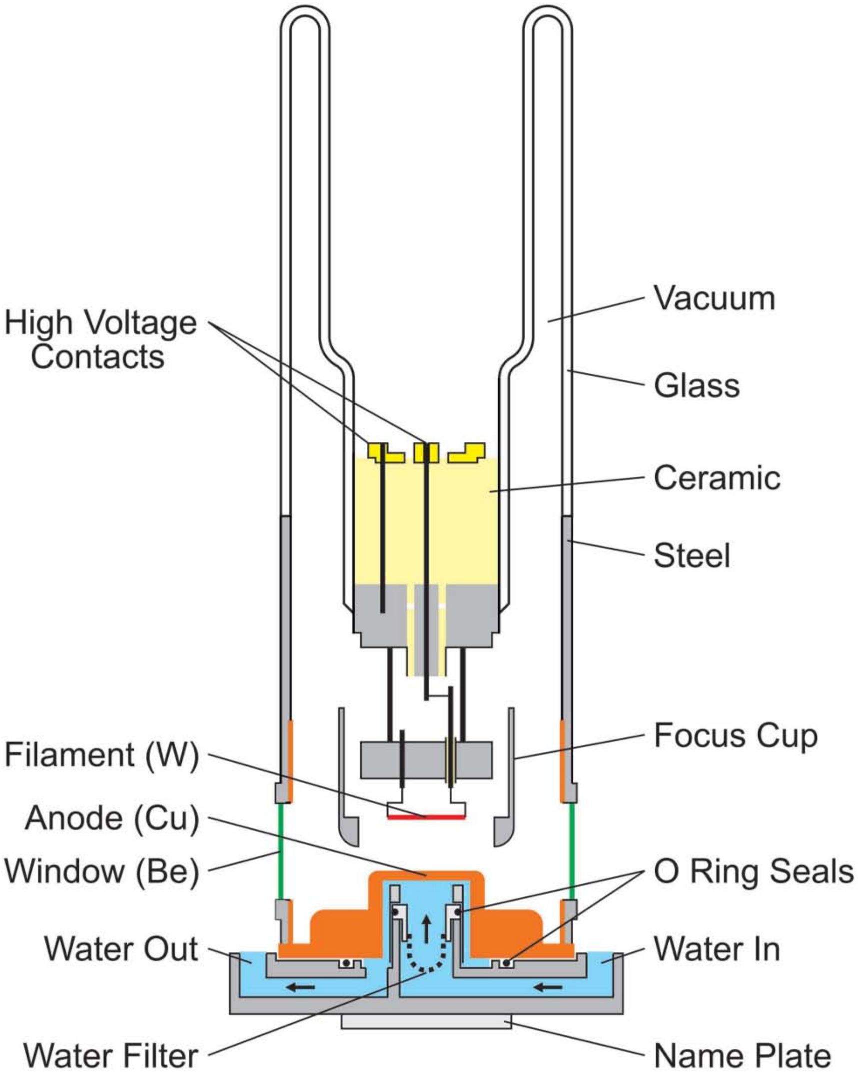
Production of X-Rays

X-rays are produced when high-speed electrons collide with a metal target.

Elements of laboratory X-Ray tube

- Cathode - a source of electrons – hot tungsten filament
- Accelerating voltage - between the cathode and the anode
- Anode -a metal target, Cu, Al, Mo, Mg.
- Anode cooling
- Vacuum
- Window
- Rays




High Voltage Contacts
Vacuum
Glass
Ceramic
Steel
Focus Cup
Filament (W)
Anode (Cu)
Window (Be)
O Ring Seals
Water Out
Water In
Water Filter
Name Plate

X-Ray spectrum

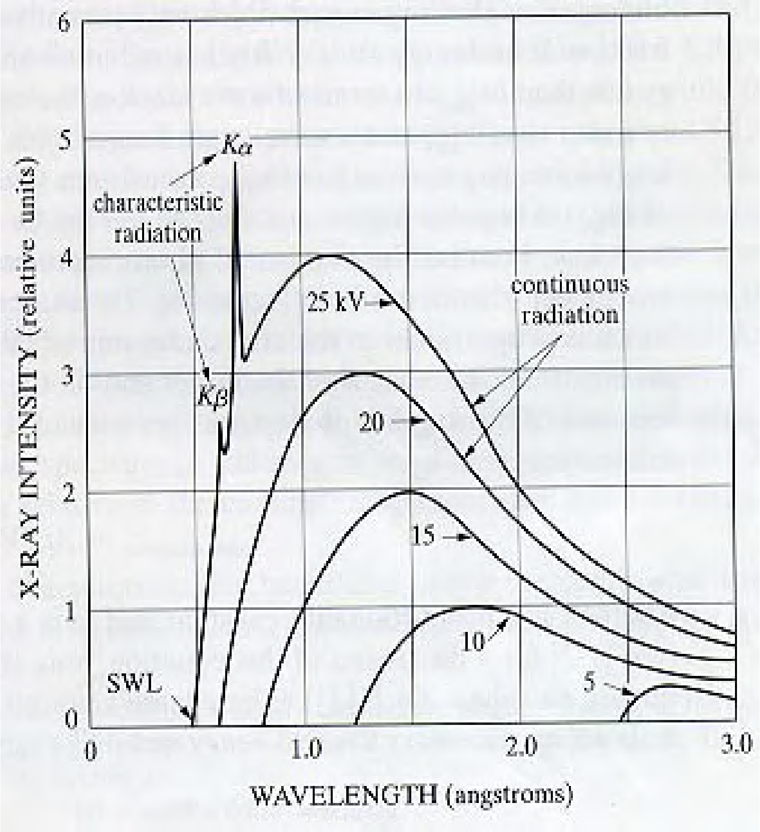
- Continuous X-Ray spectrum - due to braking radiation of electrons

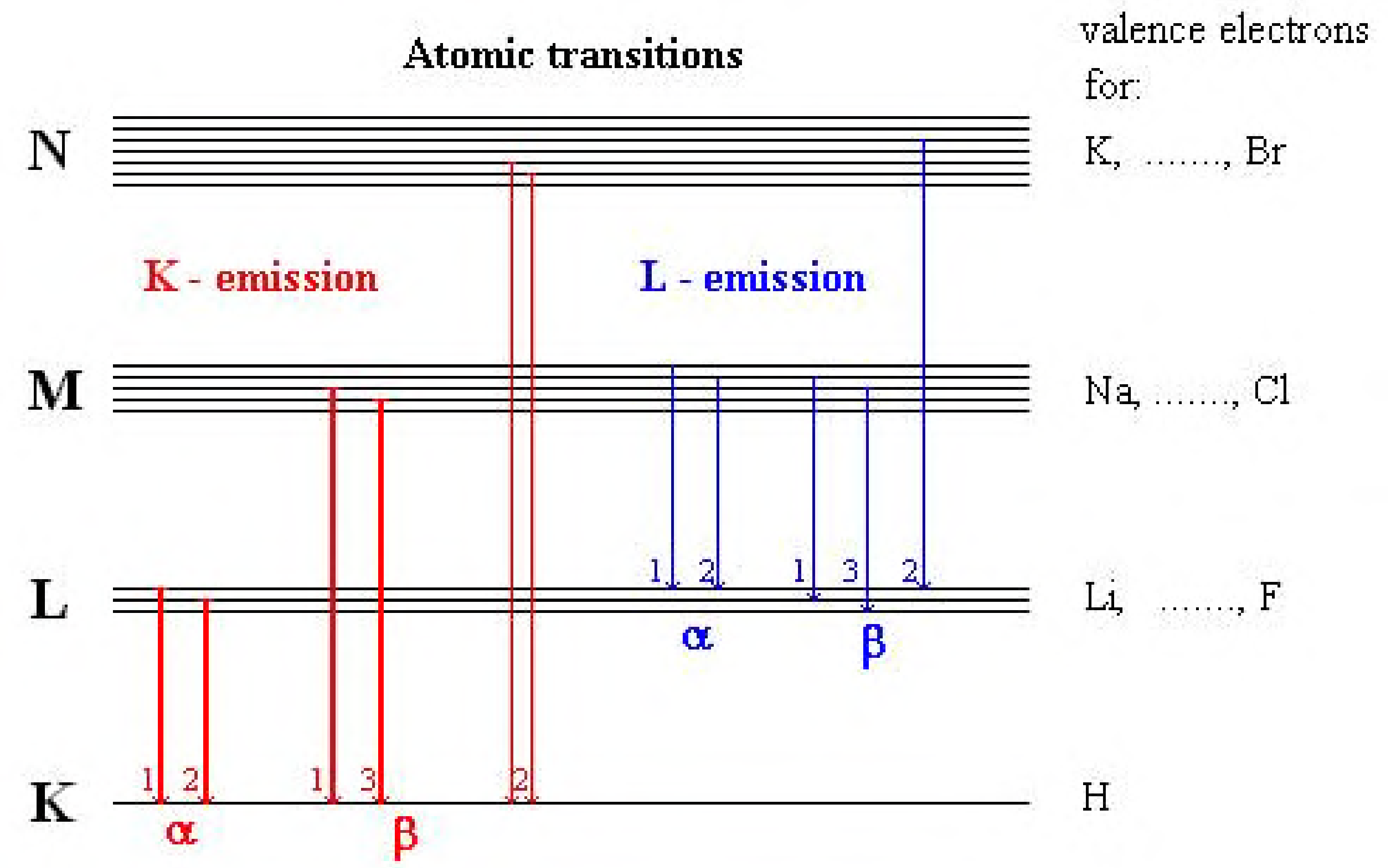
-short-wavelength limit

$\lambda_o = hc/eV$

(depends on the accelerating voltage) The intensity depends on the material of the anode as Z^2.

- Characteristic (discontinuos) X-Ray spectrum - characteristic radiation depends on the material of the anode.





K, L, M, etc. series of characteristic lines due to transitions of the atoms of the material of the anode from excited to the ground state.
Sharp,
Monochromatic

Interaction of X-Rays with matter

X-rays interact with matter through the electrons of atoms. When the electromagnetic radiation reaches an electron which is charged particle it becomes a secondary source of electromagnetic radiation that scatters the incident radiation.

Interaction of X-Rays with matter

According to the wavelength and phase relationships of the scattered radiation, we can refer to:

1. depending if the wavelength does not change or changes,

- ***elastic scattering -*** changing the trajectory of photons, but its energy is retained
- ***inelastic scattering -*** reduction in the energy of the scattered photon

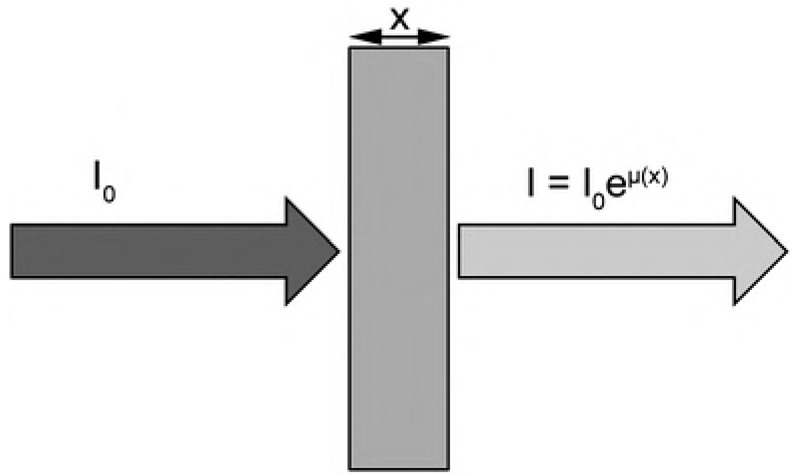
2. depending if the phase relations are maintained or not maintained over time and space

- ***coherent scattering***
- ***incoherent scattering***

refraction, *fluorescence*, *Compton scattering*, *Rayleigh scattering, absorption*, *polarization*, *diffraction*, *reflection, est.*

Interaction of X-Rays with matter

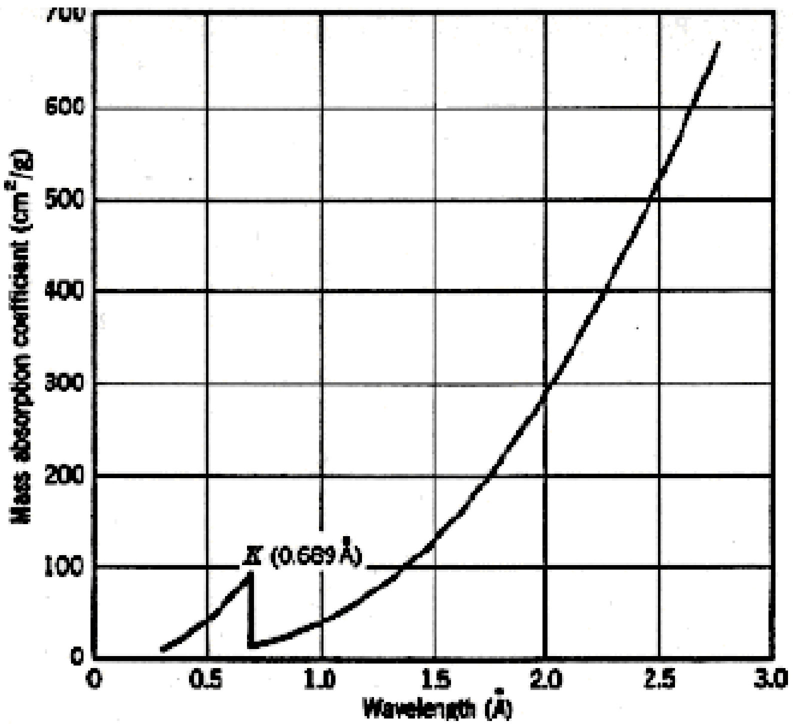
Absorption means an attenuation of the transmitted beam, which loses its energy through all types of interactions, mainly thermal dissipation, fluorescence, inelastic scattering.



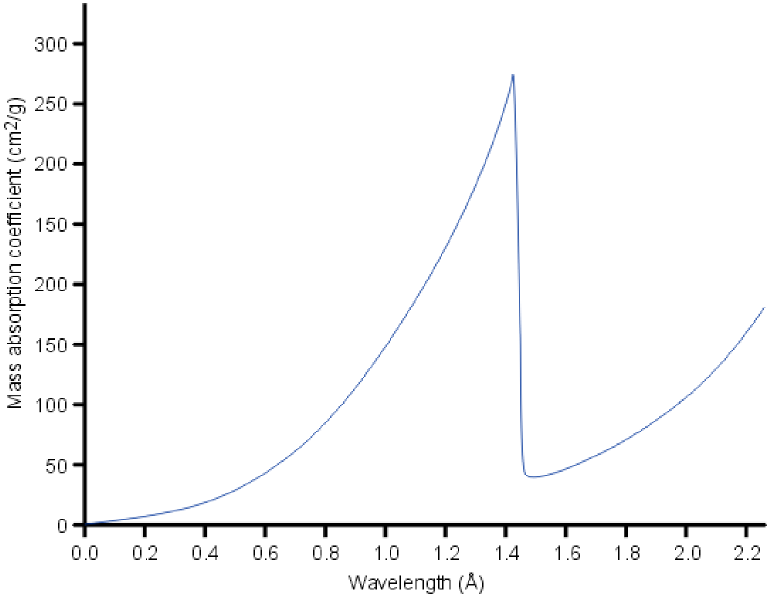
The intensity decrease follows an exponential model dependent on the distance crossed and on the linear absorption coefficient which depends on the density and composition of the material.

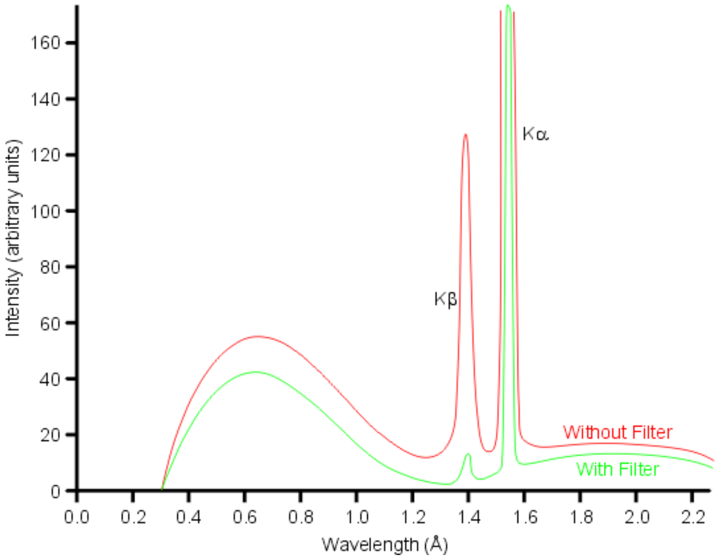
$$I=I_0 exp(-\mu t)$$

The mass absorption coefficient μ/ρ does not depend on the physical and chemical state of the material and as a rule increases with wavelength, with the exception of so-called absorption edge.



http://pd.chem.ucl.ac.uk/pdnn/inst1/filters.htm





The edges occur at wavelengths where the energy of an absorbed photon corresponds to an electronic transition or ionization potential. In this case μ/ρ increases dramatically in the edge region.

This effect is used for partial monohromatisation (removal of Kβ lines of the spectrum).

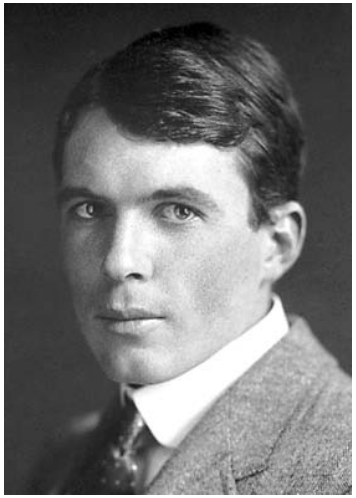
Kβ-filters are made of metals whose atomic number Z is one less than that of the metal used as anode target in the X-ray tube.

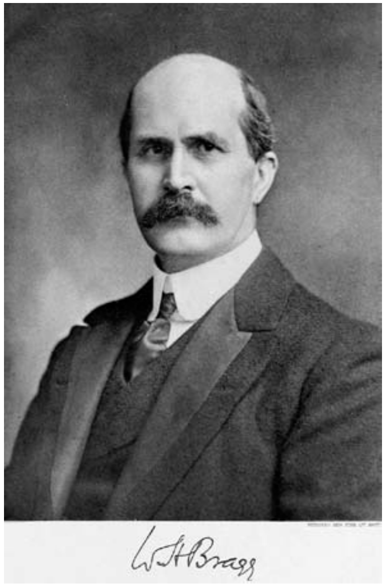
Anode	Cu	Co	Fe	Cr	Mo
Filter	Ni	Fe	Mn	V	Zr

Year 1912

The theory of diffraction of X-rays by crystal lattice summarizes the results for the three-dimensional case of well developed in optics and acoustics theory of diffraction grating.

Nobel Prize in Physics in 1915: *"For their services in the analysis of crystal structure by means of X-rays"* an important step in the development of X-Ray crystallography.





Sir William Lawrence Bragg and Sir William Henry Bragg

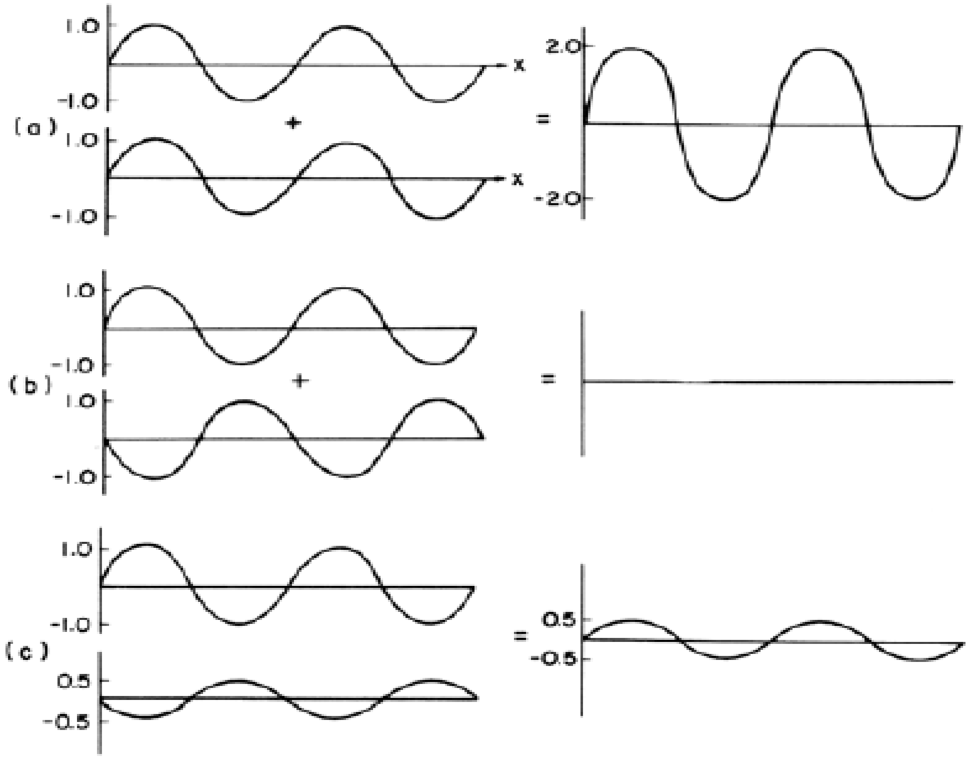
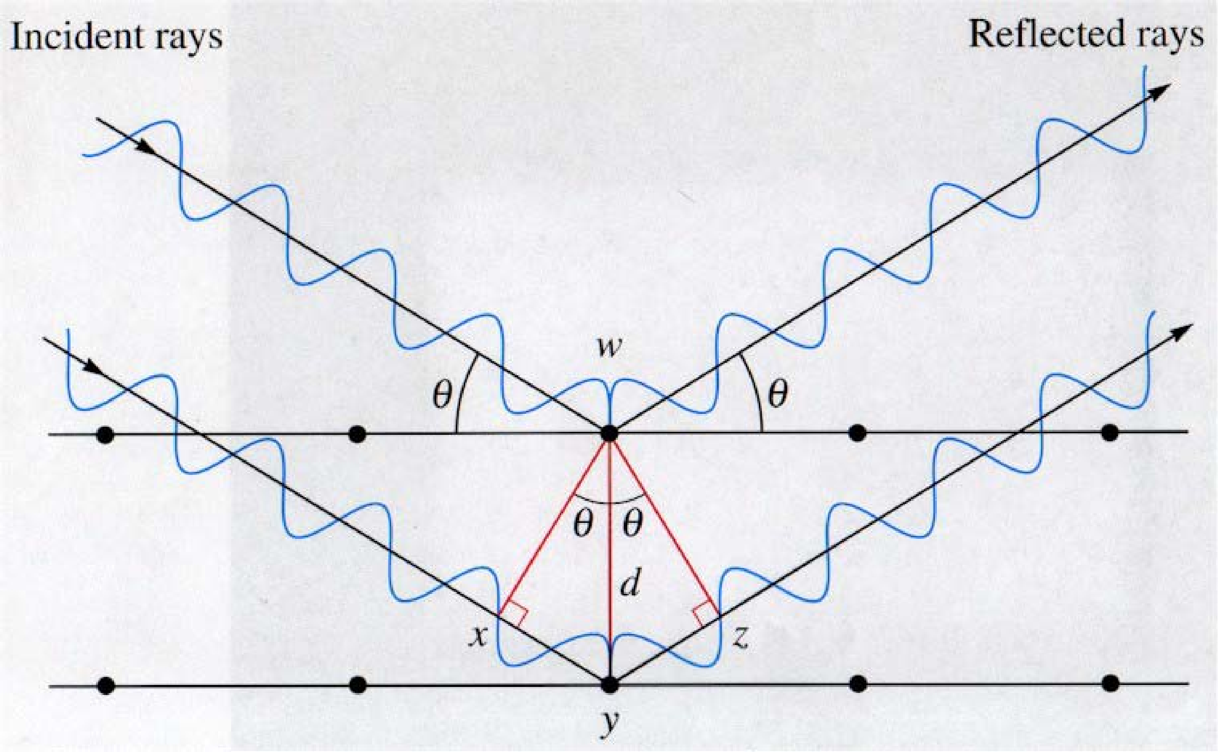


FIG. 3-2. Interference between two waves. Both waves are assumed to have the same maximum amplitude (unity) except in (c) and the same wavelength in all cases. (a) Constructive interference; (b) complete destructive interference; (c) partial destructive interference.

Bragg considered monochromatic X-ray beam incident on the crystal, in which scattering centers are arranged in a system of parallel planes at a distance d from one another, which act as mirrors reflecting X-rays. The condition for amplification the reflected waves from two such planes is Bragg equation.



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

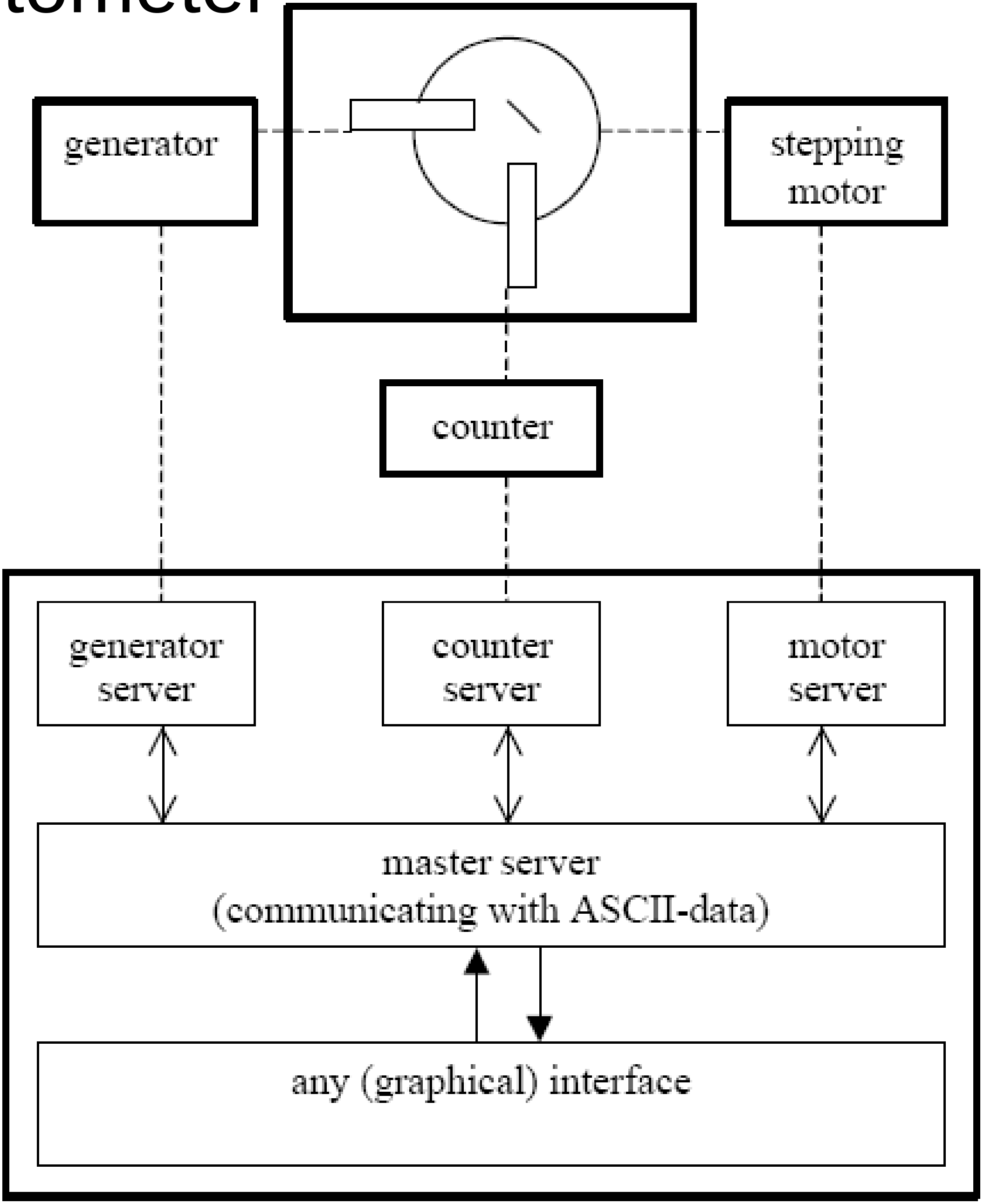
Powder X-Ray diffractometer

Generator of high
Voltage
Current stabilizer

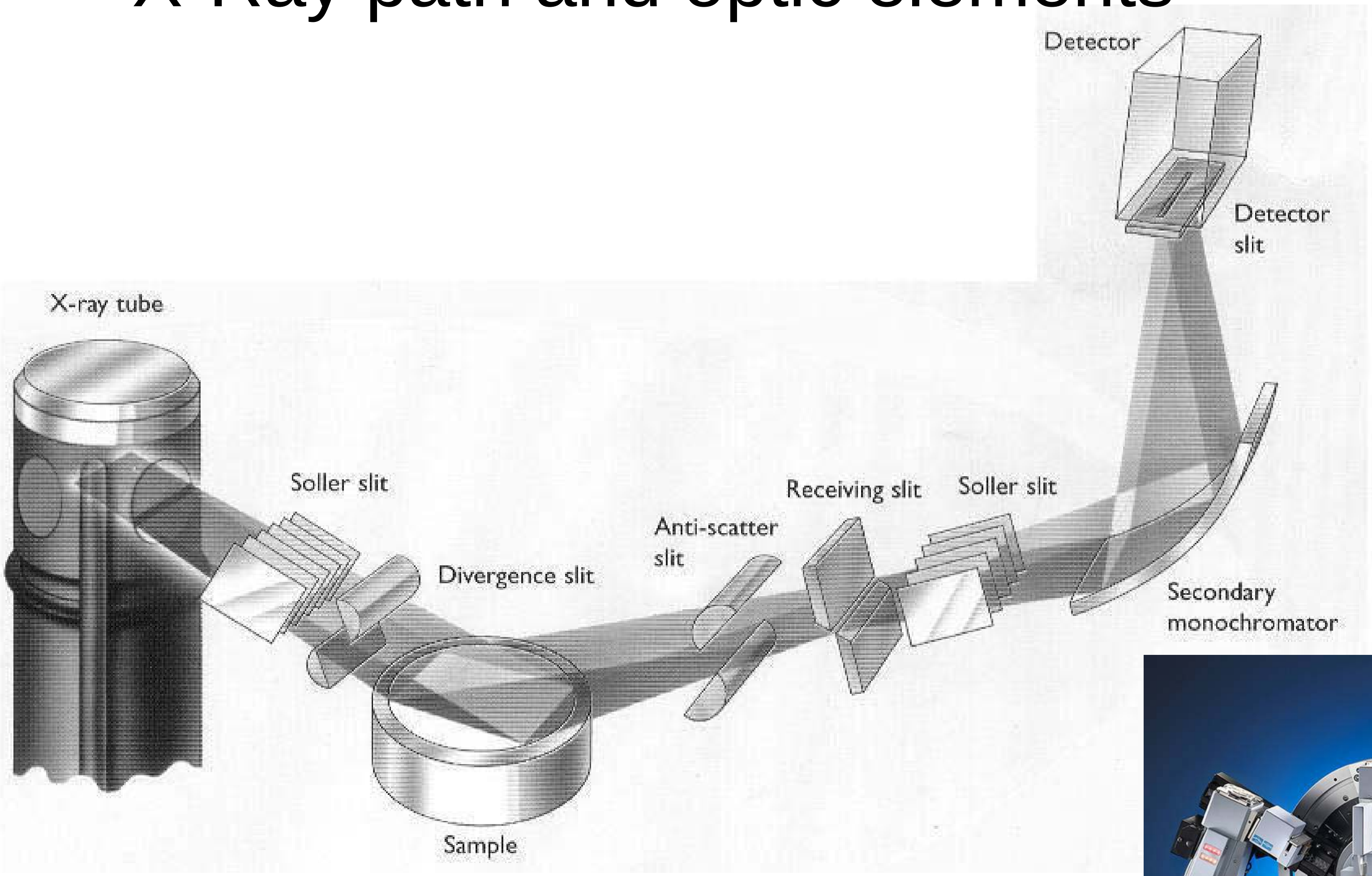
Goniometer
(Tube - Sample - Counter)

Enhancement and
matching signals schemes

Registration (file).



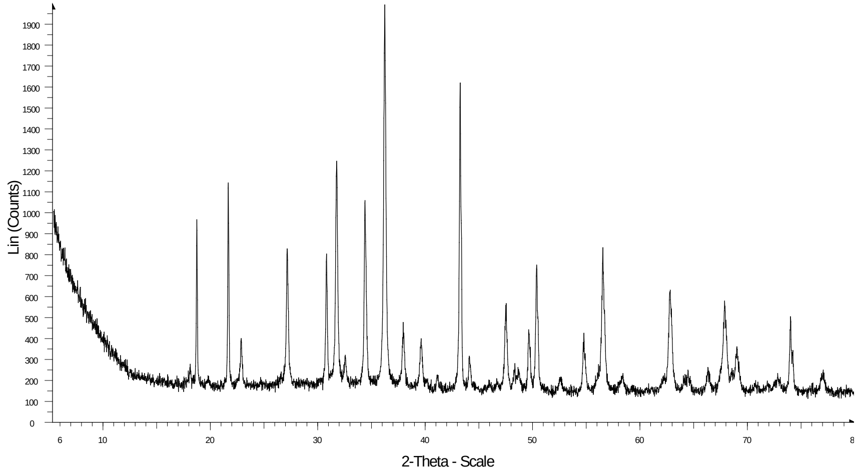
X-Ray path and optic elements



Powder diffraction pattern

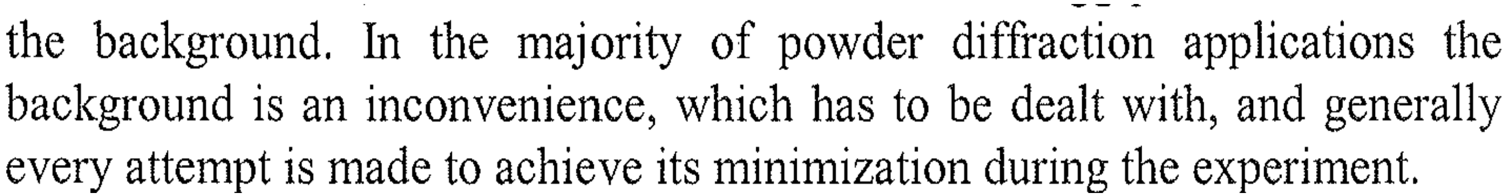
The powder diffraction pattern represents the intensity distribution of the diffracted radiation depending on the angle of diffraction.

- Background
- Peaks - Position (2θ)
- Peaks - Intensity



File: 429_Poznan-AM-goren.raw - Type: 2Th/Th locked - Start: 5.300 ° - End: 79.994 ° - Step: 0.020 ° - Step time: 17.5 s - Temp.: 25 °C (Room) - Time Started: 10 s - 2-Theta: 5.300 ° - Theta: 2.650 ° - Chi: 0.00 ° - Operations: Import

Background and diffuse scattering


the background. In the majority of powder diffraction applications the background is an inconvenience, which has to be dealt with, and generally every attempt is made to achieve its minimization during the experiment.

From V.K. Pecharsky and P.Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, (Springer, NY, 2008)

The diffuse background intensity in a diffraction pattern comes from many sources, both inside and outside the crystal, including:

•Static crystal disorder - Crystals are often idealized as being *perfectly* periodic. In that ideal case, the atoms are positioned on a perfect lattice, the electron density is perfectly periodic. In reality, however, crystals are not perfect - there may be disorder of various types – the presence of amorphous component, the presence of 1, 2 and 3-d defects, occupational and positional disorder, heterogeneity in the conformation of crystallized molecules e.t.c.

•Therefore, the Bragg peaks have a finite width and there may be significant *diffuse scattering*, a continuum of scattered X-rays that fall between the Bragg peaks.

•Thermal disorder - The thermal vibration of atoms has another effect on diffraction patterns. Besides decreasing the intensity of diffraction lines, it causes some general coherent scattering in all directions. This is called thermal diffuse scattering; it contributes only to the general background of the pattern and its intensity gradually increases with 2θ.

•Inelastic scattering (Compton, fluorescent)

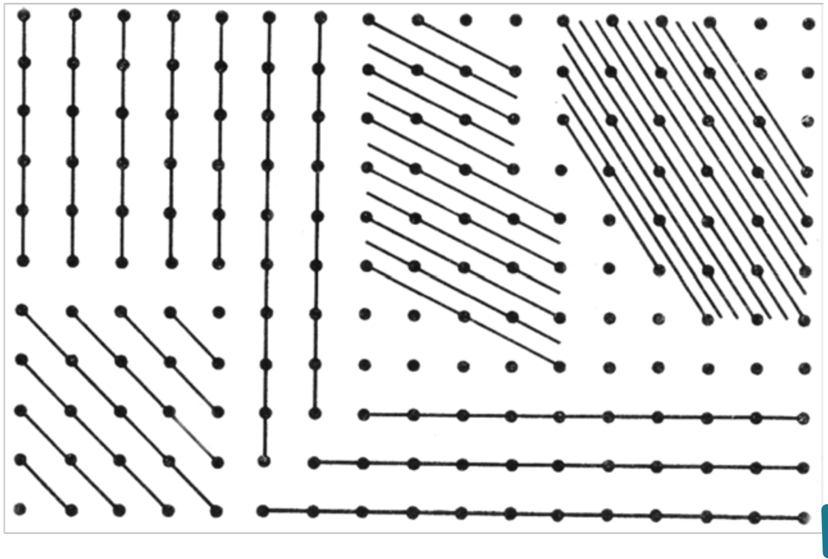
•The sample environment – sample holder. Air along the beam path between source and detector.

Peaks

Particularly important is the information in the diffraction pattern of the crystalline structure of the phases, which comprises:

- the type and dimensions of the unit cell,
- the type and position of atoms within the unit cell,
- occupancy of each position and the nature of the thermal motions of atoms.

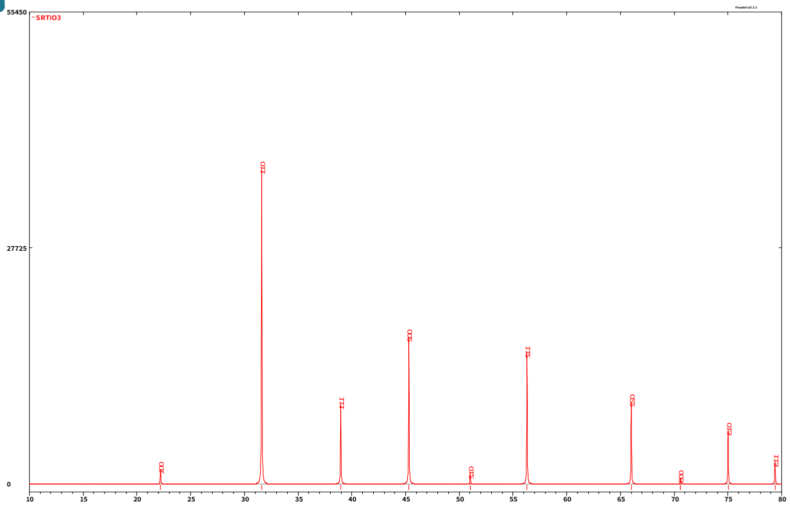
Peaks

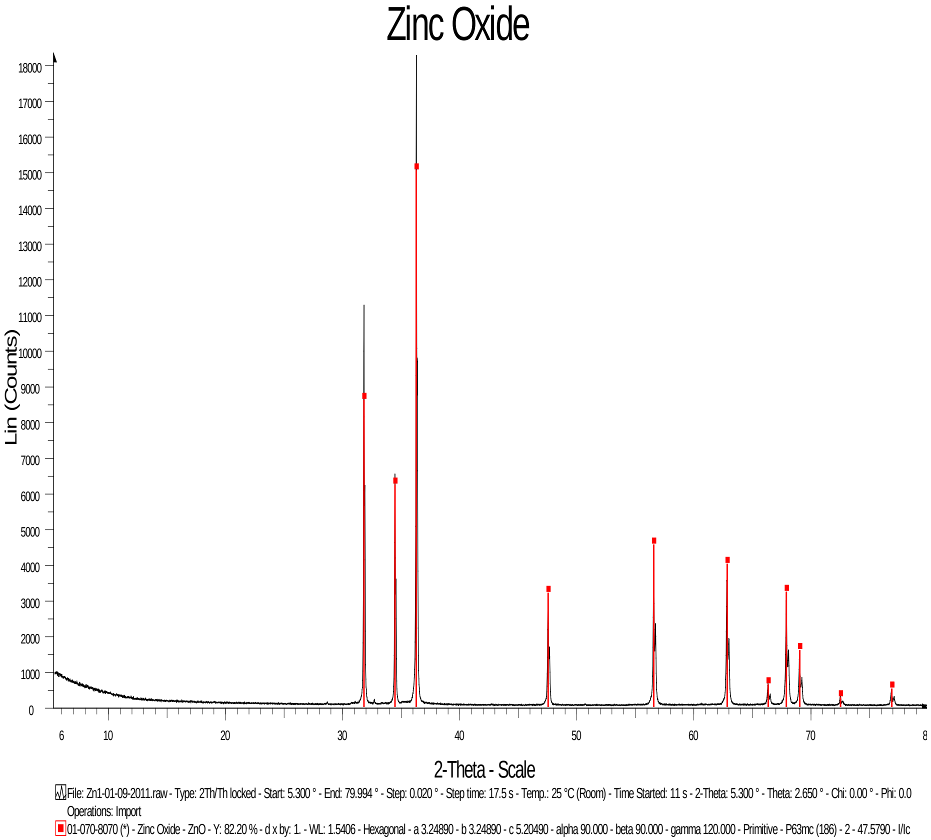


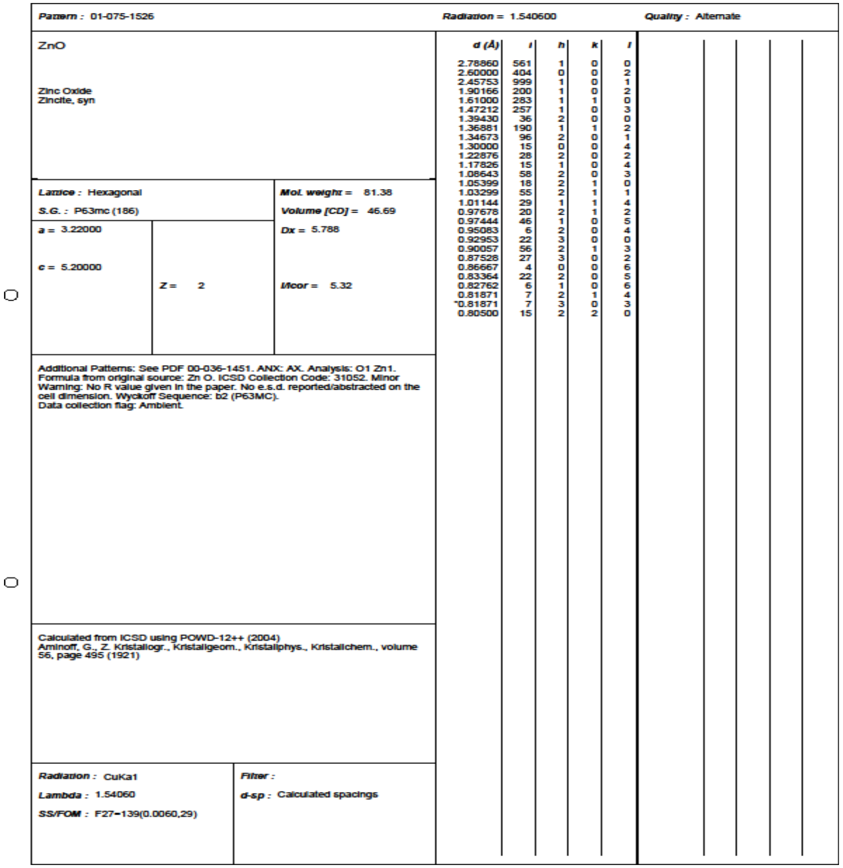
$$d_{hkl}=n\lambda/2\sin\theta$$

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

After producing a diffraction pattern from a crystal from the positions of the peaks of the pattern (theta) we can calculate interplanar distances and the corresponding parameters of the unit cell of the crystal under study.







Pattern : 01-075-1526 ***Radiation =*** 1.540600 ***Quality :*** Alternate

ZnO

Zinc Oxide
Zincite, syn

Lattice : Hexagonal
S.G. : P63mc (186)
a = 3.22000
c = 5.20000
Z = 2
Mol. weight = 81.38
Volume [CD] = 46.69
Dx = 5.788
I/Icor = 5.32

Additional Patterns: See PDF 00-036-1451. ANX: AX. Analysis: O1 Zn1. Formula from original source: Zn O. ICSD Collection Code: 31052. Minor Warning: No R value given in the paper. No e.s.d. reported/abstracted on the cell dimension. Wyckoff Sequence: b2 (P63MC).
Data collection flag: Ambient.

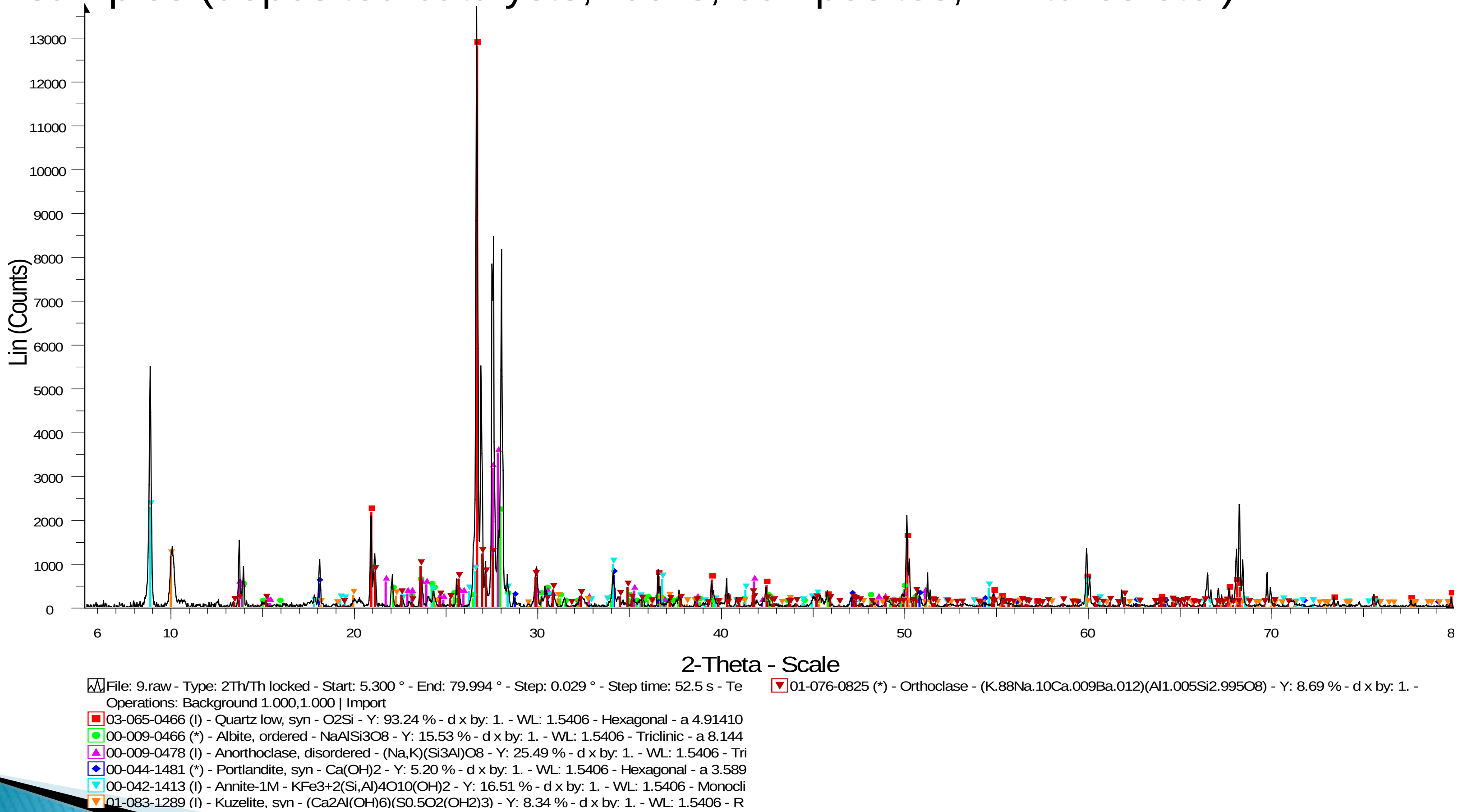
Calculated from ICSD using POWD-12++ (2004)
Aminoff, G., Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., volume 56, page 495 (1921)

Radiation : CuKa1
Lambda : 1.54060
SS/FOM : F27=139(0.0060,29)
Filter :
d-sp : Calculated spacings

d (Å)	*I*	*h*	*k*	*l*
2.78860	561	1	0	0
2.60000	404	0	0	2
2.45753	999	1	0	1
1.90166	200	1	0	2
1.61000	283	1	1	0
1.47212	257	1	0	3
1.39430	36	2	0	0
1.36881	190	1	1	2
1.34673	96	2	0	1
1.30000	15	0	0	4
1.22876	28	2	0	2
1.17826	15	1	0	4
1.08643	58	2	0	3
1.05399	18	2	1	0
1.03299	55	2	1	1
1.01144	29	1	1	4
0.97678	20	2	1	2
0.97444	46	1	0	5
0.95083	6	2	0	4
0.92953	22	3	0	0
0.90057	56	2	1	3
0.87528	27	3	0	2
0.86667	4	0	0	6
0.83364	22	2	0	5
0.82762	6	1	0	6
0.81871	7	2	1	4
*0.81871	7	3	0	3
0.80500	15	2	2	0

- Powder diffraction pattern of a given phase is **unique** and plays the role of a "fingerprint", allowing its identification.
- For phase identification programs that compare the experimental pattern with standard diffraction patterns of known phases collected by ICDD (International Center for Diffraction Data) are used.

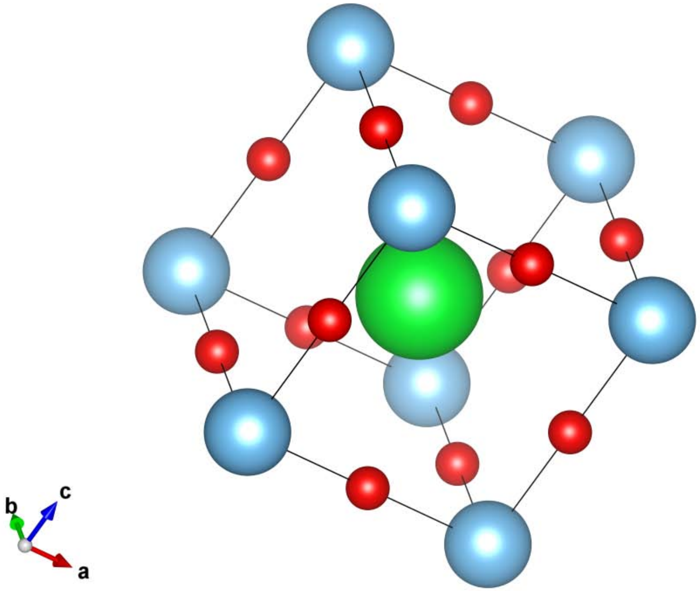
- Powder diffraction pattern of a mixture of phases is a **superposition** of the individual diffraction patterns of the phases presented in the mixture. That is why phase identification can also be done on multiphase samples (deposited catalysts, rocks, composites, mixtures etc.).



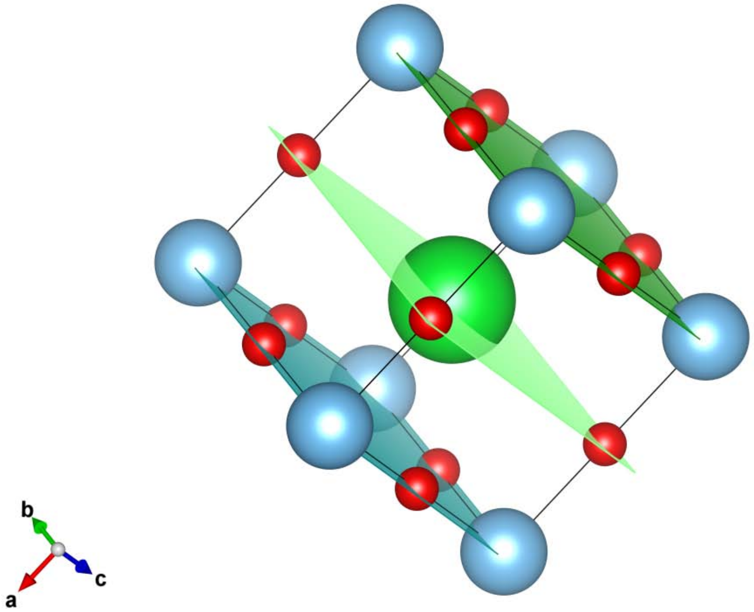
Powder diffraction pattern

Particularly important is the information in the diffraction pattern of the crystalline structure of the phases, which comprises:

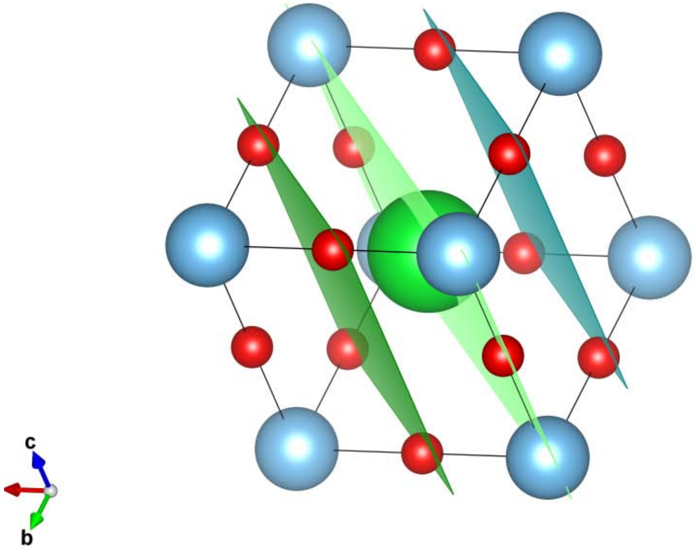
•the type and dimensions of the unit cell,
→ •the type and position of atoms within the unit cell,
•occupancy of each position and the nature of the thermal motions of atoms.



(h00)



(hh0)

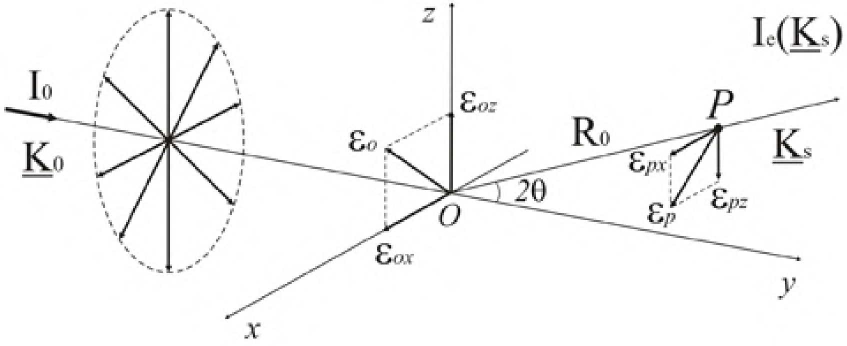


X-Rays scattering from electron – Thompson scattering formula

$$I_p(2\theta) = I_0 \frac{e^4}{m^2 c^4 R^2}\left(\frac{1+\cos^2 2\theta}{2}\right)$$

Where: R is the distance to the observation point,
2θ is the angle between the incident direction and the direction where the scattering is observed,
e and m are the charge and mass of the electron,
c is the speed of propagation of radiation in the vacuum.

The formula provides the intensity of scattered electromagnetic radiation as a function of the scattering angle θ.
The intensity is proportional to $1 + \cos^2 2\theta$.
Ip (max) at θ = 0 and 90 degrees
Ip (min) at θ = 45 degrees



Atomic scattering factor (form factor)

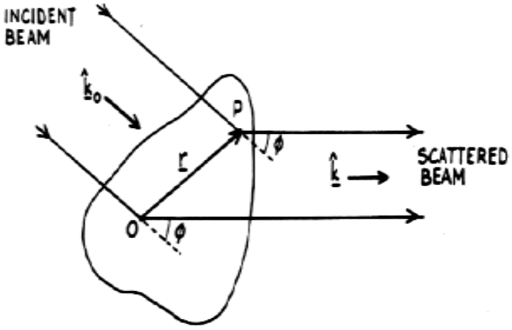
The atom represents a positively charged nucleus of very small size and electron shell.

The electrons form a complex system as a result of interactions with each other.

We may consider the atom as a *spherically symmetric* with a function of the density distribution of the negative charge ρ(r), ρ(r) - electron density at a distance r from the center of the atom.

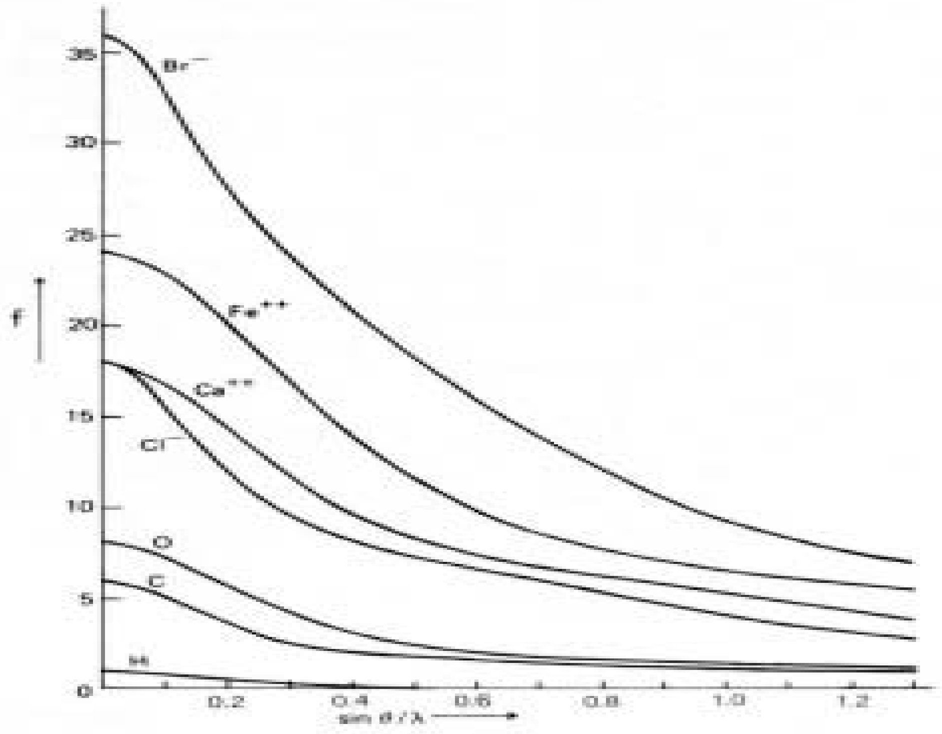
The atomic scattering factor is the ratio between the amplitude of the scattered radiation from the atom and that of one electron under the same conditions. It has the following form:

$$f = \frac{4\pi}{e}\int_0^\infty r^2 \rho(r) \frac{\sin kr}{kr}\, dr$$



Where $k = 2 \sin\theta/\lambda$ is the length of the scattering vector

K=Ks-Ko

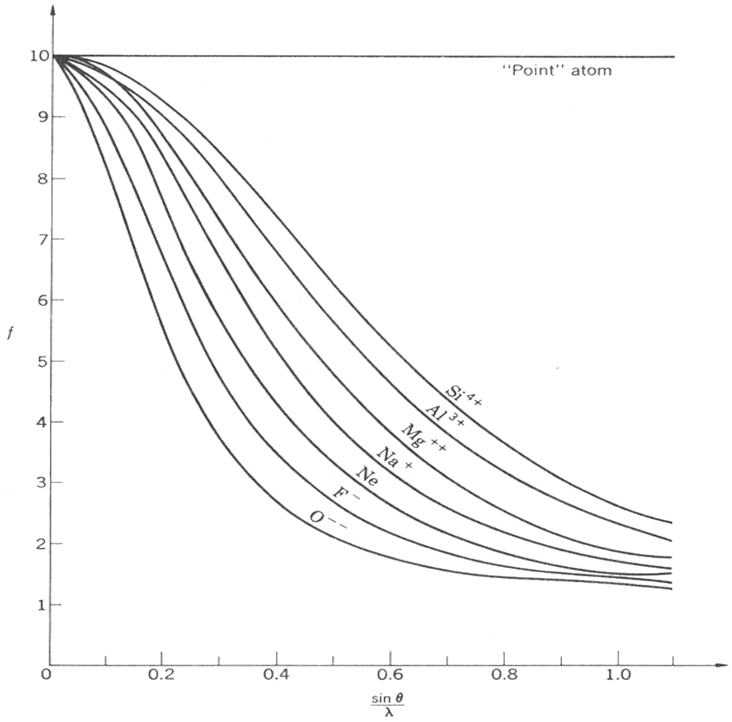


The atomic scattering factor depends on the number of electrons in the atoms or ions, on the diffraction angle and of the wavelength of X-ray radiation.

At a scattering angle θ=0, the scattering factor of the atom is equal to the number of electrons on the atom.

The X-ray scattering factor is the Fourier transform of the electron density distribution the atom.

The atomic scattering factor decreases with the increase in the angle of diffraction, as a result the peaks in the high angle part of diffraction pattern are usually with low intensity.



X-rays are not very sensitive to light atoms (hydrogen, lithium). There is very little contrast between elements adjacent to each other in the periodic table.

The refinement of the positions of such atoms in the crystal structure may be a significant problem.

Structure factor

As the atom may be regarded as a spatial distribution of charges, the unit cell can be regarded as a region with inhomogeneous distributed electron density ρ(r), which is significantly different from zero at the places where the atoms are and close to the zero elsewhere in the unit cell.

Structure amplitude is the ratio of amplitudes of the diffracted radiation from unit cell to this distracted by an electron under the same conditions.

Structure factor

The structure factor is a mathematical function describing the amplitude and phase of a wave diffracted from crystal lattice planes characterised by Miller indices *h*,*k*,*l*.

$$\mathbf{F}_{hkl} = \mathrm{F}_{hkl}\,\mathrm{exp}(i\alpha_{hkl}) = \sum f_j \mathrm{exp}[2\pi i(\mathrm{h}x_j + \mathrm{k}y_j + \mathrm{l}z_j)]$$

$$= \sum f_j \cos[2\pi i(\mathrm{h}x_j + \mathrm{k}y_j + \mathrm{l}z_j)] + i\sum f_j \sin[2\pi i(\mathrm{h}x_j + \mathrm{k}y_j + \mathrm{l}z_j)]$$

$$= \mathrm{A}_{hkl} + i\mathrm{B}_{hkl}$$

where the sum is over all atoms in the unit cell, x_j,y_j,z_j are the positional coordinates of the *j*-th atom, f_j is the scattering factor of the *j*-th atom, and α_{hkl} is the phase of the diffracted beam.

The intensity of the diffracted beam is directly related to the amplitude of the structure factor, but the phase must normally be deduced by indirect means.

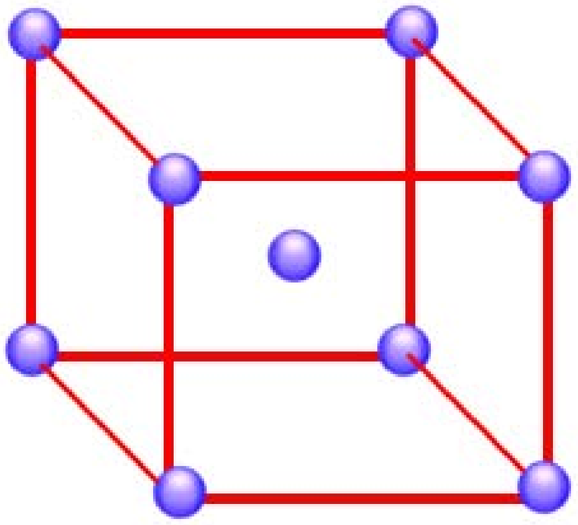
$$\mathrm{I}_{hkl} \approx |\mathrm{F}_{hkl}|^2$$

Some important notes from the general form of the formula for the structure factor. Friedel law.

$$F(hkl) = F(\overline{h}\,\overline{k}\,\overline{l})$$

This means that at X-ray diffraction pattern a center of symmetry is always presented even it does not really exist among the elements of symmetry of the class to which belongs the crystal.

Therefore, diffraction patterns can be regarded within the 11 Laue classes, which are obtained from 32 crystal classes by addition of a center of symmetry.



Another important consequence of the type of structure factor is systematic extinction of some reflexes due to the presence of elements of symmetry (nonprimitive cells, screw axes, glide planes).

Example – body-centered cubic lattice with identical atoms.

$$F(hkl) = f\left[e^{2\pi i(h.0+k.0+l.0)} + e^{2\pi i\left(h.\frac{1}{2}+k.\frac{1}{2}+l.\frac{1}{2}\right)}\right] = \begin{cases} 2f, & \mathrm{h+k+l=2n} \\ 0, & \mathrm{h+k+l=2n+1} \end{cases}$$

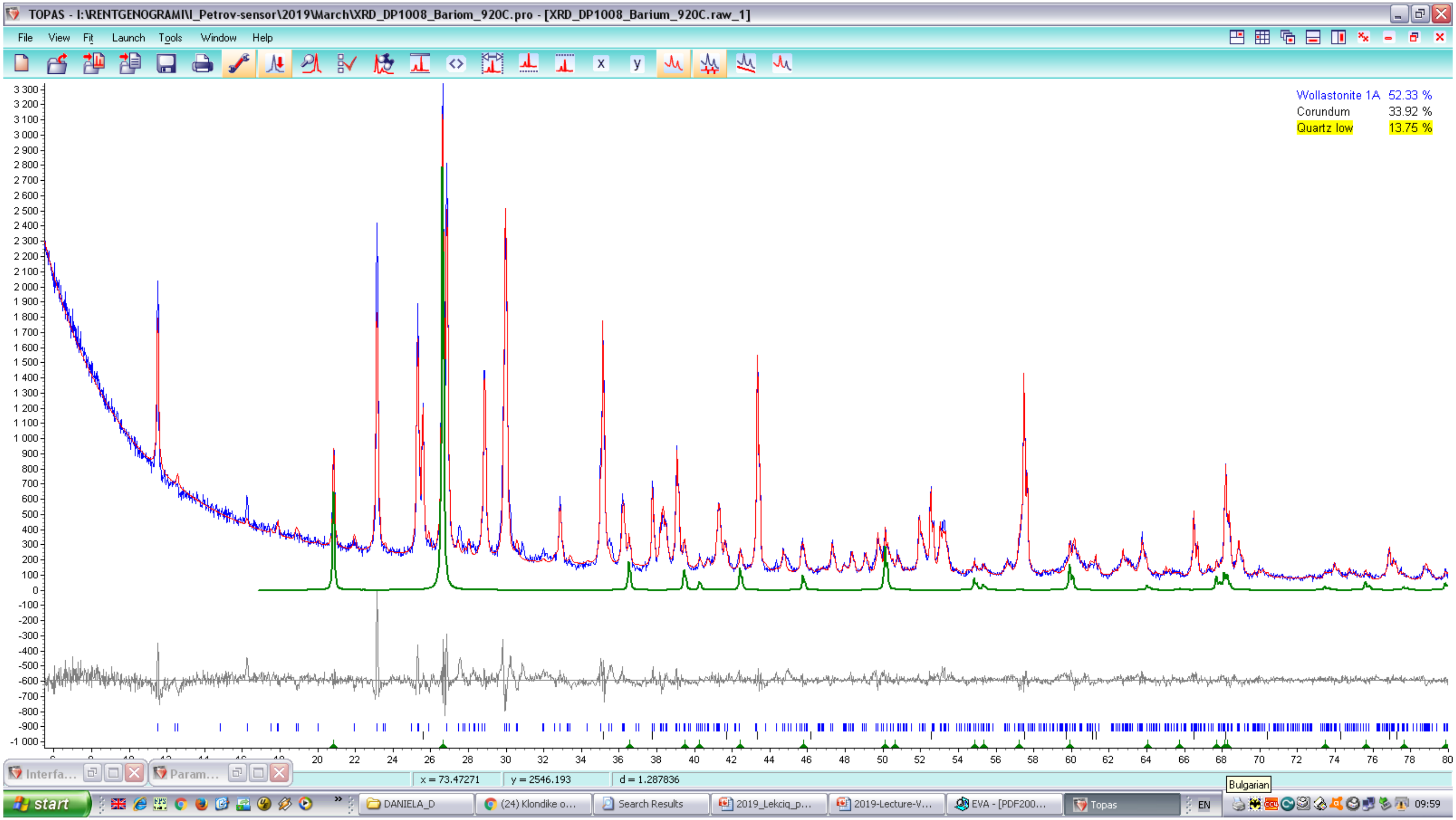
Quantitative phase analysis

•Sometimes the exact composition can be simply determined by the change of the unit cell parameters by the Vegard low (for example $Na_{1-x}K_xCl$).

• The quantities of the different phases can be determined by different methods (calibration curves, standard additives, etc.) or by the Rietveld method.

•Certain problems originate by mixtures of phases with very different densities or crystallite sizes

•The accuracy of quantitative X-ray analysis is in the order of several percent and the lower detection limit is about 0.5-1%



TOPAS - I:\RENTGENOGRAMI\I_Petrov-sensor\2019\March\XRD_DP1008_Bariom_920C.pro - [XRD_DP1008_Barium_920C.raw_1]

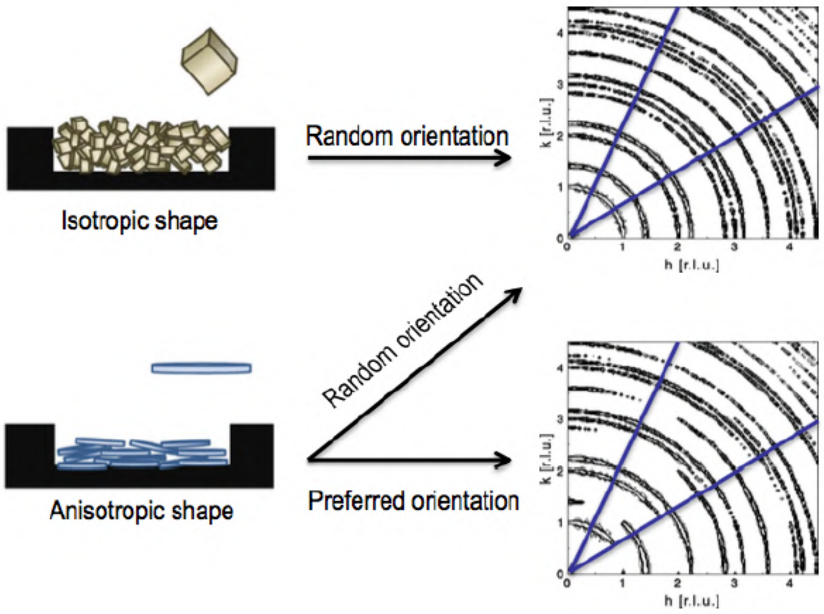
Wollastonite 1A	52.33 %
Corundum	33.92 %
Quartz low	13.75 %

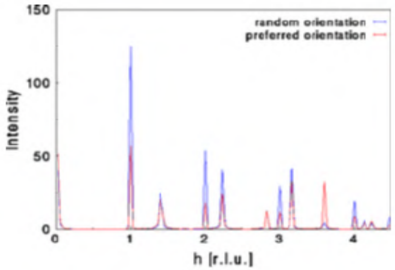
x = 73.47271 y = 2546.193 d = 1.287836

Some phenomena during crystallization and growth, processing, or sample preparation have caused the grains to have preferred crystallographic direction normal to the surface of the sample.

The preferred orientation creates a systematic error in the observed diffraction peak intensities.

Careful sample preparation!!!





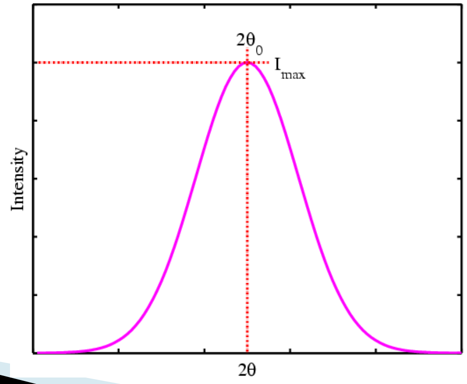
Broadening of diffraction peaks

The diffraction line can be modeled theoretically by a profile function.

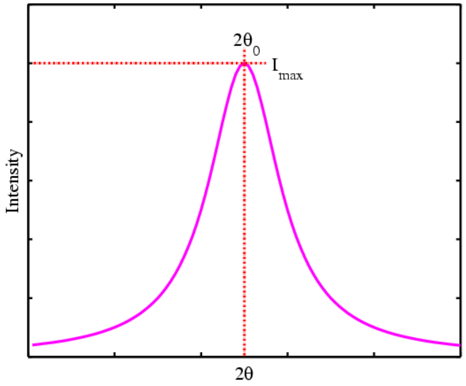
This feature includes both **instrumental** effects and effects resulting from the specific composition and microstructure of the **sample** as follows:

- Crystallite size (2-200 nm)
- Micro stresses (deformation of the crystal lattice)
- Structural defects (packaging defects, antiphase boundaries, etc.)
- Concentration gradient in non-stoichiometric samples

- Gauss

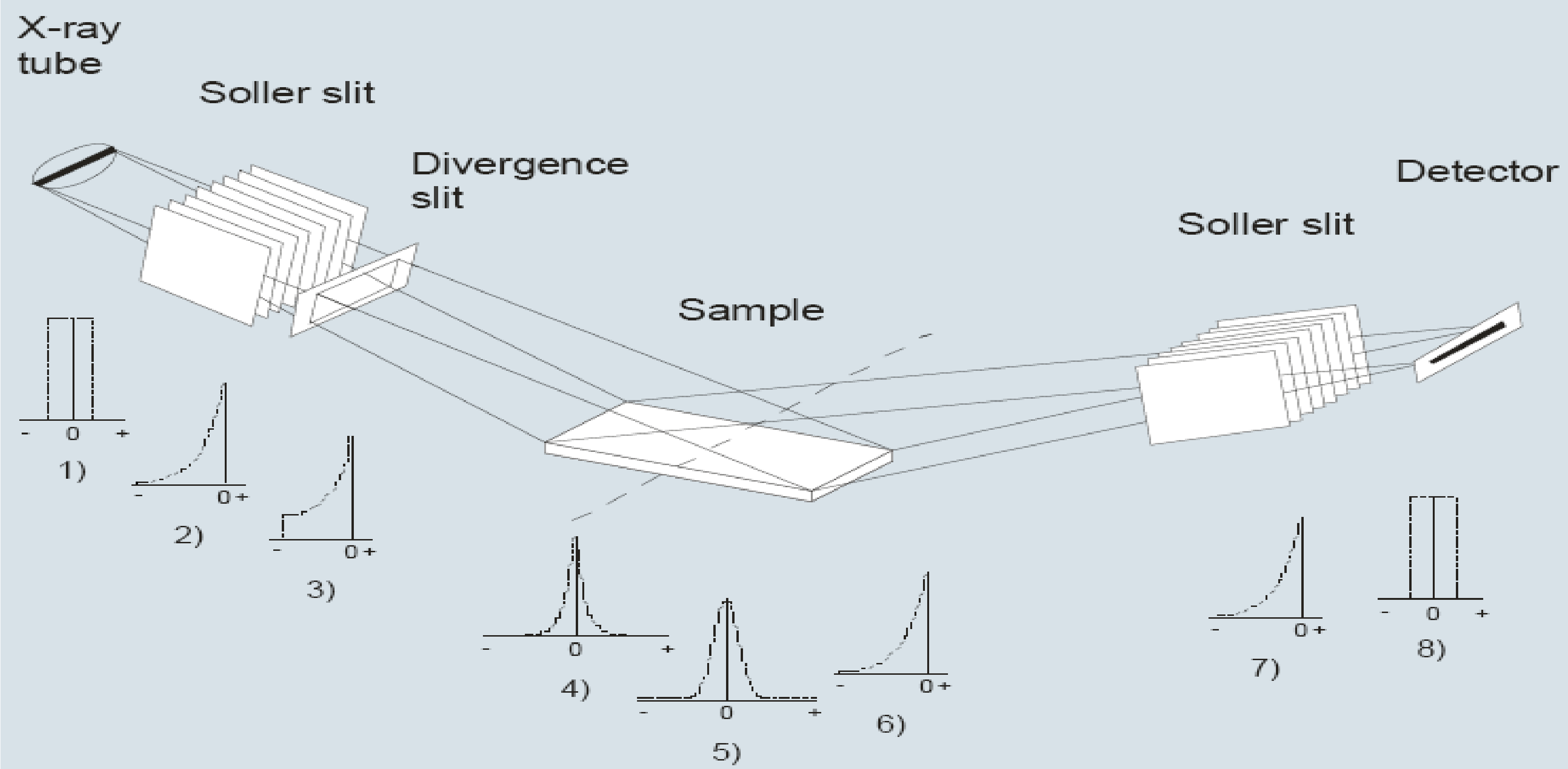


Lorentz



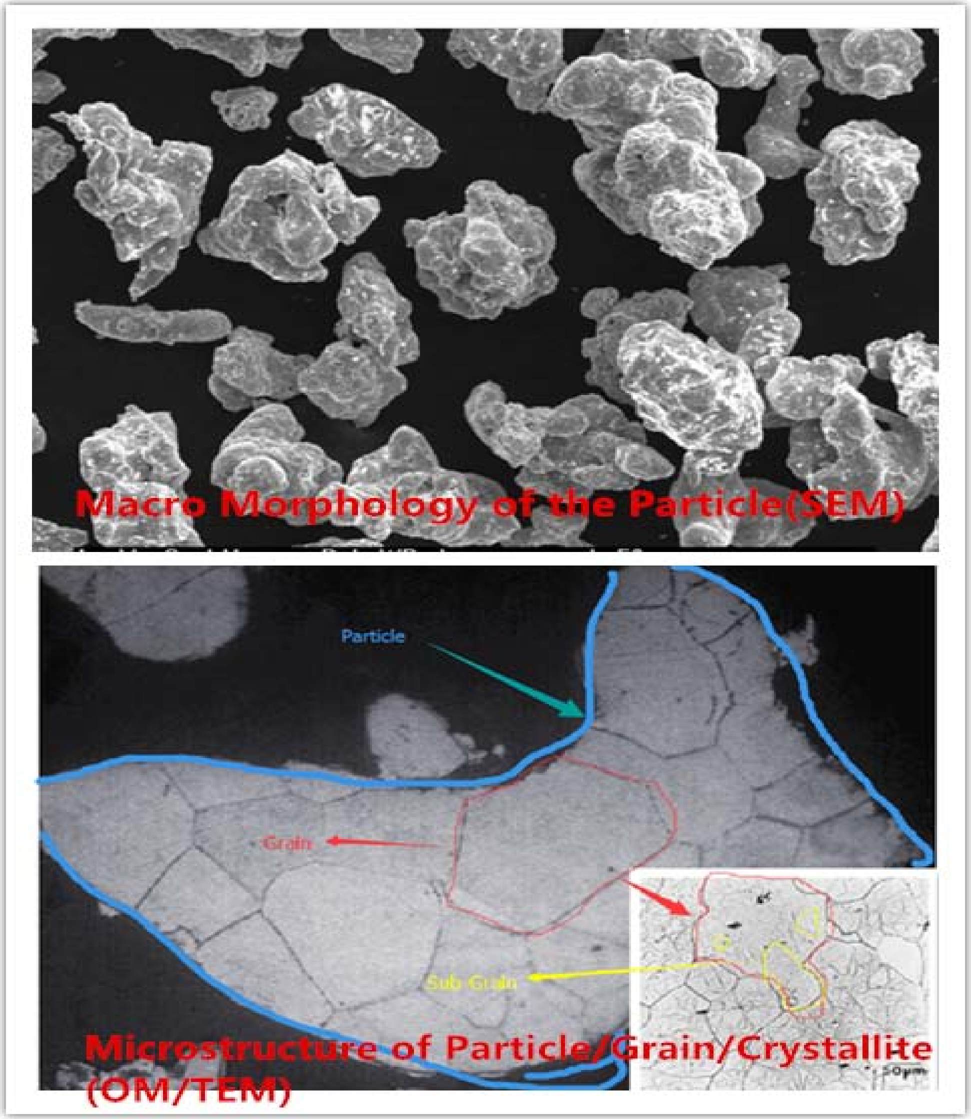
The geometry of the diffractometer introduces deviations in the pure diffraction profile that make it be:

- asymmetric
- broadened
- displaced from its theoretical position



The ideal crystal is infinite, so one of the defects of real crystals is their limited size.
This "imperfection" causes the diffraction lines to be extended to crystals smaller than 200nm in size.
The size measured by X-ray diffraction is the so-called “size of the coherently scattering domains“ of the crystal.

!Make difference with “size” measured by TEM, SEM, DLS and Low temperature nitrogen adsorption!



Crystallites, particles, grains

The grains (particles) may be crystalline or amorphous.

Coherently scattering domains (crystallites) are crystalline regions of a material that are subject to the conditions for coherent scattering. (which may not be consistent with neighboring ones).

They are single crystals in powdered material (from the diffraction point of view).

The particles may contain several grains.

A grain can contain several domains (for example, two domains that are highly disoriented).

Grain size and domain size are rarely the same in a polycrystalline aggregate but may be the same in a some nanosized powders

Scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta}$$

D - volume average size of crystallites in a given direction
k - a constant between 0.87 and 1
λ - X-ray wavelength
β - integral half-width of the line in radians (2θ)

Width of the peak(deg)	Size (nm)
2	4
1.5	6
1	9
0.75	12
0.5	18
0.25	35
0.1	88
0.05	177
0.02	442

Broadening from micro strains

Strain is a term more commonly used by engineers.
They define it as the ratio of the deformation of an object to its initial length.

$$\Delta d/d = \varepsilon$$

Two types of strains are observed in crystals:
Isotropic - leads to an increase or decrease in the parameters of an elementary cell and a displacement of the position of the diffraction lines. An example is thermal expansion. It does not observe an additional extension of the diffraction lines.
Non-isotropic - leads to the systematic displacement of atoms from their ideal positions and to the broadening of diffraction lines.
This type of stress is caused by point defects such as vacations, plastic deformation during cold working of metals, for thin layers on a substrate, etc.

Stokes and Wilson Formula (1944)

$\zeta = B/4tg\theta$

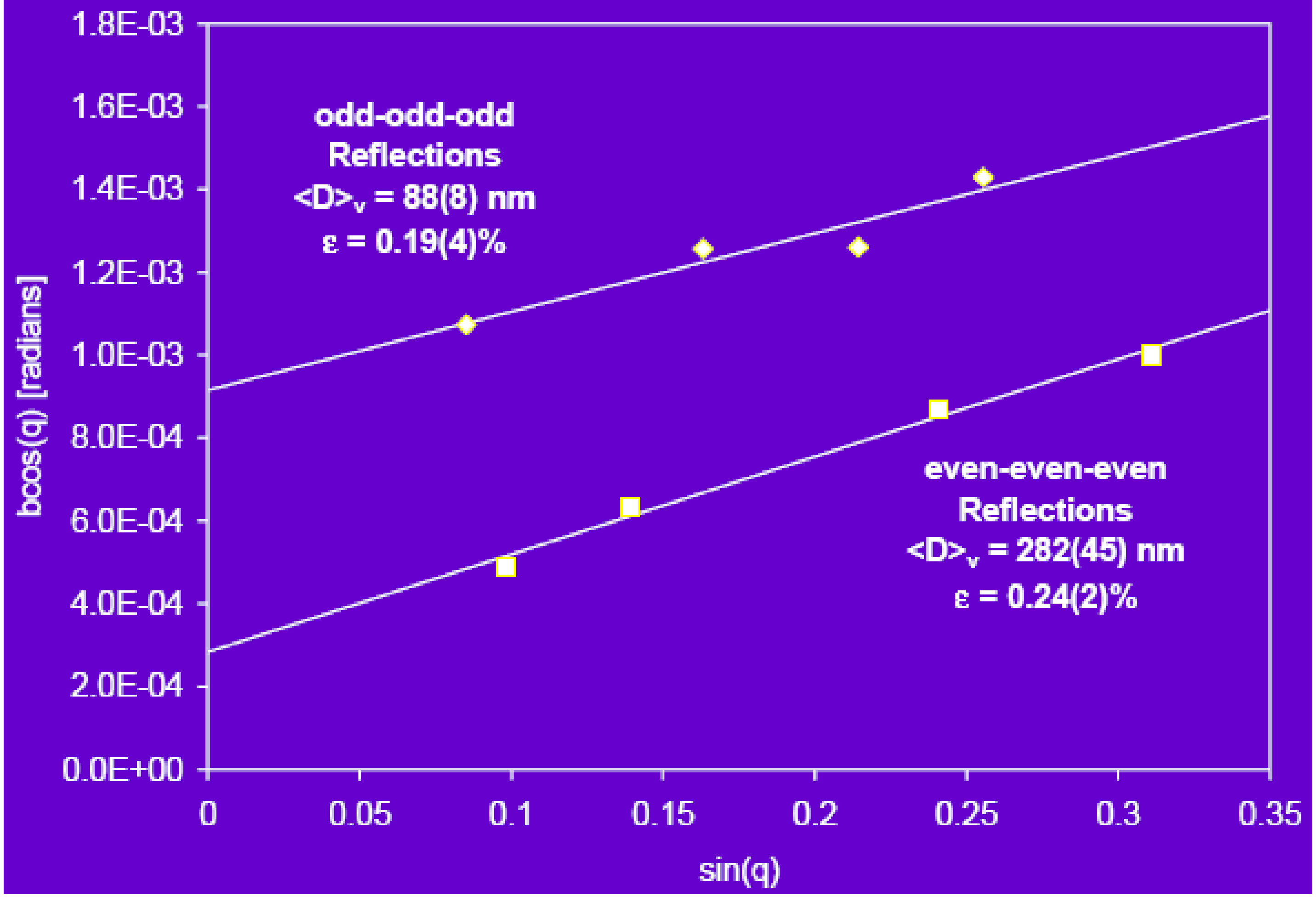
Where - ζ is the mean stress by volume, - B is the integral half-width of the diffraction line in radians 2θ.

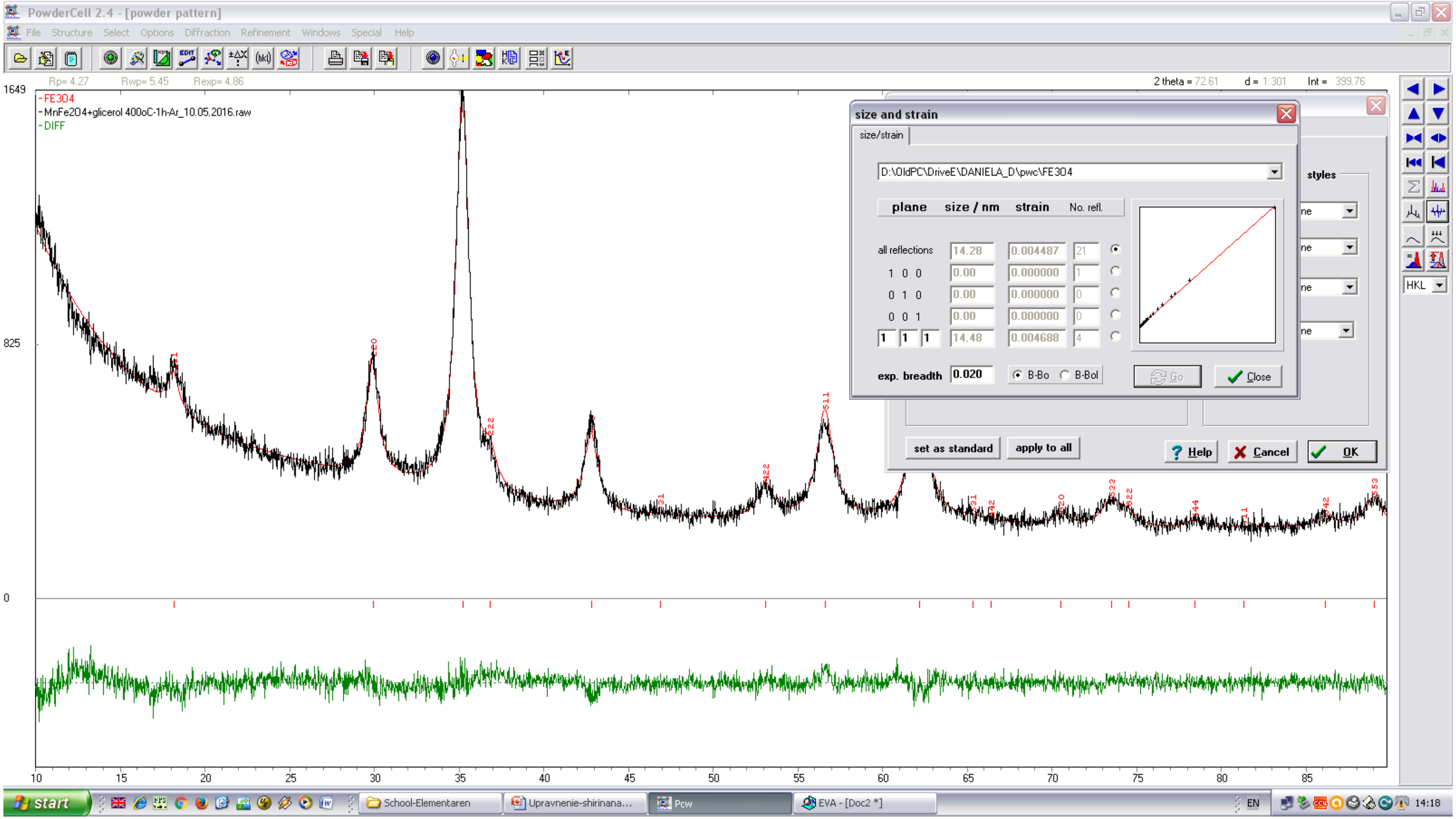
Hence $B = 4\zeta tg\theta$,

and by comparison with the Scherer formula $B = \lambda/(D\cos\theta)$,

it can be seen that the angular dependence of the width of the diffraction lines on the sizes of crystallites and on the stresses is different.

Williamson-Hall Plot





Rp= 4.27 Rwp= 5.45 Rexp= 4.86

2 theta = 72.61 d = 1.301 Int = 399.76

size and strain

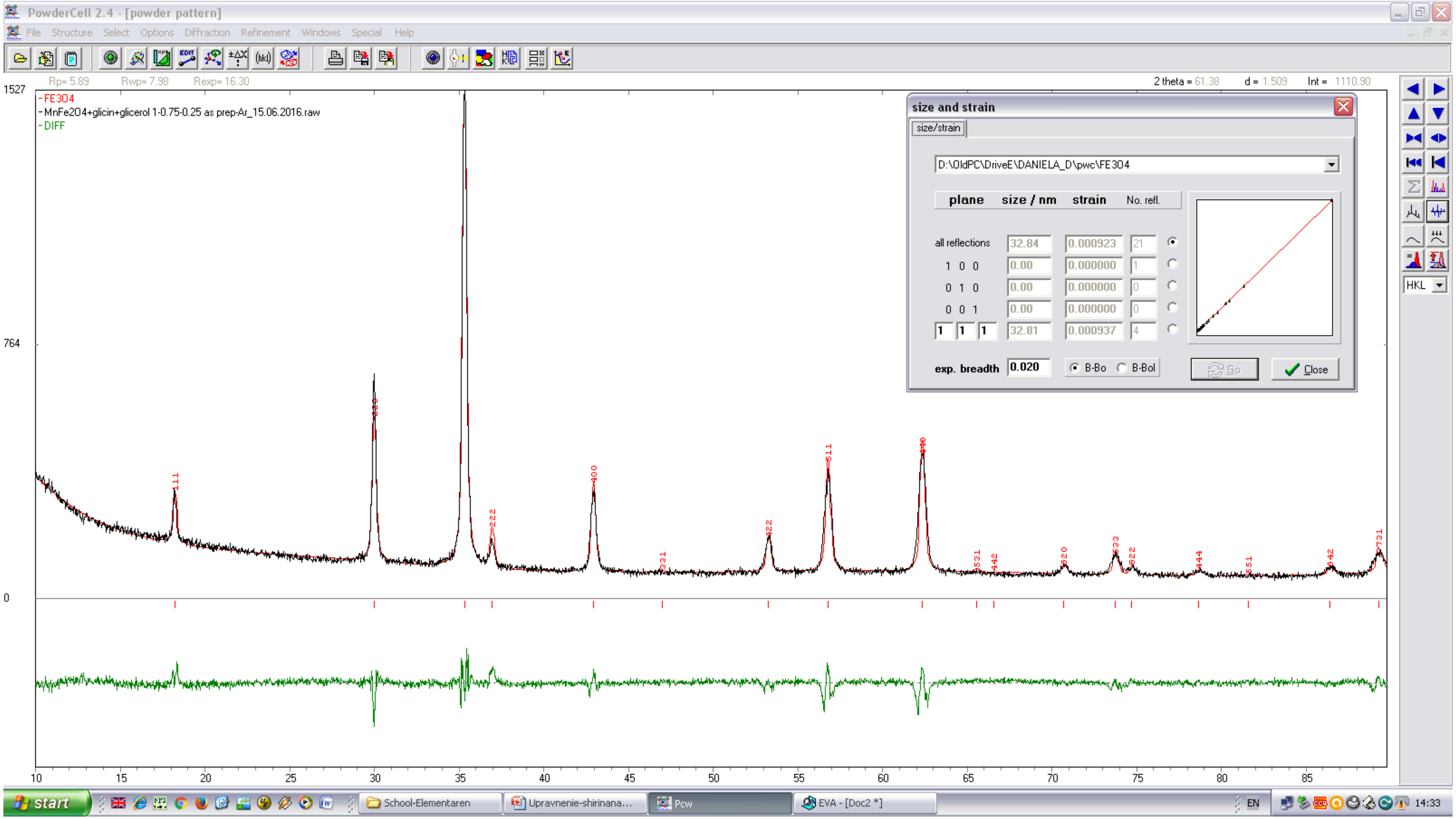
size/strain

D:\OldPC\DriveE\DANIELA_D\pwc\FE3O4

plane	size / nm	strain	No. refl.	
all reflections	14.28	0.004487	21	●
1 0 0	0.00	0.000000	1	○
0 1 0	0.00	0.000000	0	○
0 0 1	0.00	0.000000	0	○
1 1 1	14.48	0.004688	4	○

exp. breadth 0.020 ● B-Bo ○ B-Bol

Go Close



Rp= 5.89 Rwp= 7.98 Rexp= 16.30

2 theta = 61.38 d = 1.509 Int = 1110.90

- FE3O4
- MnFe2O4+glicin+glicerol 1-0.75-0.25 as prep-Ar_15.06.2016.raw
- DIFF

size and strain

size/strain

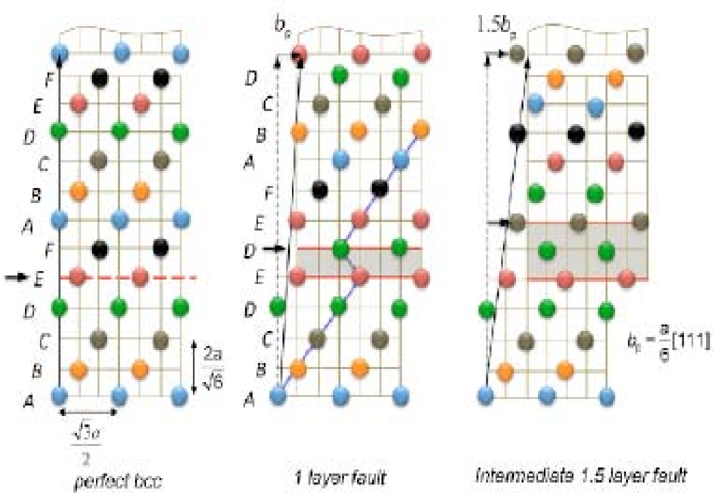
D:\OldPC\DriveE\DANIELA_D\pwc\FE3O4

plane	size / nm	strain	No. refl.	
all reflections	32.84	0.000923	21	●
1 0 0	0.00	0.000000	1	○
0 1 0	0.00	0.000000	0	○
0 0 1	0.00	0.000000	0	○
1 1 1	32.81	0.000937	4	○

exp. breadth 0.020 ● B-Bo ○ B-Bol

Go Close

The broadening from the existence of packing defects differs from the broadening of the crystallite size in which all diffraction lines are involved. In the presence of packing defects, there are planes where these defects are located, and therefore, only the reflexes of the corresponding peaks will be broadened. Other peaks will remain unchanged.



perfect bcc

1 layer fault

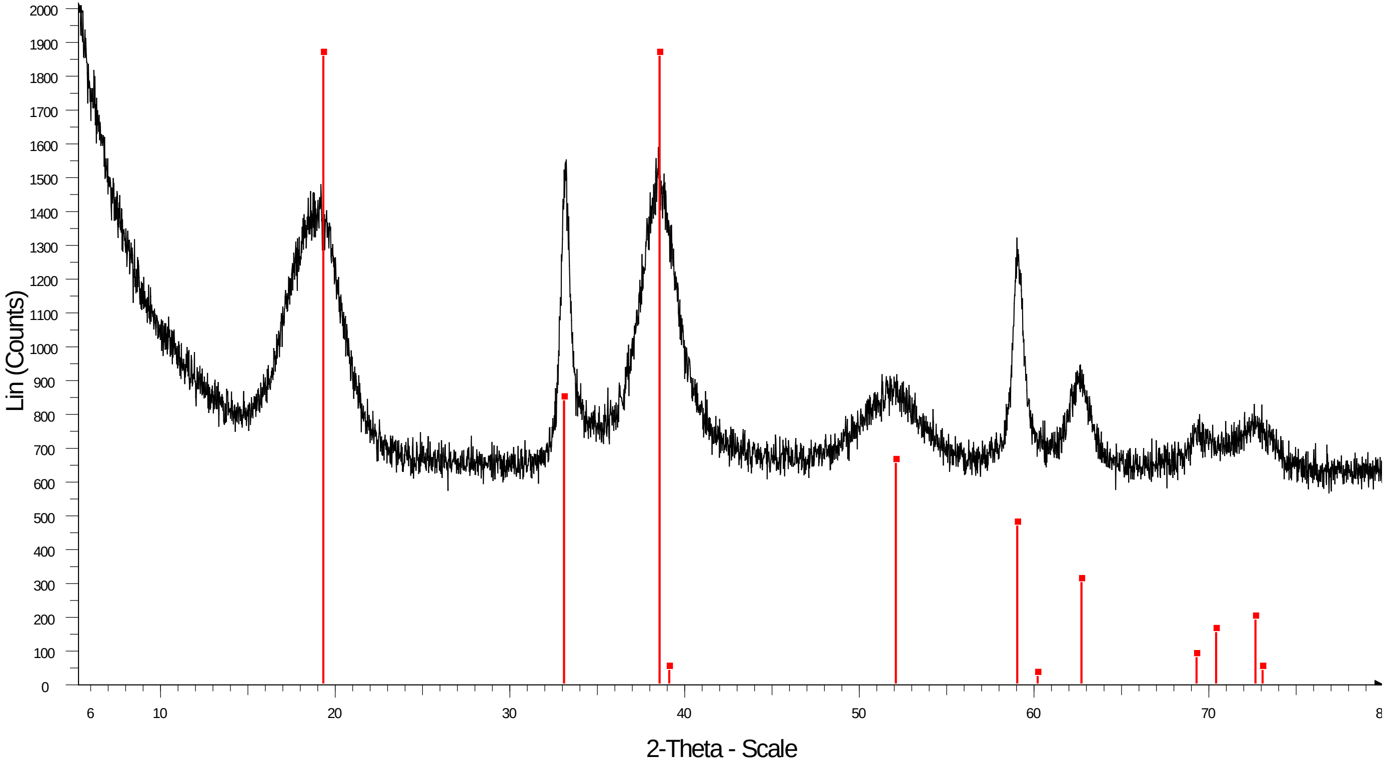
Intermediate 1.5 layer fault

Normal	subtraction	introduction	twinning
B	C	B	C
A	B	A	A
C	A	B	B
B	C	C	C
A	A	A	A
C	C	C	C
B	B	B	B
A	A	A	A

line displacement

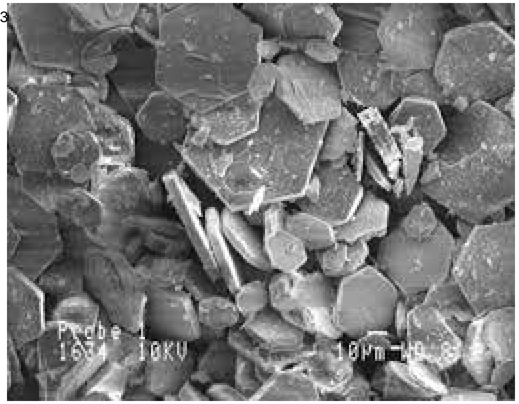
asymmetric broadening

Theophrastite, syn



File: Ni(OH)2-A-13-12-12.raw - Type: 2Th/Th locked - Start: 5.300 ° - End: 79.994 ° - Step: 0.020 ° - Step time: 17.5 s - Temp.: 25 °C (Room) - Time Started: 11 s - 2-Theta: 5.300 ° - Theta: 2.650 ° - Chi: 0.00 ° - Phi:
Operations: Import

🟥 00-014-0117 (*) - Theophrastite, syn - $Ni(OH)_2$ - Y: 92.41 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 3.12600 - b 3.12600 - c 4.60500 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P-3



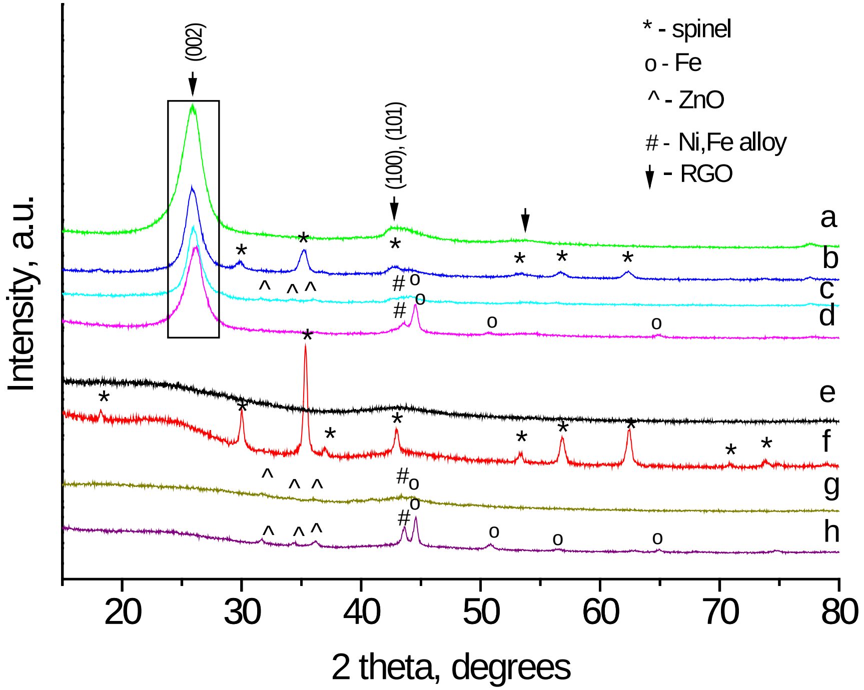
Other defects leading to broadening of the diffraction lines

Dislocations in layered materials (graphite, MS_2, Clays, ZrNCl, etc.)

Antiphase boundaries occurring in partially ordered materials (Cu_3Au, Sr_2AlTaO_6, etc.)

Crystalline size analysis applied to a sample containing longitudinal defects can be used to estimate the size of coherent domains (or the size of defect areas) in the same way that standard analysis is used to determine the crystallite size.

A typical catalyst



sample	Carbon material	$Ni_{0.5}Zn_{0.5}Fe_2O_4$	Fe	(Ni,Fe)	ZnO
NiZn/RGO	a=2.451(1) Å c=6.785(3) Å 8nm	a=8.379(2) Å 15nm	-	-	-
NiZn/RGO spent	a=2.444(1) Å c=6.782(9) Å 9nm	Traces	a=2.901(5) Å 7 nm	a=3.579(2) Å 8 nm	Traces
NiZn/RGO after TPR	a=2.451(2) Å c=6.789(8) Å 9nm	-	a=2.855(1) Å 46nm	a=3.575(2) Å 19 nm	-
NiZn/AC	amorphous	a=8.4067(6) Å 32nm	-	-	-
NiZn/AC spent	amorphous		a=2.888(5) Å 11 nm	a=3.641(7) Å 10 nm	a=3.252(7)Å c=5.210(2)Å 20 nm
NiZn/AC after TPR	amorphous	-	a=2.867(1) Å 49nm	a=3.584(1) Å 35 nm	a=3.249(1)Å c=5.197(2)Å 23 nm

Thank you for your attention!