Advanced Methods for Materials Research

Materials Structure Investigations

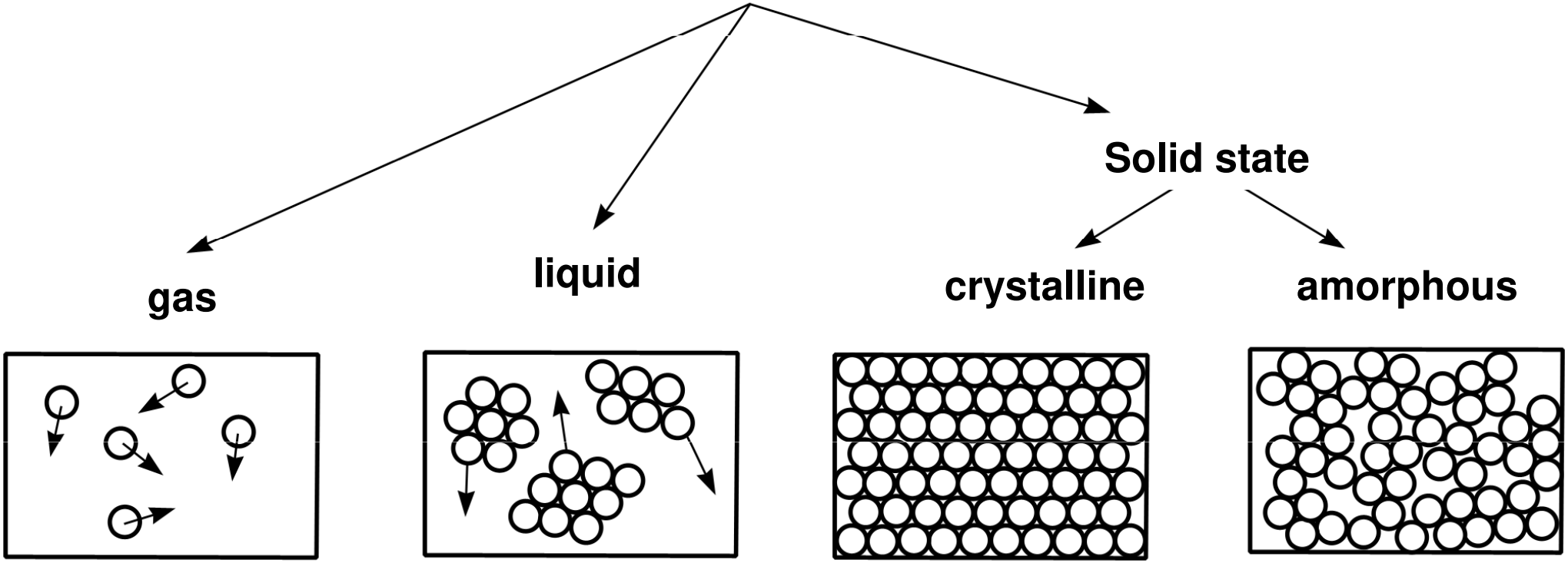
Materials Properties Investigations

Advanced Methods for Materials Research

1. The structure and property of sample and methods of their research
2. The division of structure and property research methods
3. X-Ray diffraction methods
4. The interaction between X-Ray radiation and the matter
5. Bragg-Wulf theory
6. X-ray diffractometer
7. X-Ray diffraction analysis: qualitative and quantitative

The inanimate matter

States of matter



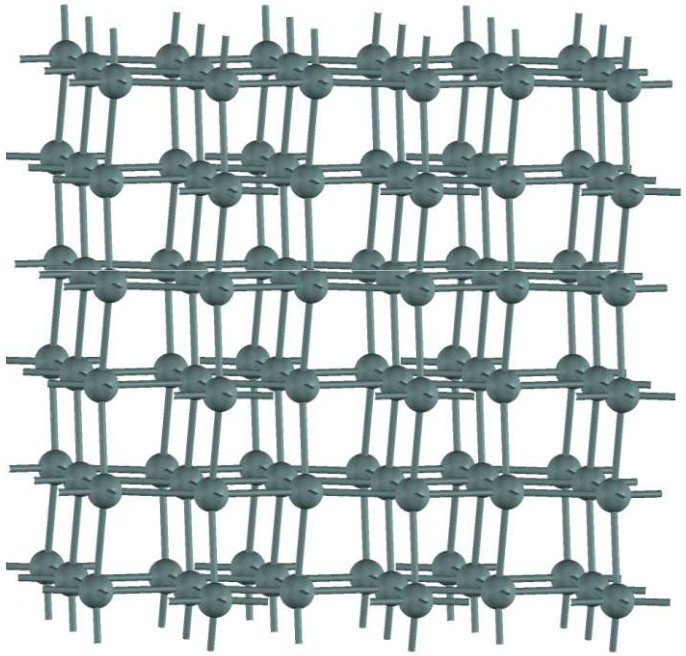
The solid state

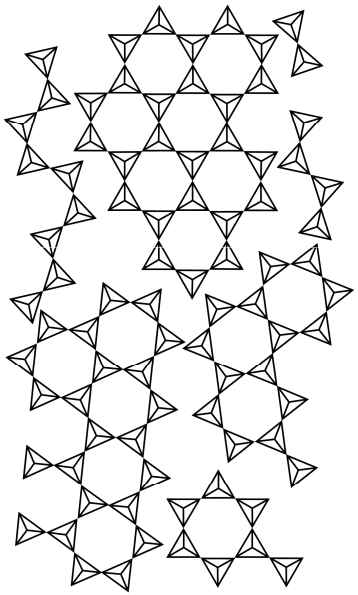
crystalline:

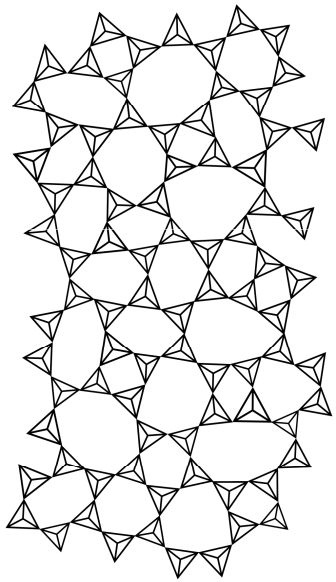
- short- and long-range order (arrangement)
- the anisotropy of properties

amorphous:

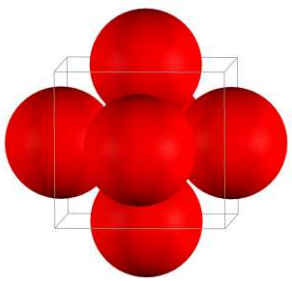
- only short-range order
- the isotropy of properties

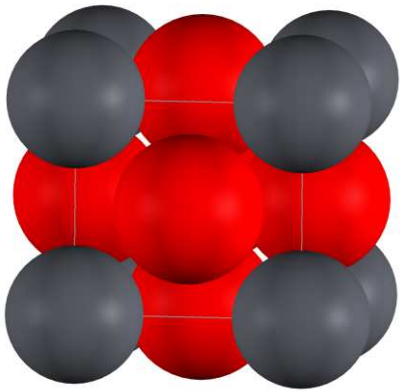


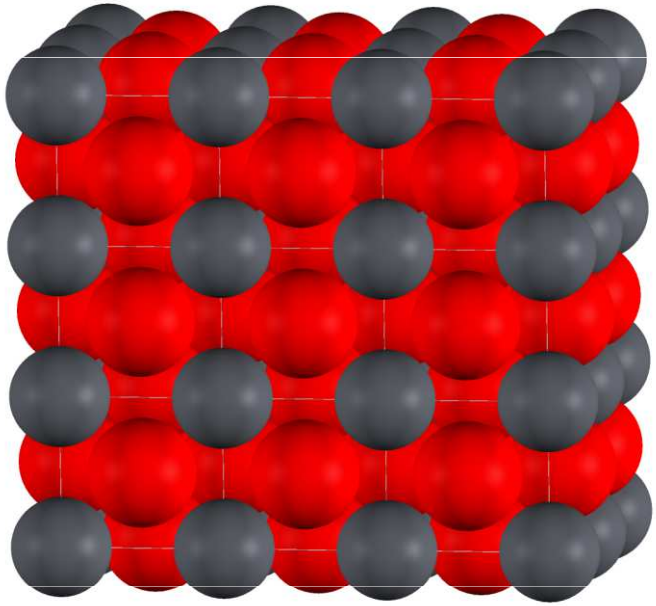




The type of order and the proper method of structural research







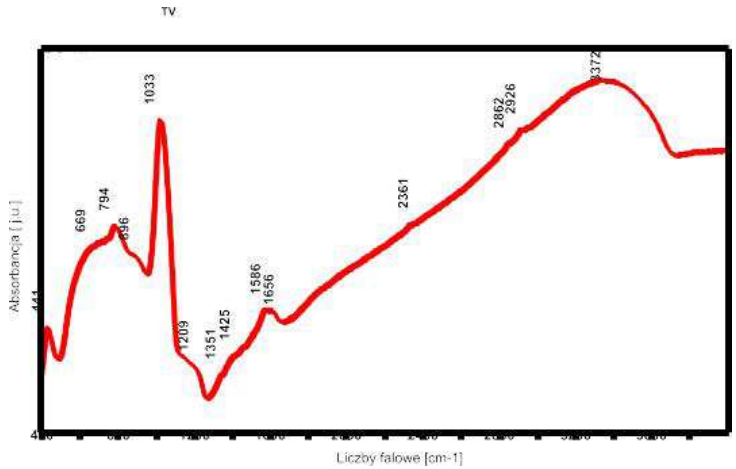
Optical Spectroscopy

Scanning microscopy

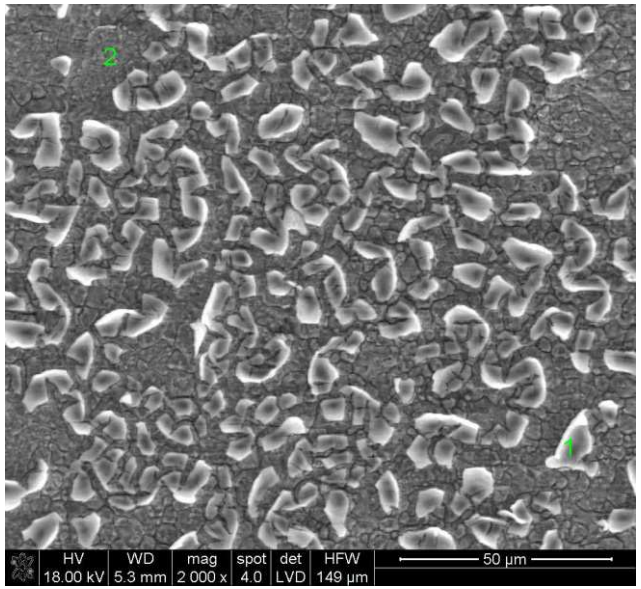
X-Ray Diffraction

Atomic Force Microscopy

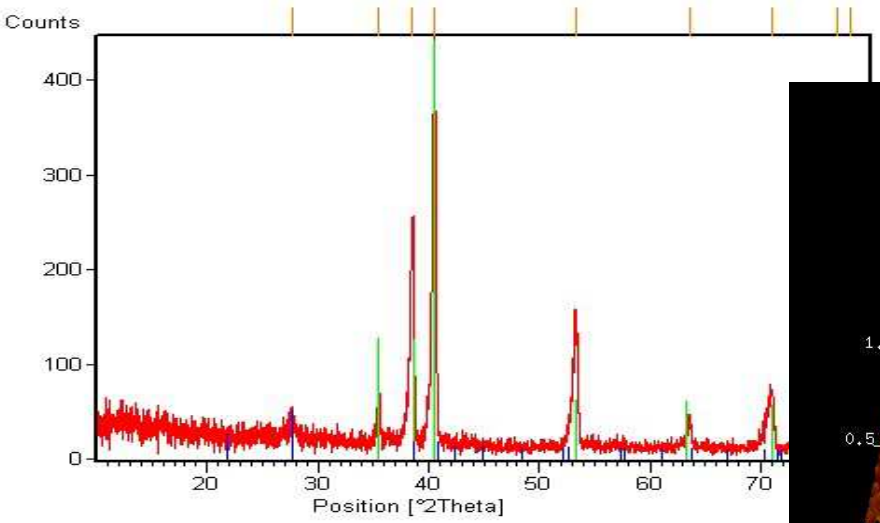
Results of measurements



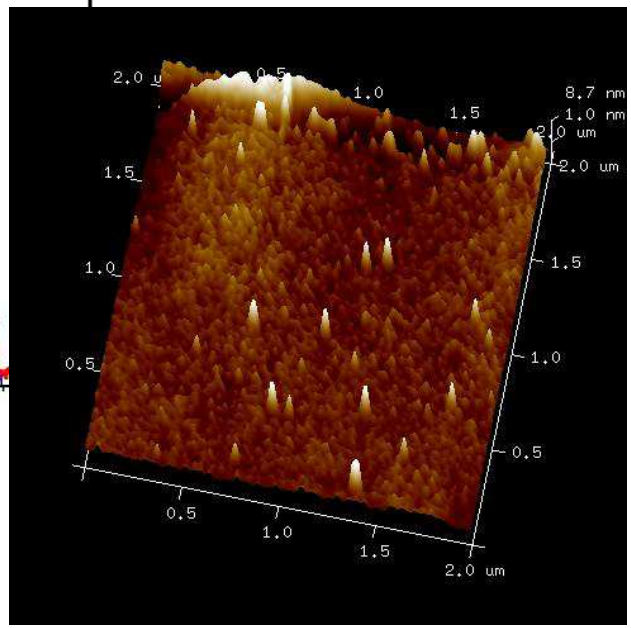
IR spectrum



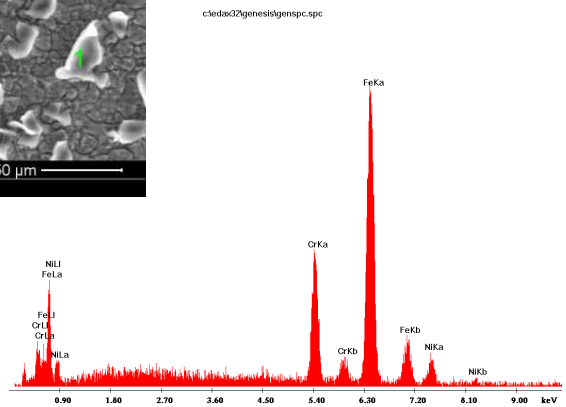
SEM image



XRD diffraction pattern



AFM image



EDX spectrum

Properties of materials

Thermal methods - allow to trace changes of selected phisical properties of materials in relation to temperature changes

the research of chemical reactions

the research of phase transformations

↓

the possibility of analysis of the phase and chemical composition of materials

the research of purity of materials

The structural methods

Spectroscopic methods (the dispertion of energy):

IR spectroscopy (FTIR and Raman effect)

- UV-Vis spectroscopy
- Fluorescence spektroscopy
- Fotoelectron spectroscopy
- Magnetic resonance spectroscopy
- Mössbauer Spectroscopy

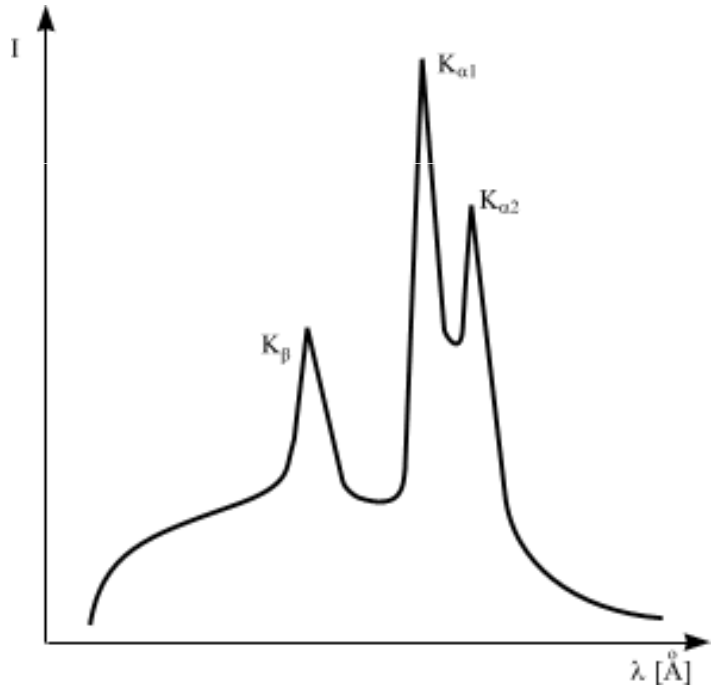
Diffraction methods (elastic scattering-dispertion):

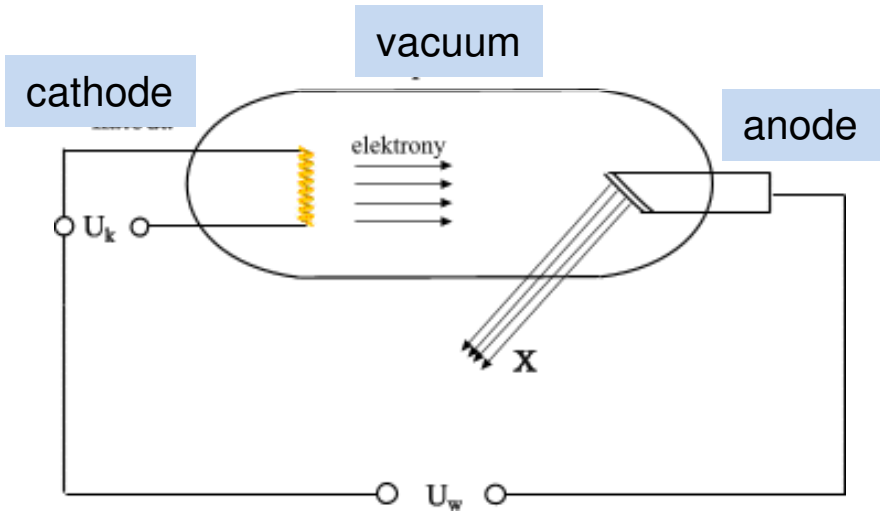
- **X Ray diffraction**
- Neutron diffraction
- **Electron diffraction**

Microscopic methods (Scanning Probe Microscopy):

- Scanning Tunneling Microscopy
- **Atomic Force Microscopy**

X-Ray spectrum



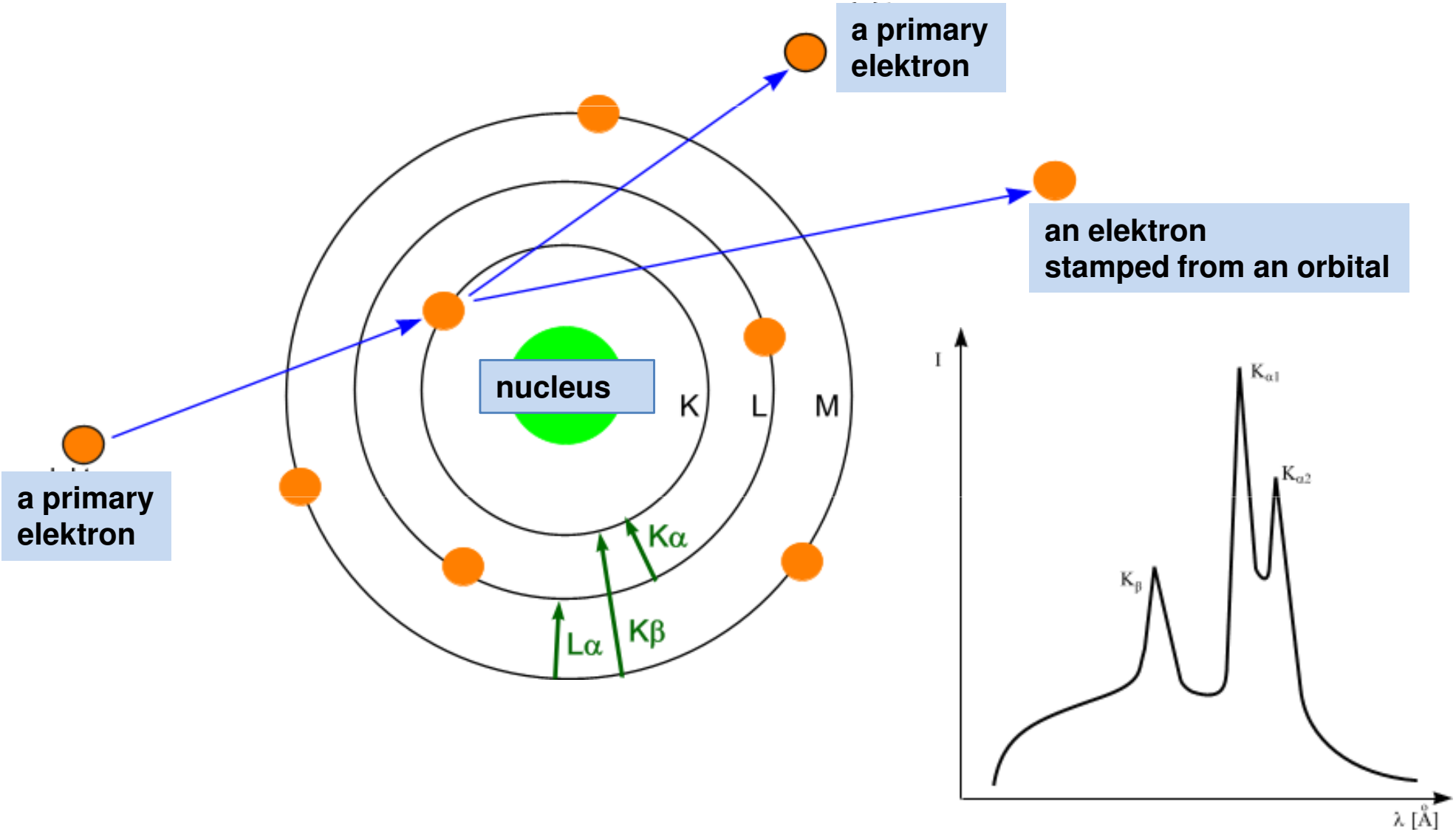


X Ray radiation range:
0.05 - 500 Å

X Ray applied in the structural methods: 0.2-2.5 Å

Anode	K_β [Å]	$K_{\alpha 1}$ [Å]	$K_{\alpha 2}$ [Å]	Filter	Av. K_α [Å]
Mo	0,63225	0,70926	0,71354	**Cu**	0.71069
Cu	1,39217	1,54051	1,54433	**Ni**	1.54178
Co	1,62075	1,78892	1,79278	**Fe**	1.79021
Fe	1,75653	1,93597	1,93991	**Cr**	1,93597

The emission of characteristic X-Ray

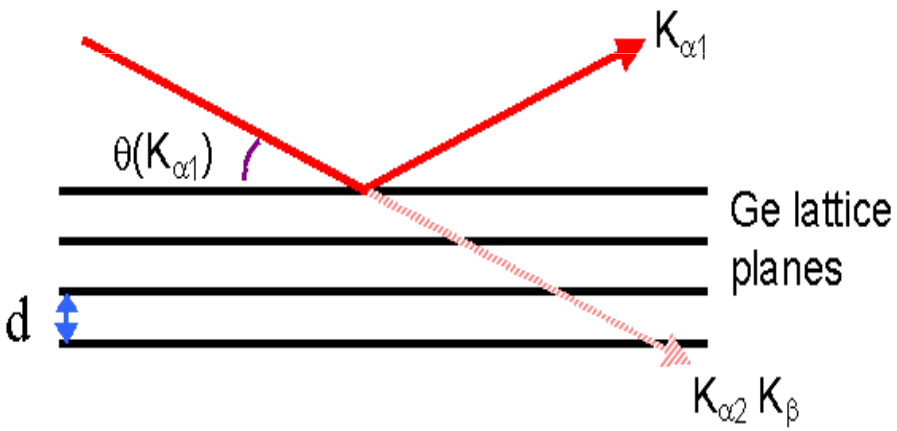


X Ray monochromators

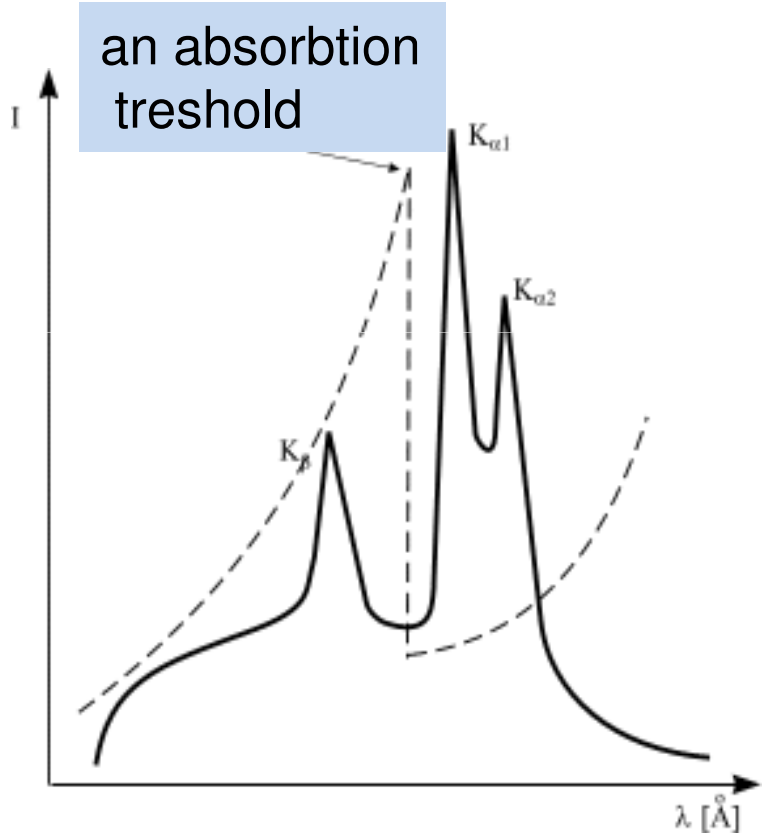
a monochromator - the polished in a proper way crystal (quartz, germanium, ...etc) , strongly reflected **$K\alpha_1$** from one group of parallel lattice planes

a monochromator influences on:

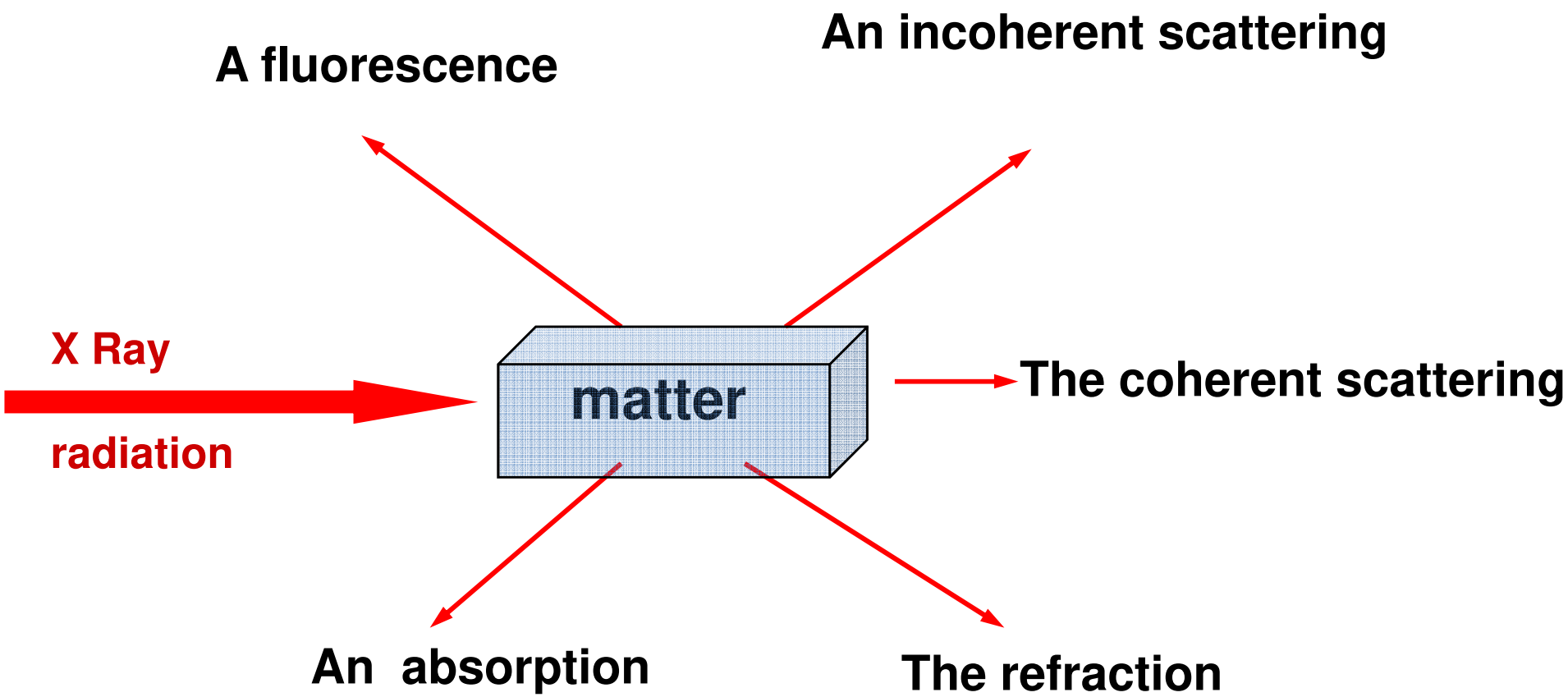
- **K_β;**
- **the background**
- **the sample fluorescence;**



a filter – fitted depending on an anode substance, absorbs K_β



X Ray vs the matter



Bragg-Wulf theory – the diffraction of X Ray on lattice planes

$\Delta S = AB + BC = n\lambda$

$AB = d_{hkl} \sin\theta$

$BC = d_{hkl} \sin\theta$

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

where:

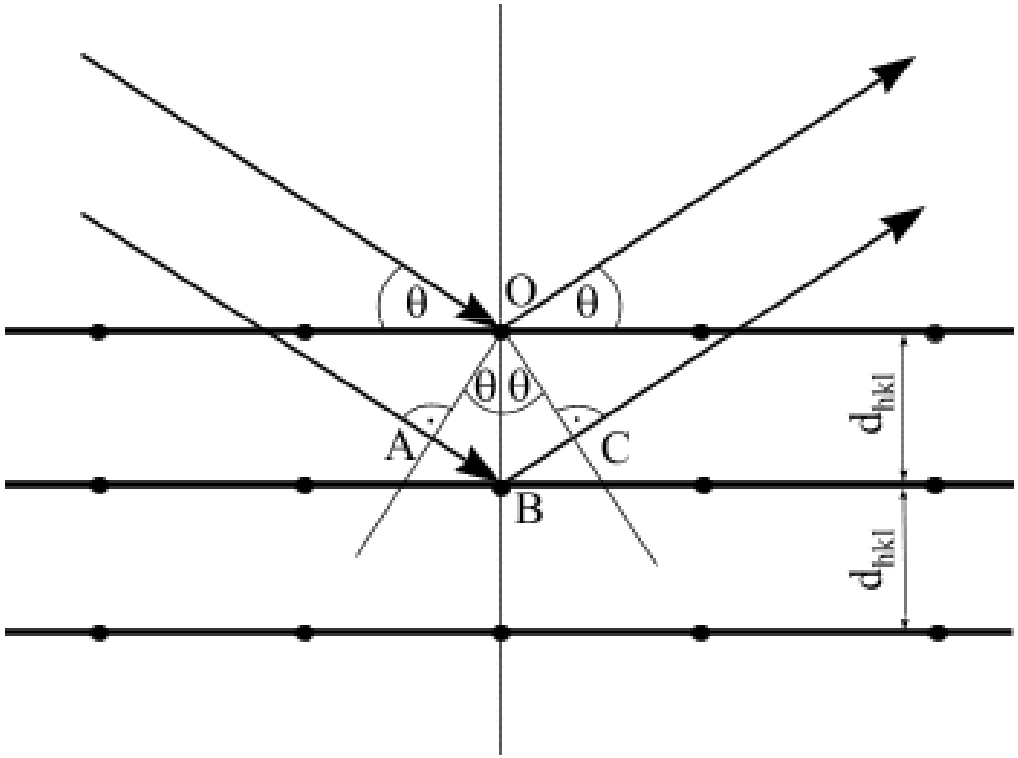
d_{hkl} – the shortest distance between two parallel lattice planes

θ - the reflection angle

n – integer, rank of reflection

λ - X Ray length;

ΔS – optical path difference



The intensity of X Ray reflection in one component system

$$J_{hkl} = C \cdot |F_{hkl}|^2 \cdot LP \cdot p \cdot A$$

$/F_{hkl}/^2$ – structure factor,
LP –Lorentz and polaryty factor (the angle factor);
p – the multiplicity factor;
A – the absorption;

$$C = J_o \cdot \lambda^3 N^2 \cdot \left(\frac{\mu_o e^2}{4\pi mr} \right)^2$$

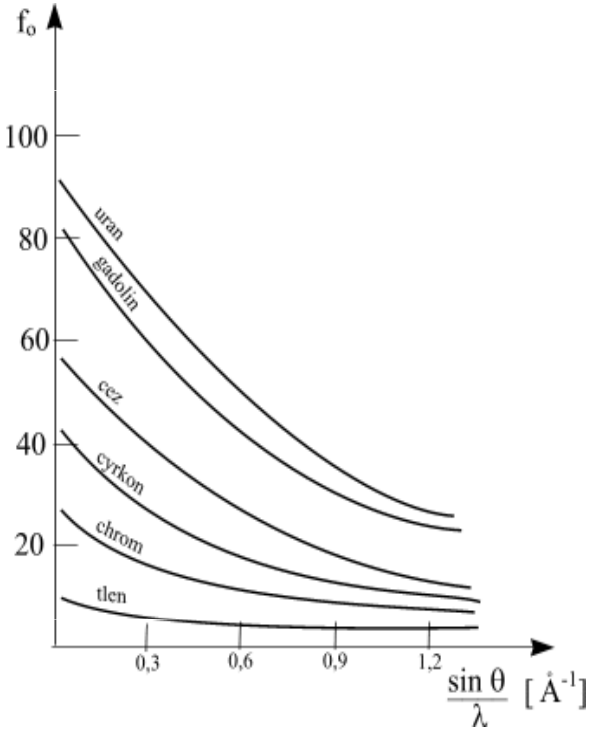
J_o - the intensity of primary been
λ - X Ray radiation lenght
μ_o – the magnetic permeability in vacuum
e - the electron charge
m - the electron mass
r - the distance between the electron and the detection point
N - the number of unit cells in 1 cm^3

The structure factor F_{hkl}

$$F_{hkl} = \sum_{n=1}^{N} f_n \exp(i\psi_n)$$

f_n – atomic scattering factor of n-atom in a unit cell

ψ_n – phase angle of X Ray scattered on n-atom in relation to the X Ray scattered on atom placed in the origin



$$\psi_n = 2\pi(hx_n + ky_n + lz_n)$$

$$F_{hkl} = \sum_{n=1}^{N} f_n \exp[2\pi i (hx_n + ky_n + lz_n)]$$

The structure factor $|F_{hkl}|^2$

$$|F_{hkl}|^2 = [\Sigma\ f_n \cos 2\pi(hx_n + ky_n + lz_n)]^2$$

$$+ [\Sigma\ f_n\, i \sin 2\pi(hx_n + ky_n + lz_n)]^2$$

The squered structure factor occurs always as the positive real number

The structure factor F_{hkl} of containing the center of symmetry structures:

$$F_{hkl} = \sum_{n=1}^{N} f_n \cos 2\pi\,(hx_n + ky_n + lz_n)$$

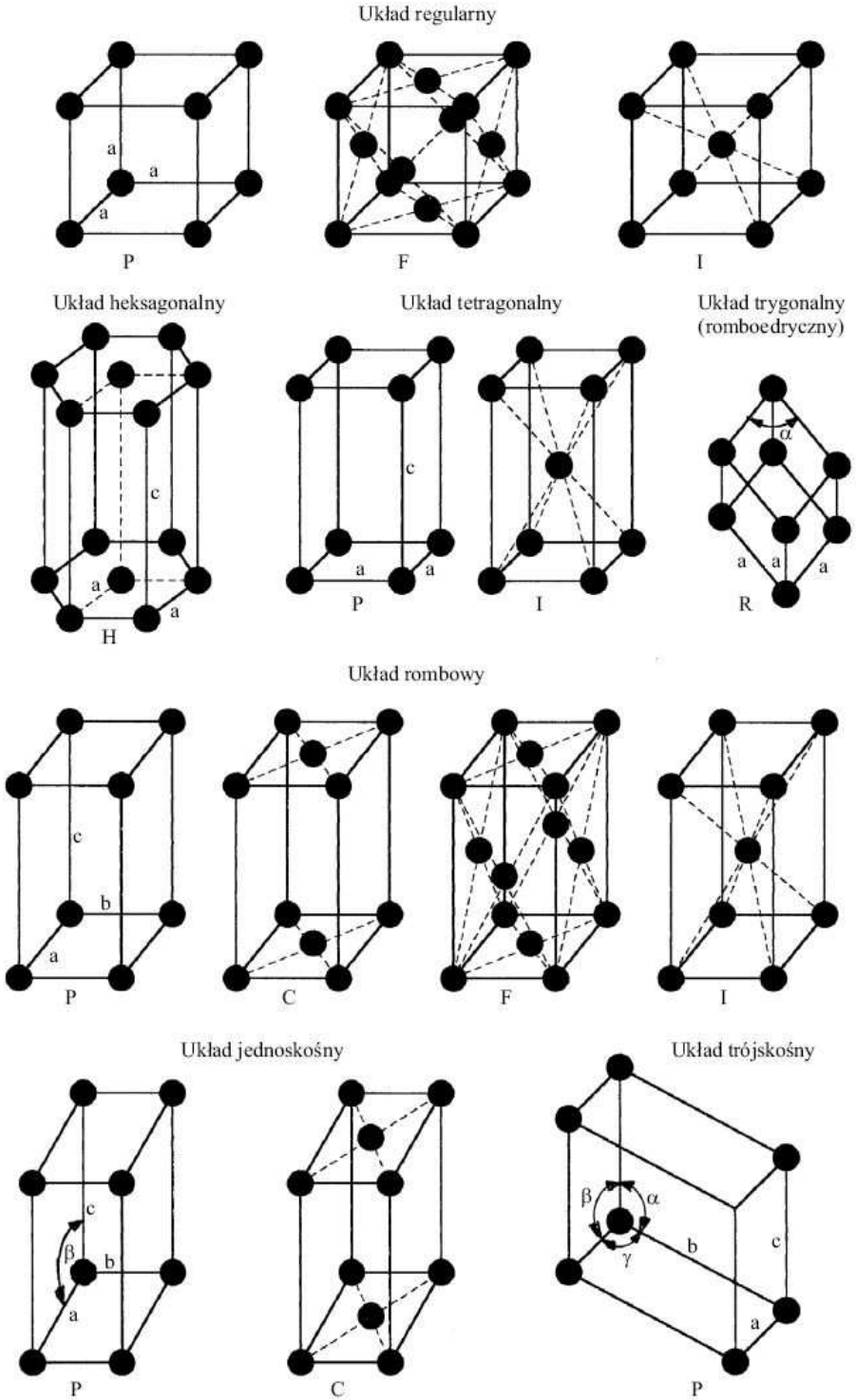
The possible unit cell shapes in the particulate crystallographic systems

crystallographic systems

- cubic
- tetragonal
- orthorhombic
- hexagonal (together with trigonal one)
- monoclinic
- triclinic

Lattice parameters:

a, b, c, α, β, γ



Structure factor vs reflection conditions (systematic extinctions)

Primitive cell (one type of atoms of f_1):

$$F_{hkl} = f_1 \cos 2\pi (h \cdot 0 + k \cdot 0 + l \cdot 0)$$

$$F_{hkl} = f_1$$

no reflection conditions

Primitive cell (two types of atoms of f_1 and f_2):

$$F_{hkl} = f_1 \cos 2\pi (h \cdot 0 + k \cdot 0 + l \cdot 0) + f_2 \cos 2\pi (h \cdot ½ + k \cdot ½ + l \cdot ½)$$

$F_{hkl} = f_1 + f_2$ dla $h + k + l = 2n$ (even sum)

$F_{hkl} = f_1 - f_2$ dla $h + k + l = 2n + 1$

no reflection conditions

Structure factor in I and F lattices

Inner centered cell I (one type of atoms f_1):

$$F_{hkl} = f_1 \cos 2\pi (h\cdot 0 + k\cdot 0 + l\cdot 0) + f_1 \cos 2\pi (h\cdot ½ + k\cdot ½ + l\cdot ½)$$

$F_{hkl} = 2 f_1$ dla $h + k + l = 2n$ reflection conditions

$F_{hkl} = 0$ dla $h + k + l = 2n + 1$ extinctions !

Flat centered cell F (one type of atoms f_1):

$$F_{hkl} = f_1 \cos 2\pi (h\cdot 0 + k\cdot 0 + l\cdot 0) + f_1 \cos 2\pi (h\cdot ½ + k\cdot ½ + l\cdot 0)$$
$$+ f_1 \cos 2\pi (h\cdot ½ + k\cdot 0 + l\cdot ½) + f_1 \cos 2\pi (h\cdot 0 + k\cdot ½ + l\cdot ½)$$

reflection conditions

$F_{hkl} = 4 f_1$ for h, k, l even or odd indexes)

$F_{hkl} = 0$ for hkl mixed (e.g. 223, 230) extinctions!

The research metods based of X Ray diffraction

a) The type of radiation;

polichromatic - Laue method
monochromatic - the rotating crystal method
- DSH powder method

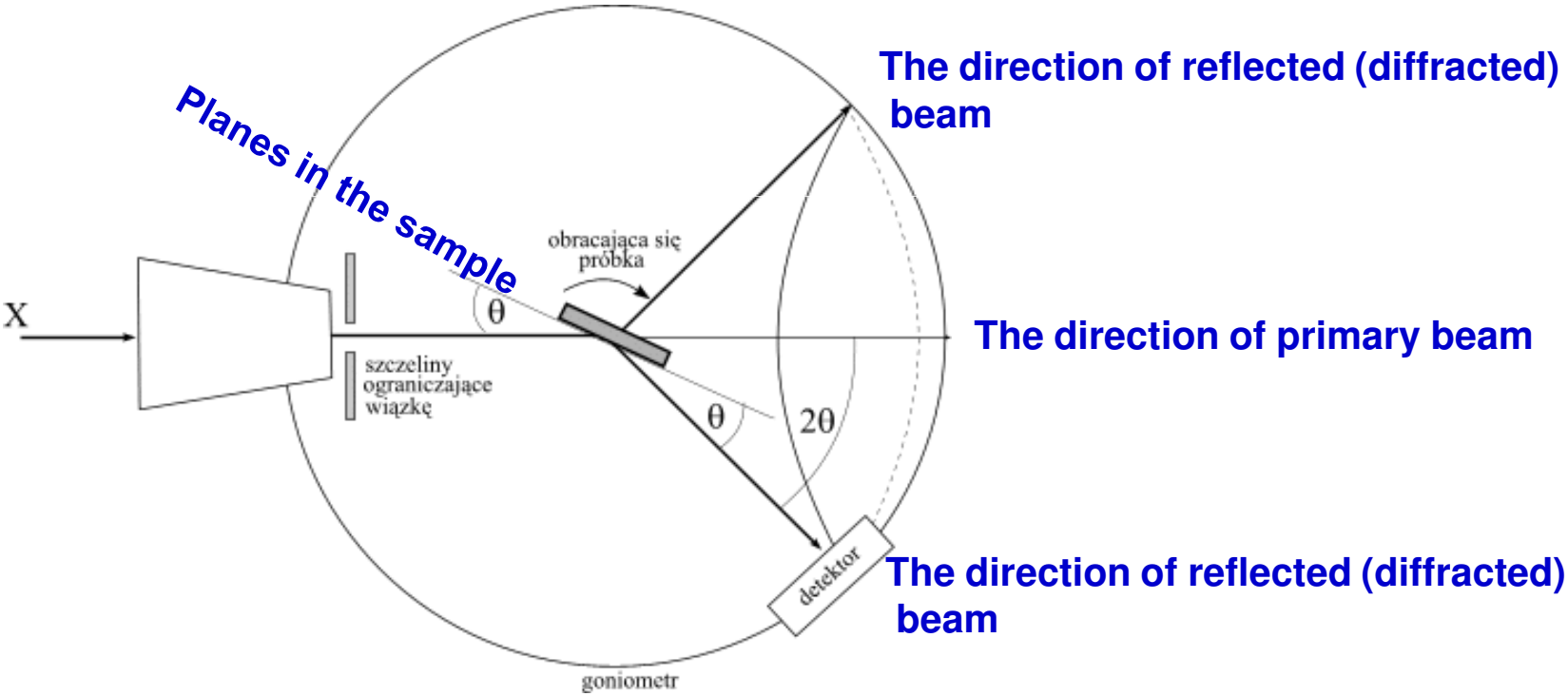
b) The type of sample:

single crystal - Laue method,
- the rotating crystal method
- X Ray four axes diffractometry

polycrystalline - DSH powder method
- **X Ray two axes diffractometry**

All nowodays X Ray structural research methods apply X Ray diffractometers.

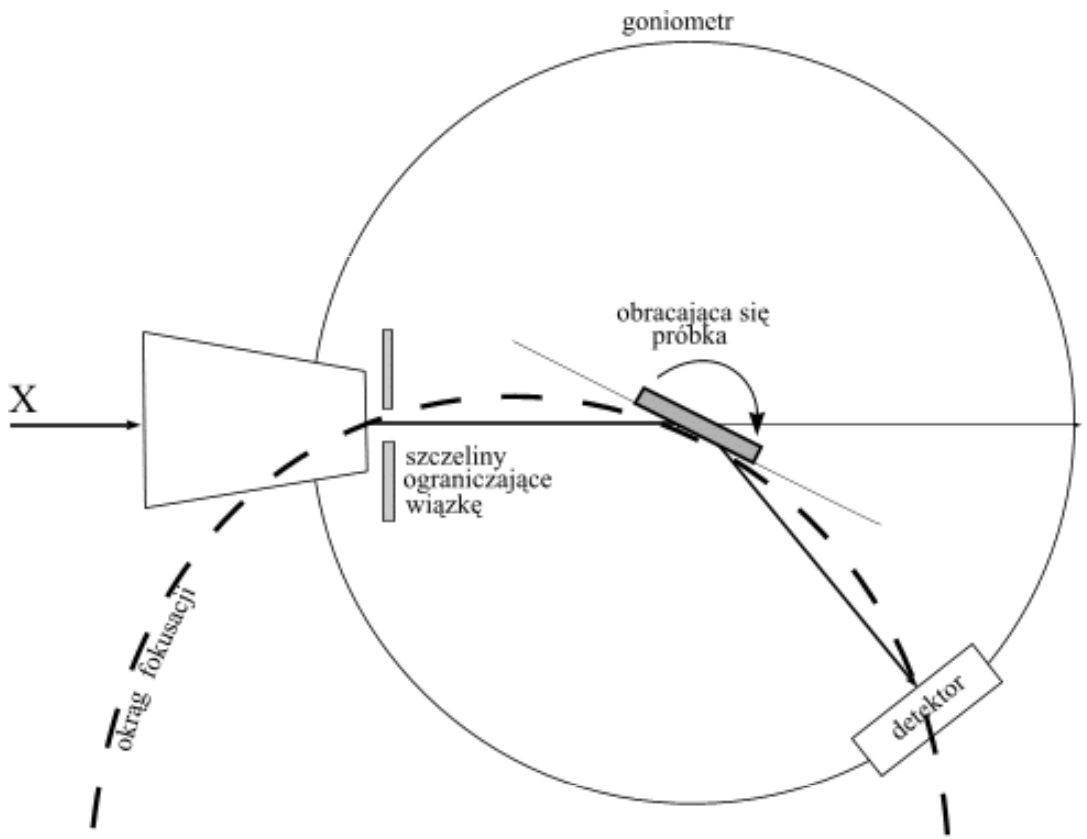
The principles of X Ray diffractometer operations – the θ-2θ configuration



θ - an angle of reflection between the defracted (reflected) beam (or primary beam) and and planes which reflect the radiation

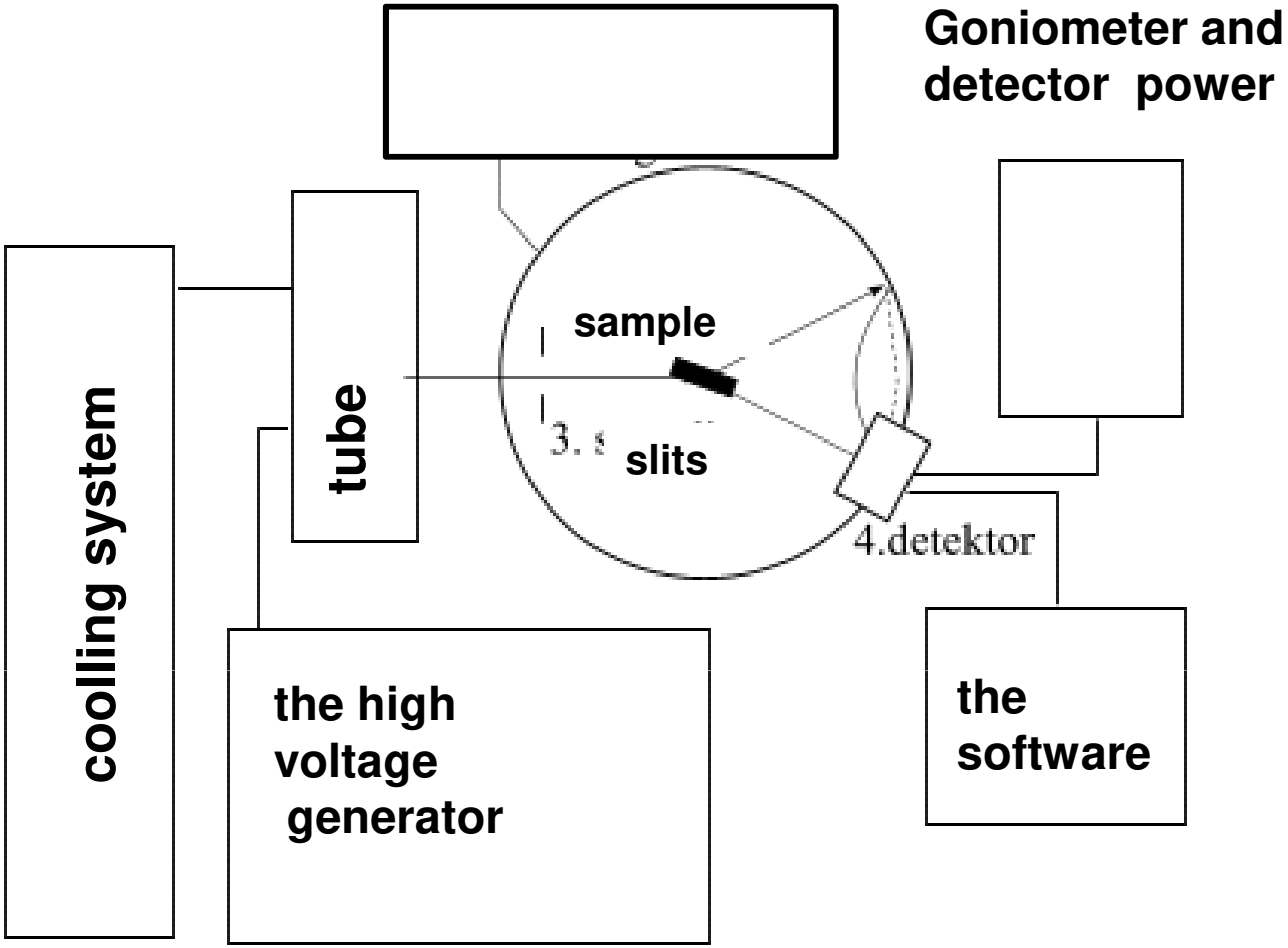
2θ - the diffraction angle between the direction of primary beam and diffracted (reflected) one

Bragg-Brentano focusing

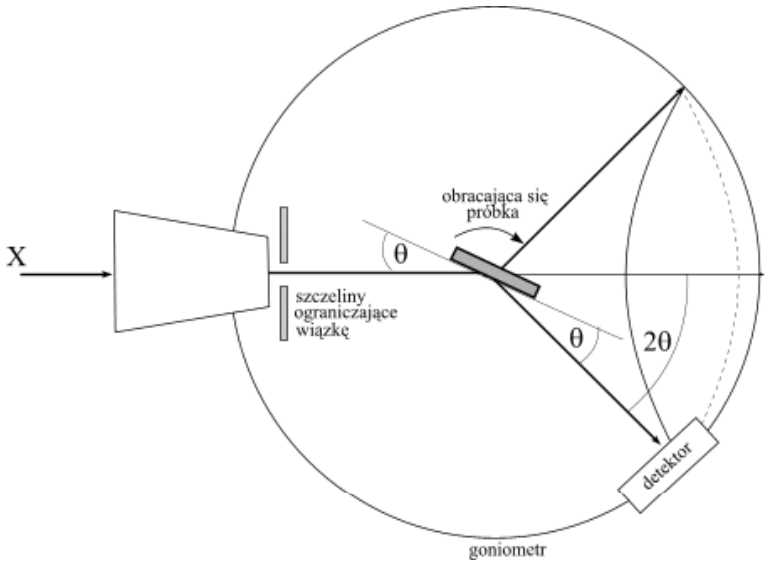


Three elements: source of radiation, sample and detector have to be placed on the same focusing circle, of changing radius r.

X Ray diffractometer parts of the device



The powder X Ray diffractometry of polycrystalline samples



The sample:

- the pollycrystalline powder sample of granulation in the range of 0,1 – 10 μm (0,0001 – 0,001 mm),
- the monolithic sample (an attention on stress and texture)

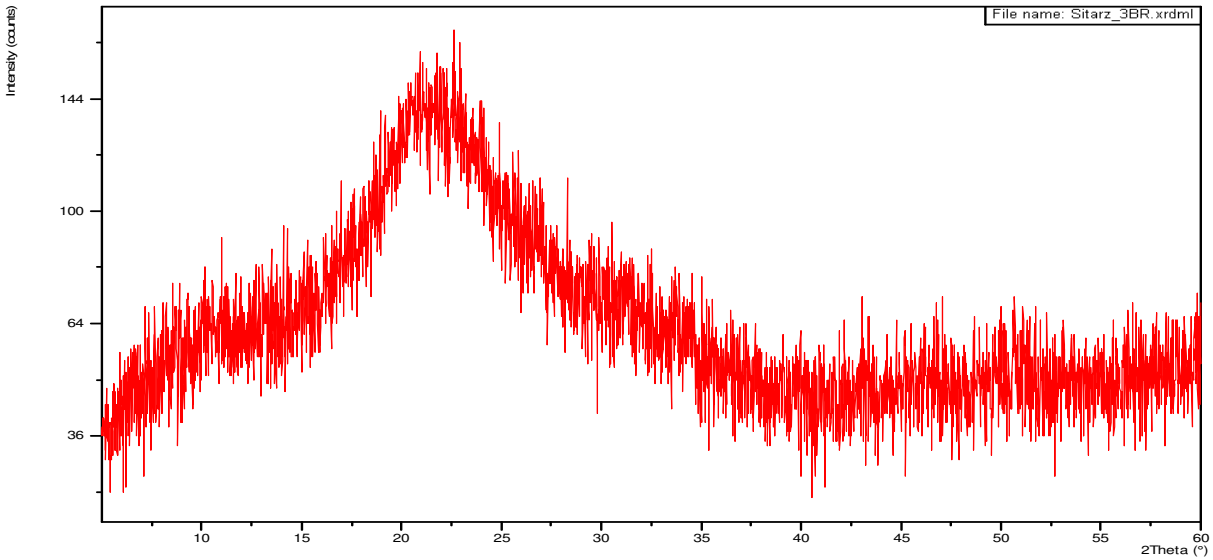
The radiation:

- the monochromatic $K\alpha$ or $K\alpha^1$,

The measurement equipment:

- two axes goniometer
- Bragg-Brentano geometry (most often)

The X Ray diffraction patterns of amorphous and crystalline samples

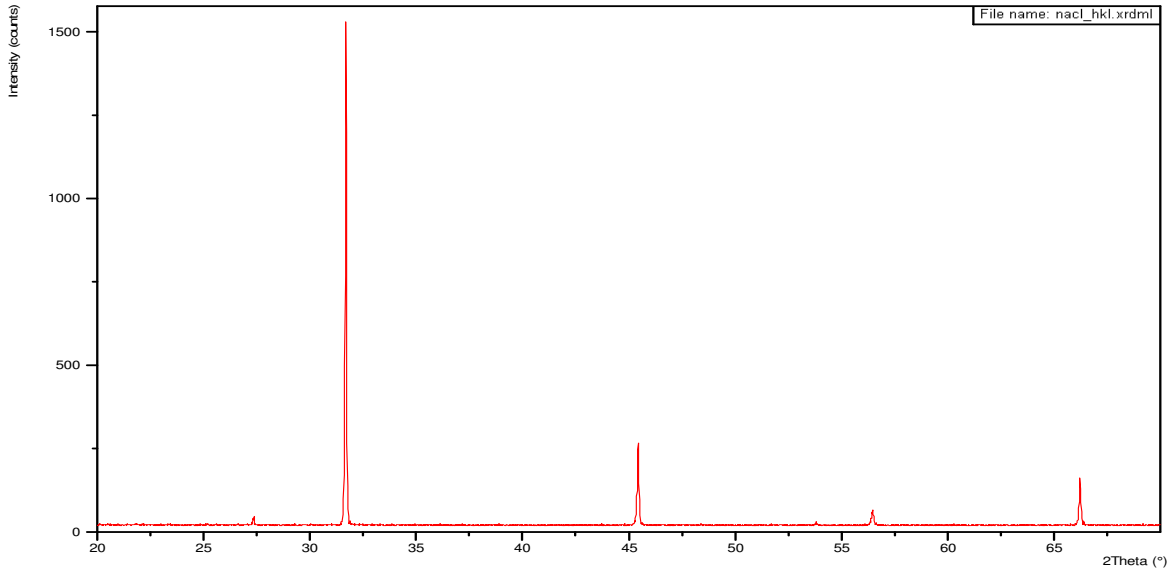


The amorphous sample :

- ✓no reflections
- ✓the typical amorphous „halo”
- ✓the low intensity of the raised background

The crystalline sample:

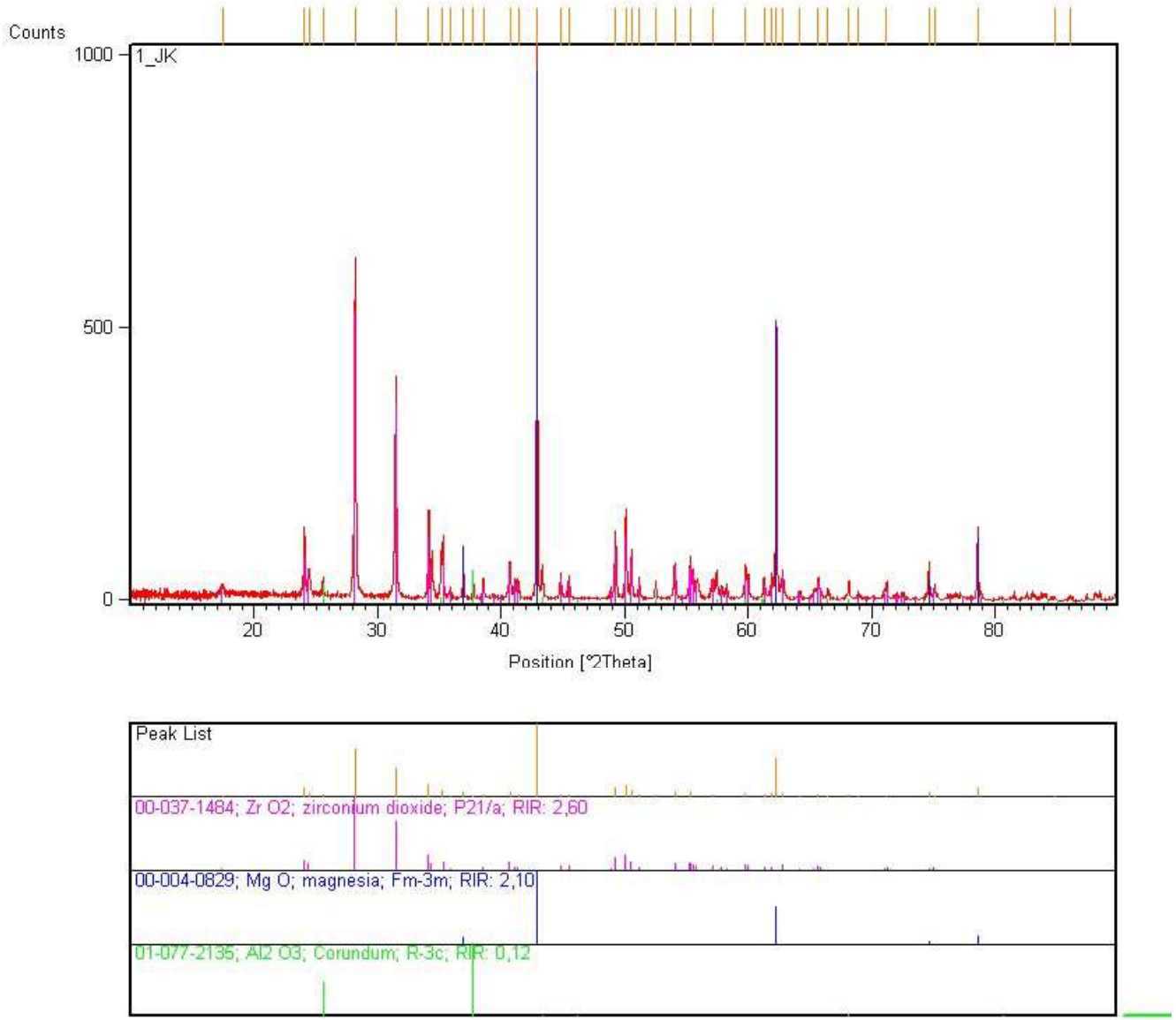
- ✓distinct reflections
- ✓significant values of intensity of reflections relative to the intensity of the background line



The description of X Ray diffraction pattern

No.	Pos. [°2Th.]	FWHM [°2Th.]	h	k	l	Area [cts*°2Th.]	d-spacing [A]	Height [cts]	Rel. Int. [%]
1	16.3505	0.1536				18.62	5.41697	90.90	7.28
2	19.3751	0.1536				12.77	4.57761	62.37	5.00
3	19.7959	0.0768				12.03	4.48124	117.51	9.42
4	22.8608	0.0960				34.58	3.88691	270.14	21.65
5	23.7880	0.0768				51.48	3.73747	502.78	40.29
6	24.3476	0.1728				68.97	3.65282	299.35	23.99
7	24.8300	0.1536				175.07	3.58293	854.82	68.50
8	25.7795	0.1728				287.53	3.45308	1247.98	100.00
9	28.3837	0.1536				11.74	3.14190	57.34	4.59
10	30.6270	0.1152				11.01	2.91669	71.65	5.74
11	33.8843	0.4608				14.08	2.64339	22.91	1.84
12	34.6529	0.2304				9.04	2.58649	29.43	2.36
13	36.3157	0.4608				11.55	2.47179	18.79	1.51
14	37.6160	0.1728				40.00	2.38928	173.63	13.91
15	38.1574	0.2304				30.53	2.35662	99.38	7.96
16	39.2492	0.1920				15.88	2.29354	62.03	4.97
17	40.1972	0.3072				10.58	2.24161	25.84	2.07
18	43.9671	0.1536				10.76	2.05775	52.52	4.21

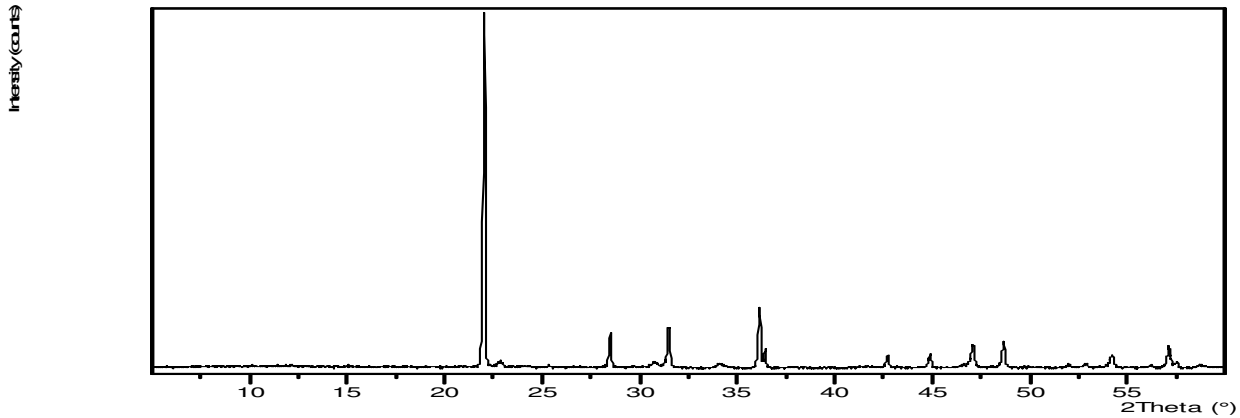
The powder X Ray diffraction pattern of polycrystalline sample



X Ray Phase Analysis

- qualitative
- quantitative

The qualitative phase analysis



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

$$I_{rel} = \frac{I_n}{I_{max}} \cdot 100$$

14-0696 Wavelength = 1.5405

BPO_4
Boron Phosphate

Rad.: CuKα1 λ: 1.5405 Filter d-sp: Guinier 114.6
Cut off: Int.: Film I/Icor.: 3.80
Ref: De WolFF. Technisch Physische Dienst. Delft
The Netherlands. ICDD Grant-In-Aid

Sys.: Tetragonal S.G. I $\bar{4}$ (82)
a: 4.338 b: c: 6.645 A: C: 1.5318
α: β: γ Z: 2 mp:

Ref: Ibid

Dx: 2.809 Dm: SS/FOM:F_{18}=89(.0102 . 20)

PSC: tI12. To replace 1-519. Deleted by 34-0132. Mwt: 105.78
Volume [CD]: 125.05

d (Å)	Int	h	k	l
3.632	100	1	0	1
3.322	4	0	0	2
3.067	4	1	1	0
2.254	30	1	1	2
1.973	2	1	0	3
1.862	8	2	1	1
1.816	4	2	0	2
1.661	1	0	0	4
1.534	2	2	2	0
1.460	8	2	1	3
1.413	1	3	0	1
1.393	1	2	2	2
1.372	2	3	1	0
1.319	4	2	0	4
1.271	1	1	0	5
1.268	2	3	1	2
1.211	2	3	0	3
1.184	2	3	2	1

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