Analiza materialelor prin difractometrie de radiatii X

Obiective:

- de a cunoaste principiile de baza privind analiza WAXD
- de a cunoaste principiul de functionare a unui difractometru
- de a cunoaste performantele si posibilitatile D8 ADVANCE Bruker
- cunoasterea termenilor din literatura de specialitate
- limbaj comun cu operatorii de la laboratorul RX
- cunoasterea modului de a pregati probele aduse si de a prelua rezultatele
- cunoasterea informatiilor care se pot obtine dintr-o difractograma

Curs 1

Principiile de baza privind tehnica WAXD – Wide Angle X-Rays Diffraction

📄 Istoric

📄 Radiatia X: tuburi, spectrul continuu, spectru caracteristic, interactiunea cu substanta,

📄 Elementele de cristalografie

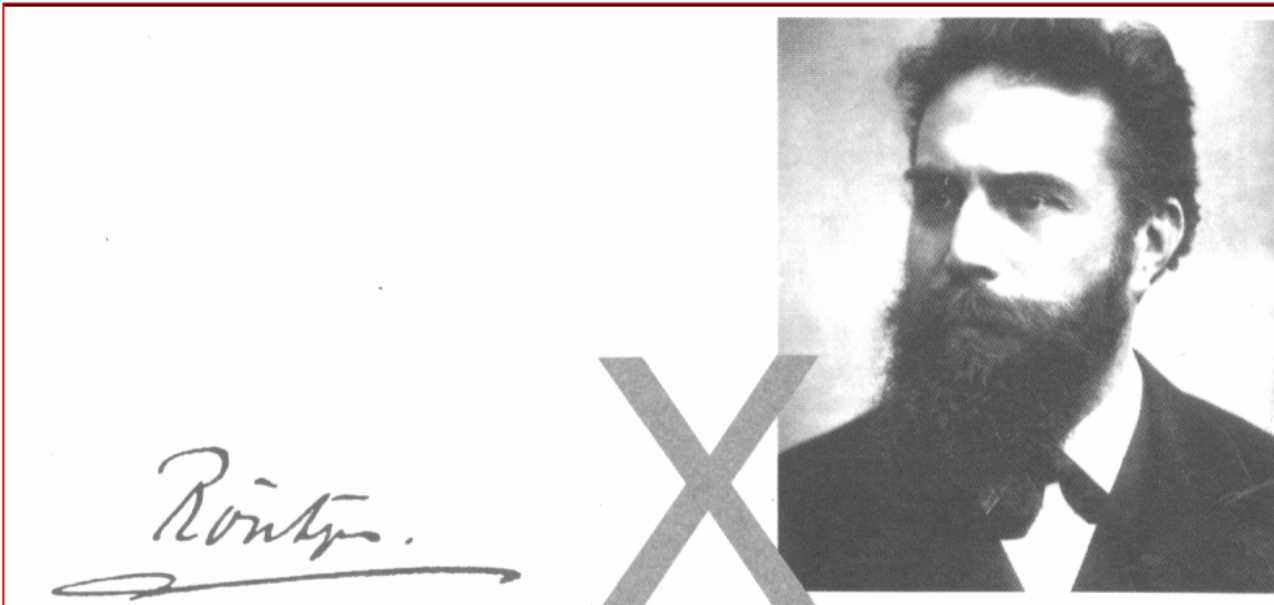📄 Conditiile pentru difractia radiatiilor X

📄 Intensitatea liniilor de difractie
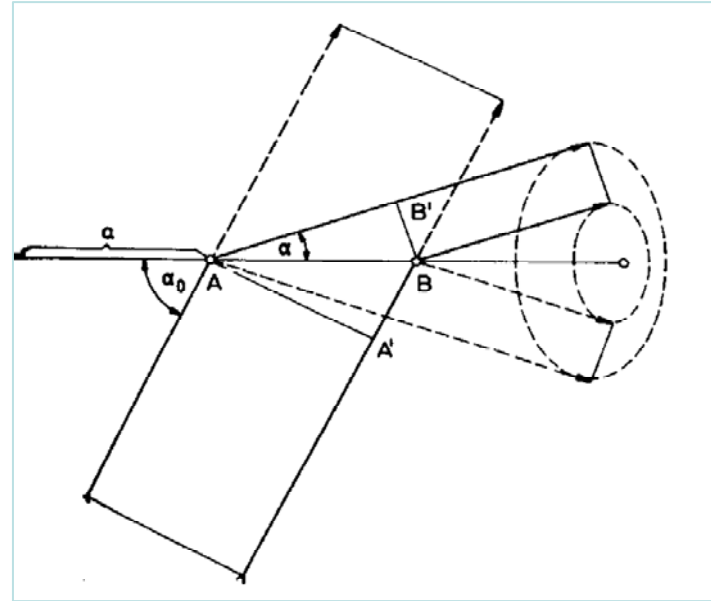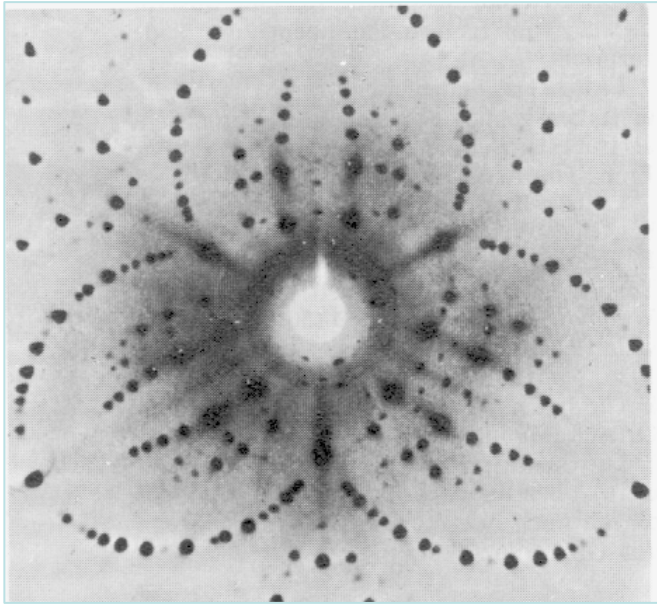
📄 Metode de analiza

Istoric (1)

Wilhelm Conrad Röntgen

**Wilhelm Conrad Röntgen a descoperit radiatiile X in 1895.
In 1901 a primit premiul Nobel in fizica.**
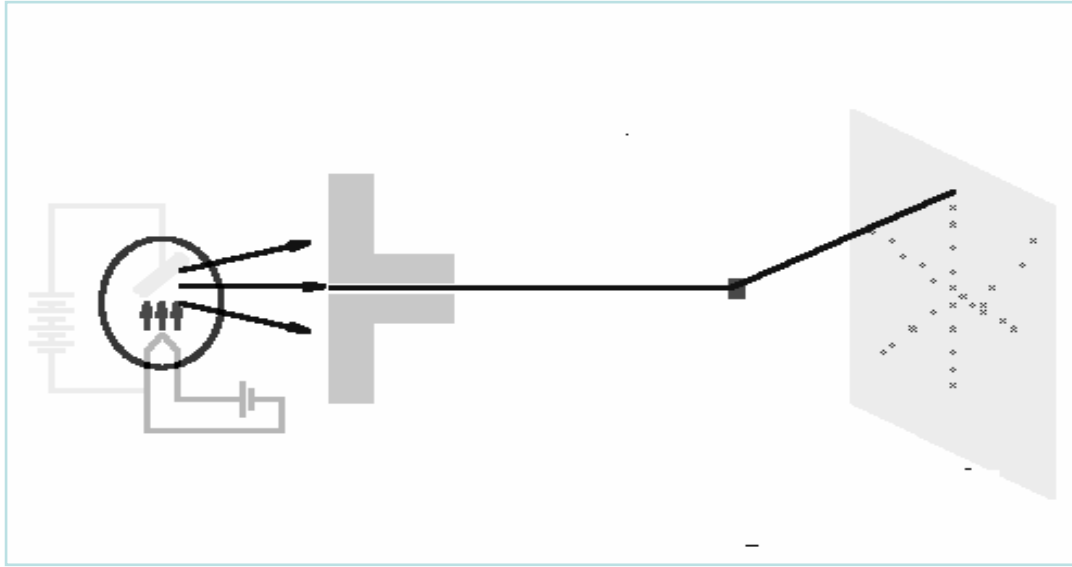
Istoric (2)
Max Theodor Felix von Laue

$$a(\cos\alpha - \cos\alpha_0) = h\lambda$$
$$b(\cos\beta - \cos\beta_0) = k\lambda$$
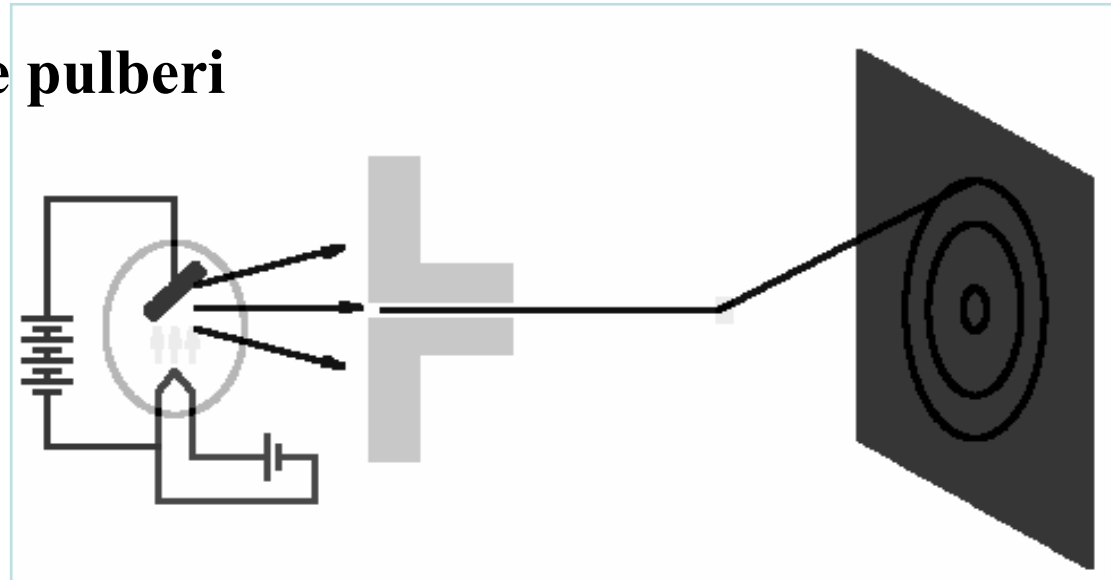$$c(\cos\gamma - \cos\gamma_0) = l\lambda$$

Istoric (3)

Experimentul lui Max Theodor Felix von Laue din 1912
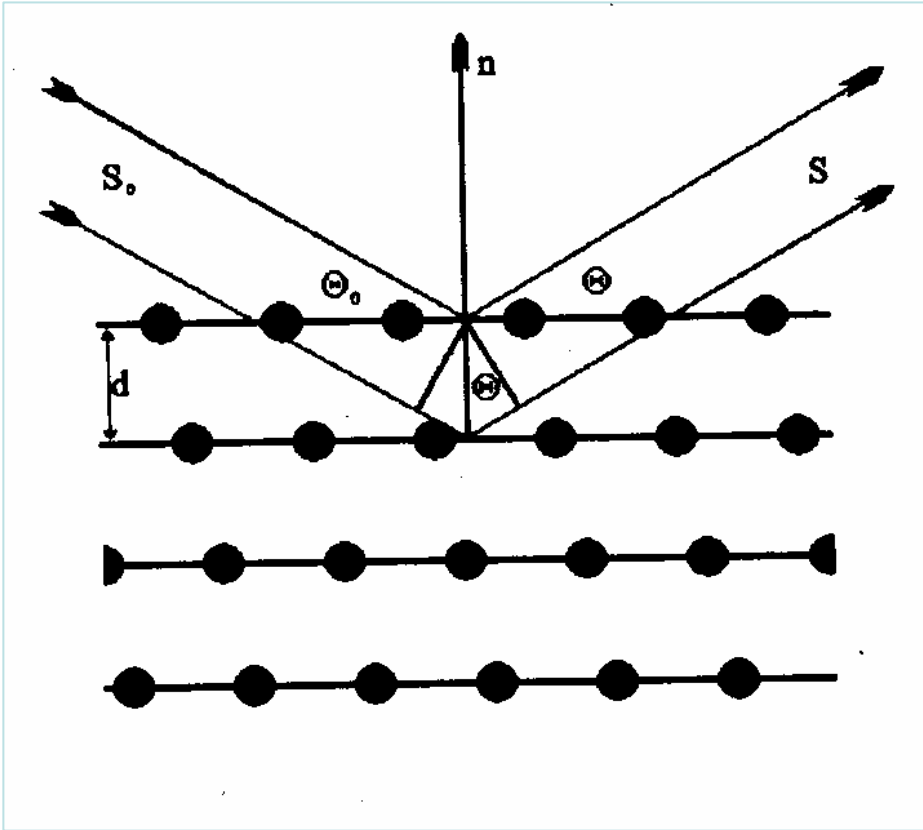**Difractia radiatiei X pe un monocristal**

Difractia radiatiei X pe pulberi

Istoric (4)

W. H. Bragg and W. Lawrence Bragg

W.H. Bragg (tatal) and William Lawrence.Bragg (fiul) au dezvoltat o relatie simpla pentru unghiul de imprastiere, numita acum
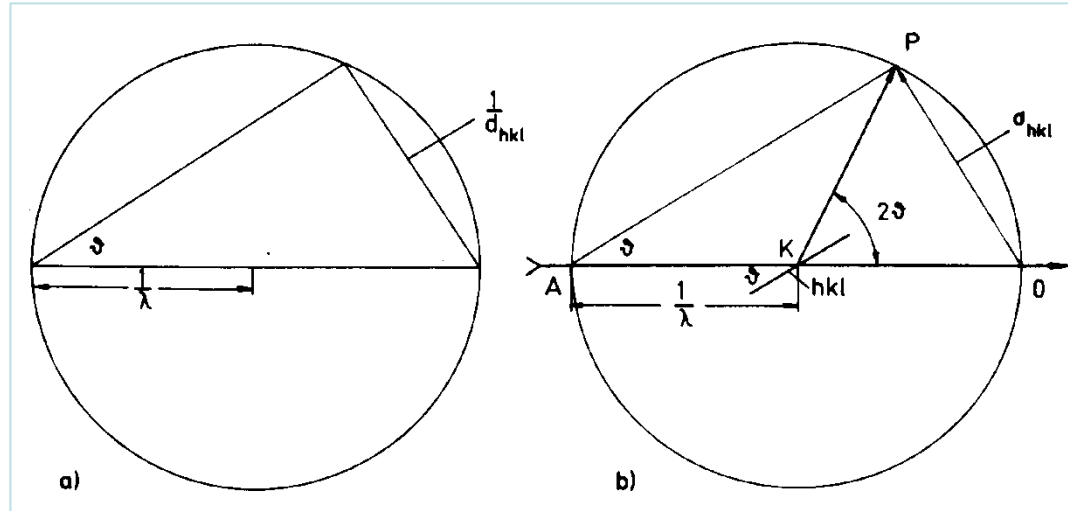
legea lui Bragg:.

$$d = \frac{n \cdot \lambda}{2 \cdot \sin \theta}$$

C. Gordon Darwin 1912, teoria dinamica a imprastierii radiatiei X pe reteaua cristalului

Istoric (5)
P. P. Ewald

P. P. Ewald a publicat in 1916 o teorie mai simpla si mai eleganta a difractiei radiatiei X, prin introducerea conceptului de retea reciproca. Prin comparare legea lui Bragg (stanga), legea lui Bragg modificata (mijloc) si legea Ewald (dreapta):

$$d = \frac{n \cdot \lambda}{2 \cdot \sin \theta} \qquad \sin \theta = \frac{1/d}{2/\lambda} \qquad \sin \theta = \frac{\sigma}{2 \cdot 1/\lambda}$$

Radiatia X – tuburi

radiatia X = unde electromagnetice, λ = 0,1÷100 A
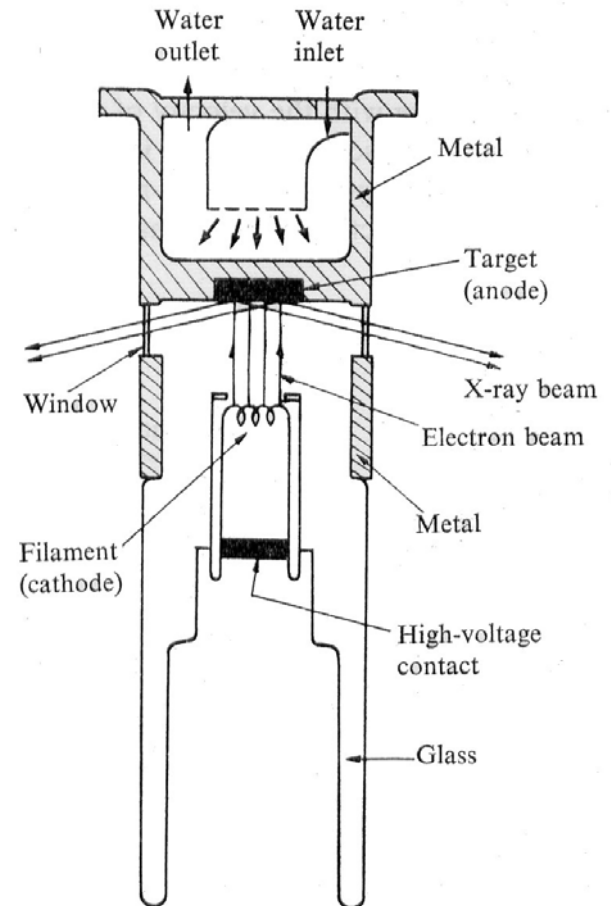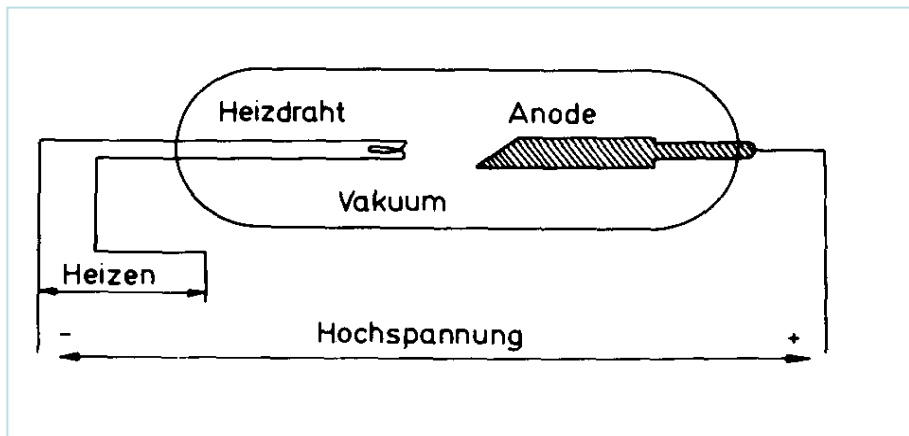
- **tuburi fixe: cu sticla, ceramice**
- tuburi rotative la P > 3kW
- **sincrotron: radiatie de putere mare, fascicul paralel, monocromatica, λ variabil, rezolutie**
  (!!! soft compatibil TOPAZ)

$U = 10 \div 200$ kV

analiza structurala: focar liniar Gotze, $1{\times}10$ mm^2, $6°$

sursa liniara: $0{,}1{\times}10$ mm^2

sursa punctiforma: $1{\times}1$ mm^2

Radiatia X – spectrul continuu

$$\Delta E = (m/2) \cdot (v_1^2 - v_2^2) = h\nu \qquad \lambda_{min}[A] = \frac{12,4}{V(kV)}$$

nu depinde de materialul anodului tinta

$$I = \alpha \cdot i \cdot Z \cdot V^2 \qquad \text{(intensitatea integrala)}$$

Electron ejectat (incetinit si cu directia schimbata)

Electron incident rapid

electroni

nucleu

X-ray

Atom din materialul anodei

9
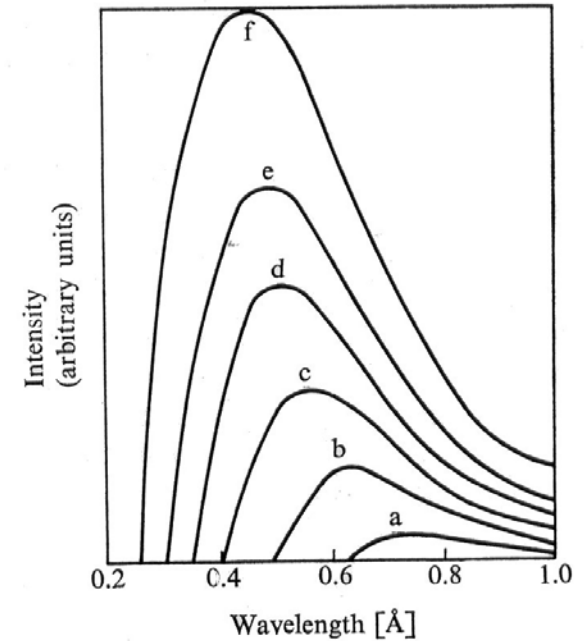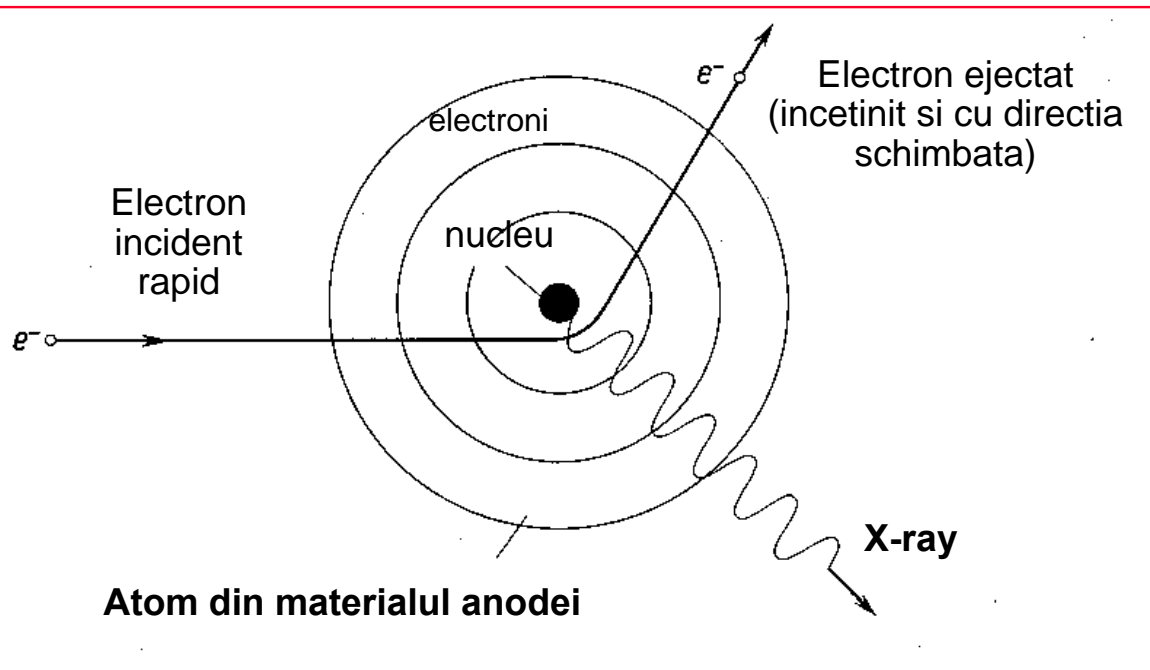
Radiatia X – spectrul caracteristic (1)
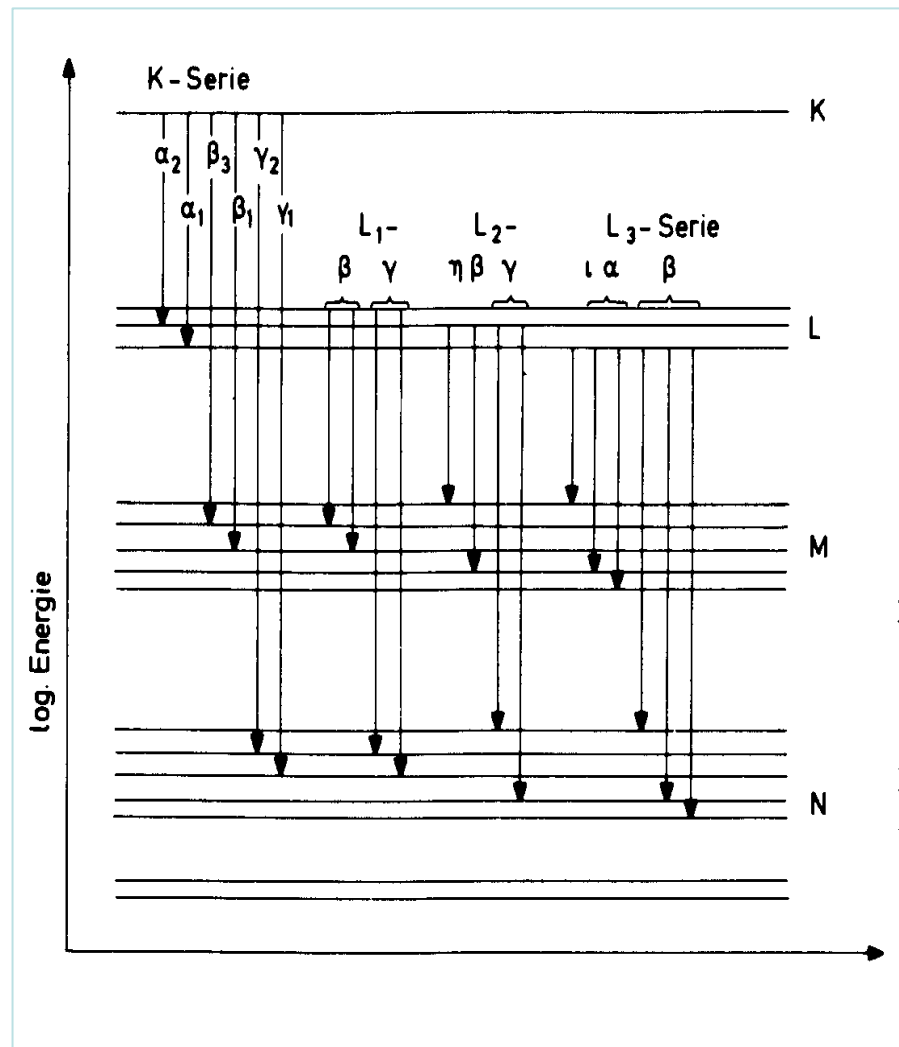
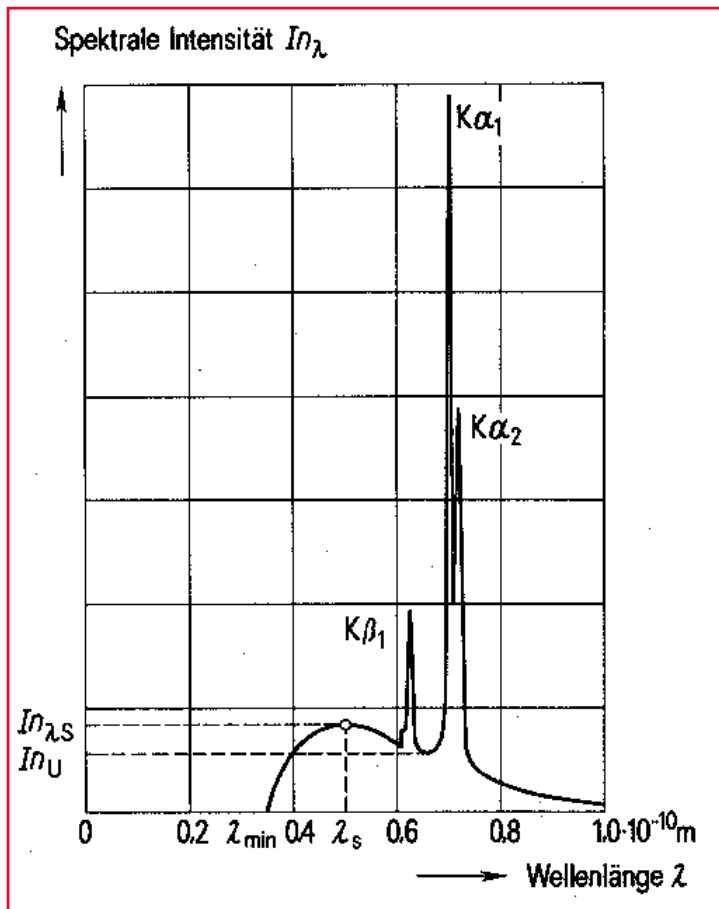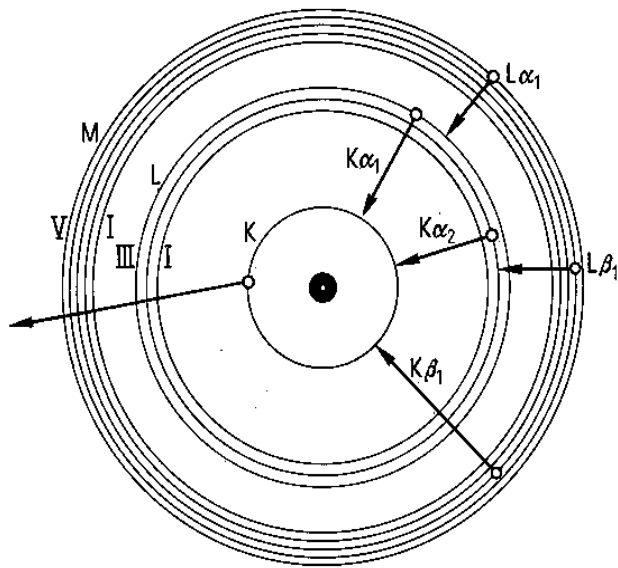$$E_i - E_f = h \cdot \nu = \frac{h \cdot c}{\lambda} \qquad I = Ai(V - V_k)^{1,5}$$
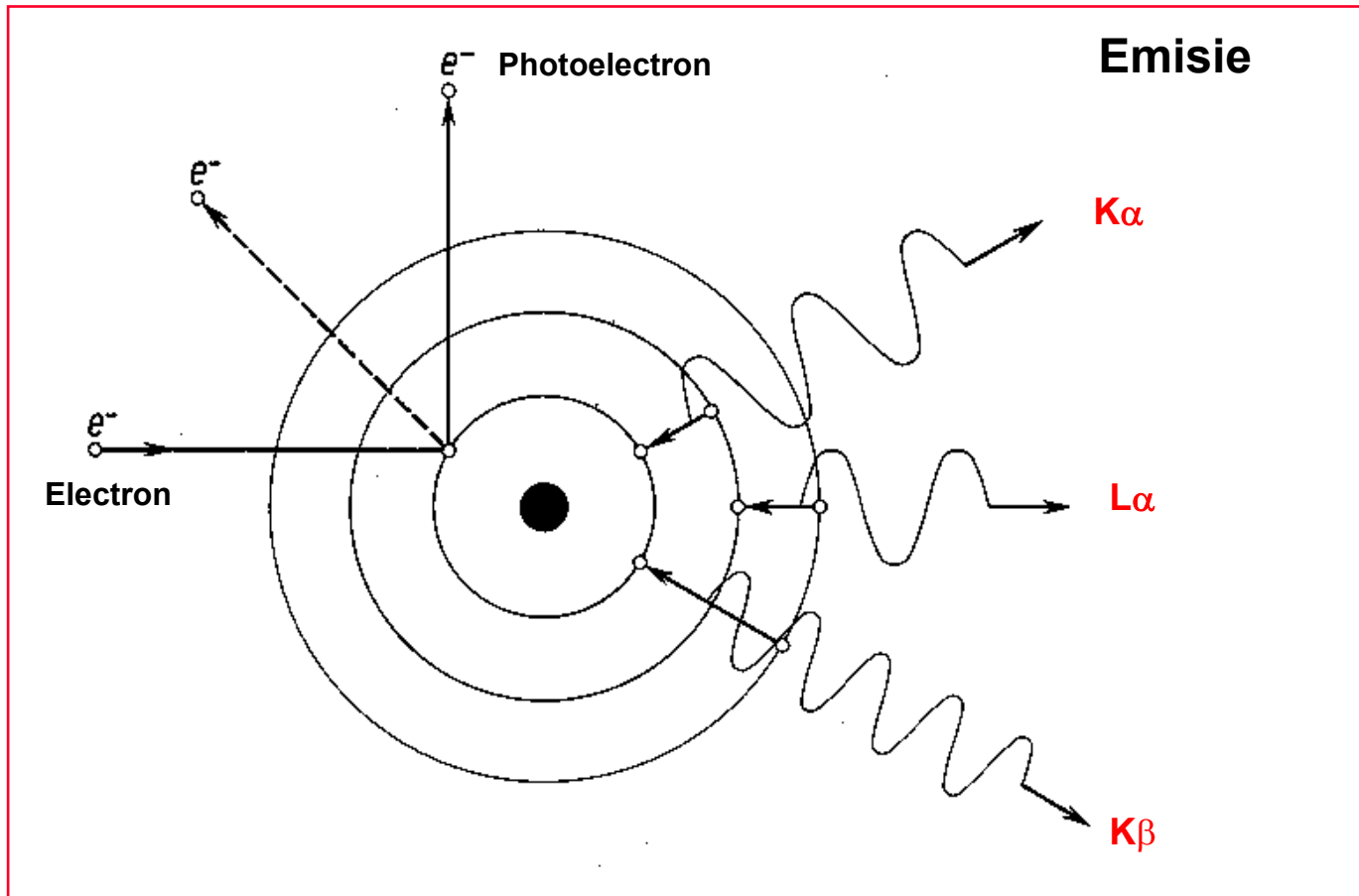
Radiatia X – spectrul caracteristic (2)

$$V = (3,5 \div 5) \times V_k \quad (kV)$$

pentru Cu: $\quad V = (3,5 \div 5) \times 9 \quad (kV)$

Radiatia X – spectrul caracteristic (3)

Modelul Bohr
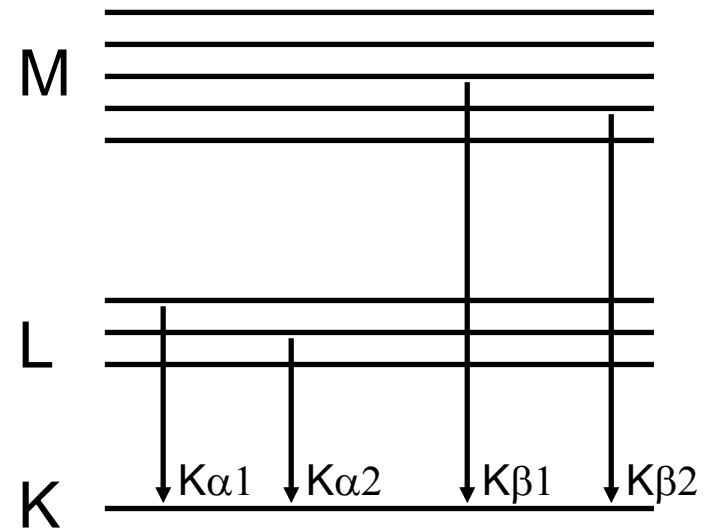
$K\alpha1$ $K\alpha2$ $K\beta1$ $K\beta2$

Raportul intensitatilor:

$K\alpha1 : K\alpha2 : K\beta = 10 : 5 : 2$

12

Radiatia X – spectrul caracteristic (4)

Lungimi de unda tipice:

Anode	Activation [kV]	Wavelength	λ [Å]	Filter	[mm]
Mo	20.0	$k\alpha1$ $k\alpha2$ $k\beta1$	0.7093187(4) 0.713609(6) 0.632305(9)	Zr	0.081
Cu	8.981	$k\alpha1$ $k\alpha2$ $k\beta1$	1.540598(2) 1.544426(2) 1.39225(1)	Ni	0.015
Co	7.709	$k\alpha1$ $k\alpha2$ $k\beta1$	1.78901(1) 1.79290(1) 1.62083(2)	Fe	0.012
Fe	7.111	$k\alpha1$ $k\alpha2$ $k\beta1$	1.93609(1) 1.94003(1) 1.75665(2)	Mn	0.011
Cr	5.989	$k\alpha1$ $k\alpha2$ $k\beta1$	2.28976(2) 2.293663(6) 2.08492(2)	V	0.011

Radiatia X – interactiunea cu substanta

- **radiatie transmisa: legea absorbtiei Beer**

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

- **caldura**

- **radiatia X de fluorescenta (secundara): spectru caracteristic $\Rightarrow$ creste fondul**

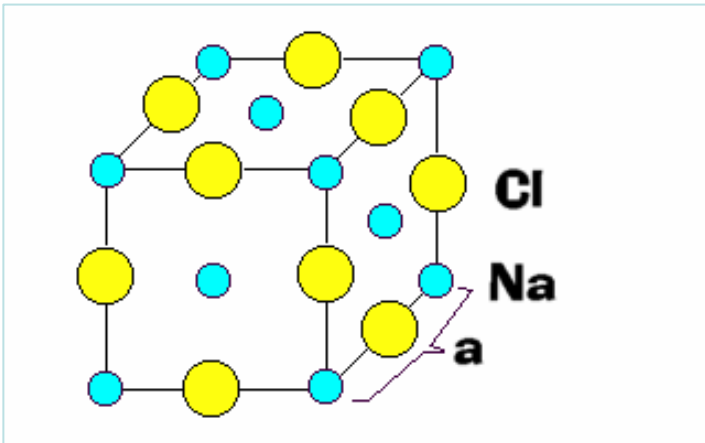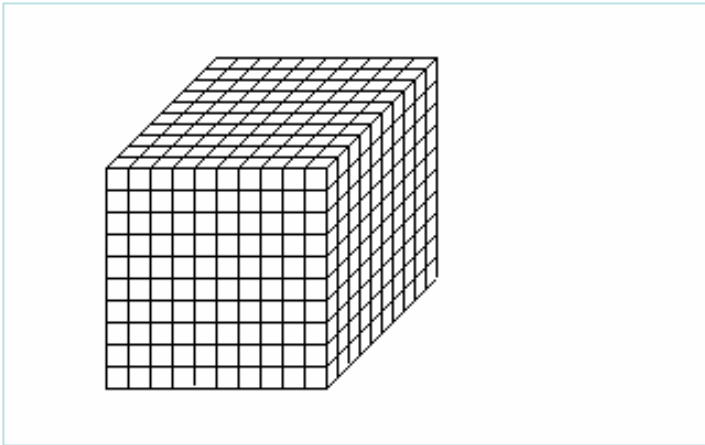- **emisia de electroni: de recul (Compton) + fotoelectroni (Auger)**

- **radiatie imprastiata incoerent (efectul Compton):**

$$\Delta\lambda = \frac{h}{m \cdot c}(1 - \cos 2\theta)$$

- **radiatie imprastiata coerent: J.J. Thompson (teoria undelor electromagnetice):**

$$I = I_0 \frac{e^4}{r^2 m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2}$$

Elemente de cristalografie (1)

Crystal and Unit Cell –celula elementara

- Crystalline materials show a 3D translatorically periodic structure.

- An ideal crystal is formed by unit cells of the same size consisting of atoms arranged in an identical manner

- The size and shape of a unit cell are described by the lattice parameters, which are the length of the edges and the angles between them.

Elemente de cristalografie (2)
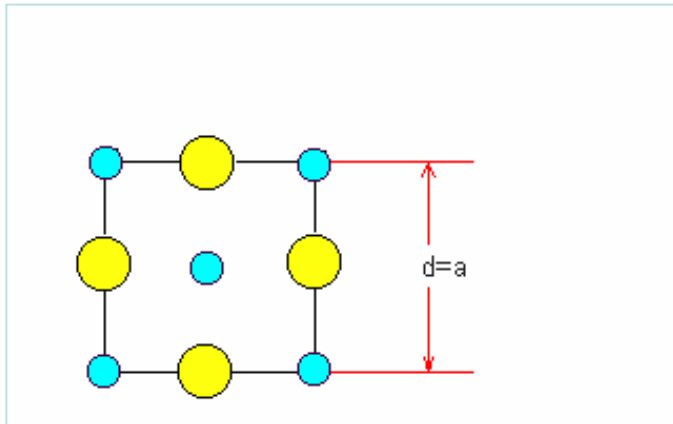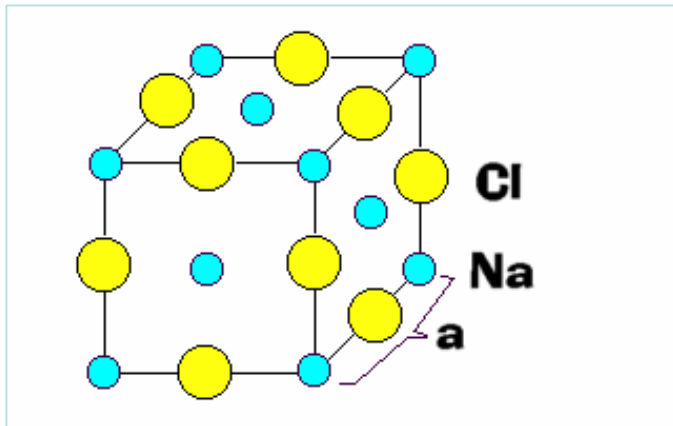
a = b = c

$\alpha = \beta = \gamma = 90^{o}$

c

a

α

β

γ

b
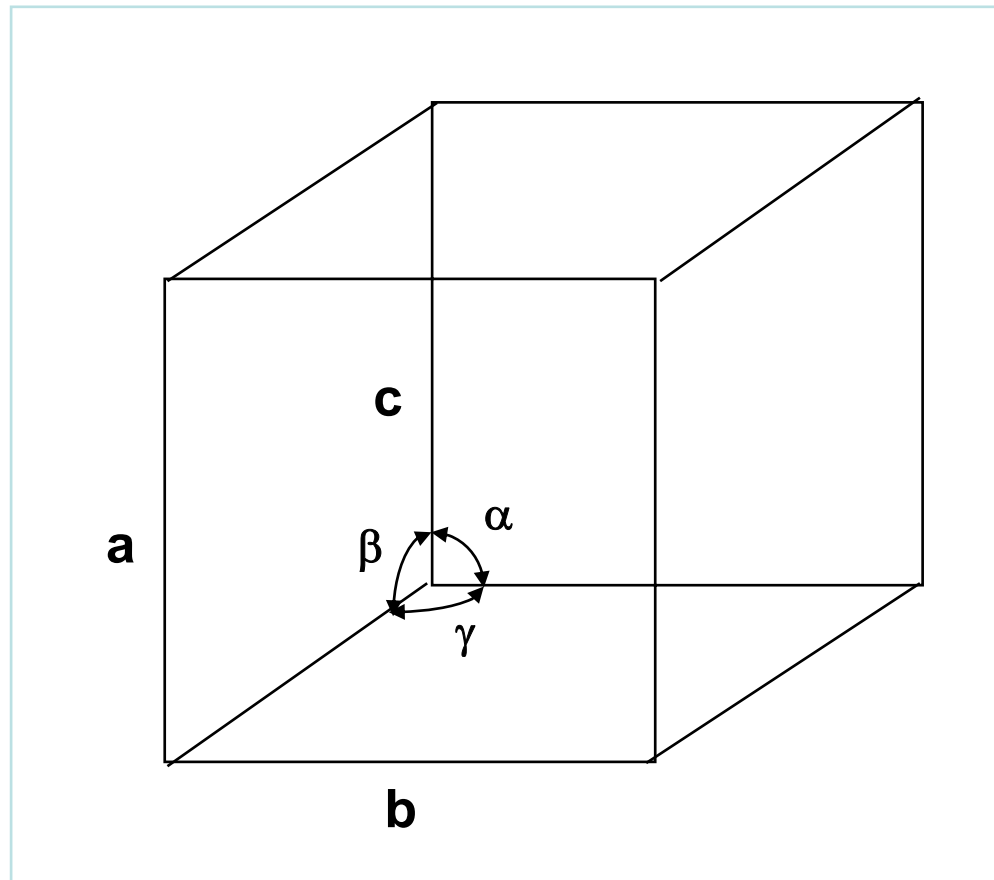
cubic

Elemente de cristalografie (3)

| Crystal systems	Axes system
cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$
Rhomboedric	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$
Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$
Triclinic	$a \neq b \neq c$, $\alpha \neq \gamma \neq \beta°$

Elemente de cristalografie (4)

- **The distances between the lattice planes according to Bragg's model may be derived from the size of the unit cell.**

- **A family of lattice planes will show the periodicity of the corners of the unit cell.**

- **Two opposite faces of the unit cell form a pair of planes of a family of lattices planes. Their shortest distance is indicated as a.**

Elemente de cristalografie (5)

Let us look at a cubic unit cell, projected in the direction of the c-axis (a_3-axis):
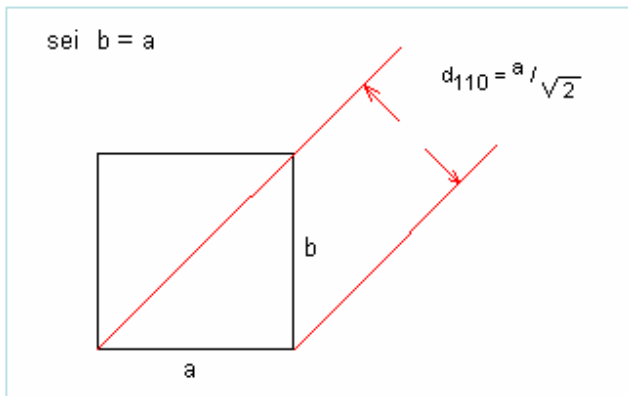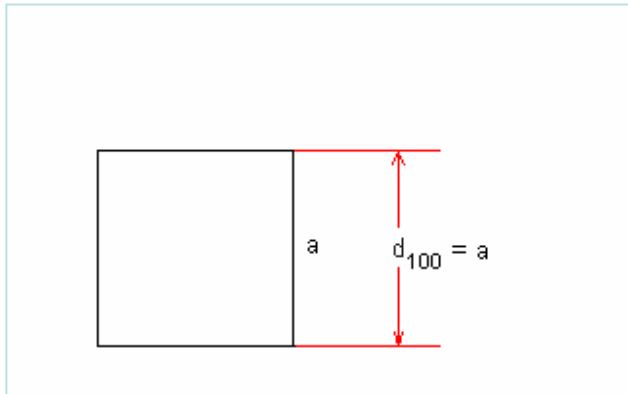
- You see the plane set up by the a- and b-axis (a_1, a_2-axis). Here b=a is valid.

- You may also find other lattice planes, which do not share the faces of the cubic cell.

- After Miller the distances of a family of lattice planes are named after the reciprocal intersections with the axes.

- The indices of a (family of) lattice plane(s) are written like other indices - for example d_{100}.

- The indices are named h, k and l.
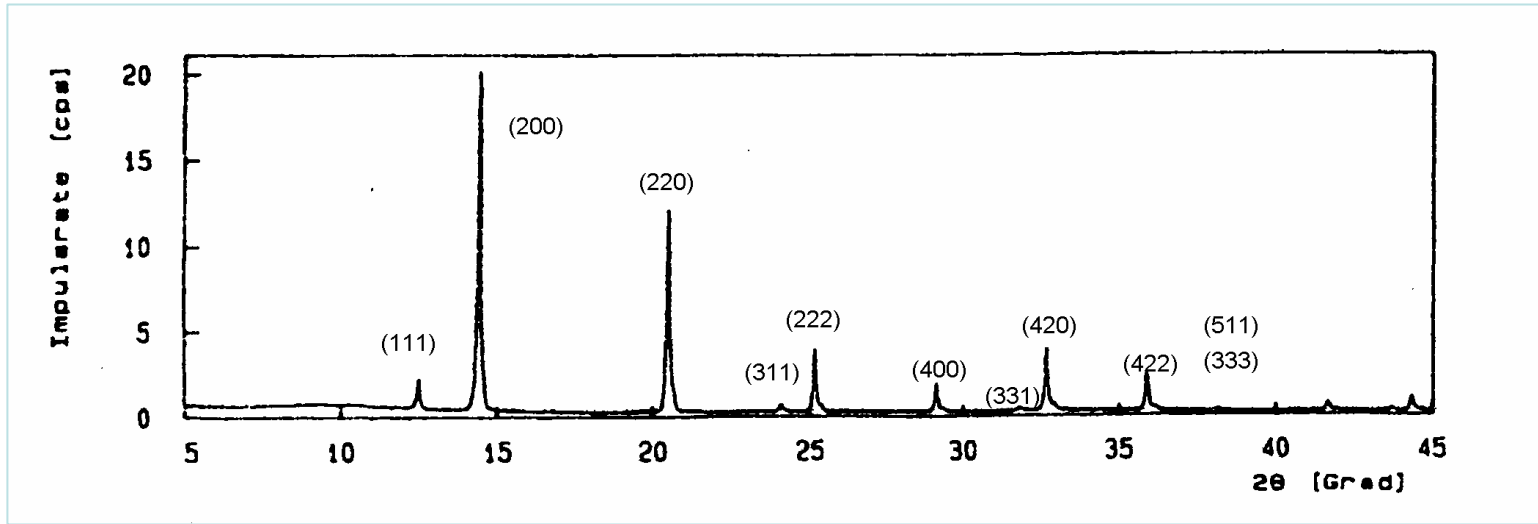
- **Each peak of a pattern of a crystalline phase may be described by its Miller's indices.**

- **Some peaks will have an identical or nearly identical position in the pattern. In cubic crystals this happens for the (333) and (511) peak. Peaks like this are named 'multiple indexed'.**

Bragg´s law

$$\lambda = 2\ \mathbf{d}\ sin\ \theta$$

- The wavelength is known
- Theta is the half value of the peak position
- d will be calculated

Equation for the determination of the d-value of a tetragonal elementary cell

$$1/\mathbf{d}^2 = (\mathbf{h}^2 + \mathbf{k}^2)/\mathbf{a}^2 + \mathbf{l}^2/\mathbf{c}^2$$

- h,k and l are the Miller indices of the peaks
- a and c are lattice parameter of the elementary cell
- if a and c are known it is possible to calculate the peak position
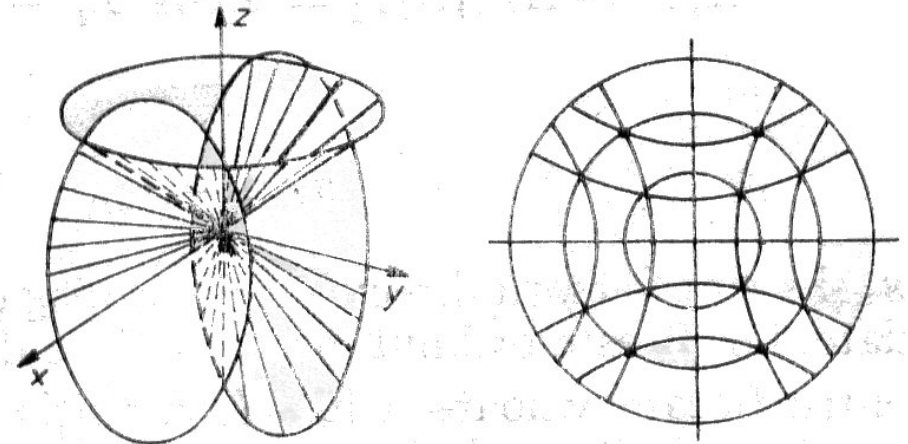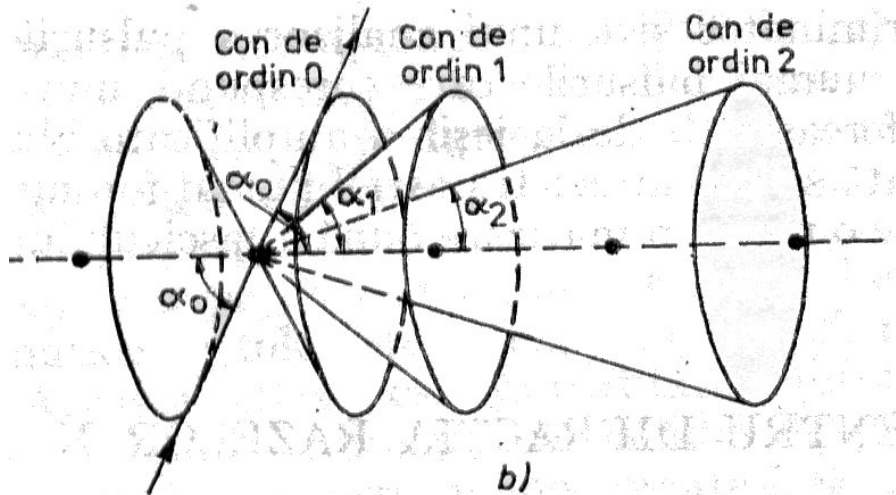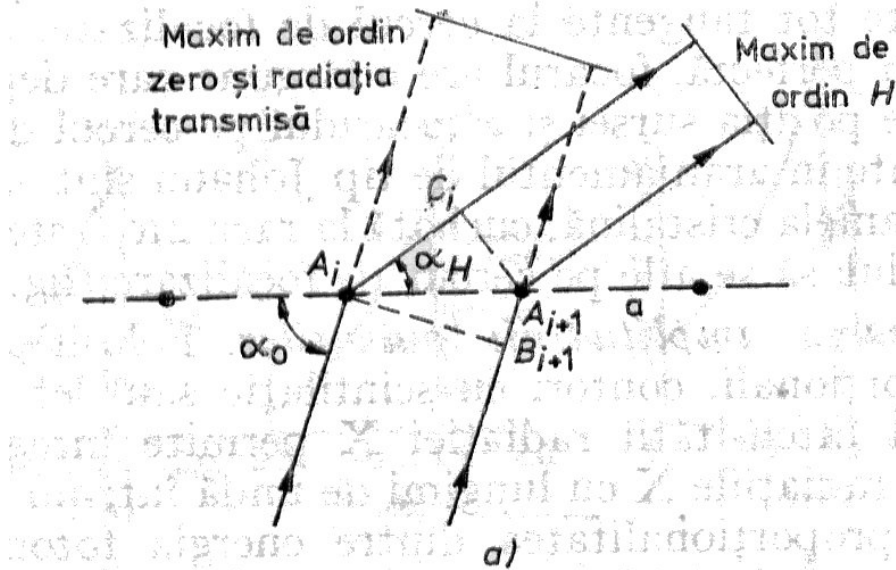- if the peak position is known it is possible to calculate the lattice parameter

Conditiile pentru difractia radiatiilor X (1)

Ecuatiile Laue:

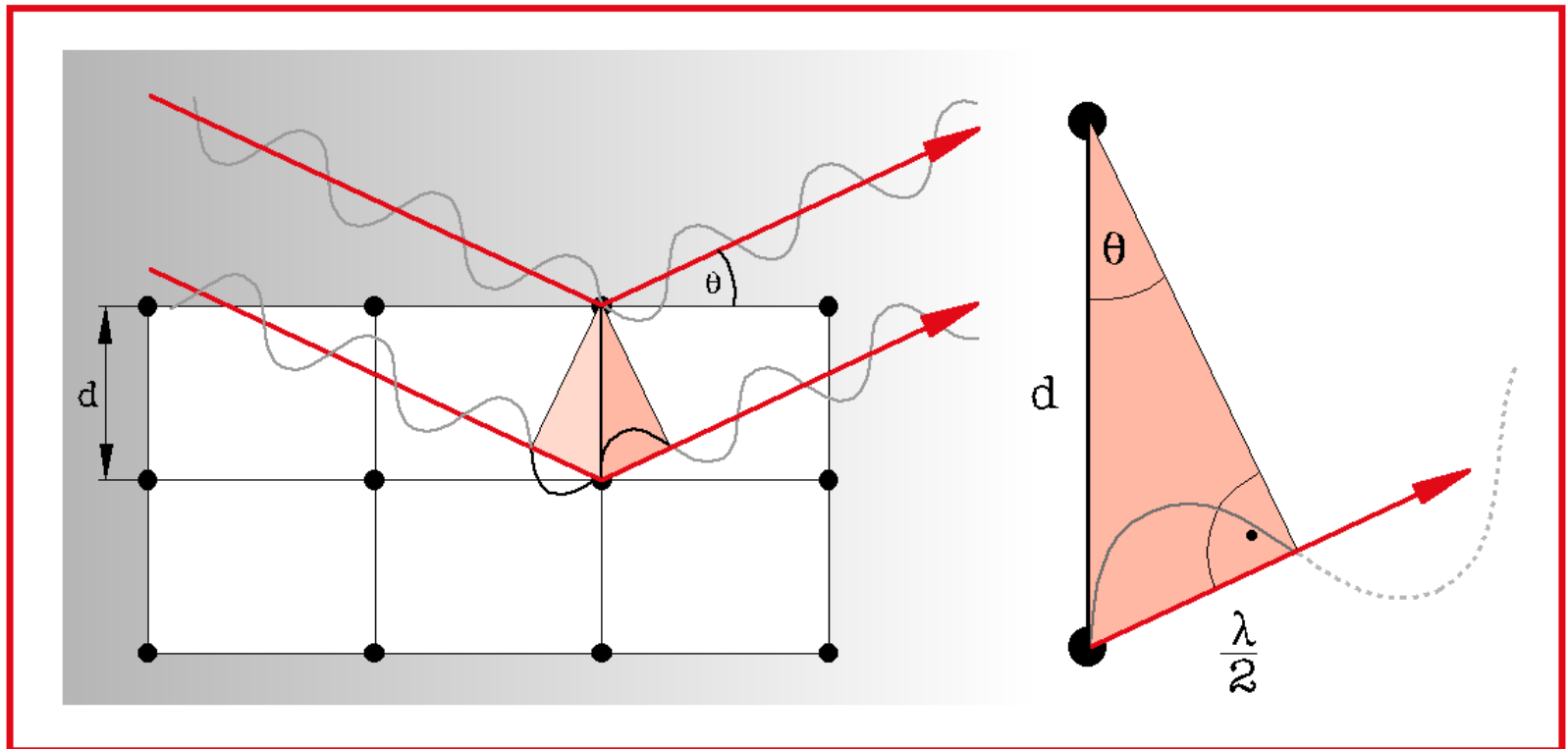$$a(\cos \alpha_H - \cos \alpha_0) = H \cdot \lambda$$

$$b(\cos \beta_K - \cos \beta_0) = K \cdot \lambda$$

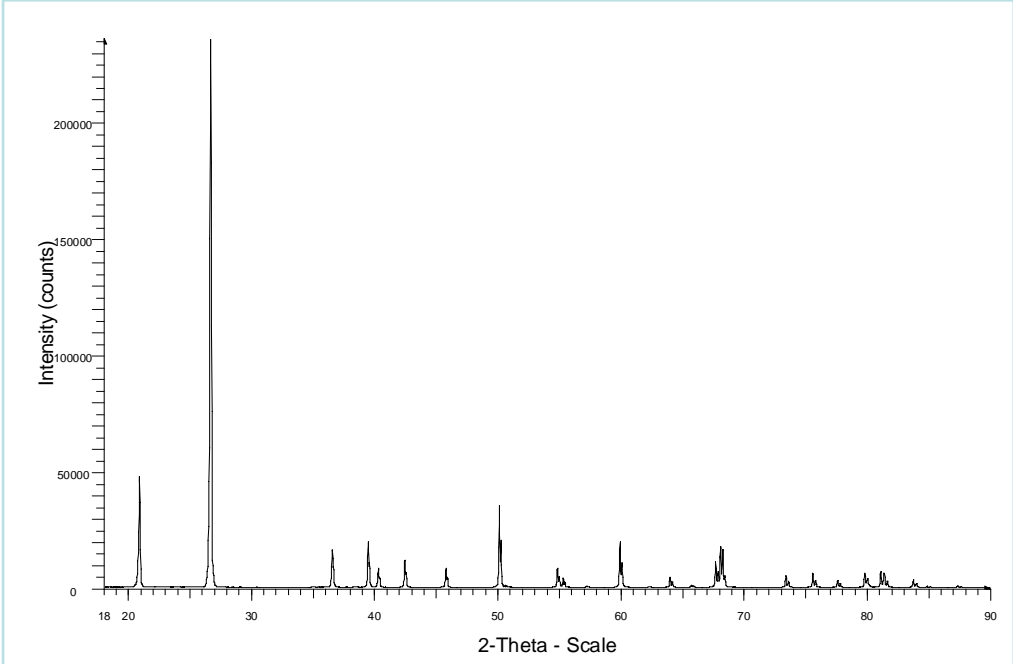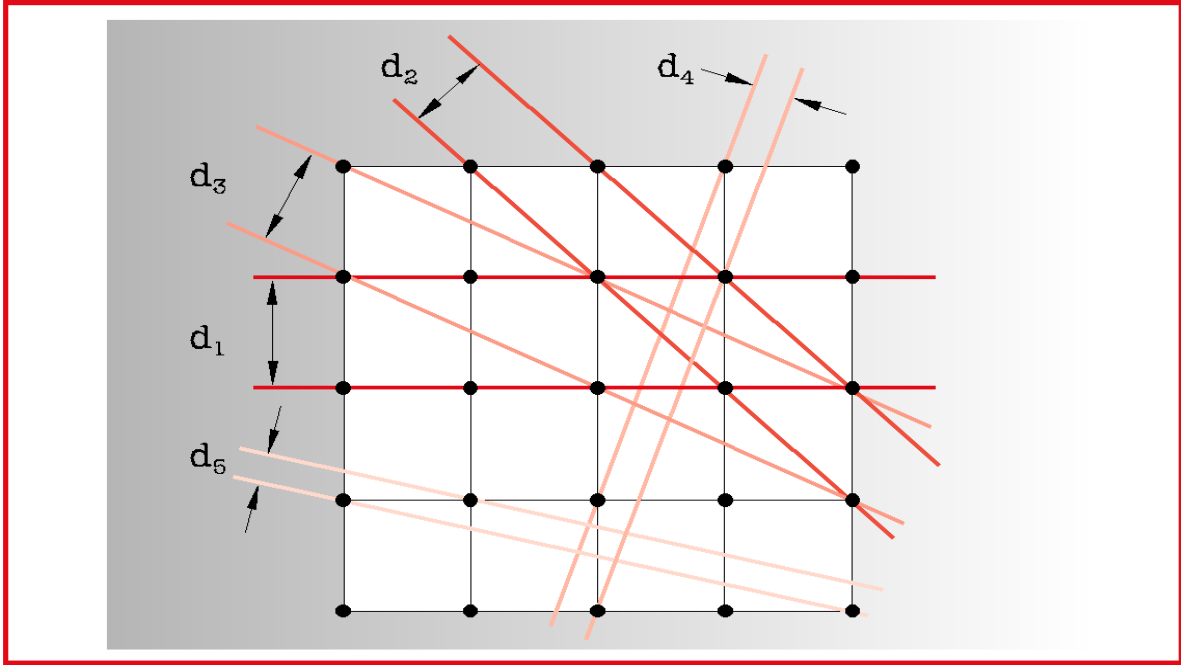$$c(\cos \gamma_L - \cos \gamma_0) = L \cdot \lambda$$

Conditiile pentru difractia radiatiilor X (2)

Ecuatiile Bragg:

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

Conditiile pentru difractia radiatiilor X (3)

Intensitatea liniilor de difractie

❑ **factorul de polarizare:**
$$I = I_0 \frac{e^4}{r^2 m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2}$$

❑ **factorul atomic de imprastiere: raportul intre amplitudinea undei imprastiata de un atom si amplitudinea undei imprastiata de un electron (pozitionarea spatiala a electronilor)**
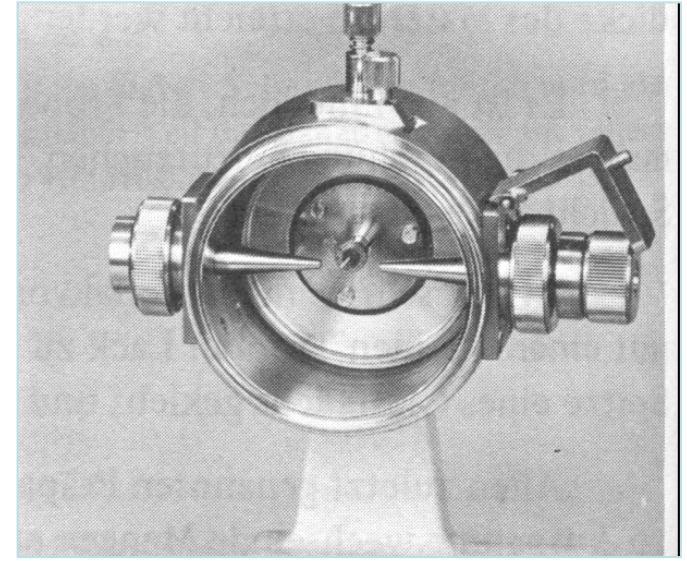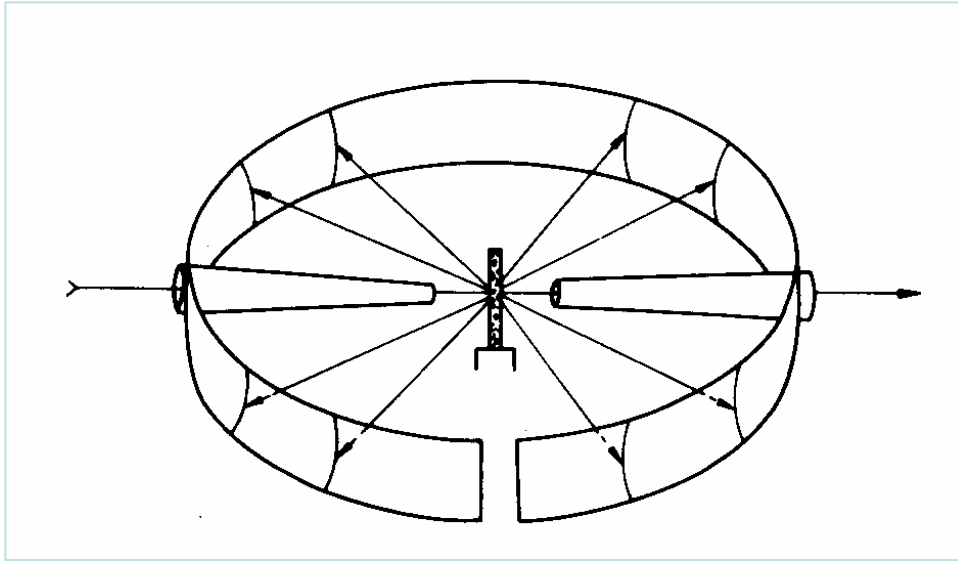
❑ **factorul de temperatura**

❑ **factorul de structura**

❑ **factorul de multiciplitate**

❑ **factorul de absorbtie**

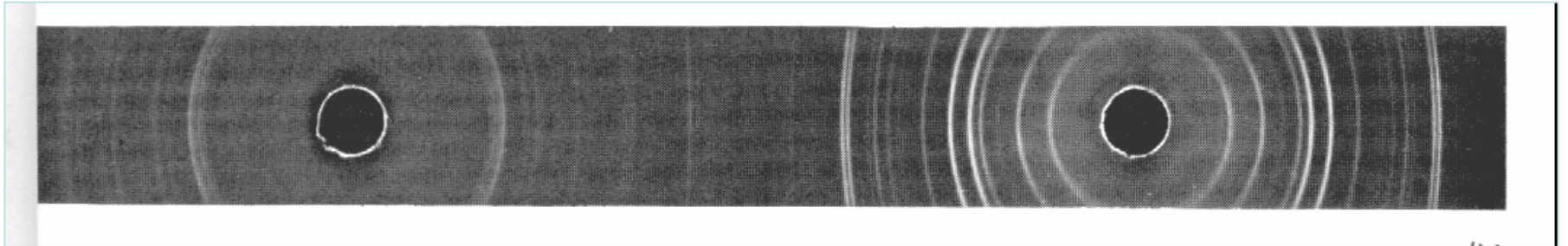❑ **factorul Lorentz (paralelism, monocromatic)**

!!! Programele soft trebuie sa tina seama de toti acesti factori

Metode de analiza (1)

Pulberea este pusa pe o fibra de sticla, intr-un capilar de sticla

- Ca detector se utilizeaza un film sensibil la radiatii X, montat ca on cilindru in jurul probei.
- Se utilizeaza colimatoare (+ vid) pentru a evita imprastierea pe aer.

$$d = \frac{n \cdot \lambda}{2 \cdot \sin \theta}$$

26