Structural rentgenography I
Introduction
Diffraction of X-ray on the crystal lattice

Nanomaterials characterization I

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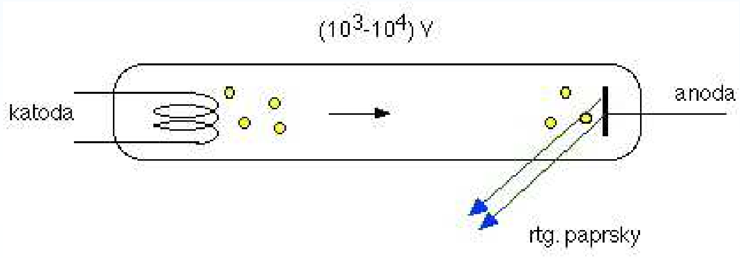
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Study of crystal structure

- Electron, neutron, X-ray photon diffraction
- Crystal $\equiv$ ideal grating for X-ray diffraction (1912), $\lambda_{rtg} \cong a$
- Development of structural rentgenography $\rightarrow$ Bragg jr., Bragg sr., Von Laue, Debye, Scherrer

X-ray formation, spectra properties

- λ_{rtg} = 1,2 nm ÷ 5 pm
- Source: vacuum tube, cathode, anticathode, difference of potential to 104 V,
impact of fast electron emitted from cathode to anticathode → X-ray formation
- → spectrum
  - a) line - characteristic
  - b) continuous



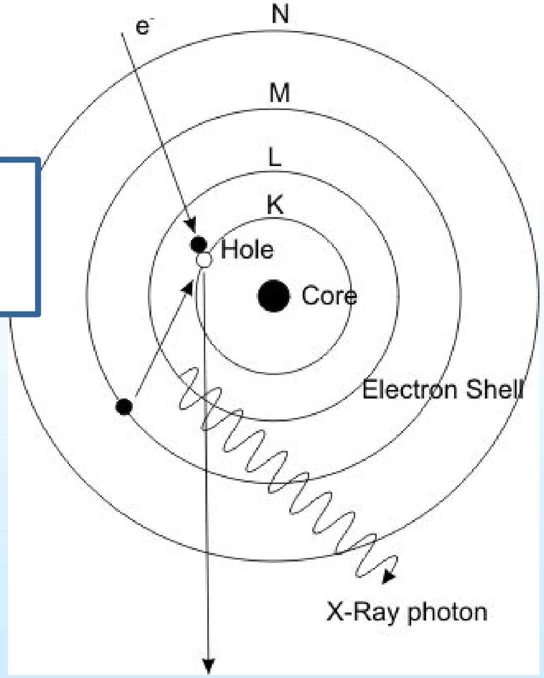
W. C. Roentgen, X-ray discovery in 1895

Continuous spectrum $\rightarrow$ electron braking in the material of the anticathode $\Rightarrow$ all possible frequencies are emitted ($\Rightarrow$ continuity of spectra). Relations: $I \sim Z$, $I \sim U^2$

Characteristic (line) spectrum

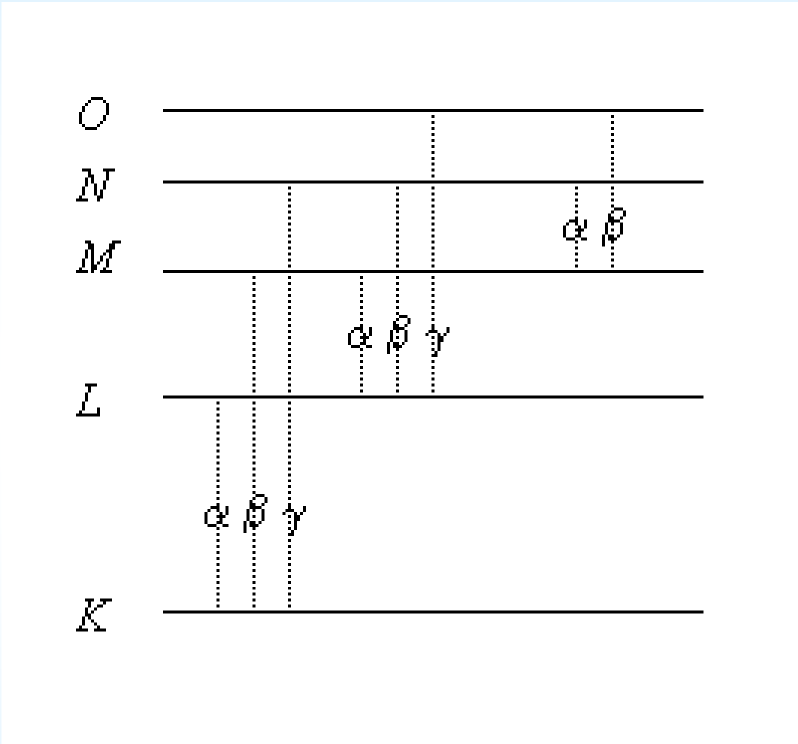
Formation: an impacted electron kicks out other electron from an anticathode electron shell, an electron from higher level pass to a vacancy $\rightarrow$ energy difference is emitted as X-ray photon with energy

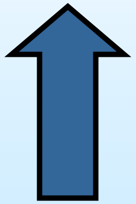
$$h\nu = E_K - E_P$$



Transitions are realized between pairs of states from discrete levels $\Rightarrow$ line spectrum (λ_{rtg} is given as levels difference)

Charakteristic spectrum - marking of lines





Spectra marking → according to emitted electron shell → series K,L,M …see pic.

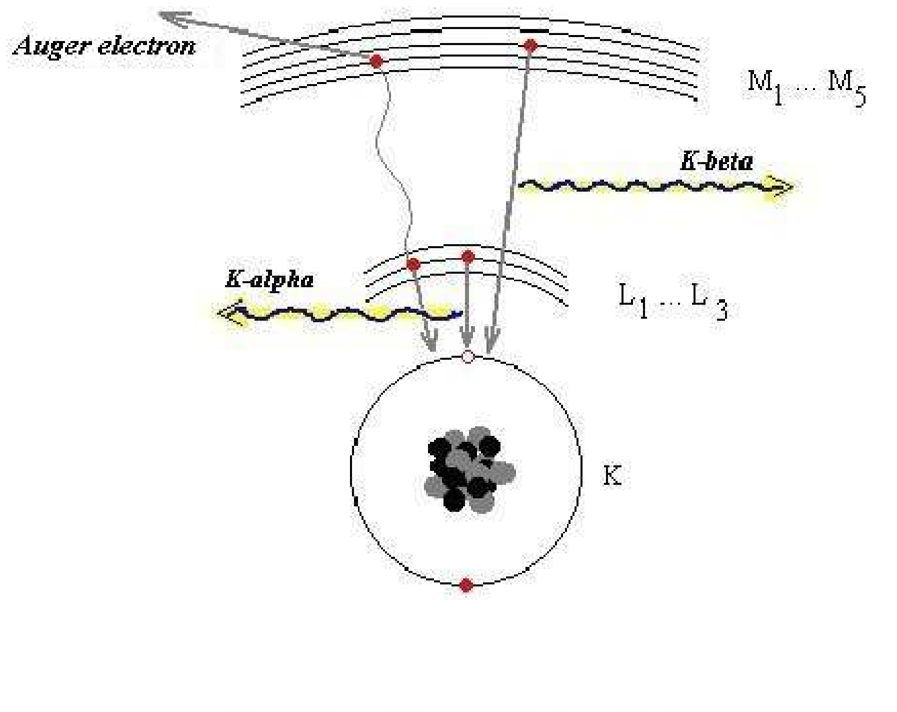
Emission of electron from K shell → series $K_{\alpha,\beta,\gamma,\delta}$ formation, emission of electron from L level → series $L_{\alpha,\beta,\gamma,\delta}$ formation, etc.

Charakteristic spectrum - splitting of levels

Interaction of atoms in solid matter ⇒ **splitting of levels**: $L \rightarrow L_I\ L_{II}\ L_{III}$ $M_I \ldots M_V$, $N_I \ldots N_{VII}$

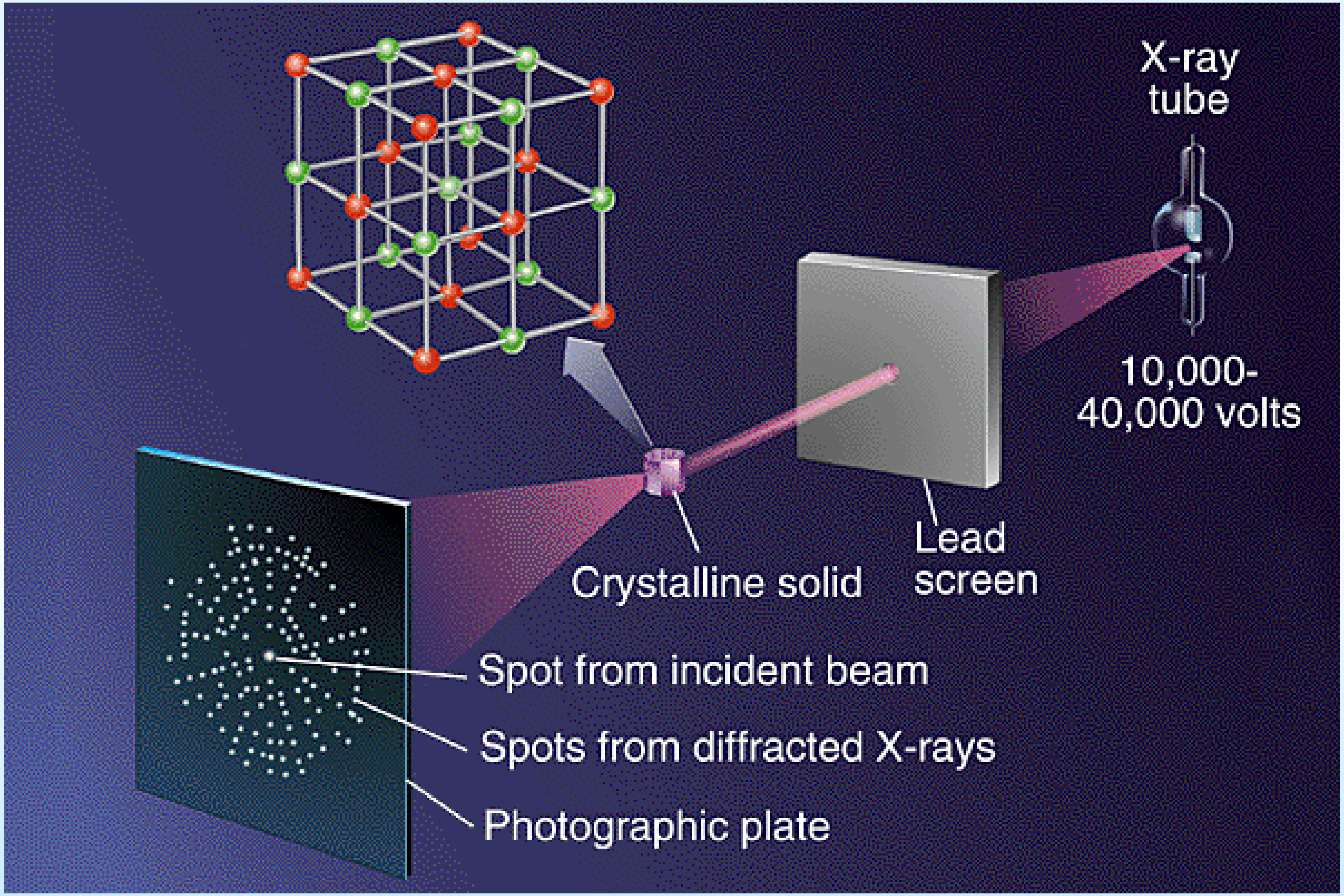
Line formation $K_{\alpha I}, K_{\alpha II} \ldots K_{\beta I}, K_{\beta II} \ldots$ etc.

Allowed transitions - **selection rules**



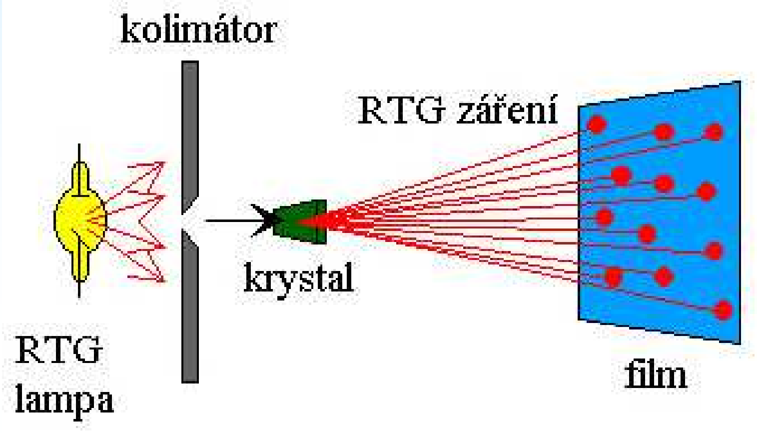
Production of Characteristic Radiation

X-ray using for crystal structure study - structural crystalography



X-ray diffraction on crystal - history

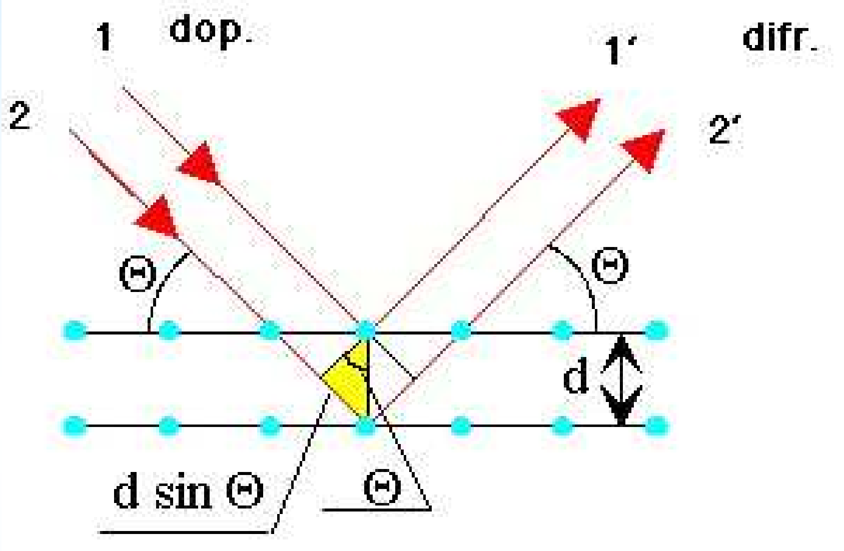
- First experiments (Von Laue) → diffraction pattern
- Diffraction spots distribution analysis (Bragg):
- Crystal ≡ set of planes, each of them scatters a small amount of X-ray
- Intensity of final scatter is sufficient for spot formation ⇔ interference of waves from all planes
- Phase difference of scattered waves are important



➤ Terms are defined in **Bragg´s law** → see next → → → → → →

Bragg´s law

Bragg´s law →
diffraction as reflection on crystal planes



⇒ **interference** arises ⇔ waves scattered on parallel crystal planes have the same phase (if their trajectory difference is equal n-multiple λ)

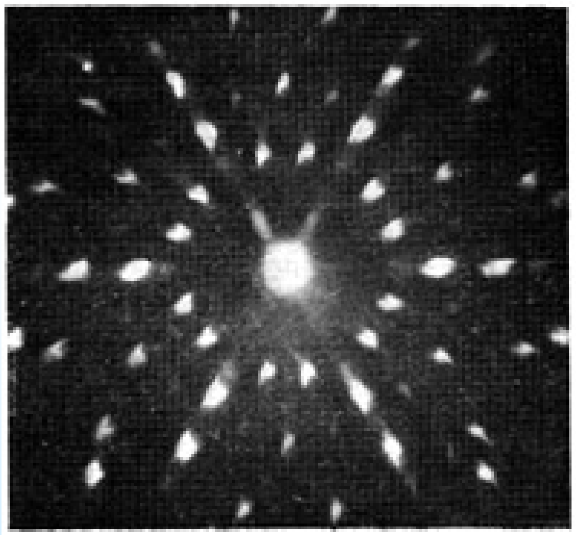
So :

$$2d_{hkl}\sin\Theta = n\lambda$$

Equation is fulfiled for definite values Θ !

Interpretation of diffractograms, reciprocal lattice

- Microscopic view ≡ image of original (direct) lattice, i.e. factual crystal structure
- By contrast: diffraction pattern (diffractogram) **does not represent** the real lattice!
- Two lattices are connected with every crystal structure – **direct** and **reciprocal**



Reciprocal lattice

- Direct lattice and reciprocal lattice $\rightarrow$ abstract construction in different type spaces (they do need to have the same origin neither scale)
- Reciprocal space $\equiv$ conjugate Fourier´s space
- Fourier´s analysis based on connection of crystal properties and electron density $n(\vec{r})$
  $\rightarrow$ electron density $\equiv$ periodical function with period $\vec{a}$
  $\rightarrow$ elaboration to Fourier´s progression is possible (electron density as progression coefficient)
- calculations of diffraction theory are based on elaboration of electron density to Fourier´s progression (amplitude of elastic scattered radiation depends on Fourier´s coefficients of electron density)

Reciprocal lattice

≡ abstract spatial construction for diffractograms interpretation; is given by basic translation vectors A, B, C (these can be defined by means of direct lattice vectors a, b, c):

$$\vec{A} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a}.\vec{b} \times \vec{c}}$$

$$\vec{B} = 2\pi \frac{\vec{a} \times \vec{c}}{\vec{a}.\vec{b} \times \vec{c}}$$

$$\vec{C} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a}.\vec{b} \times \vec{c}}$$

Planes of DL are accordant with points of RL,
points of DL ≡ planes of RL

So: **Each point (hkl) in the reciprocal lattice corresponds to a set of lattice planes (hkl) in the direct lattice**

Each of reciprocal lattice vectors is possible to write:

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

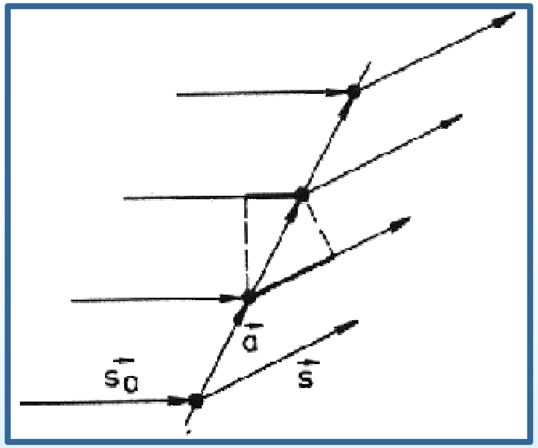
Application of Bragg´s law for 3-dim lattice → Laue´s equations

- Interference of beams in 3-dim lattice → parameters a, b, c;

  three lines of nodal points → analogical term for **every direction**:

$$\vec{a}\left(\cos\Psi_a - \cos\Phi_a\right) = h\lambda$$
$$\vec{b}\left(\cos\Psi_b - \cos\Phi_b\right) = k\lambda$$
$$\vec{c}\left(\cos\Psi_c - \cos\Phi_c\right) = l\lambda$$

Laue´s equations



1-dim lattice, periode a

- h, k, l…Laue´s indexes – they describe degree of reflection

Geometric interpretation of Laue´s equations

- Transcription of equations to vector form $\rightarrow$ by **wave vector k**

$$\vec{k} = \left(\frac{2\pi}{\lambda}\right)\cos\Phi$$

$\rightarrow$ cos Φ, cosΨ is possible to formulate through the use of wave vector impacted and diffracted beam $\vec{k}, \vec{k}^{|}$

- Then

(*)

$$\vec{a}\left(\vec{k}^{|} - \vec{k}\right) = 2\pi.h$$

$$\vec{k}^{|} - \vec{k} = \Delta\vec{k}$$

$$\vec{a}.\Delta\vec{k} = 2\pi.h$$
$$\vec{b}.\Delta\vec{k} = 2\pi.k$$
$$\vec{c}.\Delta\vec{k} = 2\pi.l$$

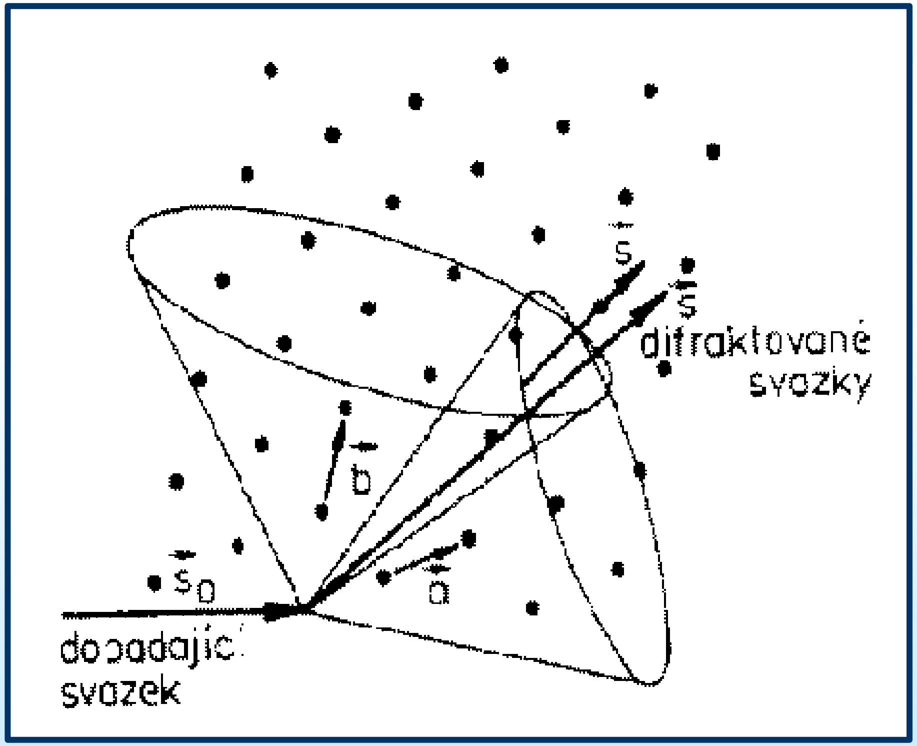
Laue´s equations in vector form

- $\Delta\vec{k}$ .....scattering vector

Geometric interpretation of Laue´s equations

From (*) $\Rightarrow$ $\Delta\vec{k}$ on the surface of cone with $\vec{a}$ axis

- By analogy - for 2-dim lattice $\rightarrow$ 2 systems of cones
- For 3-dim lattice $\rightarrow$ all of Laue´s eq. are fulfilled $\Rightarrow$
- $\Delta\vec{k}$ lies on cross points of three cone systems

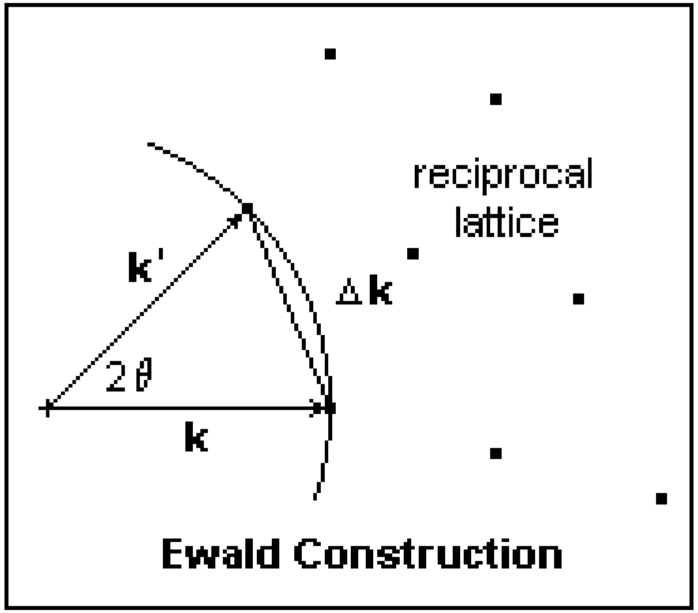


Ewald construction, geometric formulation of diffraction law

- Sphere with radius $\vec{k} = \left(\frac{2\pi}{\lambda}\right)$
- Centre in initial point of vector $\vec{k}$
- **Diffracted beam is created ⇔ if Ewald´s sfere cuts across any other point of reciprocal lattice**
- Then the beam is diffracted to the direction

$$\vec{k}^{|} = \vec{k} + \vec{G}$$

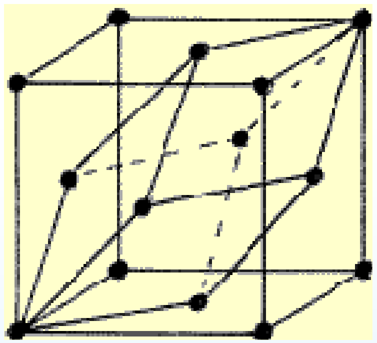
G…vector of reciprocal lattice

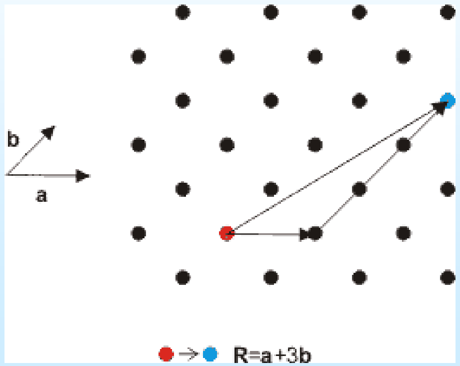


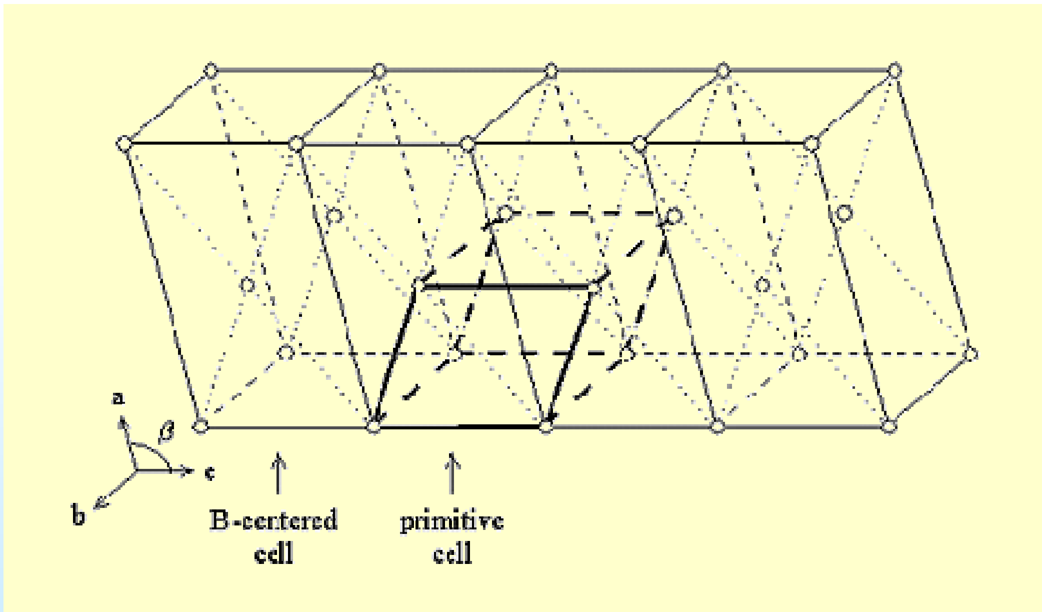
So the diffraction appears ⇔ $\Delta\vec{k} = \vec{G}$

Appendix
Basic crystalographic concepts

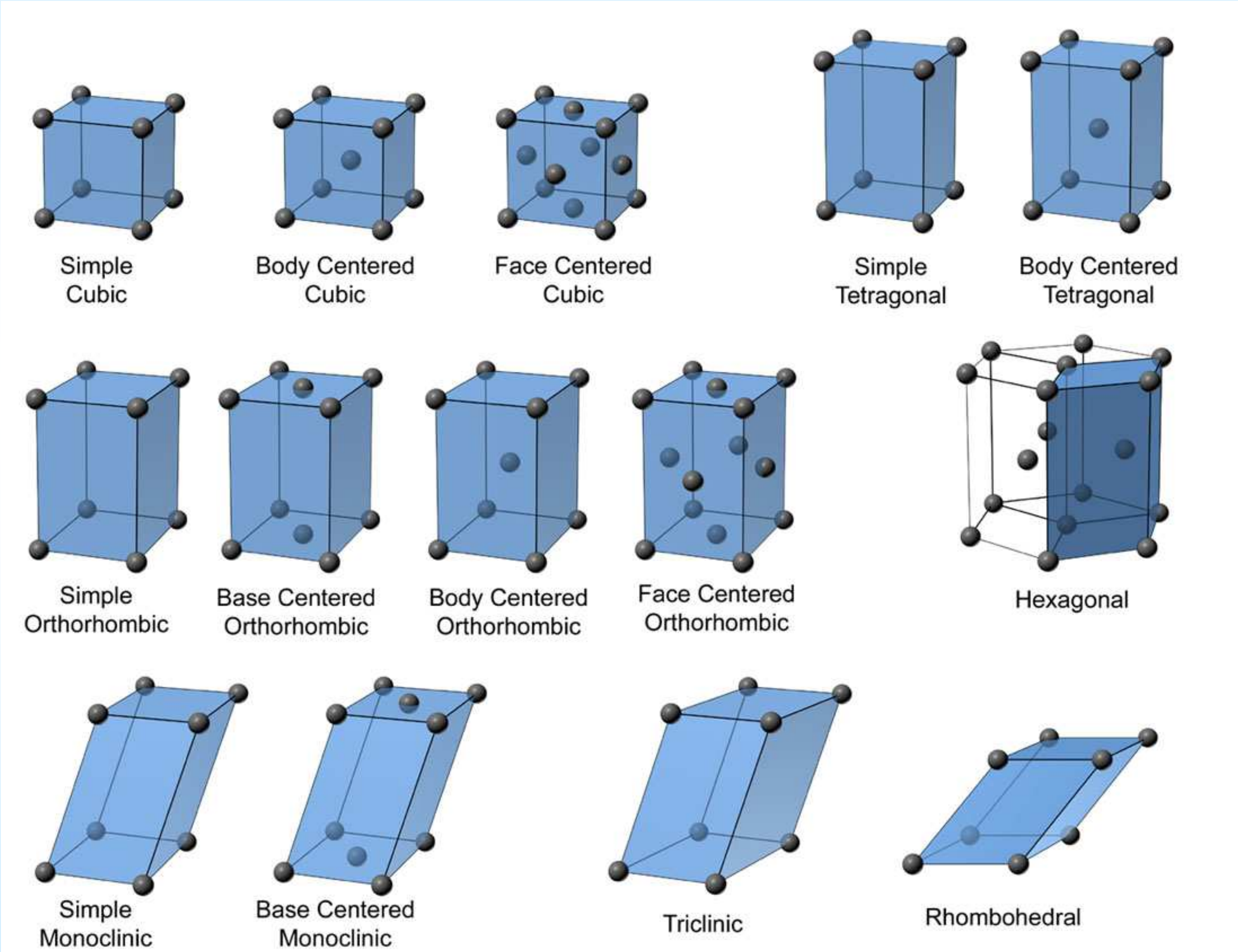
- Direct lattice, primitive cell, translation vectors
- Miller´s indices of planes and direction
- Reciprocal lattice







14 Bravais lattices
(7 Crystal Classes)



Crystal Planes describing → Miller indices

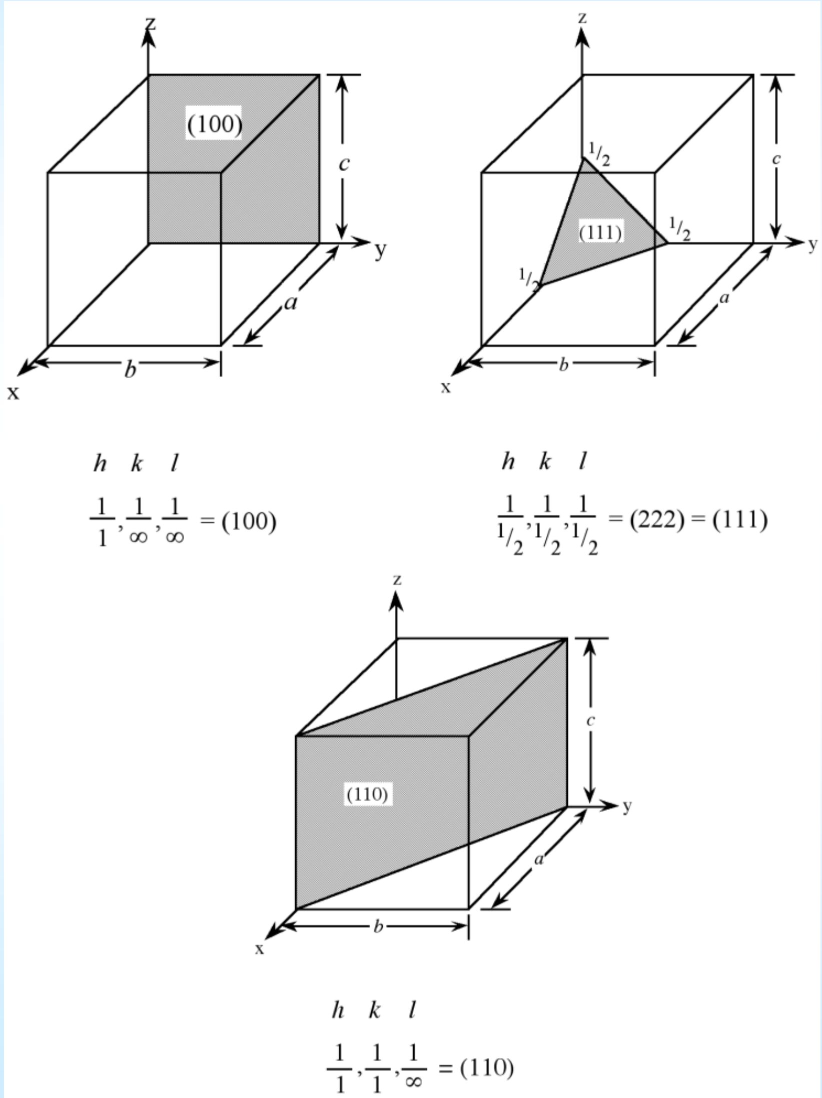
To obtain the Miller indices of a given plane:

Step 1. The plane in question is placed on a unit cell

Step 2. Its intercepts with each of the crystal axes are then found

Step 3. The reciprocal of the intercepts are taken

Step 4. These are multiplied by a scalar to insure that is in the simple ratio of whole numbers



For example, the face of a lattice that does not intersect the y or z axis would be (100), while a plane along the body diagonal would be the (111) plane. An illustration of this along with the (111) and (110) planes is given in Fig