Physics of Materials and Nuclei

CRYSTALLOGRAPHY Unit

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Crystallography

- Crystalline and amorphous solids
- Lattice and unit cell
- Seven crystal system and Bravais lattices,
- Symmetry operation
- Miller indices
- Atomic radius
- Coordination number
- Packing factor calculation for SC, BCC, FCC
- Bragg's law of X-ray diffraction
- Laue Method
- Powder crystal method.

Notation

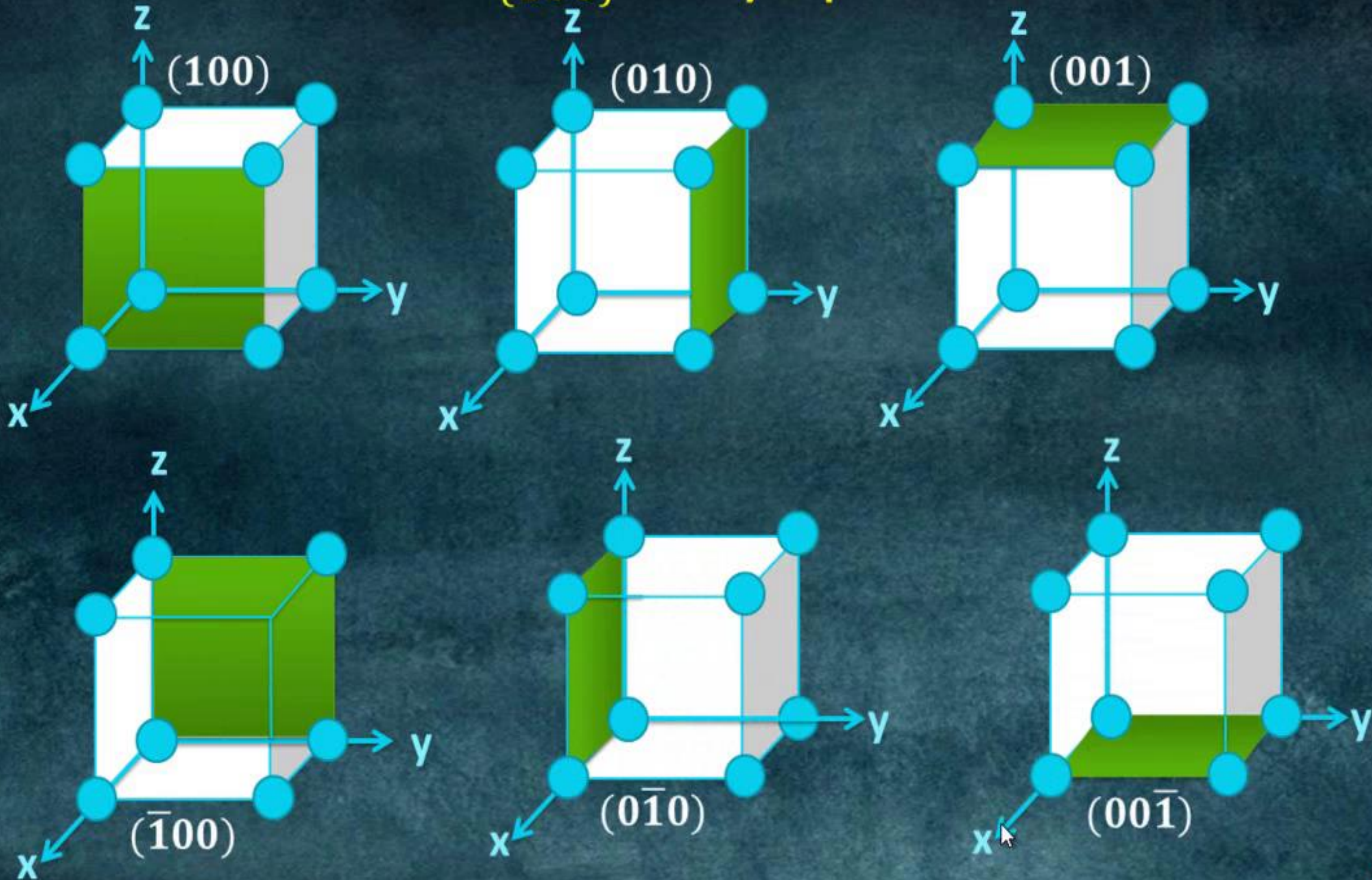
(hkl) represents a plane

$\{hkl\}$ represents family of planes

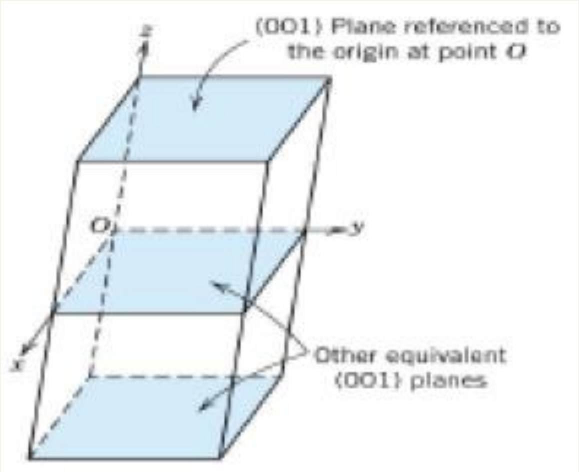
$[hkl]$ represents a direction

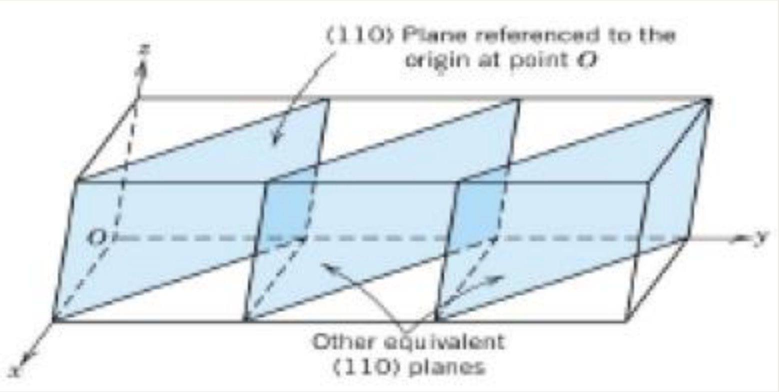
$< hkl >$ represents a family of directions

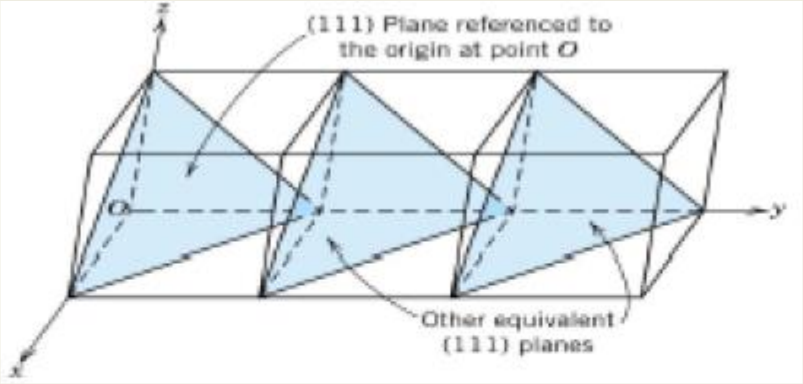
$\{100\}$ Family of planes



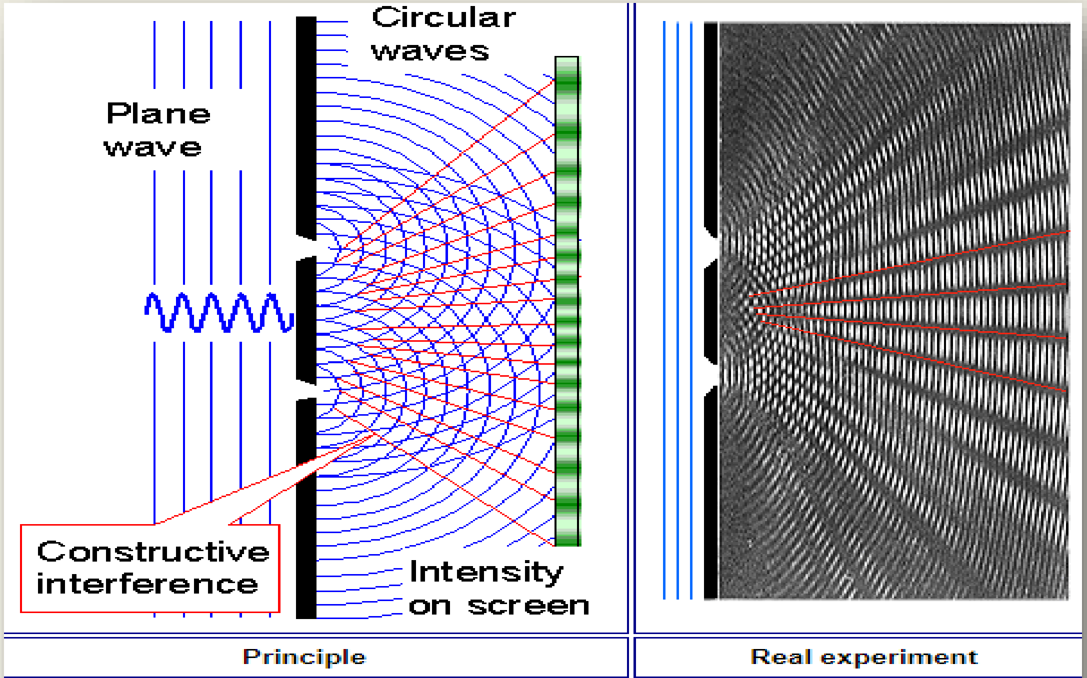
Three Important Crystal Planes







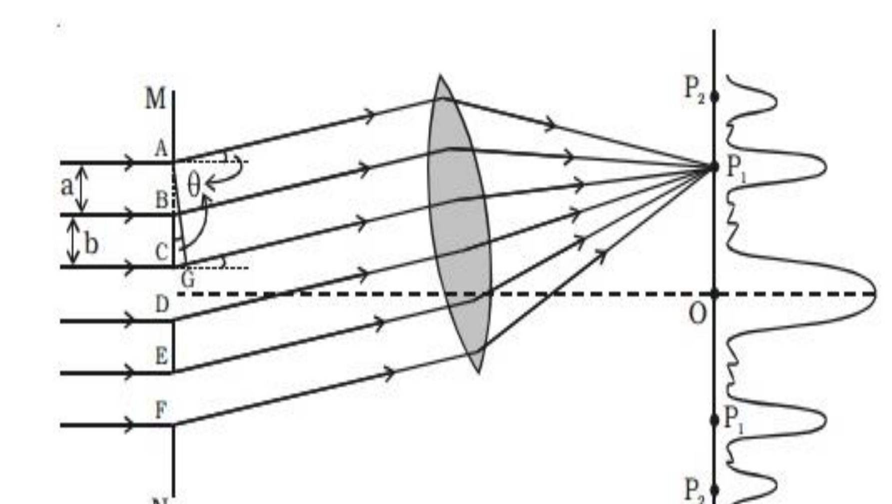
Double slit experiment



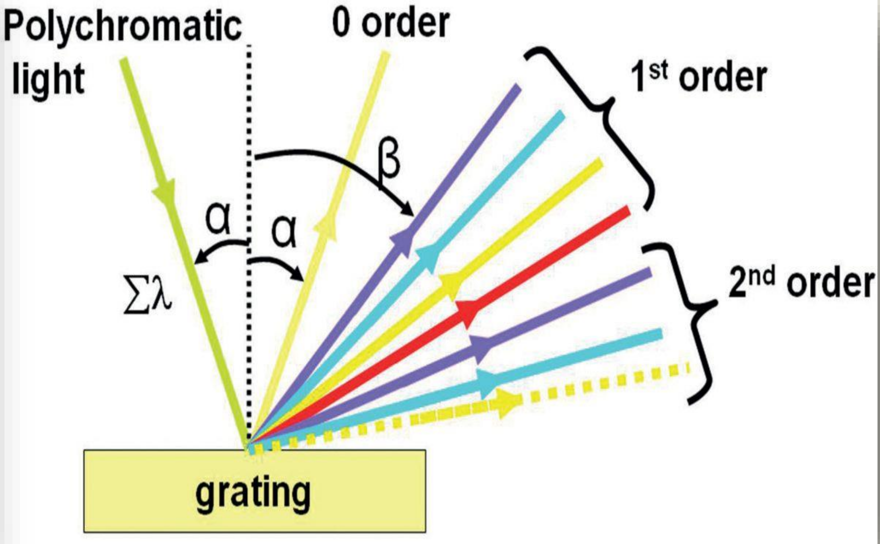
Double slit interference experiment.

- The width of the slits and the distance between the slits should be larger but still comparable to the wavelengths of the waves considered.
- For visible light, a few micrometers (μm) would be fine.
- An incoming plane wave, upon hitting small objects like slits, will continue by producing a spherical (circular) wave around the obstacle.
- The two circular waves from the two slits superimpose and interfere.

Diffraction grating – a basic optical device

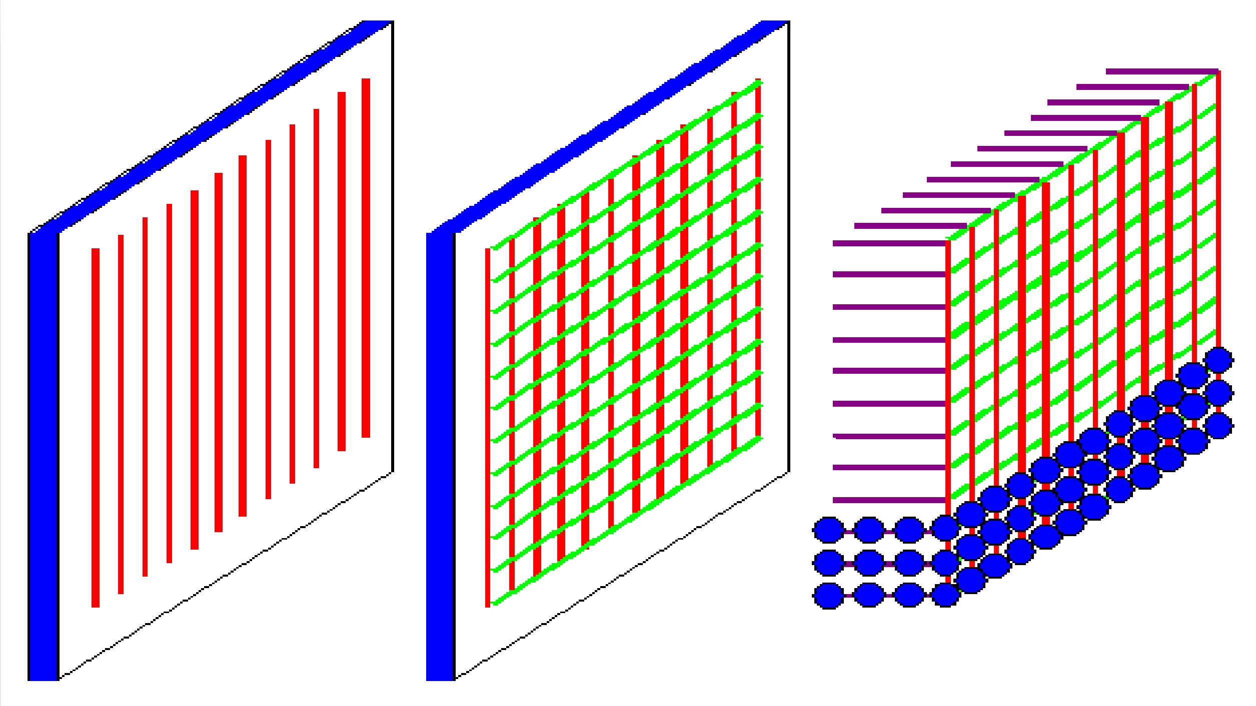


Diffraction grating



- **Diffraction grating**
  - ✓ More than 2 slits at equal distances
  - ✓ A basic optical device.
- Instead of broad lines, *fine and sharp lines* appear on screen.
- Since the position of these interference lines are different for different wavelengths, white light will produce a complete "*rainbow*" spectrum at each line.
- Making a diffraction grating for visible light is simple (as seen from the viewpoint of atoms).

Diffraction Grating in 3D



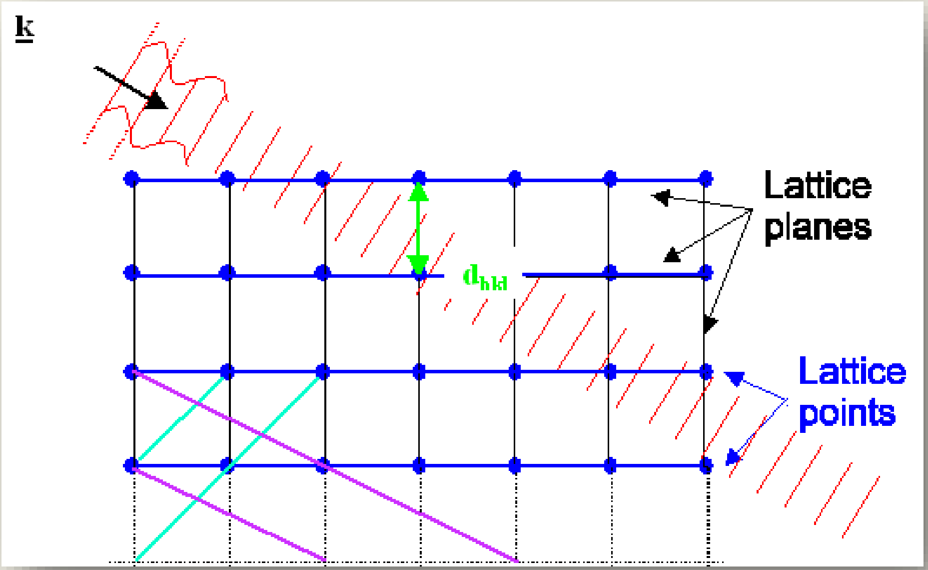
Diffraction gratings in 1, 2, and 3 dimensions

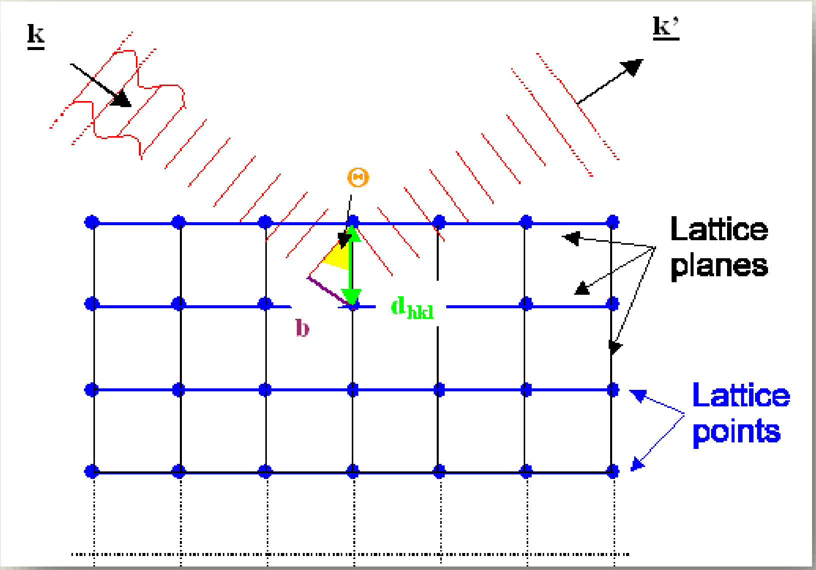
Gratings/obstacle in 3D geometry

- Atoms in crystal - A wealth of suitable gratings just at the right dimensions
- Spacing ~ nm/sub-nm
- Diffraction can be obtained if the wavelength of incoming waves ~ nm/sub-nm (Example: X-rays or electron "waves“)

X-Ray Diffraction

- X-rays $\rightarrow$ E.M. Waves $\rightarrow$ Interference and diffraction
- X-rays $\rightarrow$ $\lambda \approx 0.1$nm (1 A^o), so that ordinary devices such as ruled diffraction gratings can not produce observable effects with X-rays, but the crystals have atomic spacing ~ 2-4 A^o can produce it.
- In 1912 , German Physicist "Laue" suggested that a crystal can be used as a 3D space grating.
- Later Friedrich and Knipping demonstrated diffraction of X-rays through thin single crystal of zinc blende (ZnS).
- Bragg proposed Bragg's Law for diffraction through crystal structure.

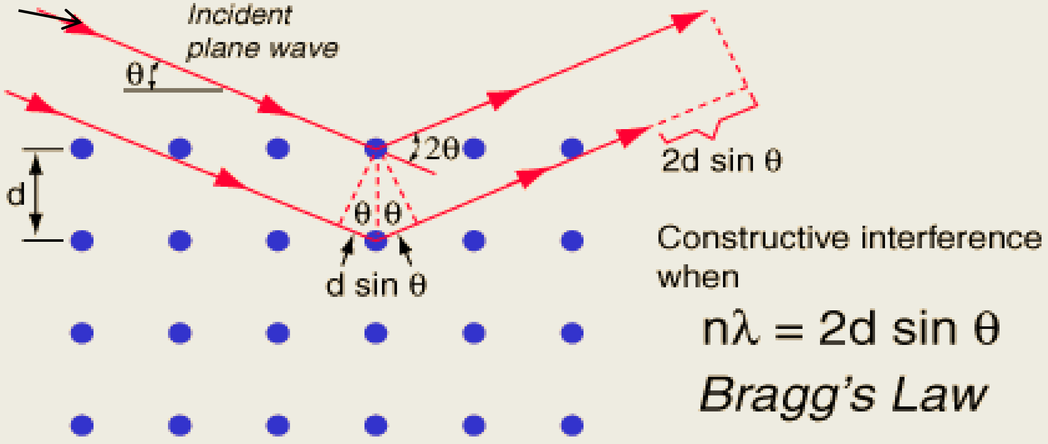




- ❑ What happens to the incoming X-ray wave ?
  - ✓ Either it just moves on and does not notice the lattice plane at all, or,
  - ✓ It gets *reflected* at the set of lattice planes considered and now moves in the ***k'*** direction.
- ❑ Reflection - will *only* happen if the angle between the incoming beam and the set of lattice planes has a specific value of θ - **Bragg angle**.
- ❑ For all other angles, interference will cancel everything.

Bragg's Law

Glancing angle



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

When X-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:

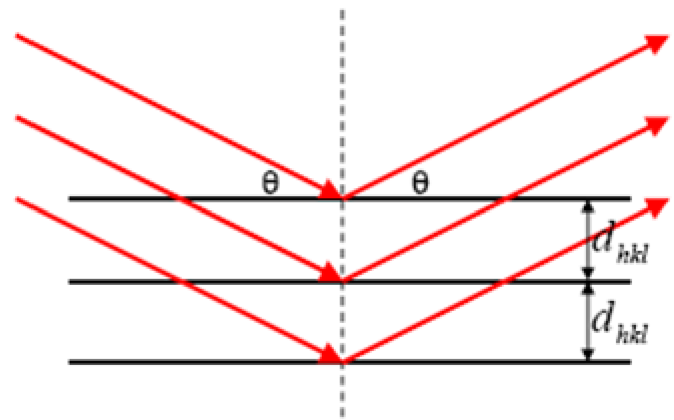
1. The angle of incidence = angle of scattering.
2. The path length difference is equal to an integer number of wavelengths.

The **condition for maximum intensity** contained in Bragg's law above allow us:

- ✓ To **calculate** details about the crystal structure, or
- ✓ If the crystal structure is known, to **determine** the wavelength of the X-rays incident upon the crystal.

Braggs Law gives conditions required for diffraction

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



- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference *only* occurs when Braggs law is satisfied.
- **Diffraction peaks**
  - ✓ Produced by a family of planes *only* at a *specific angle* θ.
- **Peak position**
  - ✓ Determined by the *Space between diffracting planes of atoms*
- **Peak intensity**
  - ✓ Determined by the *atoms present in the diffracting plane*.

Understanding the Bragg's equation

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

  The equation is written better with some descriptive subscripts:

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

If this equation is satisfied, then θ is θ_{Bragg}

- *n* is an integer and is the order of the reflection

  (i.e. how many wavelengths of the X-ray go on to make the path difference between planes).Note: if hkl reflection (corresponding to n=1) occurs at θ_{hkl} then 2h 2k 2l reflection (n=2) will occur at a higher angle $\theta_{2h\ 2k\ 2l}$.

- *Interplanar spacing* appears in the Bragg's equation, not *interatomic spacing 'a'* ($\theta_{incident} = \theta_{scattered}$).
- For large interplanar spacing, *d* increases, $sin\theta$ decreases and so does θ.

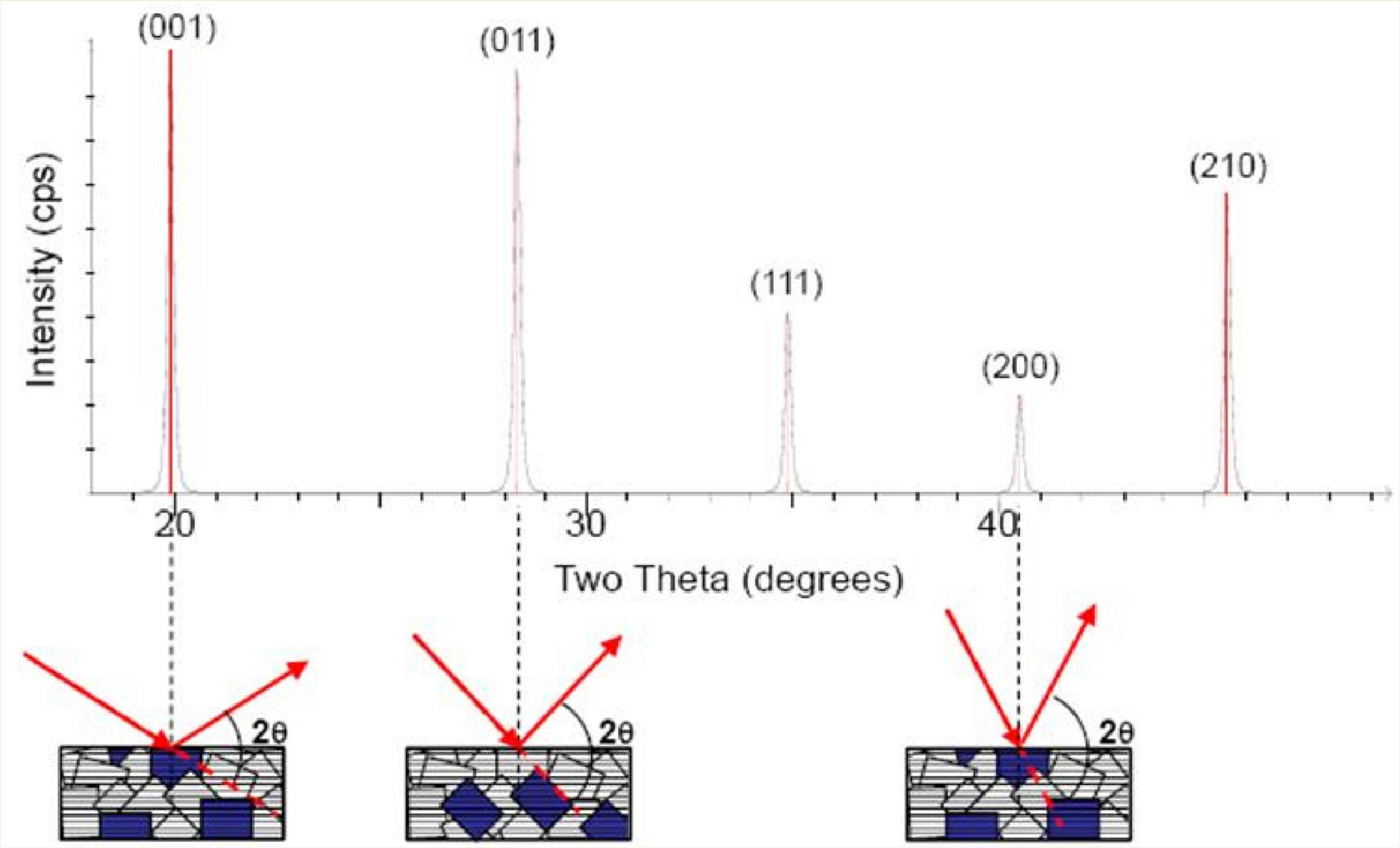
$$n\lambda = 2d_{hkl} \sin \theta_{hkl}$$ If this equation is satisfied, then θ is θ_{Bragg}

- Intensity of the diffracted lines decreases with increase in the diffraction order n or the angle θ.
- Highest possible order is determined by the condition: sin θ <= 1.
- Also, since sin θ <= 1 hence, λ <= 2d for Bragg diffraction to occur.

$$\boxed{\lambda < 2d_{\mathrm{hkl}}}$$

- Usually, d ~ 3 Angstrom

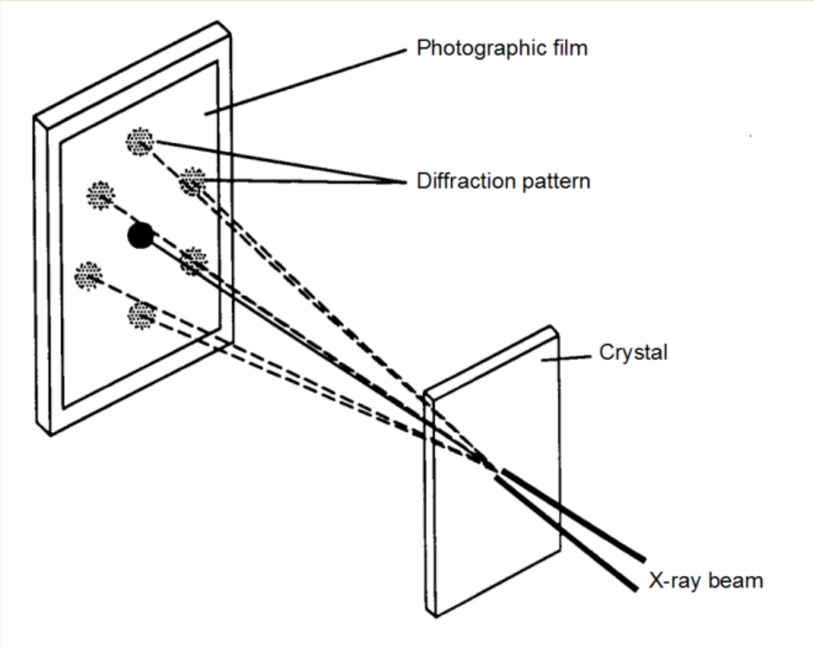
XRD Spectra: crystalline sample

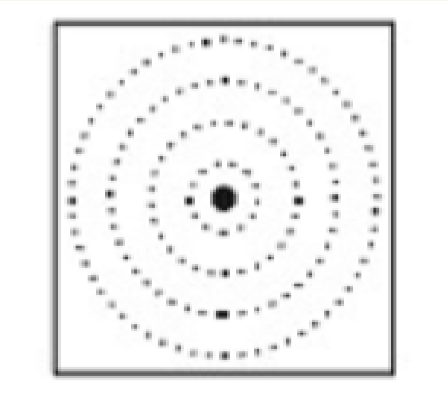


Methods of XRD

- **Laue method** (Orientation, Single Crystal, Polychromatic Beam, Fixed Angle)
- **Powder crystal method** (Lattice constant, Single Crystal, Monochromatic Beam, Variable Angle)
- **Rotating crystal method** (Lattice Parameters, Polycrystal (powdered), Monochromatic Beam, Variable Angle)

Laue method





Max Von Laue
1879-1960
Nobel Prize 1914

The Laue method is mainly used to determine the orientation of large single crystals while radiation is reflected from, or transmitted through a fixed crystal.

The diffracted beams form arrays of spots, that lie on curves on the film.

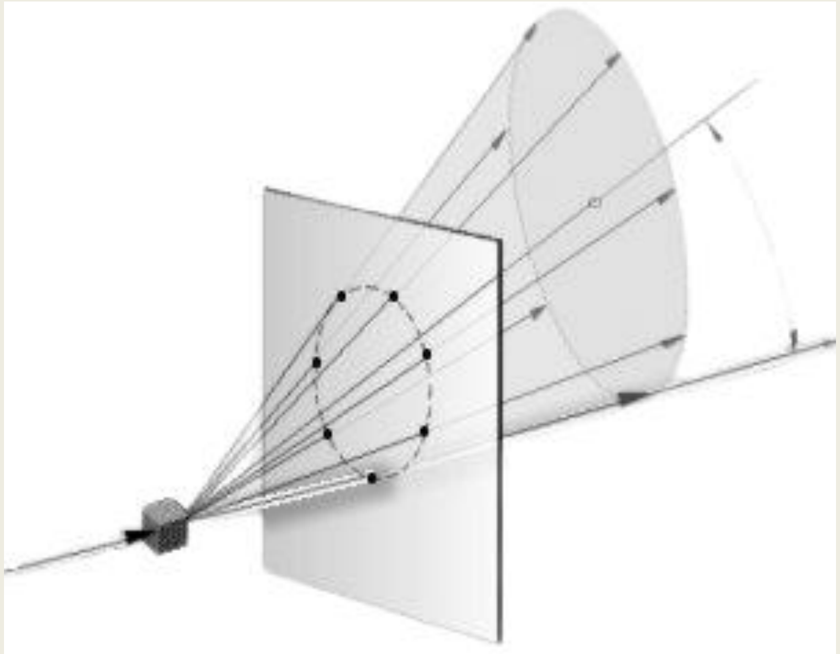
The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and θ involved.

Laue method

Transmission

In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through the crystal.

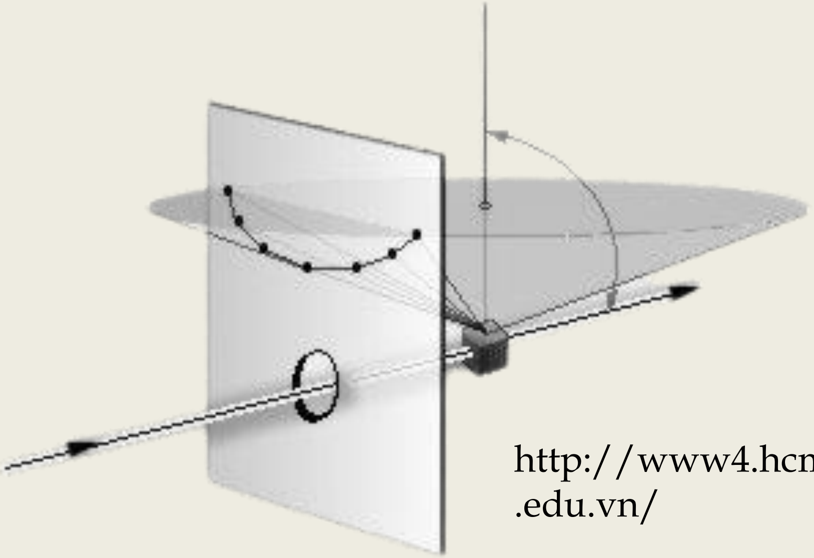
One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an ellipse.



Back-scattered

In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded.

One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola.



http://www4.hcmut.edu.vn/

Powder Crystal method

- In the powder sample there are crystallites in different 'random' orientations (a polycrystalline sample too has grains in different orientations).
- The coherent x-ray beam is diffracted by these crystallites at various angles to the incident direction.
- All the diffracted beams (called 'reflections') from a single plane, but from different crystallites lie on a cone.
- Depending on the angle there are forward and back reflection cones.
- A diffractometer can record the angle of these reflections along with the intensities of the reflection.
- The X-ray source and diffractometer move in arcs of a circle- maintaining the Bragg 'reflection' geometry.