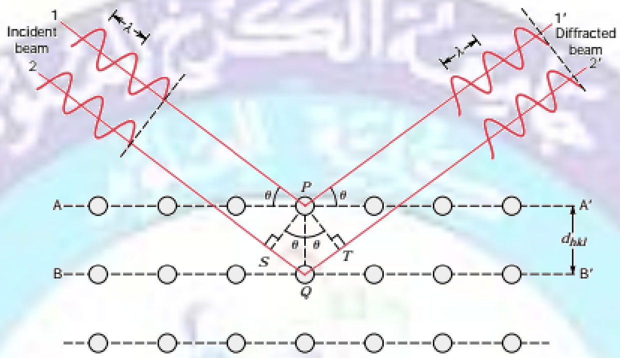
Nanomaterials

2nd year Medical Physics | Lecturer: Dr. Ghaiath A. Fadhil

Lecture 5: X-ray Diffraction



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5.1 X-ray diffraction

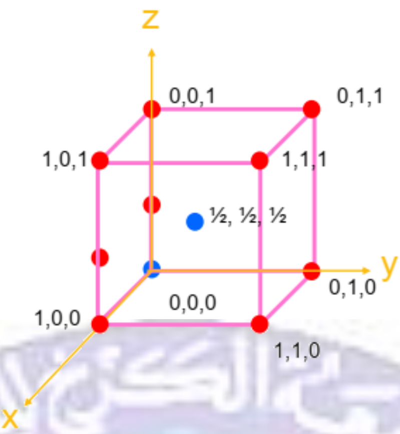
Much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations.

Furthermore, x-rays are still very important in developing new materials. A brief overview of the diffraction phenomenon and how to measure atomic interplanar distances using x-rays is following but first; we have to review Miller indices.

5.1.1 Miller indices (directions)

When dealing with crystalline materials, it often becomes necessary to specify some particular crystallographic plane of atoms or a crystallographic direction.

The basis for determining index values is the unit cell, with a coordinate system consisting of three (x, y, and z) axes situated at one of the corners and coinciding with the unit cell edges, as shown in the figure 5.1.



A crystallographic direction is defined as a line between two points, or a vector.

The following steps are used in the determination of the three directional indices:

1. A vector is positioned such that it passes through the origin of the coordinate system.

2. The length of the vector projection on each of the three axes is determined.

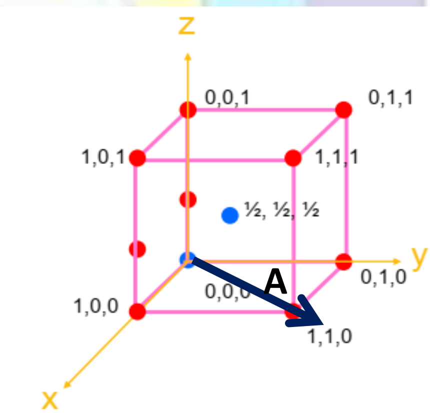
3. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.

4. The three indices, not separated by commas, are enclosed in square brackets, thus: **[uvw]**. The u, v, and w integers correspond to the reduced projections along the x, y, and z axes, respectively.

Example direction A

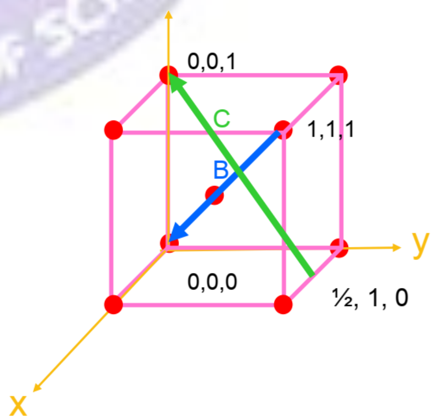
In the figure

a) Two points origin coordinates 0,0,0 and final position coordinates 1,1,0
b) 1,1,0 - 0,0,0 = 1,1,0
c) No fractions to clear
d) Direction [110]



Example direction B

a) Two points origin coordinates 1,1,1 and final position coordinates 0,0,0
b) 0,0,0 - 1,1,1 = -1,-1,-1
c) No fractions to clear
d) Direction $[\bar{1}\bar{1}\bar{1}]$



Example direction C

a) Two points origin coordinates ½,1,0 and final position coordinates 0,0,1
b) 0,0,1 - ½,1,0 = -½,-1,1

c) There are fractions to clear. Multiply times 2 ⇨ 2(-½,-1,1) = -1,-2,2
d) Direction $[\bar{1}\bar{2}2]$

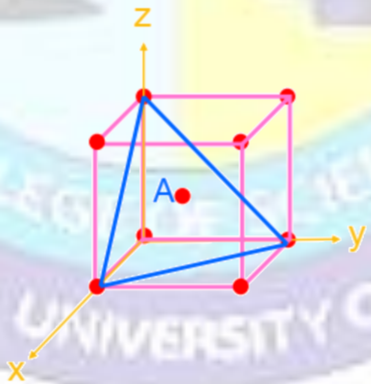
Notes on directions:

- A direction and its negative are not identical; [100] is not equal to $[\bar{1}00]$. They represent the same line but opposite directions. .
- A direction and its multiple are identical: [100] is the same direction as [200]. We just forgot to reduce to lowest integers.
- Certain groups of directions are equivalent; they have their particular indices primarily because of the way we construct the coordinates.
- For example, a [100] direction is equivalent to the [010] direction if we re-define the co-ordinates system.
- We may refer to groups of equivalent directions as directions of the same family.
- The special brackets < > are used to indicate this **collection of directions**.
- Example: The family of directions <100> consists of six equivalent directions ≡ [100], [010], [001], $[0\bar{1}0]$, $[00\bar{1}]$ and $[\bar{1}00]$.

5.1.2 Miller indices (planes)
Miller Indices for Crystallographic planes in Cubic Cells

Planes in unit cells are also defined by three integer numbers, called the Miller indices and written (hkl).

Miller's indices can be used as a shorthand notation to identify crystallographic directions (earlier) and planes.



__**Procedure for determining Miller Indices:**__

a) Locate the origin.

b) Identify the points at which the plane intercepts the x, y and z coordinates as fractions of unit cell length.

c) If the plane passes through the origin, the origin of the co-ordinate system must be moved!

d) Take reciprocals of these intercepts.

e) Clear fractions but do not reduce to lowest integers.

f) Enclose the resulting numbers in parentheses (h k l).

g) Again, the negative numbers should be written with a bar over the number.

Example plane A

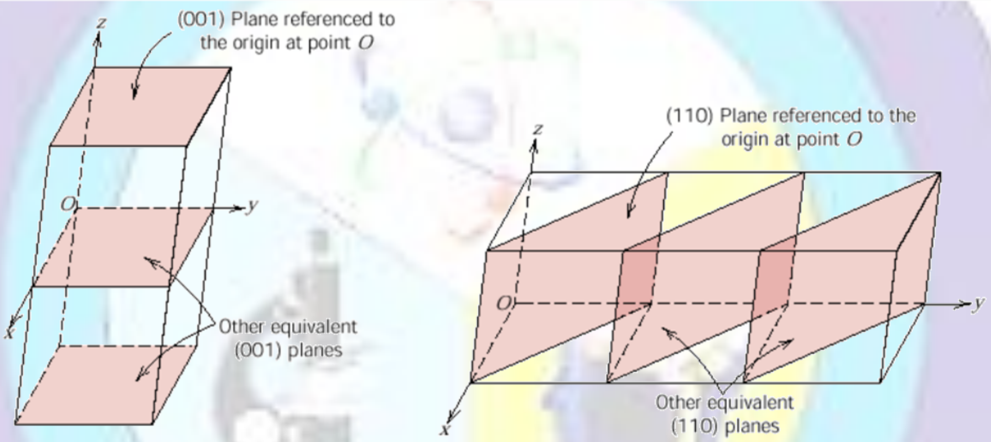
a) Locate the origin of coordinate.

b) Find the intercepts x = 1, y = 1, z = 1

c) Find the inverse 1/x=1, 1/y=1, 1/z=1

d) No fractions to clear

e) (1 1 1)



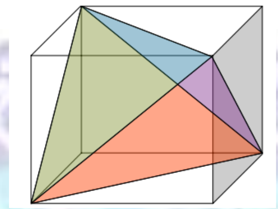
Notes on planes:

- Certain groups of planes are equivalent (same atom distribution); they have their particular indices primarily because of the way we construct the co-ordinates.
- For example, a (100) planes is equivalent to the (010) planes.
- We may refer to groups of equivalent planes as planes of the same family.
- The special brackets { } are used to indicate this collection of planes.
- In cubic systems the direction of miller indices [h k l] is normal or perpendicular to the (h k l) plane.
- In cubic systems, the distance *d* between planes (h k l) is given by the formula where *a* is the lattice constant.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- Example: the family of planes {100} consists of three equivalent planes (100), (010) and (001).

- A "family" of crystal planes contains all those planes are crystallographically equivalent.
- Planes have the same atomic packing density
- A family is designated by indices that are enclosed by braces.
- $\{111\}$:(111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$ and $(1\bar{1}1)$.



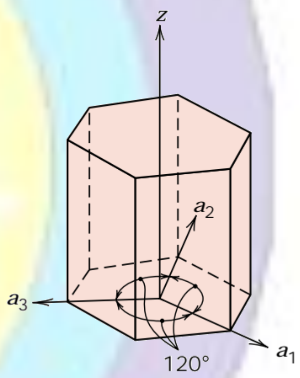
5.1.3 Miller indices (hexagonal crystals)

A problem arises for crystals having hexagonal symmetry.

This is avoided by using a four-axis, or Miller–Bravais, coordinate system as shown in the figure.

The three a1, a2, and a3 axes are all contained within a single plane (called the basal plane), and at 120º angles to one another. The z axis is perpendicular to this basal plane.

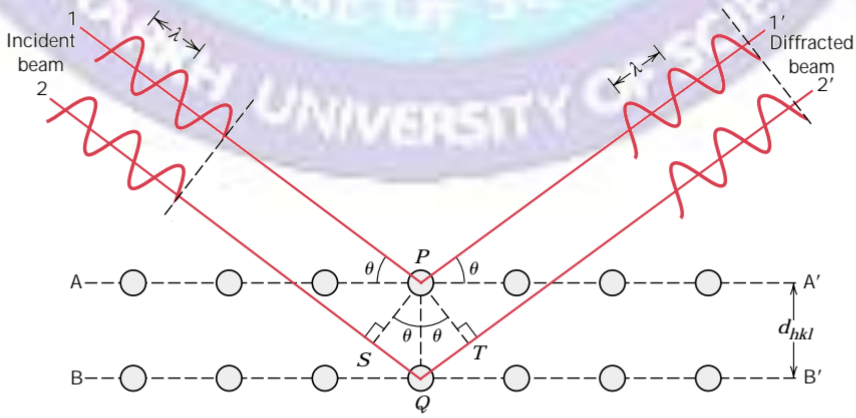
Directional indices, which are obtained as described above, will be denoted by four indices, as **[uvtw]**; by convention, the first three indices pertain to projections along the respective a1, a2, and a3 axes in the basal plane.



5.1.4 The diffraction phenomenon

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that:

1) are capable of scattering the wave, and
2) have spacings that are comparable in magnitude to the wavelength.



X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids.

When a beam of x-rays is applied on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path.

Let's now assume that a beam of x-rays of wavelength λ is incident on two planes of a material at an angle θ. Bragg's law shows that:

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

Where n is the order of reflection, which may be any integer (1, 2, 3, . . .).

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices (h, k, and l) as well as the lattice parameters. For example, for crystal structures having cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For a material with single crystal structure (similar crystal structure all over the sample), we use Scherrer's equation to calculate its size, which states:

$$D = \frac{0.98\,\lambda}{\beta\cos\theta}$$

Where D is the size of the single-crystal material and β is the peak half-width.

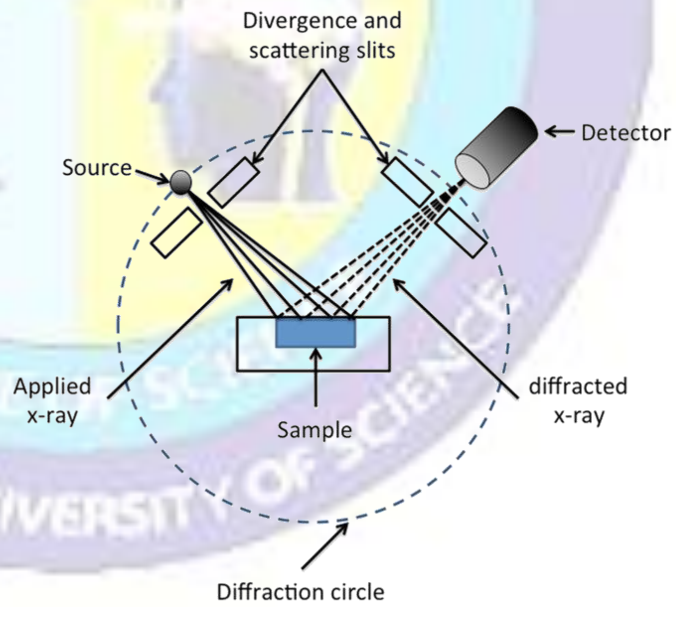
5.1.5 The diffraction technique

The diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to x-radiation.

Each powder particle (or grain) is a crystal

The large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The diffractometer is an apparatus used to determine the angles at which diffraction occurs for powdered specimens.



The X-ray diffractometer

The primary uses of x-ray diffractometer is for the determination of crystal structure, the unit cell size and its geometry, qualitative and quantitative chemical identifications and the determination of residual stresses.

The data can be presented as a spectrum of intensities of diffracted x-ray at different incident angles.