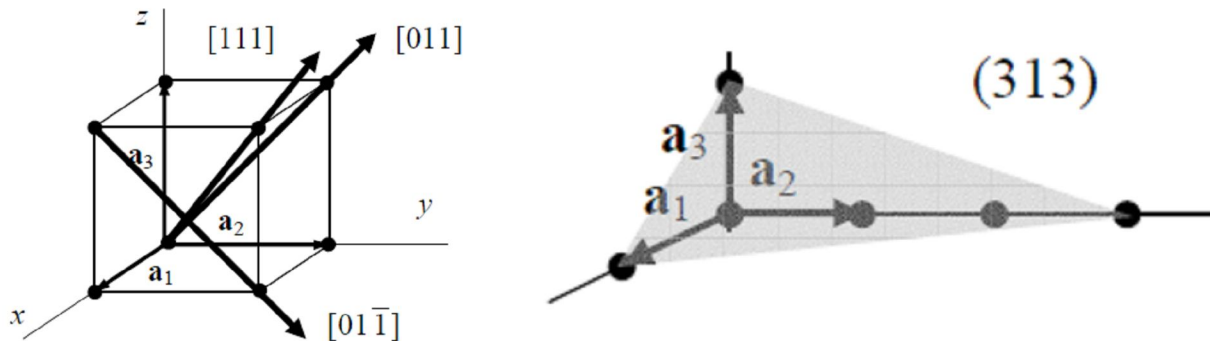


Lecture 5: Crystal planes and Miller Indices

Index system for crystal directions and planes

Crystal directions: Any lattice vector can be written as that given by Eq.(1.2). The direction is then specified by the three integers $[n_1n_2n_3]$. If the numbers $n_1n_2n_3$ have a common factor, this factor is removed. For example, $[111]$ is used rather than $[222]$, or $[100]$, rather than $[400]$. When we speak about directions, we mean a whole set of parallel lines, which are equivalent due to translational symmetry. Opposite orientation is denoted by the negative sign over a number. For example:



Crystal planes: The orientation of a plane in a lattice is specified by *Miller indices*. They are defined as follows. We find intercept of the plane with the axes along the primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . Let's these intercepts be x , y , and z , so that x is fractional multiple of \mathbf{a}_1 , y is a fractional multiple of \mathbf{a}_2 and z is a fractional multiple of \mathbf{a}_3 . Therefore we can measure x , y , and z in units \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 respectively. We have then a triplet of integers $(x\ y\ z)$. Then we invert it $(1/x\ 1/y\ 1/z)$ and reduce this set to a similar one having the smallest integers by multiplying by a common factor. This set is called Miller indices of the plane (hkl) . For example, if the plane intercepts x , y , and z in points 1, 3, and 1, the index of this plane will be (313) .

The orientation of a crystal plane is determined by three points in the plane, provided they are not collinear. If each point lay on a different crystal axis, the plane could be specified by giving the coordinates of the points in terms of the lattice constants a , b , c . A notation conventionally used to describe lattice points (sites), directions and planes is known as Miller Indices.

A crystal lattice may be considered as an assembly of equidistant parallel planes passing through the lattice points and are called lattice planes. In order to specify the orientation one employs the so called Miller indices.

For simplicity, let us start with a two dimensional lattice and then generalized to three dimensional case.

The equation of plane in 2-D and 3D having the intercepts a, b and a, b, c respectively are

$$\frac{x}{a} + \frac{y}{b} = 1 \quad \text{and} \quad \frac{x}{a} + \frac{y}{b} + \frac{z}{c} = 1$$

Crystal direction is the direction (line) of axes or line from the origin and denoted as $[111]$, $[100]$, $[010]$ etc.

How to find Miller Indices:

To determine the indices for the plane p in Figure 2,

-first we have to find the intercepts with the axes along the basis vector $\vec{a}, \vec{b}, \vec{c}$. Let these intercepts

be x, y, z . We form the fractional triplet $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$.

-Take reciprocal to this set.

-Then reduce this set to a similar one having the smallest integers multiplying by common factor.

To determine the Miller indices:

(i) Find the intercepts on the axes along the basis vector $\vec{a}, \vec{b}, \vec{c}$ in terms of the lattice constants a, b and c . The axes may be those of a primitive or nonprimitive cell.

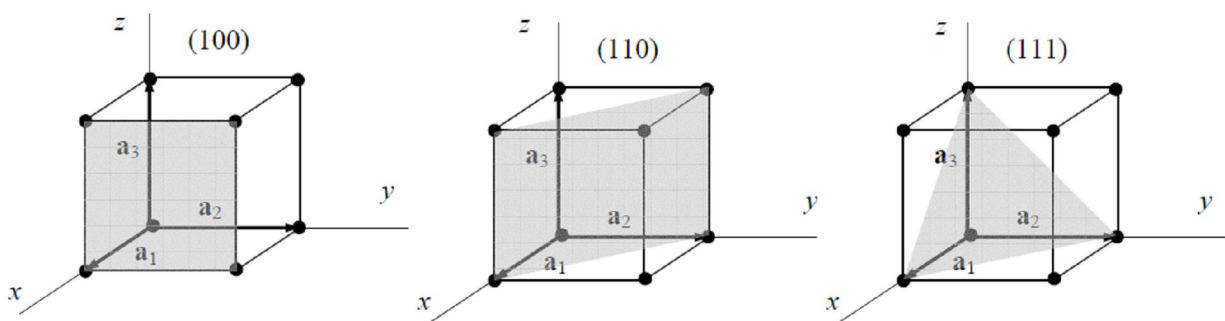
Let these intercepts be x, y, z . We form the fractional triplet $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$.

(ii) Take the reciprocals of these numbers.

(iii) Reduce the numbers to three smallest integers by multiplying the numbers with the same integral multipliers.

This last set is enclosed in parentheses $(h k l)$, is called the index of the plane or Miller Indices.

The Miller indices specify not just one plane but an infinite set of equivalent planes. Note that for cubic crystals the direction $[hkl]$ is perpendicular to a plane (hkl) having the same indices, but this is not generally true for other crystal systems. Examples of the planes in a cubic system:



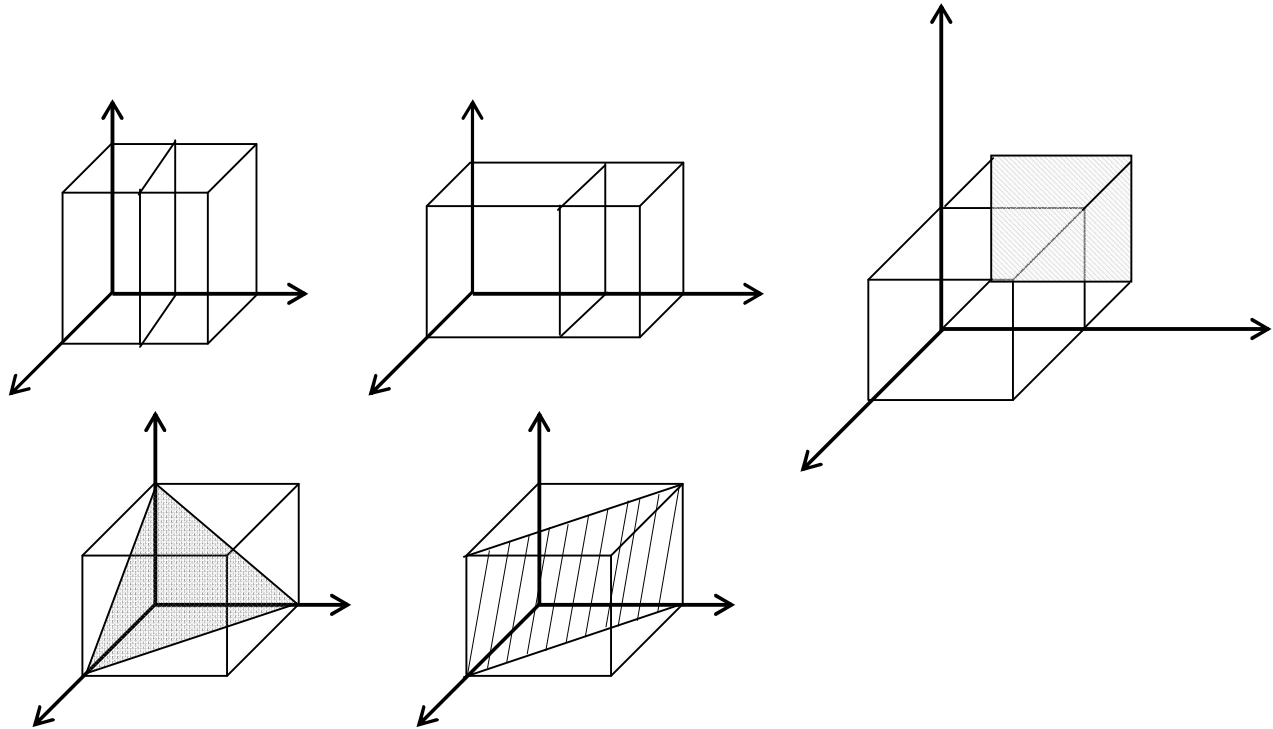
Example: Let the intercepts are $x = 2a$, $y = 3/2b$, $z = c$.

We first form the set $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right) = \left(2, \frac{3}{2}, 1\right)$,

Then invert it $\left(\frac{1}{2}, \frac{2}{3}, 1\right)$

and finally multiply by a common (factor) denominator. Which is 6, to obtain the miller indices (3 4 6).

Exercise: $x = 2a$, $y = 3b$, $z = 6c \Rightarrow (321)$.



The indices of some important planes in a cubic crystal

Relation between interplanar spacing and Miller indices:

Let us consider three mutually perpendicular coordinate axis, OX, OY, and Oz and assume that a plane (hkl) parallel to the plane passing through the origin makes intercepts a/h, b/k and c/l on the three axes at A, B and C respectively as shown in figure.

Let $OP = d_{hkl}$, the interplaner spacing be normal to the plane drawn from the origin and makes angle α , β , and γ with the three axes respectively.

Therefore, $OA = \frac{a}{h}, OB = \frac{b}{k}, OC = \frac{c}{l}$

From ΔOPA we get, $\cos \alpha = \frac{OP}{OA} = \frac{d_{hkl}}{a/h}$

Similarly, from ΔOPB we get $\cos \beta = \frac{OP}{OB} = \frac{d_{hkl}}{b/k}$

and from ΔOPC we get $\cos \gamma = \frac{OP}{OC} = \frac{d_{hkl}}{c/l}$

But, for a rectangular coordinate system, using directional cosine we have

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \tag{1}$$

Substituting the values of $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ in Eq.1 we get,

$$d_{hkl}^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 1$$

$$\therefore d_{hkl} = \frac{1}{\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}} \tag{2}$$

This is the general formula and is applicable to the primitive lattice of orthorhombic, tetragonal and cubic systems.

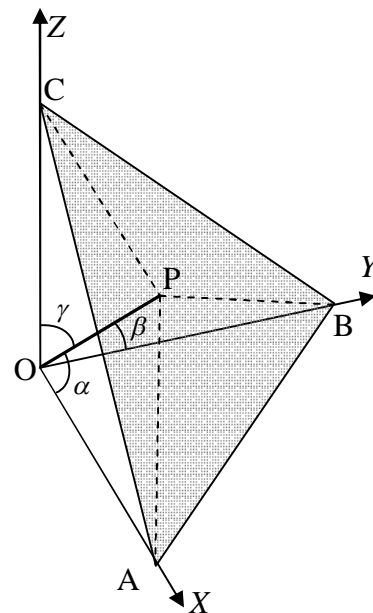
i) Orthorhombic system: $a \neq b \neq c$

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

ii) Tetragonal system: $a = b \neq c$

$$\therefore d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right)}}$$

$a = b = 2.42 \text{ \AA}$ and $c = 1.74 \text{ \AA}$
then $d_{101} = 1.41 \text{ \AA}$



ii) Cubic system: $a = b = c$

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

$$\# a = 2\text{\AA}, d_{111} = 2\sqrt{3}\text{\AA}$$

$$\# a = 421\text{\AA}, d_{321} = 1.01\text{\AA}$$

$$\# d_{100} = a, d_{110} = \frac{a}{\sqrt{2}} \text{\AA} \quad d_{111} = \frac{a}{\sqrt{3}} \text{\AA}$$

$$\therefore d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$$

For bcc $\Rightarrow d_{100} = \frac{1}{2} (d_{100,sc}) = \frac{a}{2}$

$$d_{110} = (d_{110,sc}) = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{1}{2} (d_{111,sc}) = \frac{a}{2\sqrt{3}}$$

and $d_{100} : d_{110} : d_{111} = 1 : \sqrt{2} : \frac{1}{\sqrt{3}}$

For fcc $\Rightarrow d_{100} = \frac{1}{2} (d_{100,sc}) = \frac{a}{2}$

$$d_{110} = (d_{110,sc}) = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{1}{2} (d_{111,sc}) = \frac{a}{2\sqrt{3}}$$

and $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

Ex: Determine the Miller Indices of a plane which is parallel to x-axis and cuts intercepts of 2 and $\frac{1}{2}$, respectively along y and z axes.

Solution:

i) Intercepts	∞	$2b$	$\frac{1}{2}c$
ii) Division by unit translation	$\frac{\infty}{a} = \infty$	$\frac{2b}{b} = 2$	$\frac{3c}{2c} = \frac{1}{2}$
iii) Reciprocals	$\frac{1}{\infty}$	$\frac{1}{2}$	2
iv) After clearing fraction	0	1	4

Therefore the required Miller indices of the plane (014)

Ex: Determine the M. I. of a plane that makes intercepts of 2Å , 3Å , 4Å on the co-ordinate axes of an orthorhombic crystal with $a:b:c = 4:3:2$

Solution:

Here the unit translations are $a = 4$, $b = 3$ and $c = 2$ following the same procedure

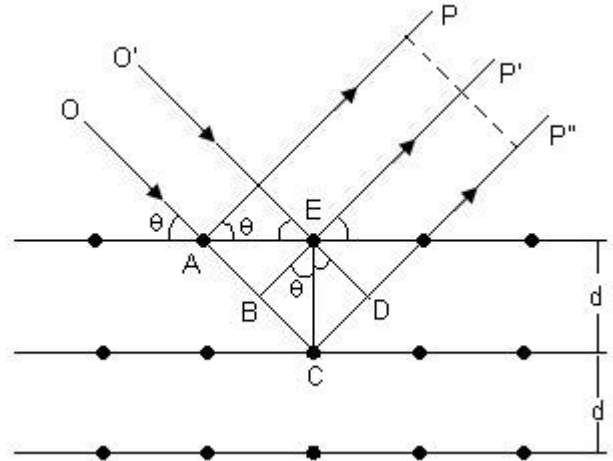
i) Intercepts	2	3	4
ii) Division by unit translation	$\frac{2}{4} = \frac{1}{2}$	$\frac{3}{3} = 1$	$\frac{4}{2} = 2$
iii) Reciprocals	2	1	$\frac{1}{2}$
iv) After clearing fraction	4	2	1

Therefore the Miller indices of the plane is (421)

Lecture 6: X-ray diffraction and Bragg's law:

The inter-atomic spacing in crystals is of the order of 1\AA . Because of the short wavelength (comparable to the inter-planer distance), X-rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction effects. When X-rays enter into a crystal, each atom acts as a diffraction centre and crystal as a whole acts like a three dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystal.

Let us consider a crystal made up of equidistant parallel planes of atoms with the inter-planer spacing d_{hkl} . Further, consider a monochromatic x-ray beam of wavelength λ having a common wave front, falls at an angle θ on the planes as shown in Figure. Each atom scatter the x-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase where they interfere constructively. In all other directions, there is destructive interference.



Consider two of the incoming x-ray OA and $O'E$ inclined at an angle θ with the topmost plane of the crystal and are scattered in the directions AP and EP' , also at an angle θ with that plane. Since the path length of the rays OEP' and $O'AP$ are the same, they arrive at P and P' respectively in phase with each other and again form a common wavefront. This is the condition for scattering in phase by single plane of the crystal.

Now, let us consider X-ray scattering from two adjacent planes $(hkl)_1$ and $(hkl)_2$ as shown in Figure. If EB and ED are parallel to the incident and scattered wavefront respectively, the total path $O'CP''$ is longer than the path OEP' by an amount

$$\Delta = BCD = BC + BD \quad (1)$$

Now, from the right angle triangle EBC and EDC, we have

$$BC = d \sin \theta = BD$$

So,
$$\Delta = 2d \sin \theta \quad (2)$$

If two consecutive planes scattered in phase with each other then we know that the path difference Δ must be equal to an integral multiple of wavelength, i.e. $\Delta = n\lambda$, where $n = 0, 1, 2 \dots$ gives the order of reflection. Thus the condition for constructive interference (in-phase scattering) by a set of equidistant parallel planes in a crystal is given by

$$2d \sin \theta = n\lambda \quad (3)$$

This is the well known Bragg's law, which was first derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. Thus diffraction (constructive) occurs for certain discrete values of θ for which the Bragg's condition is fulfilled.

As
$$(\sin \theta)_{\max} = 1, \quad \text{we get, } \frac{n\lambda}{2d} \leq 1.$$

That is, λ must not be greater than twice the interplaner spacing, otherwise no diffraction will occur.

This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

William Henry Bragg and William Lawrence Bragg were the first and (so far) the only father-son team to have jointly won the prize. Other father/son laureates include Niels and Aage Bohr, Manne and Kai Siegbahn, J. J. Thomson and George Thomson, Hans von Euler-Chelpin and Ulf von Euler, and Arthur and Roger Kornberg, who were all awarded the prize for separate contributions. W. L. Bragg was 25 years old at the time, making him the youngest Nobel laureate to date.

For certain specific wavelengths and incident angles, intense peaks of reflected radiation (known as Bragg peaks) were produced. The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes. When x-rays are incident on an atom, they make the

electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible. A similar process occurs upon scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add together to produce stronger peaks or subtract from each other to some degree), producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis.

When the energetic electrons strike the target, which is a pure metal such as copper or molybdenum, and remove inner (K) shell electrons. When this happens, other electrons from higher level shells drop into the vacant K-shell and in so doing emit a photon (X-ray) whose wavelength (energy) is characteristic of the metal target material. In order to remove the inner shell electron, the incoming electron must have an energy greater than the difference in energy between the inner (K) shell electron and a free electron in the conduction band of the target metal. This energy difference is referred to as the absorption edge energy.

Both KCl and KBr have *sodium chloride structure* shown in the figure. In this structure the two types of atoms are arranged alternatively at the lattice sites of a simple cubic lattice. The space lattice is fcc with a basis of two non-equivalent atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

In KCl the number of electrons of K^+ and Cl^- ions are equal and the charge distribution is similar. Therefore, the form factors for K^+ and Cl^- are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a . In KBr the form factor of Br^- is quite different than that of K^+ , and all reflections of the fcc lattice are present.

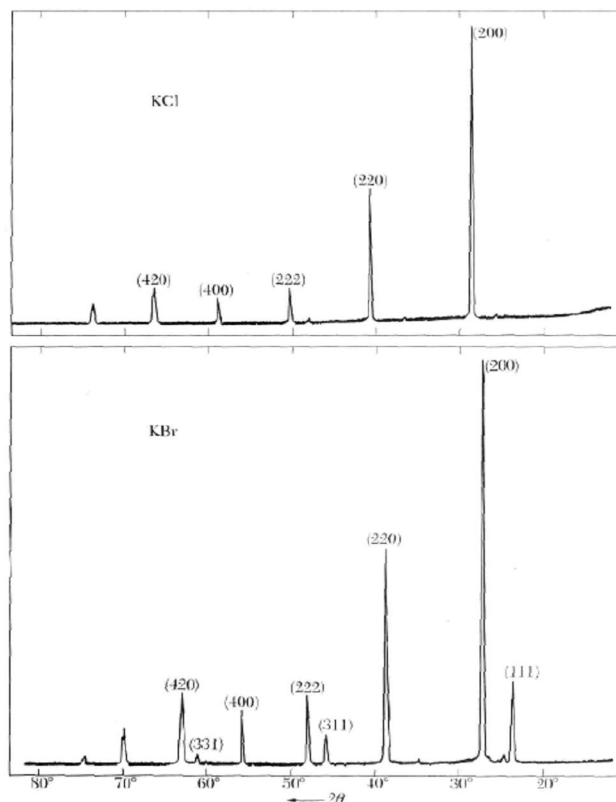


Figure: Comparison between X-ray reflections from KCl and KBr.

Exercise: Determine the angle through which an X-ray of wavelength 0.440\AA be reflected from the cube face of a rocksalt crystal ($d = 2.814\text{\AA}$).

Solution: Given $\lambda = 0.440\text{\AA}$. $d = 2.814\text{\AA}$ $\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$

1st order reflection, $n = 1$, $\theta_1 = \sin^{-1}\left(\frac{1 \times 0.440}{2 \times 2.814}\right) = \sin(0.0782) = 4^\circ 29'$

2nd order reflection, $n = 2$, $\theta_2 = \sin^{-1}(2 \times 0.0782) = 8^\circ 59'$

3rd order reflection, $n = 3$, $\theta_3 = \sin^{-1}(3 \times 0.0782) = 13^\circ 34'$, etc.

Exercise: Determine the wavelength of the diffraction beam, when a beam of X-ray having wavelengths in the range 0.2\AA to 1\AA incident at an angle of 9° with the cube face of a rocksalt crystal ($d = 2.814\text{\AA}$)

Solution:

$n = 1$	$1\lambda_1 = 2(2.814) \sin 9^\circ \Rightarrow \lambda_1 = 0.8804 \text{\AA}$
$n = 2$	$2\lambda_2 = 0.8804\text{\AA} \Rightarrow \lambda_2 = 0.4402 \text{\AA}$
$n = 3$	$3\lambda_3 = 0.8804\text{\AA} \Rightarrow \lambda_3 = 0.2935 \text{\AA}$
$n = 4$	$4\lambda_4 = 0.8804\text{\AA} \Rightarrow \lambda_4 = 0.2201 \text{\AA}$
$n = 5$	$5\lambda_5 = 0.8804\text{\AA} \Rightarrow \lambda_5 = 0.1760 \text{\AA} < 0.2 \text{\AA}$

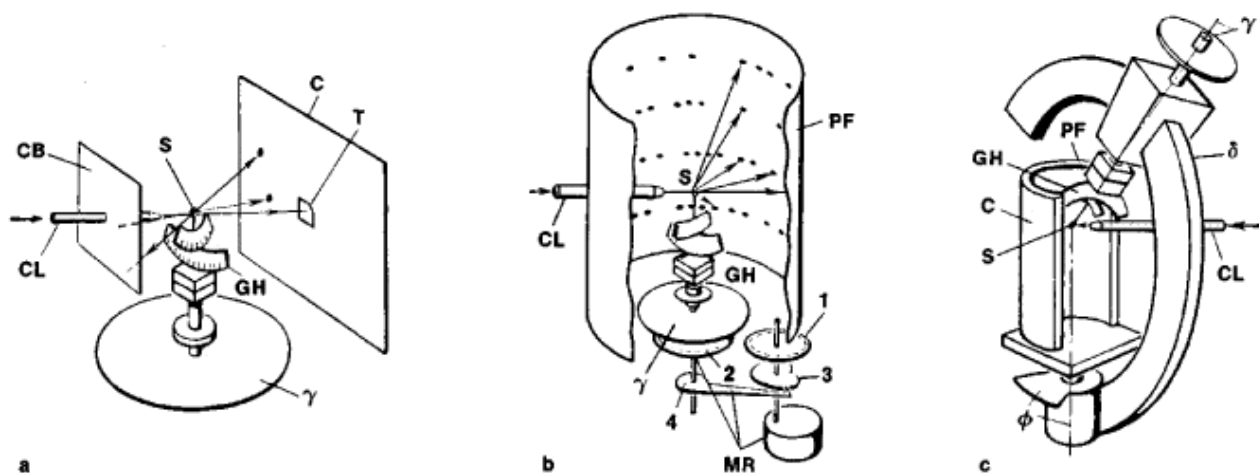
which shows the wavelength of the X-rays are 0.8804 , 0.4402 , 0.2935 and 0.2201\AA .

Experimental x-ray diffraction Methods:

To satisfy Bragg's law, it is necessary to vary either the angle of inclination of the specimen to the beam or the wavelength of the radiation. The three standard methods of X-ray crystallography are

- a) **Laue Method:** A stationary single crystal is irradiated by a range of X-ray wavelengths.
- b) **Rotating crystal Method:** A single crystal specimen is rotated in a beam of monochromatic X-rays.
- c) **Powder Method:** A polycrystalline powder specimen is kept stationary in a beam of monochromatic radiation.

Of these techniques, Laue method is used only for known crystal orientation measurement.



The powder method assumes that all orientations are present in the sample, so that regardless of the angle of incidence, there will be a grain in the proper orientation for each reflection (diffraction). The patterns are very useful for identification of unknowns. There are compiled indexes of powder diffraction data for minerals, as well as inorganic compounds and organic compounds.

If the Miller indices of the diffraction peaks are known, it is possible to determine the unit cell parameters of the material from the peak positions. Cell parameters can then be used to determine composition if the cell variation with composition is known.

If more than one mineral is present in the sample it is possible, although not easy, to determine the relative proportions of the minerals. To do this one must have a standard pattern for each pure mineral to obtain the relative intensities of the peaks from each mineral. It is then possible to use the relative intensities of non-overlapping peaks to give an estimate of the mineral proportions, called a "mode".

Exercise:

Compute the lattice spacing for the (211) reflection of olivine with $a = 4.830 \text{ \AA}$, $b = 10.896 \text{ \AA}$ and $c = 6.288 \text{ \AA}$:

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \quad 1/d^2 = (2/4.830)^2 + (1/10.896)^2 + (1/6.288)^2 \quad d = 2.2077 \text{ \AA}$$

What is the angle for this reflection using Cu k-alpha radiation ($\lambda = 1.5405 \text{ \AA}$)

$$\begin{aligned} n\lambda &= 2d \sin \theta \\ \theta &= \sin^{-1} (\lambda / 2d) \\ \theta &= 20.413^\circ \\ 2\theta &= 40.825^\circ \end{aligned}$$

Compute the spacing for (131) garnet with $a = 11.46\text{\AA}$ and Cu k-alpha radiation ($\lambda = 1.5405\text{\AA}$)

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

$$d = 11.46 / (11)^{1/2} = 3.455\text{\AA}$$

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

$$\theta = \sin^{-1}(n\lambda / 2d)$$

$$= \sin^{-1}(1.54 / 2(3.455))$$

$$\theta = 12.876^\circ$$

$$2\theta = 25.754^\circ$$

What is the energy, in joules, of an X-ray photon of Cu k-alpha radiation ($\lambda = 1.540\text{\AA}$)?

$$E = h\nu \quad \nu = c/\lambda \quad h = \text{Planck's Constant} = 6.6 \times 10^{-34} \text{ j sec}$$

$$E = hc / \lambda \quad c = \text{speed of light} = 3 \times 10^8 \text{ m/sec}$$

$$1 \text{ eV} = 1.6019 \times 10^{-19} \text{ j}$$

$$E = (6.6 \times 10^{-34} \text{ j s}) (3 \times 10^8 \text{ m/sec}) / (1.5405 \times 10^{-10} \text{ m})$$

$$E = 1.286 \times 10^{-15} \text{ j} / 1.6019 \times 10^{-19} \text{ j/eV}$$

$$\text{in electron volts } E = 8026 \text{ eV}$$

What frequency is Mo k-alpha radiation ($\lambda = 0.70926\text{\AA}$)?

$$\nu = c / \lambda$$

$$\nu = (3.0 \times 10^8 \text{ m/sec}) / (.70926 \times 10^{-10} \text{ m})$$

$$\nu = 4.2297 \times 10^{18} \text{ sec}^{-1}$$

$$= 4.2297 \times 10^{18} \text{ htz (htz = hertz = sec}^{-1}\text{)}$$

The absorption edge of Cu k-series radiation is 1.380\AA . What is the minimum KV setting on the X-ray generator required to produce Cu k-series radiation?

$$E = hc / \lambda = (6.6 \times 10^{-34} \text{ jsec})(3.0 \times 10^8 \text{ m/sec}) / (1.380 \times 10^{-10} \text{ m}) / (1.6019 \times 10^{-19} \text{ j/eV})$$

$$E = 8956 \text{ eV} = 8.956 \text{ KeV} = 8.9 \text{ KV}$$

5.4. X-ray Powder Diffraction Instruments