Condensed Matter Physics
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Module - 01
Lecture -4
Diffraction Methods for Crystal Structures

In the last lecture we saw how the symmetry of a crystal structure plays a crucial role in determining the behavior of solids in particular crystalline solids and condensed matter in general. So, the hallucination of the crystal structure namely the determination of the special position of the various atoms and molecules, which go to make up a given solid is the first important step in understanding phenomena in the solid state.

Until the discovery of x-ray diffraction by crystalline solids this was not possible, but the advent of x-ray diffraction by a crystalline solid which serves as a three dimensional grating for the x-rays. Revolutionized the situation and enabled a detailed mapping of the atomic and molecular positions inside a solid. Most of the phenomena in condense matter take place under the influence of applied electric and magnetic fields or through the scattering of particles such as electrons neutrons protons etcetera.

As well as elementary excitations such as photons, phonons, magnons, polarons, plasmons, etcetera by the atoms and molecules in the medium. So, these are all scattering events, which can also be used to reveal the details regarding crystal structure, spin arrangement, etcetera in condense matter, as well as to find, to determine the normal modes of these excitations. This is the case for example, in x-ray, electron or neutron diffraction or in roman brilone are inelastic neutron scattering. In this lecture, we describe the basic concepts which are common to these phenomena and examine some of their applications to the study of solids and liquids.

In order to do this, we have to formulate the theory of what happens, when x-rays are diffracted by a crystalline solid. We consider a perfect crystal which consists of a regular lattice of discrete atoms and molecules, when an atom is excited by an electromagnetic wave it reradiates this wave in all directions in face with the initial excitations at that atom. This is just a consequence of what Huygens postulated in wave optic much earlier. The amplitude of the beam, x-ray beam in any direction is obtained by summing up the contribution in that direction from each atom taking into account the face differences between these atoms.

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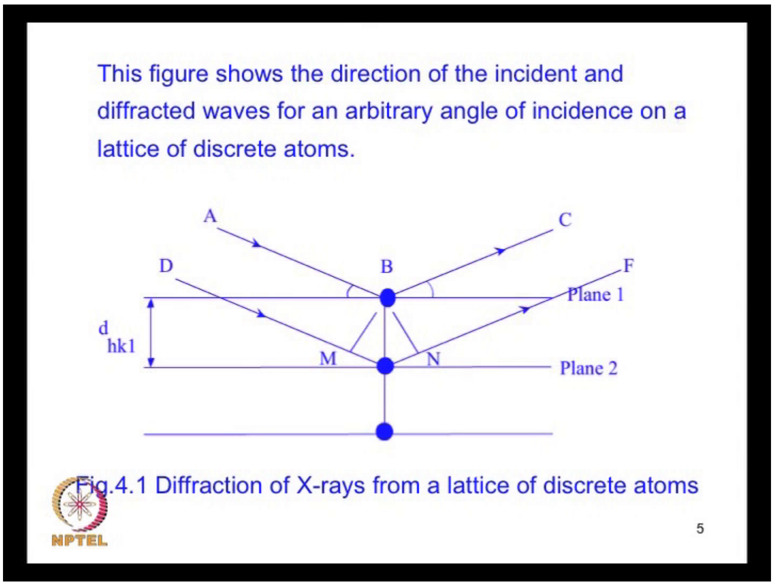

This figure shows the direction of the incident and diffracted waves for an arbitrary angle of incidence on a lattice of discrete atoms.

Fig.4.1 Diffraction of X-rays from a lattice of discrete atoms

This figure shows the direction of the incident and diffracted waves for an arbitrary angle of incidence on a lattice of discrete atoms. So, we have a lattice, which is shown by the heavy dots. So, those are the atoms and you have a pair of a set of parallel crystal planes and then the incident x-ray beam is scattered by an atom for example, at B the incident wave from A is scattered by the atom at B into a direction marked as C in this figure. So, that is the basic scattering or diffraction event.

We all know from elementary discussions, which I do not propose to go into this is based on finding this amplitude and finding the condition for constructive interference of the scattered or diffracted amplitudes. So, diffraction is known to occur when the waves reinforce each other that is what I meant by constructive interference. The condition for a diffraction maximum is given by the so, called famous Bragg law of x-ray diffraction.

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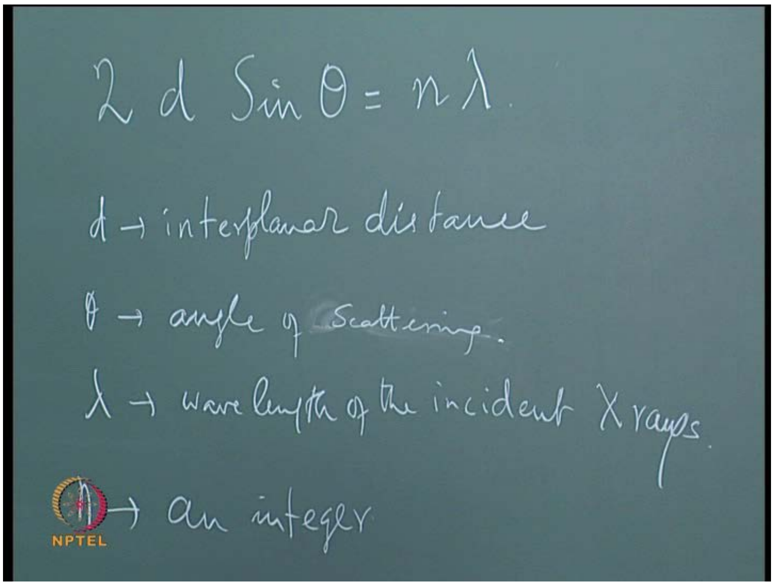

$2 d \sin\theta = n\lambda$.

$d \rightarrow$ interplanar distance

$\theta \rightarrow$ angle of scattering.

$\lambda \rightarrow$ wave length of the incident X rays.

$n \rightarrow$ an integer

Which is given as 2 d sin theta equals n lambda, here d is the inter planar separation distance, theta is the angle of incidence let me say angle of scattering and lambda is the wave length of the incident x-rays, n is any integer, corresponding to different values of n, diffraction maxima will arise. We will now try to see how this comes about by calculating the amplitude of the diffracted waves from all the atoms at a point, when a wave is incident at one of the atoms as shown in this figure.

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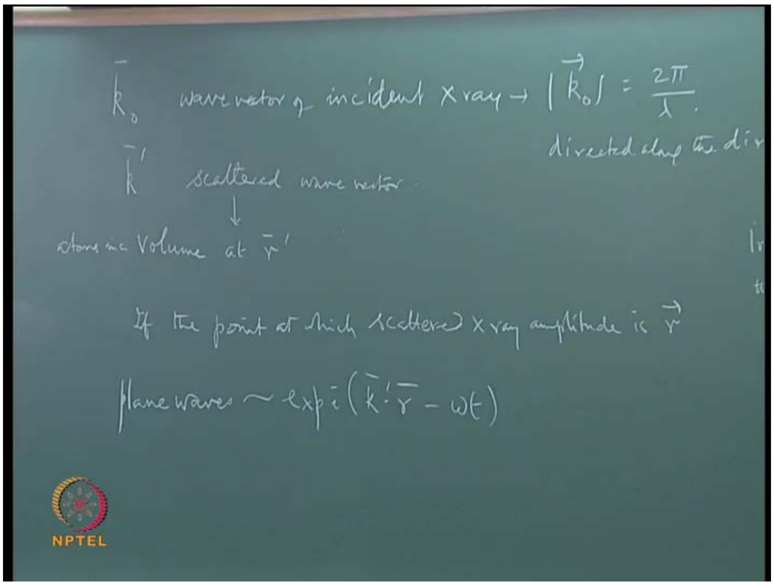

$\bar{k}_0$ wave vector of incident X ray $\rightarrow |\vec{k}_0| = \frac{2\pi}{\lambda}$.

directed along the dir

$\bar{k}'$ scattered wave vector.

$\downarrow$

atoms in a Volume at $\bar{r}'$

Ir

t

If the point at which scattered X ray amplitude is $\vec{r}$

plane waves $\sim \exp i(\bar{k}' \cdot \bar{r} - \omega t)$

So, you have an x-ray of wave vector k 0 incident x-ray. It defines a direction the magnitude is 2 pi by lambda, where lambda is the wave length and the direction is along the direction of propagation of the wave.

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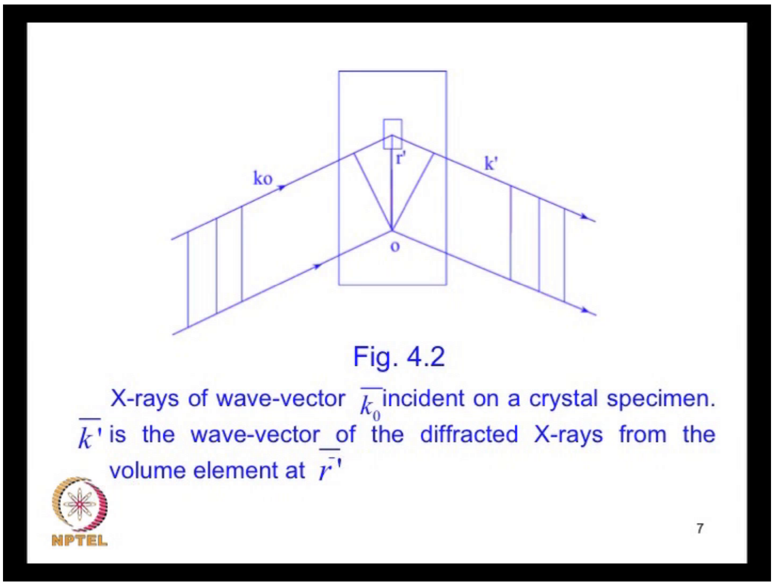

Fig. 4.2

X-rays of wave-vector $\overline{k_0}$ incident on a crystal specimen. $\overline{k}'$ is the wave-vector of the diffracted X-rays from the volume element at $\bar{r}'$

And now, k dash is the scattered wave vector, wave vector of the scattered x-rays. So, we are considering a small volume element at a point or prime. Scattered by atoms in a small volume around at position vector r prime. Now, if I consider the point at which we measure the scattered amplitude is if it is taken if the point at which scattered x-ray amplitude is calculated is given by the position vector r and if this is sufficiently far away from the arrays of atom, which do the scattering.

Then we can assume that the secondary wavelengths of Huygens theory, which originate from the scattering atoms may this spherical wave fronts of the secondary wavelets will become plane waves at sufficiently large distances and these plane waves can be written as exponential i k dash dot r minus omega t. The amplitude of the wave as it leaves the atom at r prime the incident amplitude is proportional to exponential i k 0 dot r prime minus omega t, this is the incident amplitude at the atom located in r.

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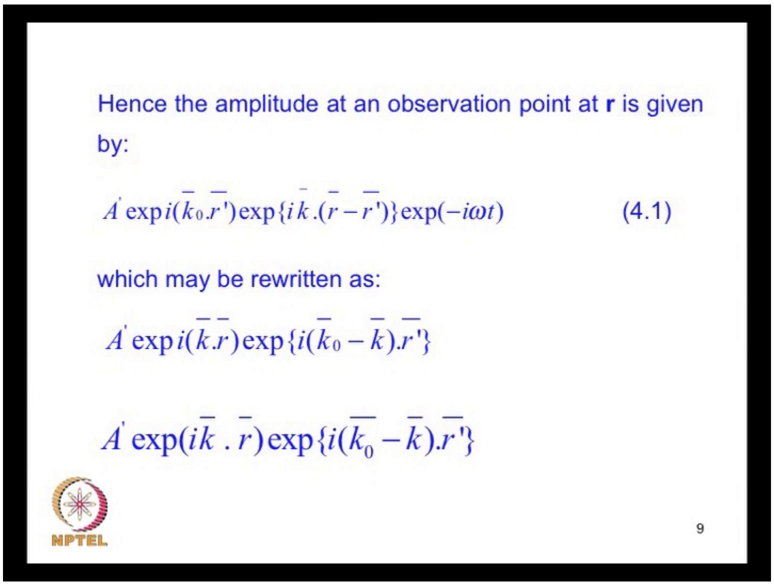

Hence the amplitude at an observation point at **r** is given by:

$$A^{'} \exp i(\bar{k}_0 . \bar{r}') \exp\{i \bar{k} .(\bar{r} - \bar{r}')\} \exp(-i\omega t) \qquad (4.1)$$

which may be rewritten as:

$$A^{'} \exp i(\bar{k} . \bar{r}) \exp\{i(\bar{k}_0 - \bar{k}) . \bar{r}'\}$$

$$A^{'} \exp(i\bar{k} \, . \, \bar{r}) \exp\{i(\overline{k_0} - \bar{k}) . \bar{r}'\}$$

So, we have a situation, where we can easily calculate the amplitude at the observation point.

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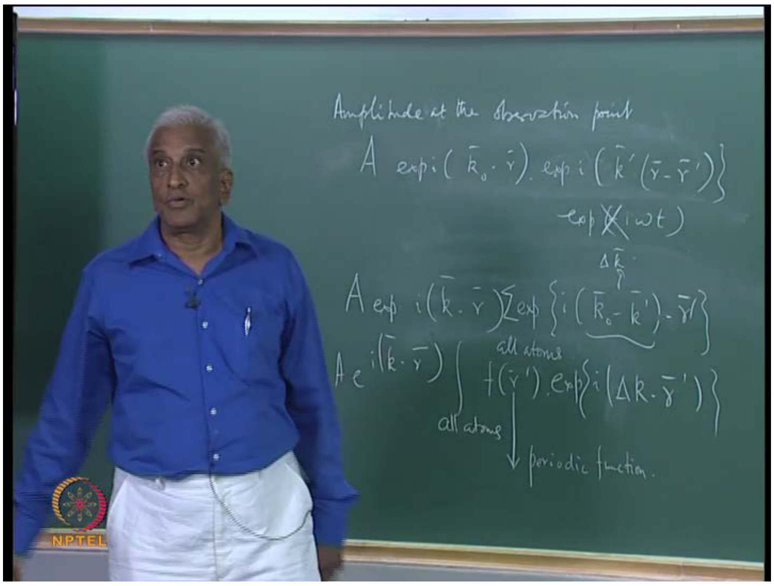

Amplitude at the observation point

$$A \; \exp i(\bar{k}_0 \cdot \bar{r}) . \exp i(\bar{k}'(\bar{r} - \bar{r}'))\}$$

$$\exp \cancel{(} i\omega t)$$

$$A \exp i(\bar{k} . \bar{r}) \sum_{\text{all atoms}} \exp\{i(\overset{\Delta \bar{k}}{\underbrace{\bar{k}_0 - \bar{k}'}}) . \bar{r}'\}$$

$$A e^{i(\bar{k} . \bar{r})} \int_{\text{all atoms}} \underset{\downarrow \text{ periodic function.}}{f(\bar{r}')} . \exp\{i(\Delta k . \bar{r}')\}$$

The amplitude the observation point of the scattered wave is proportional to or we can write as sum A exponential i k not dot r prime minus omega t.

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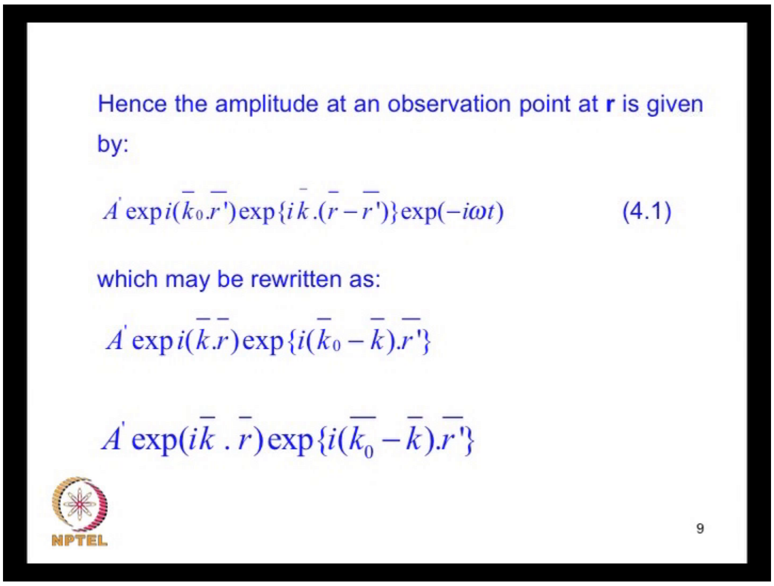

Hence the amplitude at an observation point at **r** is given by:

$$A^{'}\exp i(\bar{k}_0.\bar{r}')\exp\{i\bar{k}.(\bar{r}-\bar{r}')\}\exp(-i\omega t) \qquad (4.1)$$

which may be rewritten as:

$$A^{'}\exp i(\bar{k}.\bar{r})\exp\{i(\bar{k}_0-\bar{k}).\bar{r}'\}$$

$$A^{'}\exp(i\bar{k}\ .\ \bar{r})\exp\{i(\overline{k_0}-\bar{k}).\overline{r'}\}$$

This we will write later, times exponential i k dash dot r minus r prime that is the distance between r and r prime times exponential minus i omega t. So, that would be the amplitude. So, this can be rewritten as A exponential i k dot r times exponential i k naught minus k prime dot r prime this is simply neglecting omitting the time dependent term.

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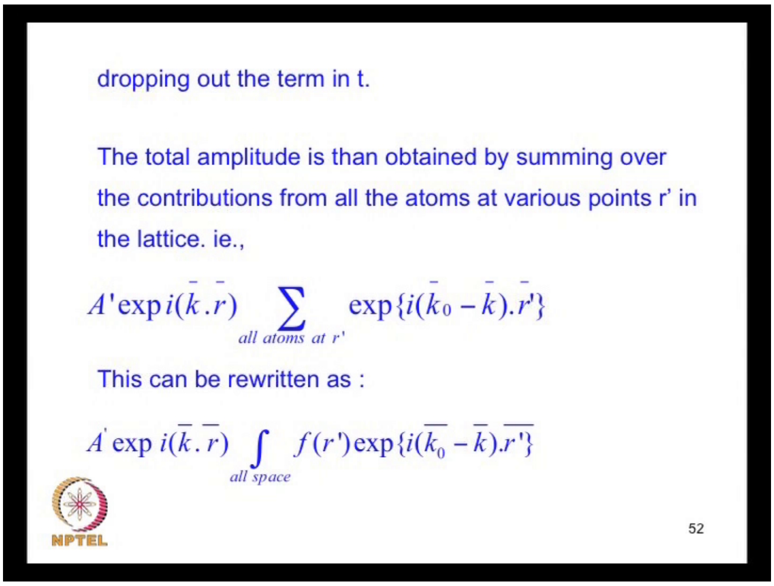

dropping out the term in t.

The total amplitude is than obtained by summing over the contributions from all the atoms at various points r' in the lattice. ie.,

$$A'\exp i(\bar{k}.\bar{r})\sum_{all\ atoms\ at\ r'}\exp\{i(\bar{k}_0-\bar{k}).\bar{r}'\}$$

This can be rewritten as :

$$A^{'}\exp i(\bar{k}.\bar{r})\int_{all\ space} f(r')\exp\{i(\overline{k_0}-\bar{k}).\overline{r'}\}$$

So, this is simply rearranged in the form. So, this is the amplitude when we drop to the time dependent the total amplitude is got by summing over all the atoms. So, the atomic terms are here. So, this is a summation over all atoms that is the total amplitude. So, that can also be rewritten as A e to the power i k dot r integral all atoms since we are having atoms, which are practically continuously distributed. So, we can write a scattering amplitude times exponential i delta k dot r prime, where delta k is just this quantity this is i write it as delta k.

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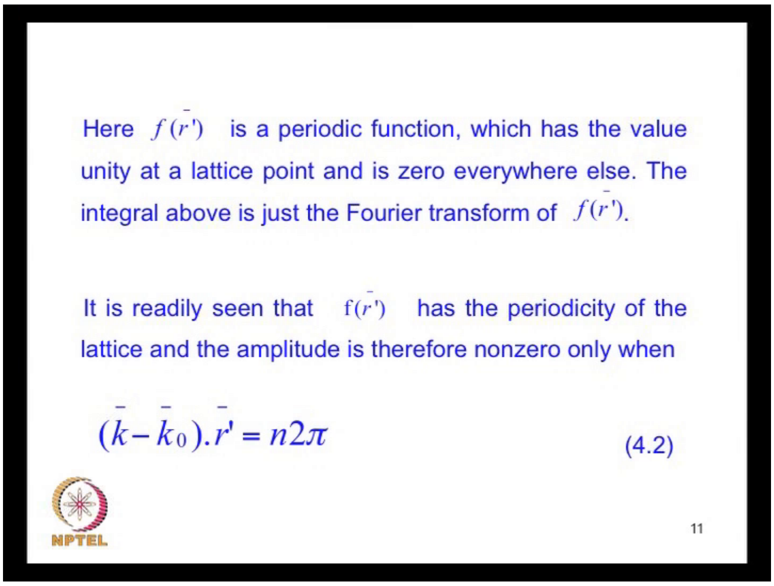

Here $f(\bar{r}')$ is a periodic function, which has the value unity at a lattice point and is zero everywhere else. The integral above is just the Fourier transform of $f(\bar{r}')$.

It is readily seen that $f(\bar{r}')$ has the periodicity of the lattice and the amplitude is therefore nonzero only when

$$(\bar{k}-\bar{k}_0).\bar{r}' = n2\pi \qquad (4.2)$$

So, this is a, this f of r prime is a periodic function depending on the distribution of atoms. So, it has a maximum value at the site of a lattice point it is unity and it is zero everywhere else where ever there is an atom there is scattering amplitude. So, it has this has which has the same periodicity is the same as that of the crystal lattice. So, it has the same thing therefore, this amplitude will be nonzero.

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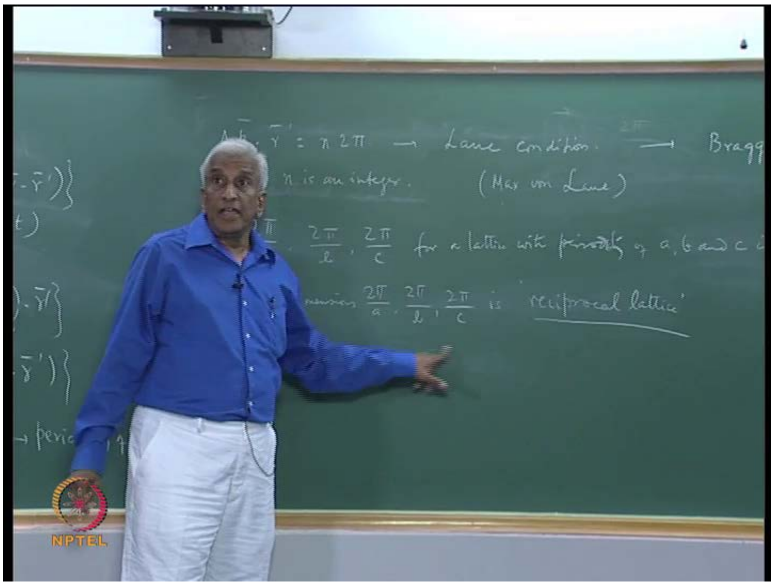

Only when this exponential term does not vanish, in other words the condition for a diffraction maximum is got as delta k dot r equal to n into 2 pi, where n is an integer this is known as Laue condition, this was first written by max von Laue. Well I will write you just keep the notation and keep the r prime. So, this is the condition for constructive interference or reinforcement of the scattered amplitudes. So, that there is a Bragg reflection so, strictly this lead to a Bragg reflection. We can write this condition in component form because this is a vector equation.

So, we can write it in component form. So, if we do this we get three conditions in terms of integers, which are 2 pi by a multiples of 2 pi by a, 2 pi by b, 2 pi by c for a lattice with periodicity of a b and c in the three mutually orthogonal crystallographic directions. So, it is now, useful to construct a lattice with unit cell with lengths of this and such a lattice is known as a lattice with unit cell of dimensions 2 pi by a, 2 pi by b, 2 pi by c is known as the reciprocal lattice in crystallography, this is a very useful concept .The concept of a reciprocal lattice it is called reciprocal lattice because it involves a unit cell whose lengths are the reciprocals of the three lattice parameters.

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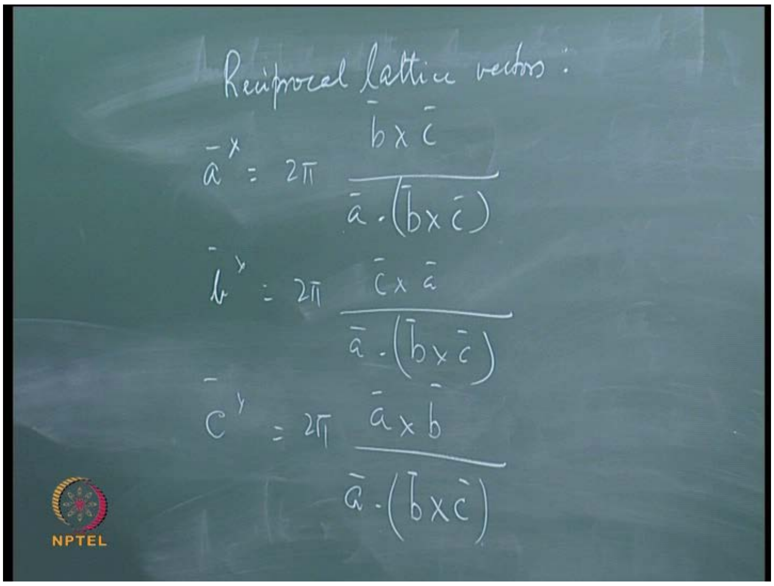

Reciprocal lattice vectors:

$$\bar{a}^{*} = 2\pi \frac{\bar{b}\times\bar{c}}{\bar{a}.(\bar{b}\times\bar{c})}$$

$$\bar{b}^{*} = 2\pi \frac{\bar{c}\times\bar{a}}{\bar{a}.(\bar{b}\times\bar{c})}$$

$$\bar{c}^{*} = 2\pi \frac{\bar{a}\times\bar{b}}{\bar{a}.(\bar{b}\times\bar{c})}$$

So, we can write the basis vectors of such a reciprocal lattice. If a b and c are the lattice vectors of the original lattice, reciprocal lattice vectors are given by a star equals 2 pi times b cross c by a dot b cross c, b star is 2 pi times c cross a by a dot b cross c.

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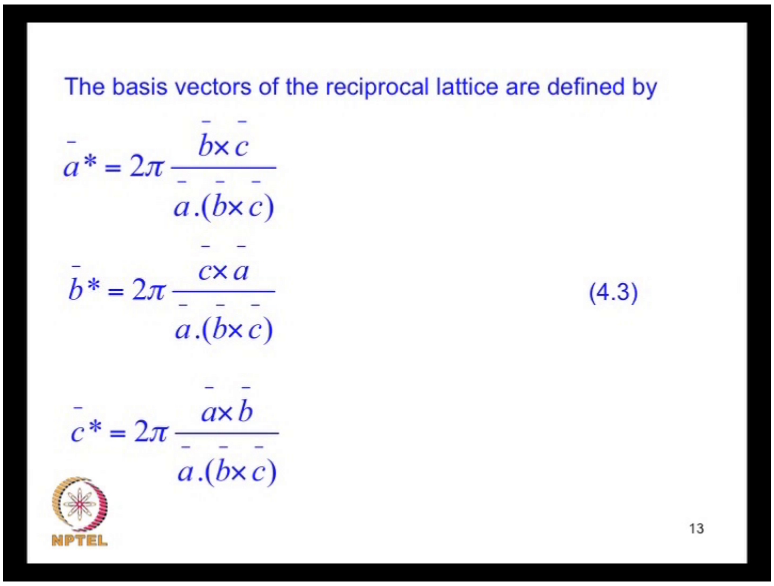

The basis vectors of the reciprocal lattice are defined by

$$\bar{a}* = 2\pi \frac{\bar{b}\times\bar{c}}{\bar{a}.(\bar{b}\times\bar{c})}$$

$$\bar{b}* = 2\pi \frac{\bar{c}\times\bar{a}}{\bar{a}.(\bar{b}\times\bar{c})} \qquad (4.3)$$

$$\bar{c}* = 2\pi \frac{\bar{a}\times\bar{b}}{\bar{a}.(\bar{b}\times\bar{c})}$$

And c star is 2 pi times a cross b by a dot b cross c. So, we define the reciprocal lattice vectors in this way and a vector, which connects two points in the reciprocal lattice, is known as a reciprocal lattice vector.

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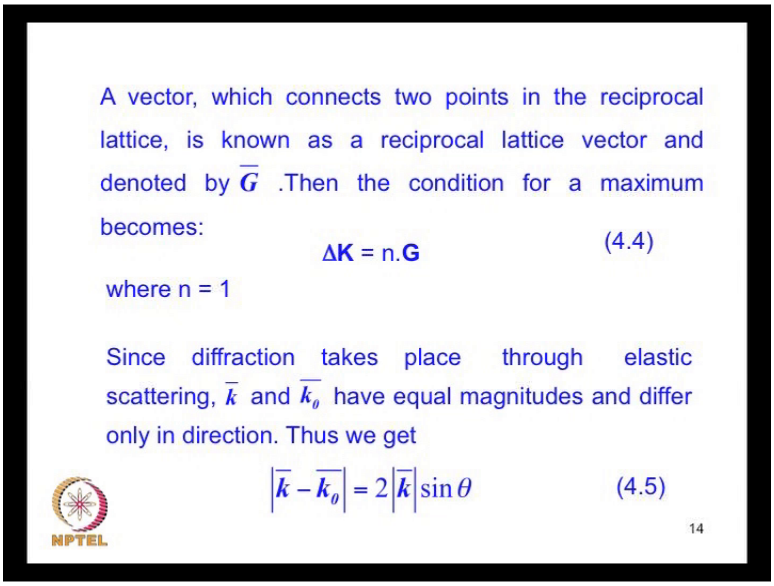

A vector, which connects two points in the reciprocal lattice, is known as a reciprocal lattice vector and denoted by $\overline{G}$ .Then the condition for a maximum becomes:

$$\Delta \mathbf{K} = n.\mathbf{G} \qquad (4.4)$$

where n = 1

Since diffraction takes place through elastic scattering, $\overline{k}$ and $\overline{k_0}$ have equal magnitudes and differ only in direction. Thus we get

$$\left|\overline{k} - \overline{k_0}\right| = 2\left|\overline{k}\right|\sin\theta \qquad (4.5)$$

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A reciprocal lattice vector is usually denoted by the symbol G.

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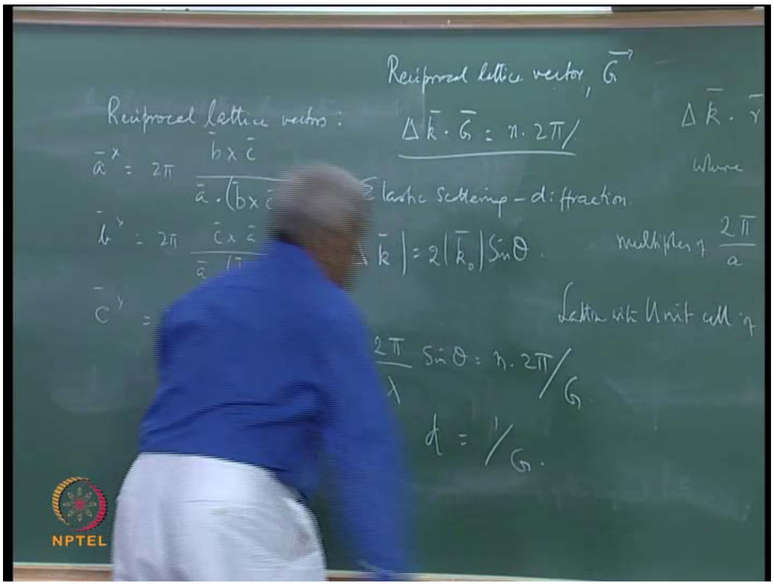

So, the condition for maximum then becomes delta k equals n dot G, since diffraction takes place diffraction means it is elastic scattering. What is elastic scattering elastic? Scattering is a scattering event in which the energy is conserved apart from momentum conservation. Energy is also conserved in the sense that the incident and scattered wave vector will have equal magnitudes and differ only in direction. So, delta k will have a magnitude equal to two times k naught sin theta. So, if you plug this in where theta is the scattering angle. So, we get two times sin theta equal to n into 2 pi.

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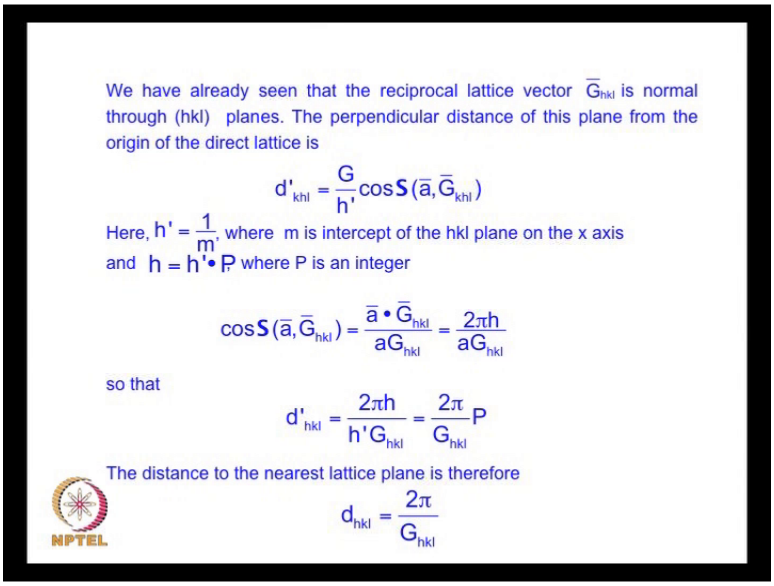

We have already seen that the reciprocal lattice vector $\bar{G}_{hkl}$ is normal through (hkl) planes. The perpendicular distance of this plane from the origin of the direct lattice is

$$d'_{khl} = \frac{G}{h'} \cos \mathbf{S} (\bar{a}, \bar{G}_{khl})$$

Here, $h' = \frac{1}{m'}$ where m is intercept of the hkl plane on the x axis

and $h = h' \bullet P$ where P is an integer

$$\cos \mathbf{S} (\bar{a}, \bar{G}_{hkl}) = \frac{\bar{a} \bullet \bar{G}_{hkl}}{aG_{hkl}} = \frac{2\pi h}{aG_{hkl}}$$

so that

$$d'_{hkl} = \frac{2\pi h}{h' G_{hkl}} = \frac{2\pi}{G_{hkl}} P$$

The distance to the nearest lattice plane is therefore

$$d_{hkl} = \frac{2\pi}{G_{hkl}}$$

And we can show that the inter planar spacing is just 1 by G therefore; we arrive at the Bragg condition 2 d sine theta equal to n lambda. So, we see that the Laue condition and Bragg condition for diffraction maximum are really one and the same. Because, the inter planar spacing in all crystals is a the order of d is the order of a few angstroms therefore, x-rays, which have the wavelength of the same order or smaller are commonly used to observe the diffraction of waves in solids. The technique of determining the structures of crystals using x-ray diffraction is known as x-ray crystallography. X-ray crystallography gives you the basic principles governing how to determine crystal structures using x-ray diffraction. There are several methods we will discuss a few of them here.

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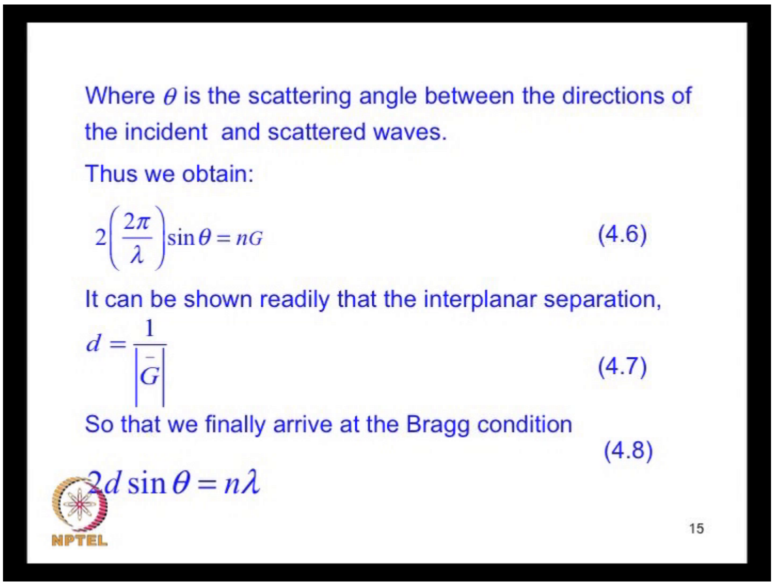

Where θ is the scattering angle between the directions of the incident and scattered waves.

Thus we obtain:

$$2\left(\frac{2\pi}{\lambda}\right)\sin\theta = nG \qquad (4.6)$$

It can be shown readily that the interplanar separation,

$$d = \frac{1}{\left|\bar{G}\right|} \qquad (4.7)$$

So that we finally arrive at the Bragg condition (4.8)

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

The first one is known as the Debye Scherrer method. This is the most popular and most commonly used method. So, I am discussing that first.

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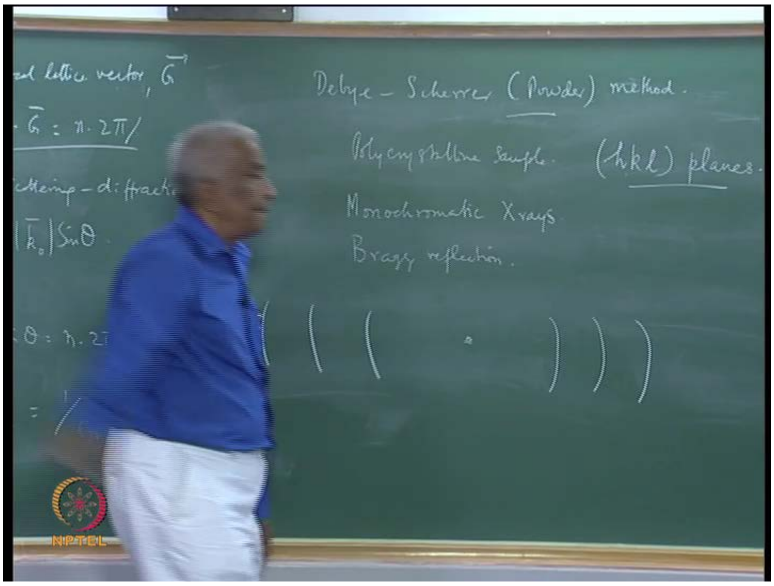

So, the first method is known as Debye Scherrer it is also known as the powder method, since it uses samples in the form of powder, powder method. So, you have a sample in the form of a powder or poly crystalline sample that is why this is very popular that you do not require a crystal you can take any solid in the form of a poly crystalline or powder sample. So, you do not have to take special efforts to grow a single crystal. So, you have a large number of tiny crystals oriented in all possible directions randomly with respect to the incident x-ray direction wherever you apply the incident x-ray direction the crystal grains will be oriented in all possible directions isotropically because, there is no way of saying, which way it will be preferably preferentially oriented.

So, all grains will be oriented randomly around the incident direction whatever be that direction. So, when a monochromatic x-rays we use a poly crystalline sample and monochromatic x-rays that is x-rays of a definite wave length. So, these are the two ingredients in the Debye Scherrer method when you have a monochromatic x-ray beam which is incident on such a poly crystalline sample, since the grains are oriented in all possible directions Bragg reflection takes place, almost all the planes because you have a large number of grains oriented in all possible directions.

So, some plane or other will satisfy the Bragg law condition. So for, every set of h k l planes containing different h k l planes, h k l or the miller indices of the crystallography planes. So, for every set of there are different planes with different values of h k and l the miller indices. So, there will be several grains in the powder sample, which are oriented in such a direction as to satisfy the Bragg condition for the given incident x-ray.

So, you take the sample in the form of very fine powder, which is usually put inside a thin glass capillary tube or is attached to a glass fiber by coating the glass fiber with grease and then rolled in the powder then this is mounted at the center of a cylindrical camera, which is shown that is known as the Debye Scherrer camera it is shown in the next figure.

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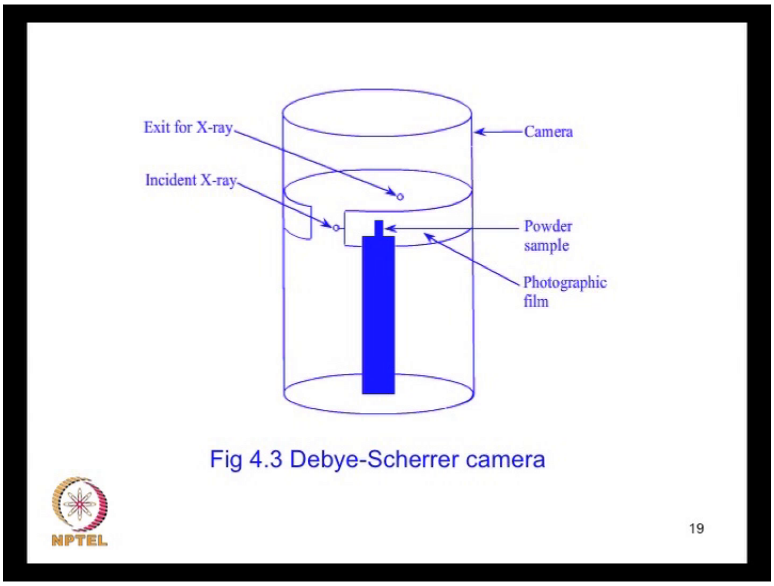

Fig 4.3 Debye-Scherrer camera

So, that is the Debye Scherrer camera and you see the sample mounted at the center. A strip of photographic plate is positioned inside the camera around the inner wall. So, you have a strip positioned around the inner wall of this camera. So, there is a photographic film. In the middle such that the films surrounds the sample, the camera has a hole for the incident x-ray and a diametrically opposite hole for the outgoing x-ray. So, there is an entrance for the incident x-rays and an exit.

So, that is the basic details of the Debye Scherrer camera when the monochromatic x-ray beam falls on the specimen the incident beam undergoes Bragg reflection from the various crystallographic planes. So, the rays reflected from one set of h k l planes making an angle theta with the incident beam will all lie on the surface of a cone, whose apex is at the point of contact of the incident radiation with the specimen this is shown in the next figure. where how the x-ray diffraction pattern is formed is shown. So, the incident x-ray beam is coming and then all the points situated on that cone will correspond to the same Bragg reflection condition. So, the diffraction beam from two sets of plane is shown in this figure.

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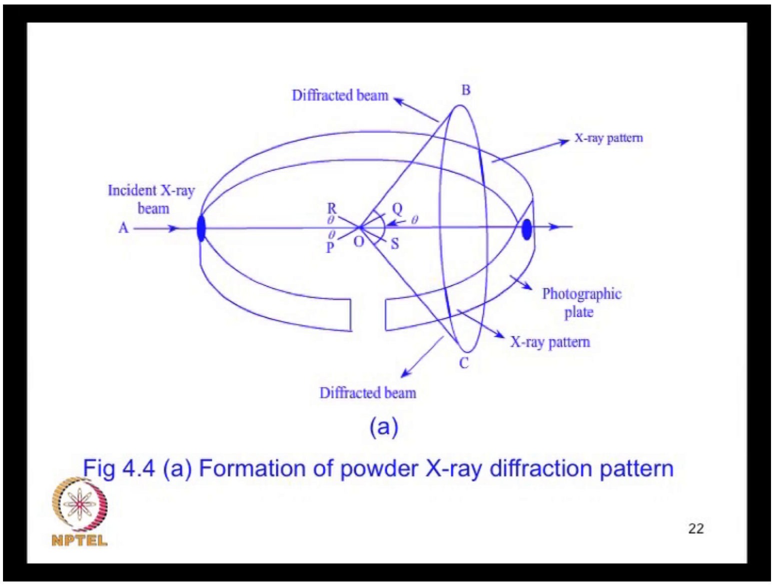

(a)

Fig 4.4 (a) Formation of powder X-ray diffraction pattern

So, from this figure you can see that the solid angle subtended by the cone is 4 theta. So, each set of planes for a given specific h k l value gives rise to a such a cone of reflected rays and therefore, these cones intersect the cylindrical photographic plate in circles as illustrated in the next figure.

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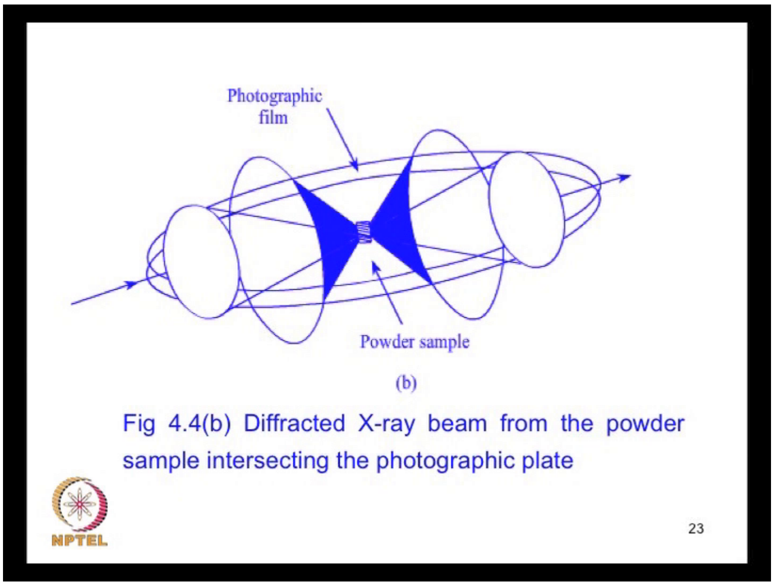

(b)

Fig 4.4(b) Diffracted X-ray beam from the powder sample intersecting the photographic plate

So, these cones intersect the photographic plate. So, you have the diffracted x-ray beam from the powder sample intersects the photographic plate. So, you get each cone generates a pair of arcs on the photographic plate. The arcs are positioned symmetrically with respect to the central hole there will be several such pairs. So, those will be different pairs of arcs each corresponding to one set of h k l planes.

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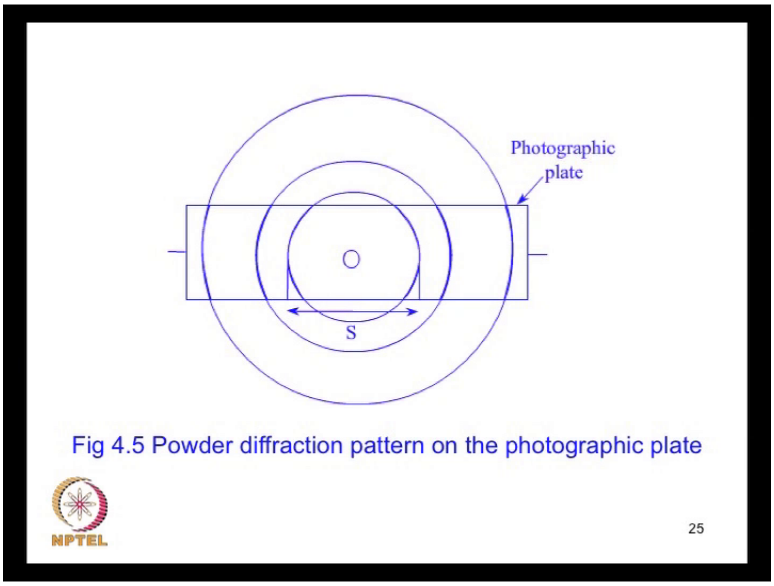

Fig 4.5 Powder diffraction pattern on the photographic plate

So, this is how a typical record will show powder diffraction pattern will be formed on the photographic plate as shown in the figure.

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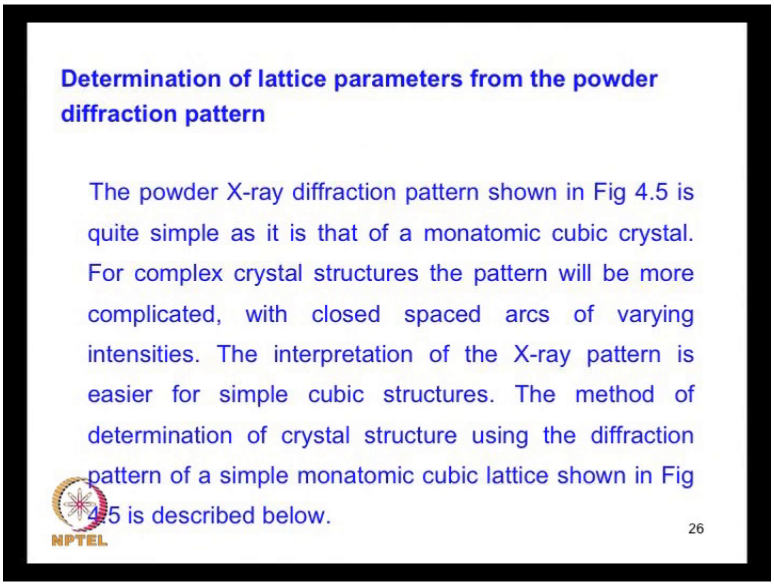

Determination of lattice parameters from the powder diffraction pattern

The powder X-ray diffraction pattern shown in Fig 4.5 is quite simple as it is that of a monatomic cubic crystal. For complex crystal structures the pattern will be more complicated, with closed spaced arcs of varying intensities. The interpretation of the X-ray pattern is easier for simple cubic structures. The method of determination of crystal structure using the diffraction pattern of a simple monatomic cubic lattice shown in Fig 4.5 is described below.

So, this is quite simple, this picture that is shown in this figure is a very simple one because, it corresponds to a simple a monatomic cubic crystal. If the crystal structure is complex this pattern also will become more complicated with closely spaced arcs of varying intensities. So, how to interpret the x-ray pattern, it is easier for simple cubic structures. So, this such a simple description of how the crystal structure can be determine using the diffraction pattern generated by a simple monatomic cubic lattice is shown in this figure is described now.

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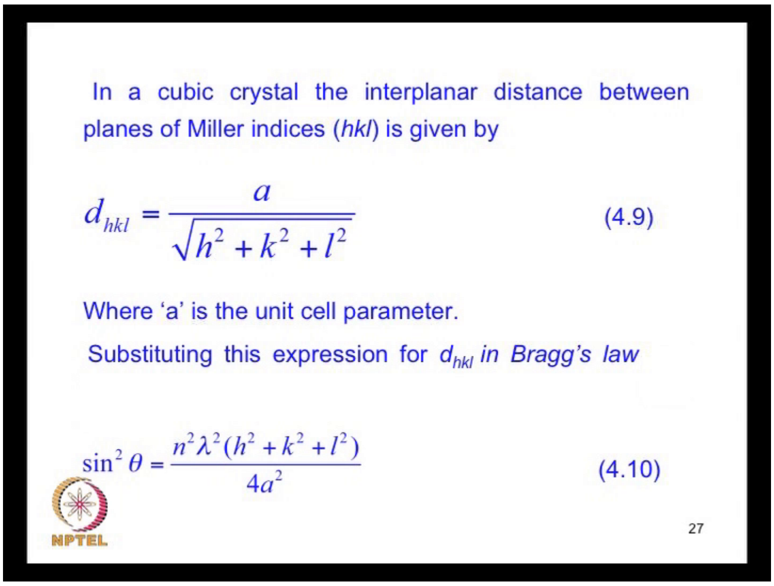

In a cubic crystal the interplanar distance between planes of Miller indices (*hkl*) is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (4.9)$$

Where 'a' is the unit cell parameter.

Substituting this expression for d_{hkl} *in Bragg's law*

$$\sin^2\theta = \frac{n^2\lambda^2(h^2 + k^2 + l^2)}{4a^2} \qquad (4.10)$$

So, if you have a cubic crystal then the condition is we already saw this mentioned this in an earlier lecture.

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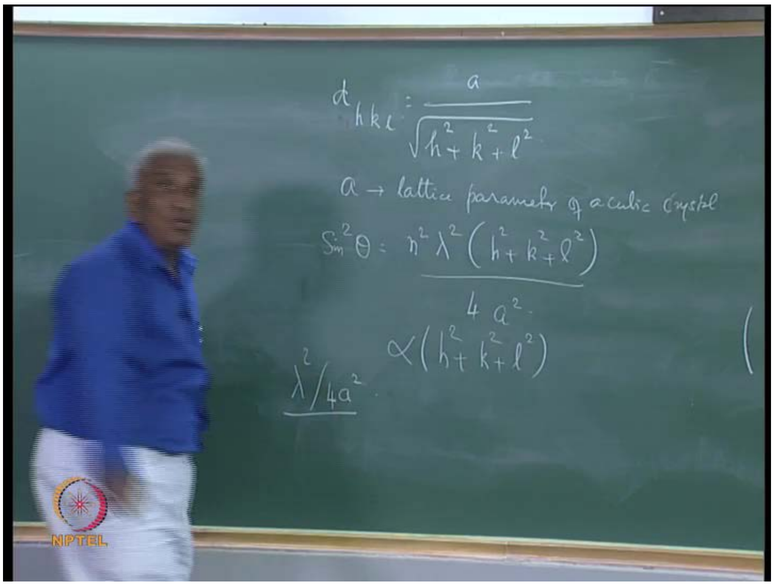

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$a \rightarrow$ lattice parameter of a cubic crystal

$$\sin^2\theta = \frac{n^2\lambda^2(h^2 + k^2 + l^2)}{4a^2}$$

$$\propto (h^2 + k^2 + l^2)$$

$$\underline{\lambda^2/4a^2}$$

Where a is the lattice parameter of a cubic solid crystal, d h k l is the inter planar spacing corresponding to a set of h k l planes, where h k l are the miller indices. So, substituting these values in the Braggs law, we get sin square theta and rearranging the terms you get n square lambda square h square plus k square plus l square by four a square. So, that is the basic equation.

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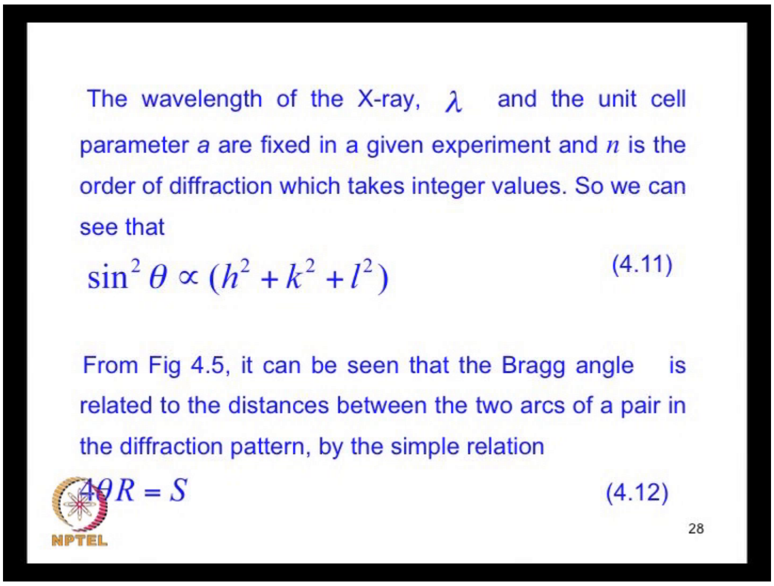

The wavelength of the X-ray, λ and the unit cell parameter *a* are fixed in a given experiment and *n* is the order of diffraction which takes integer values. So we can see that

$$\sin^2\theta \propto (h^2 + k^2 + l^2) \qquad (4.11)$$

From Fig 4.5, it can be seen that the Bragg angle is related to the distances between the two arcs of a pair in the diffraction pattern, by the simple relation

$$4\theta R = S \qquad (4.12)$$

So, the lambda is fixed in a given x-ray experiment. The unit cell parameter is fixed for the given solid, n is the order of the diffraction so, which takes integer values. So, we can see that sin square theta is proportional to h square plus k square plus l square everything else is fixed. Now, the Bragg angle is related to the distance between the arcs, this distance is what is measured and this is given by the solid angle is 4 theta times R, which is the radius of the camera gives you this distance. So, you can measure this distance and knowing the angle of scattering and knowing the radius of the Debye Scherrer camera.

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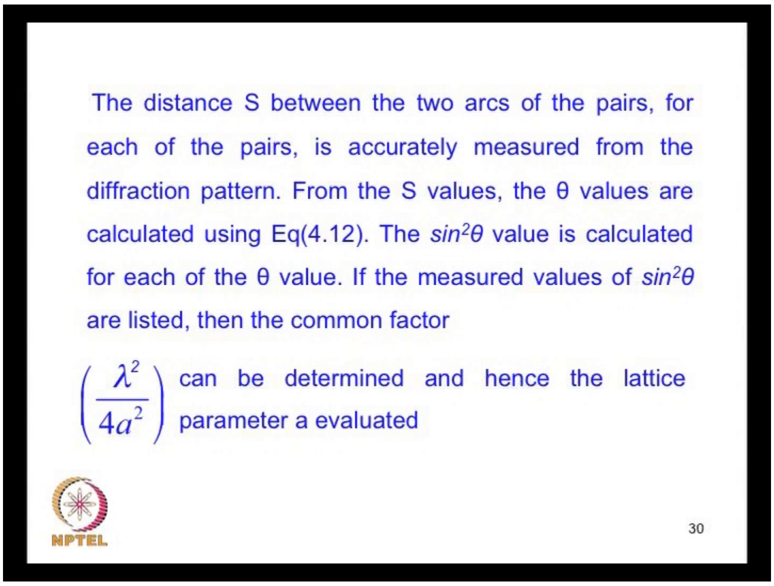

The distance S between the two arcs of the pairs, for each of the pairs, is accurately measured from the diffraction pattern. From the S values, the θ values are calculated using Eq(4.12). The $sin^2\theta$ value is calculated for each of the θ value. If the measured values of $sin^2\theta$ are listed, then the common factor

$\left(\frac{\lambda^2}{4a^2}\right)$ can be determined and hence the lattice parameter a evaluated

The distance from the distance which is accurately measured from the diffracted pattern we can calculate the theta values using this equation. So, the sin square theta is calculated then if it is tabulated the common factor between the different values of sin square theta gives you lambda square by 4 a square. So, what do you do? You write down the calculate the sin square theta and then find the common factor for example, table shows the different h k l planes and the corresponding h square plus k square plus l square. So, we can calculate the common factor lambda square by a square and hence find the lattice parameter a.

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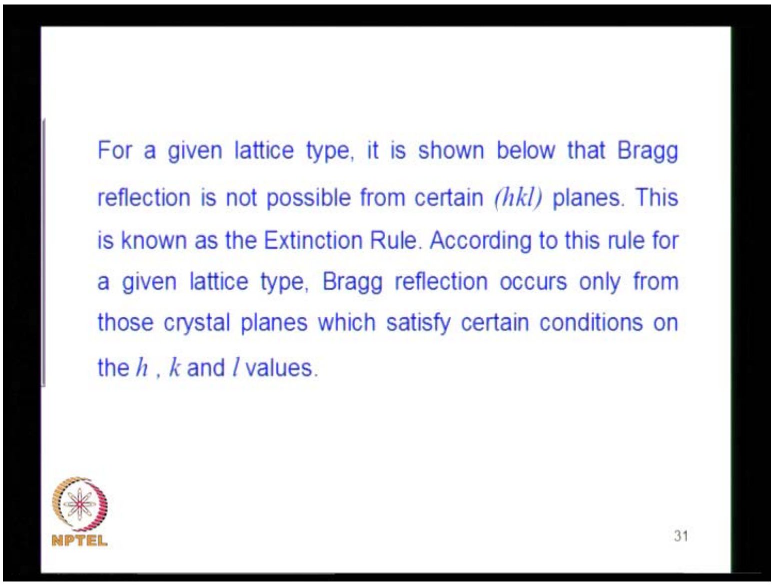

For a given lattice type, it is shown below that Bragg reflection is not possible from certain (hkl) planes. This is known as the Extinction Rule. According to this rule for a given lattice type, Bragg reflection occurs only from those crystal planes which satisfy certain conditions on the h , k and l values.

Now, we will also see that for a given lattice type Bragg reflection is possible only from certain h k l planes this is known as the extinction roll.

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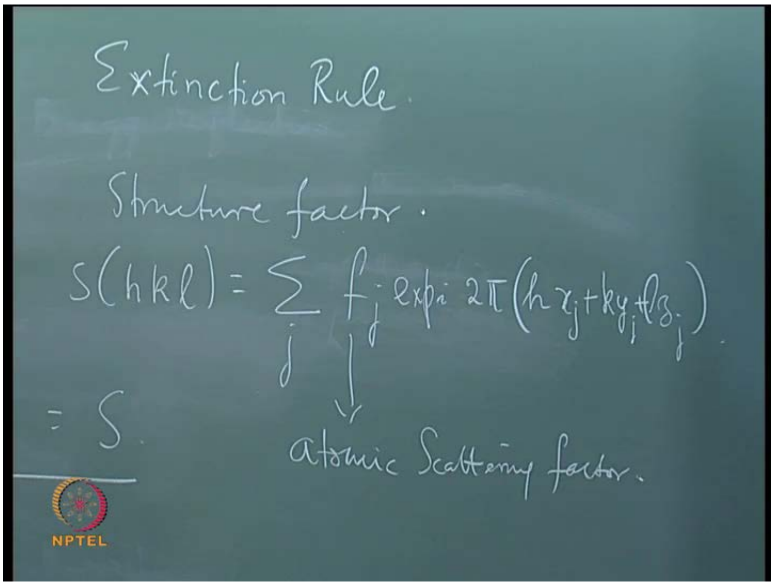

Extinction Rule.

Structure factor.

$$S(hkl) = \sum_j f_j \exp i\, 2\pi (h x_j + k y_j + l z_j).$$

$= S.$

$f_j \downarrow$ atomic scattering factor.

This simplifies the analysis of the x-ray diffraction pattern, not all values of h k l give rise to a Bragg reflection. So, depending on the given lattice type Bragg reflection occurs only from those crystal planes which satisfy certain conditions on the h k and l values.

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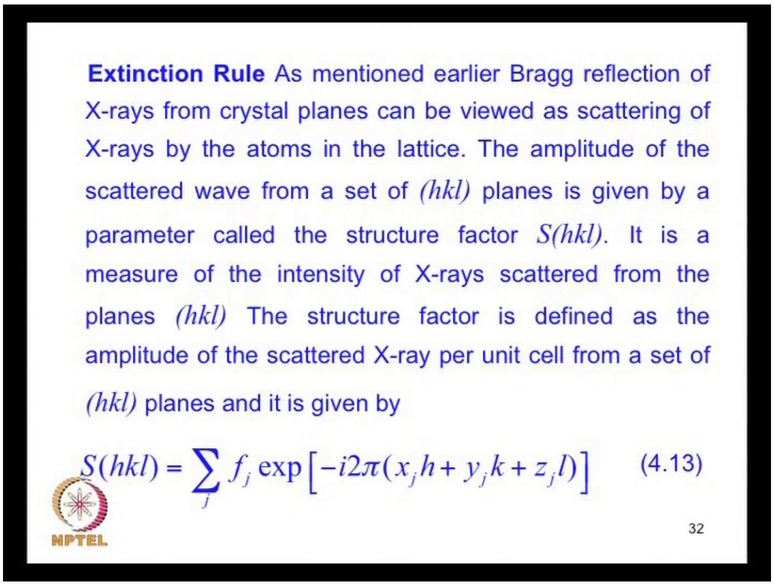

Extinction Rule As mentioned earlier Bragg reflection of X-rays from crystal planes can be viewed as scattering of X-rays by the atoms in the lattice. The amplitude of the scattered wave from a set of *(hkl)* planes is given by a parameter called the structure factor *S(hkl)*. It is a measure of the intensity of X-rays scattered from the planes *(hkl)* The structure factor is defined as the amplitude of the scattered X-ray per unit cell from a set of *(hkl)* planes and it is given by

$$S(hkl) = \sum_j f_j \exp\left[-i2\pi(x_j h + y_j k + z_j l)\right] \quad (4.13)$$

This is to understand this; we have to write down what is known as the structure factor. Which is really determined for a given h k l planes as sigma over j f j. f j is the scattering amplitude times exponential i 2 pi into h x j plus k y j plus l z j . So, that defines the where k j y j z j are the coordinates of the jth atom, which lies on a crystal lattice plane whose miller indices are h k and l. So, once you have this, the summation over j is over all such identical atoms in the unit cell, f j is known as the atomic scattering factor. Let us now evaluate the structure factor; the structure factor goes into the intensity of the diffracted beam. So, if you take a simple cubic structure.

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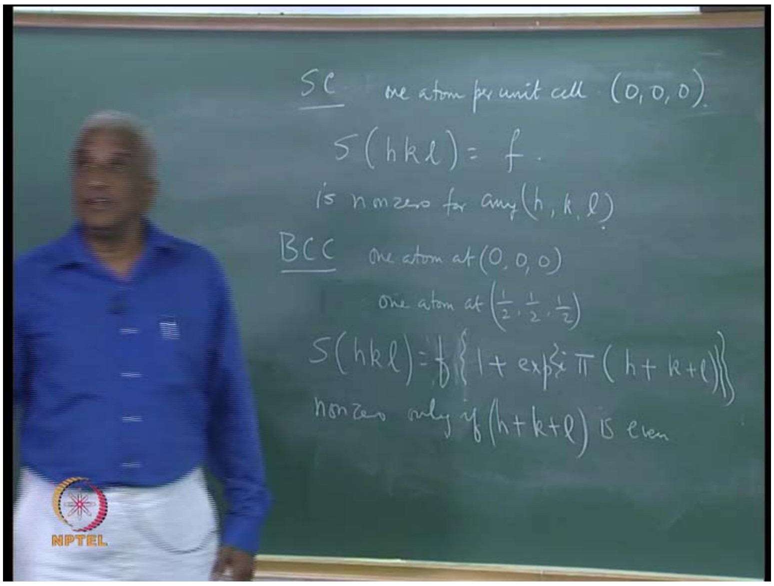

SC one atom per unit cell $(0, 0, 0)$

$S(hkl) = f$.

is nonzero for any (h, k, l)

BCC one atom at $(0, 0, 0)$

one atom at $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

$S(hkl) = f\{1 + \exp\{i\pi(h+k+l)\}\}$

nonzero only if $(h+k+l)$ is even

A simple cubic solid it has atoms at the corners of this cube, cubic unit cell which is primitive. So, there is only one atom per unit cell you may wonder there are 8 atoms why do I say there is only one atom. You must remember this unit cell is surrounded by other unit cells in all the three directions on either side therefore, all these eight atoms are shared by these adjacent atom unit cells as well.

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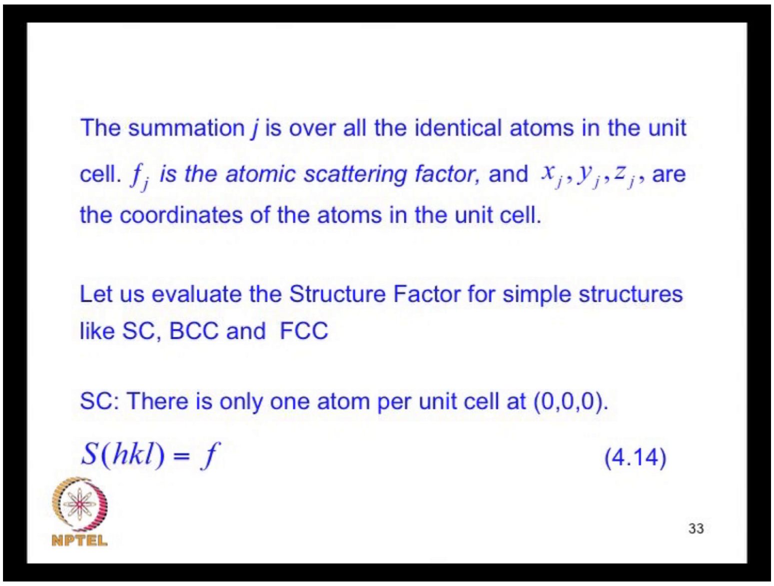

The summation *j* is over all the identical atoms in the unit cell. f_j *is the atomic scattering factor*, and x_j, y_j, z_j, are the coordinates of the atoms in the unit cell.

Let us evaluate the Structure Factor for simple structures like SC, BCC and FCC

SC: There is only one atom per unit cell at (0,0,0).

$$S(hkl) = f \qquad (4.14)$$

So, there is only one eighth of an atom which contributes to a given unit cell and since there are eight atoms at the eight vertices of a cube eight times one eight gives you one. So, that is the really the only one atom in the unit cell, which is at 0, 0, 0 the origin, we can we take this atom at the origin. So, s h k l substituting in that expression is just f because it is summation is just over one term. So, it is nonzero, the structure factor is nonzero for any sets of h k l. So, all the crystal planes give rise to Bragg diffraction. So, there is no extinction roll really, but come to a body centered cubic lattice

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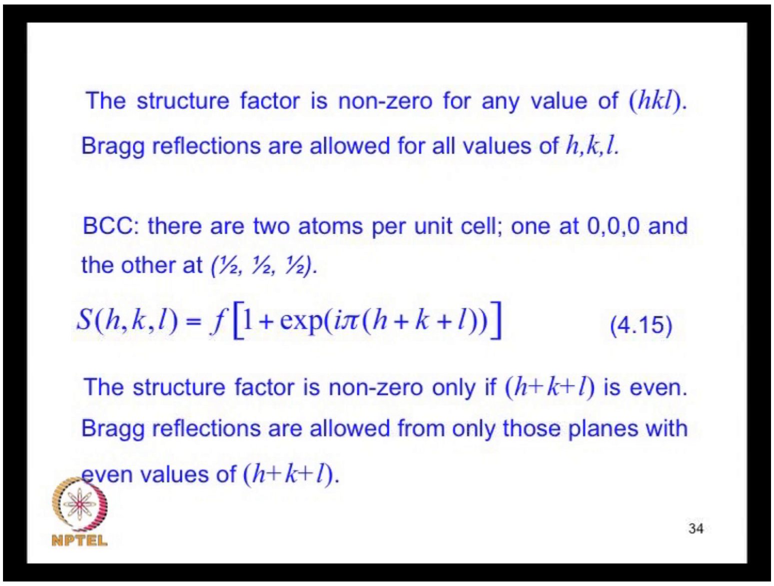

The structure factor is non-zero for any value of (hkl). Bragg reflections are allowed for all values of h,k,l.

BCC: there are two atoms per unit cell; one at 0,0,0 and the other at *(½, ½, ½)*.

$$S(h,k,l) = f\left[1 + \exp(i\pi(h+k+l))\right] \qquad (4.15)$$

The structure factor is non-zero only if $(h+k+l)$ is even. Bragg reflections are allowed from only those planes with even values of $(h+k+l)$.

A body centered cubic lattice has two atoms per unit cell one atom at 0, 0, 0 and another one atom in the body center of the cube, which is half, half, half inside the distance of half the lattice separation the distance between consecutive atoms. So, substituting this you get s h k l equals one plus f times one plus exponential i pi the 2 pi cancels with the two factor 2 cancels the 2 in the denominator.

So, I get h plus k plus l. So, that will be the scattering amplitude. So, this will be nonzero only if h plus k plus l is even. Only when this is an even number this leads to exponential i pi times 2 or 4, otherwise it becomes 0. So, only even values of h plus k plus l, the sum of h k l should be an even number. That is the extinction rule for a body centered cubic lattice. Going on to a face centered cubical lattice.

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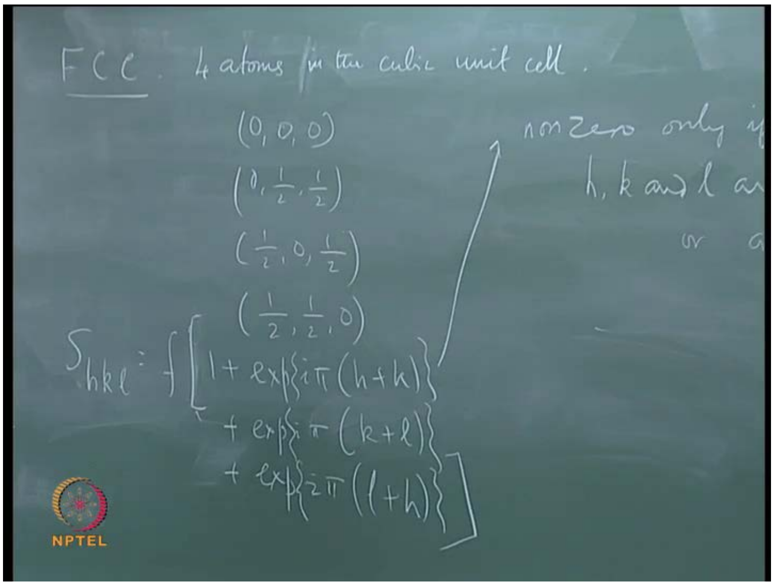

FCC. 4 atoms in the cubic unit cell.

$(0, 0, 0)$

$(0, \frac{1}{2}, \frac{1}{2})$

$(\frac{1}{2}, 0, \frac{1}{2})$

$(\frac{1}{2}, \frac{1}{2}, 0)$

$$S_{hkl} = f\left[1 + \exp\{i\pi(h+k)\} + \exp\{i\pi(k+l)\} + \exp\{i\pi(l+h)\}\right]$$

nonzero only if

h, k and l a

or a

We see that there are four atoms in the unit cell, cubic unit cell. one at 0, 0, 0 then one at 0, half, half at the face center, one at half, 0, half and another at half, half, 0 these are the coordinates of the centers of the faces. So, the s h k l in this case is going to be f times 1 plus exponential i pi into h plus k plus exponential i pi into k plus l plus exponential i pi into l plus h.

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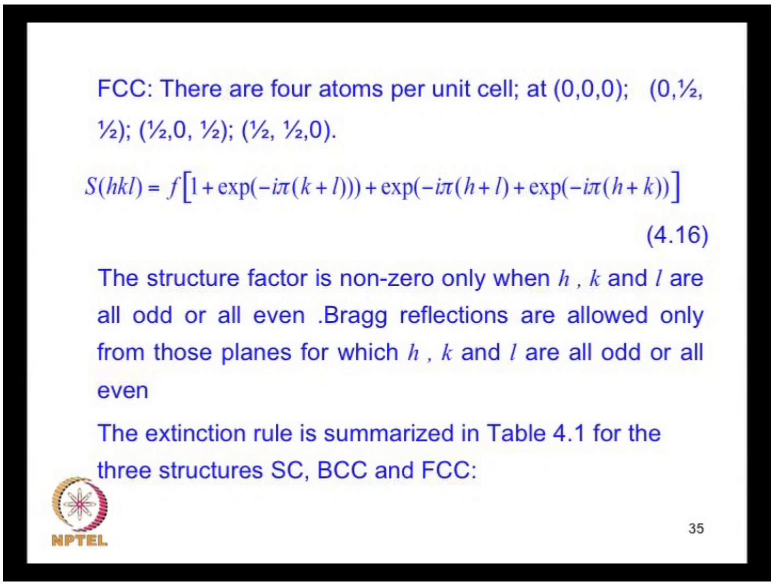

FCC: There are four atoms per unit cell; at (0,0,0); (0,½, ½); (½,0, ½); (½, ½,0).

$$S(hkl) = f\left[1 + \exp(-i\pi(k+l))) + \exp(-i\pi(h+l) + \exp(-i\pi(h+k))\right] \quad (4.16)$$

The structure factor is non-zero only when h , k and l are all odd or all even .Bragg reflections are allowed only from those planes for which h , k and l are all odd or all even

The extinction rule is summarized in Table 4.1 for the three structures SC, BCC and FCC:

So, the structure factor will be nonzero in this case only when this will be nonzero only when h k and l are all odd or are all even. So, that is the extinction rule for a face centered lattice.

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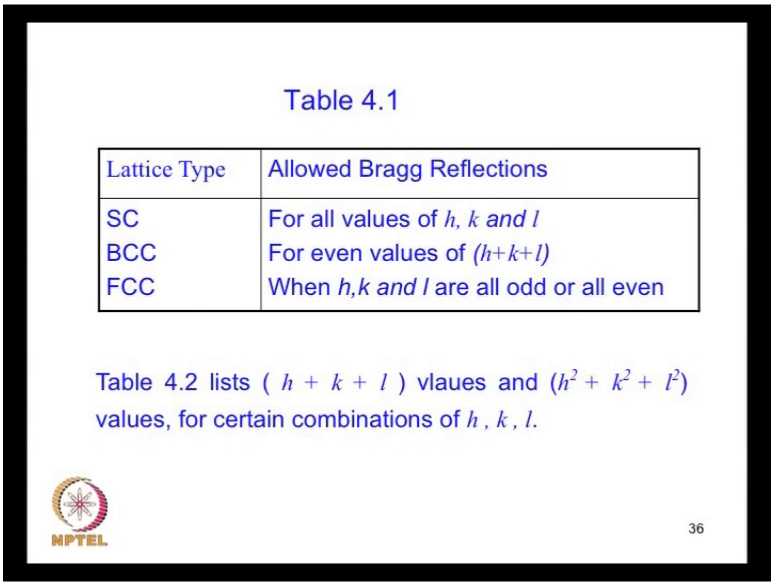

Table 4.1

Lattice Type	Allowed Bragg Reflections
SC	For all values of h, k and l
BCC	For even values of $(h+k+l)$
FCC	When h,k and l are all odd or all even

Table 4.2 lists ($h + k + l$) vlaues and ($h^2 + k^2 + l^2$) values, for certain combinations of h , k , l.

So, these three extinction rules are summarized here. In the next table and the next table as I showed you already. List the different h plus k plus l values and the corresponding h square plus k square plus l square values for these combinations, which enter into the Bragg condition.

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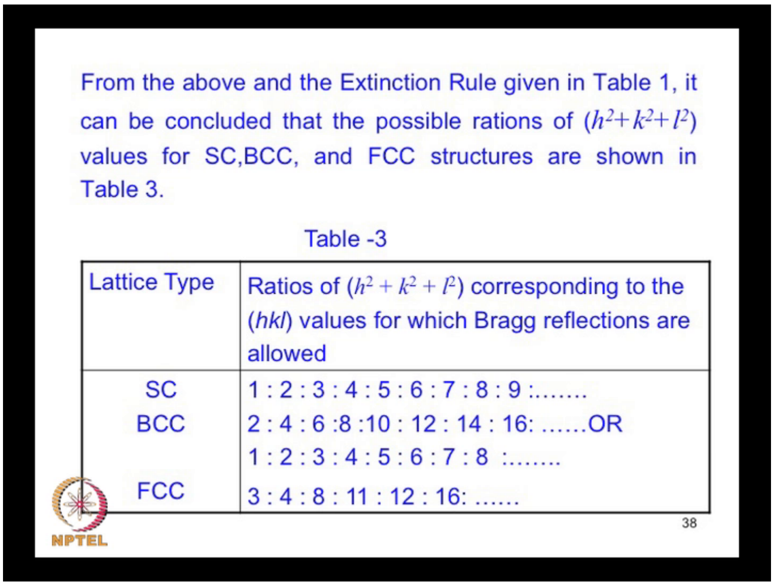

From the above and the Extinction Rule given in Table 1, it can be concluded that the possible rations of $(h^2+k^2+l^2)$ values for SC,BCC, and FCC structures are shown in Table 3.

Table -3

Lattice Type	Ratios of $(h^2 + k^2 + l^2)$ corresponding to the (*hkl*) values for which Bragg reflections are allowed
SC	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 :…….
BCC	2 : 4 : 6 :8 :10 : 12 : 14 : 16: ……OR 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 :…….
FCC	3 : 4 : 8 : 11 : 12 : 16: ……

From the above and the extinction rule it can be concluded that the possible ratios of h square plus k square plus l square values for the simple cubic, body centered cubic and face centered cubic structure these are shown in the next table. So, the ratios of the h square plus k square plus l square corresponding to different h k l values for which Bragg reflections are allowed for the case of a simple cubic ratio is 1 is to 2 is to 3 is to 4 everything all the numbers. For a body centered cubic lattice it is 2 is to 4 is to 6 is to 8 is to 10, which can be reduced to 1 is to 2 is to 3 is to 4 etcetera. And the face centered cubic lattice it is only 3 is to 4 is to 8 is to 11 is to 12 is to 16 etcetera. So, you see how there are systematic extinctions.

So, the experimentally calculated ratios knowing these h square plus k square plus l square values you can calculate the ratios of sin square theta values. And so, we can calculate, compare the h square plus k square plus l square values and the sin square theta values the lattice type is immediately found by matching these ratios. So, that is how the analysis is done for the Debye Scherrer method. The next method that we talk about is the Laue method in this technique.

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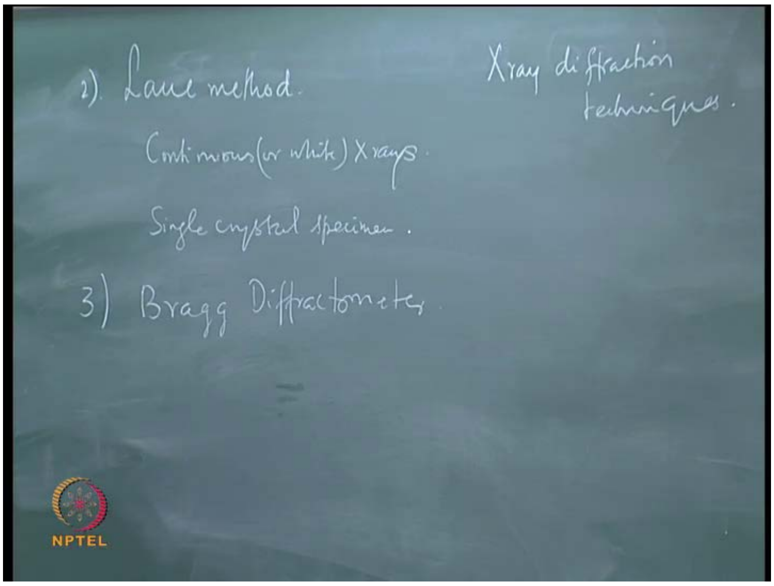

2). Laue method.

Continuous (or white) X rays.

Single crystal specimen.

3) Bragg Diffractometer.

Xray diffraction techniques.

This is the second method. The first methods were the Debye Scherrer method. In this in the Debye Scherrer method we use monochromatic x-rays, here we use continuous or white x-rays not monochromatic x-rays and in the Debye Scherrer method we use a polycrystalline sample, but here this is specimen is in the form of a single crystal specimen.

So, the diffraction pattern will be a set of spots, where there is maximum of diffracted intensity the arrangement of these spots indicates the symmetry of the crystal with respect to the incident x-ray, if the x-ray direction beam is directed along a n fold rotation axis of symmetry. The diffraction pattern will then display the symmetry of the n fold axis. So, the crystallographic directions in a crystal can be identified using the Laue method.

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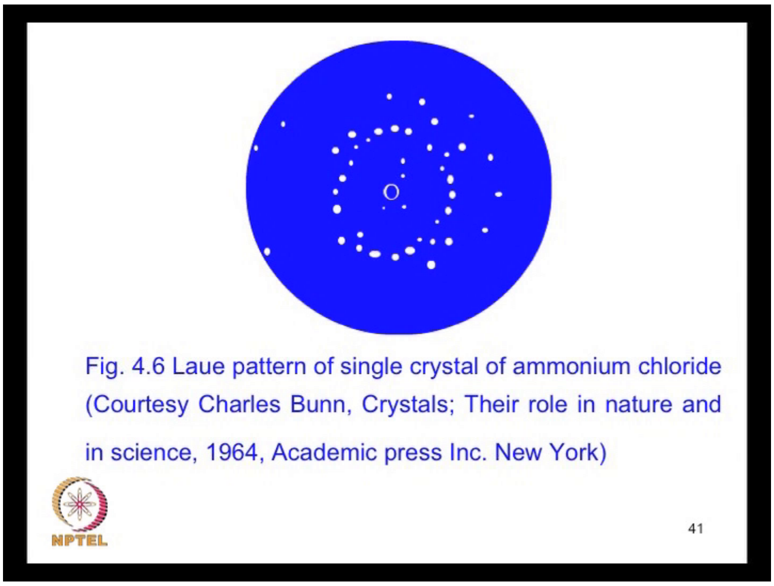

Fig. 4.6 Laue pattern of single crystal of ammonium chloride (Courtesy Charles Bunn, Crystals; Their role in nature and in science, 1964, Academic press Inc. New York)

So, the next figure shows a Laue pattern for a single crystal of ammonium chloride. So, you see how the diffraction spots are distributed.

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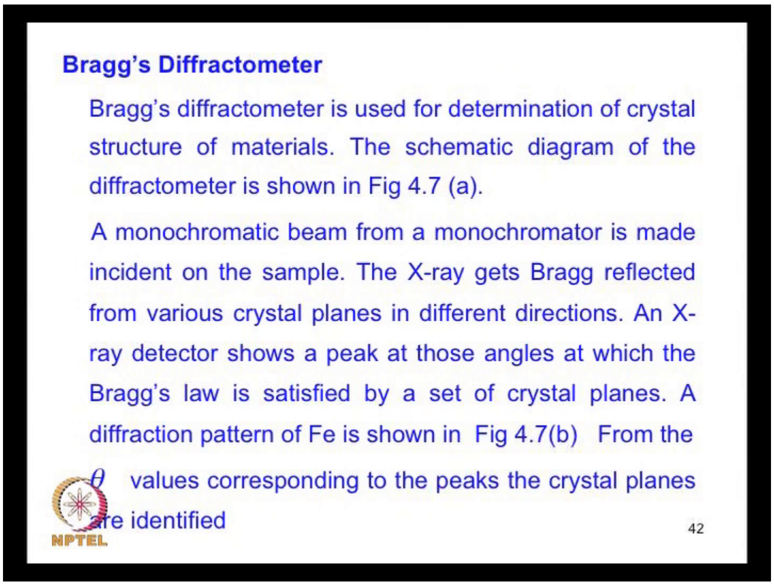

Bragg's Diffractometer

Bragg's diffractometer is used for determination of crystal structure of materials. The schematic diagram of the diffractometer is shown in Fig 4.7 (a).

A monochromatic beam from a monochromator is made incident on the sample. The X-ray gets Bragg reflected from various crystal planes in different directions. An X-ray detector shows a peak at those angles at which the Bragg's law is satisfied by a set of crystal planes. A diffraction pattern of Fe is shown in Fig 4.7(b) From the θ values corresponding to the peaks the crystal planes are identified

The third method goes by the name the Bragg Diffractometer this is the bread and butter of every x-ray crystallography. This is used for the determination of crystal structure of materials.

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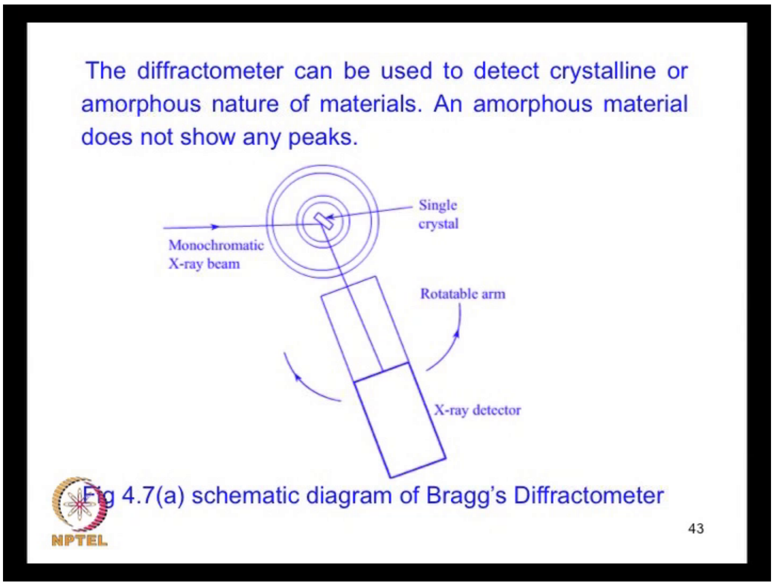

The diffractometer can be used to detect crystalline or amorphous nature of materials. An amorphous material does not show any peaks.

Fig 4.7(a) schematic diagram of Bragg's Diffractometer

And the next figure shows the experimental arrangement in a Diffractometer. You have the schematic diagram is shown with a monochromatic x- ray beam incident on a single crystal and then the diffracted beam is seen by a interms of using an x-ray detector mounted on rotatable arm the diffraction . So, the x-rays get Bragg reflected from various crystal planes in different directions the x-ray detector shows a peak at those angles at which the Braggs law is satisfied by a set of crystal planes.

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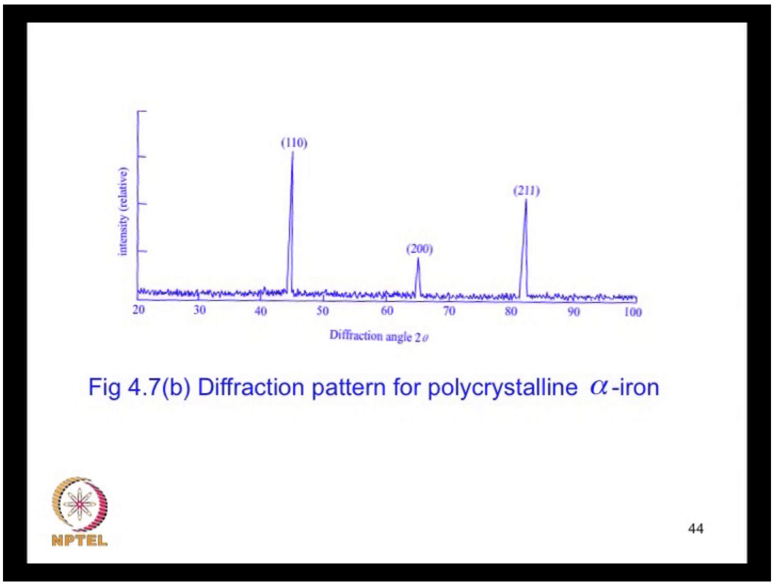

Fig 4.7(b) Diffraction pattern for polycrystalline α-iron

So, such a diffraction pattern for iron is shown in figure can see the diffraction maxima the Bragg diffraction maxima corresponding to different h k l planes. When the intensity of the scattered x-ray is plotted as a function of the diffraction angle. So, we have now, considered all the important techniques of x-ray diffraction.

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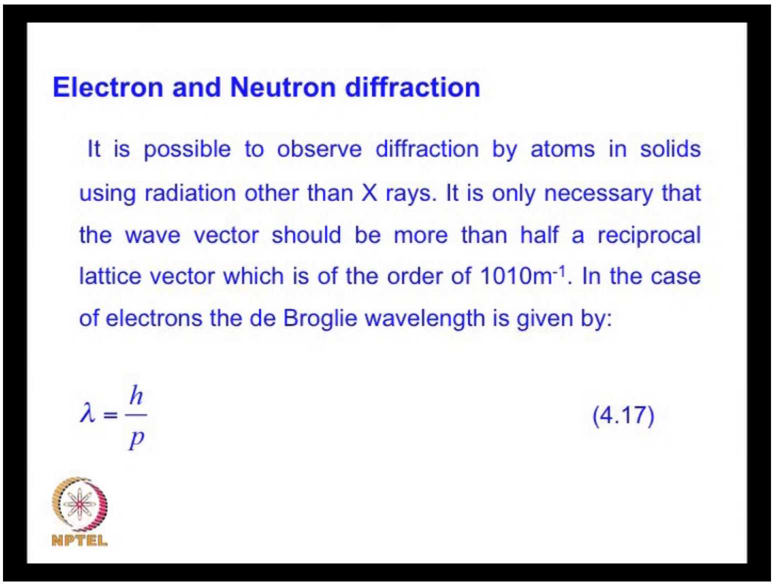

Electron and Neutron diffraction

It is possible to observe diffraction by atoms in solids using radiation other than X rays. It is only necessary that the wave vector should be more than half a reciprocal lattice vector which is of the order of 1010m^{-1}. In the case of electrons the de Broglie wavelength is given by:

$$\lambda = \frac{h}{p} \qquad (4.17)$$

We in addition to x-rays we can also use a beam of electrons or a beam of neutrons these are particles which can again get scattered and we can have electron diffraction or neutron diffraction.