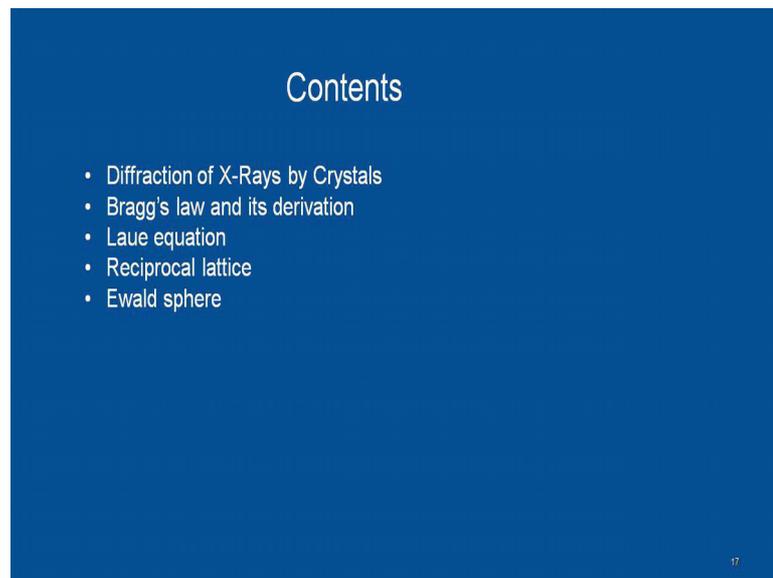


X-Ray Crystallography
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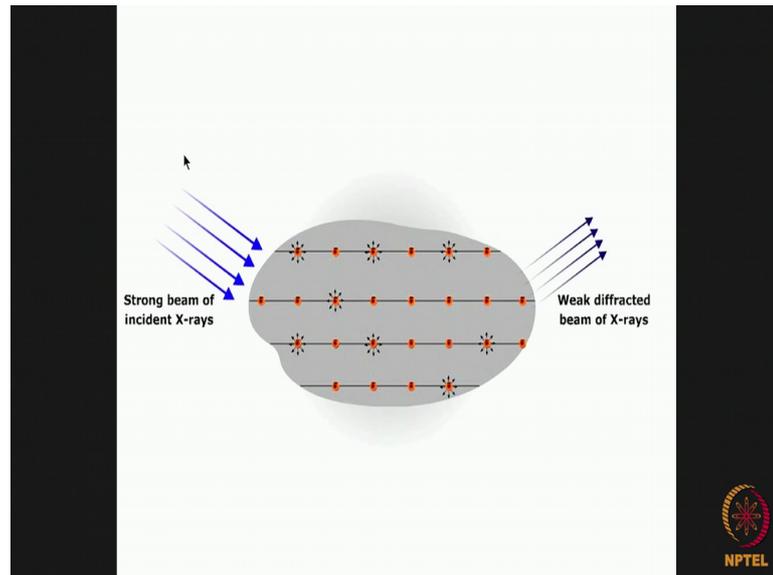
Lecture - 11
Principles of X-Ray Diffraction

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In this lecture, I shall deal with the Principles of X-ray Diffraction.

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Let us suppose that we have got a piece of metal as outlined. And we have a strong beam of incident X radiation falling on this piece of metal. Now the purpose of having the beam of X-rays falling on this piece of metal is we want to find out some pertinent information regarding what is there inside with the help of X-ray with the help of the X-rays.

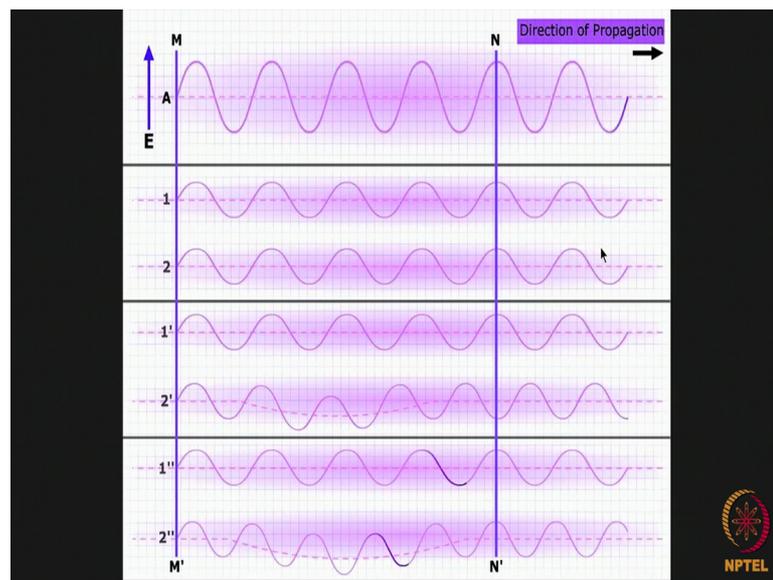
Now, we find in most of the cases when a beam of X-rays is incident on a piece of matter if we find out if there is any X-rays coming out of the matter in any direction we will score a blank. That means, under most circumstances there will be no X-rays coming out from the material only under some special circumstances a part of the incident radiation will come out of the material carrying with it all the important information regarding the crystallography of the material. Now this process is known as the process of diffraction usually the beam which gets diffracted is much weaker compared to the intensity of the incident radiation approximately one or less than 1 percent of the intensity of the incident beam is obtained as the diffracted beam from the material. So, the diffracted beam is always very weak.

Now, inside the piece of material we have a number of atomic planes as shown with a number of atoms lying on each plane. Now we know that whenever a beam of X-rays is incident on an atom these X-rays will interact with the electrons in the outer shell of the atoms and due to this interaction the incident ray will be scattered in all directions. So, in

that sense these atoms are nothing but some scattering centers and X radiation will be scattered in all directions from the scattering centers.

Under normal circumstances these X radiation which is scattered by the atoms they will interfere destructively with one another as a result of which there will not be any X-ray intensity coming out of the material; so to say only under some special circumstances which we will deal with. Now we find that there can be a weak beam of X-rays coming out of the material due to some constructive interference of the scattered radiation, and this is known as the diffracted beam. Now analyzing the diffracted beam it is possible to find out lot of information about what is there inside the material you know what are the locations of the various atoms, what is the underlined crystal structure, what is the unit cell like what is the lattice parameters of the material etcetera, etcetera.

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Now, diffraction as I said is possible only when there is a constructive interference between the scattered rays let us suppose that we have got wave propagating in this X direction. Now this wave has got an electric field attached with it. Now if the electric field is plane polarized; that means, it will be in this particular plane only this is the variation of the field from point to point. Now if we take 2 wave fronts one along M M dashed and another N N dashed and if we suppose that 2 individual waves 1 and 2 emanate from this wave front M M prime and move along the direction of propagation in the same manner then what will happen in this wave front we will have the 2 waves

completely in phase. And therefore, if we add up these 2 waves there will be a total constructive interference, and therefore amplitude will be very high or the intensity will be very high.

Now, if we consider another 2 waves say 1 prime and 2 prime they start from the same point on the same wave front at the same phase and then one travels say along a straight line another travels in a curved path and traverses a longer path than it may. So, happen that on the wave front in M prime we will have for 1 prime, 1 prime the wave; wave 1 prime will have its crest at this point and the same point the wave number 2 prime has got its crest. So, you see that if we add up these 2 waves the crest and they will nullify each other and as a result they are only any resultant wave coming out.

Let us consider a third case say 2 waves 1 prime and 2 prime emanating from the wave front M M dashed one travelling in the straight line and in the other case it is travelling in a curved path with longer way now if we measure a number of waves number of wavelengths from this point to this point. That means, from the wave front M M prime to M M prime we can see that here 1 2 3 4 4 and half waves for the wave one double prime coming over on the front M M prime. That means, if we calculate the number of wavelengths from one double prime to the wave front at M M prime. We can see that there are a number 1 2 3 4 4 and half or other 4 and a quarter 4 and a quarter wavelengths between these 2 points.

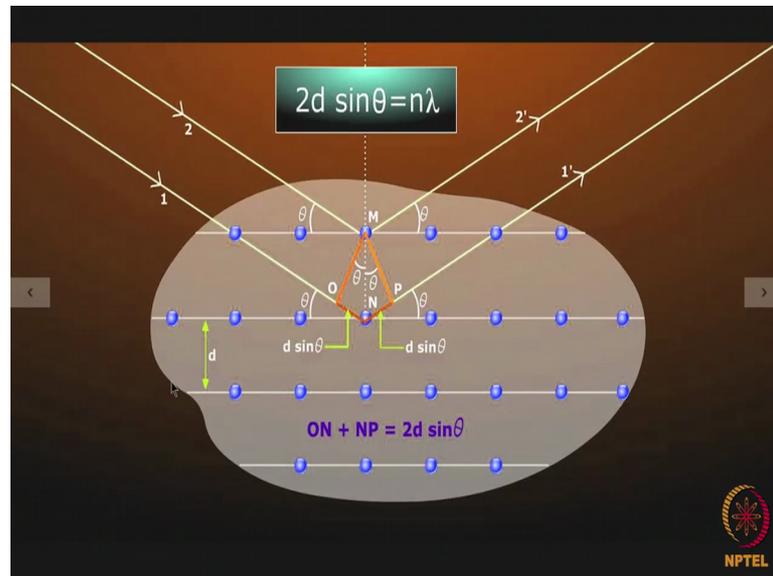
Similarly, if we calculate the number of wavelengths between 2 double prime and the wave front N N prime we will see that there are 1 2 3 4 5 and a quarter. So, there is a 5 and a quarter and in the above case there is a 4 and a quarter the result is both the waves will show their crest at the wave front N N prime. That means in this case also there will be total constructive interference.

Now in this particular case the total path difference between one double prime and 2 double prime is 1 single wavelength in case of 1 and 2 the total path difference was 0. In the other case the total you know path difference is the same and you have got the crest of one you know the crest of one line at the end of another one therefore, they nullify each other.

But in this particular case you know the path difference is such that it is one wavelength which is not true in case of the waves 1 prime and 2 prime. So, it is less than one wave.

So, we see that if there is a path difference of one complete wavelength or maybe 2 or 3 or 4 integer number of complete wavelengths there is a chance that there will be constructive interference between the waves.

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So, now let us see a particular situation say we have got a large number of atoms on a number of atomic planes in this piece of material. Now depending on the distance d between the atomic planes we find that whenever this kind of situation comes into existence that $2d \sin \theta$ becomes equal to n times λ n is an integer 1 2 3 4 etcetera and λ is the wavelength of the incident radiation and θ is the angle of incidence then we have constructive interference between the 2 waves.

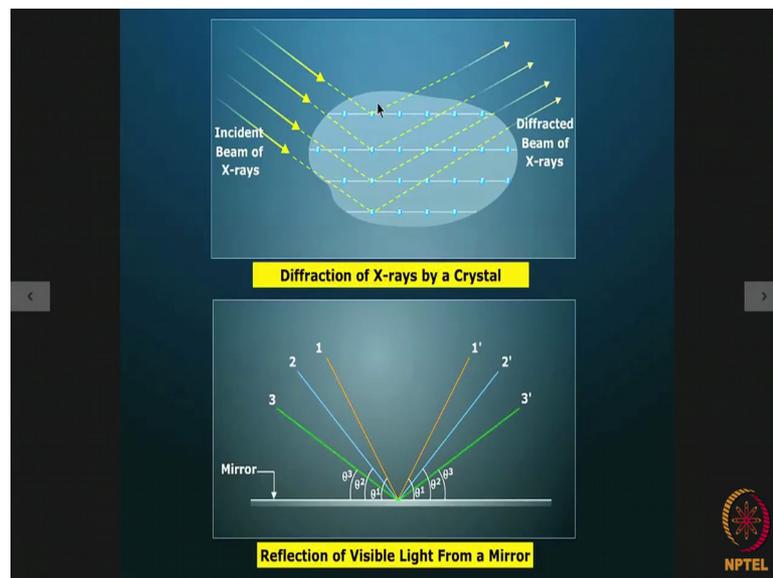
Say for example, X-ray wave 1 and 2 are incident on the atoms N and M respectively we find where this condition is satisfied there is a constructive interference between the scattered radiations now we can drop 2 perpendiculars from M over here. So, this MO is perpendicular to NN' and MP is perpendicular to this line. So, what is the path difference between ray one and ray 2 after they are scattered by the atoms at M and N the path difference is ON plus NP. So, the path difference ON plus NP if you look at that each one of these is equal to $d \sin \theta$, because this is d and this is the angle θ .

So, this is $d \sin \theta$ this also is $d \sin \theta$. So, what is the path difference between rays one and 2 after they are scattered by the atoms M and N it is $d \sin \theta$ plus $d \sin \theta$ is equal to $2d \sin \theta$. And we have already seen that if the path difference is a single

wavelength or multiple wavelengths complete wavelengths, then there will be constructive interference and will have what is known as a diffracted radiation now this particular relationship was given by Bragg and it is known as Bragg's law. So, you see that whenever there is a beam of X-rays incident on a piece of metal unless and until this condition is satisfied as we have seen we will not have any diffraction or constructive interference between the scattered x radiation by the atoms in the matter.

Now, sometimes the words diffraction and reflection are used to mean the same thing lot of people will describe the process of X-ray diffraction as X-ray reflection there is any simple the method of diffraction is such that it resembles physically the reflection of visible light from a mirror.

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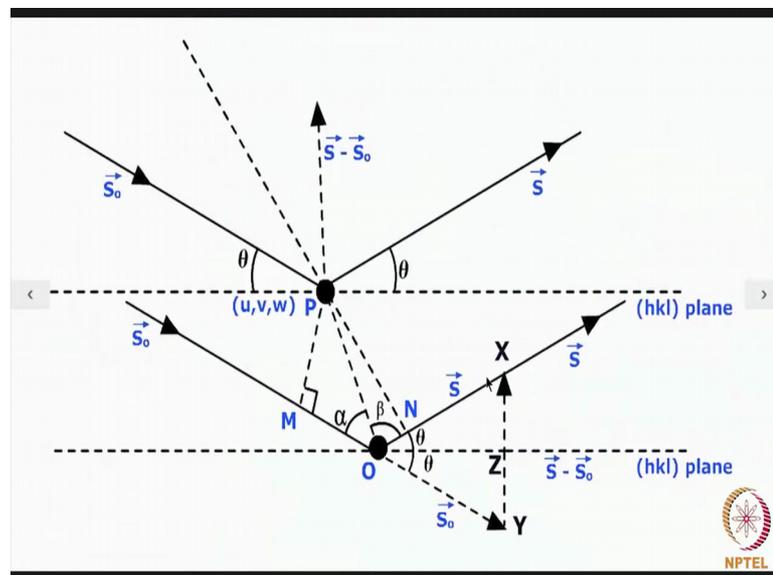
Say for example, when there is diffraction from matter then we find that the angle of incidence becomes the same as the angle of diffraction now similar kind of a situation arises when light gets reflected from a mirror. So, say this is the mirror say ray one when it gets reflected it goes in the direction 1 prime making the angle theta one on both sides say ray 2 falling on the mirror getting reflected along 2 prime making the angle theta 2 on both sides etcetera, etcetera.

And this is very similar to what happens when X-rays are diffracted in that case the angle of incidence theta is the same as the angle of diffraction theta. So, physically they look similar, but one thing we have to realize that this kind of a process for X-rays can happen

only when λ is equal to $2d \sin \theta$. That means, Bragg's law is satisfied, but here. So, it can for a particular material with a particular set of atomic planes having a particular d value this condition has to be fulfilled that to the $\sin \theta \lambda$ then and then only diffraction or reflection of X-rays will occur.

On the other hand here it does not matter whatever is the angle of incidence you know all angles of incidence for all angles of incidence there will be a reflection. So, although physically the 2 processes look like quite similar, but there is a fundamental difference between the 2 processes.

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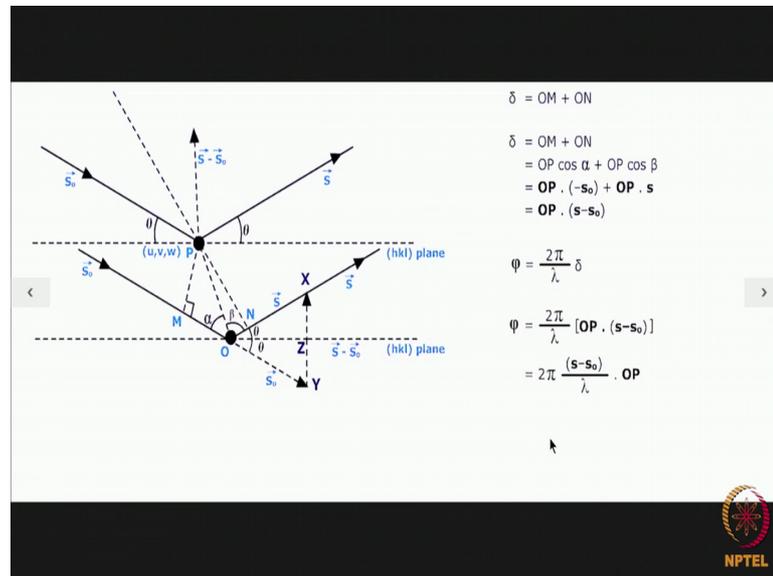


Now, let us look into the diffraction process more closely say for example, we have got an incident beam which is denoted as the unit vector \vec{S}_0 unit vector means vector whose magnitude is one and the direction is same as the given vector. So, this is a unit vector \vec{S}_0 which indicates the direction of incident radiation falling on 2 atoms 1 at P another at O and suppose this is the direction of diffracted radiation and suppose a unit vector \vec{S} denotes the diffracted vector in both the cases.

Now, angle of incidence θ is equal to angle of diffraction θ we put perpendiculars on this point P on this line P M and another perpendicular P N on this line say these are the h k l planes in the material say these are the h k l planes in the material suppose this angle here is α and this angle here is β . Now we take O as the reference origin and say P is a point whose coordinates are u v w. Now if we extend this line up to the point y.

So, that the magnitude of Oy is unity and if we extend it we cut out a length equal to unity on this line and then join this point with this point then this vector will be the vector S minus S_0 because this vector is S this vector is S_0 .

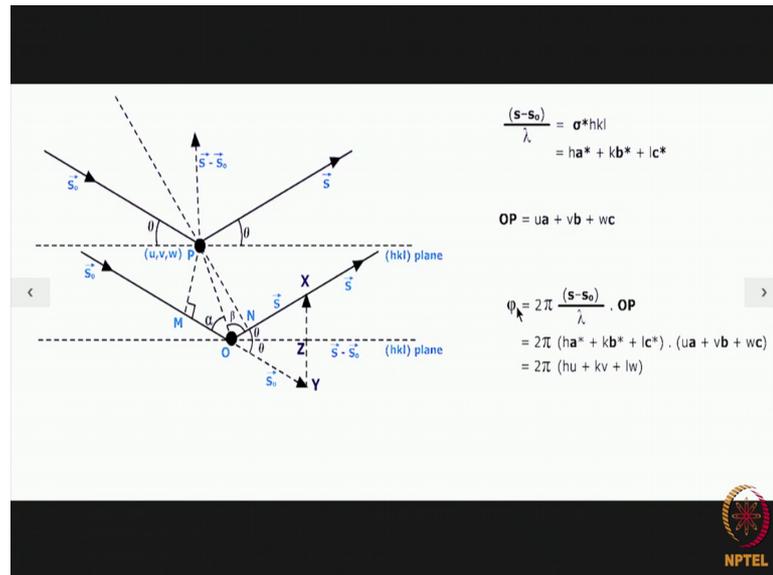
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So, this vector is nothing but S minus S_0 vector. Now the path difference between the 2 scattered rays in this from the 2 atoms at P and O will be equal to OM plus ON . So, the path difference δ will be equal to what is OM it is $OP \cos \alpha$ and ON is $OP \cos \beta$. So, we can write it as $OP \cdot (-S_0)$ vector plus $OP \cdot S$ vector now why it is minus S_0 because we take all measurements from the origin O , so, OM plus ON . So, it gives us $OP \cdot (-S_0)$ vector plus $OP \cdot S$ vector. So, it will be $OP \cdot (S - S_0)$ vector. So, what will be the phase difference between these 2 rays it will be equal to 2π by λ where λ is the wavelength of the incident radiation into the path difference δ .

So, for δ we write $OP \cdot (S - S_0)$. So, it is $2\pi (S - S_0) / \lambda \cdot OP$ let us take the $(S - S_0) / \lambda$ vector as the σ_{hkl} vector in the reciprocal lattice.

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So, sigma star h k l vector in the reciprocal lattice is nothing but h star plus k b star plus l C star vector. So, O P how much is O P we know that O P is a line joining the origin to the point u v w. So, we can write O P is equal to u a plus v b plus w C the a b C of the lattice parameters in the real lattice. So, now, the phase difference pi is 2 pi S minus S 0 by lambda dot O p; that means, is equal to 2 pi h star plus k b star plus l C star dot u a plus v b plus w C which makes it equal to 2 pi to h u plus k v plus l w.

Now, h k and l individually these are all integers again u v w individually these are all integers. So, the phase difference in case of diffraction will be an integer multiplied by 2 pi.

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$|\mathbf{s} - \mathbf{s}_0| = YZ + XZ$
 $= OY \sin \theta + OX \sin \theta$ [Since $OX=OY=1$]
 $= 1 \sin \theta + 1 \sin \theta$
 $= 2 \sin \theta$

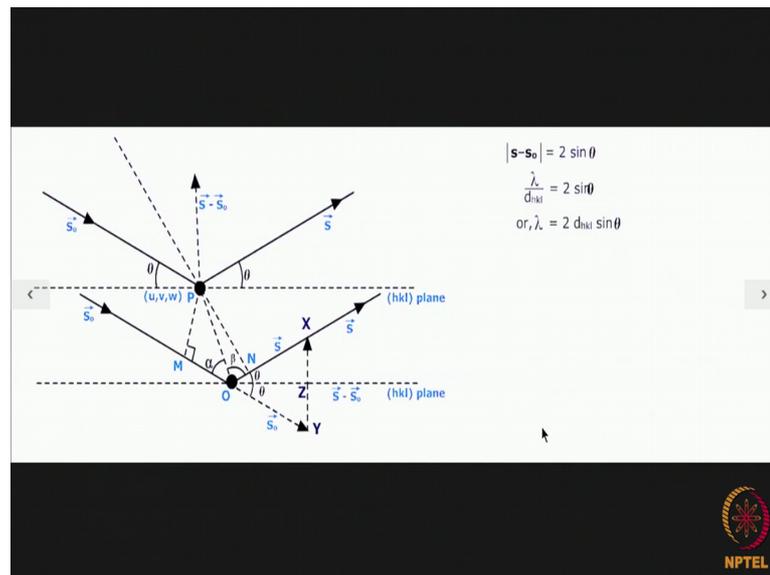
$\left| \frac{(\mathbf{s} - \mathbf{s}_0)}{\lambda} \right| = |\boldsymbol{\sigma}_{hkl}^*| = ha^* + kb^* + lc^*$
 $= \frac{1}{d_{hkl}}$
 or $|\mathbf{s} - \mathbf{s}_0| = \frac{\lambda}{d_{hkl}}$



Again we know that the vector $\mathbf{S} - \mathbf{S}_0$ if we take its magnitude it will be equal to z plus xz . So, it is equal to $Oy \sin \theta$ plus $Ox \sin \theta$, but what is Ox and Oy Ox and Oy are having unit length. So, it is one $\sin \theta$ plus one $\sin \theta$ which makes it equal to $2 \sin \theta$. Now, we can write $\mathbf{S} - \mathbf{S}_0$ by λ if this is the vector $\boldsymbol{\sigma}_{hkl}^*$ in the reciprocal lattice then the magnitude of this vector is a magnitude of this vector and we know that magnitude of this vector is nothing but one upon d_{hkl} .

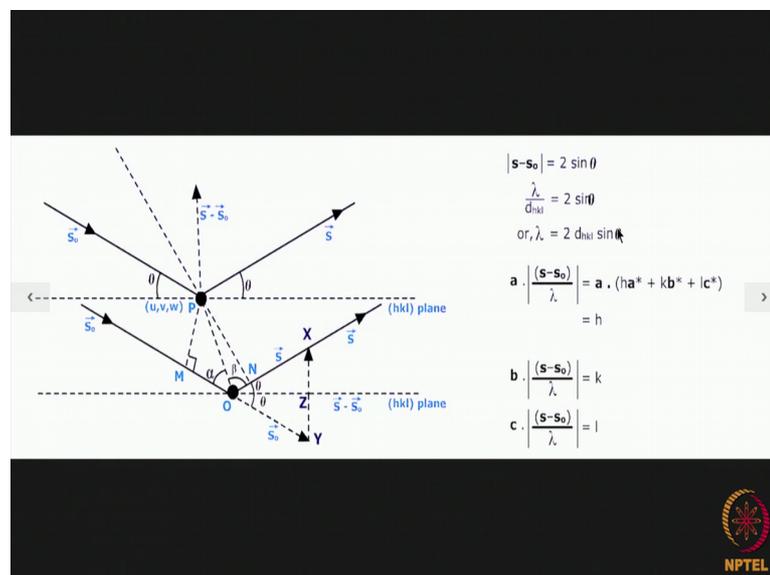
In other words we can write $\mathbf{S} - \mathbf{S}_0$ vector its magnitude S equal to λ by d_{hkl} , but again that $\mathbf{S} - \mathbf{S}_0$ vector its magnitude is $2 \sin \theta$. So, putting this value here we can see that we have got the relationship $\lambda = 2 d_{hkl} \sin \theta$.

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So, you see that this is the way reciprocal lattice concept can be utilized to derive Bragg's law of diffraction.

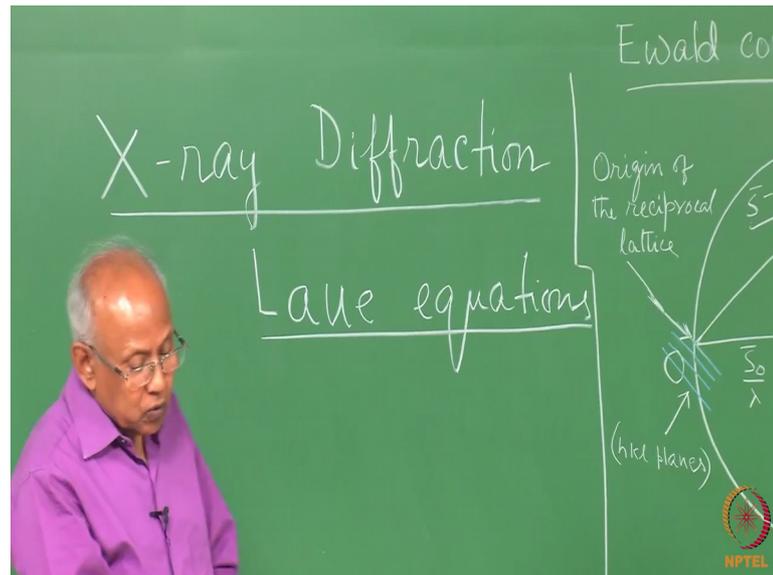
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Now, since the magnitude of $\mathbf{S} - \mathbf{S}_0$ is equal to $2 \sin \theta$ and λ is equal to $2 d_{hkl} \sin \theta$ if we make a dot product of $\frac{\mathbf{S} - \mathbf{S}_0}{\lambda}$ and the vector $\mathbf{S} - \mathbf{S}_0$ by λ then we can write it as a dot product because this vector is taken as the $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ vector. So, it will be $\mathbf{a} \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$; that means, this dot product will give you value of h only.

Similarly, if we take dot product between \mathbf{b} and $\mathbf{S} - \mathbf{S}_0$ by λ vector it will be k and C dot product \mathbf{C} and $\mathbf{S} - \mathbf{S}_0$ by λ vector it will be l . So, what we find that in order that diffraction is possible these 3 equations must be satisfied simultaneously. So, these 3 relationships must be satisfied simultaneously in order that diffraction can take place.

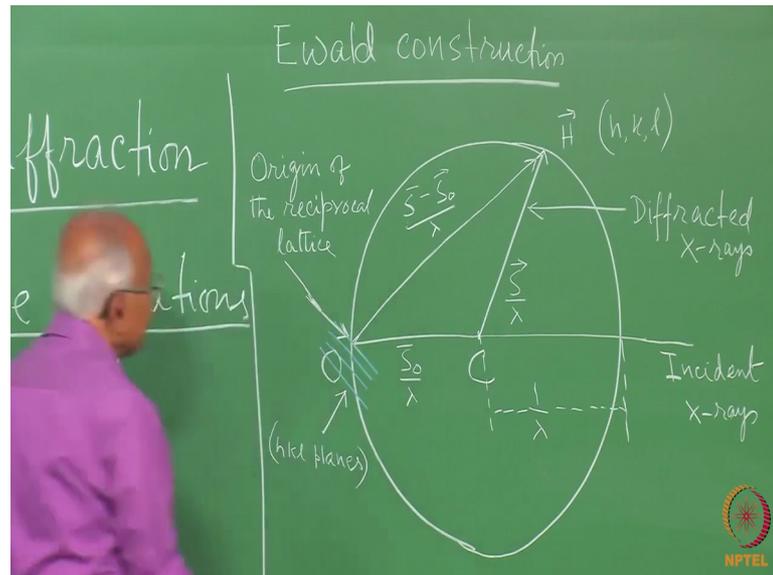
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Now, these 3 equations are known as the Laue equations. So, we can say that diffraction will be possible when the Bragg's law is satisfied or diffraction will be possible if the Laue equations are satisfied simultaneously.

The conditions of diffraction can also be shown in a pictorial way by a construction which is known as the Ewald construction

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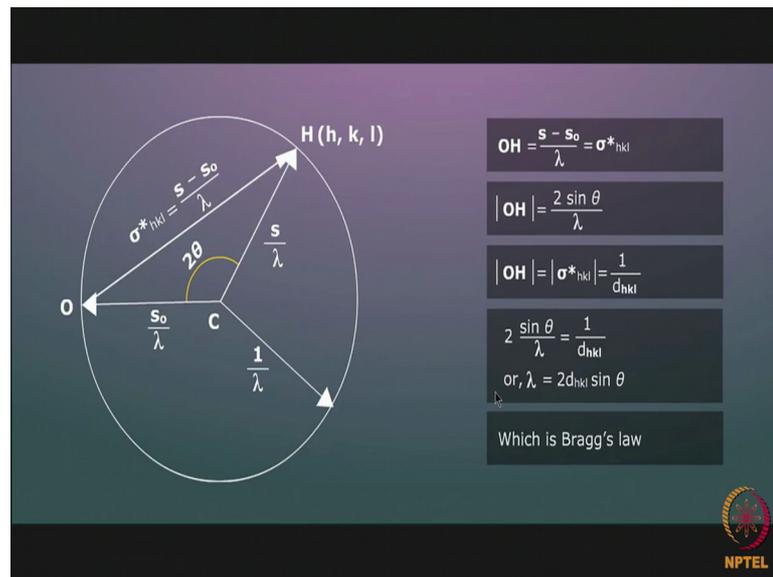


Say for example, we do a construction of this type where we draw a sphere with a radius of one by lambda where lambda is the wavelength of the incident radiation say C is the centre of this sphere now this sphere is known as an Ewald sphere. So, this vector C to O is having it is the S_0 by lambda vector because the incident x radiation is written as the S_0 vector. So, this vector denotes this is the vector S_0 divided by lambda.

Similarly, say for example, if there is a vector at an angle 2θ if there is an vector at an angle 2θ then that vector will denote the diffraction vector. So, this is the vector which denotes the incident radiation this vector denote the diffracted radiation. Now if we join this point to this point then this must be the vector $S - S_0$ by lambda say this point is a point h in the reciprocal lattice. That means, coordinates are h k l in the reciprocal lattice. And, since it is the $h^* + k^* + l^*$ vector in the reciprocal lattice it will be perpendicular to the h k l planes in the real lattice.

So, if this is the vector $h^* + k^* + l^*$ because its coordinates are h k l then we know that this vector will be perpendicular to the h k l planes in the real lattice. So, these are the h k l planes.

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Now, we know that the magnitude of the vector OH is equal to $2 \sin \theta$ by λ . We have seen from previous examples that this vector has got a magnitude which is $2 \sin \theta$ by λ . So, the magnitude of OH is equal to the magnitude of σ^*_{hkl} . So, it is $1/d_{hkl}$ because σ^*_{hkl} magnitude of this is $1/d_{hkl}$ again. So, equating these 2 we can write down $2 \sin \theta$ by λ is equal to $1/d_{hkl}$. Or in other words λ is equal to $2 d_{hkl} \sin \theta$ and this is nothing but an expression for Bragg's law of diffraction.

Now, this is a pictorial way of representing Bragg's law now it has got a very important connotation. So, in order that Bragg's law can be satisfied there is an essential condition which is dictated by this drawing. Say for example, if the point h which is having coordinates hkl in the reciprocal lattice does not lie on the surface of the Ewald sphere say if it lies you know outside the surface or inside the surface then what will happen then all this condition will not be satisfied.

So, Bragg's law will not be satisfied. So, in order that Bragg's law is satisfied completely it is essential that the vector $S - S_0$ by λ must end at a point lying on the surface of the Ewald sphere you know this vector must not end at beyond the Ewald sphere or must not end inside the Ewald sphere, but must be exactly on the Ewald sphere. So, this condition is an essential condition for diffraction to take place. Now as I

already mentioned this sphere is known as the Ewald sphere and it is also called the sphere of reflection.