Indian Institute of technology Madras
Presents

NPTEL
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture - 25
Materials Characterization
Fundamentals of X-ray diffraction

Dr. S. Sankaran
Associate Professor
Department of Metallurgical and Materials Engineering
IIT Madras
Email: ssankaran@iitm.ac.in

Hello everyone, welcome to this material characterization course, in the last class we just discussed about the properties of x-rays in terms of phase relations and then how this phase relation influence the diffraction and then we just looked at little bit elaborately how we understand the Bragg law Bragg's law and then how it explains the diffraction intensity and so on and then we have let us recall that what we have discussed in the Bragg law.

It is we just said that it is not that the diffraction intensity is coming from the first layer of the atomic plane and also the subsequent planes which is underneath the surface also contribute to these diffraction intensities through constructive interference and then we have seen that how this contribution from each atoms in the plains below the surface and how the overall diffraction intensity is envisaged.

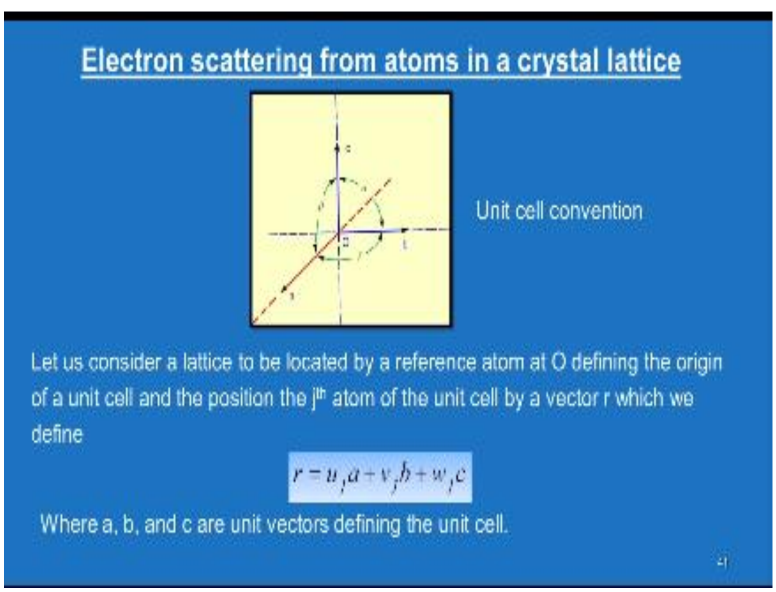
So and subsequently we looked at writing this Bragg law in a different form and then how it can be used to analyze the crystal system and then we will continue in that line today and before that I would like you to make a brief a description on the reciprocal lattice, formally we have not introduced this concept so far but in the fundamentals of this course I mean the lectures we discuss little bit about this reciprocal lattice.

However we will be using this concept throughout this course and not only this x-ray diffraction and also only now after this we will discuss about electron diffraction in transmission electron microscopy there also we will use this extensively and what I request you to do is you should go through for all the mathematical treatment of this concept which is really out of the scope of this course you should refer a physics of materials which is also there in this NPTEL portal where you have a detailed mathematical treatment is given.

And also specifically there is a 10 hour course is being offered by Professor Pratap Haridass where exclusively on the reciprocal lattice, what I request all of you to do is go through that physics of materials lecture notes or videos as well as the 10 hour course exclusively on the reciprocal lattice then if you follow this it will be very easy in order to save time I am avoiding all this basic mathematical relations.

But then I will briefly talk about it in fact we will be dealing with more practical aspects of this reciprocal lattice concept and we will be actually seeing in In-practice how we can visualize a reciprocal lattice in reality, so in our course we will look at more the application part of it and not the basic mathematical part of it but nevertheless I will keep on referring this concept and then I will try to make you understand as much as possible in terms of physical phenomenon.

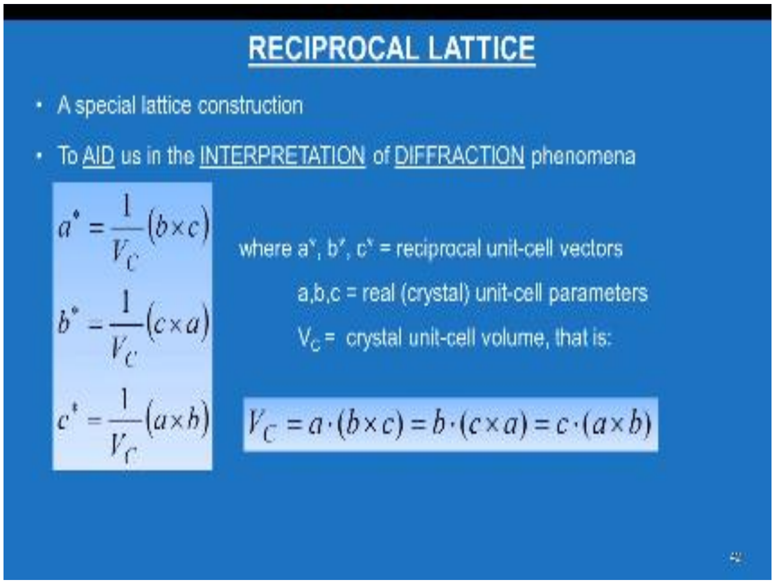
(Refer Slide Time: 04:17)



So if you look at the suppose if you want to talk about electron scattering from atoms in a crystal lattice first we have to talk about the crystal lattice and this is how we define any unit cell acre a conversion is where you have this ABC all our vectors and then the angle between them are alpha beta gamma so this is a called unit cell convention, so let us consider a lattice to be located by a reference atom at o defining the origin of unit cell and the position the j^{th} of the unit cell by a vector R which we define normally $r = u_j a + v_v b + w_j c$ where a b and c are unit vectors defining the unit cell.

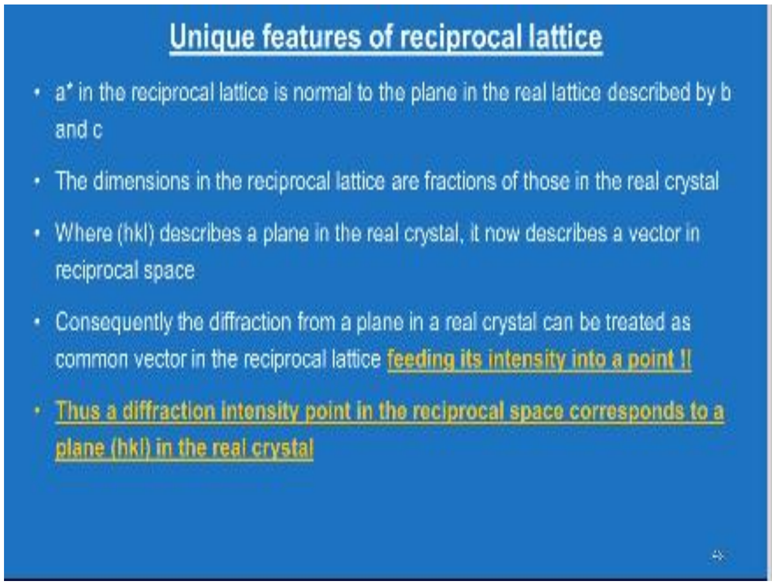
This is I am saying because we will be referring this a vector this is a vector in the real lattice which we will be using it extensively in the x-ray diffraction intensity expressions as well as when we talk about reciprocal lattice so this is the convention and it is a vector in a real lattice you have to remember that is very important.

(Refer Slide Time: 05:44)



And excuse me what is reciprocal lattice, it is a special lattice construction to aid us in interpretation of the diffraction phenomena so this is the fundamental aspect of it and how this lattice parameters are reciprocal unit vectors are defined which is $a^* = 1/V_c\,(b \times c)$, $b^* = 1/V_c\,(c \times a)$ and $c^* = 1/V_c\,(a \times b)$ where a^* $b^*$and c^* they are all reciprocal unit cell vectors where ABC they are all real crystal unit cell parameters and we see the crystal unit cell volume that is VC = a . (b x c) = b . (c x a) = c . (a x b) so these are all be fundamental expressions which you might have already studied are must have come across much before that.

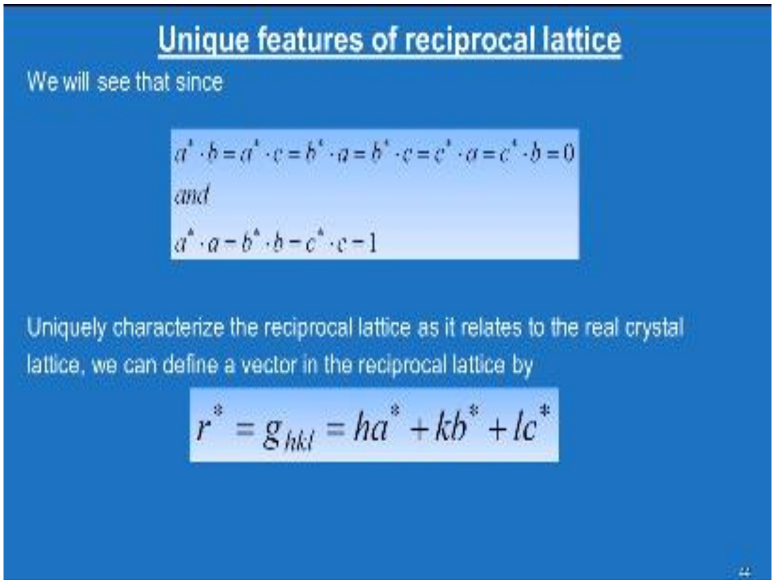
(Refer Slide Time: 06:54)



Let us now go through some of the unique features of a reciprocal lattice a star in the reciprocal lattice is normal to the plane in the real lattice described by Band C the dimensions in the reciprocal lattice are fractions of those in the real crystal where (hkl) describes a plane in real crystal it now describes a vector in the reciprocal space, consequently the diffraction from a plane in a real crystal can be treated as common vector in the reciprocal lattice feeding its intensity into a point.

Thus a diffraction intensity point in a reciprocal space corresponds to a plane (hkl) in the real crystal you see these are all the some of the basic features of the reciprocal lattice infact we will be talking about this the reciprocal point in an in a real system in a practical situation as a electron diffraction pattern well where we will try to interpret for its complete accountability what it means that we will do it detailed study and what is said here is in fact it is it is not just a one plane here it is not necessarily one plane here it could be a set of plane it is always referred as a set of HKL plane which I mean for which correspond to each reciprocal lattice points so that we will see it in a appropriate time.

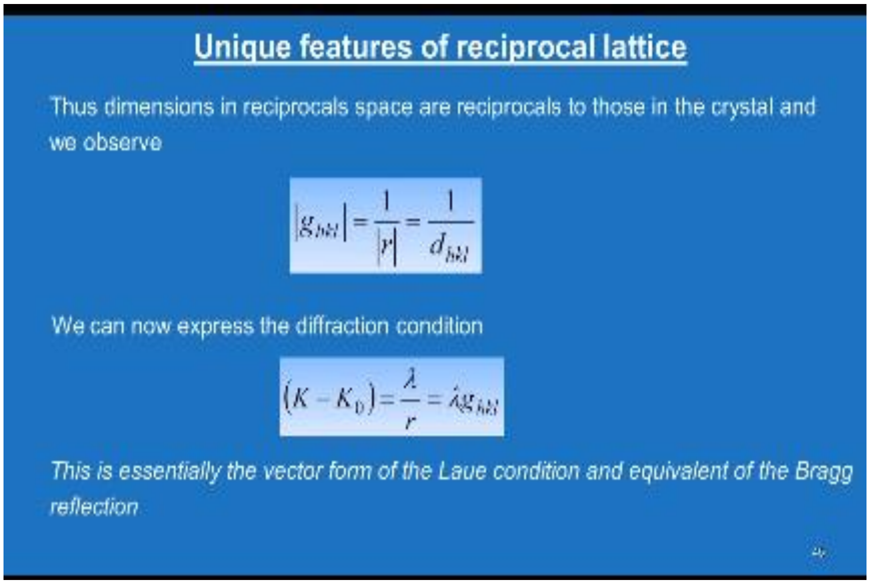
(Refer Slide Time: 08:48)



We will also see some of the other relations that a.b I mean $a^*b = a^*c = b^*a = b^*.c = c^* = c^*.b = 0$ and $a^*.a$ = b stored on b = c^* . c = 1 these are all some basic relations and very importantly now we will see the uniquely characterize the reciprocal lattice as it relates to the real crystal lattice we can define a vector in the reciprocal lattice by our star which is equal to g_{hkl} again this is which is equal to $ha^* + kb^* + lc^*$.

So this is a reciprocal lattice vector so you just compare this with the real do not confuse this with the real lattice vector this is a reciprocal lattice vector it is also called a G vector we will see inappropriate time what is the meaning of this G and how do we interpret those notations so right now you have you have to keep in mind how a vector in the real lattice is represented and how the vector in a reciprocal lattice Is represented and then what is the relationship.

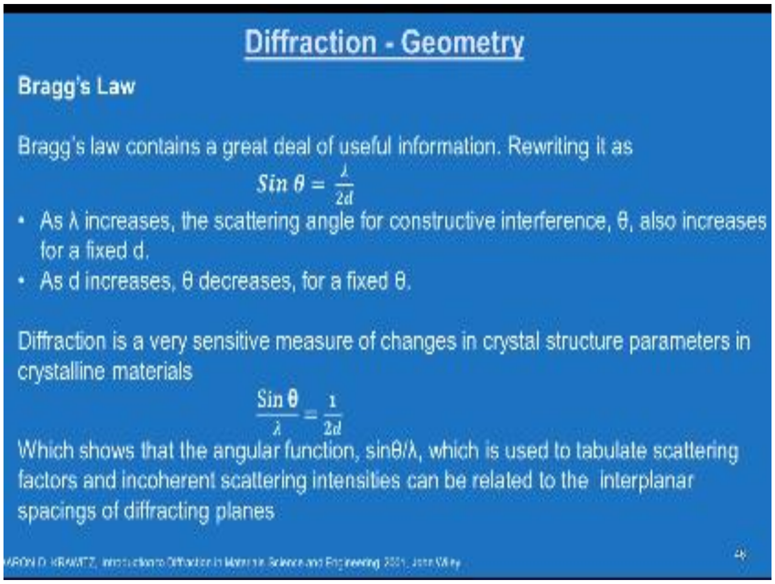
(Refer Slide Time: 10:26)



Mathematically and if you can see further the dimensions in the reciprocal space are reciprocals to those in the crystal and we observe a $|g_{hkl}| = 1/|r| = 1/d_{hkl}$ we can now express the diffraction condition in a vectorial form $K- K^{0} = \lambda/r = \lambda x\ g_{hkl}$ this is essentially a vector form of lower condition and is equivalent of the Bragg diffraction just for the completion I have brought this relation this is a I would say it is a vectorial form of a Bragg condition.

For example Bragg law describes the diffraction in terms of scalar equation what you see $n\lambda = D \sin \theta$ is a scalar equation we can also define the diffraction condition by a vector equation so this is one of the form we will now see it in much more detail in two three slides later how this law a condition our vectorial form of representation of diffraction equation.

(Refer Slide Time: 11:52)

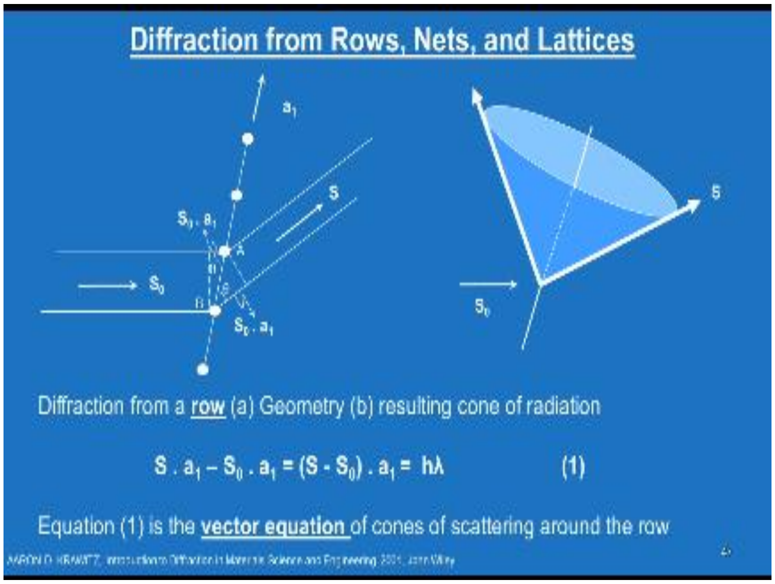


So in the last class we just looked at a Bragg law and how it can be used in analyzing the crystal system there are few more points we will see about this Bragg law so Bragg's law contains a great deal of useful information we can write sin $\theta = \lambda/ 2d$ there are two things we have to keep in mind as λ increases the scattering angle for a constructive interference θ also increases for a fixed d as d increases θ decreases for a fixed θ.

So diffraction is a very sensitive measure of changes in the crystal structure parameters in the crystal line materials hence sine $\theta/ \lambda = 1/ 2$ d which shows that the angular function sine θ/ λ which is used to tabulate scattering factors and incoherent scattering intensities can be related to the inter planar spacing of diffracting planes, so the diffraction is very sensitive measure of changes in the crystal.

So this that is why this particular parameter is used as an angular function to identify the changes in the crystal structure which we will see in the subsequent slides.

(Refer Slide Time: 13:36)



Now as I just mentioned before what we have seen so far as a diffraction condition in terms of Bragg law I are I would say Bragg's law it is in a scalar form there we just try to use a parallel planes one after the other so the all that we have showed in the form of animation is only the race which are subjected to constructive interference or a diffracting beams but we have not seen a diffraction condition for an individual atom such as rows area 2d or 3d lattice.

So now we will get into that I mean discussion where we will try to arrive at a diffraction condition in a one dimension to dimension and then and see three dimension and see what is the difference between what we have seen in a in a Bragg's law condition and what we are going to see in this discussion, so look at the schematic I have just drawn here a scatters I would say it is a repeat distance in a 1d lattice or rows of atoms.

The repeat distance is described and the direction is described by the vector a1 and then you have the incident x-rays s naught which is falling on this row and s is the scattered raise we will say that it is a deflected ray as well provided it follows some condition and in order if you look at the in order to define s as a diffracted beam we need to look at the condition whether it obeys the a kind of diffraction I mean a condition or whether it obeys a diffraction condition are whether it facilitate the diffraction condition interms of its geometry so now what you can see here is you see the atom a and B which scatters and then this is the θ and this is the θ from this side and this is a perpendicular I have drawn for this line and this is a perpendicular drawn for this line now in order to be in the same phase of s and s^0 they should have the a path difference should be having some certain conditions what is that condition.

Suppose if you look at this atom and then look at this ray after scattering this is the path difference and similarly if you look at this way which hits on the atom a and then it scatters this way and this length this is the path length so there is a difference these two rays are having two different path length so mathematically if you see what is this length this length is nothing but s^0 . a1, similarly here this length is s. s^0 .a1.

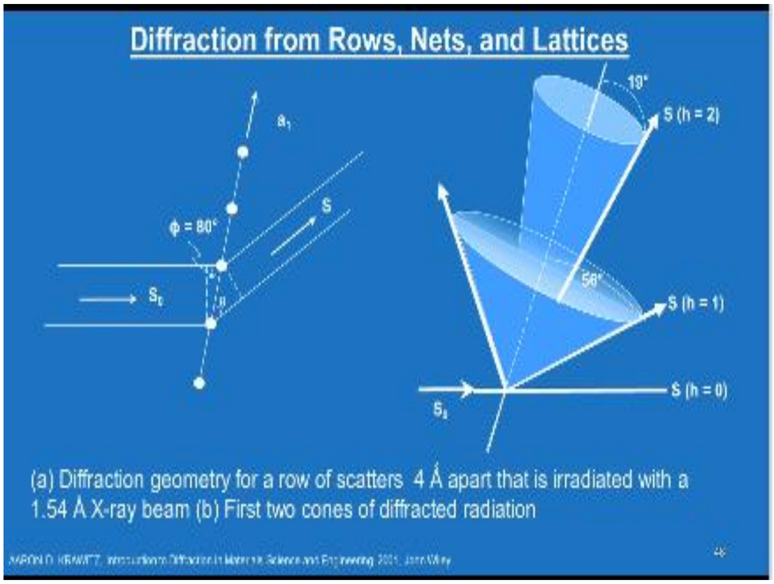
This is s^0 is an incident wave vector and this is the lattice repeat distance that is also in vector and this distance is s not a one similarly this distance is s^0 a1 and that is how the path length differs, so now we have already seen that in order for the S rays that is the scattered ray to be in the on the same phase of $s^0$the path length our path differences should be a integral multiple of a wavelength so that is what we have written here.

So you see that s. a1 that is this minus s. s^0. A1 that is the path difference between these two should be equal to an integral multiple of wavelength h λ and equation one is a vector equation of codes of scattering around the row so what actually we are seeing is this there is a intensity cone which Is spread like this so this is an incident intensity and this is scattered intensity actually this kind of a cone of intensity is generated or around the row.

And we will now see one example how this cone is related to the angle of incidence θ and then how it changes with the angle and the wavelength and the inter-atomic distance and so on so now you remember that this particular equation accounts for a diffraction in atoms lying in a row so now we are just said that if this path differences is in the integral multiple of λ then these two waves that is incident wave as well as diffracted beam will be in the same phase and then constructive interference takes place.

So the diffraction happens so this is a condition for that now we will look at one example.

(Refer Slide Time: 20:33)

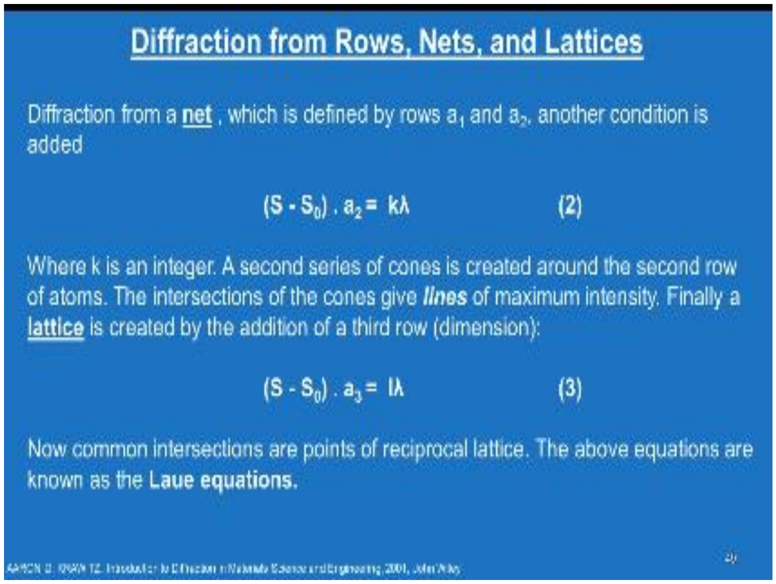


To look at the effect of the angle similar schematic where the incident angle is about 80 and then let us assume that the defection geometry for a row of scatter this is a row of scattering row of scatter is for angstrom that is irradiated with the1.5 for angstrom x-ray beam so now you see that the value for λ is equal to I mean θ is equal to a t 56 and 19 corresponding to H is equal to 0 h is equal to 1 and h is equal to 2 and so on.

And how this intensity cone going to be different you see that when the H is equal to 0 you can see that incident beam is almost on the same direction of the diffracted beam and as the value of the H increases you can see that the angle decreases you can see that it is 56 and 19 and you can also see that are the H is equal to 0 the cone is completely opened up you can you can assume that it is completely opened up and as the H value increases you can see that how the θ is decreasing.

So this is another one example to visualize the How this the intensity cone varies with the different values of θ.

(Refer Slide Time: 22:36)



Now we will move on to the two dimension so diffraction from a net that means two dimension which defined by rows a1 and a2 another condition is added to the previous condition that is the $s – s^0$ .a2 that is a path difference is also should also be equivalent to multiple I mean multiple of integral multiple of a $\lambda k\lambda$ where k is an integer a second series of cones is created around the second row of atoms the intersections of the cones give lines of maximum intensity.

So this is where you have to be a little bit careful we are now talking about intersections of cones from the two different rows if we talked about a single row now we talked about at two dimension that means one more row is added and then where that repeat distance is a two and this also is going to produce a counts of radiation for a given θ around each scatter that is here lattice positions you can say our atoms.

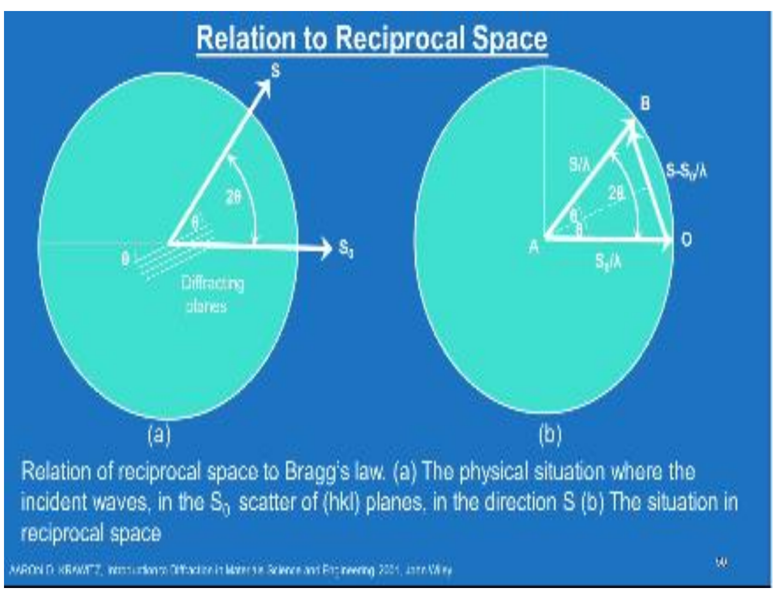
Whatever it may be each one is going to produce a code around it and these two cones are going to intersect so all the cones are going to intersect and that they are going to form a line of maximum intensity finally a lattice is created by addition of a third row that is one more dimension where the path difference necessarily to be $S - S^0$. a3 = i λ which is an another dimension so this is again has to be satisfied for the diffraction to be occurring.

Now common intersections are points of reciprocal lattice so now we talked about one point and from there we talked about a line of maximum intensity and then now the line has become a point of intersection where we will have a maximum intensity that is where the reciprocal lattice point comes, all this equations one two three are known as the LAVA equation please understand in the Bragg diffraction schematic we were talking about only a parallel planes.

And then we said that the diffraction intensity comes from each of the rows or in fact all the atoms which are in phase or in other ways contributing to the constructive interference then account for the diffraction intensity but in a Lava equation it is in a vectorial form of no I mean concept mathematically where we talk about an individual atom where in the form of a row or a 2d lattice as well as 3d lattice and then how each one is contributing to the diffraction or I would say that the each of the equation derives a condition for the diffraction to take place.

So there is a difference between the concept discussed in a Bragg's law or a condition for a diffraction through Bragg equation as well as conditions for the diffraction to take place through a lava equation so in fact lava equation is much more general and you can talk about an individual scatters in the 2d or 3d lattice.

(Refer Slide Time: 26:52)



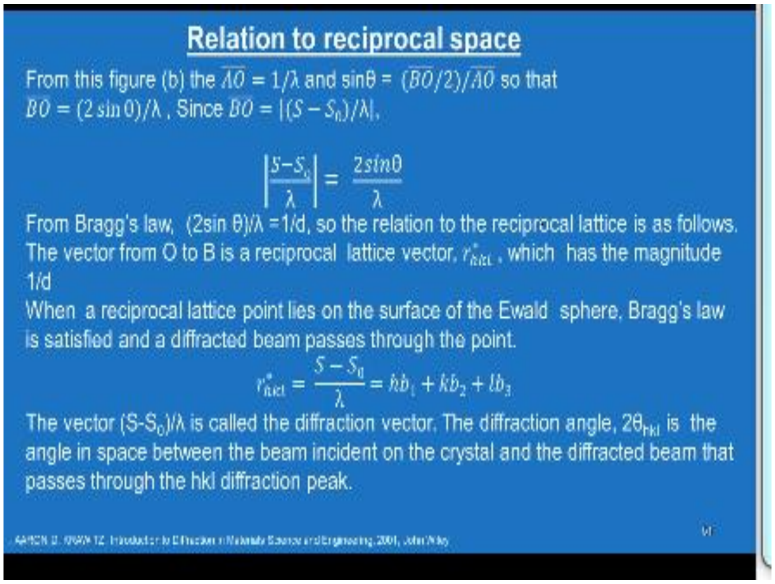
Now we will try to relate this reciprocal space I mean as well as the Bragg law look at this schematic I have just drawn a cross-section of a solid sphere that is why the inside of the circle is shaded that means a cross section of the sphere were inside you are seeing that at a plane and then this is incident ray and this is a diffracted ray and then you have the two θ angle is shown like this and let us now look at the remarks relation of reciprocal space to Bragg's law how we can relate to the Bragg law.

The Bragg law is related to reciprocal space through a wall sphere the another concept similar to reciprocal concept for a diffraction it in a waltz fear so what you are now seeing on the schematic is a cross-section of in world sphere so that is what you are seeing let us see A is the physical situation where the incident waves in the s not scatter of HKL planes in the direction S, B is the situation in the reciprocal space.

So this is an a is a real space like you have s naught and s and what you are seeing is an actual condition for the diffraction through an Evolved sphere you see that let us assume this as a and this is B and this is O from the geometry we will be able to derive some expression based on which the diffraction condition can be arrived so suppose if you define this a row vectors naught by λ and AB vector s/λ and you can look at this is called a diffraction vector $s - s^0 / \lambda$ by this relation.

You see that the evolve sphere radius is 1/ λ so that is something which you have to remember the evolve sphere radius is 1/ λ and then now we will see how this geometry can be related to a diffraction so from the figure b, aO = 1/ λ and sine θ = BO/ 2/ AO so let us see what is that so this is the triangle we are talking about so this is BO, so Bo by two for sine θ we can write like this.

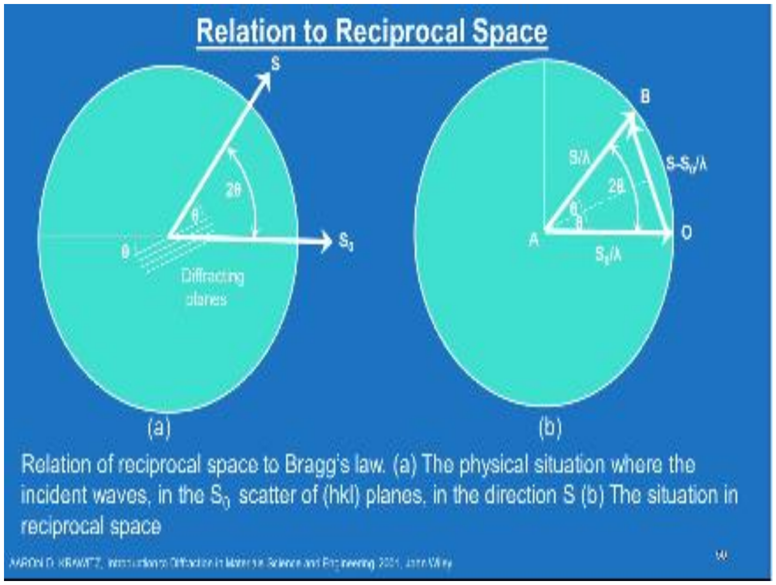
(Refer Slide Time: 30:26)



BO/ 2 divided by AO so that BO can be written as 2 sine θ/ λ and then since BO = $|S - S^0| / \lambda$ which is nothing but this distance. Which is which can be rewritten like this $|S - S^0| / \lambda$ = 2 sine θ / λ from Bragg law 2sine θ/ λ can be written as 1 / D so the relation to the reciprocal lattice is as follows the vector O to B is a reciprocal lattice vector R^*hkl which has the magnitude 1/ D when a reciprocal lattice point lies on the surface of the evolved sphere Bragg's law is satisfied.

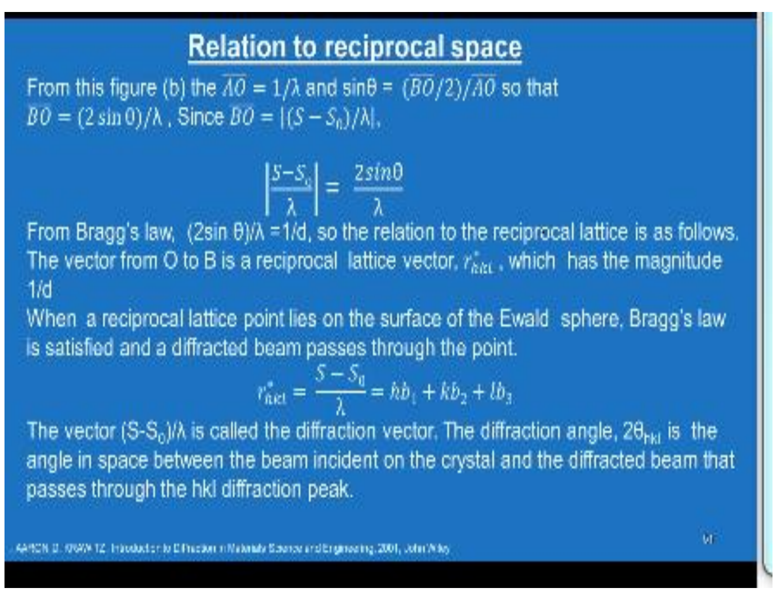
And a defector beam passes through the point so now you write the reciprocal lattice vector R star hkl = $|S - S^0| / \lambda$ = hb1 + kb2 + lb3 the vector $|S - S^0| / \lambda$ is called a diffraction vector which is nothing but R^*hkl in a reciprocal lattice space the diffraction angle to θ hkl is the angle in the space between the beam incident on the crystal and the diffracted beam that passes through the HKL diffraction P. So you have to remember this how this is related to a diffraction condition through this diagram.

(Refer Slide Time: 32:35)



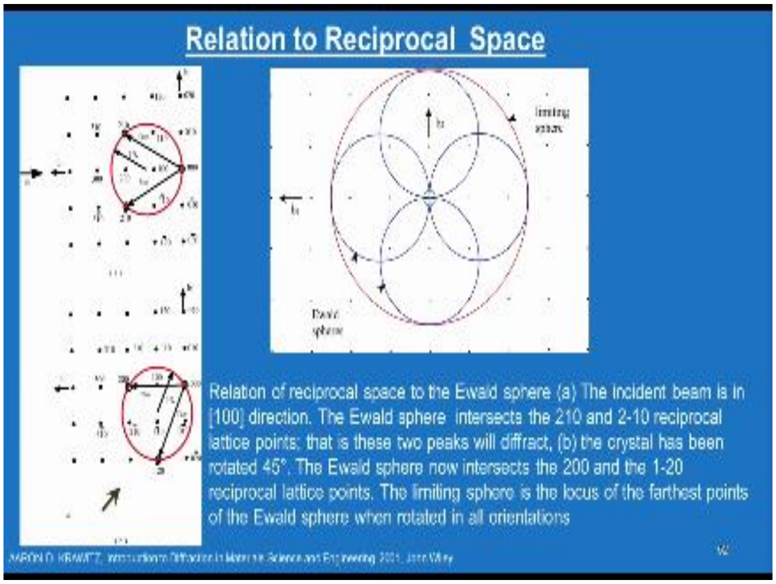
So what it says is this is the diffraction vector s which is nothing but R^* hkl in a reciprocal space so whenever this point hits on the surface of this sphere then the diffraction condition is satisfied and that is what is stated here.

(Refer Slide Time: 33:02)



And now in order to visualize this concept little more.

(Refer Slide Time: 33:11)



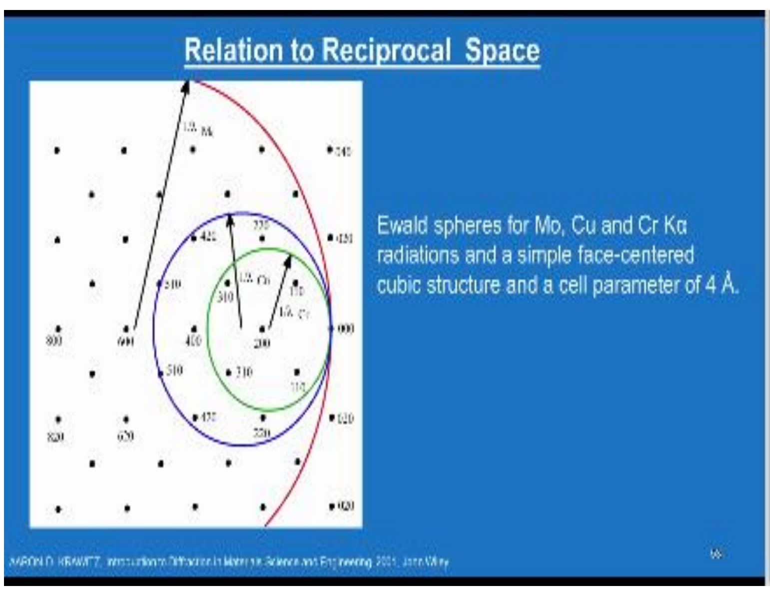
We will look at some more a schematic what we are seeing here is in a schematic a and B a relation of reciprocal space to the evolve sphere here, a is the incident beam is in 100 direction suppose this is the s^0, s^0 is in the 100 Direction 100 direction so the evolved sphere intersects the red markers in a waltz fear which intersects 210 and 21 – 0 reciprocal lattice points that is here as well as here that means these two peaks will diffract these two reciprocal points are diffracting set of planes.

And what we are seeing in the schematic b is now the crystal has been rotated to 45degree so the crystal has been rotated to 45 degree then what happens is the evolve sphere now intersects 200 and 12 - 0 reciprocal lattice points you can see that 12 - 0 + 200 reciprocal points which are coming on the intersecting the a evolve sphere so between these two rotation no other points are possible for the diffraction that is what it means.

So if you look at the diffraction spots 21- 0 and 210 after rotating to 45 degree you have a new planes 200 or 12- 0 and between these two rotation there are no other possibilities for the diffraction that is what it means so this is one way of interpreting the whole sphere concept and what is this schematic shows, this is also a set of evolve sphere but it says the limiting sphere what do you mean by limiting sphere the limiting sphere is the locus of the farthest point of the evolve sphere when rotated in all orientation so right now we have seen that rotating into two direction and suppose if you rotate another 45 degree another 45 degree another 45 degree what are all the points will intersect in the reciprocal lattice that is this is the reciprocal lattice were all it will intersect that is a maximum possible planes which will contribute to the diffraction are the planes maximum number of planes that will intersect the evolved fear that is called limiting sphere.

So that is what shown here in a in a plane of b1 and b2 lattice and this defines the limiting sphere like this and another very interesting example I would like to show.

(Refer Slide Time: 36:40)



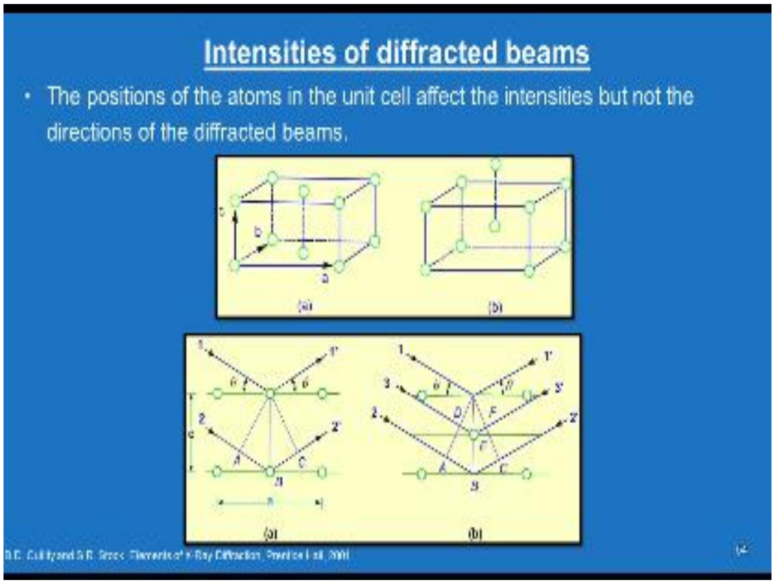
Where the evolve sphere for molybdenum copper and chromium k alpha radiations in analyzing the simple face centered cubic structure with the cell parameter for angstrom, suppose if you use one of this radiation for example let us use a chromium radiation so which is 1/λ of chromium which forms the evolve sphere around these lattice points I mean reciprocal lattice points which have only 110, 310, 200 since your reciprocal I mean your revolves fear radius is 1/λ which is a function of a wavelength of a given radiation it can explore the possibility of finding the reciprocal planes only in a limited number that is 110, 310 and 200 type suppose if you use a copper radiation then our radius increases then you are a evolve sphere becomes little bigger and now you see in addition to their 110 and 310 and 200 planes you have were able to examine ϕ10, 420, 220 etc.

So as the λ changes you are able to incorporate large number of reciprocal lattice points that means you are able to get into atomic planes more atomic planes which are satisfying the Bragg conditions so the one last one is a molybdenum radiation you see that it covers quite a bit of reciprocal points that means it forms a huge sphere evolve sphere which will interest which will intersect through many reciprocal point including large number of planes.

So there is this is what the evolve sphere concept is readily visualized so what you are now seeing is the black spot is as I said it is a reciprocal lattice points and then we will also look at this similar electron diffraction pattern and then again we will come back with the evolve sphere concepts to understand little more on the diffraction phenomena but to start with this is very nice exam and schematic to understand the relation between the Bragg's law and reciprocal lattice and evolve sphere.

So the wall sphere actually links the Bragg law and the reciprocal lattice that way we can consider it is a very nice concept too and just appreciate the diffraction phenomena.

(Refer Slide Time: 40:08)



Now we will move on to intensities of diffracted beam at the end of the day if you are interested in analyzing the crystal with x-ray diffraction we are interested in intensities and we will account for the intensity expressions and then we will see what are all the parameters which will influence the diffraction intensities when it when it happens with the amorphous material when it happens with the crystalline material or a single crystal or a poly crystal and soon so the intensities are important and their quantification is important.

But we should know what all the parameters which will control the diffraction intensities of x-rays so we will begin never a discussion with this let us look at the two I mean crystal structures simple crystal structures what you are seeing in the schematic a is a a base centered a unit cell and b is the a body centered unit cell, the positions of the atoms in the unit cell affect the intensities but not the direction of the diffracted beings.

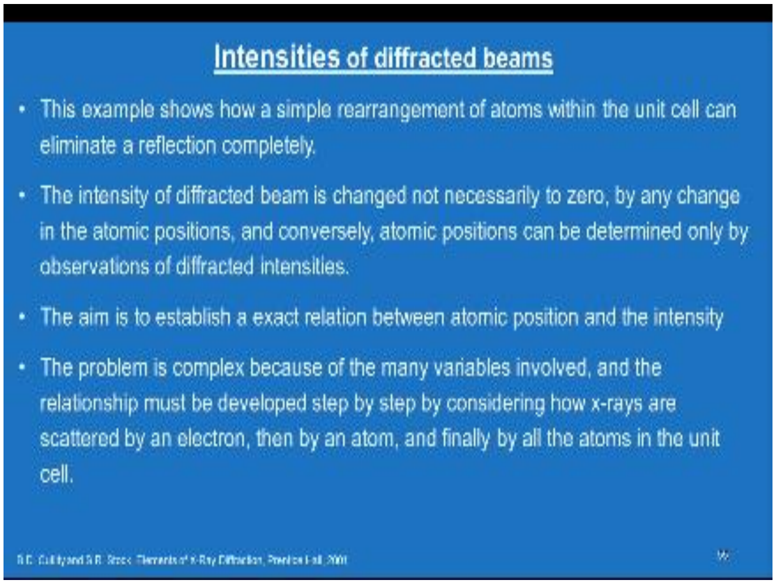
So to prove this concept how the positions of the atoms in the unit cell is going to affect the diffracted beam we are going to illustrate through this two examples one is a base centered unit cell another is a body centered cell and if you assume that x rays are coming and then diffracting through both the unit cells and then you will get the corresponding ray diagram like this a and then b, I would like you to look at this rate diagram carefully the Ray 11' and 2 2' and the distances C and this two diagrams we have already seen on the in the previous classes you will recall when I talked about the importance of 200 planes for example if you see that what is the path difference between these 211' and 2 2' they are out of phase by a one wavelength or would say that the path difference AB + BC is equal to some h λ something like that.

So but if you come to this unit cell the situation is slightly different suppose if you assume that these two planes diaphragm the x-ray and then their face differences is about 1 λ here it is exactly half of that phase difference for example if because we have the other plane which is inserted in between so the 3E3' prime ray will have the phase difference exactly half of the the previous one.

So that means this phase difference is going to completely annul the intensity is of the x rays diffracted by this ray 11'as well as to be 2' so that means you are not going to get the intensities from 100 plane at all so I hope you get this idea this has been already I had told you and the phase difference I also separately discussed how you have to visualize the phase difference and how they annoy each other or they contribute to the constructive interference.

So in this type of a crystal where you have this the path difference or the phase difference exactly half of this unit cell they are going to lose the intensity from 100 so that is what we are concluding.

(Refer Slide Time: 45:22)



This example shows how a simple rearrangement of atoms within the unit cell can eliminate a reflection completely the intensity of a diffracted beam is changed not necessarily to 0 but any change in the atomic positions and conversely the atomic questions can be determined only by the observation of diffraction intensities so the aim is to establish the exact relation between atomic position and the intensity.

The problem is complex because of the many variables involved and the relationship must be developed step by step by considering how x-rays are scattered by an electron then by an atom and finally by all the atoms in the unit cell, so we would like we would look at the how the defected intensities are changing by step by step first by scattering by the electron then by the madam and then by unit itself then we will look at the whole expression for the x-ray intensities diffracted by a crystal.

So we will continue to look at this diffraction phenomena and then we will in the next class we will start with the x-rays which when they are scattered by an electron what are all the physical phenomenon we will go through those things we will look at in the next class, thank you.

IIT Madras Production

Funded by

Department of Higher Education

Ministry of Human Resource Development

Government of India

www.nptel.ac.in