Characterization of Construction Materials
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Lecture 15
X ray Diffraction Crystal Systems and History of XRD Part 2

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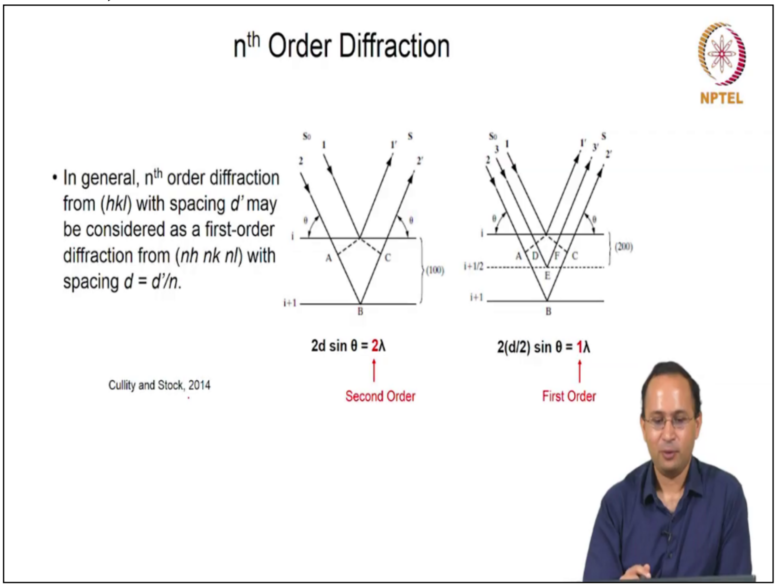

In this lecture, we will now look into n th order diffraction. So, far we looked at a,b as you know we have surface atoms then, one layer is there below surface atoms. But there could be further more. So, in general you see nth order a diffraction from hkl which is defined as plane with spacing d' may be considered as the as a first-order diffraction from nh, nk, nl with spacing d as d'over n.

So, let us look at the left one so you have 1 0 0 plane and you see here ABC is path difference that will be 2d sinΘ so if you have to write the Brag's law will be 2d sinΘ equals to 2 λ where n equals to 2 here. Now consider there is another plane now we are talking about 2 0 0 planes.

So this is a plane 2 0 0, now we talked about the ray 1 and 3, there has to be diffraction the spacing will be d by 2. So, 2d by 2 sinΘ equals to 1 λ, so see overall we get that d sinΘ equals to λ and this is the second order for this plane.

Suppose, this is one then we get λ by 2 which means there will be destructive diffraction. In general in nth order diffraction from hkl with spacing d'may be considered as first-order diffraction from nh nk nl.

So, first-order diffraction from 2 0 0 is equivalent to second-order diffraction from hkl. Second-order diffraction from 1 0 0 plane is equivalent to first-order diffraction from 2 0 0 plane.

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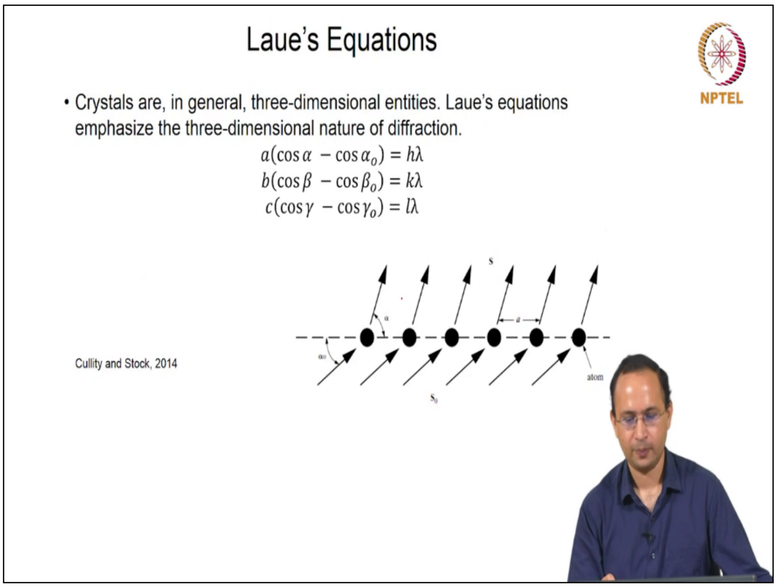

So, far we are talking about one dimension but in real life we will have the diffraction occurring in all 3 dimensions, Bragg's law simplifies it. The Laue's equations can be used for writing more general equations. Since, crystals are in general 3 dimensional entities, the Laue's equations emphasize the 3-dimensional nature of diffraction. the scatters atoms in one dimension.

We have incident beam and diffracted beam and all we need to calculate is the path difference. Suppose in one dimension you have the spacing between the atoms is 'a' and similarly spacing 'b' in y direction and 'c' in z direction. So in just to simplify we are saying let us look at the one dimension a where they are distance between atoms is a. So, 'a' times cos α- cos α_o is the path difference which is equal to h λ if the diffraction condition has to be satisfied in that particular direction.

You can calculate the power difference using the same principle in this case. In similar way b times cosβ - cosβo is equal to k λ for other direction.

These are the general equations written in 3 dimensions. So, all have to be satisfied if you want to see the diffraction where h, k, n, and l are integers. This is just to highlight the 3-dimensional nature but for simplification Bragg's law is much easier as it gives scalar quantity.

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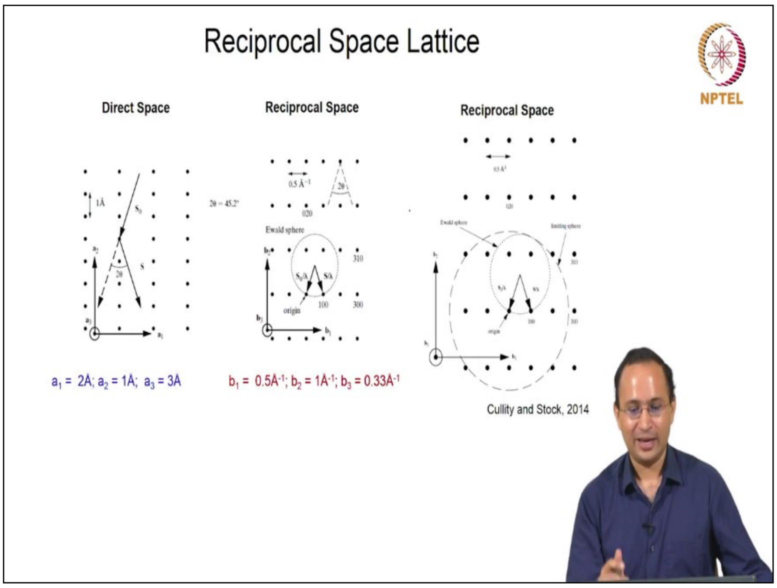

So, in the last lecture we discussed about the reciprocal space as it helps you visualize things and identify the diffraction planes. So, again here what you see in the direct space is we have these arrangement of atoms. You have incident beam as 0 and diffracted beams s and here suppose you have these are the lattice parameters a_1 is 2 Angstrom, a_2 is 1 Angstrom, a_3 is 3 Angstrom. a_1 is in x direction, a_2 in y direction and a_3 in direction coming out of plane.

This is just arrangement of atoms we are talking about now a plane this plane where you have this plane where you have incident beam as '0' and the diffracted beam as 's'. You know that the angle between diffracted beam and transmitted beam is 2Θ. Now to construct the reciprocal space we use the same principle to write for b_1.

You will find that b_1 is 0.5 Angstrom inverse. b_1 has to be perpendicular to a_2 and a_3 by using the right hand thumb rule; it is used for the reciprocal space. The rays are usually parallel in direct and reciprocal spaces.

So as 0 is the incident ray and you draw a parallel ray of the length will be as 0 over λ because we are talking about the reciprocal space. You start from a point and go parallel to 0 and you stop at specific point; if you construct a sphere if it cuts at some particular points that is the diffraction plane, so that tells you that at that point Bragg's law is satisfied.

For the 1 0 0 plane, wherever it cuts that means at that location Bragg's law is satisfied. We see 1 0 0 is the diffracted beam and is parallel to diffracted beam in direct space. Incident beam in reciprocal space is parallel to incident beam in direct space and the deflected beam in reciprocal space is parallel to deflected beam in direct space.

Now so you know 1 0 0 is basically the origin of the reciprocal space where you end it. And now we can rotate this sphere and you will find another sphere is called a limiting sphere. So, you can rotate the sphere and move the sphere. This limiting sphere tells you that the planes outside it will have no diffraction.

Only diffraction will occur for the points which lie inside limiting sphere. The point where this sphere cuts is called Ewald sphere and where it cuts those points the Bragg's law is satisfied.

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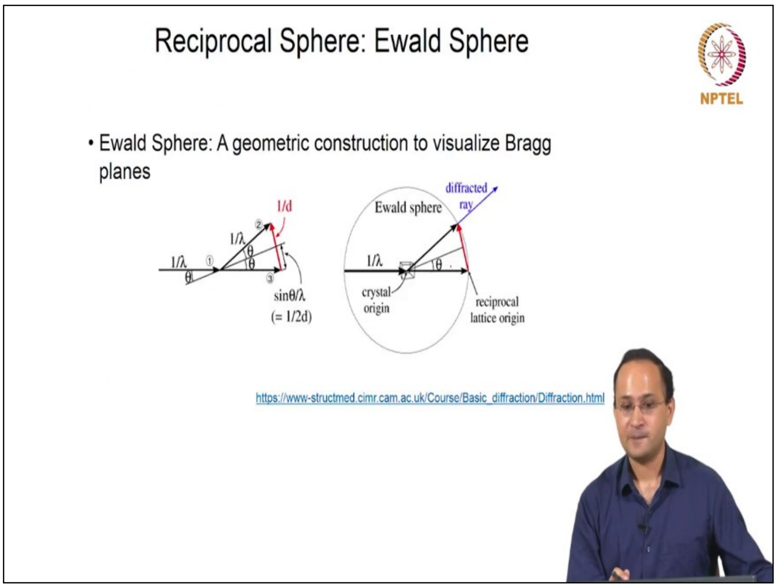

If you have a point on Ewald sphere then you will meet the Bragg's condition. Assuming you have an incident ray coming in a certain way and there is the diffracted beam and we are talking about the reciprocal space so length is 1 by λ. Now so this specified distance is 1 over d.

So this is 1 over d and can be written as 1 over (1/2) because it is half. Now if you have to write a condition sin Θ equals to 1 over 2d; this is your sphere we are talking about and the length will be equal to this 1 by λ. If you solve it you will get sinΘ equals to λ over 2d or basically 2d sinΘ equals to λ.

So, now it tells you if you have a point on the reciprocal space at that point your Bragg's condition will be satisfied and it can be seen from this geometry. So, this is 1 by λ and this is the reciprocal lattice origin. So, how do we construct it is by the drawing incident beam in reciprocal space which is parallel to incident beam in direct space.

So, the length will be s_0 by λ, where this meets is the origin in reciprocal space. Now considering this as a center you can draw the sphere that will cut; if there is a diffraction for 1 0 0 plane it will cut and this vector which you can find by joining this line so this one will be your deflected b.

So far, we focus on only one plane but there will be diffraction from other planes and we get that by considering this as origin and rotate this as sphere. Think of it as rotating then you will get a limiting sphere. So, this will tell you that all the diffraction plane are contained in this space.

When you rotate the Ewald sphere and see where it is cutting and if it that point is on that sphere means at that point Bragg's law is satisfied. If it is on the sphere then you see that the Bragg's law is satisfied. So, basically idea of reciprocal is just to visualize these planes of diffraction and you see the patterns and the periodicity.

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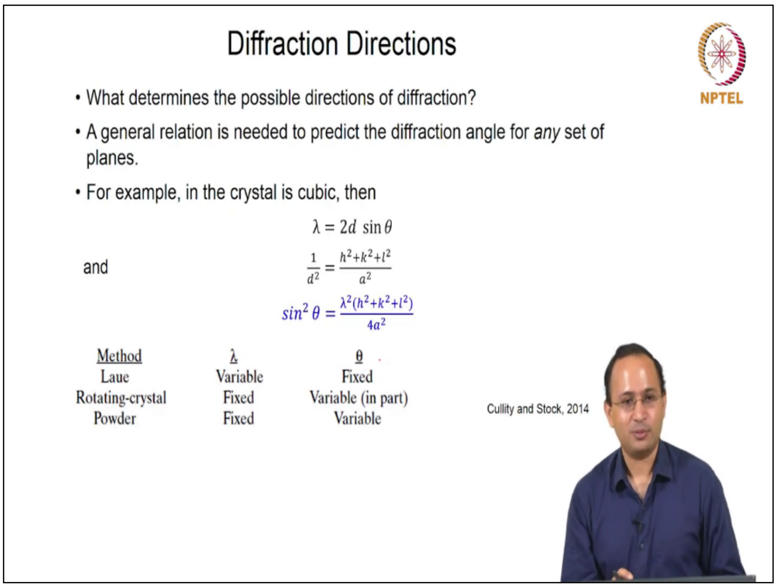

Now the question comes what determines the possible directions of diffraction, for that a general relation is needed to predict the diffraction angle for any set of planes. Suppose for any set of plane we want to calculate; what are the directions so let us try that for cubic crystal. We know from the Bragg's law λ equals to 2d sinΘ.

Now we discuss in the last lecture, you have planes and there is a spacing between the planes and this is for the cubic system, what you see. Now by combining the two equations we get you know the particular if you know the hkl plane

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

Suppose, you know a plane and the λ and you have a particular crystal structure for example cubic system you can find out all the Θ where you will have a diffraction.

So, this relationship can be used to predict the angle and the diffraction directions. This relationship is for cubic system and it will be different for tetragonal system. But this relates the Θ and the plane hkl.

Now the second question is which are the planes and what are the angles at which will get diffraction. Laue method is basically when λ is varied and theta is fixed. Rotating crystal method, you have fixed λ and Θ is variable. For Powder method, you have fixed λ and theta is variable.

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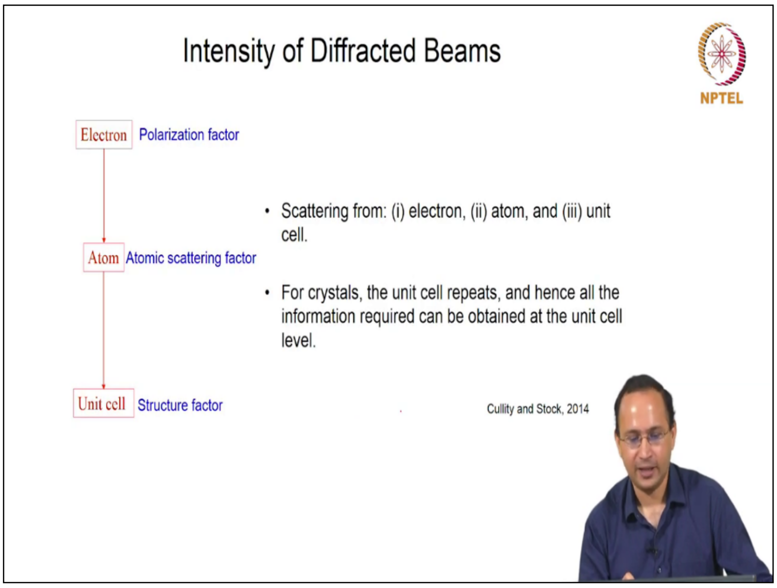

So far we know the about the diffraction and where the Bragg's law is satisfied. Now the question arises what happens to the intensity because eventually we want to get a pattern of x-ray detection. In the next lecture, we look into the intensity of diffracted beam and the factors which influence the intensity.