Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 23
Bragg's Law in Reciprocal Lattice and Origin of Systematic Absences

Welcome back to the course of Chemical Crystallography. In the previous lecture, we discussed about the origin of reciprocal lattice, how to construct a reciprocal lattice from a direct lattice and we learnt that every reciprocal lattice point in reciprocal space represents a particular plane in the direct lattice. So, by doing this what we have done is, we have constructed a reciprocal lattice from the planes that are having corresponding miller indices hkl in the direct lattice. And then, towards the end, we will learn how to construct the reciprocal lattice in case of orthorhombic system and how to get the corresponding reciprocal lattice parameters a star, b star, c star and the volume.

So, now we will try to construct the same. In case of monoclinic lattice, as you know for monoclinic lattice, the angle between a and c is not 90 and this is called beta.

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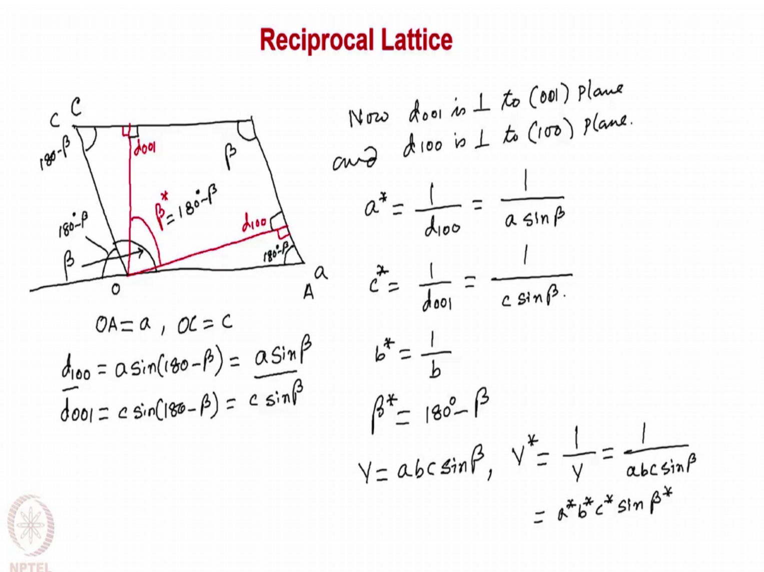

So, I am drawing AC plane of a monoclinic unit cell. So, this angle is beta. So, now if we drop a perpendicular from the origin to the plane which is parallel to C, this plane this perpendicular will correspond to d 1 0 0. In the same manner if we construct the perpendicular from origin O to AC plane here to the plane parallel to A axis is like the distance is d 0 0 1 and then, the angle between the two normals is my beta star.

So, now if the angle on that other side is beta, then the angle here is 180 degree minus beta which is same as this angle and this angle is also 180 minus beta. So, now OA where I construct that as a and that as c OA is equal to a and OC is equal to c, then if we want to write down the value of d 1 0 0 in terms of a and beta, this is d 1 1 0. So, we consider this particular triangle and then, we can write d 1 0 0 at equal to a sin 180 minus beta which means it is equal to a sin beta. Similarly d 0 0 1 is equal to c sin 180 minus beta. We are talking about triangle here which is again equal to c sin beta.

Now, d 0 0 1 is perpendicular to 0 0 1 plane and d 1 0 0 is perpendicular to 1 0 0 plane. So, the reciprocal lattice distance a star is nothing, but equal to 1 by d 1 0 0 and c star is equal to 1 by d 0 0 1. So, now a star is equal to 1 by d 1 0 0 and d 1 0 0 is a sin beta. So, a star is equal to a sin beta and correspondingly c star equal to c sin beta and obviously, if since the direction b is perpendicular to both c and a b star is same as 1 by b as one seen in orthorhombic system.

So, the angle beta star is equal to let us see that this is 180 minus beta, this angle is then beta. In case of this figure, you have this angle and that as 90 degree. So, in case of this quadrangle two angles are 90 degree. So, this is 180 plus beta. So, this angle is nothing equal to 180 minus beta because these two angles should correspond to 180 degree because the other two angles correspond to 180.

So, beta star is equal to 180 minus beta. So, if we try to calculate the volume of a monoclinic system which is equal to a b c sin beta, the reciprocal lattice volume is nothing, but 1 V star is equal to 1 by V which is equal to 1 by a b c sin beta or equal to a star b star c star sin beta star. So, this is how one can calculate the reciprocal lattice parameters for monoclinic system.

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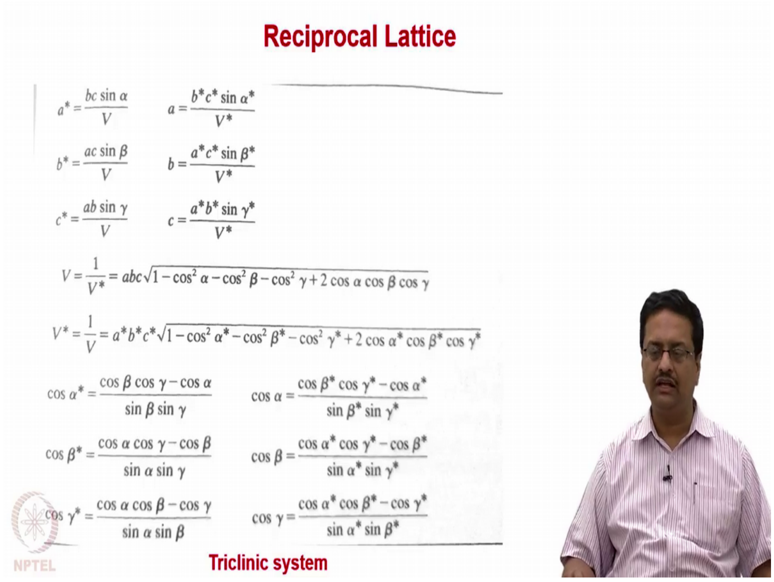

In case of triclinic, this representation becomes even more complicated because the angles; alpha, beta, gamma are all not 90 and hence, the relationships are more complicated as I have shown here in this presentation which is also taken from a text book.

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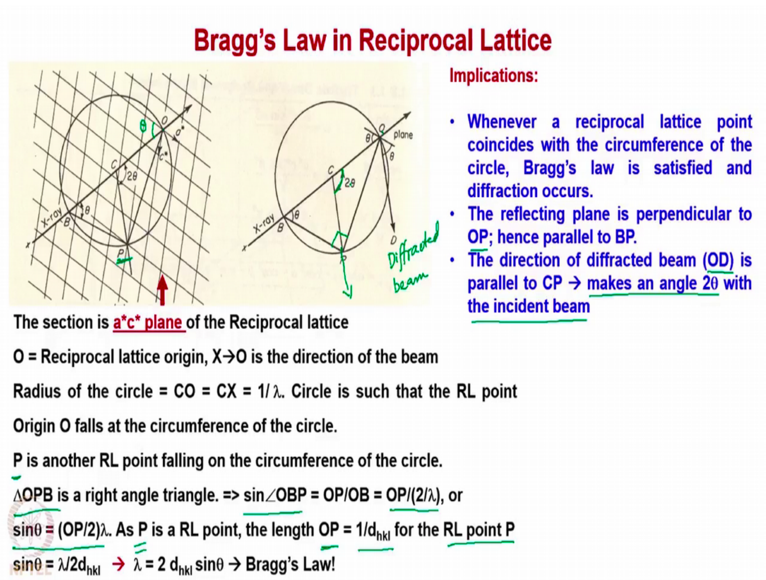

Now, let us see how we can visualize Bragg's Law in reciprocal lattice. Here in the figure on your left I have taken the section of a star c star plane of reciprocal lattice. So, the grid lines that are visible here, it corresponds to the reciprocal lattice points. So, every point of intersection of these lines presented a reciprocal lattice point in the a star c star plane and we assume that O, this O as the reciprocal lattice origin and the direction XO is the direction of x-ray beam that is falling on this particular crystal.

So, now what we are trying to do is to draw a circle in such a way that O falls at its circumference, C is the center of the circle and OC is equal to CX equal to 1 by lambda. That means, we are trying to construct a circle with radius equal to 1 by lambda. Lambda is the wavelength of a standard deviation. So, this circle is formed in the plane of the a star c star reciprocal lattice plane and O falls at the circumference of the circle. After drawing this circle, we find that another reciprocal lattice point P which is here is falling on the circumference of this particular circle of radius 1 by lambda.

So, then we consider a triangle OPB which is here OPB which is a right angle triangle and then, we try to calculate sin OBP sin of OBP where the angle OBP is equal to theta because when we are trying to see. Now, let us concentrate on the figure on the right hand side. The incident takes a beam is making an angle theta with this particular reciprocal lattice plane which means this angle is theta. As a result the angle OBP is also theta. So, OB and sin OBP is equal to OP by OB OP by OB and now OB is nothing, but the diameter of the circle which is equal to 2 by lambda. So, we can rewrite as sin theta equal to OP by 2 into lambda.

Now, as P is another reciprocal lattice point, then the distance OP must correspond to 1 by d hkl for the reciprocal lattice point P because this OP is perpendicular to OB. So, we are dropping a perpendicular from the origin and coming to a point and cutting it at P which is a reciprocal lattice point. So, the corresponding distance OP is supposed to be 1 by t hkl that is the underlined principle of generating the reciprocal lattice points. So, we replace OP equal to 1 by t hkl and we write sin theta equal to lambda by 2 d hkl or we can write lambda equal 2 d hkl sin theta. That means Bragg's Law condition is satisfied for this particular reciprocal lattice point P.

So, what are the implications of this understanding? Whenever a reciprocal lattice point coincides with the circumference of the circle drawn like this with the lambda with the radius 1 by lambda, Bragg's Law is satisfied and the deflection occurs. The reflecting plane is perpendicular to OP, hence parallel to BP.

So, the plane which is the reflecting plane is perpendicular to P which means parallel to BP, where BP is perpendicular to OP. The direction of diffracted beam is OD is parallel to the direction CP. That means, it makes an angle 2 theta with the incident beam as shown here. That means, when we try to observe a diffraction coming out of a set of parallel planes, we measure it at an angle 2 theta with respect to the incident plane.

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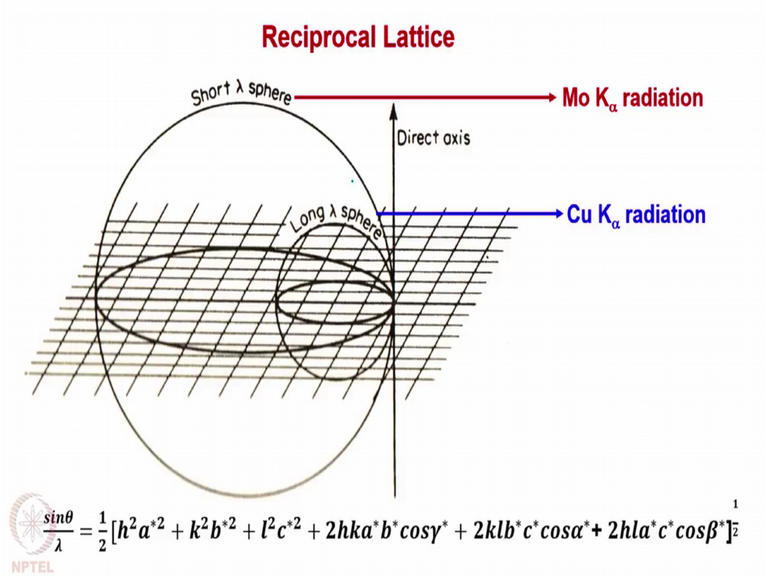

So, now this particular drawing which we have seen here is only in one particular reciprocal lattice plane of a star c star like that you have sets of planes. In a star b star direction or c star, b star planes as a matter of fact these reciprocal lattice points are there in all directions in three-dimension and if we consider those points, it actually represents a sphere. So, when you represent a sphere like that, immediately the size of the sphere is related to 1 by lambda. That means, smaller the value of lambda, larger the value of 1 by lambda; larger the value of lambda, smaller the value of 1 by lambda.

So, for radiations with smaller wavelength, we should have a larger sphere as shown here in case of M o k alpha radiation and in case of longer wavelength like copper k alpha radiation, where the wavelength is nearly double that of molybdenum, the sphere that is constructed is of smaller volume, a smaller diameter and when we have understood the formation of reciprocal lattice from a direct lattice, this equation at the bottom is another representation of Bragg's law in reciprocal space. So, this expression is one of the most important expressions in the theory of x-ray diffraction a representation of Bragg's Law in terms of reciprocal lattice constants.

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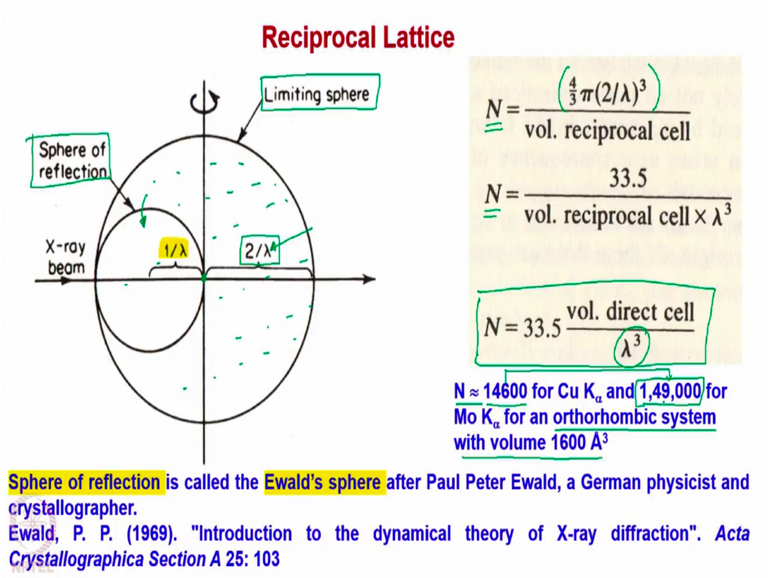

So, now if we consider this sphere with radius 1 by lambda as shown here, we kept a smaller sphere with radius 1 by lambda and then, with radius of 1 2 by lambda which is the diameter of the smaller sphere. If we construct another sphere having the center at the point of intersection here, a sphere with radius 2 by lambda is called a larger sphere and this larger sphere is called the limiting sphere and the smaller sphere with radius 1 by lambda is called the sphere of reflection.

So, this sphere of reflection is also called the Ewald's sphere after the name of Paul Peter Ewald, a German Physicist and Crystallographer and he introduced this concept of sphere of reflection and limiting sphere in his article in 1969 in Acta Crystallographica. The reference is given here. What are we trying to understand from here in the next slide? I will show you a representation where we will see that all the reciprocal lattice points which are falling within this limiting sphere of reflection can be made to pass through this sphere of reflection.

So, from limiting sphere the reciprocal lattice points which come within this limiting sphere by rotating the crystal in front of the x-ray beam, one can melt those reciprocal lattice points to pass through the Ewald's sphere and once a point is passing through the circumference of this Ewald's sphere, the periphery of Ewald's sphere it makes a diffraction to happen.

So, utilizing this concept and thinking that assuming that there is one reciprocal lattice per unit, reciprocal lattice volume one can calculate the number of reflections that can be originated from a given crystal. So, the number of reflections that can happen that can be obtained from a given crystal can be calculated as four-third pi 2 by lambda cube 2 by lambda is the diameter of this particular limiting sphere.

So, whatever reflections fall within this limiting sphere of this volume can be recorded and one can get the data for those reciprocal lattice points. So, then the value of n can be calculate in terms of direct volume of the direct lattice, that is volume of direct unit cell in terms if we know the wavelength of diffraction.

So, just for one example when we have an orthorhombic unit cell of volume about 1600 cubic angstroms, if you use copper k alpha radiation which has wavelength of 1.54 angstrom, one can get about 14,600 reflections whereas, if somebody is using molybdenum k alpha radiation, this number of reflections suddenly jumps to 1,49,000 reflections using molybdenum. That means, by using a smaller wavelength one can achieve a larger number of reciprocal lattice points. That means, one can achieve much higher resolution.

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So, in this particular presentation I will take help of this animation which is available in the website of Professor Brenton Campbell and let us try to.

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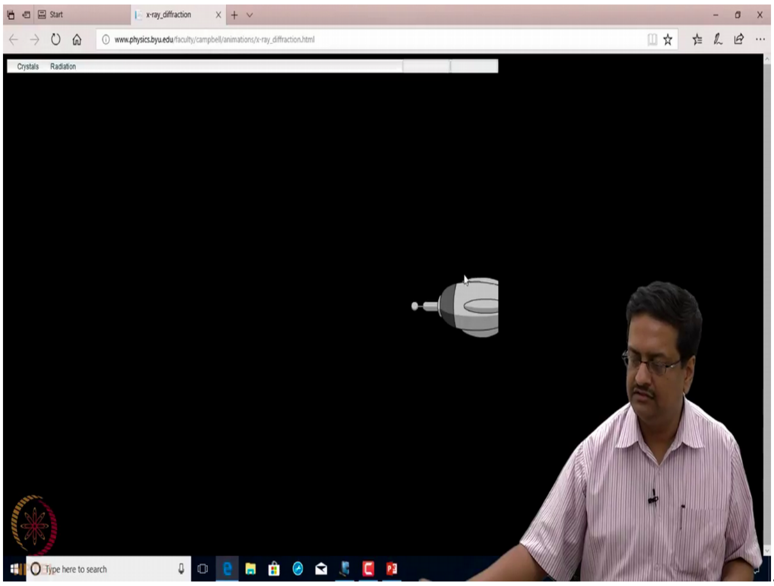

So, here this point is the source of x-ray as we can see and then, we choose a crystal oriented in a particular direction and we choose a radiation of molybdenum.

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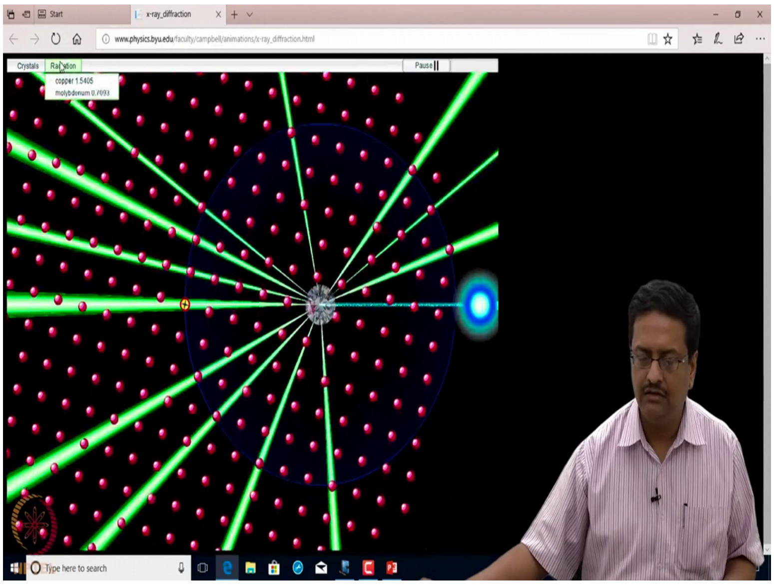

So, in this presentation what is visible is that these bright red spots are reciprocal lattice points and the crystal in the center is rotated in such a way that these reciprocal lattice points are rotating in front of the beam, and as and when a reciprocal lattice point is crossing the Ewald's sphere, it is making diffraction. So, now if we change their radiation from molybdenum to copper, you see that the size of the sphere has become much smaller. So, the number of reciprocal lattice points falling with beam, the limiting sphere of diameter 2 lambda has reduced. So, the number of reflections that one can achieve has drastically reduced.

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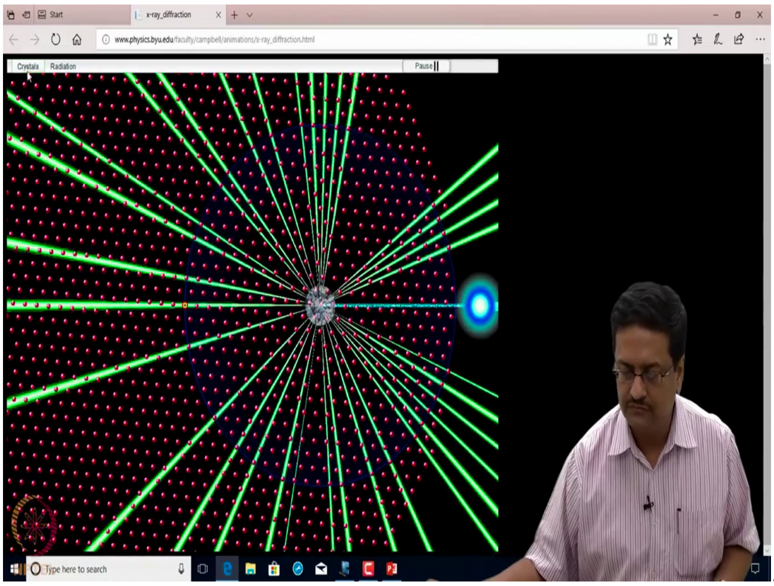

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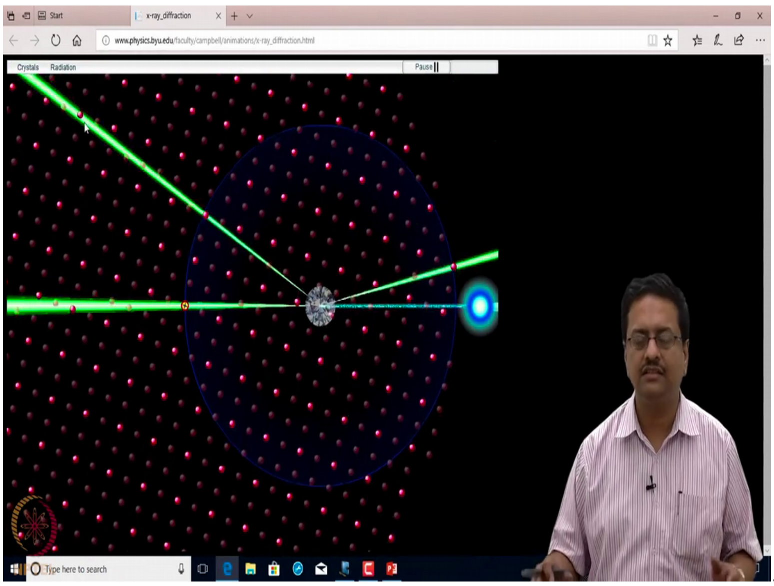

If I choose one different lattice different crystal here, what you can see? It is a zinc blend crystal in a particular plane and in the reciprocal lattice, what you can see some bright red spots and some red spots which are not bright, which are sort of disappeared and when those bright spots are crossing the Ewald's sphere, it is making a diffraction and when those dull spots are crossing Ewald's sphere, it is not making any diffraction. This indicates that not all reciprocal lattice points while crossing the Ewald's sphere will make a diffraction to happen. So, what is happening, this is the phenomena called systematic absence which we will learn in the next slide. There are cases where a set of reflections will be systemically absent and will not be absorbed for various symmetry constraints and only some of those reflections which are bright in this presentation will be visible.

Again if you change the radiation to copper, you can see that the total number of accessible reflections has reduced drastically.

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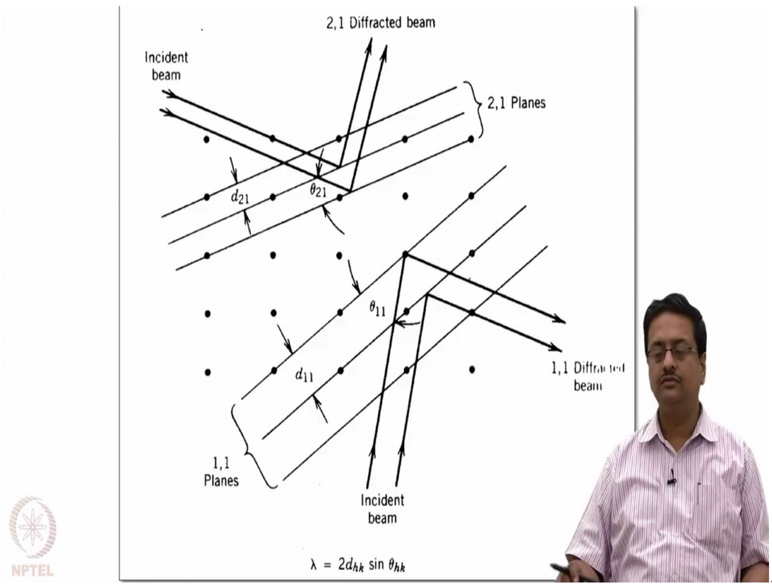

So, now in order to understand the origin of this systematic absence, I once again would take help from a two-dimensional presentation. Suppose this is a two-dimensional primitive lattice where you have lattice points; only at the corners as shown here.

So, now if we draw set of planes one which is passing through the corners like that, these planes will always have there corresponding incident beam and coming out diffracted beam and at some particular angle of theta, the diffraction angle it will give you x-ray diffraction from 2 1 set of planes. Similarly if we construct the set of 2 1 planes which means it connects from one unit cell, the corner of the other unit cell passing through the midpoint of the our direction.

So, this 2 1 set of planes having a distance d 2 1 will always meet the condition for Bragg's Laws in reflection.

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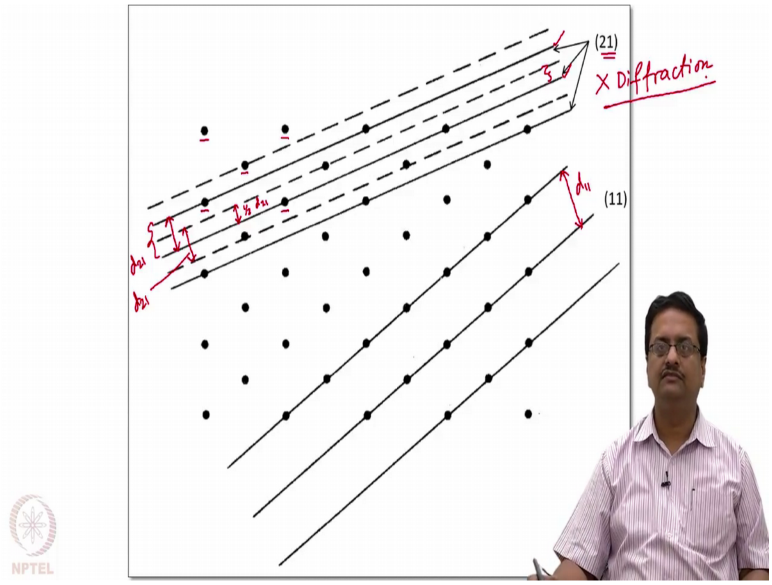

Now, if we consider a centered lattice in two-dimension where we have atoms at 4 corners and an atom at the center of the lattice, in that case when we try to construct the 1 1 set of planes where this distance is d 1 1, there is no problem. A diffraction would occur at a suitable direction where the Bragg condition is met, but in this case of 2 1 set of reflections suppose the dark lines are parallel and these dark lines, the interplanar distance is d 2 1, once again the lines which are dashed lines, the distance between them is also d 2 1. You see both the dark and the dashed lines represent, the same set of plane 2 1. That means, the planes with dash and the bolt line have the same miller indices.

So, that means this distance is half of d 2 1. What will happen, the planes at a distance d 2 1 meets the Bragg condition of integral multiple of wavelength is equal to the path difference. Then, obviously this will not meet diffraction condition. As a result the constructive interference will not happen and in this particular case, only the destructive interference will happen and we will not see any diffraction from the set of 2 1 planes.

So, from a diffraction pattern of a centered lattice like this in two-dimension, the 2 1 set of planes will be systematically absent for the time being.

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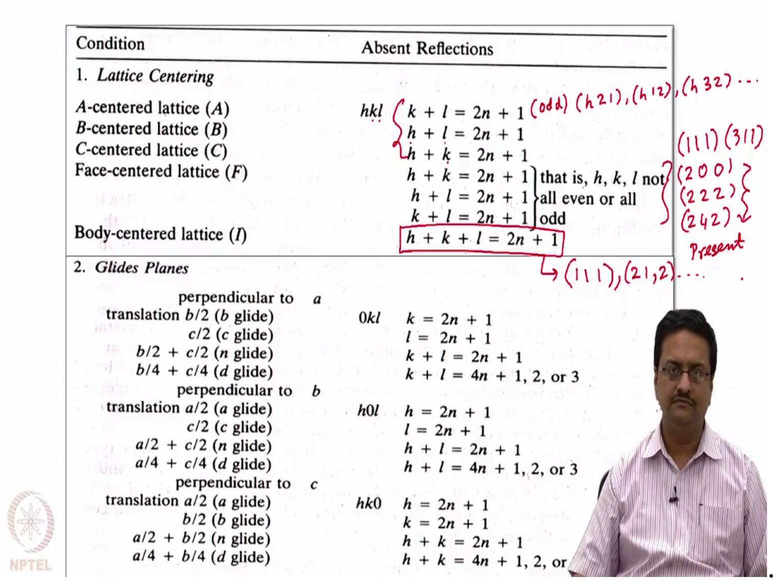

I am only introducing you to this lattice centering and the corresponding systematic absence conditions, but at a later stage we will be able to derive these conditions using some equations.

So, in case of a centered lattice, that means the b c face is centered b and c means k and l. So, for general reflections h k l k plus l when it is odd 2 n plus means it is odd. The reflections will be absent; that means, in case of a centered lattice with any value of h, when k plus l is odd say for example, 2 1 h 1 2 h 3 2 and so on. These reflections will be absent systematically in case of a centered lattice. Similarly for b centered lattice h plus l will be odd and for c centered lattice h plus k will be odd.

Now, in case of face centered lattice when all the three conditions need to be simultaneously fulfilled, that means for face centered lattice in all the cases h plus k should be odd, h plus l is odd, k plus l is odd. That means, h k and l not all even or all odd. So, in this case only reflections which are like 2 0 0 2 2 2 2 4 2, these type of reflections will be present and any other reflections, it will be absent.

Similarly, all even all odd also will be present. So, 1 1 1 3 1 1, these are all odd set of reflections and they will be systematically present. All others will be systematically absent. Similarly for body centered lattice, this condition has to be fulfilled that is h plus k plus l is odd will be systematically absent. So, the absent reflections will be of this type 1 plus 1 plus 1 3 2 1 2 and so on where the sum is 3.

So, in the next lecture, we will try to understand how the systematic absence conditions for glides and screw axis to be followed.