Chemical Crystallography
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Lecture – 22
Origin of Reciprocal Lattice

Welcome back to the course of Chemical Crystallography. In the previous lecture as if you remember, we were discussing about Bragg's Law and its applications and we were trying to understand the choice of radiations for different purposes.

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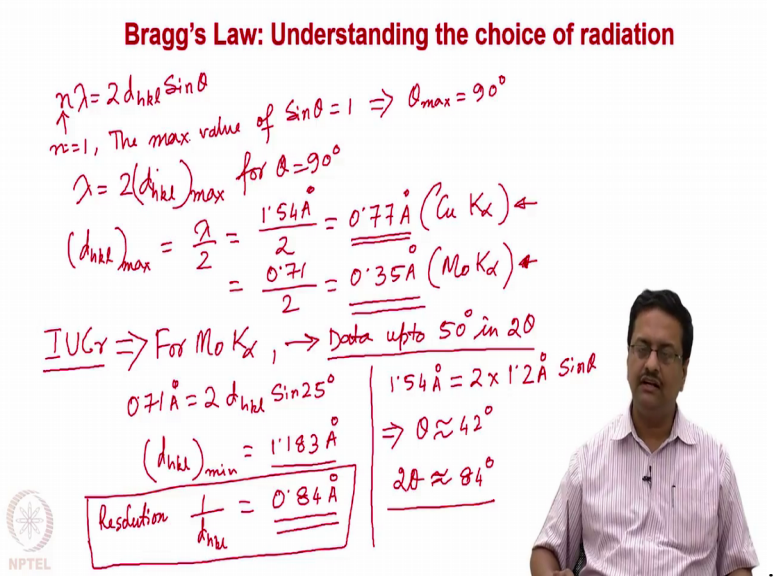

In that we identify that if we use copper K alpha radiation. You can achieve a maximum resolution of 0.77 angstrom while if you want to use molybdenum radiation, you can achieve a very high resolution of 0.35 angstrom.

So, with this I would like to continue in this lecture and see what happens if we try to use these different radiations for different purposes.

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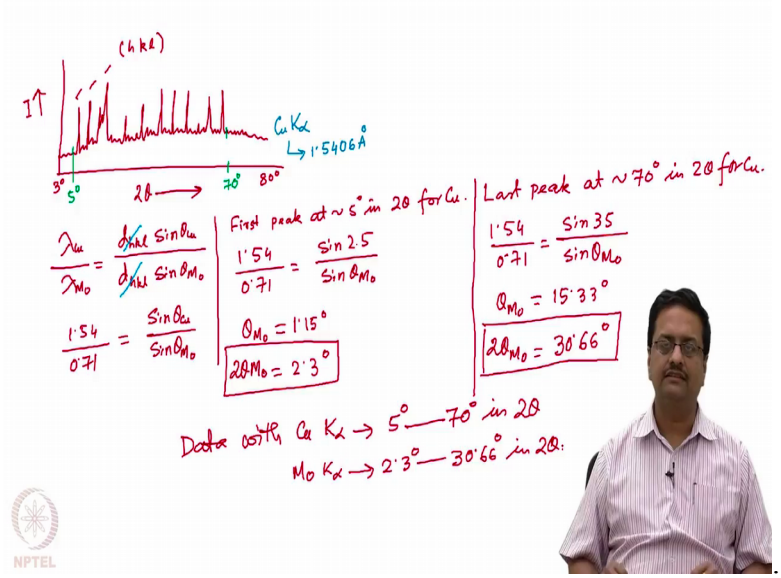

Suppose if we are trying to do a powder x-ray diffraction experiment, where we are going to record a peaks RD data which generally we obtain as intensity versus 2 theta plot and as we have already indicated something like from 3 degree to 80 degree, we measure in 2 theta and what we see are sets of peaks and these peaks correspond to every Bragg reflections which correspond to the diffracts which satisfies Bragg's diffraction condition.

So, every such reflection is identified with unique h, k and l values and we have also seen in case of cubic system, how those h k l values can be identified and from that how one can determine the unit cell parameter and then also, you can identify the lattice center.

Suppose in this particular case which I have drawn here, the peaks that has arised that has come in this diffraction pattern ranges from about 5 degrees in 2 theta to about 70 degrees in 2 theta and this suppose I have recorded using copper k alpha radiation. What is the wavelength of copper k l alpha? It is 1.5406 angstroms.

So, now if somebody wants to use a molybdenum radiation for the same purpose, what should happen? So, suppose for lambda copper divided lambda M o that is I am writing Bragg's Law in two different wavelengths which could mean d hkl sin theta for copper by d hkl sin theta for molybdenum.

So, now since if the crystal is same, the d values are going to be same for a particular reflection. So, they can be cancelled and what we end up is the sin theta copper versus sin theta molybdenum is just a ratio of the corresponding wavelengths.

So, if I try to calculate this ratio 1.54 approximately divided by 0.71 is equal to sin theta for copper by sin theta for molybdenum. So, now in this particular data where we have the first peak coming around 5 degree in 2 theta for copper, so for the first peak we can write 1.54 by 0.71 equal to 0.25 divided by sin theta molybdenum. So, for this situation for the first peak that we found, the theta M o can be calculated as which means 2 theta M o is 2.3 degree. Note this number

Similarly, the last peak for copper k alpha radiation is at about 70 degree in 2 theta. So, now again we apply the same method at this last peak. So, 1.54 divided by 0.71 equal to sin 35 by sin theta M o and then, if we solve for theta M o, we would get theta M o as equal to 15.33 degree that is 2 theta M o as 30.66 degree.

So, the data which was collected using copper k alpha, data with copper k alpha it is spanned from 5 degree to 70 degree in 2 theta, but if we collect with M o k alpha radiation, the same data would span from 2.3 degree to 30.66 degree 2 theta. What does it mean? It means the powder pattern which was quite broad over a range of 2 theta using copper is now squeezed in a small region of 2 theta and it appears as if the peaks are very close.

So, what can happen in this case is that the two peaks which are having very similar d values, the difference in the two theta value for their diffraction angle will be very close and in many cases, those reflections can overlap with each other and we may miss some important reflections and two reflections or more reflections can merge together to give you one peak if you try to use molybdenum radiation. So, the entire pattern is going to be squeezed until and unless we use a very high intensity synchrotron radiation for this kind of applications with a very small wavelength. We cannot actually segregate these reflections appropriately with a smaller wavelength.

So, as a result we now generally use copper k alpha radiation for recording powder x-ray diffraction data whereas, in case of single crystal x-ray diffraction when these diffractions spots appear at different places of your detector and they are all way resolved

at all possible angles, we use molybdenum k alpha radiation to achieve higher resolution with your given crystal.

So, what we now know is that the Bragg's Law applies to a set of planes which we imagine to be inside the crystal lattice and those planes contain a number of scatters and those scatters are responsible for x-ray diffraction.

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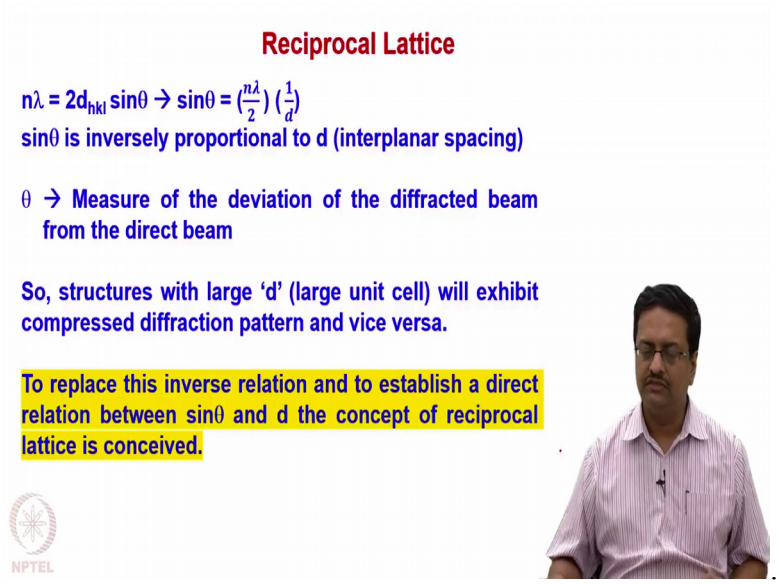

If we look the Bragg's Law, it shows that n lambda equal to 2 d hkl sin theta which means the sin theta which is the measure of diffraction of x-rays is inversely proportional to the interplanar spacing d.

So, this sin theta being inversely proportional to d gives you an impression that there is some reciprocality in it and theta being the measure of deviation of the diffracted beam from the direct beam, we would like to get a direct relationship between sin theta and d.

So, because of this inverse relation, the structures with large d, that means structures with large unit cells will exhibit compressed diffraction pattern and vice versa. So, to replace this inverse relationship and to establish a direct relations between sin theta and d, the concept of reciprocal lattice is conceived.

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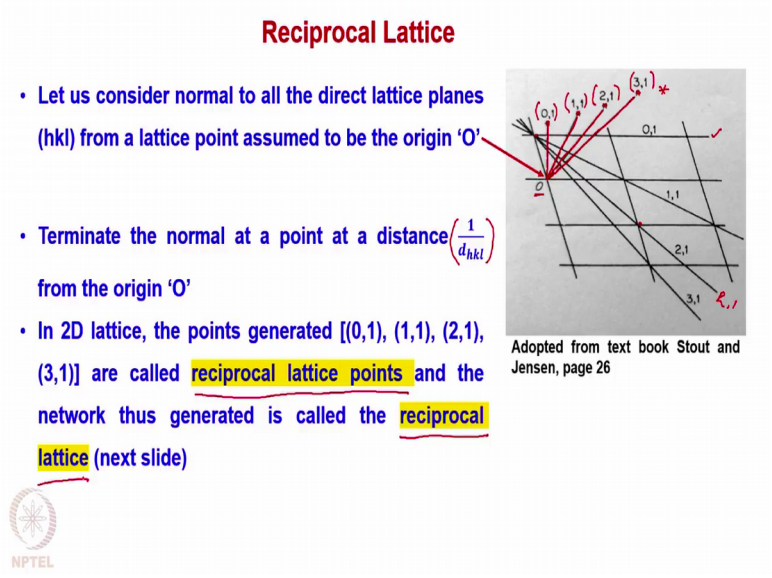

Let us see what you mean by a reciprocal lattice. On your right, we have a two-dimensional lattice which is adapted from Stout and Jensen book. Here let us consider that the lattice point o is considered to be the origin of the lattice and let us consider normal to all the direct lattice planes hkl from these lattice point o assumed to be the origin.

So, what we have here is the plane going like this which we have miller indices 0 and 1 is one set of parallel planes and then, the plane which is going through the middle of this unit cell is having miller indices 1 1. The plane which starts from this point and goes through the second unit cell is corner and continues is termed as 2 1 and that one which cuts the third x unit cell is called as 3 1. So, we have four sets of different direct lattice planes drawn here. So, what we try to now do is, we are turning to draw perpendicular from this reciprocal lattice origin to each one of those planes that is 0 1 1 1 2 1 and 3 1.

So, we are drawing these normals. So, from o this is a normal that is a perpendicular drawn on 0 1. This line is perpendicular drawn on 2 1 and the fourth line is perpendicular drawn on 3 1. So, now we are drawing, after drawing these perpendiculars to those direct lattice planes, we terminate each of these perpendiculars at the point marked as star at a distance equal to 1 by d hkl. That means the distance between the set of 0 1 planes is d 0 1. So, we cut it at 1 by d 0 1 distance from the reciprocal from the origin o.

So, now as we find in these 2 d lattice, we now have points 0 1 1 1 2 1 and 3 1 which represent a individual lattice planes in the direct lattice. So, what has happened is that the planes, the crystallographic planes containing scatters atoms are now considered to be imaginary points in space and these imaginary points are now called the reciprocal lattice points and the network that can be generated using those points is called the reciprocal lattice.

So, what is happening is in this particular case, we have a two-dimensional network and then, we have a set of planes. I have one fixed origin and from that fixed origin, I am dropping perpendicular to each one of those planes terminating the perpendicular at a distance 1 by d hkl and then, the point of termination is marked as a point which corresponds to a direct lattice plane. So, these lattice planes are now converted to lattice points in the reciprocal space and that is why these are called reciprocal lattice points and if we construct the same in three-dimension, it will generate a network, it will generate a 3D network and it will called as reciprocal lattice.

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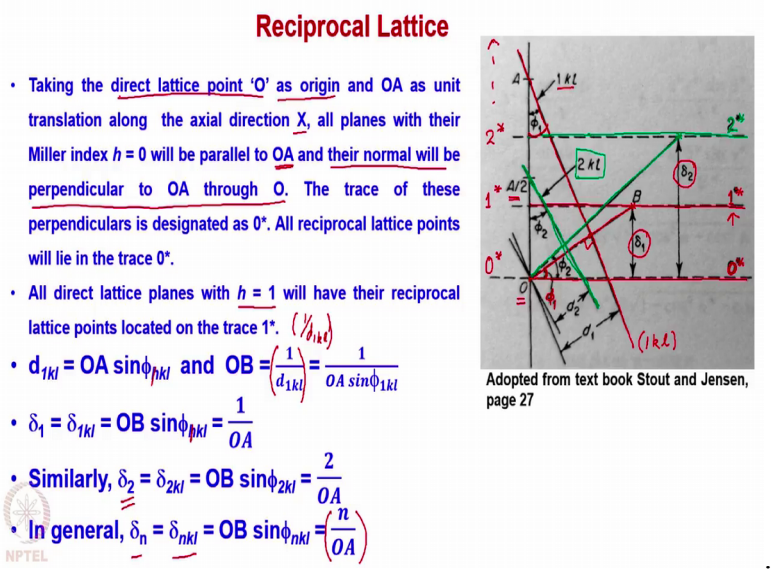

So, now let us consider the drawing here once again adapted from Stout and Jensen's book page number 27. So, taking the direct lattice point O, this is this point O is a direct lattice point O as the origin and the distance OA as the unit translation along the axial direction x. All the lattice planes which has the miller indices 0 will be parallel to OA. That means, if you have one axis like this pointing from me towards you and then, any

plane which is parallel to this axis be it here like that or be it like this or be it like that in any direction, any reciprocal lattice, any direct lattice plane parallel to this axis will have their h index 0 because this plane do not meet the axis x.

So, if we have such planes which are parallel to x axis, then if we draw perpendicular from O, their normal will be perpendicular to OA through O. That means, the perpendicular that we draw from the origin to this will be perpendicular to OA which is along the x axis and all these reciprocal lattice points suppose you have a plane parallel here, then a plane parallel there and a plane parallel there and a plane parallel there, these are all parallel planes at a given distance from the axis to OA. If we draw perpendicular from this point in the origin to these planes and cut those distances at 1 by d, all those reciprocal lattice points that would generate would fall on these line which is marked as 0 star.

Similarly, all the direct lattice planes with h equal to 1 which means the direct lattice plane is now passing through A and goes like that which has the h index of 1, other two indices can be k and l which is written here as well 1 k l set of planes if we draw perpendicular to those 1 k l set of planes which is shown here and we terminate each one of those normals at a distance 1 by d 1 k l at 1 by d 1 k l, they would come and fall on a line which is marked here as 1 star.

In the same manner, the planes which will pass though the midpoint of OA which is A by 2, the plane which I am drawing in green is marked all here as well it is 2 k l plane. So, the normal from reciprocal this direct lattice origin O to that is then terminated at one place which once again falls in the line marked as 2 star.

So, if we try to apply a simple mathematics, what we can find is d 1 k l is equal to OA sin 5 hkl where 5 is the angle here. So, d 1 k l is equal to d 1 k l is the distance from here to there and that distance is nothing, but OA sin 5, 1 or sin 5 hkl which actually should be 1 k l and similarly OB is a distance which is 1 by d 1 k l, right. We cut this normal at point B which is at a distance 1 by d 1 k l. So, OB is equal to 1 by OA sin 5 1 k l.

So, now if we want to know what is the value of delta 1 which is delta 1 k l is nothing, but OB sin 5 hkl or rather sin 5 1 k l because if that angle is 5 1, the angle here is also 5 1. So, now if we compute OB sin 5 1 k l, it is equal to 1 by OA because OB equal to 1 by OA sin 5 1 k l. So, OB sin 5 1 k l is nothing, but 1 by OA. In the same manner one can

show that delta 2 which is this is equal to delta 2 k l which is equal to OB sin 5 2 k l which is equal to 2 by OA.

So, for a general hkl reflection or nkl reflection where n can be 1 2 3 4 anything. In general delta n is equal to delta nkl is nothing, but n by OA. This indicates that the reciprocal lattice points having a particular index h, k or l as fixed and then, if we vary the values for other two indices, in this case we are keeping h fixed. So, 0 k l means we can vary k and l, 1 k l means we can vary k and l, 2 k l means we can vary k and l. So, two other indices can be varied. What it generates is that sets of reciprocal lattice points falling on the lines drawn as 0 star, 1 star, 2 star and so on and this is considered only in one direction that is the direction of OA.

The same can be considered in all the three directions.

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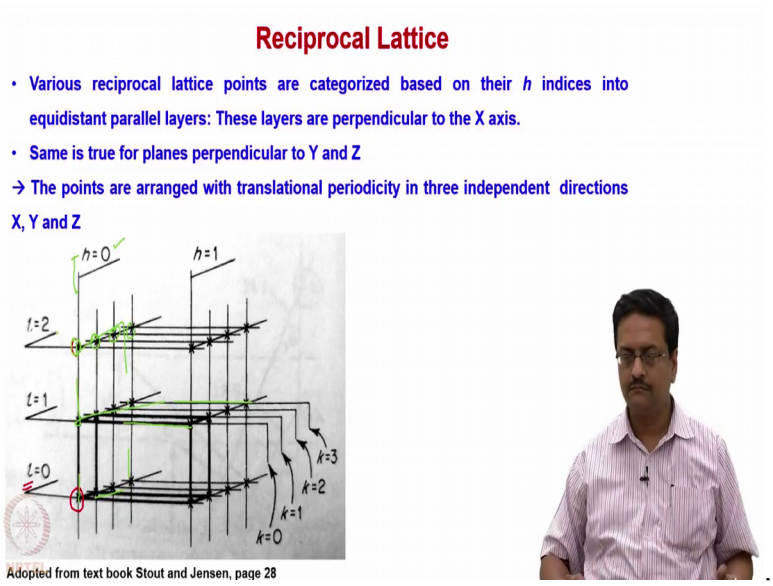

So, when you expand the concept in all the three directions, what we get is a three-dimensional network of reciprocal lattice points and every reciprocal lattice point in the reciprocal space signifies a particular plane in the direct lattice. So, various reciprocal lattice points are categorized based on their h indices into equal distant parallel layers and these layers were perpendicular to X axis. We expand it along Y and Z and then, the points are arranged in with a translational periodicity in three independent directions X Y and Z as shown here.

So, the reciprocal lattice points which are marked here as star, these points on that particular layer has l index 0. The points which are falling on this plane, that means all those points correspond to h index 0 and similarly all the points which are falling in this region are called are having the k indices 0 and then, all these correspond to a three-dimensional network very similar to the one in the direct space.

So, let us see what happens if we try to construct the reciprocal lattice for an orthorhombic system.

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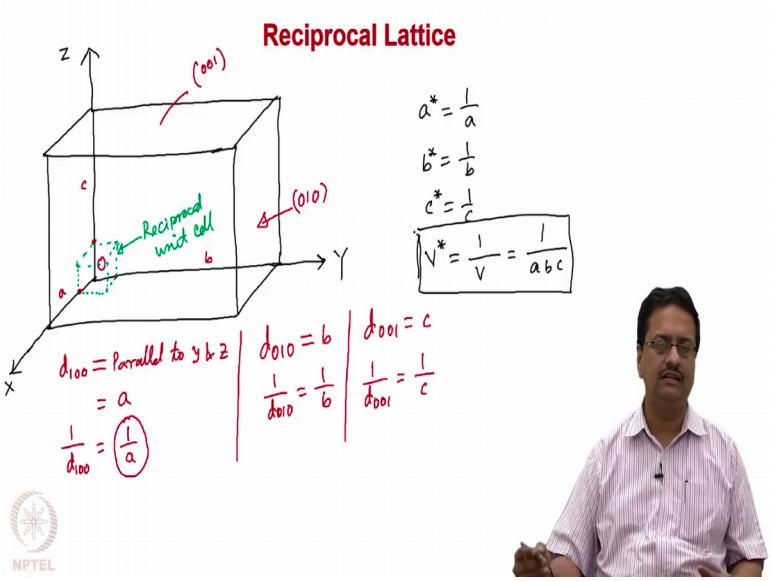

In case of an orthorhombic system, we have a naught equal to b naught equal to c and alpha equal to beta equal to gamma equal to 90 degree. So, this is the orthorhombic lattice with x pointing this with y pointing here and z pointing upwards. The h lengths are: a, b and c.

So, the plane which is perpendicular to X axis, that is the Y Z plane has a distance with the plane Y Z the d 1 0 0 set of planes, they are parallel to Y and Z. So, the distance is d 1 0 0 which is equal to nothing, but a. So, 1 by d 1 0 0 is 1 by a. So, the reciprocal lattice point corresponding to 1 0 0 plane is supposed to be at a distance 1 by a from the origin.

So, now if we consider that 1 by a to fall at this point and then, the 0 1 0 is equal to b because this is 0 1 0 set of plane, so the normal form of origin to this plane is 0 1 0 which

is equal to b and we chop it at 1 by d 0 1 0 which is a distance 1 by b. We put a point here and similarly 0 0 1 is the distance of this plane which is 0 1 1 set of planes.

So, this is equal to c. So, 1 by d 0 0 1 is nothing, but 1 by c. So, we chop it at a distance 1 by c. So, if we now try to draw the corresponding lattice connecting these three sets of points, what we would get is a reciprocal unit cell as is drawn here. So, this is the reciprocal unit cell for this orthorhombic system.

So, in this case the reciprocal lattice distance a star is equal to 1 by a b star is equal to 1 by b c star is equal to 1 by c and reciprocal lattice volume is equal to 1 by V which is equal to 1 by a b c. So, for crystal systems where you have these angles 90 degree, it is very easy to construct the reciprocal lattice as I have shown in this presentation.

So, today in this lecture we have learned how to generate what is a reciprocal lattice, what are reciprocal lattice points and how to construct a reciprocal lattice for a crystal system with the angles equal to 90 degree. In the next lecture, we will discuss about the reciprocal lattice for a triclinic unit cell.