Chemical Crystallography
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Theoretical Understanding of Crystal Packing and X-Ray Diffraction in Direct and Reciprocal Space
Lecture - 20
Theory of X-Ray Diffraction

Welcome back to the course of Chemical Crystallography. This is the beginning of 4th week. So, in the previous 3 weeks, we have learned some of the basic aspects of crystallographic symmetry, point group, space group. Then we understood the aspects of planar density, linear density and from there we are calculating the atomic packing factors and all that.

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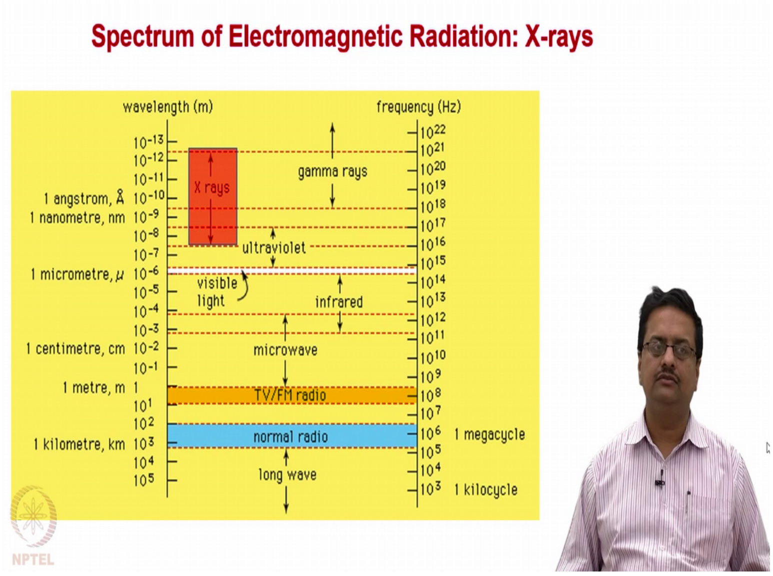

Spectrum of Electromagnetic Radiation: X-rays

So, today we will start the Theory of X-ray Diffraction. And we would like to introduce you to the Bragg's law, and then the concept of reciprocal lattice. As we are intended, we are interested to learn the X-ray crystallography using X-ray radiation, and all of us are aware about this spectrum of electromagnetic radiation in terms of wavelengths. Once again to remind you that the X-rays fall in the region of 10 to the power minus 10 about that kind of wavelength 10 to the minus 10 meter, so the wavelength is extremely small and highly penetrating in nature. So, we use X-ray radiation to identify the crystal structures.

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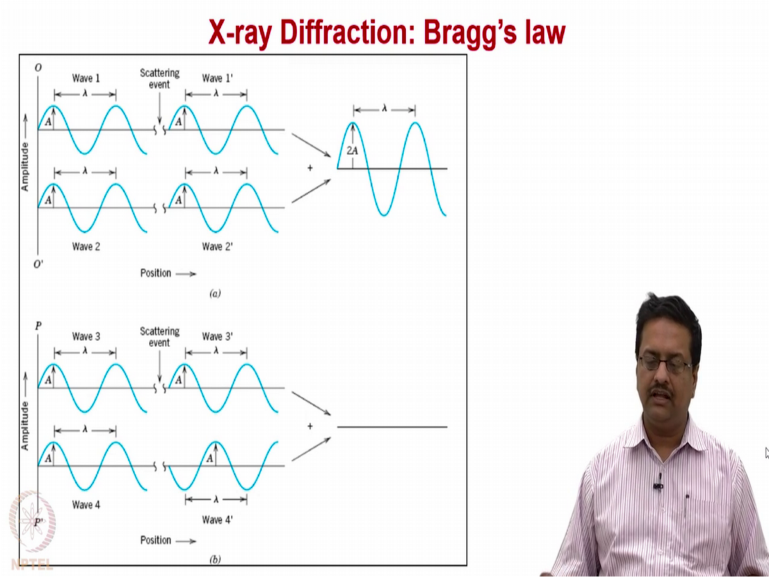

X-ray Diffraction: Bragg's law

The theory of diffraction goes like this, when a set of parallel beam of X-rays fall on a scattering substance like a crystal. Two things can happen those 2 a set of parallel beams can get scattered or diffracted from the source of scattering, which is which is a crystal. So, the source of scattering can do two things; one is that the waves that are falling on the scattering substance. The wave 1 and wave 2, they can be diffracted having the same phase as that of the incident radiation.

So, when such scattering happens, the scattered radiation is enhanced in their intensity that means the amplitude of that scattered radiation is twice the amplitude of the incident radiation and what we see is a diffraction that takes place. On the other hand, when two waves suppose wave 3 and wave 4 undergoes a scattering event through a crystal. And they come out as offset that means they are not like before, and they do not join combine together to give a diffraction data, what we get is something like that which means there is no diffraction, the interference is out of phase, and hence we do not see any diffracted beam.

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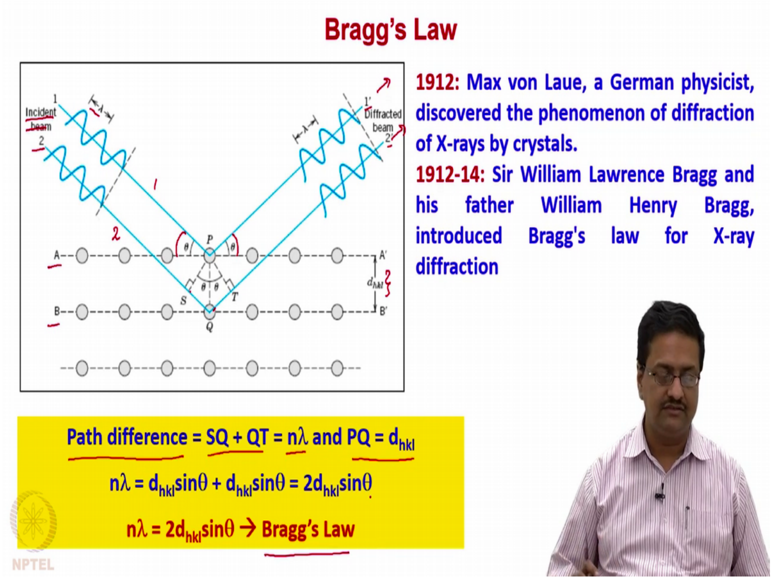

Bragg's Law

1912: Max von Laue, a German physicist, discovered the phenomenon of diffraction of X-rays by crystals.

1912-14: Sir William Lawrence Bragg and his father William Henry Bragg, introduced Bragg's law for X-ray diffraction

Path difference = $SQ + QT = n\lambda$ and $PQ = d_{hkl}$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta = 2d_{hkl}\sin\theta$$

$n\lambda = 2d_{hkl}\sin\theta$ → Bragg's Law

So, this phenomena it was observed by Bragg's in 1912 for 1914 immediately following the different immediately following the discovery of scattering of X-rays by Max von Laue wave in 1912. So, the father and son Bragg's they introduced they world famous Bragg's law in X-ray diffraction. So, how they interpreted this diffraction is very important.

So, here if we have two sets of crystallographic planes A and B containing a set of scatteres, those are scattering centers may be atoms. And when they are particular set of parallel planes, which are planes of A and B at a distance d h k l, which we have identified on the right hand side that these two planes are facing the incident beam as we are indicating here. So, two set a set of parallel beams 1 and 2 of the particular wavelength lambda is falling on a crystal, what can happen is they can get diffracted in the direction of 1 prime and 2 prime. So, the angle of incidence is theta, and angle of diffraction is also theta here. So, now these two waves 1 and 2 are getting deflected from two parallel layers of scattering centers, and going back to the viewer.

So, what Bragg and Bragg propose that the path difference of these two waves that is the wave number 1 and wave number 2, if it is integral multiple of the wavelength, then the scattering is in phase a coherent scattering, and as a result a diffraction is observed. So, by doing a simple geometric calculation, we try to understand how the Bragg's law can be derived. So, here the point P and Q from where the diffraction takes place, So, the beam 1 gets diffracted from point P, and beam 2 gets diffracted from point Q.

So, now if we drop a perpendicular from P to the line number 2, and from P to the line number 2 prime as S and T, which means that the portion before diffraction up to P is same as up to S in case of 2. After diffraction P 2 to 1 prime, and P 2 to 2 prime is again same. So, the path difference between the diffracted beams 1 and 2 is nothing but S Q plus Q T. And what Bragg proposed is that this path difference S Q plus Q T should be integral multiple of the wavelength to observe any X-ray diffraction from a set of planes kept at d h k l distance.

So, now if we want to see what is S Q, we look at S Q and very simple geometric understanding can indicate that the theta here is same as the theta here in big triangle SPQ and similarly PQT. So, now as we know PQ is equal to d h k l the distance between a set of h k l planes. So, n lambda is equal to S Q which is d sin theta that d sin theta and Q T is also this Q T is also this h k l sin theta, which means n lambda equal to 2 d h k l sin theta. And this is the famous Bragg's law and it is so simple, but so important in X-ray diffraction. So, about 100 years ago this particular law was proposed by Bragg's, and it opened up a new area of X-ray crystallography is instant.

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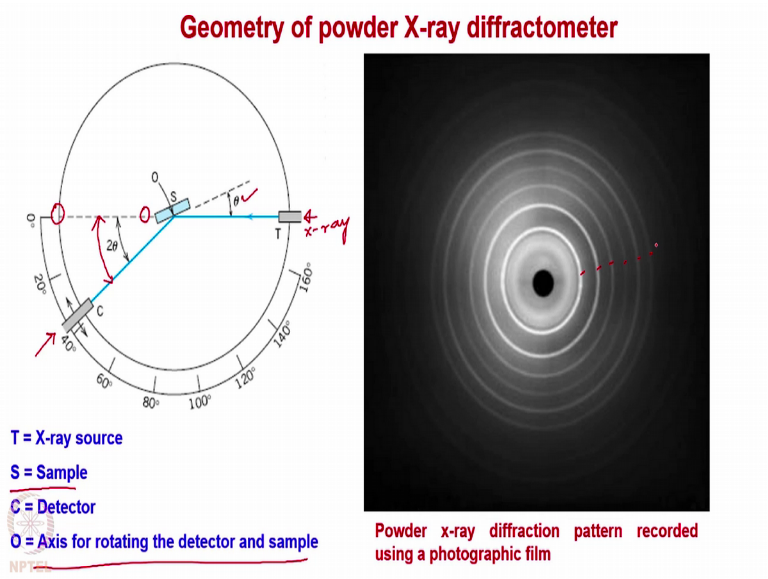
Geometry of powder X-ray diffractometer

T = X-ray source

S = Sample

C = Detector

O = Axis for rotating the detector and sample

Powder x-ray diffraction pattern recorded using a photographic film

So, at this point, I would like to draw your attention to the geometry of a powdered X-ray diffractometer. The geometry is like a circle; this circle is called the angle the cycle of diffraction, where we have a source of X-ray at the point T. So, this can be if any kind of X-ray source like the sill T X-ray or micro focus or whatever, we have understood, we have learned before. And then we have a sample at S, which is the center of the circle, and the detector C is kept on the circumference of this particular circle.

And the O is the axis for rotating the detector and the sample. So, now when the beam falls on the sample S at an angle theta, we measure the diffraction from that sample at an angle of 2 theta and then the diffraction is recorded and it presented. Here I would like to show you 1 very ancient days powder X-ray diffraction recorded on a photographic film. So, what we see here is the at the center the dark spot indicates that there is a beam stop somewhere here, which stops the beam from falling on the X-ray plate. So, the dream beam stop can be here, it can be placed very close to the sample as well depending on the geometry of the diffractometer. And then when the diffraction happens from the powdered sample it happens in a conical manner.

So, if you have a sample here, the cone behind this is the angle or diffraction. And then if you place a photographic film behind it, what you would see as the concentric circles of bright lines. Those concentric circles of bright lines indicate that the diffraction is happening at different angles for the particular set of crystal. In case of powder diffraction as we know it is a collection of large number of micro crystallites, and they are all oriented in all kinds of different directions, so what we get to see is a two-dimensional pattern of intensity versus 2 theta using a modern days diffractometer.

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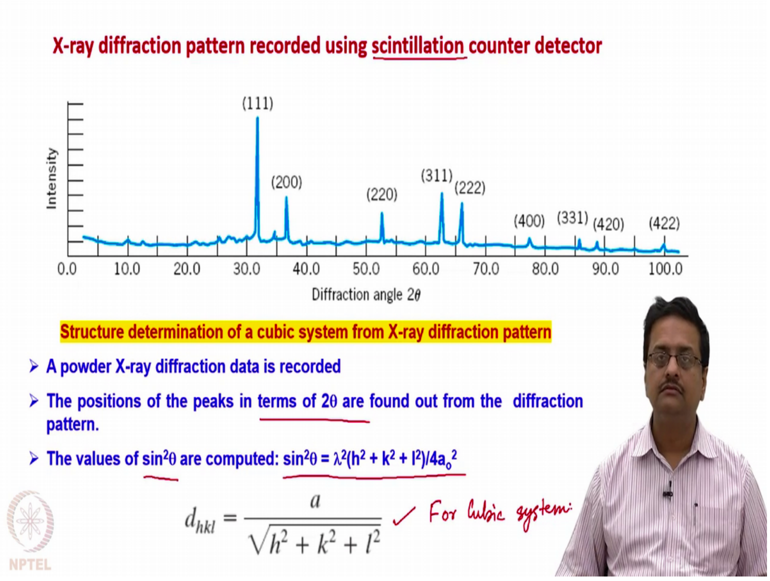

X-ray diffraction pattern recorded using scintillation counter detector

Structure determination of a cubic system from X-ray diffraction pattern

- A powder X-ray diffraction data is recorded
- The positions of the peaks in terms of 2θ are found out from the diffraction pattern.
- The values of $\sin^2\theta$ are computed: $\sin^2\theta = \lambda^2(h^2 + k^2 + l^2)/4a_o^2$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$ ✓ For cubic system:

This is a data recorded using a scintillation counter detector, which is a point detector, and it detects only 2 theta of a particular width at a given point of time, so, when we record this X-ray diffraction data. We get to see a set of peaks, these peaks indicate that those particular d values at which the Bragg’s law is met, we see a diffraction and wherever we do not see any peak means there is no constructive interference of those X-ray beams.

Using this very simple technique of powdered X-ray diffraction one can identify the type of lattice that one is examining in a given sample, if it is a cubic system. For monoclinic or triclinic or any other symmetry things are slightly difficult, but for a simple system like cubic system powder diffraction data can be used very easily to identify the lattice centering. So, what we do is we record a powder X-ray diffraction data from about 3 to 50 to 100 degree in 2 theta.

And then we find out the 2 theta positions, where all we get peaks, and then we try to calculate the sin squared theta value for each of those peaks, and we apply the Bragg’s law in the slightly different manner where it is sin square theta equal to lambda square h square plus k square plus l square by 4 a 0 square. And we use the simple equation d h k l equal to a by square root of h square plus k square plus l square for cubic systems to calculate the lattice parameter a.

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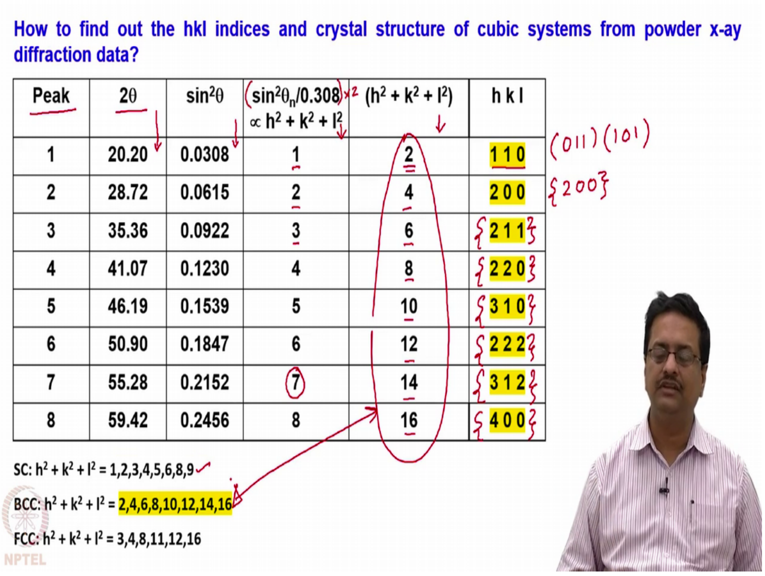

How to find out the hkl indices and crystal structure of cubic systems from powder x-ay diffraction data?

Peak	2θ	$\sin^2\theta$	$(\sin^2\theta_n/0.308)\times 2$ $\propto h^2 + k^2 + l^2$	$(h^2 + k^2 + l^2)$	h k l
1	20.20	0.0308	1	2	1 1 0 (011) (101)
2	28.72	0.0615	2	4	2 0 0 {200}
3	35.36	0.0922	3	6	{2 1 1}
4	41.07	0.1230	4	8	{2 2 0}
5	46.19	0.1539	5	10	{3 1 0}
6	50.90	0.1847	6	12	{2 2 2}
7	55.28	0.2152	7	14	{3 1 2}
8	59.42	0.2456	8	16	{4 0 0}

SC: $h^2 + k^2 + l^2 = 1,2,3,4,5,6,8,9$ ✓

BCC: $h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,16$

FCC: $h^2 + k^2 + l^2 = 3,4,8,11,12,16$

Let us see with 1 example, how to find out the h k l indices and crystal structure of a cubic system from powder X-ray diffraction table. So, to start with what we have is a set of peaks, and the corresponding 2 theta values as listed in column 1 and 2. So, now we calculate the corresponding sin square theta values for each of those peaks and write it down. Now, we try to find out a common factor in this column of sin square theta, where if we divide all these numbers by that common factor, we should end up getting integers.

So, in this particular case, what we find is the first term 0.0308 such the purpose of a common factor, so that common factor is used to divide all the values of sin square theta on this column and is written in the 4th column. So, now these are integers. And as we have seen in the previous slide, where sin squared theta is proportional to h square plus k square plus l square with a constant lambda square by 4 a 0 square, we multiply this fraction by 2 a constant quantity, and get the set of integers like this.

So, now this h square plus k square plus l square corresponds to 2, 4, 6, 8, 10, 12, 14 and 16. Why did we do that, because we see that if h square plus k square plus l square is 1 we are not able to write unique values for h k and l for all these numbers.

Why are we multiplying it by 2 because, when we try to understand if the h square plus k square plus l square is equal to 1, what are the possible values of h, k and l, it can be 1 0 0 0 1 0 0 0 1. When it is 2, it can be 1 1 0 0 1 0 1 0 0 1 1; in case of 3 it can be 1 1 and 1; in case of 4, it can be 2 0 0 0 2 0 2 and 0 0 0 2; in case of 5 it can be 2 2 1 that is 2 square plus 2 sorry, it can be 2 0 1 so 2 square is 4 plus 1 5; in case of 6 it can be 2 1 1, which means 2 square plus 1 plus 1 is 6. But, now for 7, we are stuck, 7 cannot be represented as squares of 3 integers, and then we first it multiplied by 2. And see if all the numbers that we generate on the column 4, whether it can be written as a combination of 3 sets of integers.

So, now when we have multiplied by 2, we have the numbers 2, 4, 6, 8, 10, 12, 14 and 16. So, now 2 can be written as 1 0 actually it can be 0 1 1 or it can be 1 0 1; 2 0 0, which means it can be family of planes of 2 0 0; 6 is 2 1 1 so it can be family of 2 1 1 planes; 8 can be written as 2 2 0 that is family of 2 2 0; 3 1 0 and so on.

So, what we can see here is that only a set of h k l planes are allowed in this particular diffraction pattern not all possible values of h k l. For the time being, make a note that for single simple crystal, if it is a simple cubic system. The combination of h k and l the h square plus k square plus l square should be equal to 1, 2, 3, 4, 5, 6, 8, 9 and so on.

For body centered cubic lattice, it has to be 2, 4, 6, 8, 10, 12, 14 and 16, which is the case here. And in case of face centered cubic, it has to be 3, 4, 8, 12, 8, 11, 12 and 16. So, by looking at the 5th column and comparing it with the value for body centered cubic, we conclude that this is a body centered cubic lattice.

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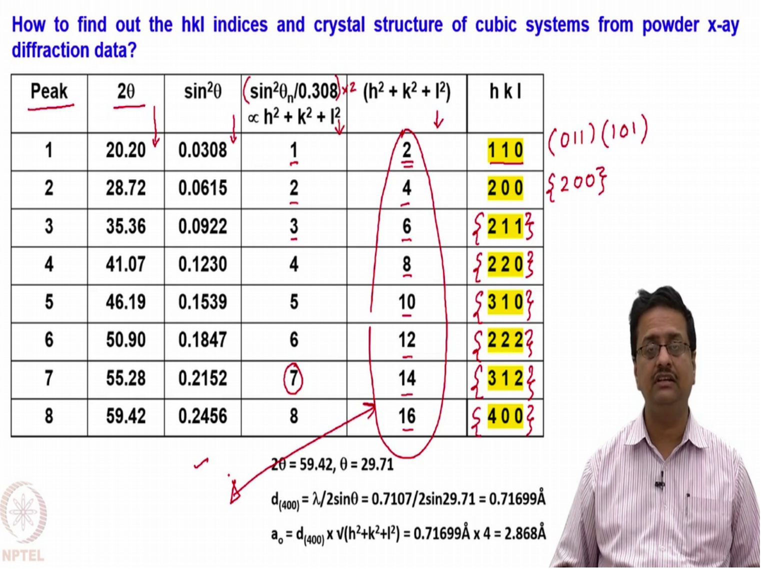

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7	55.28	0.2152	7	14	{3 1 2}
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$2\theta = 59.42,\ \theta = 29.71$

$d_{(400)} = \lambda/2\sin\theta = 0.7107/2\sin 29.71 = 0.71699\text{Å}$

$a_o = d_{(400)} \times \sqrt{(h^2+k^2+l^2)} = 0.71699\text{Å} \times 4 = 2.868\text{Å}$

And then if we try to calculate the lattice centering, lattice parameters. we take one of these 2 theta values, suppose we take the last one 2 theta for 4 0 0 reflection as our standard reflection, so theta is 29.71. So, we calculate the d 400 as equal to lambda by 2 sin theta, because if we are applying Bragg's law. So, we calculate the d 400 to be this number 0.71699 angstrom. And then from that we calculate a 0 equal to d into square root of h square plus k square plus l square.

So, we multiplied d mean square root of h square plus k square plus l square, which is 4 because here h k l is 4 0 0. So, 4 0 0 square is 16 and square root of that is 4. So, a 0 can be calculated as 2.868 angstrom. So, this is how one can calculate the lattice parameter, and identify the lattice centering of simple cubic systems. It is it can be simple cubic, body centered cubic, or face centered cubic, one can determine the lattice centering correctly.

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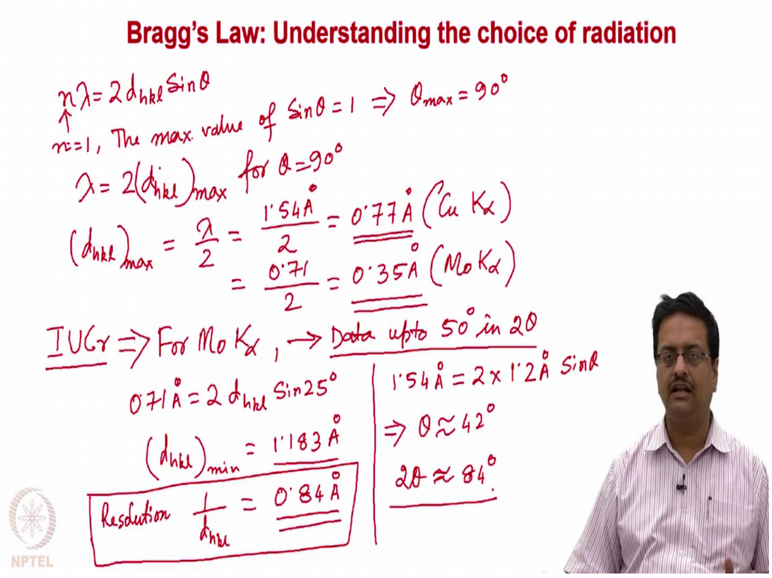

Bragg's Law: Understanding the choice of radiation

$n\lambda = 2d_{hkl}\sin\theta$

$\uparrow$

$n=1$, The max. value of $\sin\theta = 1 \Rightarrow \theta_{max} = 90^\circ$

$\lambda = 2(d_{hkl})_{max}$ for $\theta = 90^\circ$

$(d_{hkl})_{max} = \frac{\lambda}{2} = \frac{1'54\,\mathring{A}}{2} = \underline{\underline{0'77\,\mathring{A}}}\ (Cu\ K_\alpha)$

$= \frac{0'71}{2} = \underline{\underline{0'35\,\mathring{A}}}\ (Mo\ K_\alpha)$

$\underline{IUCr} \Rightarrow$ For $Mo\ K_\alpha$, $\rightarrow$ $\underline{\text{Data upto } 50^\circ \text{ in } 2\theta}$

$0'71\,\mathring{A} = 2\,d_{hkl}\sin 25^\circ$

$(d_{hkl})_{min} = \underline{1'183\,\mathring{A}}$

$\boxed{\text{Resolution } \frac{1}{d_{hkl}} = \underline{\underline{0'84\,\mathring{A}}}}$

$1'54\,\mathring{A} = 2 \times 1'2\,\mathring{A}\sin\theta$

$\Rightarrow \theta \approx 42^\circ$

$\underline{2\theta \approx 84^\circ}$

Now, let us try to understand, how this Bragg's law can be applied to understand the choice of radiation. As we know we write Bragg's law as n lambda equal to 2 d h k l sin theta and we generally construct n equal to we write n equal to 1. So, the maximum value for of maximum value of sin theta can be 1, which indicates theta max can be 90 degree.

So, lambda equal to 2 d h k l max is for theta equal to 90 degree. So, d h k l max is equal to lambda by 2. So, now, if the wavelength is copper k alpha, my lambda is about 1.54

angstroms by 2, which is equal to 0.77 angstroms for copper k alpha radiation. And the same is equal to 0.71 by 2 as 0.35 angstrom for Mo k alpha radiation.

This mind you these are very approximate values; I have not taken values up to 4 decimal places, which indicates that using molybdenum k alpha radiation one can go to a very high resolution of 0.35 angstrom in d values. And get the information on that particular crystal structure to a very high resolution. Whereas, using copper k alpha, you can only achieve a resolution of 0.77 angstrom.

Now, I would like, now I would like to introduce you to the IUCr limits. What is IUCr? IUCr is the short form of International Union of Crystallography. And it is a big association of crystallographers across the world and there, there it is recognized that for molybdenum radiation, one has to achieve a data up to 50 degree in 2 theta for an acceptable crystal structure solution.

So, what does it mean the 50 degree 2 theta means 25 degree in theta. So, for molybdenum radiation, which is about 0.71 angstrom is equal to 2 d h k l sin 25 degree, which meant means d h k l can be calculated as 1.183 angstroms. So, we write the resolution in terms of reciprocal distance that is 1 by d h k l as equal to 0.84 angstrom inverse. So, this is the resolution that is minimum required for a publishable data in any crystallography journal.

So, if you do the calculation for the same, using copper radiation, and if you want to achieve this resolution, what should be the 2 theta value for that particular case. So, when you use copper k alpha radiation, you use wavelength of 1.54 angstroms, which is equal to 2 into the corresponding d should be about 1.2 angstrom. And I need to know the corresponding sin theta. So, if you do this calculation, you will find that theta is about 42 degree, which means 2 theta is about 84 degree.

So, in case of copper you need to collect data up to a very higher much higher angle compare to a molybdenum data to achieve the same resolution. So, this indicates that by using copper data, you should collect data up to a high angle. If you are collecting using molybdenum, you restrict yourself up to 50 degrees of 2 theta to collect a routine X-ray diffraction data.

So, from here we will continue in the next lecture to discuss about the choice of appropriate radiation for macromolecular crystallography and small molecular crystallography. And we will see why do we need to use copper radiation for powder X-ray diffraction, and why do we use single molybdenum for single crystal X-ray diffraction. From there, we will start discussing about the introduction of reciprocal lattice, and we will try to understand the theory of X-ray diffraction using reciprocal space.