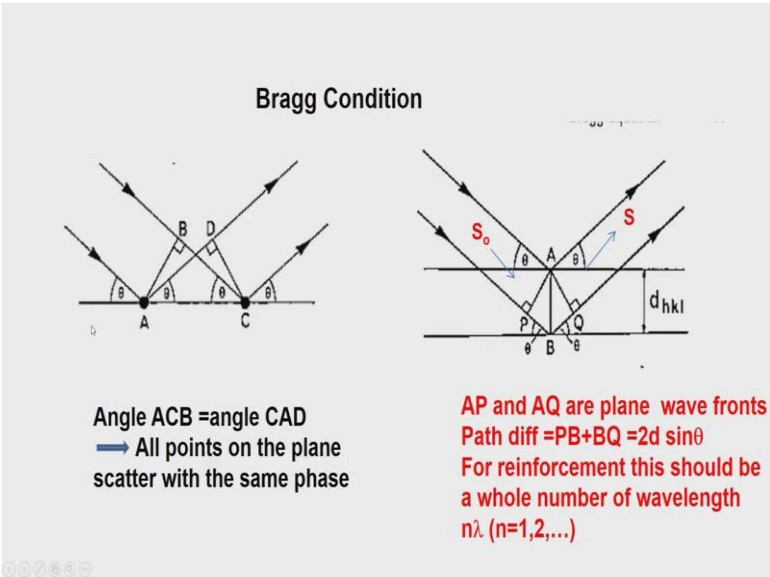
Symmetry and Structure in the Solid State
Prof. T.N. Guru Row
Department of Solid State and Structural Chemistry Unit
Indian Institute of Science, Bangalore

Lecture – 36
Bragg's Law in Reciprocal Space 1

We have been looking at the Bragg condition. A few issues with Bragg conditions still left undiscussed. I left this diagram for you to analyse, but I thought that maybe I should explain it a bit more.

(Refer Slide Time: 00:44)



Other than that this new diagram I have put in. This new diagram will tell you that if you consider a this that is say is the plane from which the diffraction or the reflection of the incoming radiation is giving us the diffracted beam. Now, essentially the diffraction from all practical points of view under the Braggs law we consider it as a reflection; that means, the angle of incidence and the angle of diffraction they are one and the same and because of the fact that this distance AB in fact, AB will represent now the wave front associated with the incoming, that is the incident radiation and CD will represent the wave front which is going out after this scattering.

So, that would mean that this angle is 90^o and that angle is 90^o. So, which essentially tells us that if you take any point on the plane take any plane and take any point on the plane the diffraction condition is still the same; that means, if you see this angle ACB and angle CAD these two angles are one and the same which happens to be equal to θ and because these two angles are equal to θ by construction it means that all this points any point in this plane will scatter with the same phase. So, if you assume that there are different kinds of atoms in different parts of a given phase all those atoms will scatter in phase.

Suppose, you consider this as the plane passing through the origin and that along different directions different distances different atoms lie on the on that particular plane, as far as the phase associated with this plane is concerned it is always 0 because it is passing through the origin. And if atom sit on this particular plane the phase that is scattered by these atoms will also be 0. So, this is a very important point that this scatter with the same phase if you consider any point on the plane.

So, which means to say that in a given plane any plane for that matter it need not pass through the origin any plane there may be several atoms sitting. This is again taking you back to the bread analogy where we take a slice out, there may be several pieces of different things which we have added in the piece of bread and therefore, different electron different electron densities associated with different atoms may coincide with that particular plane. All these now will scatter in a with a single phase and this is a very important phenomena because then we need not have to worry about the what are the contents of that plane as for as phase determination is concerned.

Suppose, in this particular plane there is a carbon there is a nitrogen, there is a bromine, there is a iodine and things like that which parts of it ϕ of course and all these electron density therefore, will all scatter with the same phase associated with the plane. So, this factor will help us in actually determining the structural details in a later point. So, what we have to take home the take home lesson from this particular diagram is that these scattering is associated with the same phase and that particular phase angle is now with respect to the plane.

So, suppose these atoms are not in this plane and somewhere else the contribution of this plane to the scattering will still have the same phase. So, the phase angle is therefore, a property associated with the plane and the contents of the plane now whatever be the contents the phase angle will still be the same and this is the phenomena which in fact, will come in handy when we toss determine the structure later date.

Now, regarding this diagram which we already discussed a bit in a last class we see that the wavefront again here in this case is a is shown as AP. So, this difference this defines the incoming unit vector S_0 and this the vector S which is the scattering vector and the what is represented here are the two different plane separated by a distance d_{hkl}.

So, whatever are the atoms on this plane they will all scatter in phase whatever are the atoms in this plane they will scatter with that particular phase and if the first we consider the first plane which is out of the; out of the origin suppose A is the origin position then the first plane out of the origin will scatter with a path difference of λ and therefore, a phase difference of π. So, that defines in fact, the Braggs law that is because of the fact that this little geometry construction will tell us.

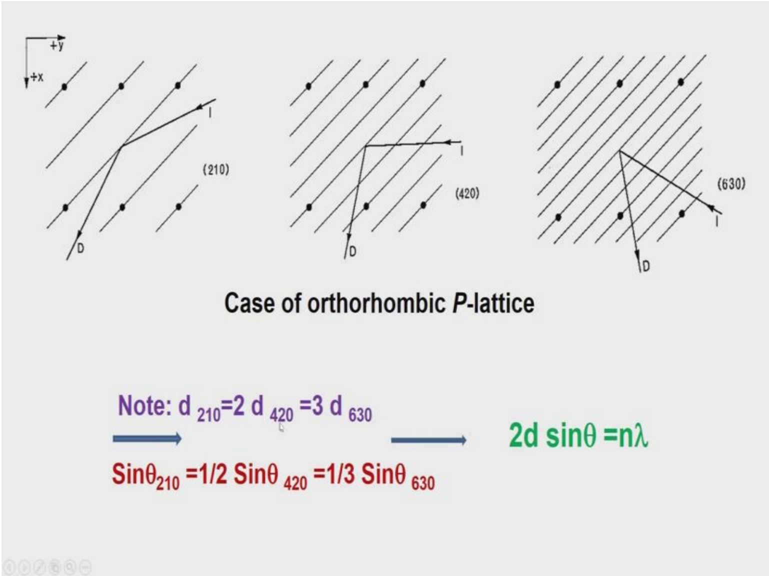
So, if you look at AP and AQ this AP and AQ are plane wave fronts the path difference is that if you consider this particular wave on the second wave which is going up here, the path difference will be additional PB+BQ. So, the additional path the second wave is travelling is PB+BQ. Now, the value of PB+BQ can be calculated as based on this diagram because this is the angle of incidence this is the angle of diffraction and therefore, this is the angle of incidence and this is the angle of diffraction.

These two triangles are similar triangles. So, APB and ABQ are similar triangles in as a property of the similar triangle is that the external angle will be equal to the internal angle. So, these two angles will also be θ and therefore, this will be one side one d sinθ the other side another d sinθ. So, it accounts for 2d sinθ. So, PB is d sin θ, BQ is also d sinθ. So, PB+BQ is 2d sinθ.

So, in order for the reef reinforcement occur in order this two waves now overlap with each other they should be a whole number; in other words if the diffraction has to take place these two have to be a whole number of n number of wavelength. So, the first one will be 1λ, second one plane will be 2λ, third plane will be 3λ and so on. So, therefore, they satisfy this equation 2d sinθ is equal to nλ. So, you get the Braggs equation, 2d sinθ is equal to nλ that is the condition which is derived from this particular diagram.

So, therefore, these two diagrams tell us two major things one is that when there are points any point on this given plane will always scatter in the same phase, irrespective of where the point is on that particular plane and when we consider parallel planes like this with are separated, but a distance of d_{hkl} we get the condition that 2d sinθ is nλ and that is the way in which the Braggs law appears.

(Refer Slide Time: 07:51)



To see what is the value what is the role of this n which is referred to as the order of the reflection we have already discussed this, but we will again look at it from the point of view of how the angle changes with respect to the variation in the values of h, k and l.

Suppose, this hkl is 210 the value of 210 if you consider the value of 2 times d_{420} where you have now taken 2h, 2k and of course, you can call it 2l, but it 0. 3 times d_{630} that is the 3 times. So, we therefore, see that the value of the d_{210}; this is the value of d_{210} the spacing between these two planes is twice 2 times that of the plane distance between these two and 3 times that of the distance between these two and therefore, d_{210} is equal to 2 times d_{420} equals 3 times d_{630}.

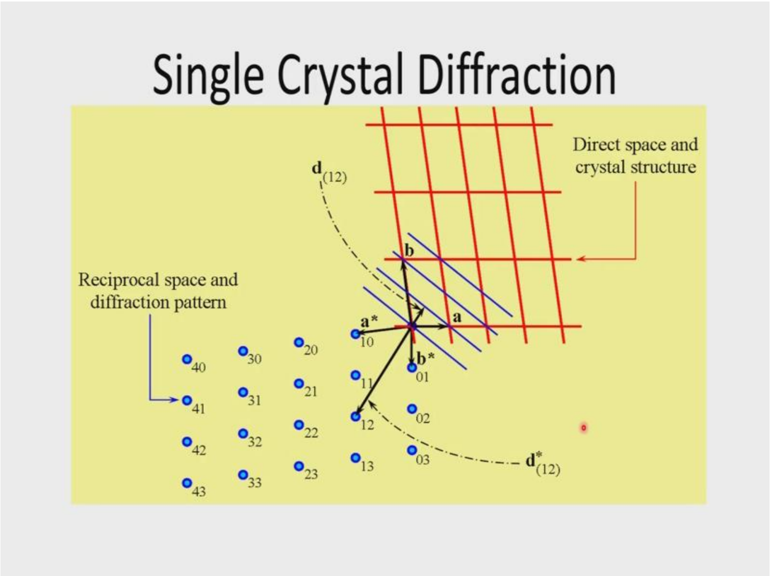
So, as a consequence what will happen to the sinθ value? The sinθ value which is again following this formula 2d sinθ = n λ, we see that sin θ_{210} will be half that of sin θ_{420} as is illustrated here; this is the θ angle, this is the θ angle the angle of the of the between the incident and the diffracted. So, this is the incident angle θ; this is the diffracted angle θ. So, the angle between these two therefore, will be 2 θ.

So, this I and D now come at an certain angle sin θ_{210}. This now becomes one half of that angle and this now becomes one third of that angle and if you consider the fourth order reflection it will be one fourth of that angle. So, the order of the reflection therefore, tells us what should be the angle that is at which the diffraction occurs. So, at which the incident ray comes and falls on the plane and these are of course, all parallel set of planes.

So, from the X-ray diffraction point of view and when we do an X-ray measurement even though this is a general equation 2d sinθ is n λ your n value can be different from each other when the diffraction spots come. So, when you have the reciprocal lattice points these reciprocal lattice points can have different values of n. So, therefore, we get 2d sinθ equals λ for the first case, 2d sinθ equals 2 times λ, 2d sinθ 3 times λ and so on. So, as a result the position of individual reciprocal lattice points will already put a formula which is 2d sinθ equals λ.

So, the order of the reflections will appear in a diffraction geometry in such a way that each of them will represent a separate position for the reciprocal lattice point because this now will occur with this point, this will that point that will occur at that point and that depends upon the angle between the incident and the diffracted rays which is given in terms of this values. So, therefore, in general 2d sinθ is n λ, but for all practical purposes in a diffraction experiment we take it n equals 1. So, we therefore, get 2d sinθ equals λ which is what we will be using in the entire analysis associated with the reciprocal lattice.

(Refer Slide Time: 11:17)



Now, we discussed a little bit of this diagram yesterday, but we will re-do that in the sense that we have to now consider the relationship between the direct space and the crystal structure and the reciprocal space on the diffraction pattern. Now, this is a factor which is of crucial importance because what we will observe from a diffraction experiment are these.

What we will observe from a diffraction experiment are these reciprocal lattice points, so, when you put crystal in the X ray beam and diffraction occurs you will get spots depending upon the quality of the single crystal and this particular spots will tell us the points of the reciprocal space lattice. So, this therefore, defines the reciprocal lattice.

Now, what is the relationship between the direct lattice which is up here which is our unit cell defined suppose you take this as a 2-dimensional crystal you see that this is represented by the a value and this is represented by the b value therefore, this red square here will be the unit cell. Now, this unit cell repeats itself because it is a crystal in all both the directions. So, this therefore, now defines the crystal space. So, this is the lattice representing our crystal.

So, the angle between a and b which is γ will also decide the orientation of these a and b with respect to each other. So, in other wise this angle which is here could be γ. So, that is because of the fact that this two are identical I can show the γ here, I can show γ here, I can show γ here, I can also show it here. So, this you know already.

So, we have therefore, a direct space and the corresponding crystal structures. So, the atoms are all lying here in this part of the diagram. So, there here wherever depending upon where the atom wants to be and where the molecular structure develops or the ionic structure develops and so on. The atoms are connected to each other as we discussed yesterday, these scattering is done basically by the atoms; that means, the electrons associated with the atoms. So, X-rays when they fall on this crystal they will be diffracting based on where the electron density is found. So, the larger is the electron density the more intense will be the diffracted spot.

But, the observations which we are going to make is with respect to the individual planes which are defined in the direct space. Now, what are these individuals space planes we define in the direct space? We will define for example, a plane which is not going through the origin and therefore, as we discussed all the atoms which may lie on this will scatter in phase Φ in the phase we the scatter with the same phase a 1 with 0 and that particular case will be 0 this the phase angle will be 0.

The plane which is coming out from here we have we can consider several planes which come out from here, but what we have done is a set of parallel planes. So, we have drawn here the plane which is now represented by a line because we are shown it in 2-dimensions. So, plane is perpendicular to us. So, if you now consider this particular plane a in two-dimensions it can be represented as 1,2. Now, why 1,2 because we see that this blue line intersects these red unit cell at 1 unit along a and half unit along b.

So, we said already that the indexing is done in such a way that if there is a cut of half it will be actually 2 in terms of the identification. So, therefore, d_{12} go back to the bread analogy where we took the central slice and said it is at half position along a, but that would mean that it is a 200 reflection if we are considering the reflections along the a direction. So, the same analogy brings up here the value which is the distance the black line here indicates the distance here indicates the where position of d_{12} the this the length of d_{12} that is the value of the d value of 12; 12 being the plane which we are representing here.

So, if this is the 12 plane the next parallel plane will be what? The next parallel plane will be 2 and 1. So, this is 2 and 1, this is sorry this is 1 and 2 and this will be; this will be 2 and 1 and this will be 3 and find out. Now, you have gone into the next unit cell up here if you consider the intersection, but it is a parallel plane to this one. So, all parallel lines with respect to 12; so, 12, 1 along the a direction and 2 along the b direction that becomes half of that. So, this will therefore, be 13 right 23, 33 sorry. See, 1,2 is up here the parallel plane to that will be what? This will be 2,1, the next parallel plane will be 3 something.

Now, if we consider this as 1, this will be now 3/2 one and half and therefore, this intersection point will be what? So, if this is 3 that will be what? Find out and then you see that these are now a set of parallel planes ok. These set of parallel planes let us go further these set of parallel planes are represented by this vector in this case the plane 1 2 is represented by d_{12}, the distance of 1 2.

Now, the corresponding reciprocal lattice vectors will occur with respect to *a*, 1/*a* this is the vector direction 1/*a* vector direction represents *a** and 1/*b* vector direction represents *b** this is now the value *γ* and therefore, this will be the value *γ** to define the 01 and the 10. So, the reciprocal lattice points are now represented as 10 and 01 with respect to the reciprocal lattice and this angle will become *γ**; *γ** is 180-*γ* where *γ* is this angle. Suppose this is angle is exactly 90^{o} this will also will be 90^{o}. So, a will be 1/*a*, *b* will be 1/*b*. Here also as far as vector directions are concerned it will be 1/*a*, 1/*b*.

So, these therefore, now represents the *a** *b** axis and this is 10 in this direction and 01 this direction. So, if we now take all the reciprocal lattice points along the *b* axis *b** axis we will have 01, 02, 03 and so on and the corresponding values in the a direction are 10, 20, 30, 40. We will therefore, get the intersection of 1 and 1 as 11 then 1 and 2 as 21 and so on. So, if we are now looking at a plane d_{12} the corresponding reciprocal lattice vector will be now we have to look for 12 that is one intersection along a 1 along a and 2 along b.

Now, this what this represent is the reciprocal point that is d^*_{12}. If this is the d_{12} we represent this as d^*_{12}. So, this therefore, now defines the diffraction pattern, it also defines the reciprocal space. So, if you sit down and study this diagram a little carefully you will definitely see that the one to one relationship between the direct space and the reciprocal space. And that one to one relationship will therefore, tell us that if this is a lattice if this is the red one is a lattice, then the collection of all this blue dots should also be a lattice and therefore, this we call as the direct lattice this now becomes the so called reciprocal lattice.

So, in the reciprocal lattice we have two vectors *a** and *b** with an angle of *γ** defining this particular nature of this lattice. So, the distribution of the diffraction spots therefore, should come at these blue points. So, keeping this in mind we will see how we can use this idea of reciprocal as because we always see the reciprocal lattice in an experiment.

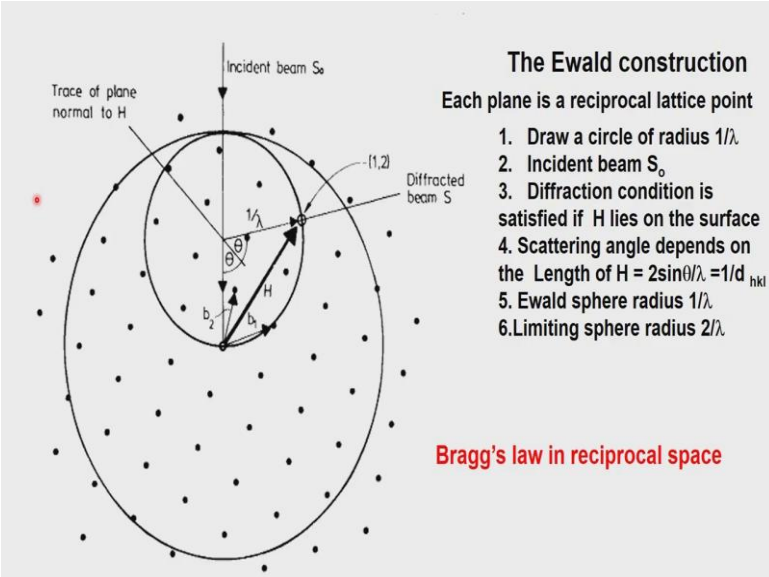
So, when we do the experiment we put an X-ray we send an X-ray beam onto the crystal a collimated X-ray beam onto the crystal. The crystal now diffracts, so, it will follow the Bragg's law and therefore, we have an incident ray and a diffracted ray according to the Bragg's law satisfaction $2d \sin\theta = n \lambda$ and therefore, we will get to positions which are now the reciprocal lattice positions and therefore, we will get spots.

Now, these parts which we will get in a single crystal are therefore, each and every spot now is a representation of a plane in the direct space. So, every plane in the direct space gets represented by a point in the reciprocal space and this a very big advantage because we do not have to look at the plane we look at only the reciprocal lattice point. We also know another factor that every plane therefore, if any atoms are lie on that particular plane they will all correspond to the same phase and therefore, when we get this reciprocal lattice point let us say 21 here; 21 will contain information of all the atoms in that particular plane in the direct lattice. And therefore, 21 is something which is one once we get the coordinates of 21 it is important to see what is the intensity that is associated with 21.

So, before we go to the analysis of the intensity we have to do one other way in which we can look at the Braggs law. Whatever Braggs law we derived earlier is in the direct space, we took the parallel planes, we did the construction then we found the phase angle and so on and showed it is 2d sinθ equals to λ or nλ where n is the order of the reflection on the other hand when we do a diffraction experiment what we see is the reciprocal lattice image; that means, we see the spots. So, it is always good to see whether we can actually think of deriving the Braggs law in that space itself.

So, in other words, can we have a Braggs law in reciprocal space can we derive Braggs law in reciprocal space? This was thought process which was put to develop what is known as the Ewald construction. So, it was developed by a person by name Ewald. So, it is known as the Ewald construction. You can directly visualize the diffraction conditions by means of which reciprocal lattice points come and that is how it is done which is shown in the next view graph.

(Refer Slide Time: 22:31)



Here you see something which we have to do a construction. What you see are the points here which are the reciprocal lattice points. So, I have drawn the reciprocal lattice. So, the reciprocal lattice is similar to the reciprocal lattice shown here. So, all these points which come we know now how they are coming and knowing that how they are coming we have taken these points and we have transferred it on to the plane.

Now, therefore, this is now a planar representation of the reciprocal lattice points. Then what we do is we do what is known as a Ewald construction. So, each plane is a reciprocal lattice point as we saw just now. So, what we do is we just take a circle, we draw a circle of radius 1/λ; λ is the wavelength. Remember that the reciprocal lattice is represented in inverse of length the dimensions of inverse of length.

So, we therefore, take a circle and draw the circle of radius 1/λ. That particular circle we can draw with some centre here and you see that this is the circle which we have drawn. This is a circle drawn with the radius 1/λ. So, if you consider the centre as here this to this distance or that the distance is 1/λ.

Now, we define on this particular circle this circle can be anywhere ok, it can be anywhere in 3-dimensional in the 2-dimensional space we have drawn here it is 3-dimensional because we are now going to eventually change the circle in a sphere, but at this moment this is a 2-dimensional diagram and so we have a circle. Now, this circle can be drawn anywhere, but it should have a diameter of 2/λ or a radius of 1/λ. So, this radius of $1/\lambda$ is with respect to some origin. So, we take this the one of the reciprocal lattice points to be an origin. So, if you take this as a origin of the reciprocal lattice point (0, 0) now this is the circle with a $1/\lambda$ radius which is drawn in such a way that the circle passes through our (0, 0).

So, remember the circle is passing through our (0, 0) on the circumference. So, this is the circumference of our $1/\lambda$ sphere. So, there is a centre up here. Now, let us say we send an X-ray beam from the top. The X-ray beam from the top now comes and falls on this particular origin which is a reciprocal lattice point so, it is scatters. Now what it therefore, tells us is that any point which intersects with the circumference of the circle because we set the circle is arbitrary it can be put anywhere. So, any point which intersects with the surface of this particular circle will give us therefore, the diffraction condition that satisfied. So, can we use this method to find out what is the diffraction condition that has to be satisfied.

So, therefore, we see here in this particular example we have taken the reciprocal lattice points and we see that this is the vector b_1, the reciprocal lattice vector and this is the vector b_2 which is the second vector. So, b_1 and b_2 now represent the reciprocal lattice vectors, reciprocal lattice dimensions. So, b_1 and b_2 are the reciprocal lattice cell dimensions or reciprocal cell dimensions.

So, having seen b_1, b_2 being representing this is let us say one direction this is the other direction. You see we go up in this direction drawing these points on, these are all the points which are lying with their origin here and these are all the points which lie with the origin with respect to the b_2. So, we have an we have *a* b_1 here and a b_2 that is defined, so, this is the origin.

Now, you see in the diagram which I have drawn it so, happens that the point which is now 2 along 1 along the; 1 along the one direction that is this point this is the if you consider b_1 the and this is the point 1 along the *b* direction. So, we see that this coordinate therefore, which lies on this is 2 this one in this case of b_1 and b_2 is 1 and 2. So, there are 2, this is a second position; that means, this vector H is represented by (1, 2).

So, since this vector is this is the crystallographic directions in some in some sense, so, it is (1, 2). So, the diffracted beam is now shown as S in that direction. So, therefore, what happens is this is the incident beam, this is the diffracted, beam you remember the diagram with we draw the diagram will be this will be the angle 2θ between the incident beam and the diffracted beam. Now, if you take the bisector of that we already know that should be the direction of what we call as the scattering vector. So, this is written as the trace of plane normal to H. So, this will be the direction of this scattering vector.

So, we therefore, have a θ here and a θ there and this is the centre of the circle and we have the incident beam and the diffracted beam. Now, what happens is that as you see here the there are several reciprocal lattice points which on this grid, but none of them are intersecting except the one which you are taken as an example the reason is obvious because we are keeping the reciprocal lattice fixed; that means, we are keeping the crystal in one position and then sending in the X-ray beam.

So, if we keep crystal in one position and then send an X-ray beam very often there not there may be no diffraction coming no reflection are observed or we may observe a reflection by chance like what we have seen here and we will see this particular reflection we do not see any other reflection; that means, to say that whenever the reciprocal lattice intersects with the Ewald sphere on the surface. Now, instead of the circle I am going to call it a sphere because we are now going into 3-dimensions. So, we call it as the Ewald sphere.

So, anywhere anytime an Ewald sphere intersects with a reciprocal lattice point the surface of the Ewald sphere then can we get the diffraction condition satisfied and this diffraction condition is satisfied if H lies on the surface and if H lies on the surface of this sphere then the scattering angle we know it depends on the length of H the Laue condition; the length of H, $S-S_0/\lambda$

So, the length of H therefore, is equal to $2\sin\theta/\lambda$ in magnitude. We have shown this magnitude of H is $2\sin\theta/\lambda$, so, it is $2\sin\theta/\lambda$. Now, what is $2\sin\theta/\lambda$? It is $1/d_{hkl}$. So, therefore, you equate these two, you will get the Braggs law $2d \sin\theta = \lambda$

So, therefore, the Ewald sphere has a radius of $1/\lambda$. So, what is the catch here? The catch here is the following that we have kept the crystal in a single position sent in the X-ray beam, by chance it so happens that in this diagram which we have shown purposely there is a point which intersects with the surface of the Ewald circle or the Ewald sphere and therefore, it satisfies the Bragg condition. See in order to satisfy the Bragg conditions we have to have this equation satisfied that is because of the fact that the vector H which is the reciprocal lattice vector should have a magnitude which is equal to $2\sin\theta/\lambda$ then and only then we get diffraction.

So, we see here that in this entire diagram we have shown only one possibility of a diffraction point. Then how do we get all these reciprocal lattice points to diffract? The solution is very simple, you rotate the crystal. Now, as you rotate the crystal this reciprocal lattice itself will start rotating. So, as the reciprocal lattice rotates different points in the reciprocal lattice can come and intersect with the Ewald sphere here, the surface of the Ewald sphere.

So, as and when any of these for example, here there is a nearest intersection it may slightly turn around and then next point will be intersecting here this will intersect and like that. So, all these points will start intersecting. Now, what is the limiting condition for that? The limiting condition is that now this becomes the radius, $2/\lambda$ becomes the radius and therefore, this circle which we are drawn outside or the sphere which we can draw outside in 3-dimensions which is referred to as the limiting sphere, so, this has a radius of $2/\lambda$. And this $2/\lambda$ is now the limitation. So, all those reciprocal lattice points which lie within the $2/\lambda$, have a chance to intersect with the Ewald sphere which has a radius of $1/\lambda$.

So, the radius of the limiting sphere is $2/\lambda$. So, the reciprocal lattice points which lie within that particular sphere have a chance whenever when the rotation takes place the 360 rotation of the crystal will bring all these points which are shown within the limiting sphere to intersect with the Ewald sphere and whenever there is an intersection with the Ewald sphere you get diffraction. So, it may so happen that in as you rotate the crystal.

There may be positions of more than 3 or 4 reflections satisfying the Braggs condition then you at that particular angle of rotation of the crystal you will get more than one reflection. So, it is not necessary that one at a time should come, you can get any number of reflections at a given angle theta in different directions see the directions are different this point and let us say this point were to intersect. We will get one diffraction in this direction another diffraction in that direction and so on, so, it goes in that particular fashion.

So, what we therefore, do is to see that this set of points which will now present or which are present in the limiting sphere will have a chance to intersect with the Ewald sphere and this is a point which therefore, allows us to do look at Braggs line reciprocal space. So, we now know what under what co conditions and under what circumstances a crystal can give diffraction. So, we have a crystal, we get the diffraction spots and these diffraction spots will follow this particular equation which is the Braggs equation. So, I think at this level we have now just understood the Braggs law, both in the direct space as well as in the reciprocal space.