Symmetry and Structure in the Solid State
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Lecture – 35
X Ray Scattering; Laue conditions to Bragg's Law, Introduction to Reciprocal lattice

So, the Laue's conditions form the basis of all diffraction.

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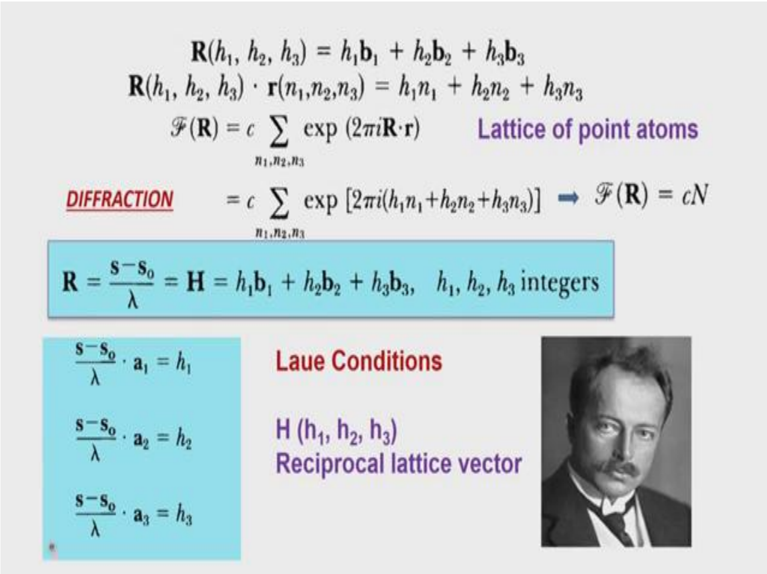

So, whenever Laue's conditions are satisfied we get diffraction. So, you would have seen the X ray diffraction patterns of crystals and you will see they come with various spots. We also discussed that in the diagram earlier on when we discussed the way in which the we can compare microscopy ordinary microscopy with X ray diffraction.

We showed some points which come out from the scattering experiment and these whenever scattering experiments are done on crystalline objects if it is a 3 dimensional crystal; we will get spots. And these spots therefore, now represent the values of h_1, h_2, h_3 that is where the spot will occur with respect to the reciprocal lattice. And therefore, we will be able to not only find the coordinates of the reciprocal lattice point in terms of h_1, h_2, h_3 which can be replaced later by h, k, l these are called miller indices.

Now, this is where Laue completed this work and he got the Nobel Prize in 1949. Then the famous work of Bragg and Bragg father and son Bragg came up and what is done is essentially we start from the Laue's condition. So, we start with these 3 conditions ok.

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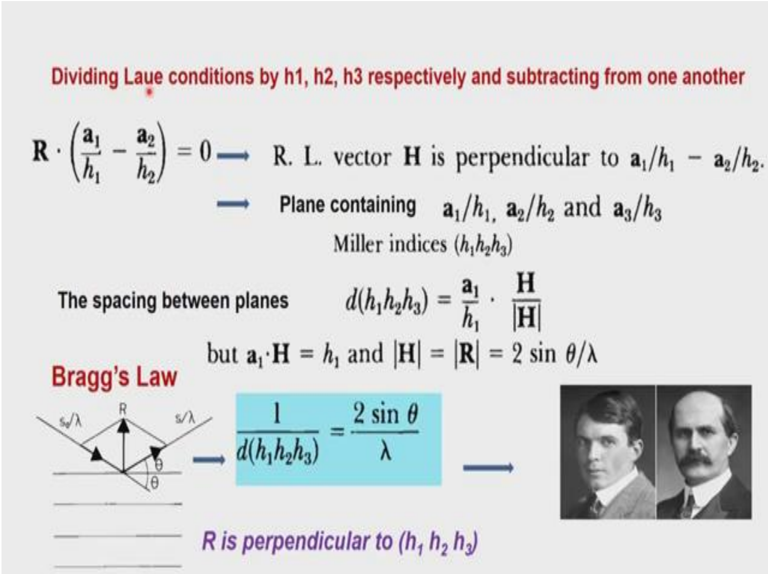

And then after starting from these 3 conditions we divide the Laue conditions by h_1, h_2, h_3 respectively and subtract from each other. So, take the Laue condition divide by h_1, h_2, h_3 and you subtract. So, we get $R\,.(\,a_1/h_1 - a_2/h_2) = 0$.

So, whenever we have an expression like this 2 vectors $a\ .\ b = 0$; that means, a is perpendicular to b; this is vector analysis. So, therefore, we see that the reciprocal lattice vector h is perpendicular to $a_1/h_1 - a_2/h_2$. The same logic we can apply to the other two sets that is $R\,.(\,a_2/h_2 - a_3/h_3)$. So, reciprocal lattice will be perpendicular to $a_2/h_2 - a_3/h_3$ and the third one as 1.

So, which essentially means that the vector R is perpendicular to the plane containing a_1/h_1; a_2/h_2 and a_3/h_3; so h_1, h_2, h_3 are refer to as the miller indices. We can replace h_1, h_2, h_3 by h, k, l because most of the textbooks follow h, k, l but this particular textbook which I have followed is that of Jack Dunitz, where this nomenclature has been used.

So, the fact that R is perpendicular to a_1/h_1, a_2/h_2, a_3/h_3 essentially tells us that if you have now the s_0/λ coming in here; you remember the picture we drew we have just reorganized that picture, I have rotated the picture such that I now represent a plane and that plane is in terms of h_1, h_2, h_3.

So, this particular plane is characterized by the miller indices $(h_1\ h_2\ h_3)$ or $(h\ k\ l)$. So, this is a plane $(h\ k\ l)$; so, s_0/λ comes here and then it is scattered you remember we wrote the angle 2θ for the s_0/λ to s/λ direction. So, this angle is 2θ, but since this plane is perpendicular to this vector R you see that these 2 is divided into θ and θ. And therefore, we get the vector R to be perpendicular vector R is perpendicular to the plane containing a_1/h_1, a_2/h_2, a_3/h_3 and that is this particular plane.

So, vector R therefore, now is being perpendicular the direction of s/λ is indicated here. And if you look at this very carefully essentially what we see is that this plane is like a mirror and we are actually seeing the X ray pattern because of the fact that the incoming radiation and the scattered radiation or the diffracted radiation or essentially a reflection from the plane.

So, what Bragg and Bragg called this as a reflection. So, the this can be approximated to a reflection of course, radiation may go through into this crystal and so on, but from this particular plane in the crystal we therefore, have this s/λ coming out as a reflection.

So, the diffraction now becomes reflection. So, whenever we now see a spot in a diffraction pattern; we identify the spot with the miller index $(h_1\ h_2\ h_3)$ and we say that is the reflection because of this particular plane which is at $(h_1\ h_2\ h_3)$; the reflection of the incident ray is measured here. So, this is now coming as a point source from a point source and this falls on the mirror. So, this again becomes a point and that is how we get a collection of points.

Depending upon the various orientations of the planes we can think of inside the crystal which we have already discussed in the previous classes. We can get diffraction say these scattering or diffraction or reflection all three are one and the same now they come in specific directions they obey the of course, the laws of Laue the conditions of Laue and we get this one.

So, if we now call the spacing between planes; this placing if we call that spacing as d_{hkl} that is the distance of the plane where between the two planes d_{hkl} then we can write this expression $a_1 \cdot H$. Because you can now see that if you go to the Laue's condition we are essentially writing the Laue condition $a_1 . H$ is the Laue condition; this is $a_1 . H$; this will be equal to h_1. So, $a_1 . H$ which is actually h_1; $a_1 . H$ is h_1; now this is divided by h_1 and |H|.

So, this represents the distance between the planes. So, we can calculate d_{hkl} as $a_1/h_1 . h/|H|$. We know the $|H|$ is 2sin θ/λ; $a_1 .H$ is h and therefore, we get an expression which is 1/ d_{hkl} is equal to 2sin θ/λ or 2d sin$\theta = \lambda$.

So, this is the so called Bragg's law and this got the Nobel Prize in 1950. So, very interesting it is just a mathematical jugglery a little bit of reorganization of the equations which Laue derived, but why did it get also a Nobel Prize? It got a Nobel Prize because of its simplicity number 1 and secondly, because of the fact that here after we can get to the distances associated with the planes directly by measuring the scattering angle and the wavelength.

So, if we know the θ value and λ we know the value of d_{hkl} and d_{hkl} is what we are interested in terms of the spacing between planes. Now what you see here is 1/ d_{hkl}; so the so called vector R has still got the dimensions of reciprocal length. So, the dimensions of reciprocal length associated with R will be associated with d_{hkl} also. So, the distance between the planes now is a real space quantity d_{hkl} is therefore, a real space quantity; this is something which is important and you should remember because this is essentially telling that R is perpendicular to $(h_1\ h_2\ h_3)$. Now R is H the reciprocal lattice vector and both the Laue conditions and the Bragg equation are satisfied when the diffraction occurs.

The other advantage is that now diffraction can be very easily understood as though it is a reflection. And the use of the Bragg equation will allow us for a direct determination of the reciprocal lattice quantities, which was not probably possible if we has use the 3 conditions of Laue. And that way practically this equation is the one which now tells us the entire geometry of the diffraction experiment which you have done.

So, we not only get the information about the real space geometry; we also get information about the reciprocal space geometry and the 2 geometries are related to each other. That means, if you have a well defined crystal with the symmetry which we have defined over the year over the weeks then that particular symmetry is reflected; also into the reciprocal lattice. We will have to examine that more carefully as we go along, but essentially this is therefore, the one of the key equations.

In fact, along with this the key other 2 equations which we wrote earlier for the structure factor and the electron density these 3 are the 3 key equations. Now why do you ask that question? We asked that question because this now just gives us only the geometry associated with the crystal; it will tell us in fact, with based on this equation we can calculate the cell dimensions and therefore, the crystal system *a, b, c α, β, γ* can be determined by using these expression. So, if we do an experiment using X rays; the scattered X rays will now follow the rules of Laue's conditions and as a result they satisfy these equation.

So, using this particular equation we get information about the d spacing; we also get the values of $1/d$ and $1/d$ we can call it as d^* a vector in reciprocal space. So, we can get solutions to a^* b^* c^*; the values of the reciprocal lattice directly from these expression. Once we have the reciprocal lattice information we can convert it into the direct space information.

So, the geometry of the unit cell and its *a, b, c, α, β, γ* values and its corresponding spacing of the planes inside the crystal both will be we will be able to get using this equation, so the entire geometry of scattering can be obtained. The other 2 equations which we discussed earlier on discuss scattering factor and the electron density represent essentially the presence of the electron density inside this crystal.

So, a combination of this to give us the geometry and a combination of the Fourier transform equation to give the electron density in principle therefore, should help in solving the structure. Finding out where the atoms are what are the atoms is left to the other 2 equations; finding out the environment in which that electron density is stuck because of obeying the Laue's conditions and following the Bragg's law; we will get the geometry that is associated with the crystal.

So, therefore, the beginning of crystallography was done by these 3 gentlemen Bragg and Bragg and Max Von Laue. So, both of them; in fact, both groups all 3 of them deserved therefore, the Nobel Prize in those days because this now forms the basis of structural determination fine.

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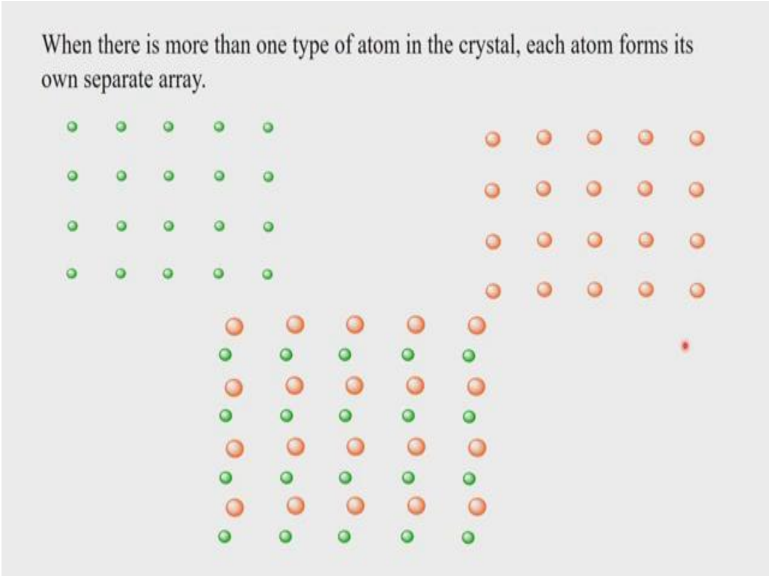

So, let us go further and see the more detail of this; how the diffraction is occurring how the Bragg's law is coming into the picture. Bragg's law is now coming into the picture as we see the intensities that come out from a diffraction experiment do not depend upon the lattice points because the lattice point need not contain any atom.

So, if what in a unit cell when you are putting these atoms they form their own array. So, suppose you have one type of atom in the crystal let us say the green type; they will form an array of their own satisfying this as the *a* direction; this is the *a* direction and that is the *b* direction. So, because of the periodicity they will repeat itself in both these directions. So, this defines a lattice of atoms now it is no longer a lattice of points which is a lattice of atoms. Now when we say it is a lattice of atoms, then the intensities should come out when the scattering occurs.

Similarly, we can have another atom which defines a lattice of atoms and these 2 can be put inside the crystal. So, inside the crystal we have now a diatomic molecule let us say. So, this is one atom that is the other atom. So, we have a diatomic molecule defining the crystal so; that means, now these crystal dimensions can be built in. So, this will be the *a* direction of the crystal that will be the *b* direction of the crystal and inside that we have the atoms located at (x_1, y_1, z_1); (x_2, y_2, z_2).

So, the presence of (x_1, y_1, z_1) and (x_2, y_2, z_2) therefore, is crucial with respect to the location inside the crystal.

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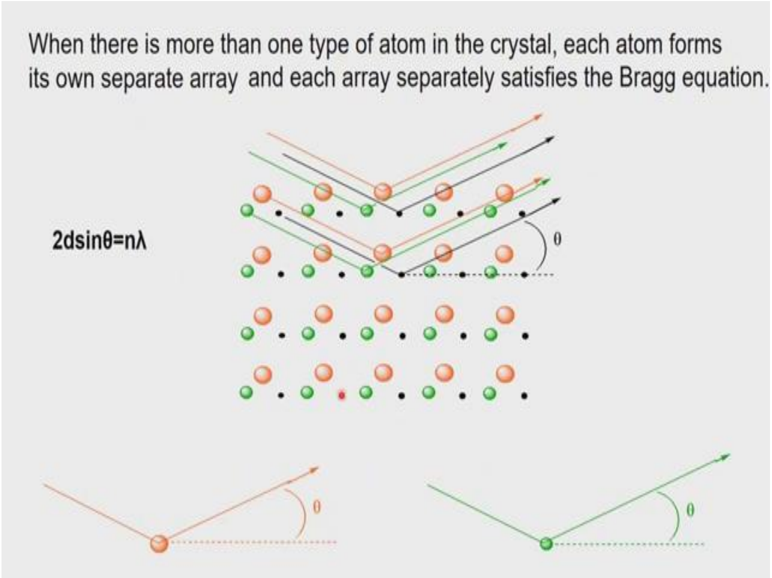

The location inside the crystal is with respect to the lattice points. So, the lattice points will be now associated with this black dots which we have shown here; the black dot here the black dot here. So, this now defines our lattice; so if these are the lattice that is defined this is we are in the direct space, then when X rays are shown each and every atom will follow the Bragg's law.

So, there let us say 20 atoms associated with this one lattice point each of them will follow the Bragg's law. So, the red atom will also scatter at θ the blue atom will also scatter at θ, but what you measure is the reflection which is coming from the plane. Now each and every plane is now a point represented in this 2 dimensional diagram and therefore, this particular point is a plane which satisfies the Bragg's condition or the Laue's conditions.

So, therefore you get now from this point you have let us say the X rays coming in this direction, the scatter from this point go in that direction. So, this is what we measure what we measure is therefore, the black arrows, but remember the black arrows are coming originating from the positions of the atoms. And they contribute even parallel to the intensity that is coming out from the plane. So, when we measure the intensity from the plane; we have a collective measure of all these atoms scattering in that particular θ value.

So; obviously, the intensity will be dependent upon where these atoms are located and that is the main issue. We have to find out where these atoms are located, but the fact that we are getting it from the various planes which we can locate by Bragg's law or for that matter the Laue's condition will tell us that it is in principle possible to find where these atoms are depending upon the intensity now.

So, until now we dependent upon the directions to get the geometry the intensity associated with the diffraction spot we will tell us where the atoms are; if for example, if this red atom is associated with this lattice point then the intensity will be totally dominated by the presence of that red atom ok. So, that is the logic which we will follow in getting into the details of how this scattering occurs.

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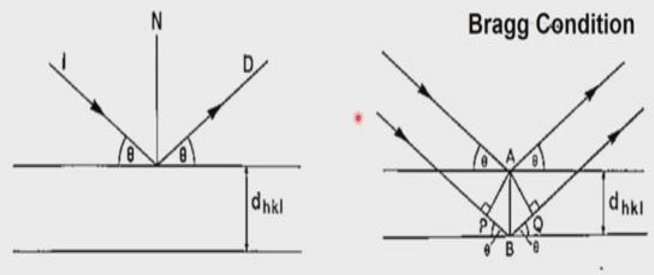

Fig 6.8 The Bragg Equation. The diffracted beam D can be regarded as a reflexion of the incident beam I by a set of lattice planes (*hkl*) when the angle of incidence θ satisfies the equation $\lambda = 2d_{hkl} \sin \theta$.

Here is a little example of the whole process for example, if there is an incident beam; the Bragg equation is satisfied the diffracted beam D can be recorded as a reflection of the incident beam I by a set of lattice points represented by (*hkl)*. So, these now represent the lattice points; remember when we say a (*hkl)* all the parallel (*hkl)* planes are considered and therefore, we show the (*hkl)* in brackets.

Now what how each and every one of them contributes is very important because we want to get contribution from every plane even if they are parallel to each other we will see how that behaves in a little while from now. So, whenever the angle of incidents satisfies the equation 2d sinθ = λ we get this scattering ok.

So, suppose we now consider 2 the spacing between these 2 is d_{hkl} now we found that $1/d_{hkl}$ is related to 2sinθ/λ; how does that come about is shown in this construction. I have left it unexplained because I want you to get an explanation for that and you already know these from your college days, how these Bragg's law comes up I will just give you the idea about it. So, suppose you take this ray 1; it gets reflected from this plane and goes off and here is a parallel plane, which is placed at a distance of d_{hkl}.

So, now we can we can see that this second ray is up to here if we drop a point here which goes to P. So, this drop a point here you get perpendicular here you go to Q. So, the extra length that is travelled by this second ray is PB + BQ. Now, therefore, this ray has travelled PB + BQ, but then the scattering occurs at an angle of θ the spacing is d_{hkl}. Now making use of the fact that the addition distance is PB + BQ; in principle you should be able to find out what is d_{hkl} because 1/ d_{hkl} corresponds to 2sinθ/λ.

Now, you have to therefore, calculate the values of PQ and BQ in terms of the θ value. So, you see that this is also θ that is also θ. So, you can calculate the length of PB and length of BQ that will be equal to the d_{hkl}. So, the additional distance that the ray travels is equal to d_{hkl} because these 2 rays are parallel to each other. So, this is purely a geometrical phenomena and therefore, we should be able to find out and this satisfies the Bragg's condition.

So, the Bragg condition is satisfied because of the fact that **λ is 2 d sinθ** and how do we get this? PB + BQ is what? You have to calculate PB + BQ. PB + BQ will give us $1/d_{hkl}$ equals 2sinθ/λ right. And therefore, that will give us the value of sinθ and this value of sinθ take the two sinθ values and then you will get the value of 2 times d_{hkl} how does $2d_{hkl}$ come up?

So, discuss this diagram in your mind I want you to take it as a home lesson to find out that this diagram now illustrates the Bragg's law has 2 d sinθ = nλ. The reason why I am not explaining it is because I want you to think about it with simple geometry how PB + BQ add on and what are the values of PB and BQ, which essentially, now gives us this parallel beam and that will satisfy the Bragg condition.

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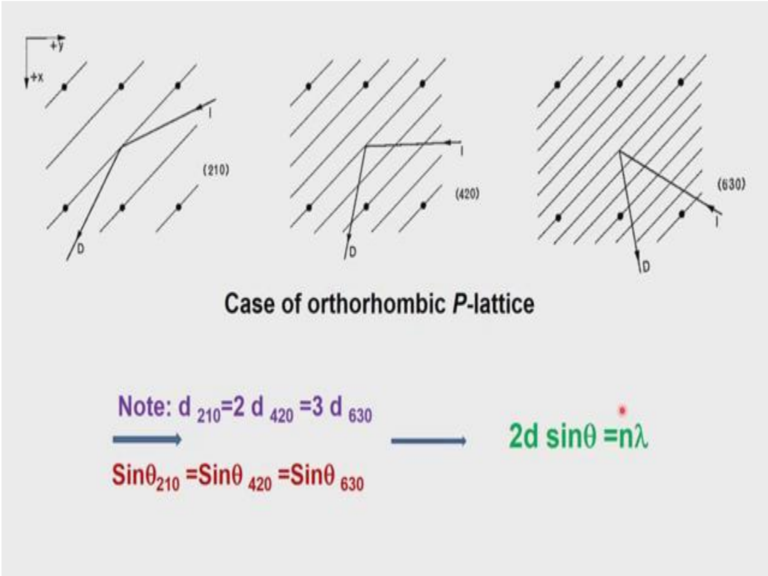

The other issue which I will discuss now and probably leave you after this is to essentially consider 3 different planes. This will also give you a hint of how to look at the previous diagram and arrive at 2d sinθ = nλ.

Now the hint is the following you see that you consider plane (210) alone; the plane (210) is parallel to several planes. So, if you consider (210) only you will see that the incident ray is here and the deflected ray goes like that, I have indicated + and *y* as the directions. So, you will get a value of $\sin\theta_{210}$.

So, since 2d sinθ = nλ you get a value of $\sin\theta_{210}$; d_{210} this value. In fact, is equal to 2 d_{420} because you are now making 2X2 and 1X2. So, this distance by reciprocity will become half. So, if you double the (*h k l)* values by reciprocity it becomes half you have studied it already. So, you have (420) you also have (630) which is by 3 times. So, what you see here is the effect is to change the angle θ. the sin θ_{210} is in fact, this is I made a mistake here; I should correct it. So, you see that the angle here which is the 2θ angle or the sinθ, the θ angle will now ensure that sin θ_{210} is half of 420 and one third of 630**.**

So, this means that if we consider the order of the reflection if we consider let us say (210) as n = 1; (420) as n = 2 and (630) as n = 3 then the value of n comes up here. So, we therefore, have 2d sinθ = nλ. So, this is the general expression which you find in many textbooks; so, where does these n come from? n comes from the fact that there are orders of reflections.

So, n = 1, n = 2, n = 3 and so on when we do the X ray diffraction experiment ;the X ray diffraction experiment will individually give the reflection idea; that means, $2d \sin\theta = n\lambda$ for each one of them separately because the angle θ is different from each other. So, this essentially now will tell us that the; if this the equation $2d \sin\theta = n\lambda$ is the one which is which is essentially covering the thing.

So, let me expand this and show this is what he was telling. So, (210), (420) and (630); I am showing the diagram again because I have a not showing it in slide mode. So, I will show it again and to confirm that d_{210} is 2 d_{210}; so one half of $\sin\theta$, one third of $\sin\theta$. So, the angle you see here is becoming different from each other. So, when you do an X ray diffraction experiment, you can get these individually the intensities because of the values are being different.

So, $2d \sin\theta = \lambda$ for all practical purposes, but when we deal with other issues like X ray spectroscopy for example, then all the orders will appear together and therefore, we have to use this formula $2d \sin \theta = n\lambda$. So, basically n can take different values and that represents the so called order of the reflections. So, the order of the reflections come up as a consequence of the *h* and *k* doubling here and tripling here, which is resulting in the variations in the $\sin\theta$ angles.

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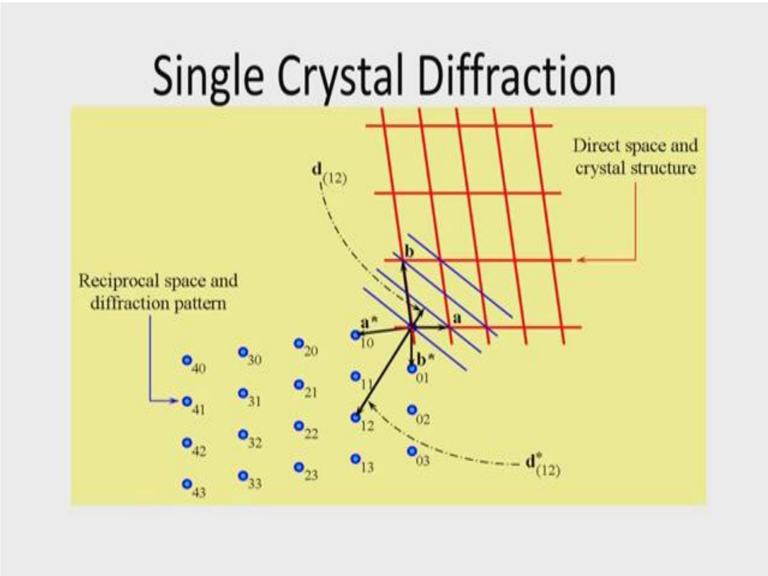

So, this having seen this now we will see what happens in the diffraction condition. So, this is a very important slide for all practical purposes I will use this slide to describe how the scattering experiment is happening and how we get to the diffraction conditions and how we get the reciprocal lattice points.

So, what we do is we put a crystal layer at the origin. So, the crystal is now having a dimension a in this direction *a* dimension *b* in that direction. So, I am taking a 2 dimensional plane into account and this 2 dimensional plane therefore, will start from the origin 0 here, I will also say that the reciprocal lattice origin and the direct space origin coincide.

Now, what happens is that the value of this is a 2 dimensional example. So, $d_{(12)}$ is represented in these direction that is because you see that the plane that is considered here the second plane which we have drawn here this is (000) plane; the plane which we have drawn here which is (120). So, one along the *a* direction half along the *b* direction. So, this makes it (120). So, this plane is now (120) if you consider this plane, then it will be (210) it is a parallel plane.

So, this is (120) and this is (210). So, if this is (120) this is (210) what would be the next plane. So, these are parallel planes anyway. So, if you have (12) then this plane will be 2 this plane will be 2 along these direction and this in this direction it is 1. So, you see that the bread analogy which we discussed. So, you essentially have the planes going through this is the loaf of bread which is now having a orientation like this. So, we are cutting the bread piece along the (12) direction in this case and in this case it is along the $a = 2$ and $b= 1$ and in this case it is $a = 3$, $b = 2^1/_2$.

So, the corresponding value will be the reciprocal value of that. So, we can read out the corresponding planes associated with this. So, what happens is this is $d_{(12)}$ when we do the scattering experiment the corresponding reciprocal point will appear at here position and that represents $d^*_{(12)}$ notice that, now this vector is in the reciprocal space. And since this vector is in the reciprocal space we will therefore, generate corresponding to each one of these parallel planes different points in the reciprocal space.

So, suppose I take this as (12) ok. So, this is now cutting at 1 and this is cutting at $^1/_2$ the position. So, this then will be what? It will be (24). So, this will be (24) which is not shown here, but we can show the other example which is a essentially telling us that if you take this point (000) and go along these direction by 1 unit ok; then you will have the (10) a^* coming up here and the b direction will be representing b^*; it depends upon what is the angle of β here the values between a and b which is γ.

So, the value of γ now decides what should be the value between a^* and b^*. So, the value between a^* and b^* will be 180 - γ; so, because this whole thing has to be 360 degrees. So, you have therefore, the γ value here and 180 - γ will define the a^*b^* direction. And once we have the a^*b^* direction you will have the planes will be identified by points that is how you get the diffraction in terms of spots. The spots which you see from the diffraction experiments correspond to these reciprocal lattice points.

So, one once we have the dimensions of a, b and c in principle we should be able to find out and index these spots. This process of finding out what are the values corresponding to h and k in these 2 dimensional plane is referred to as indexing. So, each and every point therefore, is indexed with respect to the value of h and k. So, you see here that this particular point which is indexed is now corresponding to (12).

Now, please notice that these (12) is the same as (12) up there. So, there is no change there so; that means, the value of h and k will still remain the same whether in the direct space or in the reciprocal space. It is essentially the way in which the reciprocal space develops with a value of which is proportional to 1/distance. So, in a in other words it generates the reciprocal lattice point. So, planes in the direct space will generate points in the reciprocal space and therefore, we call them as the reciprocal lattice points and each and every reciprocal point therefore, correspond to the plane in the crystal.

So, the planes in the crystals will now, therefore, can be identified in the direct space by looking at spots and a indexing those spots. So, when I index this spot as (12); that means, I am referring to the plane (12) in the real crystal. So, that way we can do these values find all these values and these values now represent the reciprocal space and the diffraction pattern. So, this is the direct space and the crystal structure. So, if there is an atom now sitting here; if there is an atom now sitting here its contribution to this plane needs to be calculated in order to find the intensity of this spot.

So, if there is an atom sitting here for example, very close to (12) how are we going to calculate the intensity that can be associated with this part and that is something we will have to evaluate in the coming classes. So, at this time we have a few questions left unanswered which you have to answer. One is the answer to this diagram and as a home exercise you can work it out how to arrive at the formula $2d_{hkl,}$ 2d $\sin\theta = \lambda$ from these expression from these diagram.

So, you have to find out the perpendicular distance from this point to this perpendicular distance from this point to this. So, the path difference is now PB + BQ. So, the it has traveled by that extra path there is a corresponding phase difference. The phase difference will now introduce what? It will tell us at what θ angle the scattering is occurring and therefore, the $\sin\theta$ values can be calculated one once we know the value of θ and if we know the $\sin\theta$ value; then we can possibly use $2\sin\theta/\lambda$ which will give us the value of d_{hkl}.

So, d_{hkl} is $1/d_{hkl}$ sorry $1/d_{hkl}$ will be $2\sin\theta/\lambda$ and that is how we calculate these particular value. So, what I want you to do it as a home exercise; the second one is a is an understanding of how 2d $\sin\theta$, $n\lambda$ comes up, n is the order of the reflection these 3 diagrams will help you in principle to identify how these diagrams are coming and what are the angles inter axial angles between them between I and D and that will tell us the relationships and therefore, we get the different values of n going from 1,2,3 and so on.

So, essentially what we have just a quick revision of what we did until now we started with the scattering from a periodic array. And then we derived the expression using their Laue conditions and having done the Laue conditions we derived the Bragg's law. And having done the Bragg's law we try to understand in terms of the diffraction as a reflection from a plane.

And then we identified that the scattering is coming from atoms and not from the planes, but then the atoms are now associated with the planes. We will do in the coming class how this association with the plane will generate the intensities how what is the contribution of each one of these atoms to this particular lattice point.

And then we saw the 2d $\sin\theta = n\lambda$ and then 2d $\sin\theta = n\ \lambda$ and then we are now trying to get to an understanding of the reciprocal lattice points which come from the direct space lattice. This is something we will discuss again and then see how we can arrive at the Bragg's law in reciprocal space. Because we have the recording in reciprocal space whatever we get from a diffraction experiment gives us parts in reciprocal space.

And so the geometry associated with this can be identified one once we index this spots and once we have this indexation done, then in principle we should therefore, see how Bragg's law behaves in the reciprocal space and that is the material for our coming classes.

Thank you.