An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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Lecture - 34
X-ray Diffraction (contd.)

So again, we begin with a new lecture. We will continue about X-ray diffraction as we are talking in the last lecture. So, in the last class we are talking about the X-rays basically the absorption edge in of various materials, and how that absorption is edge can be used in one, choosing appropriate filter to allow certain radiation to go through certain radiation for you to use. And secondly, knowledge of absorption edge can also be useful in choosing appropriate radiation for a particular material. For example, for iron it is not appropriate to use copper, but you can use cobalt chromium radiations. So now, let us look at representation of X-ray diffraction in crystals, we will not look at the physics of X-ray diffraction in crystals because of lack of time.

But if you are interested you can go through any standard book on X-ray diffraction such as X-ray diffraction by bd quality, or even there is a good interpretation of X-ray diffraction in Charles Kittel solid chess physics; which talks about diffraction, and essentially what happens in these cases those cases is that since X-rays are radiation they have a wave vector this wave vector is reciprocal of the wavelength. Since so, the reciprocal is basically the reciprocal of length ok, so, it has a unit which is meter inverse. So, in order to deal with X-ray diffraction in that case one also has to consider lattice in reciprocal terms.

So, use reciprocal lattice vector instead of real lattice vectors. And then you can understand diffraction in the form of what we call as Laue equations or a waltz fear which gives you a certain diffraction condition which gives you a diffraction condition which ultimately can be reduced to a scalar form which is called as Bragg’s law. So, we will straight away look at Bragg’s law in terms to interpret the X-ray diffraction in crystals.

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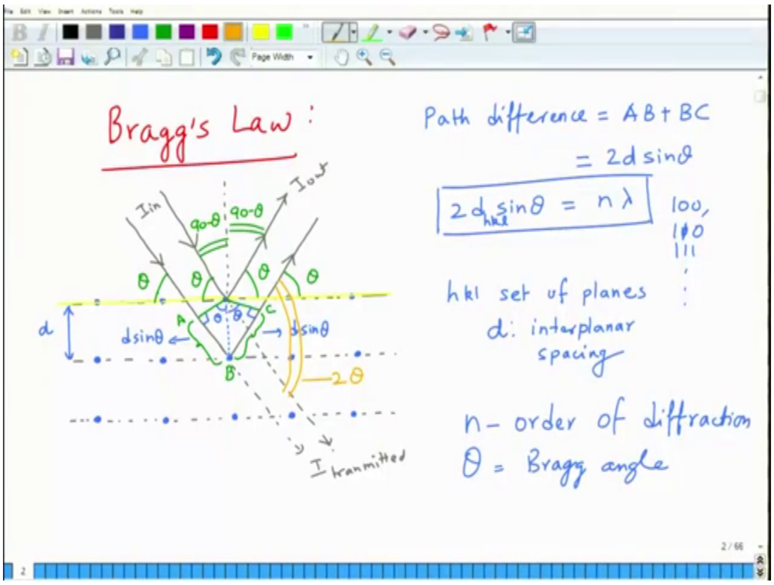

Bragg's Law:

Path difference = AB + BC

= 2d sinθ

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

hkl set of planes

d: interplanar spacing

n - order of diffraction

θ = Bragg angle

So, we begin with Bragg's law. Now Bragg's law basically you consider you have a these parallel plane of atoms. So, let us say this is a this is the plane which is hkl (refer time: 03:00) to and a blue one certain atoms. So, these are the atoms, and hence so, this is hkl set of set of planes. And the inter planar spacing between these is d. D is the inter planar spacing; so, d is inter planar spacing. To what you have here is you have a X-ray beam that comes from certain direction, let us say (Refer Time: 04:04) in green. So, so, let me first draw the normal to this.

So, we have X-ray beam which comes along this direction, and it gets refracted in this direction ok. And this will be the outgoing beam right. So, this is I in, this is I out. And this is to this is let us say transmitted beam. So, let me just write it differently because transmitted. And this is let us say I out there is the outgoing or diffracted beam. So, we have a parallel beam coming from here as well, and this parallel beam comes in such a manner. So, that hits so, sorry I little bit weird. So, I have to draw this in this fashion so that it comes in. So, you have a parallel beam which comes like this. And then this also gets deflect transmitted in this fashion, and this goes through the lattice in this form angle between this angle the angle which it makes through with the plane so, this is the plane here. So, this is if I draw this as yellow let us say. So, this angle here is theta, right this is also theta, and this is also theta, this is also theta, and this angle will be 90 minus theta. And this is also 90 minus theta.

So, in some sense it looks like as if it is having it is a reflection ok, but it is not reflection because reflection can occur at any angles as we will see it does not happen at any angle. So now, here if I do some now for diffraction to occur basically the path difference must be equal to the multiple in integral multiples of wavelength. That is the condition for diffraction to occur which comes from Thomas Young's experiment. So, if I now make a geometry like this, the path difference is some of these right.

So, this is A, this is B and this is C. So, the path difference I can write as is equal to AB plus BC ok. Now by geometry, I can say that this is this is 90 degrees, this is 90 degrees, this is theta and this is also theta. So, this becomes d sine theta, and this also becomes d sine theta. So, this is basically 2 d sine theta. And this 2-d sine theta the diffraction Bragg's law says that this must be equal to n lambda integral multiples of the wavelength. So, this is what is basically the Bragg's law. So, here n is defined as order of diffraction, theta is the Bragg angle or the diffraction angle lambda is the wavelength. So, you can see here, since so, since you are using a let us say if you are using a fixed lambda. If you are using a fixed lambda, and you know from the knowledge of so, this is d hkl, all right? D hkl is not a random value ok. So, if you have 1 0 0, plane if you have 1 1 0 plane, if you have one 1 1 plane and so on and so forth, they have a specific values, all right.

Specific values will mean you have a specific d h k ls specific, d h k ls will mean you have a specific theta values to satisfy this equation, because lambda is fixed ok. So, for a given value of n and lambda your d sine theta product is it has to be equal to n lambda divided by 2. So, which means if your d is fixed theta is fixed; that means, diffraction cannot occur at any random angle it can only happen at those angles at which this equation is satisfied. So, that is why there is a different fundament difference between diffraction reflection all that looks like reflection, it is not reflection it is diffraction which satisfy the Bragg's law whereas, a reflection can occur at any angle. Secondly, the reflection is only a surface effect diffraction is a subsurface effect, the information from the surface below the surface also comes out ok.

So, the path difference must be equal to the integral multiples of wavelength. And theta n must be equal to theta out. And you can see the angle between the diffracted beam and the transmitted beam what is this angle? This angle? This angle is 2 theta, the angle between the diffracted beam and the transmitted beam is 2 theta corresponding to the

Bragg angle. So, this is a typical Bragg's law, essentially and you can see now for crystals we have let us say a cubic crystal.

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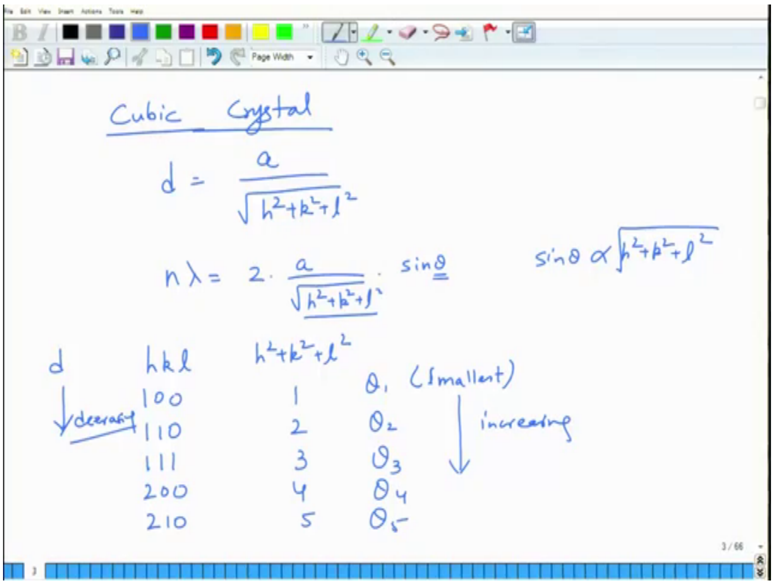

Cubic Crystal

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$n\lambda = 2 \cdot \frac{a}{\sqrt{h^2+k^2+l^2}} \cdot \sin\theta \qquad \sin\theta \propto \sqrt{h^2+k^2+l^2}$$

d	hkl	$h^2+k^2+l^2$	
↓ decreasing	100	1	θ_1 (smallest)
	110	2	θ_2 ↓ increasing
	111	3	θ_3
	200	4	θ_4
	210	5	θ_5

So, cubic crystal if you say for a cubic crystal d will be equal to a divided by root of h square plus a square plus l square, all right. So, n lambda will be equal to 2 into a divided by square root of into sine theta.

So, you can see that your theta will depend only on square root of h square plus a square plus l square. So, that is how you index your planes; so, when you go from various h k l values. So, you start from 1 0 0 your h square plus k square plus l square will be equal to 1. What is the next value for h square plus k square plus l square? That is for so, this will be theta 1, this will be theta 2. And as you go to what is the next one 1 1 1 this will give you a value of 3, this will occur a value 3.

So, this will be the so, for this h square plus k square plus l square is a smallest, theta 1 will be the from this you can the reciprocal right. So, basically you can say that sine theta is proportional to right. So, theta 1 is the smallest and it increases right. So, as you know what is happening to d spacing. That d spacing is decreasing. So, this is decreasing your theta is increasing. So, theta is increasing and d is decreasing. So, 1 1 1 you can go to now 2 0 0, that will give you 4 theta 4, and then you go to 2 1 0 that will give you 5 theta 5 and so on and so forth.

So, basically when you look at the X-ray diffraction for a cubic crystal, at least when you look at the X-ray diffraction peaks, they go in the order of increasing values of h square plus k square plus l square as a function of theta. So, as theta increases h square plus k square plus l square increases.

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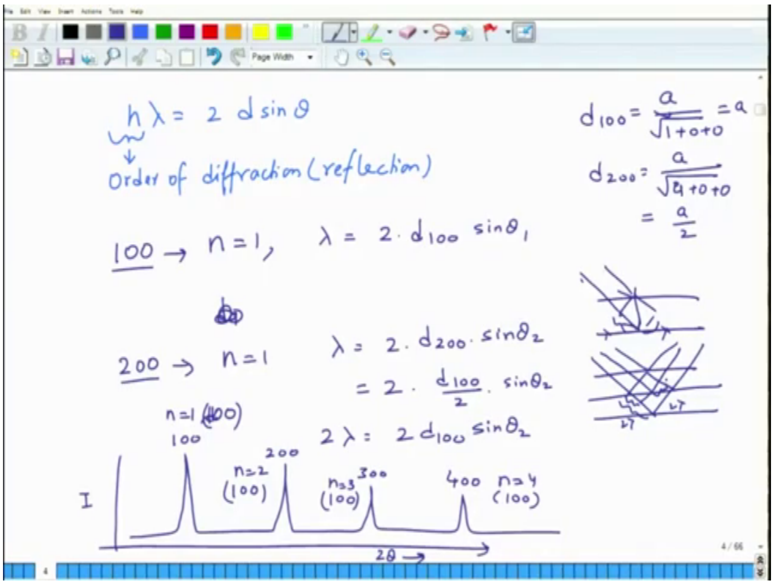

$n\lambda = 2\, d \sin\theta$

Order of diffraction (reflection)

$\underline{100} \rightarrow n=1, \quad \lambda = 2 \cdot d_{100} \sin\theta_1$

$\underline{200} \rightarrow n=1 \quad \lambda = 2 \cdot d_{200} \cdot \sin\theta_2$

$= 2 \cdot \frac{d_{100}}{2} \cdot \sin\theta_2$

$2\lambda = 2 d_{100} \sin\theta_2$

$d_{100} = \frac{a}{\sqrt{1+0+0}} = a$

$d_{200} = \frac{a}{\sqrt{4+0+0}} = \frac{a}{2}$

Now, next thing I would like to come upon is; what is the significance of in the equation and lambda equal to d sine theta. What is the significance of this factor n? Which we said it was order of diffraction in some cases they also called as order of reflection ok. Reflection is a misnomer, but it is used very frequently ok.

Now, what it means basically is that, let us say if you have 1 0 0 plane. For 1 0 0 plane imagine n is equal to 1, then this becomes n is equal to do d 2 d 1 0 0 sine theta 1 ok. Fine, now, what does d 1 0 0 mean? Now if you want to look at d 2 0 0 now. So, this will be again we take n is equal to 1. So, this will become 2 d 2 0 0 sine theta 2, what is d 2 0 0? It is nothing but d 1 0 0 divided by 2. Because d 1 0 0 is a divided by square root of 1 plus 0 plus 0, and d 2 0 0 is a divided by square root of 4 plus 0 plus 0 ok. So, this is a, this is right. So, by you can see that d 2 0 0 is half of d 1 0 0.

So, this becomes 2 lambda is equal to 2 d 1 0 0 sine theta 2. So, basically it means a 2 0 0 peak is the diffraction peak from 2 0 0 plane is nothing but second order 1 0 0 reflection or diffraction peak. So, when you have these deflection peaks you will have diffraction peaks in modern machines like these so on and so forth. This is intensity this is 2 theta.

So, let us say if this is 1 0 0, this is I am not drawing other peaks, this will be 2 0 0, this is 3 0 0, this is 4 0 0. You can call this as first order 1 0 0, this as first order 2 0 0, this as first order 3 0 0, this as first order 4 0 0. Or alternatively you can say this is first order 1 0 0, this is second order 1 0 0, this is third order 1 0 0 0, and this is 4th order 1 0 0. That is a significance of n; so, this n which is called as order of direction is meaningful in this manner.

So, this is nothing but n is equal to 1 for 1 0 0, this is n is equal to 2 for 1 0 0, this is n is equal to 3 for 1 0 0 reflection ok. And this is n is equal to 4 for 1 0 0 reflection ok. Basically, the order of reflection, the same peak can give you same plane can give you diffraction peaks at different angles. So, there may be no atom sitting at 1 0 0, 2 0 0, 3 0 0, 4 0 0; it is just that the wavelength is now diffracting in such a manner.

So, that first it was lambda, then it became 2 lambda, then it became 3 lambda, then it became 4 lambda ok. So, it is as if in the first case it would be in this fashion. So, this was one lambda lambda this so, this is lambda. This is lambda ok, in the second case it became this was 2 lambda 2 lambda. It is as if you have a plane sitting here, because if you had a plane sitting here, this would be lambda this would be lambda.

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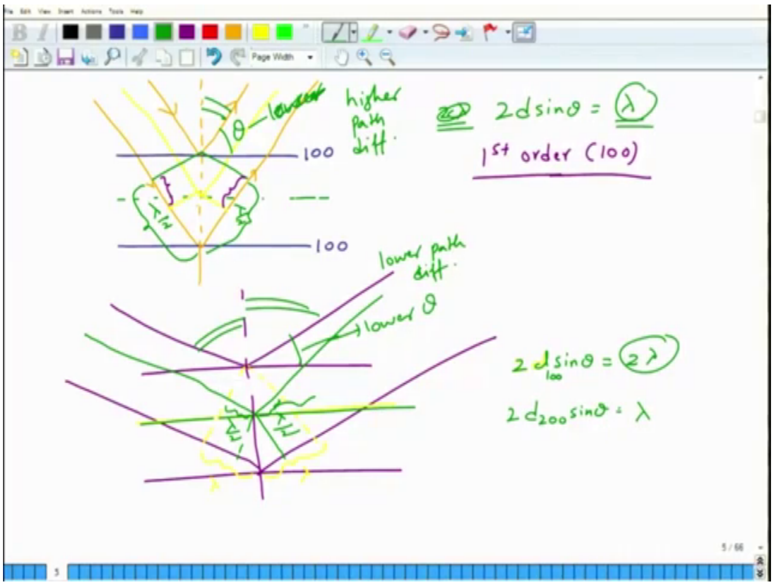

$2d\sin\theta = \boxed{\lambda}$

1st order (100)

$2d_{100}\sin\theta = \boxed{2\lambda}$

$2d_{200}\sin\theta = \lambda$

So, let us say this is the first set of planes. You might have a plane here sitting here. Let us say it may or may not be sitting, you may or may not have atoms. So, let us say this is 1 0 0, this is 2 0 0, this is this is; so, they are all hkl planes, but it is not rights to draw them in this fashion. So, if you say that this is 1 0 0, and this is 1 0 0, then the middle of it will be 2 0 0. Then you can also define this as 2 0 0 ok.

So, let us first let us not talk about 2 0 0 at all, it let us talk about the 1 0 0. Now if you have incoming beam in this fashion, let me use a different color. This is the incoming beam, this is outgoing beam. And this is let us say the other beam, that is coming parallel to this, this is let us say the other one which is going parallel to it. This is the path difference, the path difference is this and if this was lambda ok, then the path difference is lambda a 2-lambda alright. So, this is 2 lambda, 2 d sine theta basically, it is in this case it is the path difference is 2 d sine theta, and if this is equal to lambda. So, which means this is lambda by 2 this is lambda by 2 then this is one lambda ok. Now if you had a plane sitting somewhere here let us say, then what would be the path difference B, if I now draw a hypothetical beam coming here, then what would this part difference be? This would be lambda by 4, what would the path difference be for that? it is destructive interference.

So, which means for a first order 1 0 0 there could be no second order 2 0 0 or there could be no 2 0 deflection because 2 0 0 plane, does not diffract at that position. For that to occur now beam has to bend ok, it has to change the angle in such a manner so that the path difference changes. So now, when the path difference has changed, let us say the beam has bent in this fashion now. So, that you are now when you draw this is now since the angle has increased the path length is increased let us say this is now equal to lambda this is now equal to lambda ok. So, your 2-d sine theta 2 d sine theta has now become equal to 2 lambda, all right. What it make? So, this is d 1 0 0, if you had a if you had a plane in between, and let us say the beam you draw another beam in between. The path difference for this would be now half of that. You just draw a perpendicular here this would be half, this would be lambda this would be lambda by 2 this would be lambda by 2.

So, you can say that for 1 0 0, it is second order diffraction, but for 2 0 0 it is first order diffraction, this is what it means ok. Similarly, you can draw for third order 4th order, the multiples will get increasing 3 lambda 4 lambda. So, when the path difference between successive 1 0 0 plane is 4 lambda; which means you will have forethought of diffraction you. So, even whether you have plane or not if you have a plane if you have really a physical plane present then the position of atom will determine whether diffraction will take this or not that we will discuss later on, but if you didn't have those effects taking place then you will have a 4th order 1 0 0 if the path difference is 4 lambda.

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A different angle because, now you have now the theta has increased right. So, that is why it comes on the higher angle because the path difference has to increase ok. So, this theta is lower this is lower, and this is smaller angles, and this is at higher. Basically, you can say with respect to this ok. So, with respect to the normal you can say not this, but with respect to that. So, normal the beam has to flatten out ok. Or rather other way around actually this should be lower theta. So, this will give you. In fact, so, here you will have higher difference as compared to the previous case. So, this will have higher path difference, and this will have lower path difference ok, all right.

So, I hope this is clear now, the now when you when you want to use when you want to you analyze crystals using diffraction methods there are depending upon the type of crystal we use different methods.

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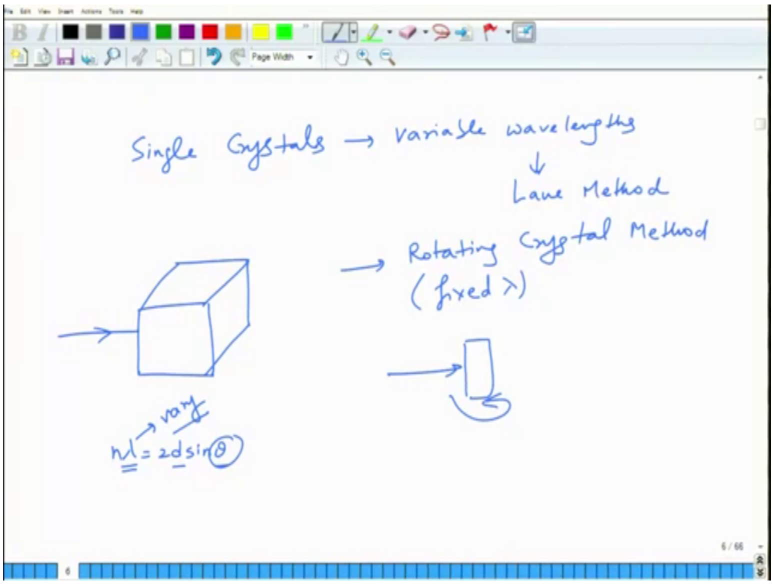

So, if you have single crystals, single crystals generally do not give you multiple freedom of orientation because the faces of crystals are fixed, as a result in single crystals we generally use variable wavelength so that you have multiple peaks coming out of the sample at various. So, you want to get more data to analyze it. So, variable wavelengths are used this method is called as Laue method. There is another method for single crystal which is called as rotating crystal method. In that method again, the wavelength is; however, not fixed a wavelength is fixed. So, it is a fixed lambda, but crystal rotates ok. So, you have a crystal which undergoes rotation, and this is the incoming beam of fixed lambda.

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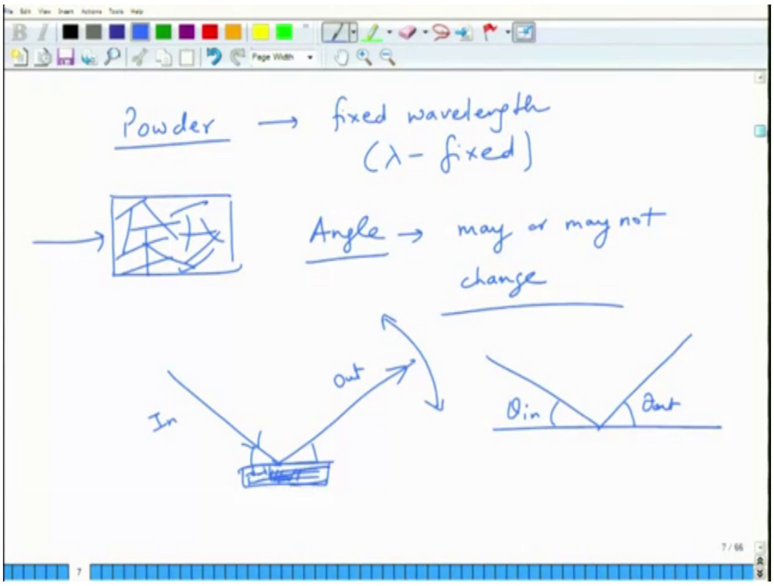

Powder → fixed wavelength (λ - fixed)

Angle → may or may not change

However, in case of poly crystals, let us say powder specimens where every plane is randomly oriented in a space. So, you have every possible orientation available to the incoming X-ray beam. See the problem with single crystals is that, if I have a single crystal specimen then, let us say my incoming beam is this is my incoming beam. And there are only a very few planes which may be appropriately oriented with respect to the incoming beam. Especially, if your sample orientation is fixed, because remember, you have to follow n lambda is equal to 2 d sine theta. If your lambda is fixed, then the only 2 things are d and theta which are dependent upon each other right.

So, orientation of a particular plane with a particular d spacing will not guarantee whether you will have Bragg's law satisfied or not. So, as a result you need to increase your you need to change lambda, so that a particular plane will diffract ok. And there is no guarantee that all the planes will diffract because there are very few orientations available. So, that is why you need to vary lambda. If you do not want to vary lambda and you need to create more opportunities for theta which means you need to rotate the crystal ok, for diffraction to occur. So, that you can get some data out of it; however, in case of powder specimens in case of powder specimens if you have bunch of powder one hkl might be like this another hkl might be late like this another hkl could be this another hkl could be this another hkl could be this. So, you can have multiple orientation of hkls. So, when the beam comes it will always find a peak for do it will always find some plane for diffraction which is oriented perfectly according to Bragg's law.

So, for powder specimens we generally used fixed wavelength ok. So, lambda is fixed and angle may or may not be changed, the sample may remain stationary or sample may rotate, then by large we can keep it fixed. But we need to change the detector position. So, if this is your incoming X-ray beam, if this is your sample, if this is your detector. So, this is in, this is out, if the sample is single crystal, then you need to if you move the detector.

So, detector will move in this direction, you are normally your beam is fixed, you will not get much diffraction only from those planes which are favourly oriented not from anything else, then because you know you need to satisfy this 2-theta geometry 2 theta. Remember, for diffraction to occur you have to have for a given plane, theta n theta out as equal. If this geometry is not maintained then you will not get diffraction, alright. So, in case of powder specimen since there are multiple orientation present all over the place.

So, you will have diffraction taking place all you need to do is that. You can keep that X-ray beam fixed you can keep even your sample fix you can just move the detector whereas, in case of single crystals you may have to move the sample you may have to move the incoming beam as well to get the maximum deflections occur maximum diffraction possibility. So, this is what is these are the 3 methods which we use for diffraction in crystals. The Laue method for with which has variable wavelengths for single crystals, rotating crystal method with fixed wavelength for again for single crystals, then we use powder method for the powdered or poly crystalline specimens.

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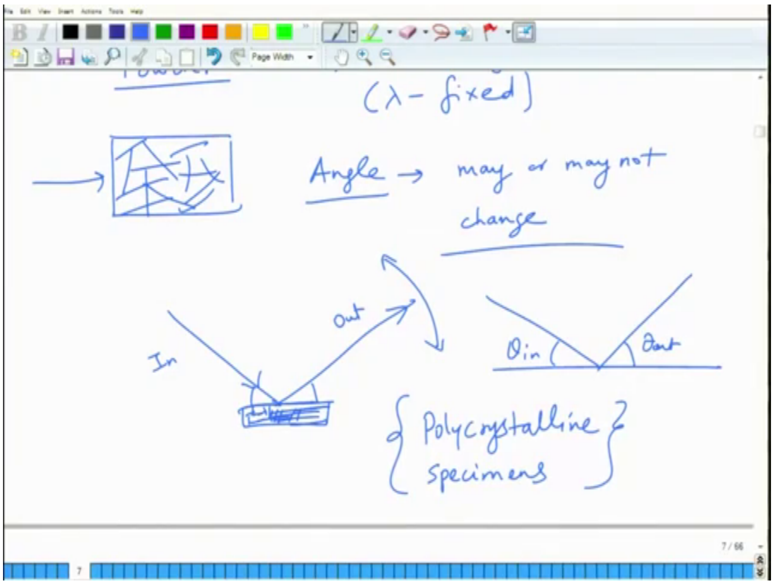

(λ- fixed)

Angle → may or may not change

{Polycrystalline specimens}

So, this is for poly crystalline, specimens if you are not clear about what poly crystalline a single crystal specimen are I will explain that a little bit in the next class ok. So, in the next class we will again discuss X-ray diffraction it is utility to crystals and give you certain examples. Before we move on to, finally the defects in the materials.