Indian Institute of Technology Madras

Presents

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture -21
Materials Characterization
Fundamentals of X-ray diffraction

Dr. S. Sankaran

Associate professor

Department of metallurgical and materials engineering

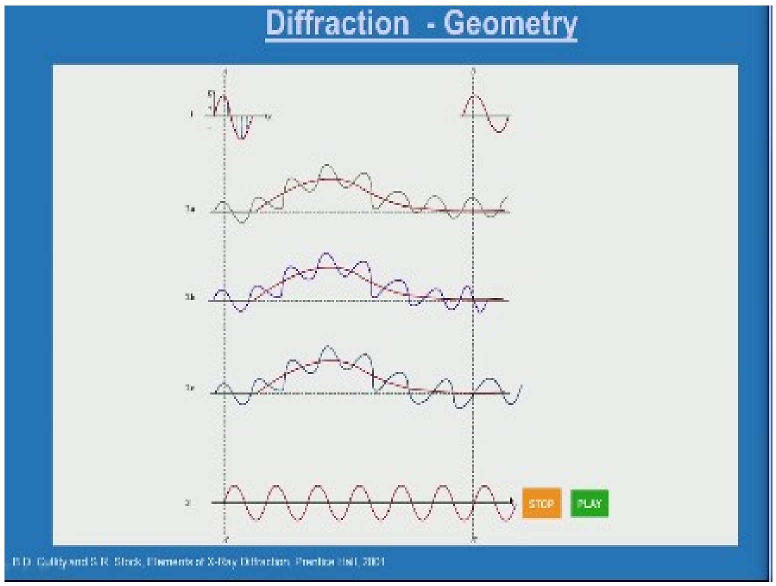
IIT madras

E-mail. ssankaran@iitm.ac.in

Hello everyone welcome to this material characterization course. In the last class we just looked at the some of the fundamental properties of X-rays as a wave and then we also looked at the kind of relations that is we talked about phase relations and then and we also talked about how the X-ray waves are represent represented mathematically in the exponential component form as well as a trigonometric form and then finally how if somebody want to use it this expression for arriving at any intensity what kind of expressions we will look at it.

So in continuation with that discussion we also lightly looked at a diffraction I said that most of the phase relations we talk about in order to appreciate the phenomena, diffraction. Today I will just briefly discuss with some of the animation diagrams to illustrate how the diffraction can be appreciated using the phase relations between the waves.

(Refer Slide Time: 01:39)



So I will just start with this animation where you have let us assume this is a plane polarized wave that means their electric vector is in the same plane of the drawing and then I'm going to consider two waves like what is depicted here and then what you are now seeing is that wave is propagating in particular path and then in reaching the wave front B-B' and it starts from the wave front A-A' and what we are now interested here is just look at this wave and for the hypothetical I mean situation you imagine that this wave is spilted into two waves like 2a and then 3.

And these waves will have the amplitude one half of this wave 1. This is just an assumption and also you assume that these two waves are in the same phase and first I would like you to compare the 2a and then 3. These two waves are travelling in two different paths, the wave 3 is traveling in the straight line but wave 2 is travelling in a very different path as compared to wave 3.

In fact the amplitude as I mentioned updated of this two waves 2a and then 3A should be half of this though. This is not quite obvious from this schematic diagram please assume that these two waves are having of the amplitude of this that means we are splitting this wave into 2 for an imaginary experiment. So now you see that the wave travels this path and the arrives at the wave front B-B'

And here also you can see that the wave which travels in a straight line arrive and the wave front B-B'. You see these since these two waves have travelled in at two different path lengths and there you can see that the wave where they enter the wave front B-B' they are not the same. You can see that at this intersection you can see the wave the amplitude is zero, on the other hand the 2a wave where it try to rejoin the wave 3 where the intersection point you have the amplitude is maximum.

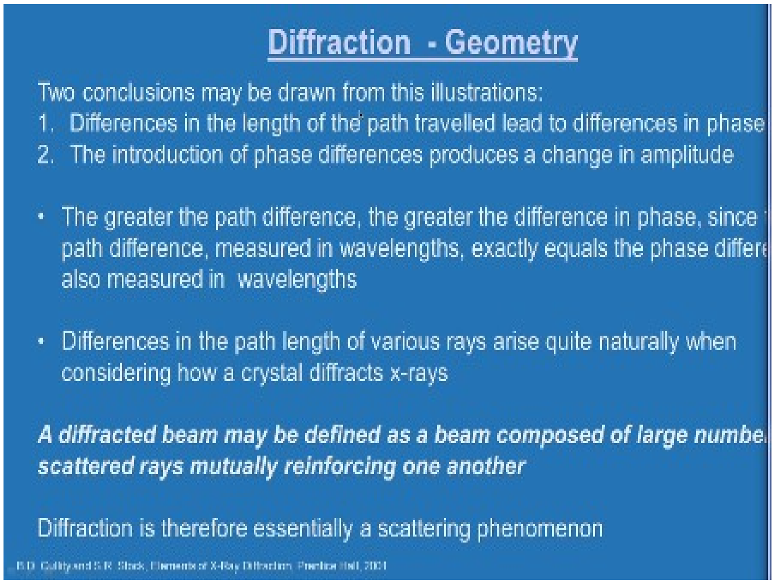
So you have very clear demonstration here when the path difference is there and there will be impact on the amplitude or there will be a change in the amplitude like this you can see. I will repeat since the wave travels in the straight line and where it enters the B-B' wave front the wavelength is I mean the amplitudes zero here you can see that interest intersection.

Since the wave has taken a different path and it causes a path difference in this case the wavelength is I would say that the wavelength is enlarged to the quarter wavelength we can assume that so their amplitude is maximum here the amplitude is zero. We can also assume suppose if you allow the travel I mean allow the wave to travel like this for example in 2b case where wavelength is, I would say that the wavelength difference if it is instead of quarter wavelength here if it is in half a wavelength then the two waves will be out of the phase by half wavelength.

The phase I mean phase shift between the 2a and 3 about a quarter wavelength. So you can see that similarly if you allow this 2c to travel in a different path and then the wavelength difference is between that the third wave and the 2c wave it is one wavelength completely then the this wave and this wave will be out of the out of phase by one full wavelength.

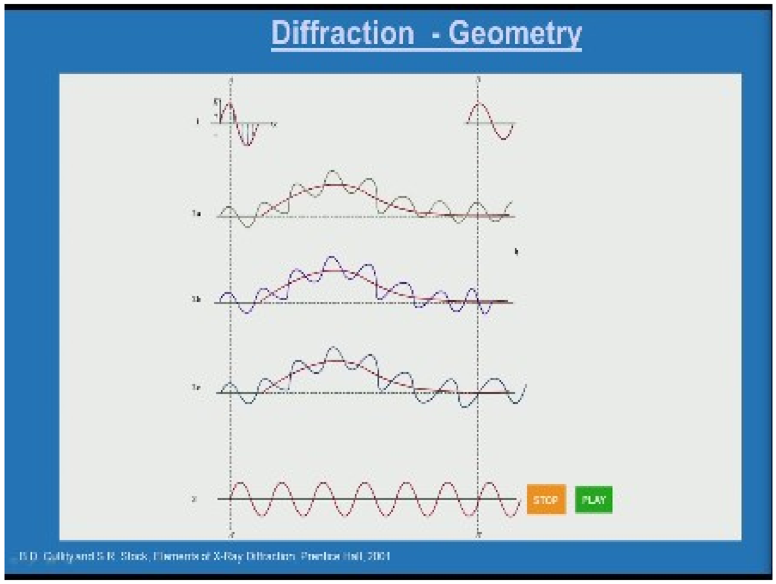
But in this time the wavelength though it is out of phase by one full wavelength and it is completely indistinguishable because it has got both I mean you can see that amplitude they are in this same phase. So certain things are very clear here.

(Refer Slide Time: 07:30)



You can just note down few points. The two conclusions may be drawn from this illustration. Differences in the length of the path travelled lead to differences in the phase. The introduction of phase differences produces change in amplitude. So I think these two points are very clear.

(Refer Slide Time: 07:50)

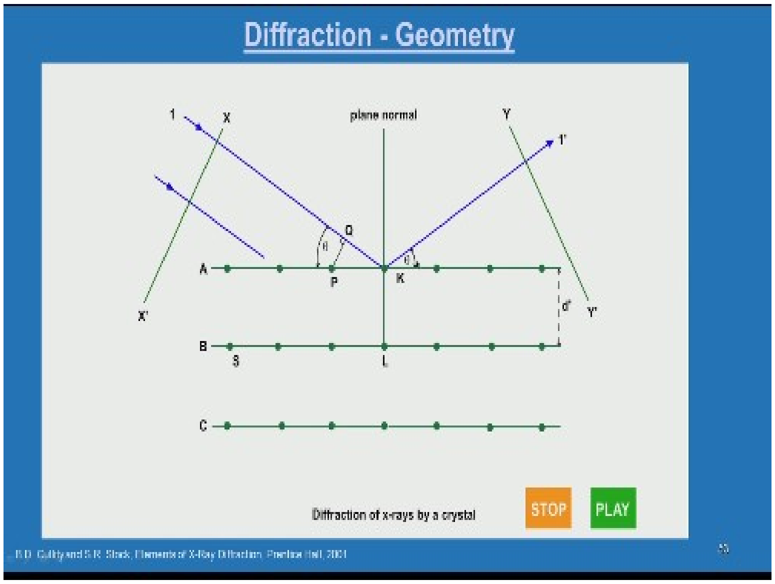


You can see in this case every wave is traveling in a different path assuming that their wavelength is different. At least I have shown at this intersection, the amplitudes are quite different if they follow a different-different travel path. So the greater the path difference the greater the difference in the phase since the path difference measured in wavelengths exactly equals the phase difference also measured in wavelengths. So this is again and a very important point though we have come across this in the light optical system also.

And we are reinforcing that understanding here with this illustration. So differences in the path length of various rays arise quite naturally when considering how a crystal diffracts X-rays. So finally we are interested in looking at the scattering of X-rays by a crystal system and then there we are going to connect this concept to a diffraction. So we need to understand how this path difference will contribute to the condition for a diffraction that is the ultimate game.

So you can see that a diffracted beam may be defined as a beam composed of large number of scattered rays mutually reinforcing one another. so this is a kind of a definition for the diffracted beam. But then how do we qualify this? This statement how do we visualize this statement and then and we can come back to this statement and then say this is what it is

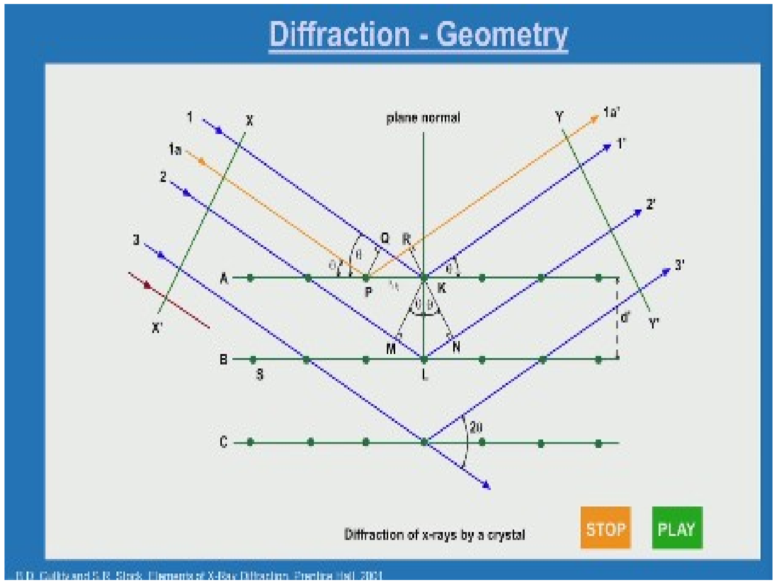
(Refer Slide Time: 10:00)



So for that what I will do is you look at this schematic again it's an animation I will play it. What you are now seeing is a diffraction of X-rays by a crystal. So okay we will stop here and then we will go one by one. So assume that this is the a 2D representation of a 3-dimensional crystal. A, B, C are different planes and then you have the perfectly monochromatic X-rays are falling on this surface.

And this is a angle of incident θ and this is angle of reflection θ. so this θ what we are seeing here in X-ray diffraction is slightly different from what we talked about in general light optics where the angle of incidence and angle of reflection is always with respect to the surface normal to the whatever the angle of incidence an angle of reflection we talk in light optics is with respect to the surface normal of the plane surface plane. But here it is slightly different.

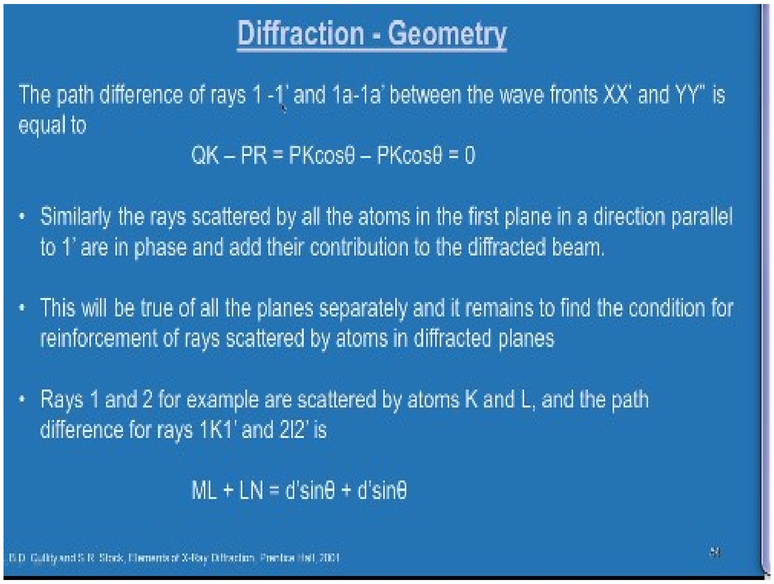
(Refer Slide Time: 11:38)



It is this θ is an angle of incident and angle of reflection is considered in this fashion and that is one point and assume that this is the wave front X' and then after the reflection it goes to the goes through the Y' the wave front and this is the normal we are trying to take a normal to this the first X-ray path that is 1-K-1' this is the wave we are now going to talk about. And now let us see I put another ray, second ray which that is 2-L again this one 2' and then you have 3 and 4 and 5 and so on it will keep on going.

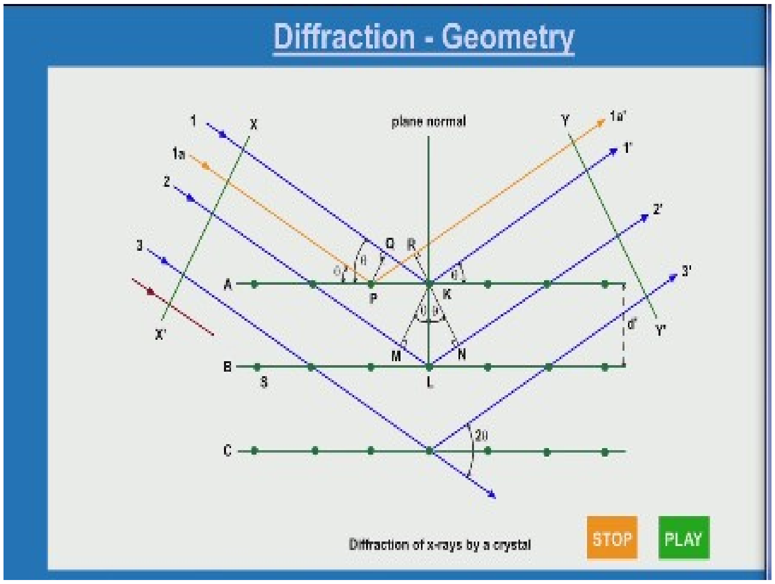
So now we will talk about the atoms sitting in that top surface plane and it is reflection and how it is contributing to the diffraction intensity. For example, this is we will talk about the second ray little later. We will talk about the first plane now. Suppose if I introduce one more ray like this and then which again comes and hits the atom P and then it reflects and then you can designate this as 1a. So now you have to rays1-K-1' and 1a-P-1a' that is two rays which are trying to diffract from the first plane. So now we have to see whether these two rays have any path difference. We were just talking about path difference just now so to understand that we will just do this.

(Refer Slide Time: 14:15)



The path difference of and 1 -1' and 1a-1a' between the wave fronts XX' and YY" is equal to **QK - PR =PK cos θ - PK cos θ = 0**. So let us go back and then look at this QK –PR.

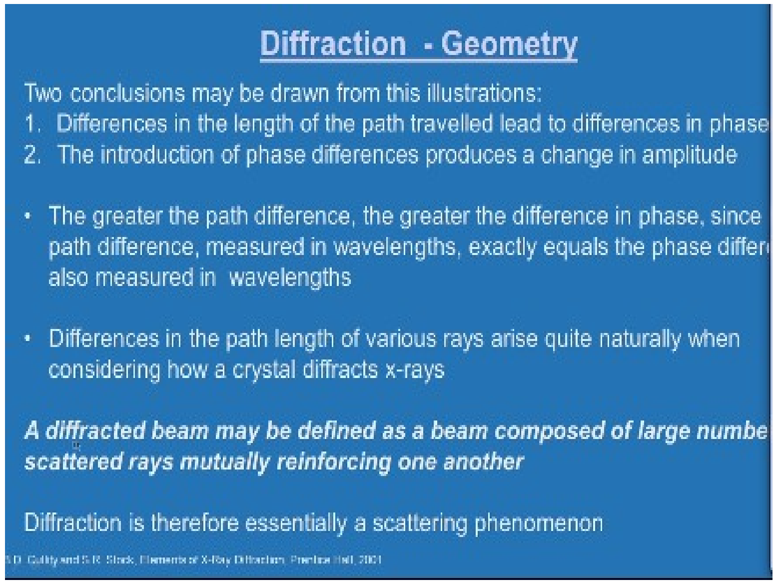
(Refer Slide Time: 14:39)



QK is there and this is PR and this is nothing but your PK cosθ. For both cases whether it is a QK or PR = PK cosθ. So in this case both the path difference is zero. It is not just this 2 rays, any ray, any number of ray which comes and hits at the plane 1 will have will not make any path difference like this. So what is the significance?

Similarly the ray scattered by all the atoms in the first plane in a direction parallel to 1' are in phase and add their contribution to the diffracted beam. So all this will be in phase and then they will contribute to the diffraction we are still we are yet to qualify the diffraction we are now saying that these two rays will have their phase I mean they will have the same phase. So that means I am also saying that any number of rays which falls on this first plane will have their phase in the same orientation we can say that.

(Refer Slide Time: 16:25)

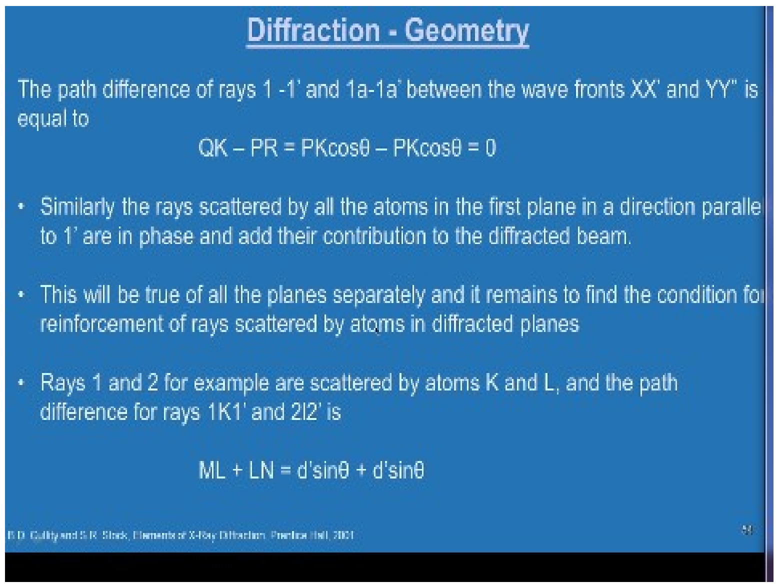


And the important point is if all this rays reinforce with each other with the same phase and then they contribute to the diffraction intensity that is what we just made a statement here. A diffracted beam may be defined as the beam composed of large number of scattered rays mutually reinforcing one another. So this is now qualified for the first line first line of atoms.

Please remember whatever the schematics shown here it is shown assuming that these rays are diffracting in fact the moment the X-rays hit on the atoms P and K it scatters all over the direction all the direction it scatters but only the 1A’ and 1’ are shown as a diffracted beam. Please we have to understand the diagram. We are assuming that only these two waves contributes to the diffraction intensity. It is not that I mean other scattering rays are not there they are there they are not in the phase they are not in the same phase. That is the that is the meaning you have to look at it.

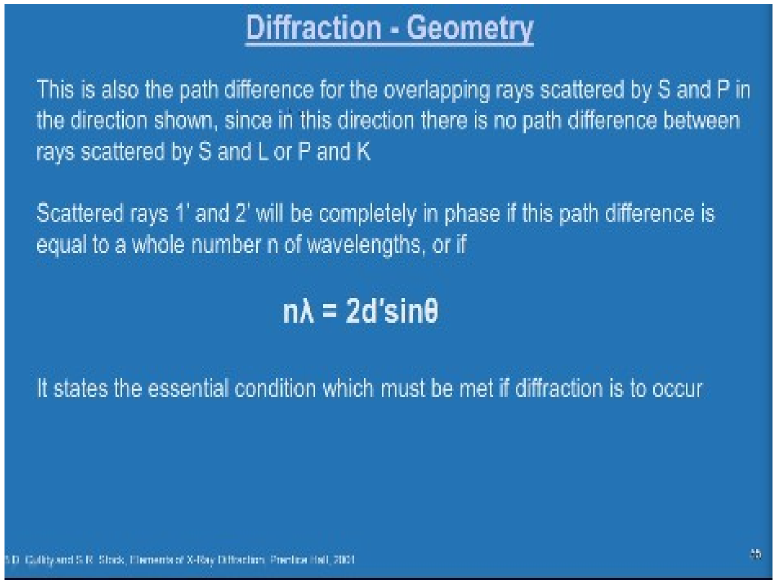
So now what about the other rays which is coming just below this plane. You have because we are talking about 3-dimensional crystal lattice and we are only representing with the 2D, I mean lattice and you will have an infinite number of planes here and above and so on. So now we will see what is that condition where the ray 2 will have to get it reinforced and contribute to the diffraction intensity. So let us talk about the ray 2-L-2' and if you look at the path difference by drawing a normal M and N and then we can look at ray 1 & 2 for example are scattered by atoms K & L and the path difference for 1-K-1' and 2-L-2' is **ML+ LN =d' sin θ +d' sin θ**

(Refer Slide Time: 19:17)



So what is that? So these planes are separated by the distance d' and the path differences M-L and L-N this is nothing but d sineθ so that is how it is measured.

(Refer Slide Time: 19:20)

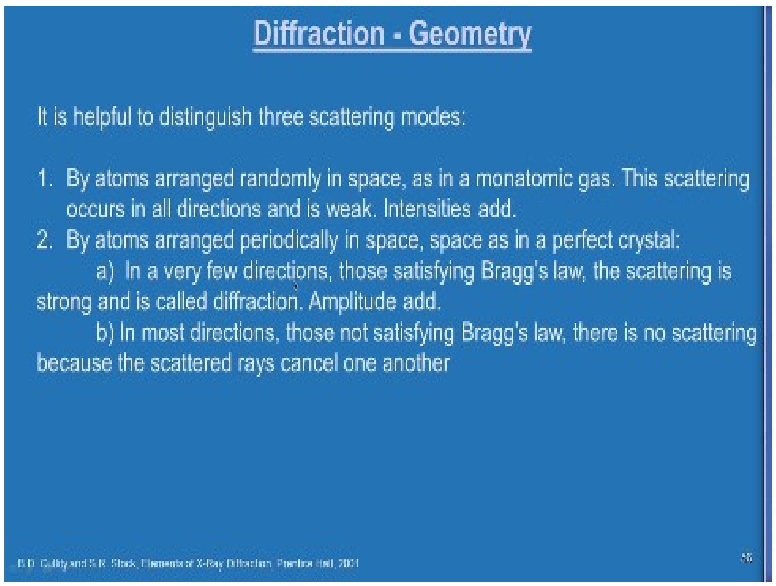


So this is also the path difference for the overlapping rays scattered by S and P in the direction shown. Since in this direction there is no path difference between the ray scattered by S and L or P and K so let us go back and see. S&L, P&K so in the same line there is no path difference similarly there is no path difference in this but when it crosses the next plane there is path difference but that is measured like ML+ LN here. Scattered rays 1' and 2' will be completely in phase if this path difference is equal to whole number of wavelengths or if **$n\lambda = 2d' \sin \theta$**.

So in order for this second ray to be in phase with the race which is diffracted from the first plane and there is a condition this is a condition which exists. So the condition is the path difference should be the integral multiple of wavelength that is $n\lambda=2\ d \sin \theta$. Now let us now play the other.

Okay if it is going to satisfy this condition like if the path difference is going to be the integral multiples of λ, they are going to get reinforced with the plane, I mean the rays which is coming out of the first plane and second plane and third plane and so on it is keep on going to reinforce provided if this condition is met. Similarly you can imagine 2a and 2a' which is going to follow this condition again. So like that you can keep on imagining any line which comes and hits any atom here and then they will follow a condition like this or this two situations in either case you will have the reinforcement of the phase will be there and then they will contribute to the diffraction intensity. So it states the essential condition which must be met if the diffraction is to occur. So this is the condition for the diffraction which is popularly known as Bragg's law.

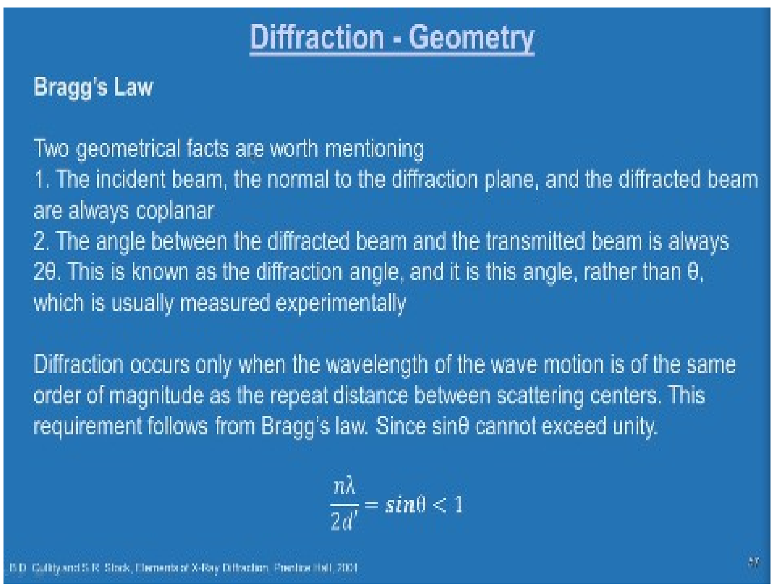
(Refer Slide Time: 22:18)



And we will now see what are the some useful remarks in considering the above schematic. It is helpful to distinguish three scattering modes by atoms arranged randomly in space as in a monatomic gas the scattering occurs in all directions and it is weak. Intensities add. By atoms arranged periodically in space as in the perfect crystal in a very few directions these satisfying Bragg law the scattering is strong and it is called diffraction. Amplitudes add. In most directions those not satisfying Bragg law there is no scattering because the scattered rays cancel one another.

So you have to just recall the phase relations what we have just gone through. You see that if the path difference is different then has got a significant influence on its amplitude and if it is out of phase by quarter wavelength or off wavelength we have seen that it is completely you know canceling that intensity if it is of opposite sign. So if the Bragg condition is satisfied you will have the rays which is diffracting will be on the same phase and then they will reinforce and contribute to the diffraction intensity. Not all the scattering waves will know this because it has got some specific angle theta by which only it will happen it is called Bragg angle.

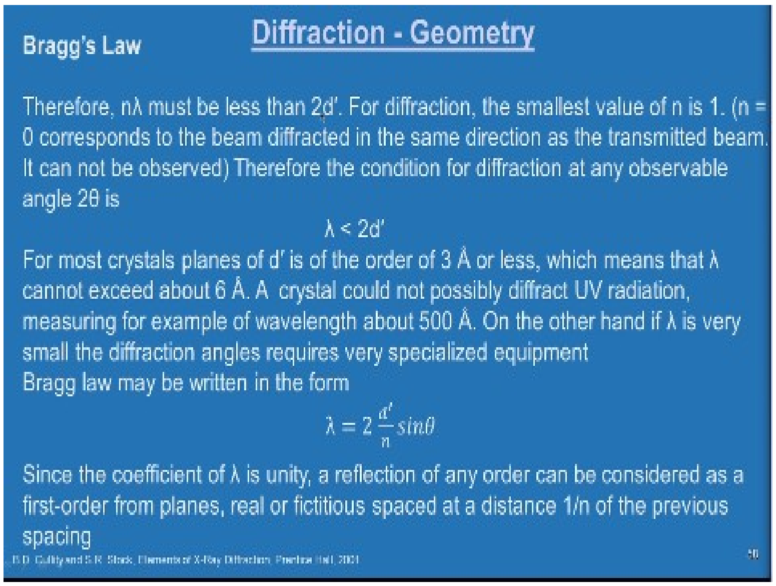
(Refer Slide Time: 24:20)



So we will see the significance of this further. Two geometrical facts are worth mentioning. The incident beam, the normal to the diffraction plane and the diffracted beam are always coplanar. The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as diffraction angle and it is this angle rather than θ which is usually measured experimentally.

We will talk about this 2θ angle when we go to the X-ray diffractometer in the laboratory and we will discuss about the significance of this 2θ versus θ. Let us look at the another important remarks diffraction occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This requirement follows from Bragg's law since sin θ cannot exceed unity, where this is very important. So that clearly implies **$(n\lambda/2d') = \sin\theta < 1$**.

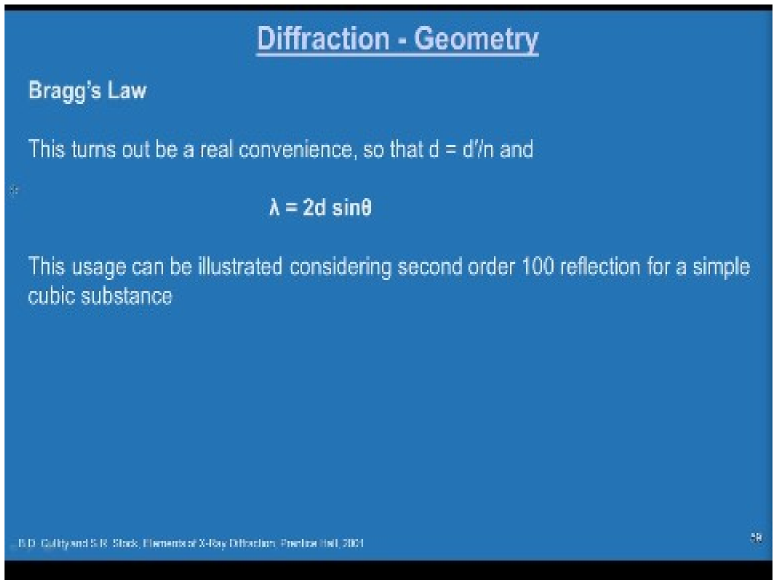
(Refer Slide Time: 25:46)



Therefore nλ must be less than 2d'. For diffraction the smallest value of n is 1. n =0 corresponds to the beam diffracted in the same direction as the transmitted beam. It cannot be observed. Therefore the condition for diffraction at any observable angle 2θ is λ less than 2d'. So what is the significance of this statement? For most crystals planes of d' is of the order of 3 angstrom or less which means that λ cannot exceed about 6 angstrom. A crystal could not be possibly diffract UV radiation measuring for example of wavelength about 500 angstroms.

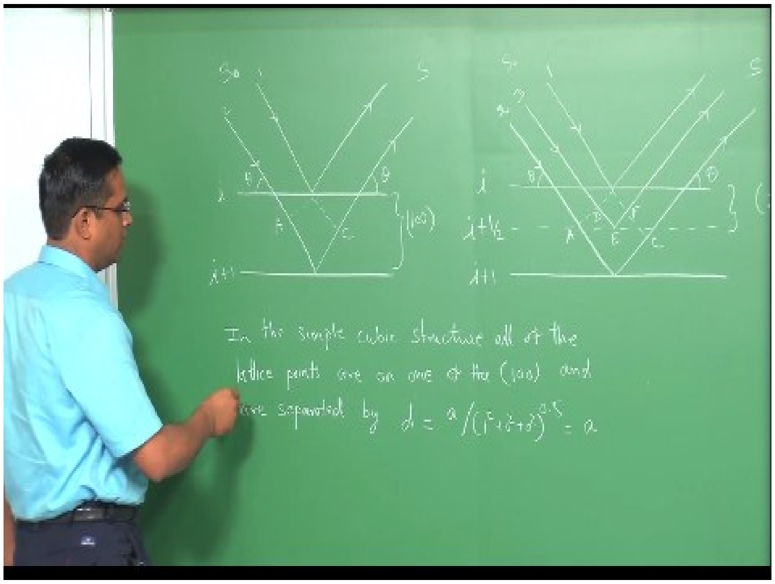
So that is the implication the your d spacing and λ are not compatible. On the other hand if the λ is very small the diffraction angles requires very specialized equipment. So we can rewrite this Bragg's law like this **$\lambda=2(d'/n)\sin\theta$**. Since the coefficient of λ is unity here a reflection of any order can be considered as the first order from plains real or fictitious spaced at a distance 1/n of the previous spacing. Excuse me.

(Refer Slide Time: 27:35)



So this turns out to be a real convenience. So the **$d = d'/n$** and we can write a general form **$\lambda = 2d \sin \theta$**. We can demonstrate this usage of this kind of writing this Bragg law by considering a second-order 100 reflection for a simple cubic substance. So what I will do try to illustrate this on the black board.

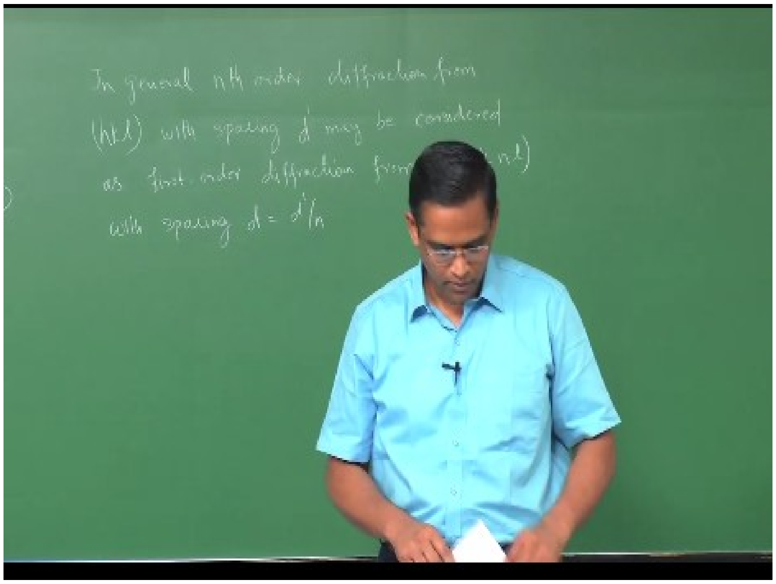
(Refer Slide Time: 28:15)



What I have just drawn here is you have 100 plane in a cubic crystal where you have i plane and i+1 plane and you have this incoming rays and this is diffracting rays and they are separated by the a. Now we will suppose if you consider the second order reflection from this that means these two planes are out of phase by 2λ. So that means suppose if there were some scatters if you assume in the i+1/2 plane, they will scatter the atoms sitting on I and i+1 atoms by λ.

You have the that this scatter I mean whether you have the atom here or not and the diffracted intensity from this plane will with respect i and i+1 will have the phase difference of λ. Here it is 2 λ.

(Refer Slide Time: 35:13)



So what we can write is, in general n^{th} order diffraction, so considering this the equivalence of a second-order reflection from 100 and the first-order reflection from 200 we can make a general statement. In general n^{th} order diffraction from hkl with the spacing d’ may be considered as a first-order diffraction from (nh nk nl) with spacing **d =d‘/n**.

So with that we'll be able to understand the kind of diffracted intensity which is coming from these crystal planes will be realized. So what I will do is I'll just stop here and then we will continue this the diffractions of X-rays and its relation with reciprocal lattice concept in the next class. Thank you