Indian Institute of Technology Madras
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NPTEL
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture -21

Materials Characterization
Fundamentals of X-ray diffraction

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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 talked about in order to appreciate the phenomena and 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

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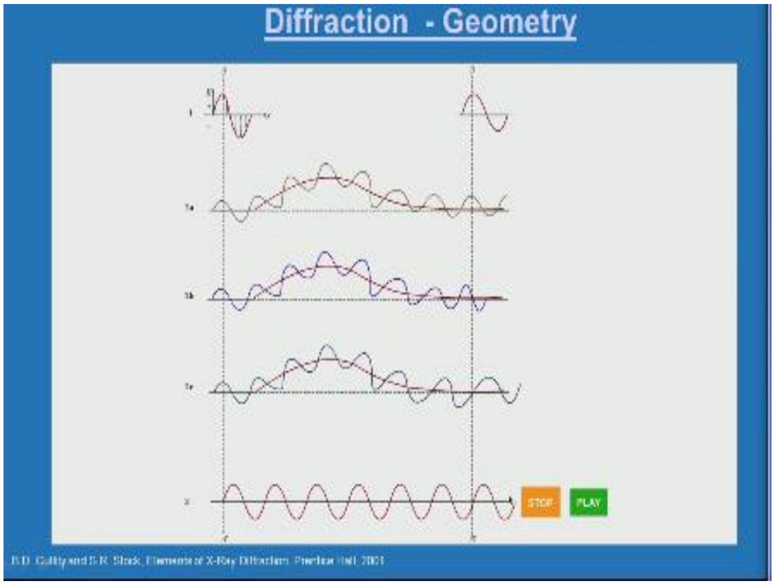

Diffraction - Geometry

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

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 BB Dash and it starts from the wave front 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 spilt into two waves like 2a and 2p then three and these waves will have the amplitude one half of this way one 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 2 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 BB

And here also you can see that the wave which travels in a straight line arrives and the wave front BB 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 VB - they are not the same you can see that at this intersection you can see the wave the amplitude is 0 on the other hand the two a 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 vb-prime wave front the wavelength is I mean the amplitudes 0 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 h.

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 mean allow the wave to travel like this for example in to be case there were wave length is in the I would say that the wave length 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 face by half wavelength the face 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 to see wave it is one wavelength completely then the this wave and this wave will be out of the out of phase by one full wave length.

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.

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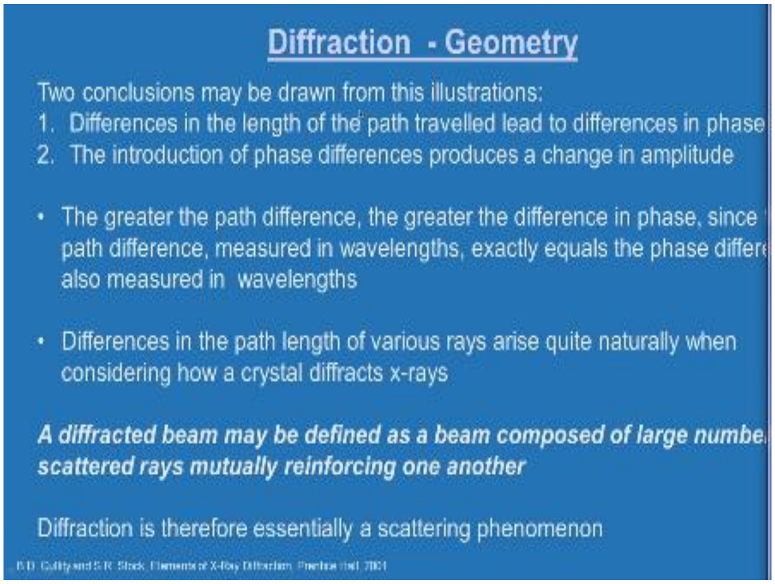

Diffraction - Geometry

Two conclusions may be drawn from this illustrations:

1. Differences in the length of the path travelled lead to differences in phase
2. The introduction of phase differences produces a change in amplitude

- The greater the path difference, the greater the difference in phase, since path difference, measured in wavelengths, exactly equals the phase differe also measured in wavelengths
- Differences in the path length of various rays arise quite naturally when considering how a crystal diffracts x-rays

A diffracted beam may be defined as a beam composed of large numbe scattered rays mutually reinforcing one another

Diffraction is therefore essentially a scattering phenomenon

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

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 face the introduction of phase differences produces change in amplitude so I think these two points are very clear

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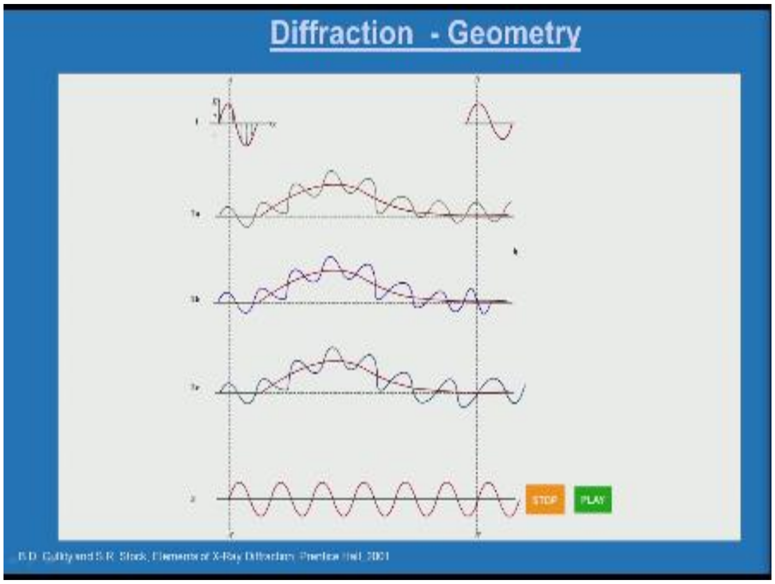

Diffraction - Geometry

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall 2001

You can see in this case every wave is traveling in a different path assuming that they are wavelength is different at least. I have shown at this intersection the amplitudes are quite different if they follow a different travel path so the greater the path difference the greater the difference in the face 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 race arise quite naturally when considering how a crystal diffract x-rays so

finally we are interested in looking at d 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 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

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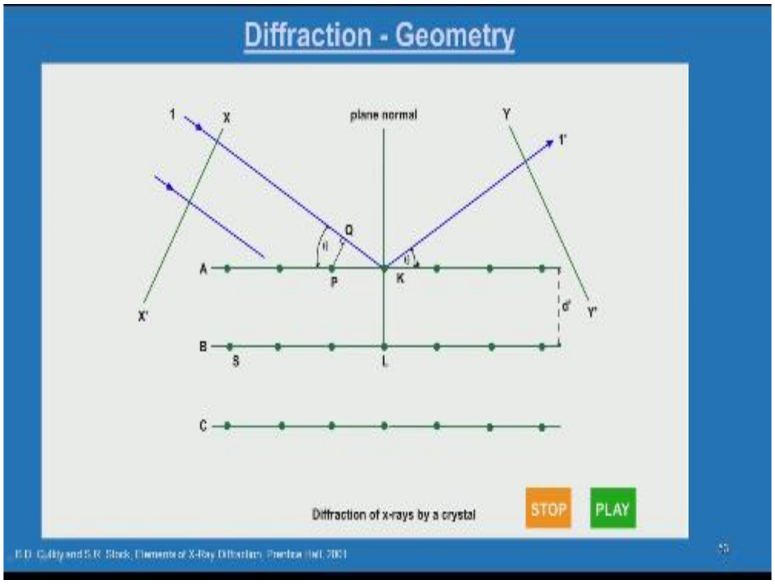

Diffraction - Geometry

Diffraction of x-rays by a crystal

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

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 ABC are different planes and then you have the perfectly monochromatic x-rays are falling on this surface.

And this is a angle of incident theta and this is angle of reflection θ so this the a 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 dangle 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.

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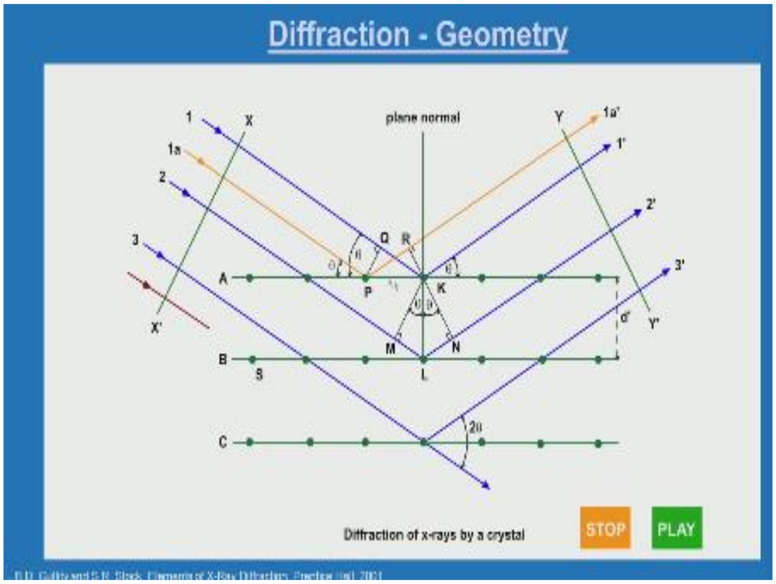

Diffraction - Geometry

Diffraction of x-rays by a crystal

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

It is this 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 prime and then after the reflection it goes to the goes through the y prime 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 k1 prime this is the wave we are now going to talk about and now let us see I put one another raid secondary which that is to yell again this one to prime and then you have three and four and five 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 secondary 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 raise1 K 1 Prime and 1Y a prime that is two rays which are trying to diffract from D the first to claim so now we have to see whether these two rays have any path difference we were just talking about what difference just now so two to understand that we will just do this.

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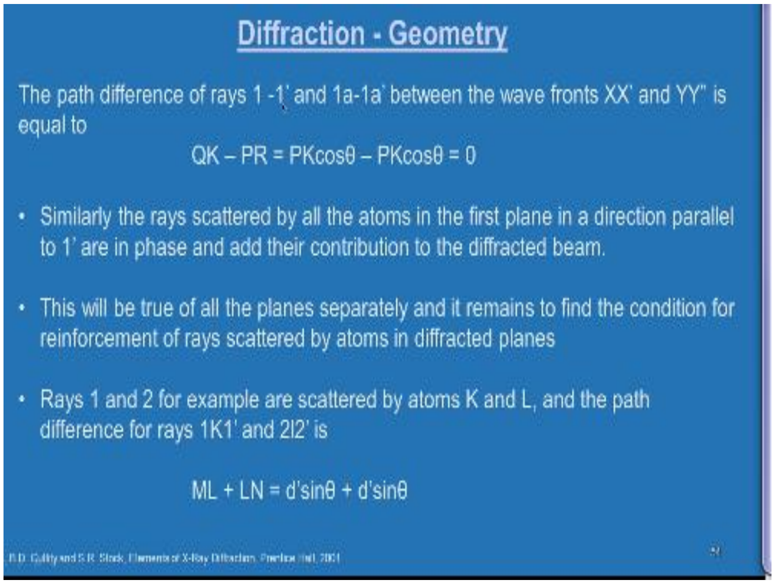

Diffraction - Geometry

The path difference of rays 1 -1' and 1a-1a' between the wave fronts XX' and YY" is equal to

$$QK - PR = PK\cos\theta - PK\cos\theta = 0$$

- Similarly the rays 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.
- This will be true of all the planes separately and it remains to find the condition for reinforcement of rays scattered by atoms in diffracted planes
- Rays 1 and 2 for example are scattered by atoms K and L, and the path difference for rays 1K1' and 2l2' is

$$ML + LN = d'\sin\theta + d'\sin\theta$$

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

The path difference of and 1 -1' and 1 and 1 EI prime between the wave friends X '+ Y' = QK -P R =PK cos ϕ -PK cos ϕ= 0. So let us go back and then look at this QK –PR.

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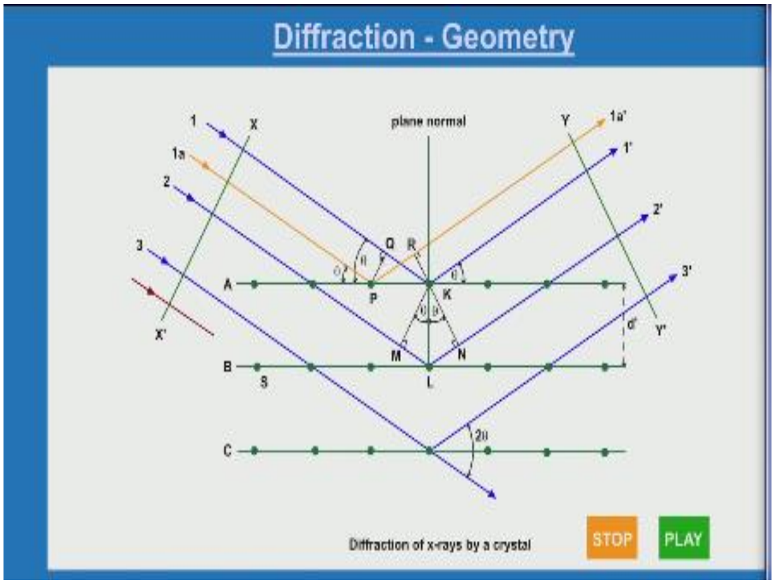

Diffraction - Geometry

Diffraction of x-rays by a crystal

QK is there and this is P R and this is nothing but URPK $\cos\phi$ 4 both cases whether it is a Q K R P R $=$P k $\cos\phi$ so in this case both the path difference is0 it is not just this to race anyway any number of Ray which comes and hits at the plane one will have will not make any path difference like this so what is the significance.

Similarly there a scattered by all the atoms in the first plane in a direction parallel to one prime R in face 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 trays will have the their face I mean they will have the same face so that means I am also saying that any number of rays which falls on this first plane will have their face in the same orientation we can say that.

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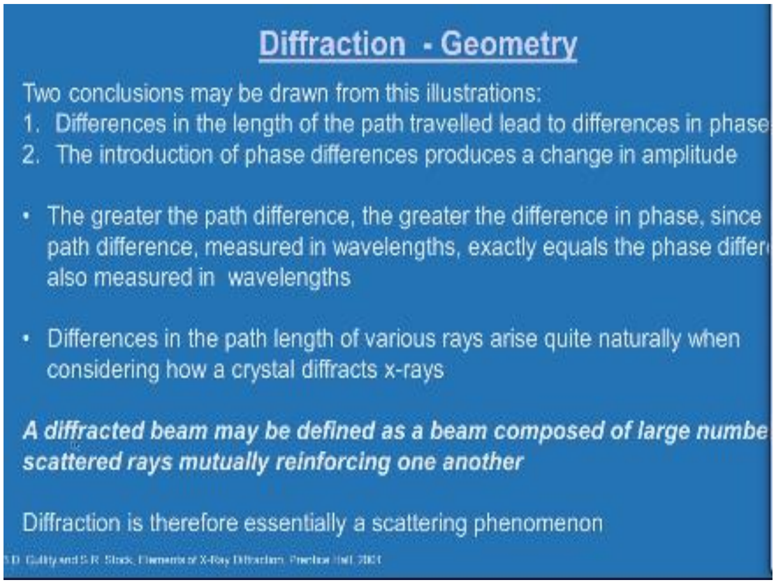

Diffraction - Geometry

Two conclusions may be drawn from this illustrations:

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A diffracted beam may be defined as a beam composed of large numbe scattered rays mutually reinforcing one another

Diffraction is therefore essentially a scattering phenomenon

D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

And the important point is if all this rays reinforce with each other with the same face and then they contribute to the diffraction intensity that is what we just made a statement here Y diffracted beam may be defined as the beam composed of large number of scattered raised 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 is 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 face 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 soon so now we will see what is that condition where the Ray too will have to get it reinforced and contribute to the diffraction intensity so let us talk about the Ray 2yell and 2P’ 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 1K1’ and 2L2’ ML+ L N =D’ sine θ +D ‘sineθ

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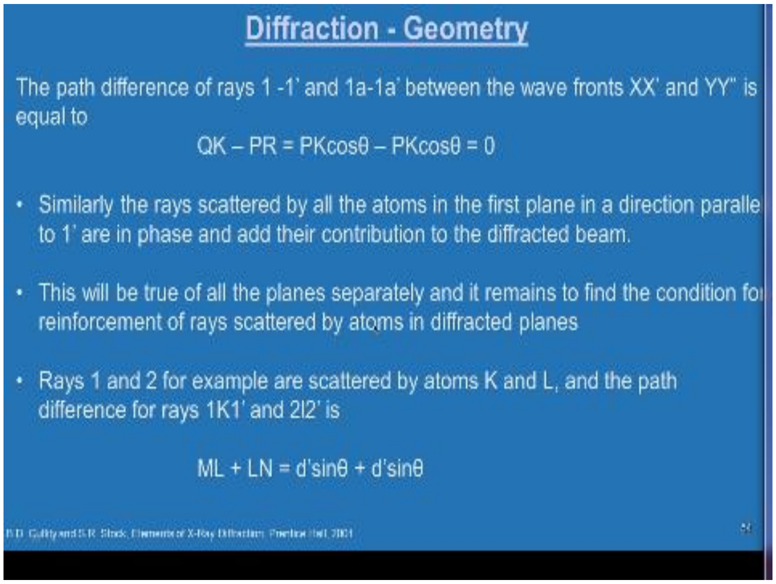

Diffraction - Geometry

The path difference of rays 1 -1’ and 1a-1a’ between the wave fronts XX’ and YY” is equal to

$$QK - PR = PK\cos\theta - PK\cos\theta = 0$$

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B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

So what is that so these planes are separated by the distance D’ and the path differences M L and LN this is nothing but D sineθ so that is how it is measured.

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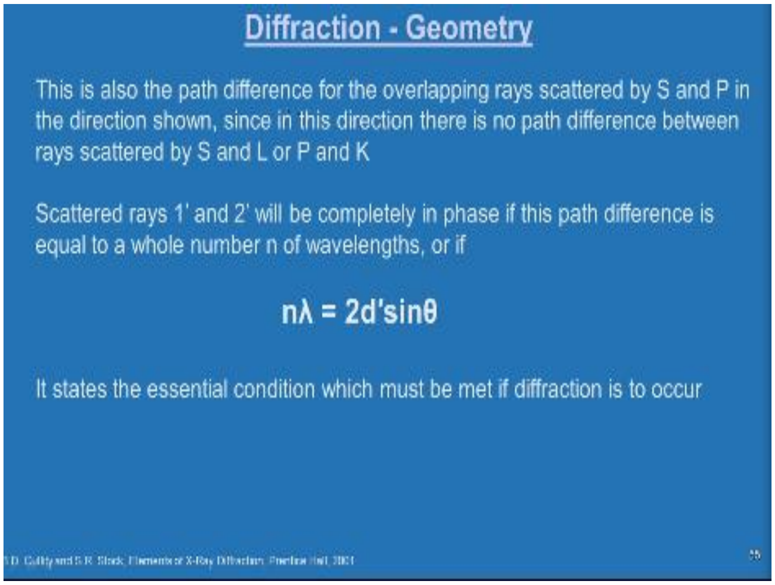

Diffraction - Geometry

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 rays scattered by S and L or P and K

Scattered rays 1' and 2' will be completely in phase if this path difference is equal to a whole number n of wavelengths, or if

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

It states the essential condition which must be met if diffraction is to occur

D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

So this is also the path difference for the overlapping race 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’ 2’ will be completely in phase if this path difference is equal to whole number of wavelengths or if nλ is 2 D’ sineθ.

so in order for this second ray to be in phase with the race which is deflected 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 λ2 D sineθ a now let us now play the other room.

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 race 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 to a and to a prime 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 face 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.

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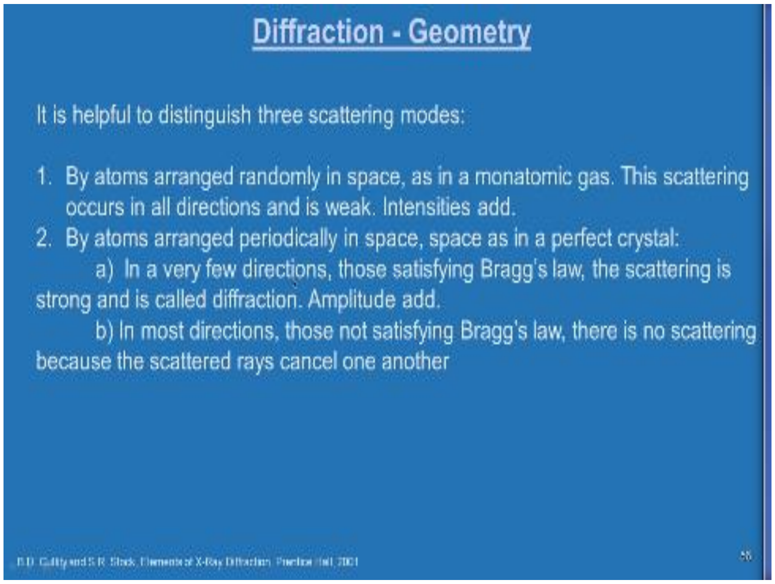

Diffraction - Geometry

It is helpful to distinguish three scattering modes:

1. By atoms arranged randomly in space, as in a monatomic gas. This scattering occurs in all directions and is weak. Intensities add.
2. By atoms arranged periodically in space, space as in a perfect crystal:
   a) In a very few directions, those satisfying Bragg's law, the scattering is strong and is called diffraction. Amplitude add.
   b) In most directions, those not satisfying Bragg's law, there is no scattering because the scattered rays cancel one another

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

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 monotone gas the scattering occurs in all directions and it is weak intensities ad 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 Brad condition is satisfied you will have the race which is diffracting will be on the same face 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.

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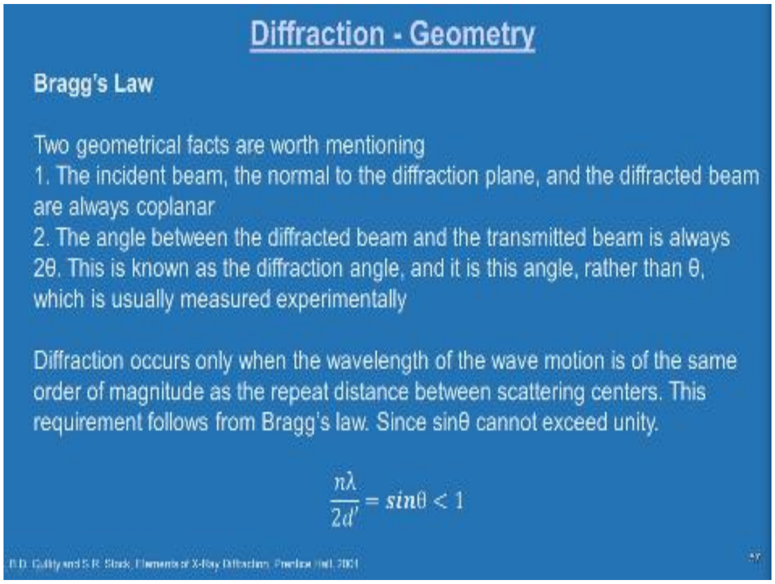

Diffraction - Geometry

Bragg's Law

Two geometrical facts are worth mentioning

1. The incident beam, the normal to the diffraction plane, and the diffracted beam are always coplanar

2. The angle between the diffracted beam and the transmitted beam is always 2θ. This is known as the diffraction angle, and it is this angle, rather than θ, which is usually measured experimentally

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 sinθ cannot exceed unity.

$$\frac{n\lambda}{2d'} = \sin\theta < 1$$

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

So we will see the significance of this further to 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 refraction 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 diffract meter in the laboratory and we will discuss about the significance of this 2θ versus θ a let us look at the another important remarks diffraction occurs only when the wavelength of the wave motion is of the same order of magnitudes the repeat distance between scattering centers this requirement follows from Bronx law since sineθ cannot exceed unity where this is very important so that clearly implies λ by 2 D prime is equal to sineθ less than 1.

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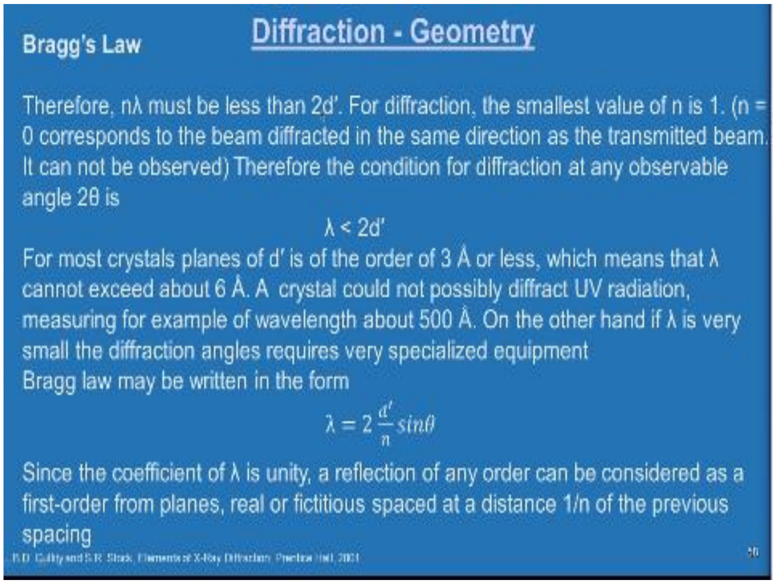

Bragg's Law

Diffraction - Geometry

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 can not be observed) Therefore the condition for diffraction at any observable angle 2θ is

$$\lambda < 2d'$$

For most crystals planes of d′ is of the order of 3 Å or less, which means that λ cannot exceed about 6 Å. A crystal could not possibly diffract UV radiation, measuring for example of wavelength about 500 Å. On the other hand if λ is very small the diffraction angles requires very specialized equipment

Bragg law may be written in the form

$$\lambda = 2\frac{d'}{n}\sin\theta$$

Since the coefficient of λ is unity, a reflection of any order can be considered as a first-order from planes, real or fictitious spaced at a distance 1/n of the previous spacing

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall, 2001

Therefore n λ must be less than 2 D ‘for diffraction the smallest value of 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 2 θ is λ less than 2 D Prime so what is the significance of this statement for most crystals planes of D prime is of the order of 3 angstrom or less which means that λ cannot exceed about 6 hang straw a crystal could not be possibly diffract UV radiation measuring for example of wavelength about 500angstroms.

So that is the implication the your D spacing and lambda 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 Bragglaw like this λ=2 D’ n/sineθ since the coefficient of lambda is unity here are reflection of any order can be considered as the first order from Plains real or fictitious spaced at stands 1/n of the previous spacing excuse me

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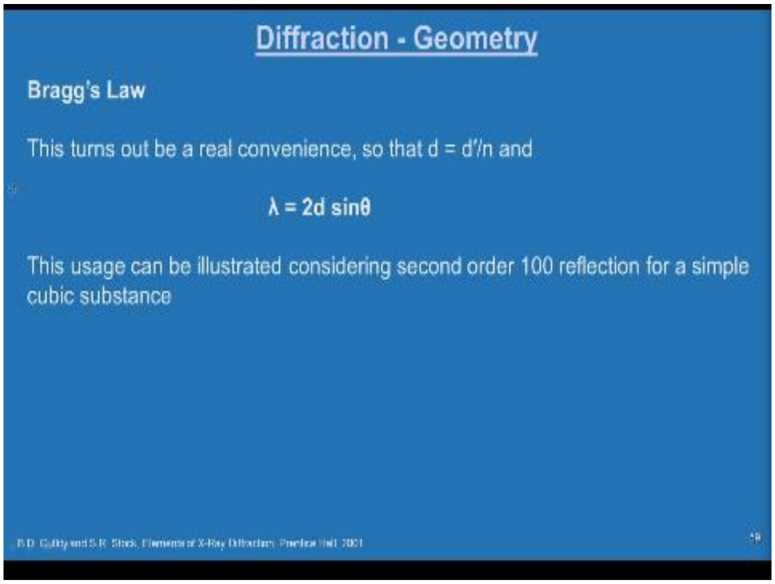

Diffraction - Geometry

Bragg's Law

This turns out be a real convenience, so that d = d'/n and

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

This usage can be illustrated considering second order 100 reflection for a simple cubic substance

B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, Prentice Hall 2001

So this turns out to be a real convenient so the D =D’/ N and we can write a general form λ=2 D sineθ. We can demonstrate this usage of this kind of writing this Bragg law by considering a second-order one zero deflection for a simple cubic substance so what I will do try to illustrate this on the black board.

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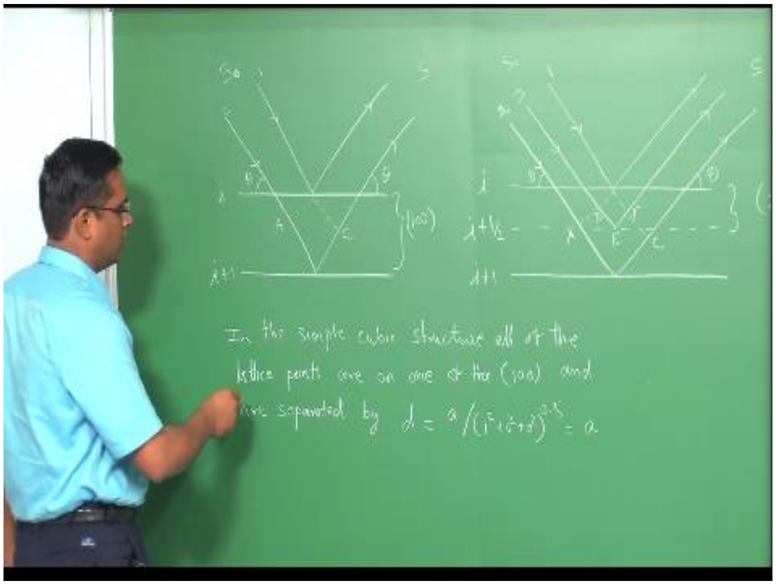

In the simple cubic structure all of the lattice points are on one of the (100) and are separated by $d = a/(1^2+0+0)^{0.5} = a$

what I have just drawn here is you have1.0 plane in a a cubic crystal where you have a plane and I a plus one plane and you have this incoming race and this is an affecting race 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 a 2lambda so that means suppose if there were some scattered if you assume in the I plus half clean they will scatter the atoms sitting on i+1items/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+I will have the phase difference of a lambda here it is2 λ.

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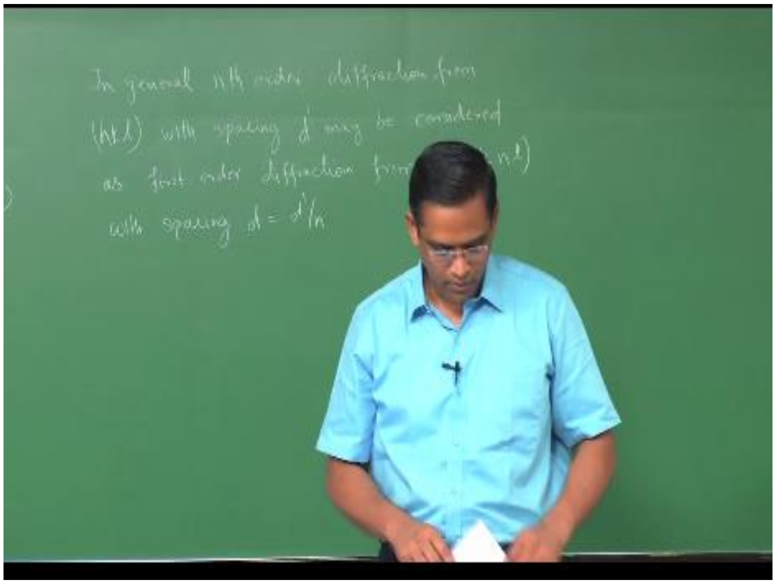

In general nth order diffraction from
(hkl) with spacing d' may be considered
as first order diffraction from nl)
with spacing $d = d'/n$

So what we can write is order diffraction so considering this the equivalence of a second-order reflection from 1 0 0 and the first-order reflection from 2 0 0 we can make a general statement in generality order diffraction from HKL with the s pacing D Prime may be considered as a first-order diffraction from NH n K genielle with spacing D =D '/n.

So with that we'll be able to understand the kind of refracted 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