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**Lecture – 04**
**X-ray diffraction: Crystal structure determination**

Hello friends, let us start with a new topic and we have already seen the different crystal system crystal structures. And one of the way of finding out that which is the crystal structure in a particular material or what is the crystal structure then that is X-ray diffraction is the technique to you find out that what crystal structure is present in the material.

So, today's topic we will see what do we mean by diffraction ok, how I can use X-ray diffraction to know that what type of crystal structure is present? Of course, we will take example of on the cubic materials till now for now. Because usually all our metallic materials either have cubic structures or hexagonal structures most of them are cubic structures.

So, we will not go into lot of details of how you can find out the intensities; X-ray intensities after diffraction of different material. We will just concentrate on that how this intensity is the diffraction intensities are affected by the crystal structure and how from my X-ray diffraction pattern, I can find out the information about the crystal structure.

So, the two son and father team of William L. Bragg and William H. Bragg in 1913; they used this concept of a spacing between two parallel planes which is called d spacing ok; they use that to mathematically determine an equation which tells us that what; at what angle the diffraction is going to take place ok. So, you have X-rays you have d spacing between two parallel planes and using that you will be able to find out that what at what angle the diffraction is going to take place.

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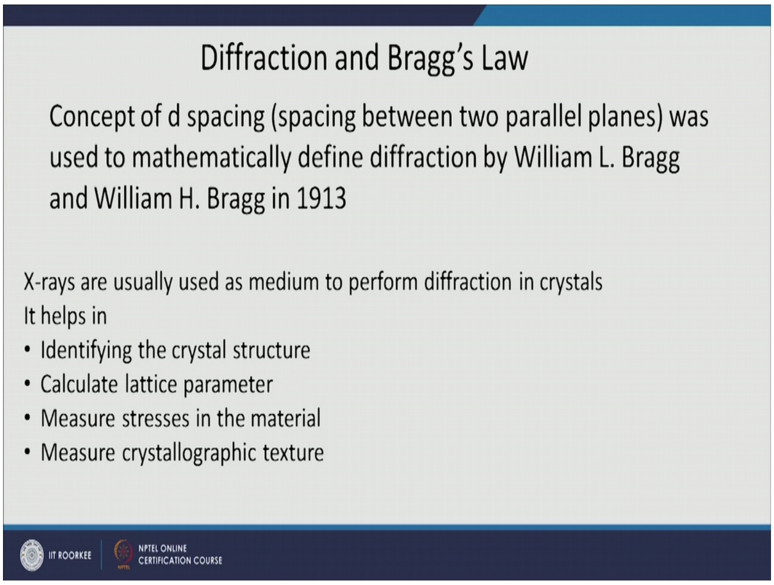


And for that they got Nobel prize and I can use this X-ray diffraction technique to identify the crystal structure as I have I have already told you and which is which is the topic of today's lecture. You can also calculate the lattice parameter of a material or of a unit cell, you can measure a stresses in the material the residual stresses when you do any metal working or you do welding for example, there are large number of a stresses which are present in the material ok.

So, you can find out or you can do some estimate of these stresses which are present in the material using X-ray diffraction. And you can also measure a what we call as crystallographic texture that is one of the characterization technique of the material by which we know that what is the preferred orientation in the in your material ok.

But we are not going to do all these three things; we will be just concentrating on the crystal structure part for now. Before coming to the diffraction part let us just see what are the properties of X-rays. Before that there is some nice trivia about X-rays that how they were discovered. So, Wilhem Conrad Rontgen accidentally discovered these rays in 1895; he was doing some experiment and he took first X-ray photograph of his wife ok.

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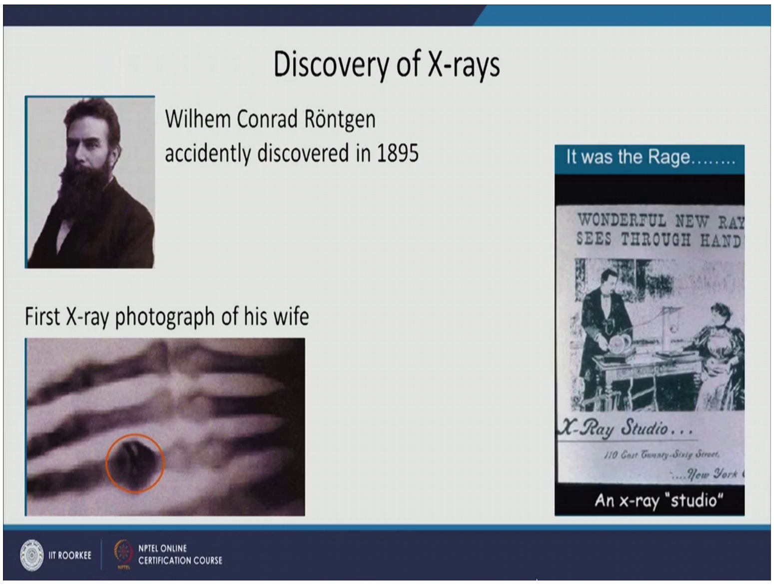


So, you can see in the bottom picture in you can see all the bone structure of a her hand ok. And in fact, you can also see the ring which she was wearing ok. So, these are all bone structure and the ring is their her middle finger.

In fact, people were using there was so, much euphoria about this new type of rays that there were X-ray studios at one point of time. And people were going there and taking photograph of their hand or any body part just to know that there was some curiosity about these rays and they were just going for fun and taking photographs.

So, that was the craze when it was discovered, some technical aspects of X-rays the range of wavelength.

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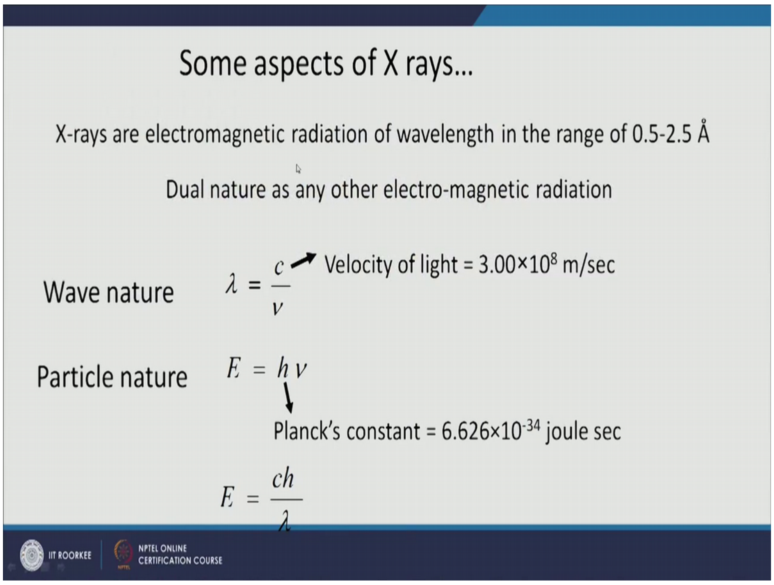


This is also an electromagnetic radiation and the wavelength is in the range of 0.5 to 2.5 angstrom depending upon which X-rays you are using. It also has a dual nature as any other electromagnetic radiation ok, it can give you a wave it also shows a wave nature ok; where wavelength you can be related to the frequency with velocity of light or it can have a particle nature where it you can give a quanta of energy to the X-ray photon which is again related to the frequency with Planck's constant the value of Planck constants is a constant is also given here.

And you can combine both the particle nature and wave nature and you can now relate the wavelength with the energy. So, if you see this equation here, if my wavelength is a small the energy of the that particular electromagnetic radiation will be very high. And that is why visible light cannot go through our body for example, where if you have any problem in our bone; if we have a fracture we go to the X-ray machine they take photograph and find out there may be a hairline fracture or something like that ok.

So; that means, it transmit through our body ok. So, they these X-rays must be having very high energy so, that they are they are able to go through the human body visible light cannot do that. So, the reason for that is that because the wavelength of X-rays is are very a small, they have very high energy as you can see there is a reciprocal relationship between the two. So, if you keep on decreasing the wavelength the energy of the; that particular electromagnetic radiation will keep on increasing.

Now, let us come after knowing something about X-rays that these are electromagnetic radiation of various low wavelength; how people thought of using X-rays for understanding something which is at atomic scale ok? The idea came from I think you must have done some physics experiment using diffraction gratings where you we use visible light and there is a ruled grating. And there you see this high more light, darker region again lighter region and so, on then that is the actually a effect of the diffraction.

Another good example of if you want to understand diffraction is that when you use any radio ok. And suppose our windows always have some kind of grill in that and this radio also has a radio some electromagnetic radiation. So, some waves are coming your radio is receiving those waves and you are listening to some beautiful song.

So, when it goes through this grating; this electromagnetic radiation now you please understand that radio waves are having very high wavelength well the wavelength is very large as compared to X-ray it is in meters or centimeters ok. So, when it is going through this grating in our window, it also gets diffracted.

Because this is also a electromagnetic radiation it is going through some grating or some regularly spaced object. And because of the diffraction you will see that your radio receives signals at some places; it is receive very high signal ok; at some places it does not receive very good signal ok. The quality of the reception changes if you roam around in your house and that is the effect of diffraction actually ok.

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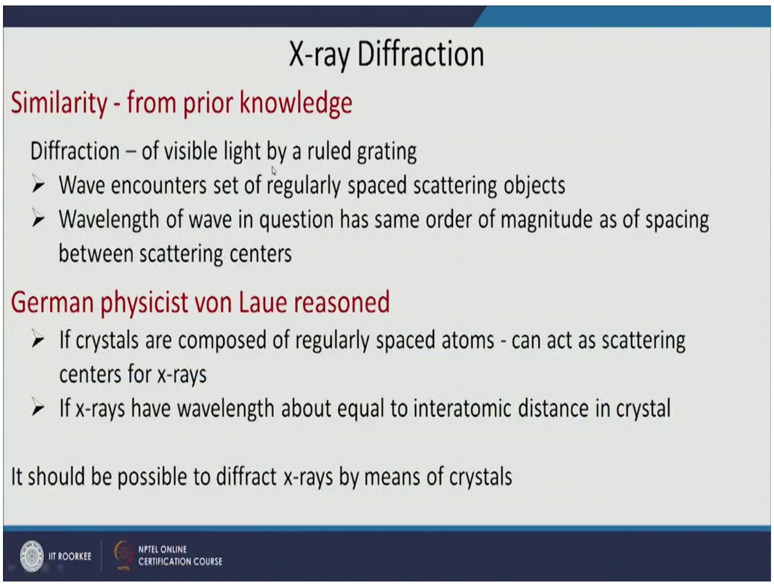

So, already people knew before a X-rays were discovered that in visible light if you take ruled grating. So, that is ruled grating means that is a regularly spaced a scattering object is there ok. So, then wave will; this particular wave the visible light will have this diffraction effect ok. And somewhere you will see a more light somewhere you will see a darker region; that means, less light is there so; that means, some diffraction effect is taking place ok.

So, when X-rays was moreover discovered then there was another German physicist one law he reasoned that atoms in the crystals are also arranged in a regular pattern ok. And they have as we have all that had already seen in lattice that there is a translation symmetry; so, these are regularly a spaced arrangement of atoms. And of course, the distance between them is in angstrom some in the some value of in angstroms; X-rays also are electromagnetic radiation which is in angstrom.

So, if my this X-ray waves interact with this regularly spaced atoms ok; there must be some effect like diffraction should happen ok. So, he reasoned that you can use X-rays to do a diffraction study in crystals and by that we will be able to know a lot of details about the crystal ok; a very nice idea. And from that the Bragg that is a actually a father son team was there they were doing experiments and they thought about this diffraction experiments. And they actually give it a very nice mathematical equation to understand the whole diffraction phenomena and this is what they thought about it ok.

So, before coming to that the diffraction effect let us see what do we mean by different type of interference when you are dealing with electromagnetic waves?. So, this is what we call as constructive and destructive interference; so, this is one wave.

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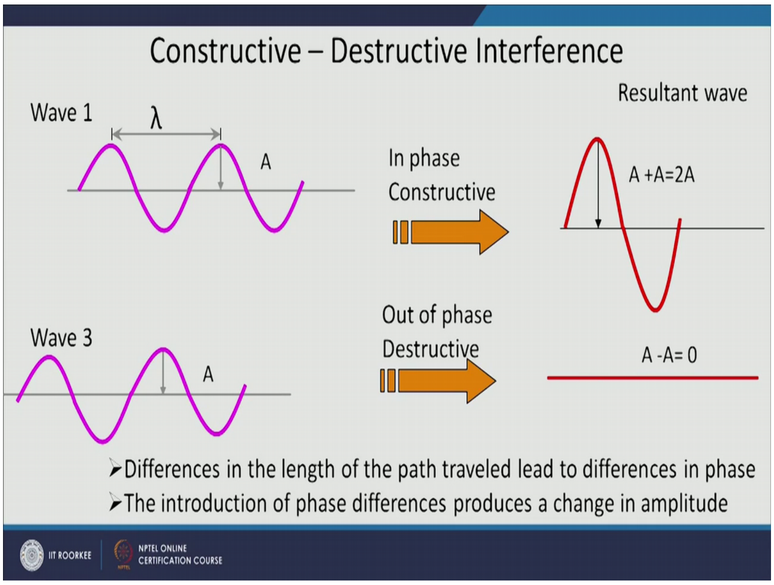


With a wavelength of lambda here and it has any amplitude A, there is another wave which also has an amplitude here sorry; another wave maybe I will show it on this I think it is going to fast there ok.

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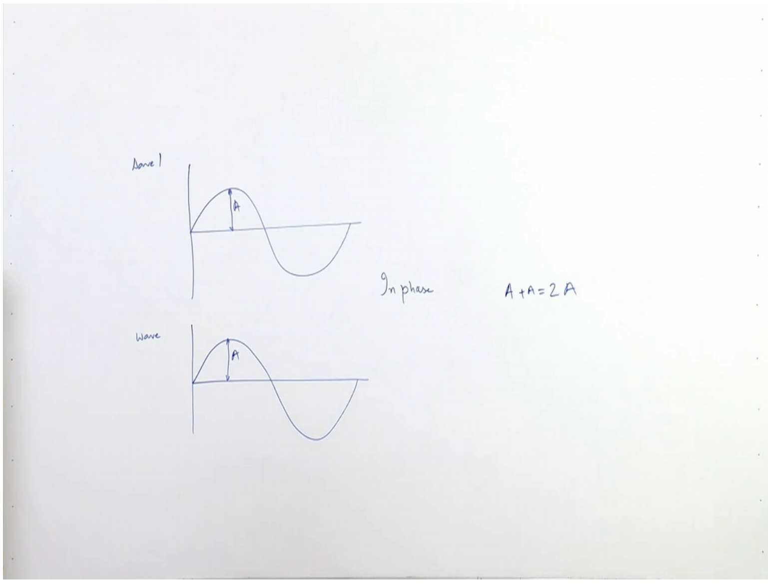


So, this is one wave 1; I am calling it as wave 1 and suppose there is another wave here which I am calling as wave 2 ok. And in this case suppose their wavelength is same and in this case they are in phase ok; you can see that their minima and maxima are matching with each other; so, they are in phase.

So, when you have this condition of in phase the resultant wave will be; if this is my amplitude A for both the waves because of they are of similar type, then the resultant wave will have an amplitude of A plus A; which is equal to 2 A. So, when you have in phase interaction or interference between two waves, then we have a constructive interference and you will have a magnitude which is summation of both the amplitudes, but we if we have a third wave ok, but now it is not in phase ok.

So, let us say this is our third wave here.

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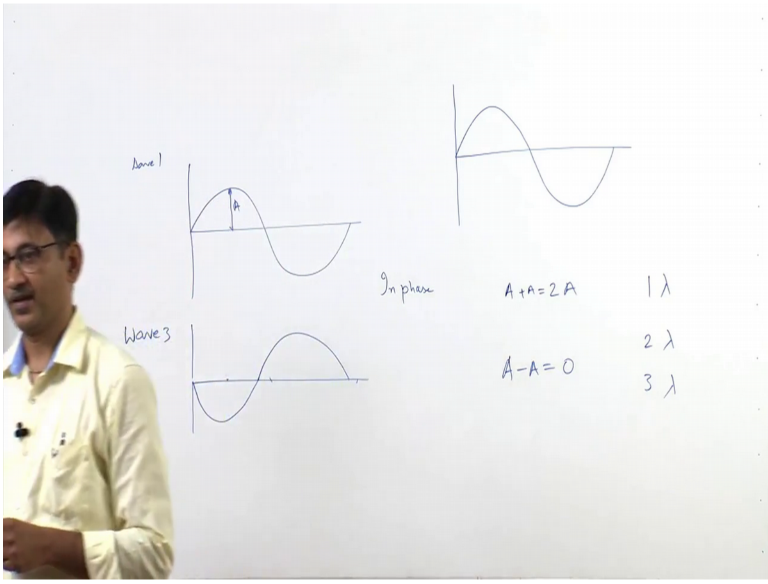


So, now I am calling it as wave 3 and now this is not in phase and where the maxima is coming let us say we have minima here and then it is going like this. So, it is completely out of phase it is at 180 degree phase difference will be in the first one ok. So, where the maxima is here you are seeing minima; so, it is cancelling out, where the minima is here it is maxima here and again it cancels out ok.

So, now, the resultant wave will be having amplitude of A minus A and which is actually 0. So, it is having a destructive interference in this case it is out of phase. So, diffraction takes place when the two waves are in phase or there what we call we they have constructive interference then only you will have diffraction ok.

So, this is what is summarized here the differences in the length of path travelled lead to differences in phase and the introduction of phase difference produce a change in amplitude ok. So, this is what now we know that X-rays have wavelength which is in atomic range or atomic scale; some angstrom. The distance between the regularly spaced atom in crystals; they are also in that range angstroms. So, some few angstrom less than 5 angstrom usually.

We also know that when X-rays interact with each other and if they are in phase; then you have a constructive interference, if they are out of phase they have destructive interference.

So, now using all this knowledge ok; we can understand that how the diffraction happen in a at in a crystal using X-rays ok.

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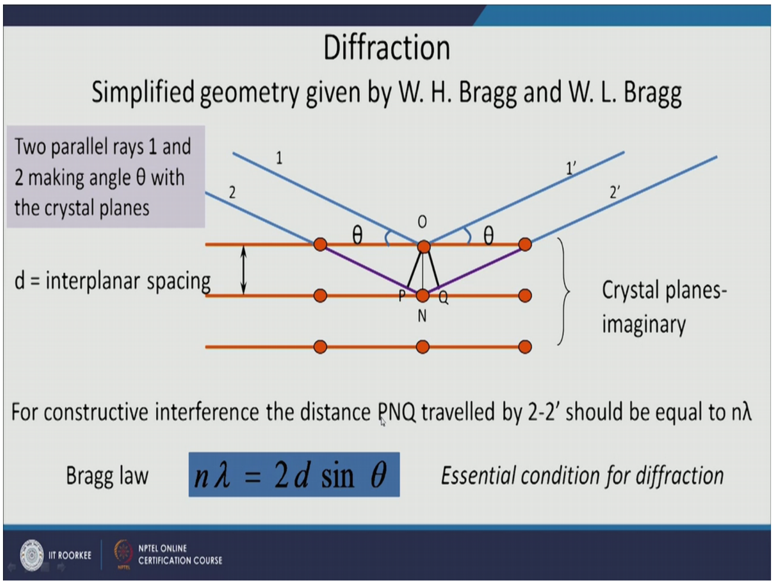


So, that is what is shown here these are atoms in a one in a particular plane regularly spaced atoms ok. So, now, we know that the atoms are regularly the; in the crystal atoms are arrange in regular pattern ok. And this distance between the atoms in is in angstrom range usually less than 5 angstrom.

The X-rays their wavelength is also in angstrom range as we have seen and when these two will interact there is going to be some diffraction ok. And the diffraction is due to when the two waves interact ok, they can interact in a constructive manner in which case the resultant wave will have amplitude of both the waves ok; addition of both the waves or if they are interacting in a destructive fashion ok, they will cancel the intensity or amplitude of each other ok.

So, the diffraction ah; the diffraction phenomena is due to in constructive interference of two waves or multiple waves. And that is what is explained by the Bragg condition of diffraction that how the X-rays are interacting with the crystallographic planes and how; when you will get the constructive interference there the condition was given by the Bragg law.

So, now there is one schematic here ok; you have the crystal planes here and the atoms are regularly arranged here in crystal planes. Now suppose there are two parallel rays; 1 and 2 which are falling on this particular crystal ok; at an angle theta it is making an angle theta with the crystal planes ok. So, let us see these two waves are coming and it got a scattered from this atom, another ray coming and it got a scattered from this atom.

So, now if you see these two parallel rays which were in phase before they interacted with the atoms ok. So, if you see the distance which they have travelled up to this particular plane which is shown by O P here; they have travelled a common distance ok. The distance travelled by these two wave is same; so, if they are in phase they will remain in phase up to this particular plane which is given by O P if they remain out of in phase after O Q ok; then you will have constructive interference ok.

So, when it will have a constructive interference? If the distance travelled between P and Q is some integer multiple of the wavelength. So, constructive interference will be there when you have the phase difference as either as 1 lambda, 2 lambda, 3 lambda, 4 lambda and so, on. So, basically the integer multiple of lambdas will give you constructive interference ok.

If my this distance which is travelled by this second wave in P and Q if that is equal to integer multiple of lambda ok; then the whatever ray which is coming as 2 prime here that will also remain in phase with the 1 prime; which is which is scattered from the this top atom ok.

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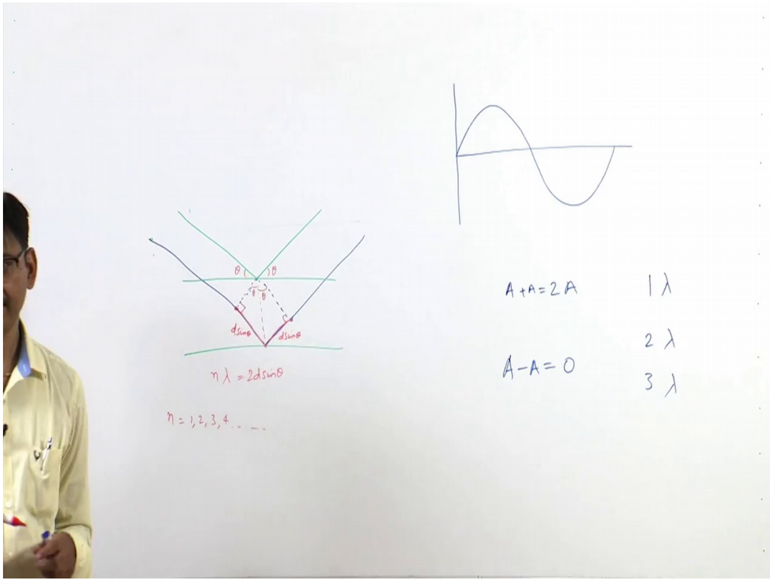


So, if this is. So, if I want to do as simple mathematics here ok. So, first ray is coming like this and going like this, the second ray which is parallel to this in phase is let us take; so, that is going like this ok. And we have drawn a perpendicular on the second ray from this point two perpendiculars. And we are saying that if this extra distance travelled by the second ray from here to here ok; if it is some integer multiple of lambda then you will have constructive interference ok.

And we know this angle is theta which is the ray is making with the crystal planes. So, if you do a simple trigonometry; you will know that this angle is going also going to be theta ok. And if this angle is theta I have to find out this particular distance here ok. And which is going to be this theta angle and this is angle 90 degree here ok. So, this is 90 degree this is going to be sin theta ok. So, I have two sin thetas; one which is here another one is here; so, sin theta plus sin theta will give you two sin theta.

So, if you do the this simple trigonometry then I will say that the Bragg law will be given by n lambda is equal to 2 d sin theta. So, this distance is going to be d sin theta and d sin theta which is 2 d sin theta. And as we have said that it should be integer multiple of lambda; this extra distance which has been travelled. So, that I am saying is equal to n lambda, where n is equal to any integer.

So, this is my essential condition for diffraction and this simple equation was given by this and the team of father and son W H. Bragg W L. Bragg and they got Nobel prize for giving this particular equation here ok. So, once I know that what is the angle theta and what is the wavelength of X-ray then I can calculate what will be the d spacing ok.

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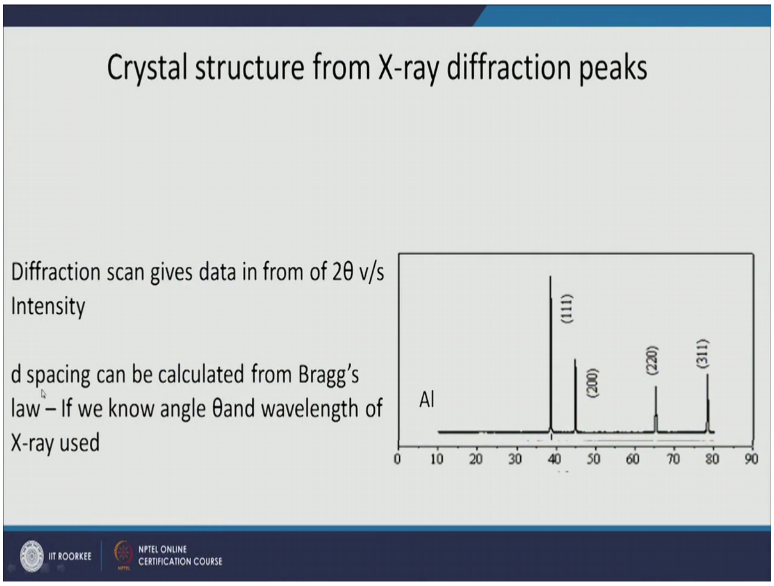


So, when you do a X-ray diffraction experiment you get what we call as this x axis is the two theta angles and the y axis is the intensity ok. So, it is intensity versus two theta angle.

So, from two theta angle we will get angle theta; so, between the angle theta and wavelength as we saw in the previous case. So, if I know the lambda and I know theta then I can find out what will be the d spacing ok. And from d spacing I will be able to tell that which are the crystallographic planes which are taking part in the diffraction ok; one simple diffraction pattern is given here for aluminum and the planes which are taking part in the diffraction is also given here ok. And at what angle they are going to diffract that is also given here and, but please remember that this axis is and 2 theta ok. So, all these intensities and what planes are taking part in diffraction these are given ok.

Now, how I can use this particular information to find out about crystal structure? For that we need to know that in a particular crystal structure which particular planes are going to take part in diffraction and which are not going to take part in diffraction.

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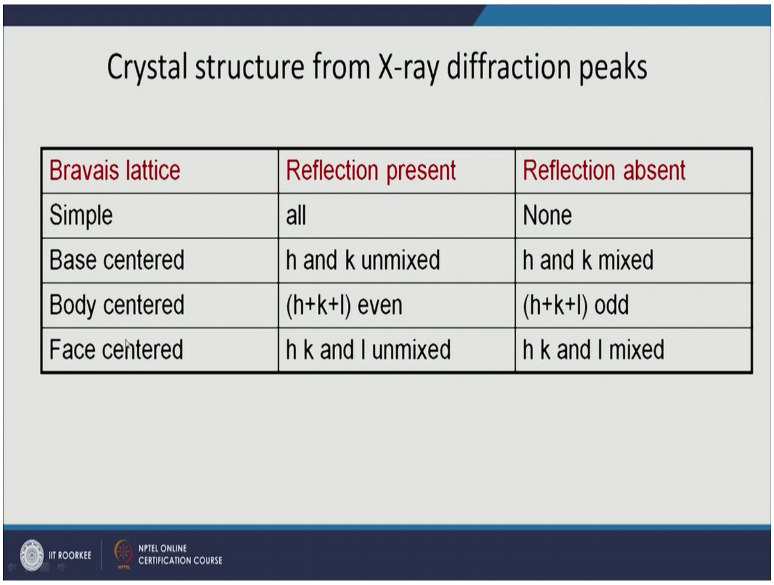

Crystal structure from X-ray diffraction peaks

| Bravais lattice | Reflection present | Reflection absent |
|---|---|---|
| Simple | all | None |
| Base centered | h and k unmixed | h and k mixed |
| Body centered | (h+k+l) even | (h+k+l) odd |
| Face centered | h k and l unmixed | h k and l mixed |

So, for example, in case of if we take different Bravais lattice here ok. So, you have simple it can be cubic, it can be any other ah; from any other crystal system you can have base centered again it can be cubic sorry it can be any other crystal system, you can have body centered which can be cubic or from any other crystal system or you can have face centered ok.

So, we are not specifying here that whether this is from a cubic crystal system or from any other system ok. What we are saying that if it is body centered, it may come in any particular crystal system or if it is face centered ok; it can be also in any crystal system ok. If it is so, then these are the rules for getting the reflection from a particular plane ok.

For example, in case of simple Bravais lattice planes are going to take part in diffraction ok; so, there will not be any plane which is not taking part in the diffraction ok. If you take a base centered crystal you will have reflection from h and k only when they are unmixed ok. So, now, what do we mean by unmixed?

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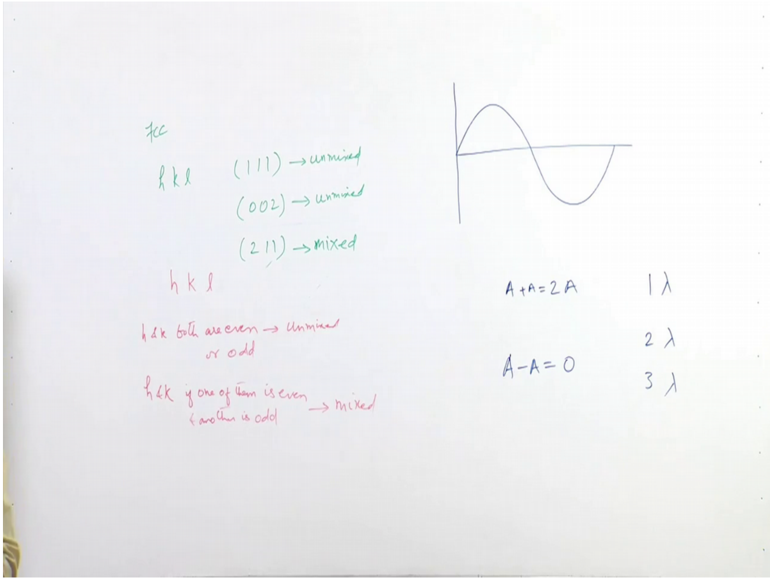


Unmixed means when you talk about the crystal planes we say h k l planes ok. So, if h and k both are even then they are suppose h and k both are even, then this is unmixed both are even or odd in both the case it is will be unmixed. If one of them is even and one of them is odd ok; if from out of h and k in this particular case right now, if one of them is even and another is odd then this is the condition what we call as mixed ok.

So, in case of base centered; if h and k are unmixed, you will have reflection will be there; that means, you will get a diffraction peak. If h and k are mixed ok; that means, one is even one, other is odd then there will not be any reflection ok. If we come to body centre if h plus k plus l is even; then you will have reflection. If h plus k plus l is odd then the reflection will be absent ok.

In case of face centered, if h k and l are unmixed again all has to be even or all has to be odd. For example, what do we mean by all even all odd? Let us say h k l in case of this face centered f c c; if I have 1 1 1 plane ok; that means, this is unmixed all the planes are odd ok.

So, this is unmixed if I have suppose let us say 0 0 2 then it is also unmixed please. Remember this the 0 here is going to be even. Whereas, suppose I take a plane like this 2 1 1; this is a mixed plane ok. So, I will not going to have any X-ray diffraction peak from this particular plane in case of f c c, but in this cases I will have a reflection ok.

Now, you can again see what I showed you in the previous slide ok. This is for aluminum the diffraction peaks for aluminum you have diffraction peak from 1 1 1 plane; which is unmixed all h k l planes values are odd. You have diffraction peak from 2 0 0 plane ok; so, all are even you have diffraction peak from 2 2 0 ok.

Again all are even you have diffraction peak from 3 1 1 again all the h k l values are odd; that means, that you will get diffraction from a face centered any Bravais lattice only when you have unmixed h k l planes ok; in case of mixed one you will not get.

So, this is how you can take help of the diffraction pattern to identify that what type of crystal system is there or what type of Bravais lattice is there; using the information from the X-ray diffraction peak ok. So, this is what is given in a tabular form; actually I am not covered in this is how it is derived because and then we have to go into lot of details about that how X-ray interact with atoms and how their phase shift is there because of the interaction ok, how the scattering takes place ok?

So, that is kind of a more involved understanding for a very advanced course in characterization if one take a course in characterization, but for this particular course ok, this much understanding is enough that we can use this X-ray diffraction studies to find out the information about the crystal system.

Thank you.