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

Prof. Ashish Garg
Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture- 35
X-ray Diffraction (contd.)

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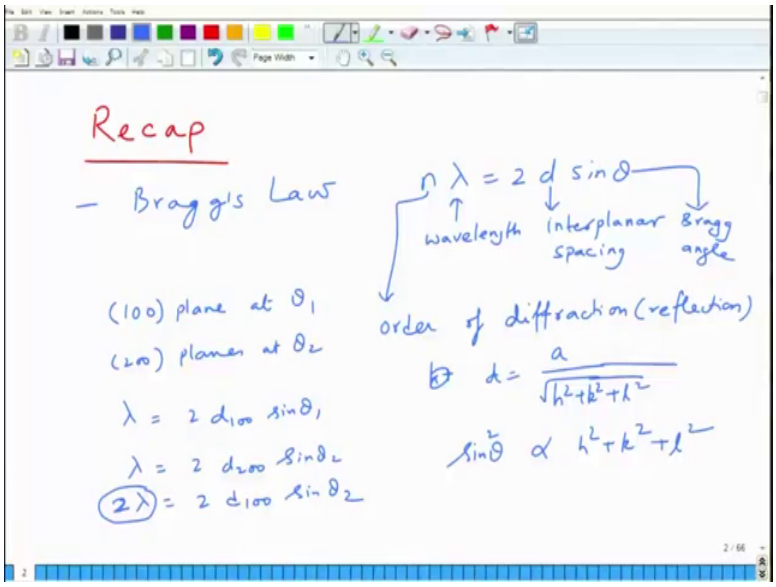

So, good morning again, we start with a new lecture 30, lecture number 35 continuing on X-ray diffraction; So, just a brief recap of last lecture that we looked at the Bragg's law. So, basically Bragg's law is the holy grail of X-ray diffraction at least for beginners, which is defined as n lambda is equal 2 d sine theta, where lambda is the wavelength of radiation which is typically around 1.5 Angstrom. d is the inter planar spacing, and theta is the Bragg angle, and n is the order of diffraction or reflection all right.

So, we discussed that we discussed the significance of all of these parameters that if you have if material has higher, so you can see that there is a reciprocal relation between d and theta. So, for as your planar spacing goes down, so as you move on from h square plus, so d is equal to a divided by square root of h square plus k square plus l square. So, basically your sine theta, sine square theta is proportional to h square plus k square plus l square.

So, as your inter planar spacing goes down, the peaks appear on higher angles because the sine theta increases. And this is for a monochromatic radiation. So, we in most cases at least for powder diffraction, we take lambda to be constant all right. And n is here order of diffraction which basically means that if you have a diffracting peak for one 1 0 0 plane at say theta 1, then 2 0 0 plane will diffract whether imaginary or not at an angle theta 2 which is higher than theta 1 because 2 0 0 plane is placing your half of 1 0 0.

But by this equation you can see that for the for 1 0 0 it is lambda 2 1 0 0 sine theta 1. Whereas, for 2 0 0 the first order diffraction would be 2 d, 2 0 0 sine theta 2 d 2 which is equivalent to writing 2 lambda 2 d 1 0 0 sine theta 2. So, essentially what I mean to say is that at higher angles, the first order 2 0 0 reflection is same as second order 1 0 0 reflection all right. So, this is what basically because your path length now has become 2 lambda. So, basically the path length is 2 lambda; in the previous case the path length was lambda, so this is what means.

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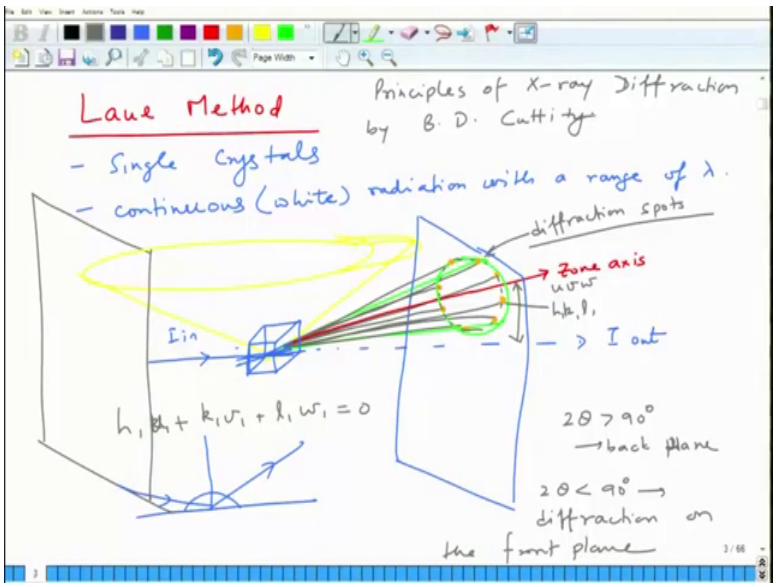

Now, let us look at the various methods, which are used for carrying out X-ray diffraction on various materials. So, we first begin with Laue method which is a method typically for single crystals. And we use basically continuous radiation or you can say white radiation with a range of lambda ok. So, basically what happens is that you have a you have a crystal like this, and this is this is a single crystal in fixed orientation all right. So, this is let us say a single crystal like this ok.

Now, single crystal will have planes at different angles. Now, if the beam orientation is fixed this is I in, and this is you can say is I out ok. If your if the plane orientation is fixed and only planes which are going to diffract are the planes whose which make appropriate angle with respect to the incident and diffracted beam which satisfy the Bragg geometry.

So, as a result, if you keep a screen on front, so if you keep a screen on front here somewhere here, so this was this is this was a X-ray screen on which the diffracted spots are going to go. So, you can have diffracted spots going in various directions; and diffracted spots go in such a manner so that they form a cone and the diffracted spots will lie like this.

So, not all not all planes will diffract only those planes will diffract which make a right angle, right means not 90 degree, but correct angle or appropriate angle satisfying the Bragg's geometry. Which means whatever plane is going to diffract must satisfy theta in is equal to theta out, and they must also satisfy n lambda is equal to 2 d sine theta.

So, only those only those planes are going to diffract, and that diffracted beam is basically going to appear like a spot on the screen. And it turns out you can prove crystallographically that these planes which will diffract they so they make a sort of cone ok. And the cone basically may lie up to the bottom. And the center of the cone is basically what we call as a zone axis, this is zone axis, and these are all diffraction spots diffraction spots.

So, then we need to carry out an analysis because if these are the spots from the diffracting planes which I have a common zone axis then we know v zone law right. V zone law says that for at least for a the dot the dot product of h, k, l, and u, v, w must be equal to 0. So, if these planes, so if this was u, v, w and these planes had a let us say h 1, k 1, l 1, and h 2, k 2, l 2, so we will have this condition as h 1, k 1, h 1, u 1 plus k 1 v 1 plus l 1 w 1 is equal to 0.

So, you will form a series of equations which you solve and determine what is the zone axis and what are these spots. You will need to do a bit of crystallography here, unfortunately we cannot get into the cannot get into the details of that, but nevertheless.

So, what basically it means is that you will have a zone, you will you will form a cone and this is the transmitted beam typically the angle. And we know that the angle between so for most of these the plane orientation would be so if you if you combine these two lines, some plane would be like, that some plane would be like this.

So, if you if you if you combine this line some plane would be like this. So, planes will have different orientations, but not all planes only those planes which have appropriate inter planar spacing and angle satisfying the Bragg's law that is why we use variable lambda that is why we use variable lambda. So, that we can we have a higher probability of finding a plane which can diffract ok.

If you have a fixed lambda then you are going to find only for a fixed orientation, you may or may not find a plane, you may not find actually any plane all right. If no plane is satisfying that orientation, you will not have any diffraction that is why you choose variable lambda, so that at least one particular lambda will find a one particular plane from which the diffraction may occur, so that is what it is going to look like. So, you will have this you can do so for angles which are smaller than 90 degree, you will have forward coming diffraction pattern.

So, you can see that if this is your Bragg angle and this is the incident beam this is you forward coming beam. So, for higher angles the peak will go on the backside because this angle is 180 degree right. So, anything which is for which 2 theta is less than 90 degree, you will have diffraction on the forward side; and for anything which has diffracted peak having 2 theta more than 90 degree it will go on the backside; So, for this kind of thing actually the cone would be little bit down. So, you will have diffraction taking place nearly close to the eye out. And this angle is the angle between the zone axis and the reflected beam.

So, the others the so for 2 theta being equal greater than 90 degree, you will have back diffraction on the back plane, so basically the screen needs to be put on the on this side on this side. And the diffraction cone would be if I draw using this, so diffraction cone would be like this will be a diffraction cone very big diffraction cone very wide diffraction cone. Whereas, for this case the diffraction cone is this kind of cone ok. So, for 2 theta greater than 90 degree you will have backplane, and for 2 theta less than 90

degree you will have diffraction on the on the front plane. So, this is a Laue method which is typically used for determining things like.

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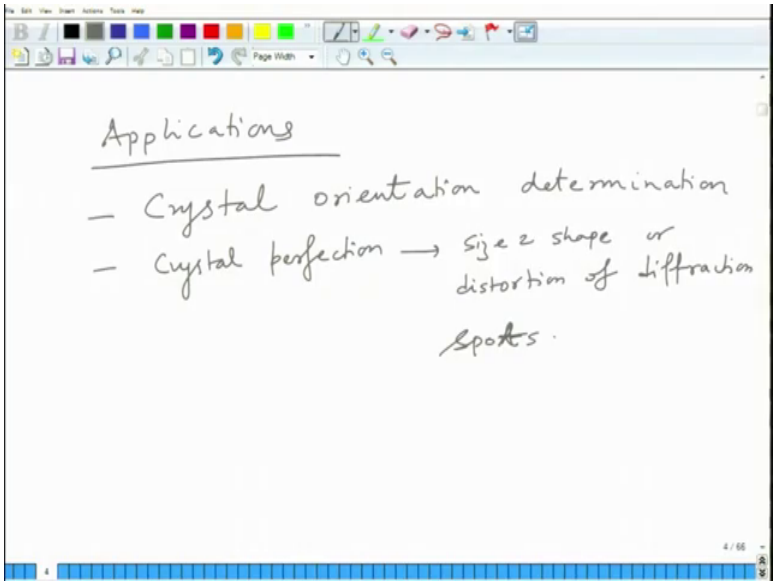

So, Laue method is used for oops applications. So, determining basically crystal orientation, if you want to get into details of it, I would suggest that you go through Principles of X-ray Diffraction by B.D Cuttity it is a very good book for beginners. So, it is useful for crystal orientation determination, it is also useful from determination of crystal perfection because from the size and shape of spots one can determine the crystal orientation from the size and shape or distortion of a spots all right.

So, this is the first method that we have here. The second method that we look for is so you can see here this these are diffracted beams right, the angle between diffracted beam and the eye out would always be 2 theta ok, just like we have in the Bragg's geometry right.

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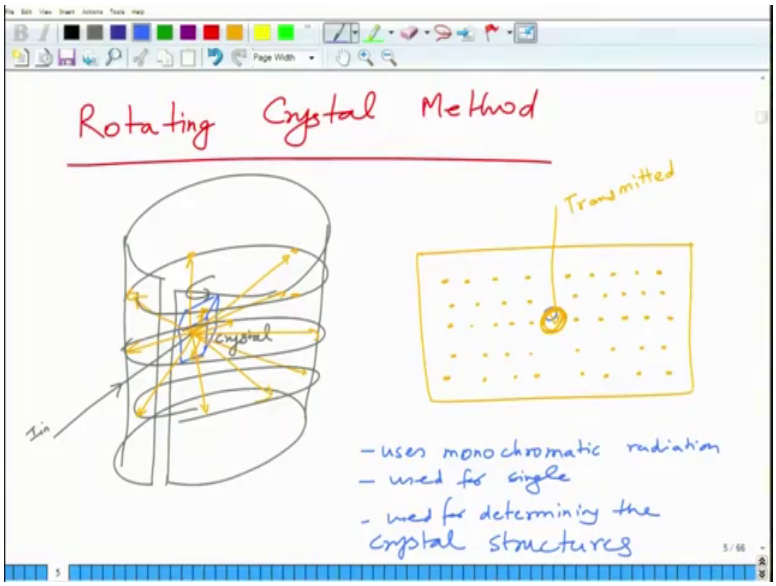

Second method that we talk about is rotating crystal method. In this method, what basically you have you have a crystal ok, the beam hits somewhere like this. This is your crystal. This is your eye in. And you are going to have diffract diffraction going on in various and it is rotating ok, it is rotating.

So, as it rotates it will expose many planes for diffraction because now you have at least one variable that your crystal is rotating ok. And you put a film around it basically you put a film around it in this fashion. And this film is going to have diffraction occurring at various angles. As a result you will have these little circles appearing on which you will have diffraction is spots. So, you will have diffraction is spots.

So, from this let us say this is one type of diffraction right, this is one angle. Second angle can give you diffraction here. Third angle can give you diffraction on the other side. So, this is how you will have a photographic film. So, when you look at the photographic, when you open the photographic film, you will have a picture like this. So, this is somewhere in between you will have transmitted beam ok, because it goes through and then you will have diffracted spots in this fashion depending upon the plane spacing and you will have these and this is the transmitted beam.

So, of course, you need to determine the distance, you need to determine the size is similar in the previous case for accurate calculation, you need to determine what is the distance, what is the size of camera film, what is the different distance between stops

spots so that you are able to convert those into angles. So, similarly here you need to know the distance between the crystal and the film size of the film, diameter of the film, and perimeter which will turn out to be. And then you determine the spacing between the spots and calculate the angles properly and then correlate with the h, k, l.

So, this uses monochromatic radiation used for single crystals. So, instead of using a white radiation, you use a rotating crystal here. And it can be used for determining for determining the crystal structures of unknown materials ok. So, this is what is rotating crystal method. These two these two methods are typically used for um analyzing the structure of single crystals.

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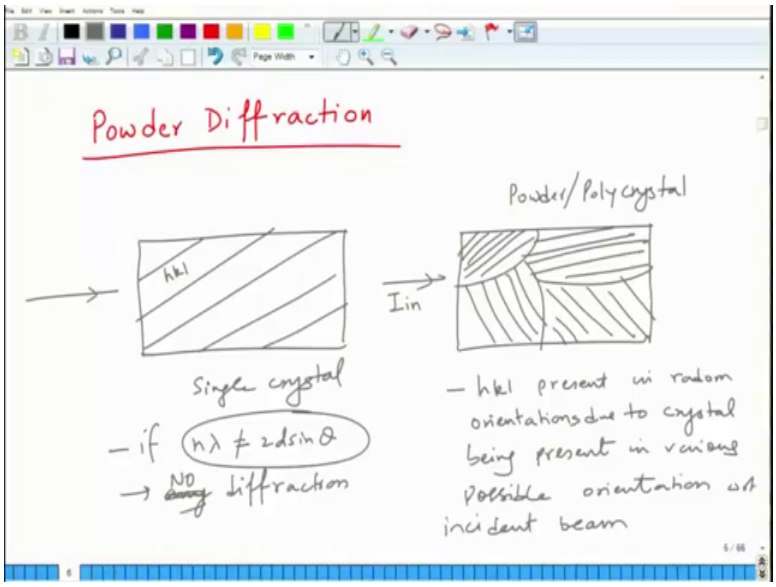

The more common method that we use generally as a material scientist is powder diffraction. And we use powder diffraction because as against single crystal we have plain orientation, there is only one set of plane at given angle with respect to the incident beam. In powder diffraction since the powder, powder is nothing, but multiple single crystals in random orientations.

So, millions and zillions of single crystals, tiny single crystals which are in random orientations. As a result what happens is that if you if you just look at a macroscopic picture of powder, so let us say you have a plane h, k, l. If this was single crystal and you will have only one set of h, k, l plane with respect to the incident radiation, and if that is

not satisfying the Bragg's condition you will not have any diffraction this is in case of single crystal.

So, if n lambda is not equal to 2 d sine theta, you will not have any no diffraction ok; if this equation is not satisfied, because you have only one set of plane at a given orientation. Now, in case of powder sample what happens is that in certain region you will have hkl like this, but in the other region your hkl will be like this.

In other region your hkl could be like this; in the other region your hkl could be like this. So, you have multiple possibilities, millions of possibilities of orientation. So, when the beam comes it will always find a plane of plane which is satisfying it is always find a set of planes which will which will satisfy the Bragg's law with respect to the, so this is I in.

So, hkl present in. So, this is powder or you can say poly crystalline material poly crystal, hkl present in random orientations due to crystals beam present in various possible orientations right with respect to incident beam. As a result you will always have some set of planes which will satisfy Bragg's law. So, one hkl will diffract, so all the hkls will diffract, in this case and you will have all you need to do is that you need to move your detector to carry out to collect those spots.

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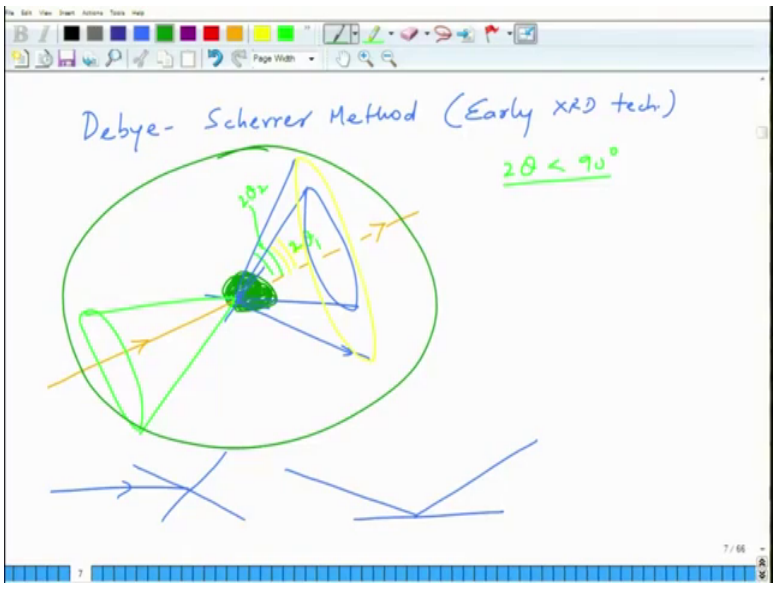

So, first initially this was done on initially people used to we did not have detectors and sources and optics as we have today. So, initially what people were using that was called

as Debye-Scherrer method you can say this is early XRD technique. So, what they used to use was you have a bunch of powders this is let us say lot of crystals here ok. Your X-ray beam comes like this, this is your beam, this is your outgoing beam.

So, what will happen is that since one set of hkl planes will diffract in a given direction, you will have one cone from one set of planes because let us say if this plane is present at this angle and it is diffracting in this direction, there is always another set of plane the same plane which is presented this angle ok. So, you will have diffraction taking place in this direction.

Similarly, in 3D you will have multiple orientation. So, if I have a plane so Bragg geometry is this direct geometry ok. If this plane so this is your incident beam ok, your plane can be present like this, your plane can also be present like that, your plane can be oblique in other direction which we cannot see. So, in 3 D, it is as if you have incident beam and that diffracted beam one this, another this, another this, another this, another this, another this, so they will form sort of a cone. So, you will have a cone of x diffracted X-rays coming out of a material. So, one cone will correspond to one set of planes. So, this is one cone ok.

You will have another cone which will correspond to another set of planes. And again you can see this angle should be 2 theta. So, this is 2 theta 1, this is 2 theta 2. So, so for again for 2 theta being less than 90 degree, you will have cones going in the forward direction; but for planes for which 2 theta becomes more than 90 degree, the diffracted beam will start going in this direction.

So, you will have diffraction in the back plane. So, what to cover all of them, you keep up you keep a ring circular ring like this which is the photographic film, so that you intercept both forward cones as well as the backward planes.

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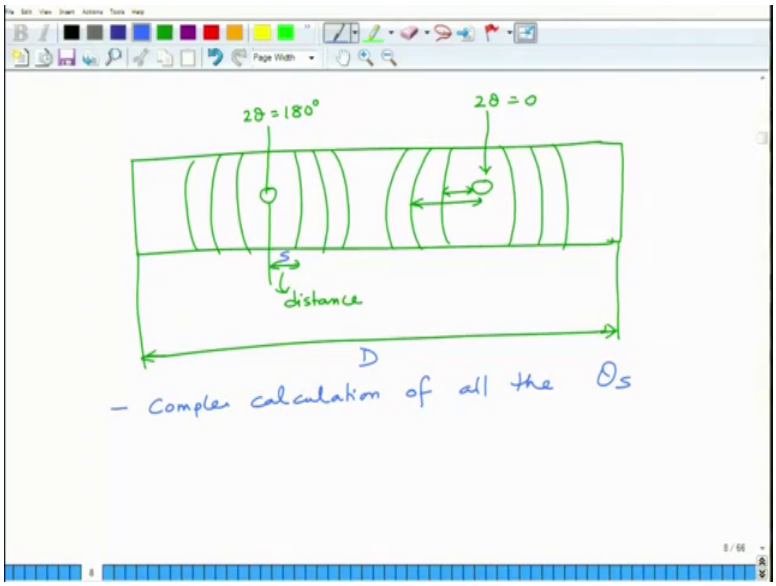

So, basically what you will have if you if you open up this film, film will be like this. This is your film all right. This is your incident beam. This is your diffracted beam. If the film is intersecting, so first cone with the lowest 2 theta, it will intercept like this right. Second one will intercept like this, this is how you will get your X-ray diffraction pattern. So, this is this is for 2 theta 0 degree. So, transmitted side this will be 2 theta 180 degree for the backward side; So, this is how you will have diffraction taking place.

So, now, what you need to know accurately a para, so you if you want to determine what is the what does this distance correspond to angles, you need to calculate the diameter, the distance and things like that. So, basically you need to know what is the distance between these two in the distance and you need to know, what is the film length right. If you know these things, then you can carry out the calculation of angles.

So, so basically what you do is that you then complete calculation of all the thetas. Once you determine all the thetas, after that you can do determination of what plane is a bit much it does it. So, now, the question that will come now is how do you determine the structure of unknown material using this kind of information. So, we will do that exercise in a little while, but from this you can determine thetas knowing these distances. So, if this is diameter d if this is distance s using S and D, you can determine what is the theta.

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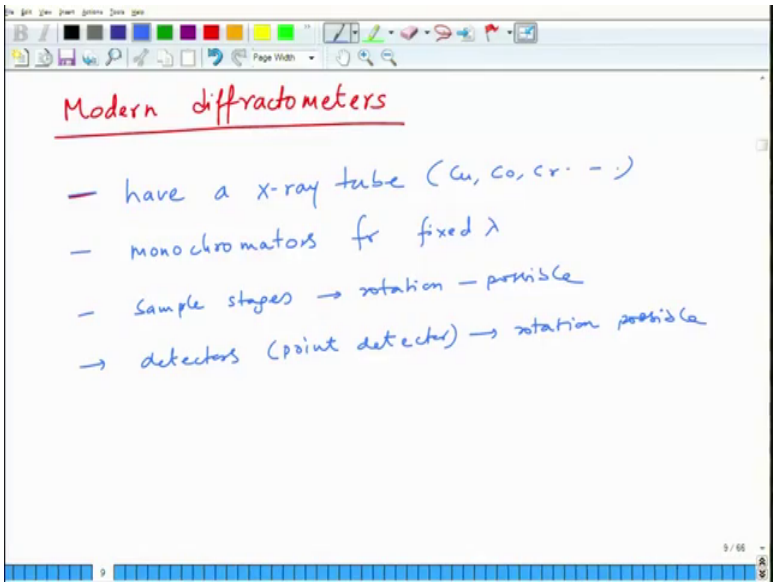

Nowadays, modern diffractometer, they look very different. So, for modern diffractometers, I will show you a slide.

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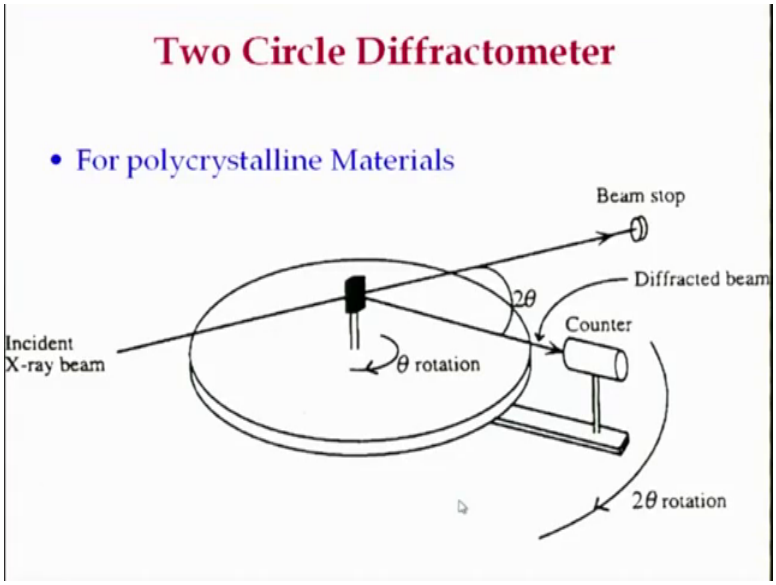

So, this is sort of a modern diffractometer that we will have. So, you have a two circle diffractometer. This is the incident beam. This is your sample. This is the beam stopper for the transmitted beam. You can so this is your incident beam the diffracted beam is going to go in this direction let us say ok. So, instead of putting a photographic film you have a counter. So, this could be a scintillation counter or some sort of detector ok. So, so

this detector rotates in this direction to collect all that all the diffracted beams at all the two thetas. So, it will start at two theta is equal to 0 degree or close to 0 degree typically we start from five degrees in the wide angle X-ray diffraction.

So, it will start at lower angles and will go up to right up to nearly 150 degrees. So, on the way, it will collect all the diffracting peaks ok. So, this is the modern diffractometer. You can also rotate the sample in this there is a possibility of sample rotation as well to maximize the probability again but you do not need to do that poly crystalline material unless you have texture or something like that you do not have to do that. So, that if so this is basically the diffractometer will the geometry will look like this.

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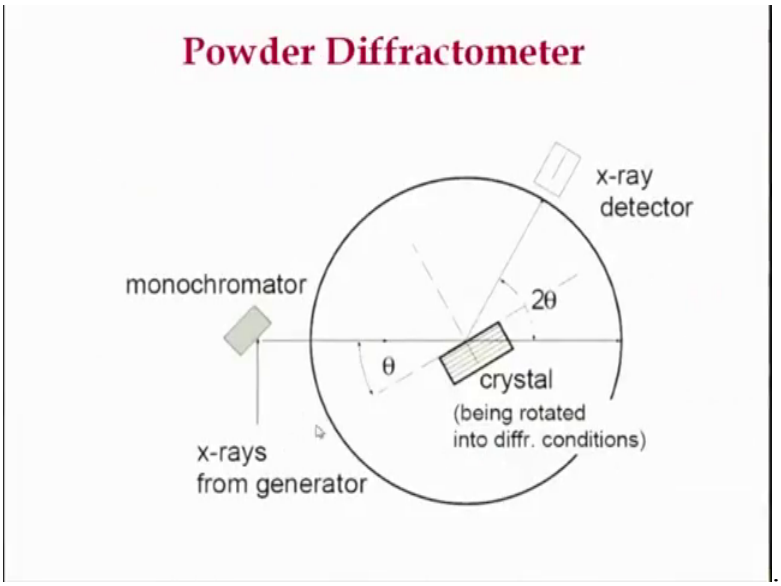

This is your X-rays they go through a monochromator, monochromator or filter. Monochromator only allows the one particular wavelength to be and to go into the crystal this is your sample. So, in this case, if this is your X-ray detector, this is your mono X-ray generator you can rotate the crystal.

So, there is a possibility of rotating the crystal as well as there is a possibility of rotating the detector. So, you can for polycrystalline material, you have to have only one of them, you do not need to rotate both of them. So, either you can rotate the sample holder or you can rotate the detector ok. And what you get at the end of it something like that.

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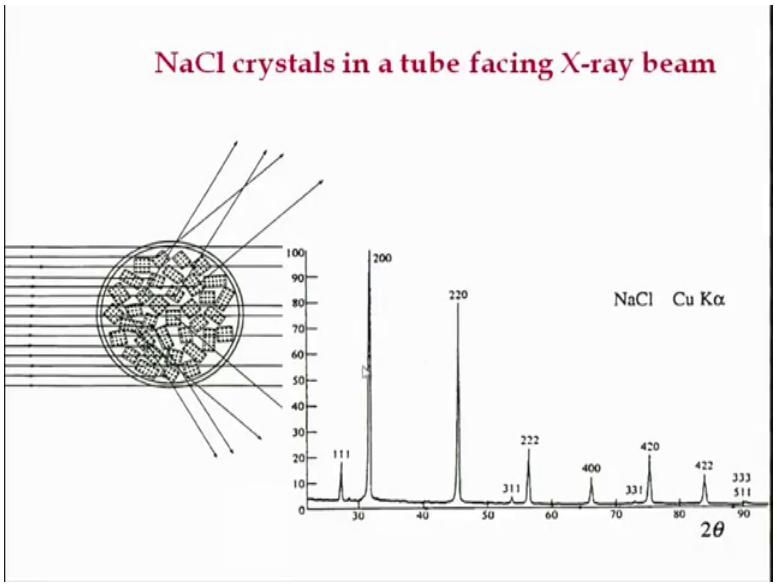

So, this is for example, for a sodium chloride crystals in which face. So, this is in a tube sodium chloride salt powder exposed to X-rays which are emitting in various directions and diffracted x-rays. And what you get a pattern like this. So, you have on the y-axis intensity and this is because X-ray is a photon right.

So, intensity of number of photons basically collected by the director this is 2 theta and you have these peaks. So, you can see that they all go in the order of increasing h square plus k square plus l square we will see now that how do you distinguish between for example, BCC, FCC or simple cubic material using the information that you get ok.

So, modern diffract diffractometers they have a have a X-ray tube which could be copper, cobalt, chromium any source. And they use monochromators for fixed lambda ok. Monochromators are basically single crystals which deflect only a particular wave particular beam.

And then we have sample stages where you can have rotation possible rotation. And then you have detectors which are point detectors basically much better than photographic plates because they give you very high intensity of diffracted peaks and these also one can rotate ok. So, this is sort of so what you get at the end is something like this as a function of 2 theta, as a function of intensity you have these peaks and so on and so forth.

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So, you have theta one you have theta 2, theta 3, theta 4 and so on and so forth. And then from this you need to work out what does it belong to so the exercise in front of ourselves I will not get into details of this, but exercise in front ourselves is what material will it belong to for example, you have a given structure the question is can you identify the structure of the material especially in case of cubic cases.

So, we will do that in the next lecture ok.

Thank you.