X-Ray Crystallography
Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 13
Debye Sherrer Camera

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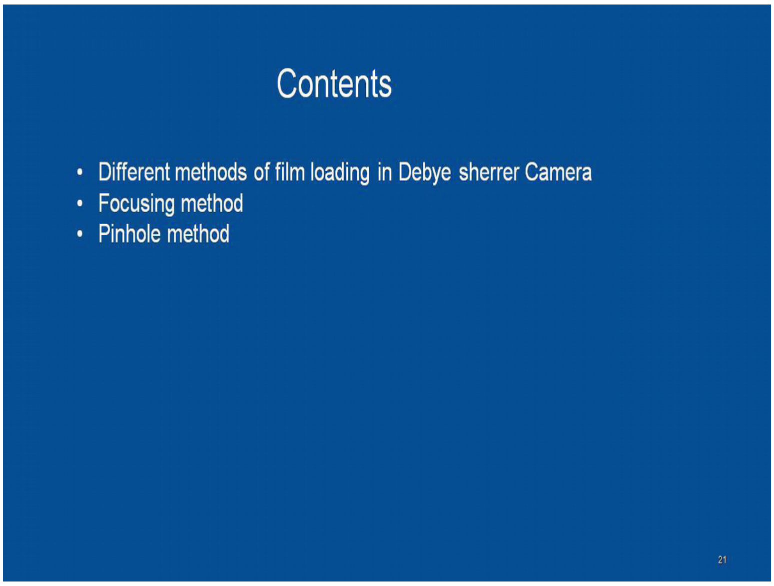

I shall now describe the different methods by which x-ray films are loaded inside the Debye Scherrer Camera.

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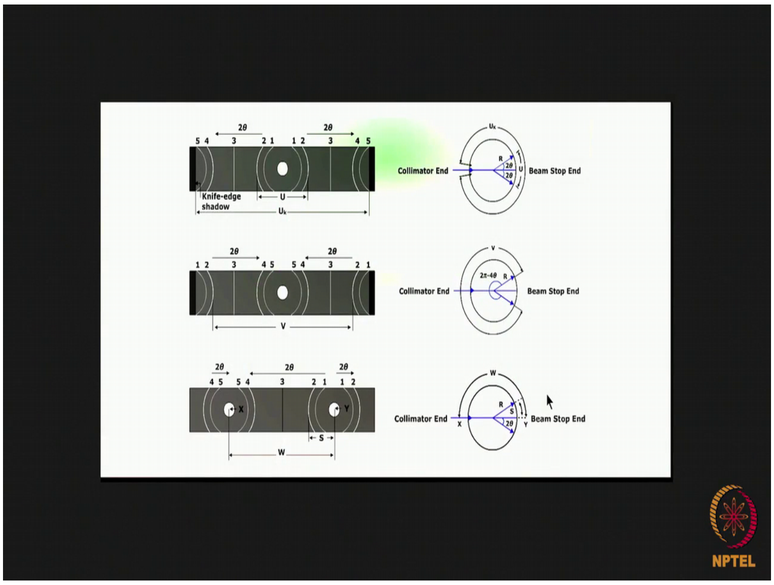

There are three such methods, in the first method we make a central hole in the film and then it is put in this fashion so that the hole goes against the beam stop and the two ends of the film come against the knife edges. So, these are two knife edges. So, this knife edges are put at the time of manufacturing of the camera and therefore, the distance between the knife edges over the circumference of the camera U k is known very very accurately. So, when X radiation strikes the sample here the diffracted beams will emanate from this point and then strike the x-ray film at these two points. So, if we have a particular h k l plane then it will give raise to this line pair say 1 1 and those will be recorded on the film at this points.

Now this angle as we known is 4 theta and the angle subtended by U k the distance between the two knife edges at the centre is also known right from the they are manufacturing of the camera. So, if we measure the distance between the two lines in the line pair 1 1, and if this distance is U we can write down U divided by U k the distance between the knife edges is equal to 4 theta divided by say 4 theta k. The angle subtended by these two points you know the entire arc at the centre this is known accurately right from the date of manufacturing.

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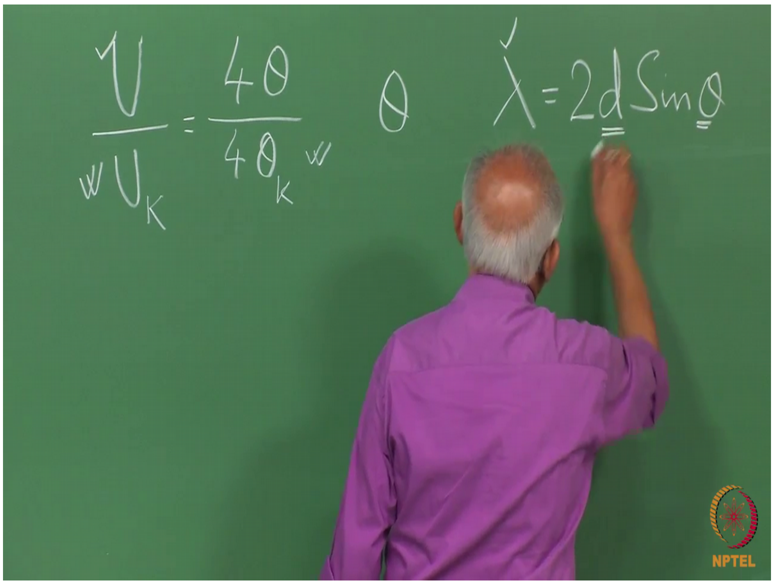

So, if we can measure this is value this particular length U this is again known accurately. So, we can find out the value of theta from this equation and once we can find out the value of theta then using the Brag equation lambda is equals to 2 d sin theta where lambda is the wavelength that has been used in this measurements and theta has been calculated. So, we can easily find out the value of d; the interplanar distance for the h k l plans we talk about. So, in this way we can find out the interplanar distances of the planes h k l between say line pair 1 1 then h prime k prime l prime from the distance between line pair 2 2 etcetera, etcetera. So, all the h k l planes which have given rise to the diffraction pattern can be found out in this manner.

Now in the second method of loading the central hole is placed over the collimator end and the ends of the film go up to the knife edges here. So, the knife edges cast a sharp shadow on the film and the actual distance between the two knife edges V is now very very accurately from the date of manufacturing of the camera and it is also known how much will be the angle subtended by this over here since we have got, say we are talking about the pair 5 5 in this case, suppose the diffracted beams strike at this two points. So, naturally this will be 2 theta, this angle will be 2 theta.

So, this angle will be 2 pi minus, this whole angle will be 2 pi minus 4 theta. You see this angle is 2 theta the bottom angle this is also 2 theta just like as over here. So, this angle the entire angle is 4 theta. So, this angle is 2 pi minus 4 theta. Now since the distance V is clearly known we can write down 2 pi minus 4 theta in to R the radius of the camera which is also known very very accurately is equal to V.

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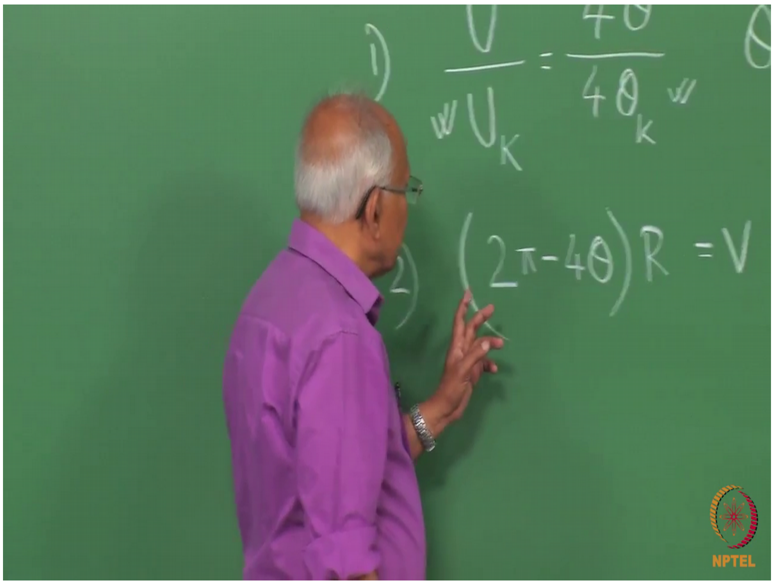

So, you see that this is the first method and this is the second method. So, in the second method what we have to do is we have to know the value of R very very accurately which is known right from the date of the manufacture of the camera, V is also known. So, we can figure out the value of theta straight away and once you know the value of theta we can write down lambda is equal to 2 d sin theta.

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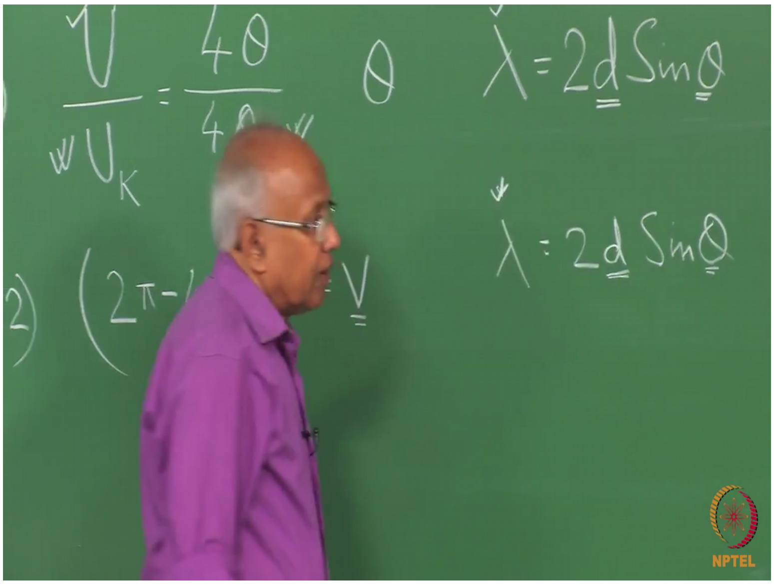

So, lambda the wavelength is used is known theta has already been determined in this manner. So, we can find out the d or the interplanar distance you know for the planes which have given rise to all the lines in the diffraction pattern. Now there is a third method which is known as Straumanis method.

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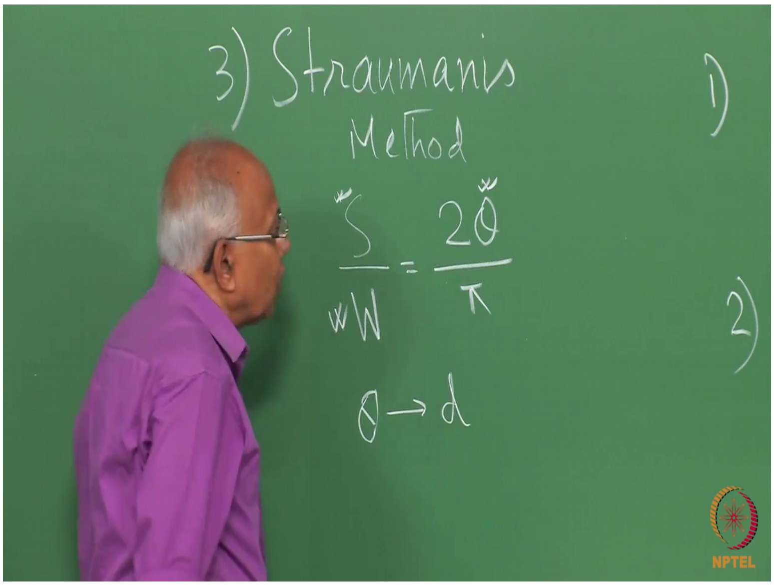

So, there is a third method which is known as the straumanis method. So, what is done here? In this method we have two punch marks two holes corresponding to the regions the collimator and the beam stop. So, the film is plays inside the camera in such a manner that this hole goes over the collimator and this hole goes over the beam stop and the distance between these two holes is known very very accurately from the manufacture of the camera.

So, this distance W is known to us already the camera radius R is also known. Now if we measure this length corresponding to the length over here the S then we can simply write down S by W will be equal to 2 theta divided by pi, we can easily write down S by W is equal to 2 theta by pi. Now S can be measured accurately. So, W is also known. So, we can easily find out the value of theta and then from the value of theta we can find out the corresponding d value.

So, in this manner we can find out the interplanar distance of all the planes which have given rise to this diffraction pattern. Now the reason why these three methods are used is a fact that when you after the exposure when you take out the extra film you have to develop it and fix it and then dry it. Now once you do that what happens is the film will shrink a little bit.

So, shrink and error will come into the picture. So, in order to avoid this we use any of the three methods. The reason is simple say for example, in the first method you know the knife edges are fixed inside the camera. So, the distance between the knife edges is a fixed quantity. Now we know that for any line this length will shrink a little bit and it will be in proportion to the length between the knife edges. So, if the distance between the knife edges is known accurately, then we can avoid the problem of shrinkage because this line between say line pair this length which in the line pair 1 1 will shrink in the same proportion as a distance between the knife edges, but since the knife edges are known accurately right from the beginning you know and since we use it in our calculations, so we can avoid the problem arising out of film shrinkage.

Similar is the case in the second case, in the third case also we avoid the problem of film shrinkage because this length between the two holes is very very accurately known you know when the manufactures make it they give this value. So, whatever shrinkage can happen you know once we take this length in to consideration we do not have the problem appearing in the measured value of theta or in the measured value of d. Now we come to the second method, second type of camera that we use in the powder method. You know we have already described the Debye Scherrer method you know and now we are talking about the Focussing method. So, as we all know in the powder photography there are 3 variations the Debye Scherrer method, the Focussing method and the pinhole method.

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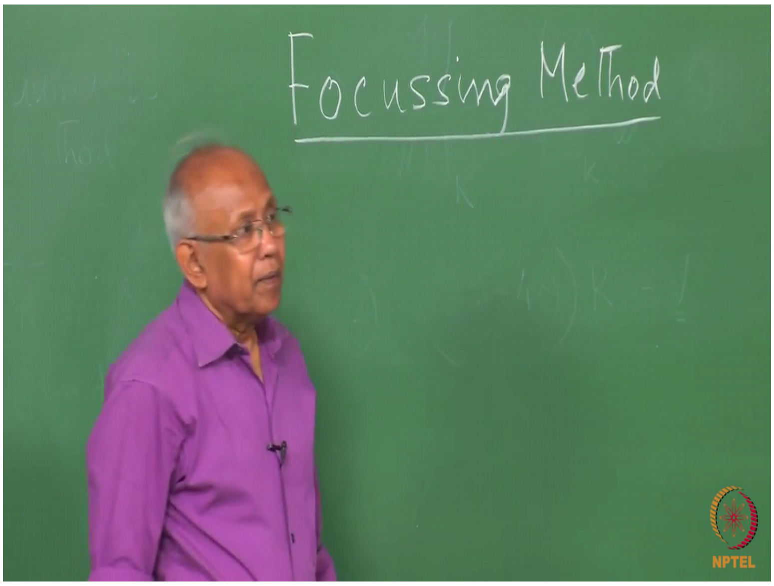

.So, we have talked about the Debye Scherrer already, now I will talk about the Focussing Method. This method is based on a well known geometrical problem which says that if angles are inscribed in a circle by an arc then all these inscribed angles will be equal to one another and this angle will be half the angle subtended by the same arc at the centre.

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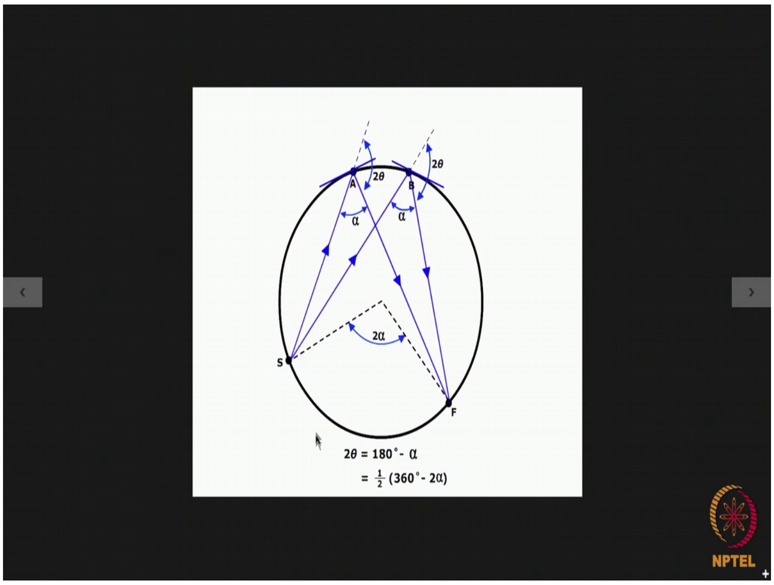

Now in the Focussing method we use an extended sample say we put a sample big enough at the circumference over here. Say these are the two h k l type of planes in the two crystallites in the sample. So, if there is an incident beam over here and it gets diffracted along a particular direction then this angle will be the 2 theta, 2 theta angle is always between the incident and the diffracted direction.

Similarly if we have a divergent beam coming from an x-ray source, another x radiation will go through this particular atomic plane fall on this particular atomic plane this is also an h k l plane like this one and it will get diffracted along. So, this angle will be 2 theta. So, if this angle is 2 theta, this angle is 2 theta then automatically this is angle is pi minus 2 theta; that means, you know all these two ray, this two rays they will be focussed at the same point f.

So, what is the advantage of this method? Here we are using the Focussing the diffracted beams in order to enhance the intensity of the diffracted beam. You see diffraction process is a very inefficient process, the diffracted radiation is much much weaker compared to the incident radiation. So, if we have a Focussing action of this kind then we can enhance the intensity of the diffracted beam to our advantage. So, in the Focussing method this is what we do.

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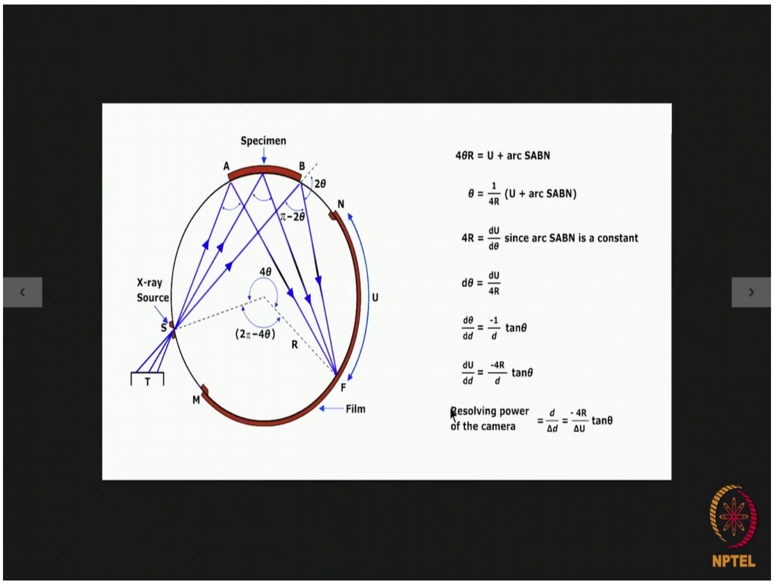

Now if we take a cross section of the Focussing camera as I always said the specimen is an extended one as shown over here. So, we can use a big enough specimen then the x-ray film is placed in this manner the source of x radiation is here and we use a divergent beam of x-rays.

So, let us suppose we have go the same kind of h k l plane at these three points on the sample, due to diffraction all these three diffracted beams must come to a focus over here and this goes on for other h k l plans also. Say for example, if we have got three h prime k prime l prime planes, one over here, another over here and third one here in three different crystallites or the sample again they will get focussed at another point over here. So, you see that we will get lines due to diffraction from different h k l planes as we get in case of Debye Scherrer Camera.

Now, there is a big difference between a Debye Scherrer Camera and a Focussing Camera. For example, we will let we say that this camera the Focussing camera has a higher resolving power than the Debye Scherrer Camera. Say for example, we can write you know 4 theta multiplied by the radius of the camera is equal to U, U is this distance plus arc SABN. So, this arc plus this, this total arc subtends on angle 4 theta at the centre. So, we can write 4 theta R is equal to U plus arc SABN. Now the arc SABN it is a fixed arc from the way the camera is manufacture. So, this is the fixed quantity. So, we can write down theta is equal to 1 upon 4 R. So, 4 R if we now differentiate both sides with respect to theta we can write down 4 R is equal to dU d theta. So, d theta is dU dR.

Again we know that by differentiation of the Bragg's law we can get this value d theta dd is equal to minus 1 by d tan theta. Now if we combine these two relationships we can write down d U dd is equal to 4 R by d tan theta or resolving power of the camera which is denoted as d by delta d that will be equal to minus 4 by delta U tan theta. So, in this equation delta U is the distance between two lines diffracted by 2 h k l planes which have got very similar value of d and d is average distance between those planes, delta d is a difference between the d of those planes. So, this resolving power is equal to minus 4 R by delta U tan theta this minus sign does not have any connotation. So, we say that the resolving power of the Focussing camera is 4 R by delta U tan theta.

If we remember for a Debye Scherrer Camera it is 2 R by delta S into tan theta where delta is the distance between the diffraction lines appearing in the film. So, we say that if R is constant for both the camera that R is same for the both Debye Scherrer and Focussing Camera. The resolving power of the Focussing Camera is just two times that of Debye Scherrer Camera. So, you see that when we want to do some very accurate we prefer using the Focussing Camera instead of the Debye Scherrer Camera.

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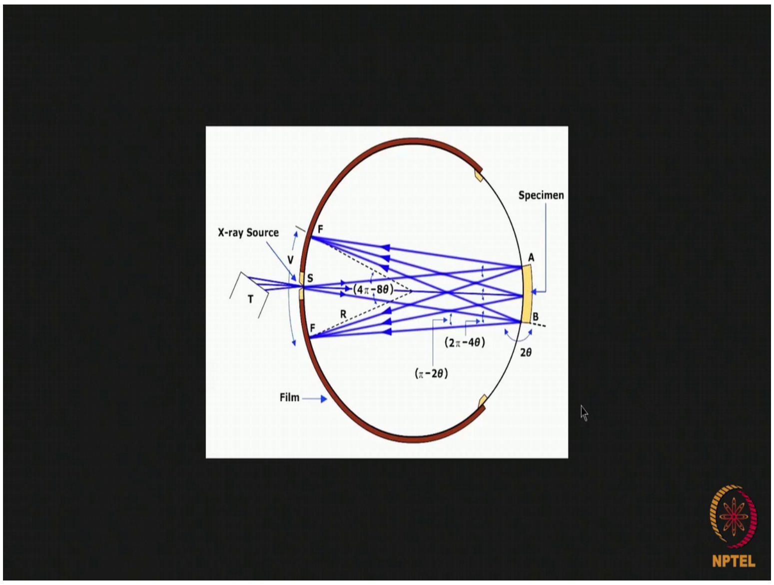

This is the arrangement of the x-ray source, the specimen and the x-ray film in a Focussing camera when we record all the back reflected diffraction beams.

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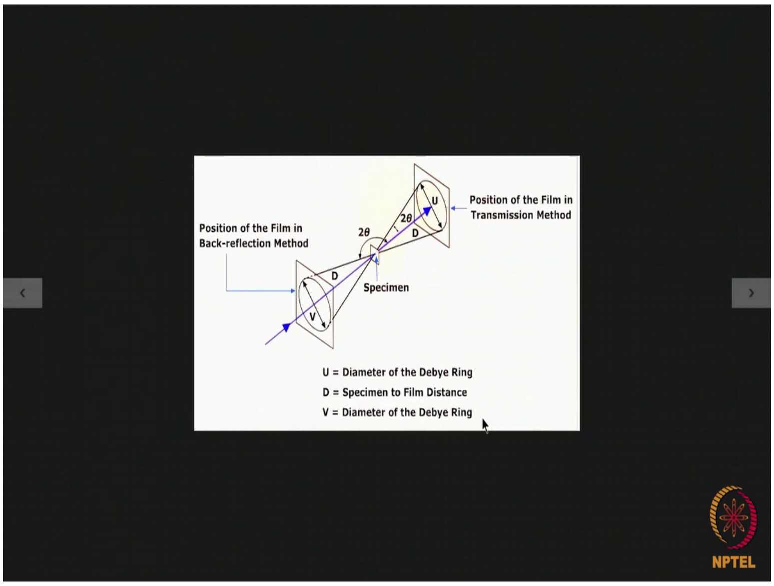

Now we come to the third method in powder photography that is the Pinhole Method. Now we talk about the third method of powder photography the Pinhole Method.

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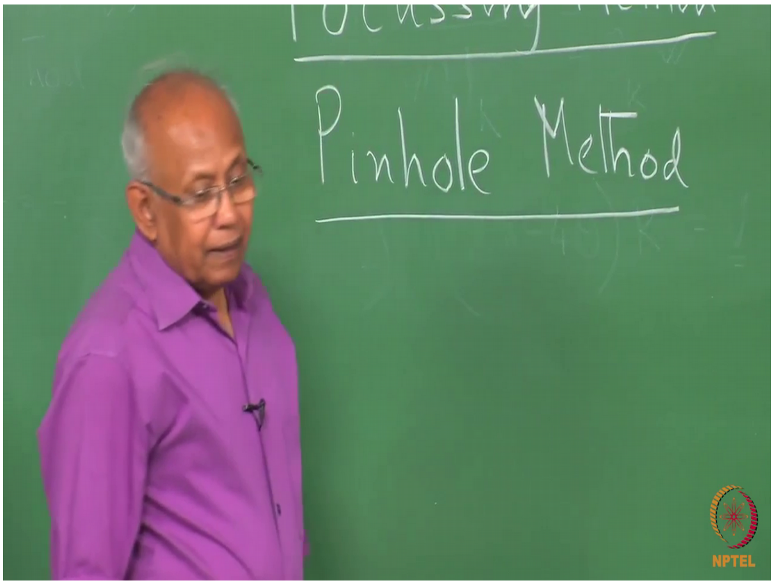

Now, in the pinhole method we can use a flat specimen as shown over here. We have a source of x-rays coming from this side and the photographic film can be placed either on this side when the method is a transmission method or it can be placed in between the source of x-rays and the specimen if we want to record the back reflected diffracted, back reflection beams. So, for forward reflection beams we put the x-ray film over here and for back reflection beams we put the film in between the x-ray source and the specimen. So, these two variations are there in the transmission method we record the x-ray that a diffracted in the forward direction in the back reflection method we record the x-rays that are diffracted in the backward direction.

Now again in this method our film is a big flat film. Now remember that in case of the Debye Scherrer method and the Focussing method we use a strip film in case of the Debye Scherrer or the Focussing method we use only a strip film, but now in this case in the pinhole method we use a much bigger sized x-ray film like this.

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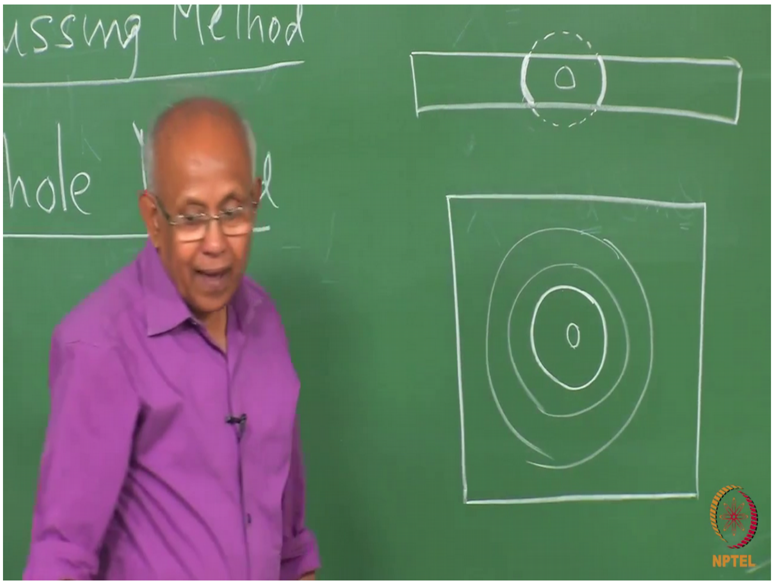

So, what happens? In case of the Debye Scherrer or the Focussing method you have you record only part of the Debye ring you know we do not; we cannot record the entire Debye ring like that which is diffracted, but we can record only this part of the entire Debye ring.

But what happens here in case of the pinhole method we can record the entire Debye ring. So, this is a basic difference. So, in case of the Debye Scherrer method we only record a part of the Debye ring, but in the pinhole method since we have got a flat film a bigger size we can record the entire Debye ring. So, depending on the planes within the specimen which give raise to the diffraction patterns we will be able to record the different Debye rings in this manner and then by doing the usual calculations by knowing the distance or the diameter of the Debye rings and the specimen to film this consist it is possible to find out the value of theta for the different Debye rings and from the value of theta since lambda is known we can find out the value of d for each and every diffraction pattern.

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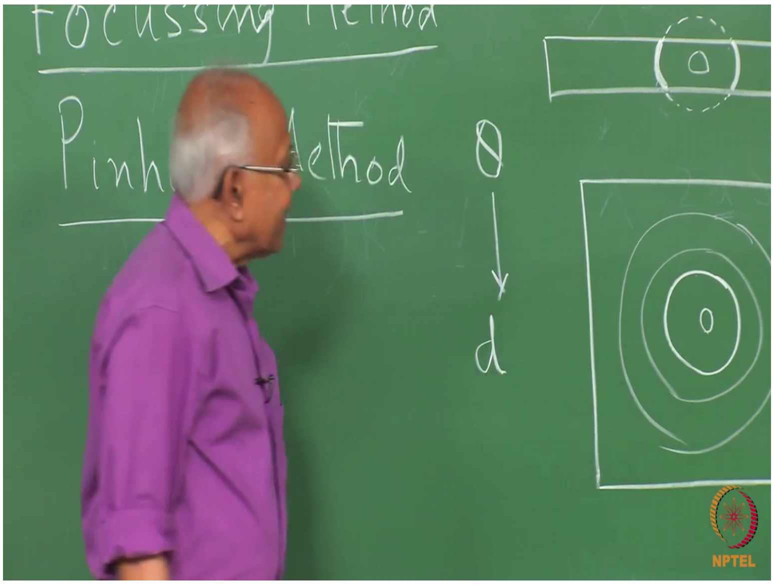

So, in this way we can find out the d values for the different planes which give raise to the diffraction patterns in the pinhole camera. Now you see the pinhole camera has got a big advantage say for example, if we take a portable x-ray machine in the fields for example, the geologist when he move to different you know unaccessible places big jungle and they have a portable x-ray machine and if find out a rock sample you know which is thick and cannot be thinned down then they can use the rock specimen for the back reflection photography without any problem.

Yes, they know they cannot do it by the transmission method, but in the field you know if you put a thick enough sample here, but can you easily, you can easily record the x-ray diffracted beams to the backward direction and from that they can make they can find out the values of d and as I will show later it is possible to find out the crystal structure and other parameters regarding the material.

Now, when you do powder photography how to choose the incident radiation?

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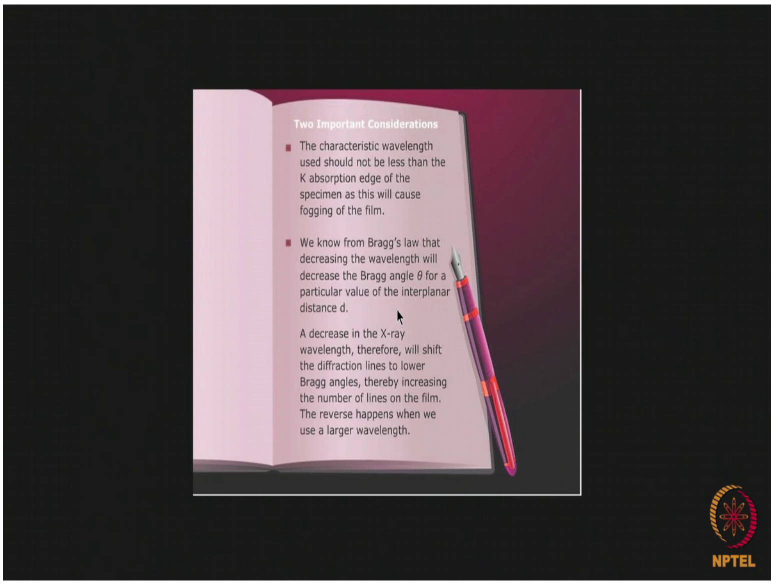

Now, there are two important considerations in this respect the first one is the characteristic radiation which would be used should not be such that it is wavelength is less than the k absorption edge of the specimen why, because this will cause fogging of the film. So, let me repeat what it say the first consideration while choosing.

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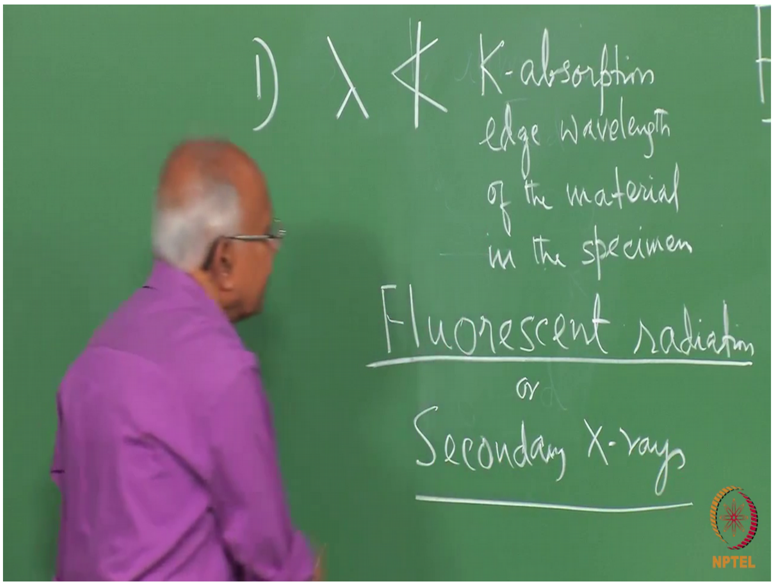

The incident is the lambda or the wavelength of the incident radiation should not be should not be less than the K absorption edge wavelength of the material in the specimen. We know that if the incident radiation is less than the K absorption edge wavelength of the material in the specimen then what will happen? This wavelength will be able to knock out electrons from the inner shells as a result of which there will be x-rays produced and those x-rays are known as the fluorescent radiation, those x-rays are known as the fluorescent radiation and this fluorescent radiation; that means, the x-ray which is produced due to the impact of the incident wavelength with the material it has got another name we also call it secondary x-rays.

So, what will be the function of these rays? They are going to fog the film they will make the x-ray film very very dark. So, if the x-ray film as you see later if the x-ray film is very very dark it will be difficult to distinguish the lines that appear on the film against the background. So, this is one of the most important considerations that we should not use a wavelength which is less than the K absorption edge wavelength of the material in the specimen.

There is another consideration which we should keep in mind.

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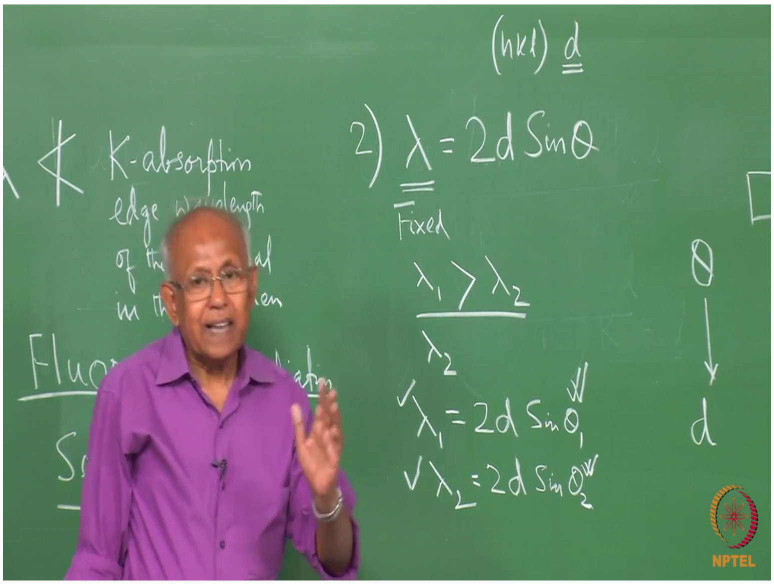

Now you see if we think about the Brag equation lambda is equal to 2 d sin theta in the powder method lambda is a fixed quantity. So, it is fixed. So, what will happen if we go for a higher lambda say instead of using a particular lambda value say we use in one case a lambda value lambda 1 and then a lambda value of two say lambda 1 is greater than lambda 2. What effect will be brought about in the values of these quantities say for example, for the same h k l plane for the h k l plane for which d is a fixed quantity if I use lambda 1 the higher wavelength then we can write down lambda 1 is equal to 2 d sin theta 1. Say we use a characteristic radiation from a different target material say that is lambda 2. So, if you use that it will be 2 d sin theta 2.

Now if lambda 1 is greater than lambda 2 then what will happen to these? If lambda 1 is greater than that is a higher value so that will mean your theta will be higher, if the lambda used has a lower value your theta will be lower because d is fixed for that particular plane; that means, you can change the relative provisions of the diffraction lines by using different incident radiations having different wavelengths. So, if suppose we want to bring all the diffraction lines closer together; that means, we would like to have theta to have theta values to have smaller values and then we use a smaller incident wavelength, but if we want to separate out the lines; that means, we want to increase the value of theta then we should use a longer wavelength radiation. So, these are the two considerations which we must remember while choosing the incident radiation.

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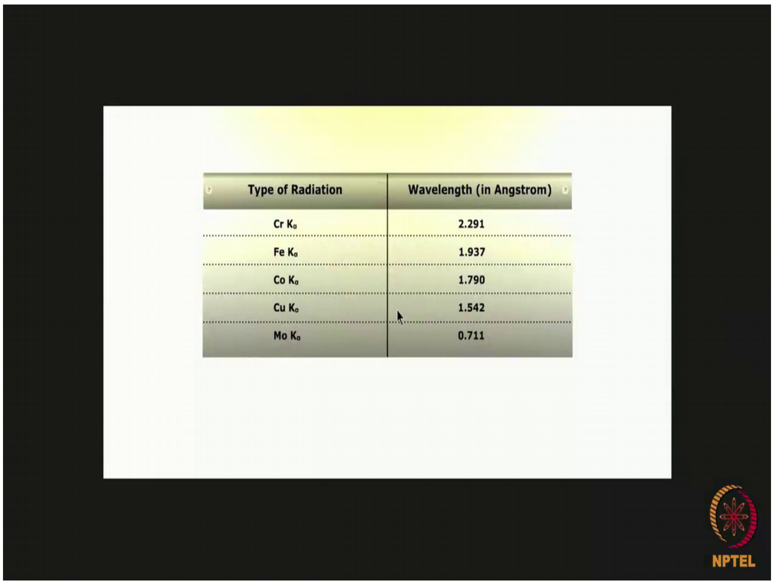

Type of Radiation	Wavelength (in Angstrom)
Cr K_{α}	2.291
Fe K_{α}	1.937
Co K_{α}	1.790
Cu K_{α}	1.542
Mo K_{α}	0.711

Say for example, if we have a case if we are going to study say a sample of iron and if we use a copper k alpha radiation then what will happen? The copper k alpha radiation has a wavelength which is one point five 4 two angstrom iron K alpha has a wavelength 1.937 angstrom and the K absorption edge wavelength of iron is also very close to this. So, naturally if we use a copper K alpha radiation to study an iron sample the copper k alpha has a wavelength which is less than that of the iron K alpha absorption edge wavelength which is very close to this. Naturally what will happen? Secondary radiation secondary x radiation or fluorescent radiation may be produced and that will fog the x-ray film so that the lines will not be properly visible.

Now say for example, we use copper K alpha radiation having a wavelength 1.542 angstrom to study a particular material. Now we find the lines are too close together in the x-ray film. So, we want to separate then out so that we can read them properly in a better way. So, we should go for a higher wavelength of the incident radiation you see that chromium K alpha will be good choice it has got a wavelength of 2.291 and as I have already said as you increase the incident wavelength the theta value should also increase because d remains a constant for a particular film. So, these are the things which we must keep in mind while choosing a radiation for the powder photography.

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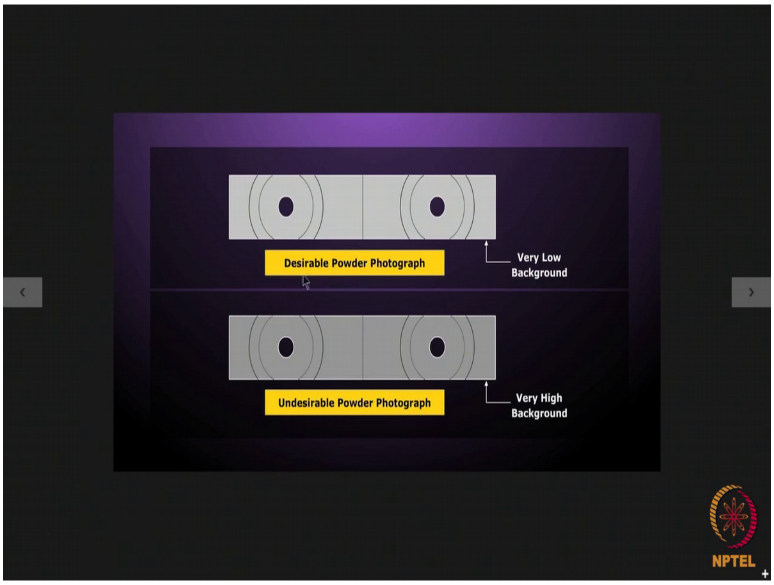

Now, as I already told you which one will be a desirable powder photograph this one or that one. Here you see you can see the diffraction lines clearly against a very light background on the other hand you have the background is very high and therefore, you know the lines are not that clearly visible here than in this case. So, this one is a very desirable powder photograph and this was is an undesirable powder photograph. So, we should see to it that the background radiation is not high.

Now what are the sources of the background radiation in case of the powder photographic methods? One is of course, the emission of fluorescent radiation by the specimen; that means, if we use an incidence radiation which has a wavelength shorter than the K absorption edge wavelength of the material in the specimen then fluorescent radiation will be produced and that will further filmed, so we must take care about that so that there is no fogging of the film due to this source.

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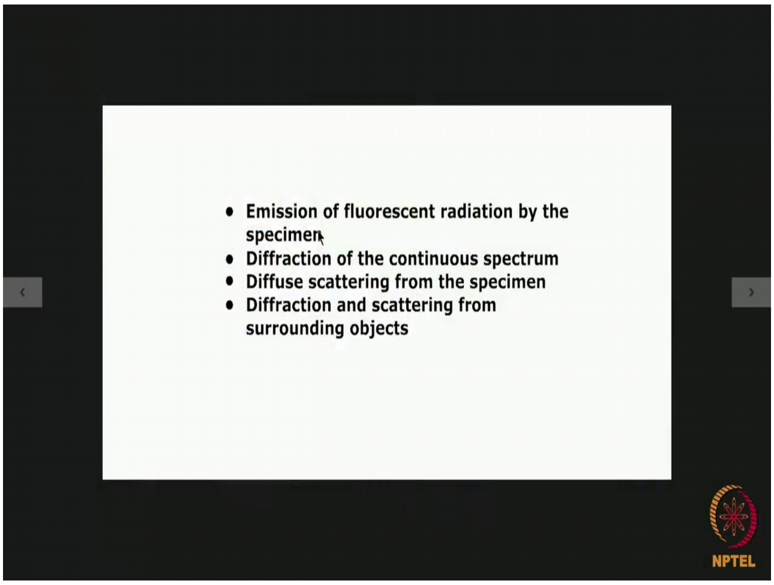

The other source second source is diffraction of the continuous spectrum. You see whenever we use a K alpha radiation you know it is not only K alpha that we use at the same time there will be some amount of the continuous white radiation and a little bit of K beta also because filters cannot efficiently filter the K alpha it is not 100 percent efficient.

You know when you use a filter against a target it is through that you will allow the K alpha radiation to pass through without much of a hindrance without much of an absorption. But the other ones are absorbed more that the K alpha, but even then you know the radiation that we get is not only K alpha it has got all the other radiations also they may have a lower intensity. So, those radiations they can also get diffracted you know and that will cause the fogging of the film.

Then comes the defuse scattering from the specimen say if the temperature is little bit high or if there are imperfections in the specimen then you will find some diffused scattered radiation from the specimen. Then the fourth source of error is diffraction scattering from surrounding objects. Say for example, when you make a needle sample for the Debye Scherrer method we use binding glue. So, some scattering might occur from the atoms present in the binding glue and if you know beam is not properly collimated there may be some diffraction and scattering from the beam stop and the collimator.

So, there are various sources of you know more sources which give rise to the fogging of the film and we must be careful you know to avoid them as far as practicable.

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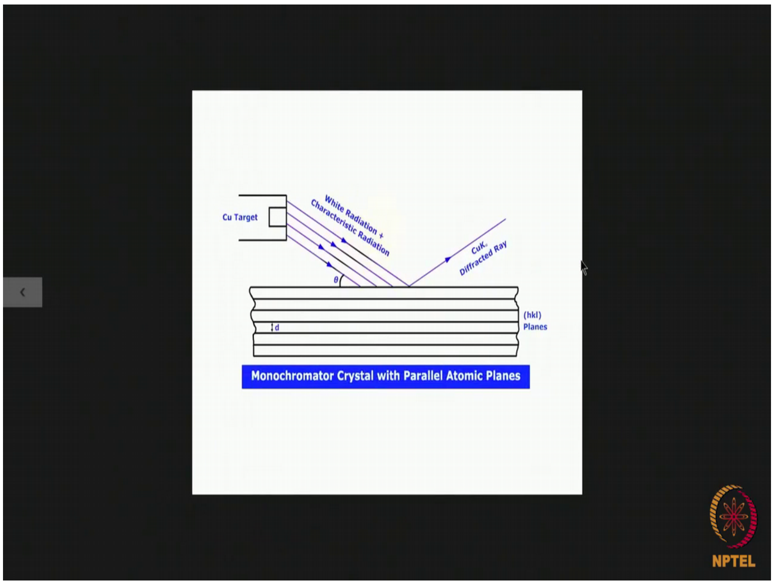

Now, so far as the second source is concerned diffraction of the continuous spectrum we can completely avoid it by using what is known as a Monochromator. So, I will tell you the principle of a monochromator. Say for example, we have a copper target in an x-ray machine. So, from this machine we will find a white radiation as well as the characteristic K alpha and K beta radiations. Now if this radiation is allowed to fall on the surface of a crystal where these are a specific atomic planes h k l planes and this is the value of d then if I put this angle you know incidence angle such that only the copper K alpha can be diffract not the others then what will happen. According to Bragg’s law only copper K alpha will be diffracted.

So, this radiation will be a perfect single wavelength radiation and this can be used for powder photography. So, what we do? This is called a monochromator crystal with parallel atomic planes and we figure out that if we want to use a copper K alpha radiation we find out what is the wavelength of the copper K alpha radiation.

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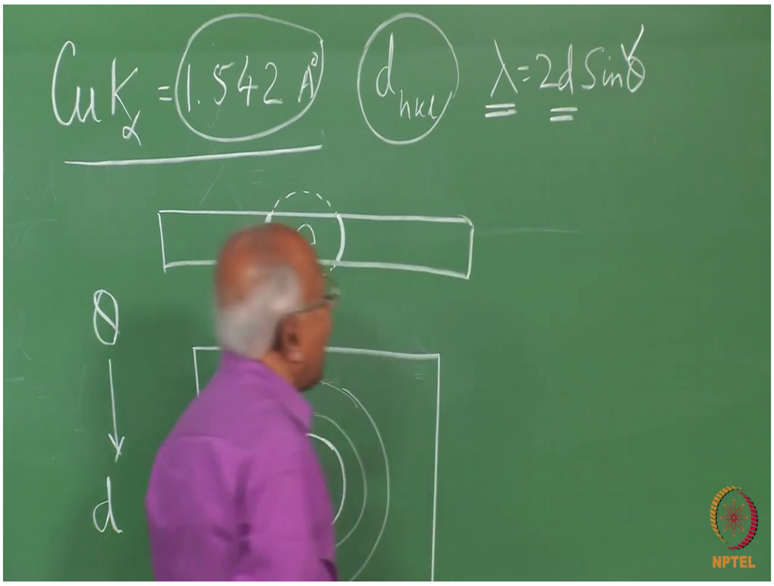

We know that it is equal to copper K alpha has a wavelength of 1.542 angstrom and we use a known monochromator crystal and we know all the planes parallel to the surface of the monochromator and naturally from the known monochromatic crystal the d of those h k l planes is also known. So, this is known, this is known. So, form Brag equation lambda is equal to 2 d sin theta since both lambda is known this is what we want to diffract, since this is a constant for the particular plane so sin theta can be found out and theta can be found out.

So, we allow the beam from the target to be incident on this monochromatic crystal at exactly that same value of theta and this will ensure that no other radiation except in copper k alpha radiation will be able to diffract although it will give away lower intensity, but this will be a perfectly monochromatic beam, perfectly single wavelength beam which is not possible to obtain using a normal filter material.