X-Ray Crystallography
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Lecture - 12
X-Ray Diffraction Methods

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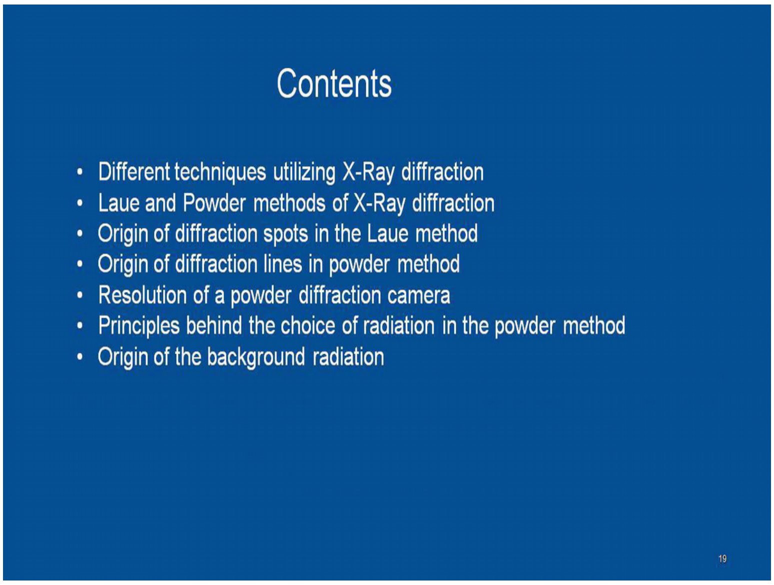

In this lecture, I shall discuss the various X-ray diffraction methods that are available to study materials, there are in general 3 different X-ray diffraction methods.

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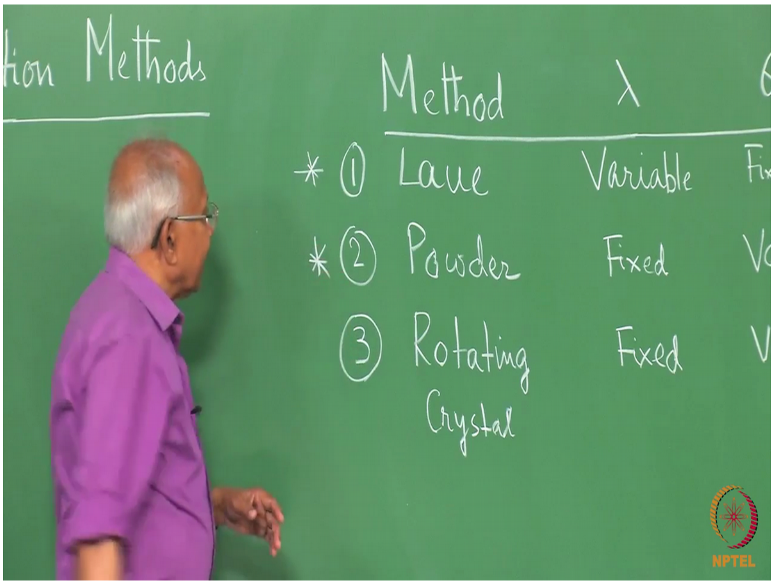

Now the 3 X-ray diffraction methods are the lave method the powder method and the rotating crystal method. Now in the lave method the X-ray that is used has an variable wavelength; that means, in this method we use a quite radiation from the X-ray tube.

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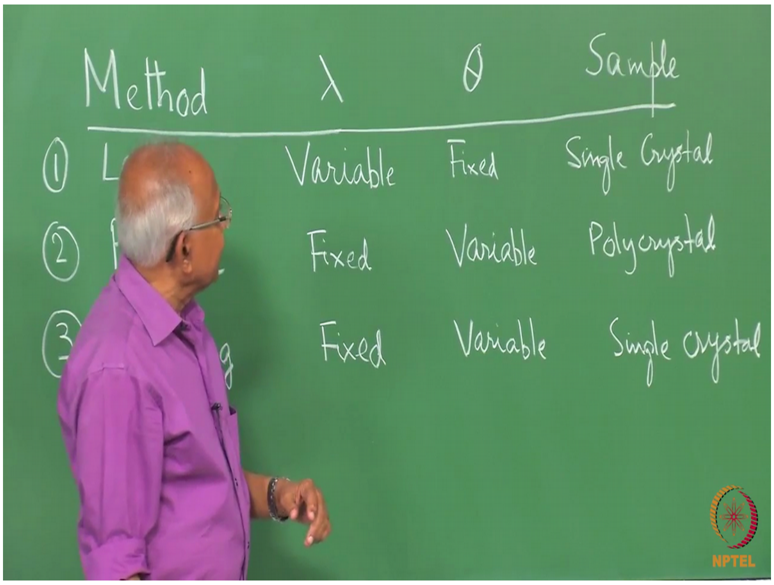

The sample in this case is a single crystal as a result of which theta the angle of incidence of X-rays on an atomic plane is fixed in the powder method we use a single or monochromatic wavelength from the X-ray tube by using the appropriate filter. Normally in this method we can examine a poly crystalline sample and in the poly crystal there are plenty of crystals available. And therefore, there will be many many atomic planes which will be in a position to diffract and we can have a variable theta or angle of incidence.

In the rotating crystal method wavelength is a monochromatic wavelength theta is variable and we can examine a single crystal now out of these three. I will discuss only the first tow namely; the lave and the powder methods.

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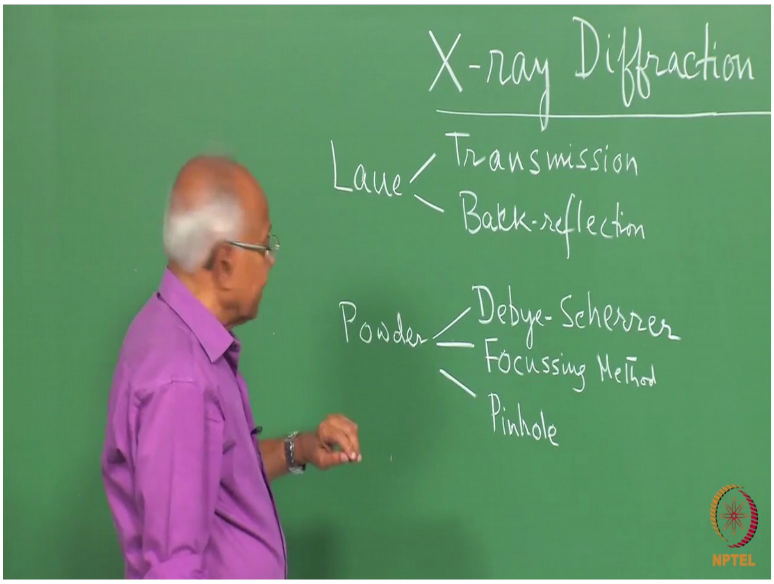

Now so, far as the lave method is concerned it has got 2 variations one is known as the transmission lave method the other one is known as the back reflection lave method. So, for as the powder method is concerned there are 3 variations one is known as the Debye Scherrer then comes the focussing method and thirdly the pin hole method. So, lave method has got 2 variations the transmissions lave and the back reflection lave the powder method has 3 variations the Debye Scherrer focussing and pinhole methods we will describe this methods one after another.

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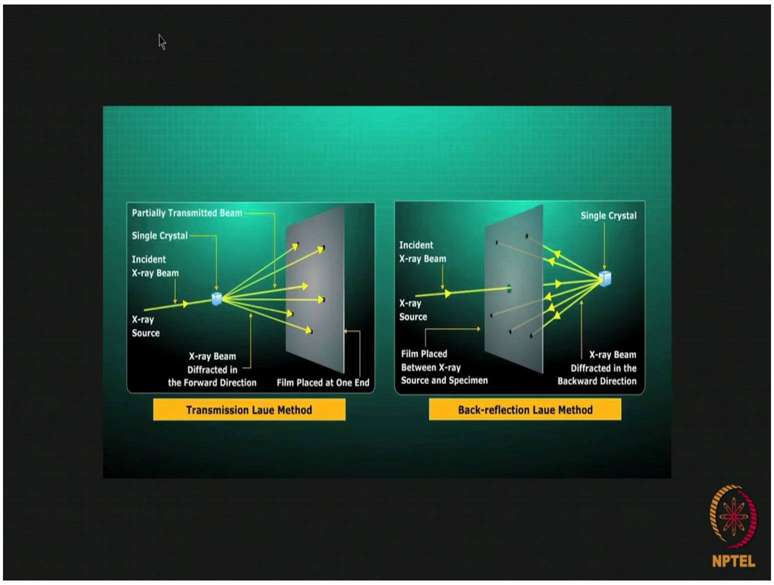

Now, this diagram shows the arrangement that we have in the transmission lave method and the back reflection lave method. So, far as the X-ray source the sample and the film to record the diffraction are concerned in the transmission lave method we use a single crystal at the at a central location from 1 side X-rays are allowed to fall on this single crystal and depending on which of the h k l planes in the single crystal that are poised for diffraction according to Bragg's law. We will get a large number of diffracted beams travelling from the sample towards a photographic film which is kept at one end. So, this is the photographic film this is wrapped in a black paper.

So, that photographic film is not affected by ordinary light in the back reflection lave method as we can see the photographic film is kept at the centre location X-rays pass through the film and fall on the single crystal and all the diffracted radiations at the back side they are recorded on the photographic film.

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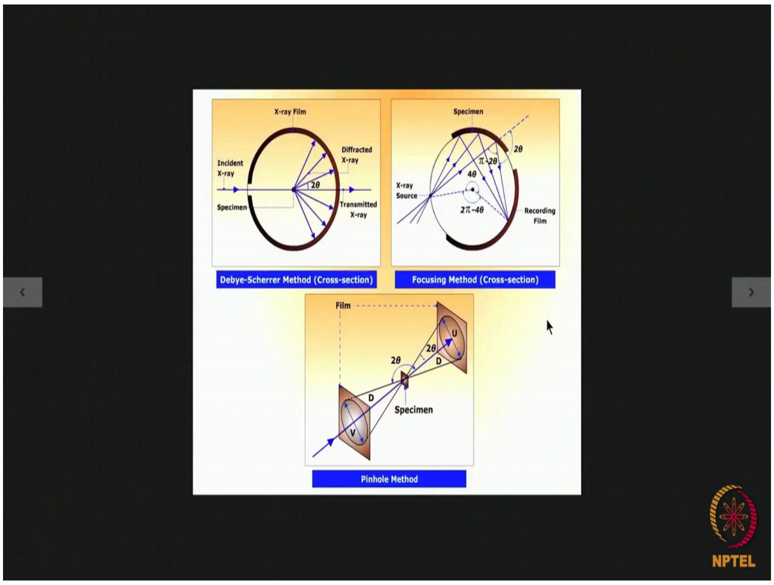

Now, so far as the powder method is concerned I have already said that there are 3 different methods like the Debye Scherrer method the focussing method and the pinhole method now here I have given a cross section of the Debye Scherrer camera. So, to say now you see in this method we put a needle like sample here, we put a needle like sample here made up of a large number of crystallides from the material to be examined. Now there is a film wrapped in this manner in the inside of a cylindrical light tight camera the x radiation falls on the sample and the diffracted radiation is recorded on this film.

Now this film after exposure is over is taken to a dark room developed and fixed and dried and then all those diffracted spots analysed in the focussing method we use a camera of this type. Again it is a light tight camera. And here instead of putting the specimen in the form of needle at the centre we put a specimen on the star face on the star face of the camera and the recording film is wrapped in a larger part of this surface 2 and X-ray source lies on the surface.

So, in this case the X-ray source specimen and the recording film are both lying on one circular area. Now in case of the pinhole method there are 2 variations one is called the transmission pinhole another is called the back reflection pinhole. So, in this case we can have a big thin sample made up of large number of crystals the X-rays will go through the sample and produce diffracted radiation to be recorded on a film on this side and all the diffracted at the backward side will be recorded on a film placed in this position this one is known as the transmission pinhole type this one is known as the back reflection pinhole type.

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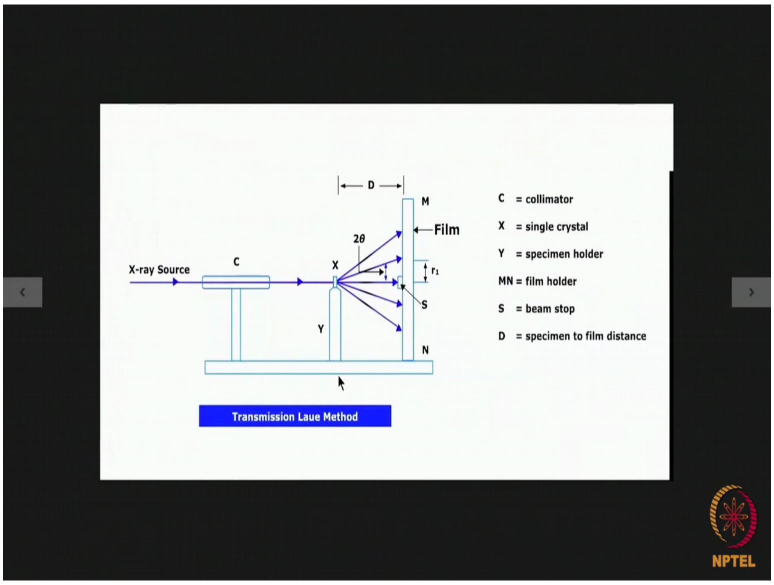

So, when we talk about all the different methods in more detail this is the transmission lave method X-rays source from the X-ray source X-ray of consisting of white radiation we know that in the lave method we need a large number of wavelengths why we need a large number of wavelengths, because in this method you have seen we have a single crystal specimen to be examined. And one a single crystal specimen is fixed we know that the angles with respect to the incident radiation for the different h k l planes they are also going to be fixed. And there may be a possibility that none of those atomic planes are in position to diffract.

So, if you use a single wavelength X radiation then the chances are none of the atomic planes in the single crystal specimen may be satisfying Bragg's law that is lambda is equal to 2 d sin theta in that case no diffraction will occur, but when we study a material by X-ray diffraction we not only want to have some diffraction taking place, because only by examining the diffracted radiation we shall be able to find out crystallographic information of the material being examined.

So, that is reason why in the lave method we use a white radiation consisting of a large number of wavelengths the idea is if a particular wavelength cannot get diffracted for a particular h k l planes then some other wavelength may satisfy brag condition and get diffracted. So, in order to improve the chances of diffraction to occur from the single crystal sample we use a white radiation or heterochromatic radiation or multiple wavelength radiation in the case.

Now c is a collimator the function of a collimator is to make the incidence X-ray beam as parallel as possible in most of the cases we will find that X-ray beam coming out of the X-ray source they are divergent type. So, in order to have a more or less parallel beam of X-rays we use a device called the collimator whose function is to make the rays more or less parallel to one another.

So, this collimator rays will fall on the sample X-ray over here and y is the specimen holder now from you know part of the radiation will pass through this sample and strike the film at the central spot this is the transmitted beam this is the transmitted beam and this S stands for a beam stop you use a heavy metal you know stop. So, that it stops here you know say for example, if some lead or lead glass is used then it cannot go out on this side because X-rays are dangerous.

At a various diffracted beams they will fall on the film at different places. So, from for particular diffracted beam we know the length R one from the centre and we also know the distance d between the specimen and the film. And therefore, we can find out what is the value of 2 theta you remember that 2 theta is always the angle between the incident and the diffracted beam.

So, for each spot 2 theta value can be found out and from that the theta value which is nothing but the angle of incidence or x radiation on a particular atomic plane can be found out now in the transmission lave method the material must be very very thin. So, that X-rays can pass through if the sample is very thick then what will happen practically no diffracted beam will come out in the forward direction. So, in order to have diffracted beams coming out in the forward direction your sample must be thin enough so that the X-rays can easily pass through.

On the other hand if may. So, happen that the material is not that thin it is a thick material in that case what will happen.

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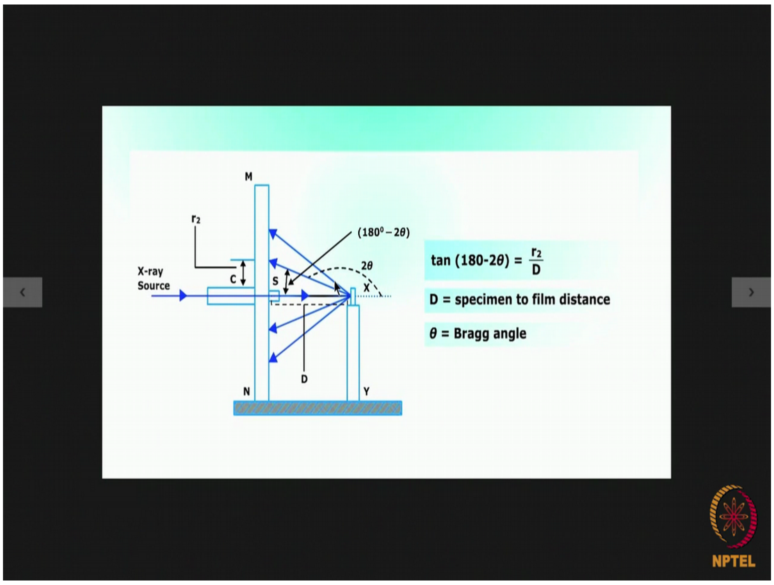

There will be no diffraction can be recorded in the forward direction and only those which are diffracted in the backward direction can be detected. So, in this particular case what happens; we allow the X-rays source to pass through the X-ray from an X-ray source to pass through the collimator. And through the centre of the through a hole in the centre of the film to strike the single crystal and all the rays which are diffracted in the backward direction they can be recorded an the film here. So, we know that for a particular diffraction spot over here this is the value of 2 theta. So, this angle here is 180 degree minus 2 theta this distance can be measured on the film.

So, this from the measured distance and the given distance here from the specimen to the film you can find out the value of theta easily you see again going back to the transmission lave method there may be atomic planes which are poised to diffract in the backward direction also. So, you can have both diffraction from forward, as well as backward direction and depending on that you can collect all the information in the forward direction or in the backward direction too.

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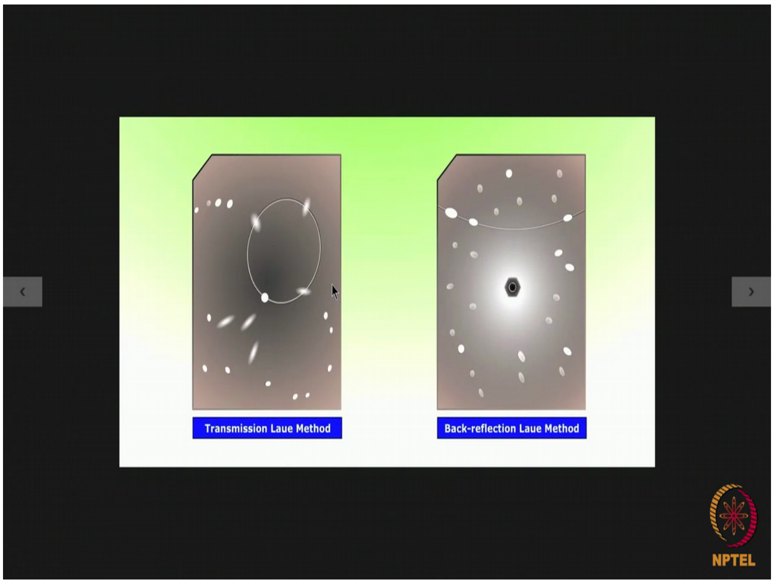

Now, the kind of diffracted spots that are obtained in the transmission lave method and in the back reflection lave method are shown in this diagram. Now if you look at the spots you can find this spots lie on the; of ellipses or hyperbolas in the cases. So, the spots will lie on ellipses or hyperbolas now we can find out why this is.

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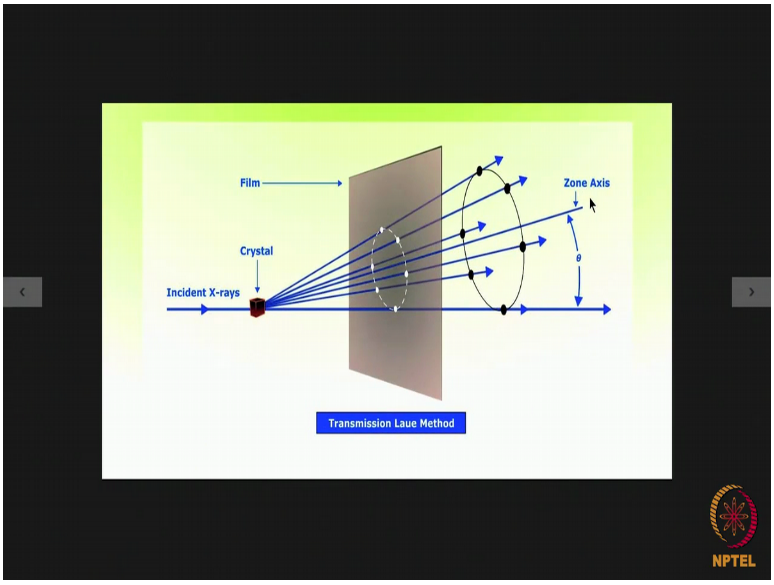

So say for example, when we use the transmission lave method the incidence X-rays fall on the crystal and all the planes which form a zone we know that a number of planes if they are individually parallel to a particular direction then we say that those planes form a zone and the direction with which each one of them is parallel is known as the zone axis now it.

So, happens that when we look at the diffracted radiation from number of planes which form a zone the diffracted radiation from all those planes belonging to a zone come out in the form of a cone of radiation there is a cone of radiation this. You know this is the base this is an emanates from this point. So, if we consider a number of planes that form a zone then if we find out the diffracted radiation from all the planes in a particular zone then we find that the diffracted radiation comes out in the form of a cone like this and when it gets recorded on the film it appears as a they appears in the form of a it appears in the form of a circle.

So, when this beam of radiation like diffracted radiation intersects the film then they come out the intersection comes out in the form of an ellipse like this at this angle you know this is the zone axis of that particular zone of planes which give raise to this diffracted ellipse. So, this is true in case of the transmission lave method.

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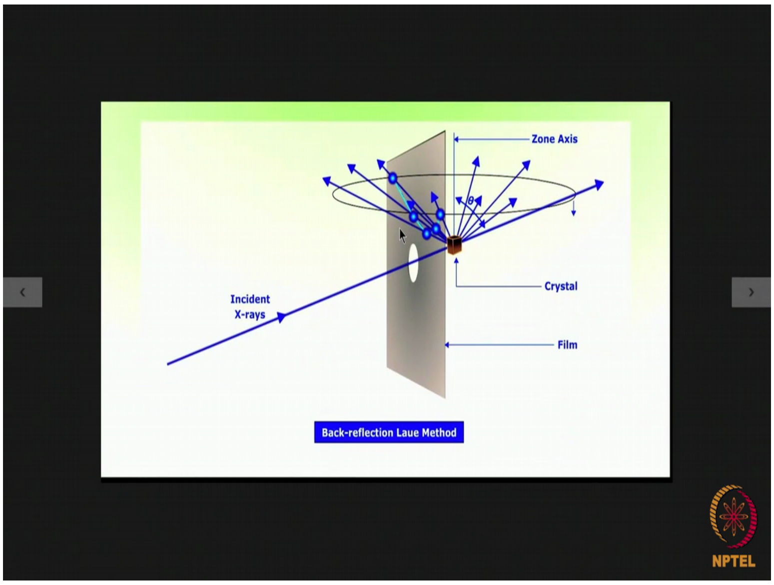

Now, when we look at the back reflection lave method again you see that from a zone of planes the diffracted radiation will come out in the form of a cone you know this is the base of the cone it will emanate from this point. And if you look at the diffracted beams they will form if you join the diffracted points on the film they come out in the form of a hyperbola.

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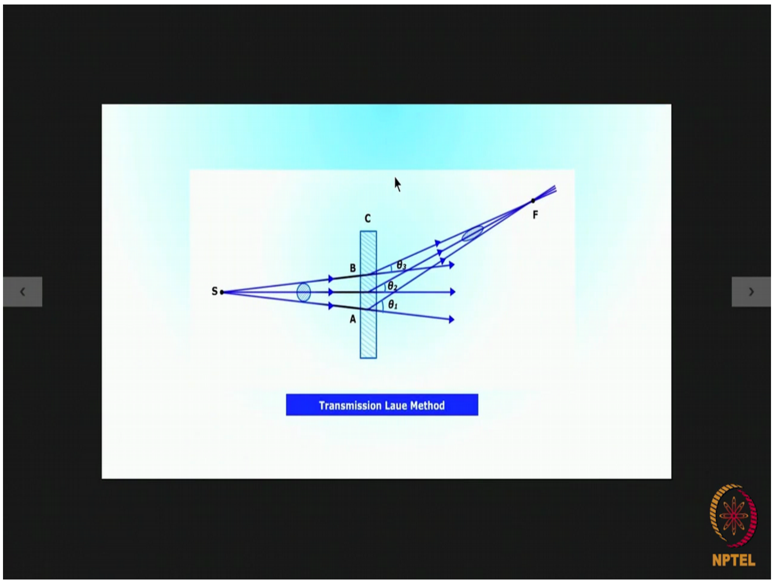

Now, looking at the diffracted radiation from the single crystal we always find that even though the incidence radiation which is a divergent one. In most of the cases it has a cross section which is circular in nature after they are diffracted by a series of similar atomic planes and they get focused to a point f over here. And the cross section automatically will not be spherical one, like in case of the incident radiation there is an ease, because they are not parallel they are incident as slightly different brag angles on the planes. And as a result of which due to the focussing action when they are focussed at particular point cross section looks like an ellipse.

So, that is why you will find that the spots are no longer spherical in case of the in the lave diffraction.

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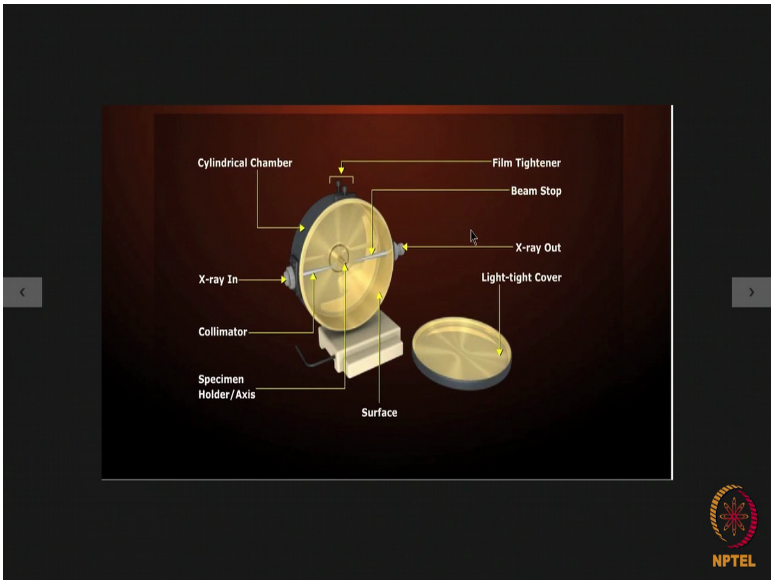

Now, let us come to the powder method in the powder method the most important method is the Debye Scherrer method. Now what happens in the Debye Scherrer method? In the Debye Scherrer method we use a camera which has the shape of flat cylinder. So, this is the flat cylindrical camera and it is covered by a light tight cover. So, the specimen is placed right at the centre and specimen is a needle shaped specimen how we produce the needle shaped specimen. We have to remember that here we examine not a single crystal, but a poly crystalline material.

So, one way of making a needle shaped specimen is to produce some fine powder from the sample by finding and then by coating a very thin glass fibre with that powder using glue or petroleum jelly. So, what we do first we produce a fine powder from the poly crystalline sample by finding the sample and then we take a very fine glass fibre coat it with glue or petroleum jelly and then coat it with the powder. So, the powder will adhere to the very thin glass fibre and then it can be used as a sample. The other method is you produce a some powder from the poly crystalline sample the take some thin valve glass tube very very thin valve glass tube made up of a non absorbing material like cellophane or lithium borate glass and fill it up with the powder that can be used as the sample.

Or if you have a thin poly crystalline sheet of a material with a pair of scissors you can cut out a thin length you know small length of very thin and small length and that can be used as the sample.

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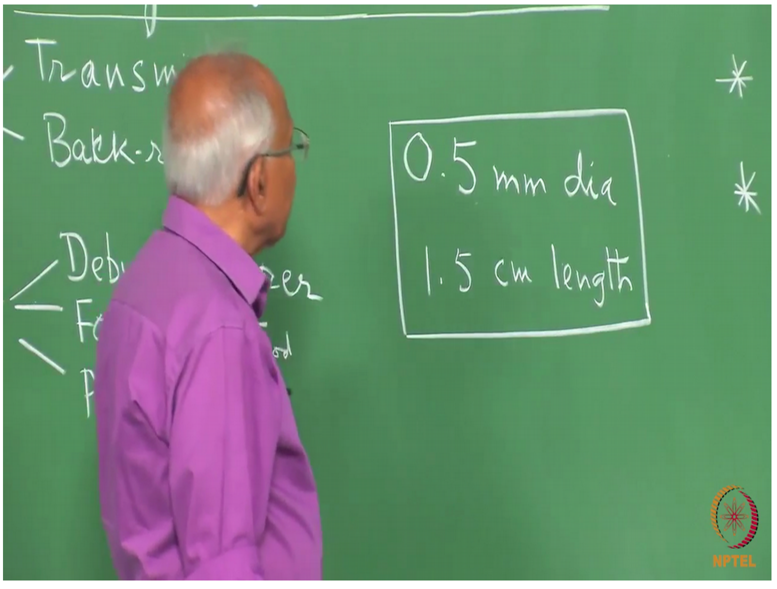

Now, normally for Debye Scherrer method the needle shaped sample should be about 0.5 millimetre diameter should be 0.5 millimetre in diameter and about one or one point five centimetre in length. So, the needle shaped specimen for powder photography has approximately point five millimetre diameter and say about one to one point five centimetre in length now if you look in this camera.

So, this is where the specimen is fixed on the specimen holder X-rays pass through a hole made over here and X-ray ray direct X-ray comes out through a hole over here now this is what is known as the beam stop and there you have a heavy metal. For example, lead glass to stop the direct beam. Now here we have got what is known as film tightener you see a we produce we keep you know for recording the diffracted radiation we use a film which is put tightly around the inside of the camera. So, a thin strip of film is kept inside the camera and it has tightened it is tightened by what is known as a film tightener.

So, this is the description of the type of camera which we use in the Debye Scherrer method the point to be remembered is because we are dealing with films which are affected by ordinary light the whole you know the positioning of the film etc must be carried out in the dark room. So, that the film does not come in contact with ordinary light and then the cover should be tightly put. And after the exposure is over the whole camera is taken in the dark room developed fixed and dried in the usual manner. Now in the powder method we have a large number of crystalloids thousands or sometimes even millions of crystalloids.

So, the chances are that a particular h k l plane in a quite a number this crystalloids will be poised for diffraction with respect to the single wavelength X-ray that is incident on it. So, in this method we use a monochromatic radiation. And, since the number of crystalloids is many may be many thousands or even millions of crystalloids in the powder sample it will. So, happen that there will be at least a few of the crystalloids for which say the h k l plane will be in a position to diffract the incident x radiation.

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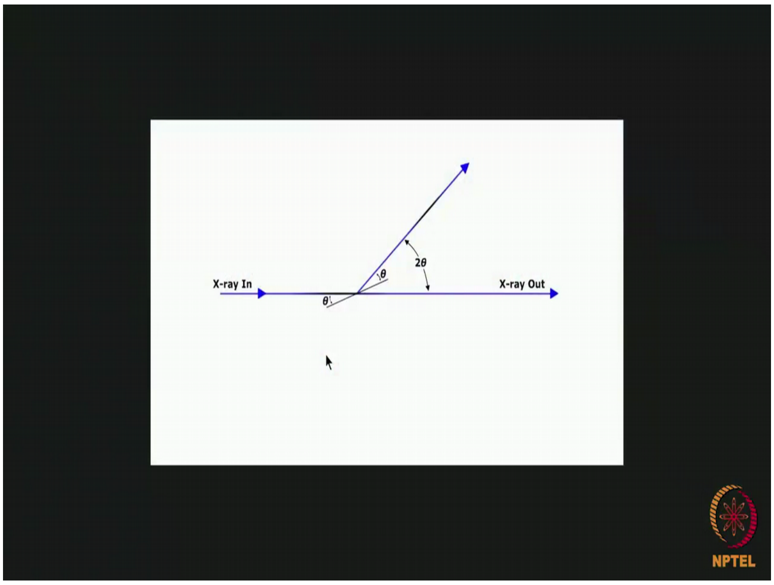

Say for example, this is a particular case say this is an h k l plane which is having an angle of incidence theta with respect to the incident x radiation. So, the X-ray if it you know follows Bragg's law X-ray will be diffracted in this direction this is the angle 2 theta between the direction of incidence and the direction of diffraction. Now in another crystal the h k the same h k l plane may be may be lying in this fashion and what will happen after diffraction it will be coming out in this direction.

So, you see if we rotate this h k l plane around this point you know at this point around the direction of the incidence X-ray then all possible locations of the same h k l plane in many many crystalloids will be found out. So, what will happen if you look at the diffraction taking place from all the h k l planes from the different crystalloids they will come out as a locus they will come out as a con of radiation it will come out as a cone of radiation.

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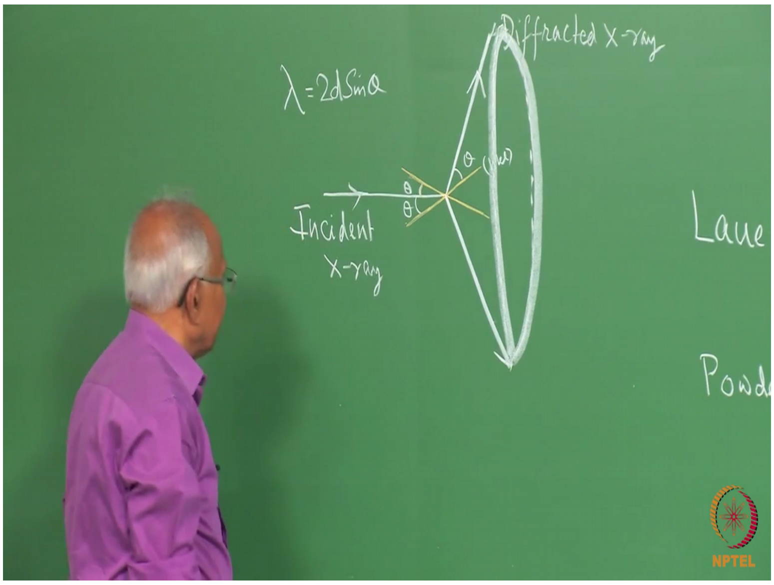

Say for example, it we have say for example, in a particular crystallite the h k l pane makes this angle theta with the incident radiation and suppose the incident radiation lambda is such that lambda is equal to 2 d sin theta this Bragg's relationship is fulfilled. So, we have a diffracted ray making the same angle theta going in this direction say in another crystallite it may. So, happen that the same h k l plane is positioned in this manner and still it makes the angle theta with the incident radiation. Say for example, you have the same h k l type of plane in another crystallite which lies like this making the same angle theta with incident radiation.

So, what will happen in that case you will have the diffracted radiation coming out in this fashion? So, if you look at the locus of all the diffracted radiation coming out from the same h k l plane in as many crystals as possible. Say for example, in one crystal the h k l may be making an angle theta with the incident radiation at the diffracted radiation come out in this direction. So, if you consider all the diffracted radiation from a particular time of h k l planes from many many crystals we will find that the whole diffracted radiation will come out in the form of a cone.

So, the whole x radiation diffracted radiation will come out in the form of a cone of radiation. So, the whole diffracted intensity you know from all the diffracted beams coming out from the same plane h k l from many many crystallites present in the sample will come out in the form of a cone of radiation.

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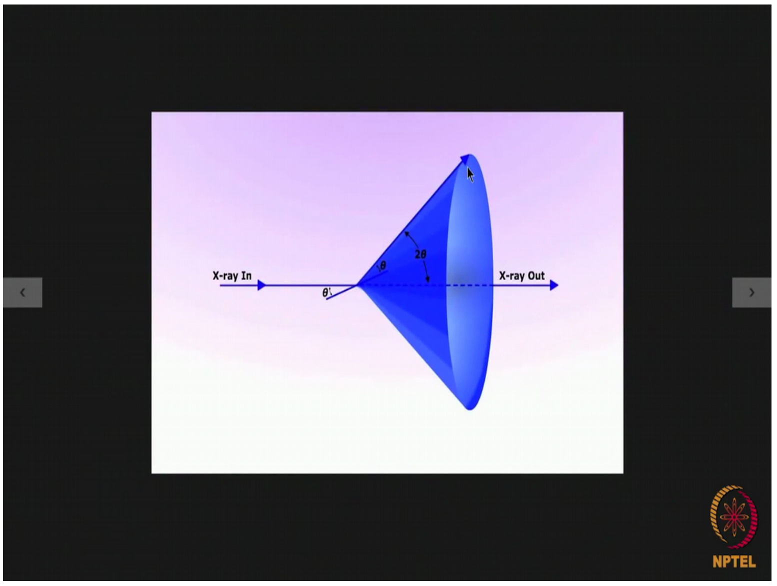

Now, so, this is the situation we have the a particular type of h k l making the correct angle for Bragg diffraction in one of the crystallites considering many many other crystallites, where also this h k l plane is in a condition to diffract looking at all the diffracted beams from this particular type of plane will find that the diffracted intensity will come out in the form of a cone.

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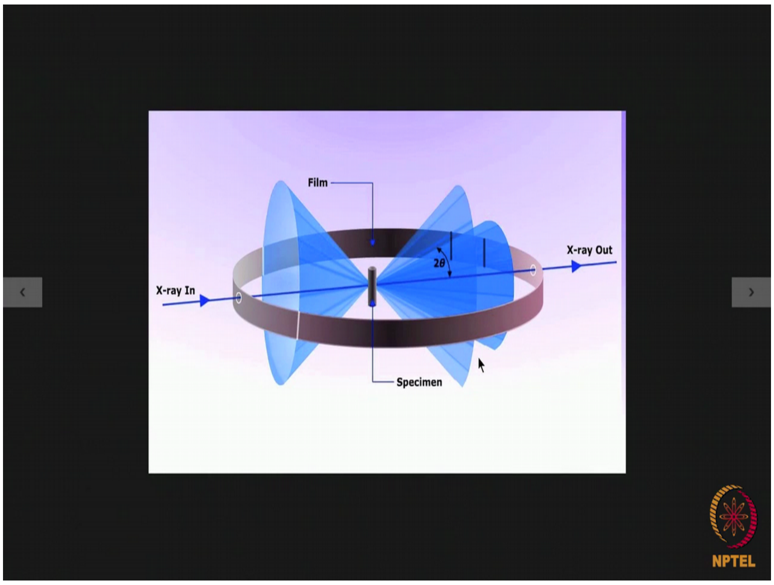

Now, if we have a thin photographic film placed in this manner then what will happen all the cones have radiation will get intersected on this film. For example, this particular cone will intersect the X-ray film at this point. And at this point this cone of radiation will intersect the film at this point and also at this point. Similarly this particular film you know cone of radiation will intersect the uh film X-ray on the film here as well as here.

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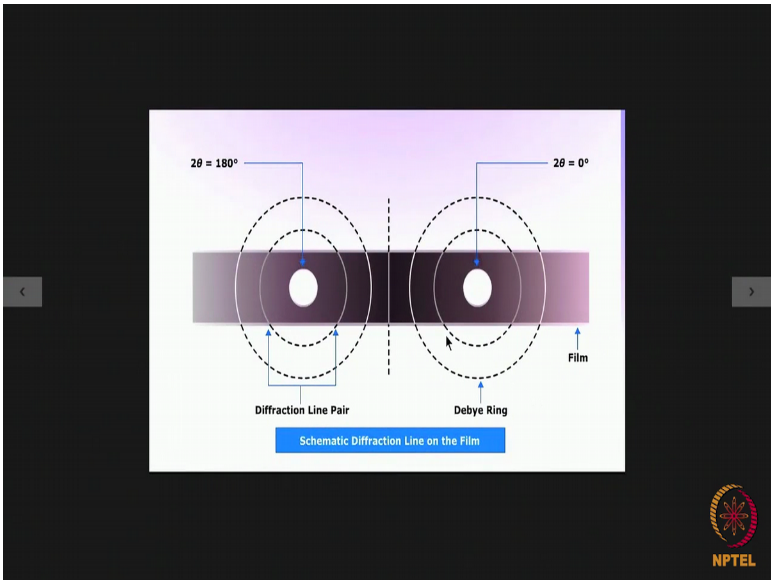

So, as a result when you look at when you take out the film develop and fix it then we find that the recording film looks like this these are the holes one for the collimator through which the X-rays get in to the chin bar and this is the beam stop region. So, these 2 holes correspond to the collimator where through which the incident X-ray beam comes and this is the beam stop region.

So, this is another hole and the diffracted radiation in the form of cone they intersect the film on these lines over here. So, the entire diffracted radiation is not recorded on the film because the film is a narrow strip otherwise the entire diffraction cones would have been recorded over there. So, so far as are concerned we will get a film of this type on which the diffracted radiation from a particular h k l plane will come as a lined pair.

So, these 2 lines will come this Debye Scherrer ring which is due to diffraction from a particular plane only, but. So, far as the recording is concerned it will be recorded as 2 distinct lines a line pair. So, to say it for another h k l plane from the poly crystal material the diffracted radiation; again will be recorded as another line pair in this manner a third h k l plane the diffraction on it will be recorded as a line the line pair and for another as a line pair etcetera, etcetera on some cases where the diffracted. Say for example, if we have a diffracted cone which cuts the film at this point.

So, instead of 2 lines we will have a single line. So, it will appear like this. So, this is a schematic diffraction lines on the films as we recorded. Now this end through which the X-ray enter naturally 2 theta is 180 degree you must remember 2 theta is the angle between the incident and the diffracted direction and here at this point to theta is 0 degrees.

Now, whenever we deal with a Debye Scherrer camera one very important thing to understand is what is the resolving power of the camera now what we mean by a resolving power of a camera. Say for example, if it. So, happens that the 2 h k l planes which diffract the radiation from many many crystallites say the h k l planes are having very very close inter planar distance.

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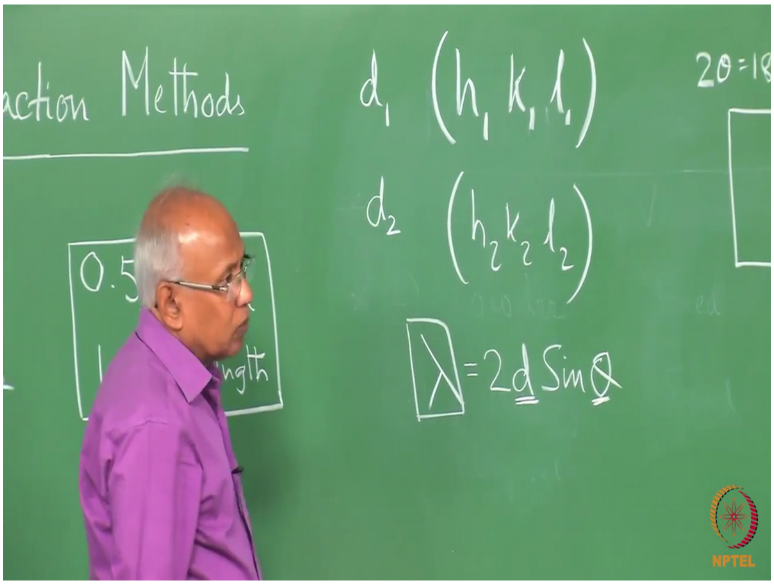

So say we have a situation where say we have 2 plains h one k one l one and h 2 k 2 l 2 in the material. So, the h 1 k 1 l 1 planes from many of the crystallites in the powder sample they will diffract the radiation and the diffracted cone will be recorded partly on the X-ray film. Similarly, say the h 2 k 2 l 2 planes in many of the crystallites they will also diffract the radiation and the diffracted radiation will be recorded as a part on the X-ray film.

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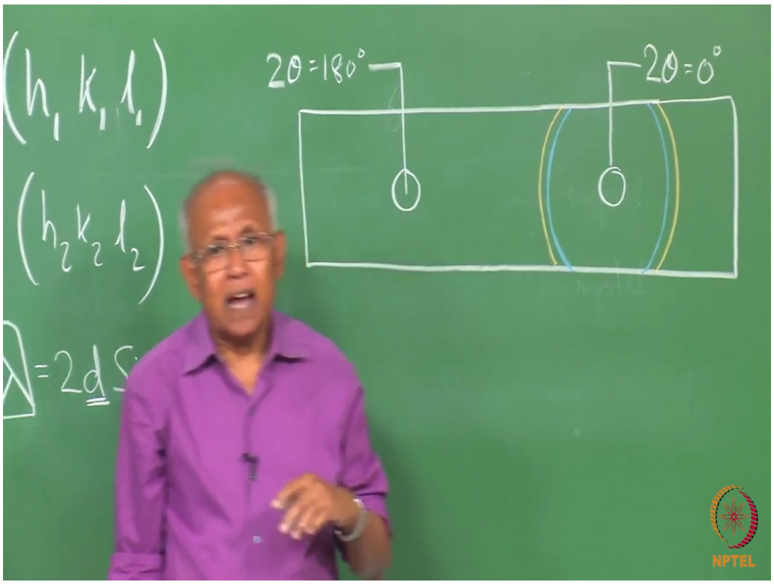

Say for example, this is the situation this is where 2 theta is 0 degrees this is where 2 theta is equal to 180 degrees. Say for example, we have got a diffraction from h 1 k 1 l 1 planes say this blue lines they give you this line pair stands for diffraction from the h 1 k 1 l 1 planes hence they from the h 2 k 2 l 2 planes after diffraction we get these line pair now if it.

So, happens that the interplanar distance of the h one k one l one planes which is say d 1 and the interplanar distance of the h 2 k 2 l 2 which is say d 2 if d 1 and d 2 are very very close if d 1 d 2 are very very close, then what happens lambda is equal to 2 d sin theta the Bragg's law tells us that if d of the planes are very very close; since lambda is a fixed quantity then what will happen this thetas will also be very very close. So, the 2 cones of radiation from this plane and that plane they will be almost similar as a result the. So, happens that the distance between the 2 lines will be. So, small that it may be difficult to identify the 2 lines from the 2 planes as separate lines. So, what property of the X-ray camera will determine that? Well, in one case the 2 lines from the 2 planes with very similar d values can be seen as distinct lines? So, that will depend on what is known as the resolving power of the camera.

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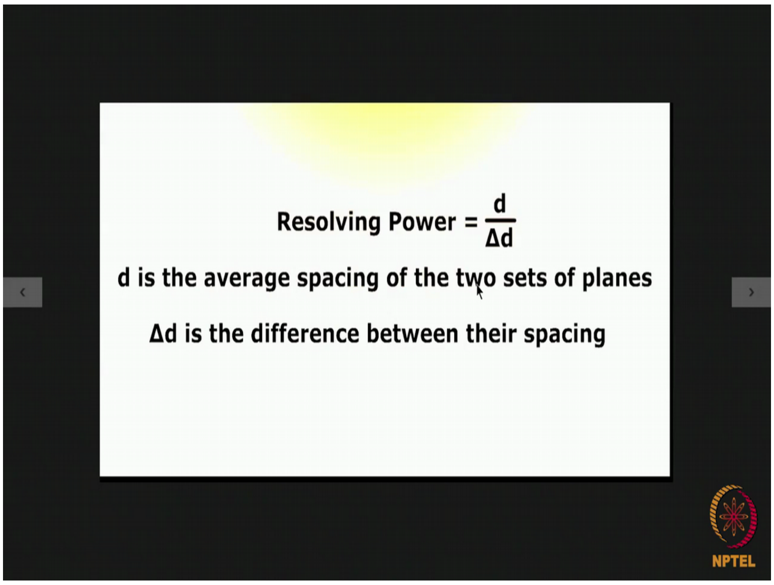

So, we define the resolving power by term d by delta d. So, what is d? D is the average spacing of the 2 sets of planes that we are considering here. So, d is the average spacing of these 2 and what is delta d delta d is the difference between their spacing.

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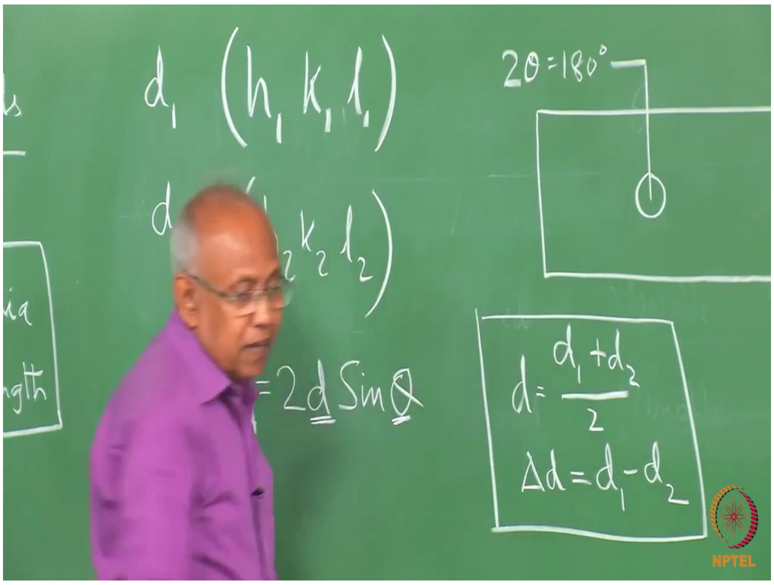

So, we have got d is equal to d 1 plus d 2 by 2 the average spacing and delta d is nothing but the difference between the 2 d S d 1 minus d 2 as for in this case. So, d S average spacing of the 2 sets of planes and delta d is the difference between their spacing’s. Now we will find out an expression for this quantity the resolving power of the camera. Now how we do it?

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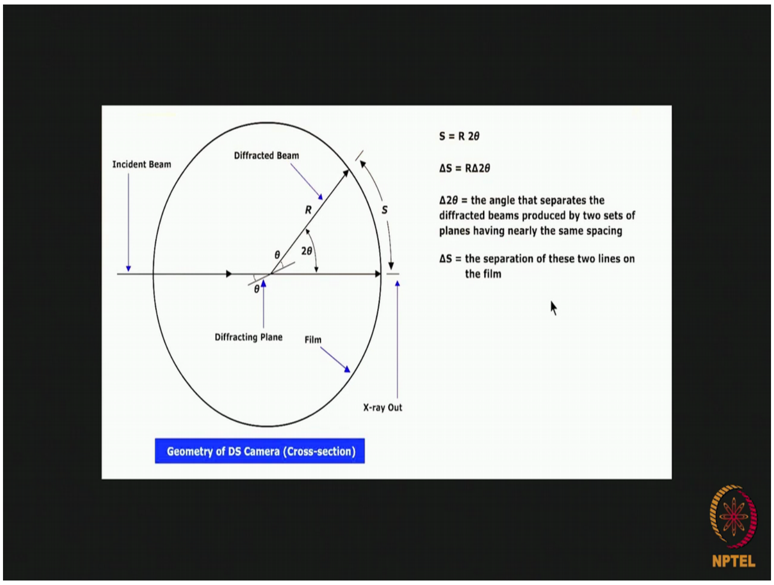

Say for example, this is the geometry of a Debye Scherrer camera this is just a cross section this is where we have got the needle sample perpendicular at a plane of the figure this is the direction of the incident radiation this is the for where the direct radiation goes out and say this is a diffracting plane making the correct brag angle.

So, there will be a diffraction along this now this distance can be measured on the film after the exposure is over now say this distance is s. So, we can write it S equal to R; R is a radius of the camera in to 2 theta 2 theta is the angle between the incident and the diffracted beam. So, S equal to R into theta or delta S is R delta 2 theta; what is delta 2 theta this is the angle that separates the diffracted beams produced by 2 sets of plains having nearly the same spacing.

So, in this case say you have the diffracted beam from this plane having say the interplanar distance d 1 over here and if you have another plain d 2 close to it may be these line will be somewhere here very close to it. So, delta theta you can calculate from the position of the 2 diffracted lines. So, delta 2 theta is the angle that separates the diffracted beams produced by 2 sets of planes having nearly the same spacing and what is delta S this is a separation of these 2 lines on the film. So, for one set of planes if this is the where the diffracted radiation intersects may be the other one the diffracted intersects very close to it and thus distance is delta S.

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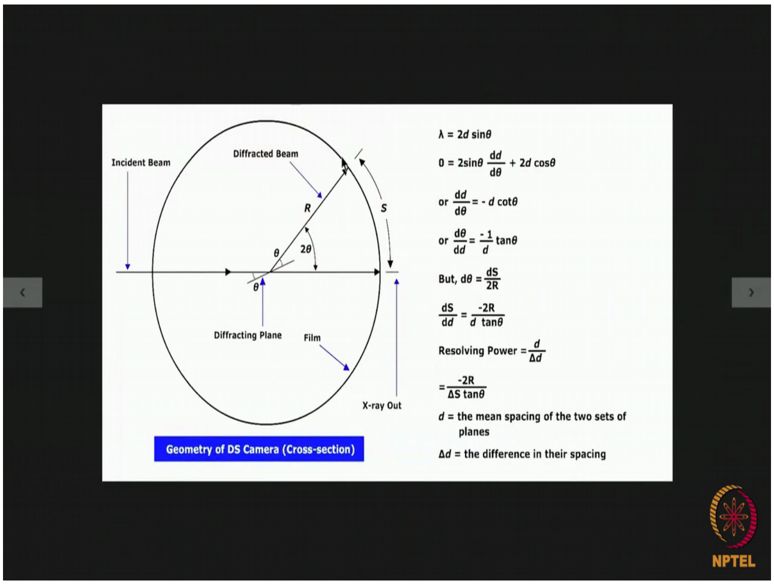

Now, the Bragg's law states the lambda is equal to 2 d sin theta. So, if we differentiate both sides with respect to theta we come to this kind of a situation or if we write d d d theta is equal to minus d co tangent or d theta d d will be minus 1 by d tan theta, but we know that d theta is d S by 2 R, because is S equal to R 2 theta where R is the radius of the camera. So, we can write d S d d is equal to minus 2 R by tan thet.Nnow we know that the resolving power is d by delta d.

So, we can write d by delta t is equal to minus 2 R divided by delta S tan theta the negative value here does not have any meaning. So, the resolving power here can be taken as 2 R divided by delta S tan theta. So, how you increase the resolving power the resolving power can be increased by increasing the R. Please remember the negative value here does not have any meaning at all. So, the resolving power can be increased simply by increasing r. That means the diameter of the cylindrical camera bigger it is better will be the resolution.

So, this is what we find in case of a d S or Debye Scherrer camera. Again we know that d is the mean spacing of the 2 sets of planes and delta d is the difference in the spacing.