X-Ray Crystallography
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Lecture - 27
Particle Size Determination by XRD

In a polycrystalline material; grain size is a very important parameter. Since, the mechanical property of a polycrystalline material depends very much on the grain size. For example, the tensile strength and hardness of a polycrystalline material will continuously increase as the grain size becomes finer and finer. It is therefore, very important to device suitable methods by which grain sizes can be accurately measured.

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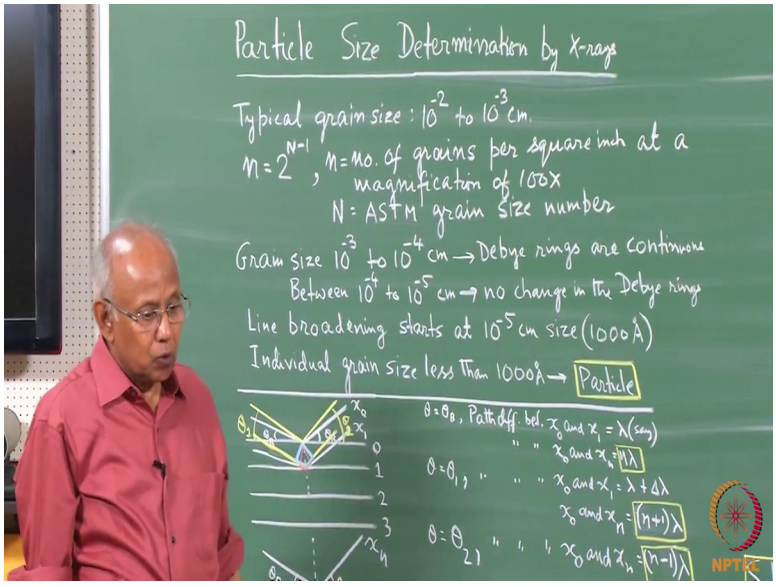

Now in a normal polycrystalline material, we find that the average grain size varies between 10 to the power minus 2 to 10 to the minus 3 centimeter. Now it is quite usual practice to describe the grain size of a polycrystalline material by mentioning; what is known as the ASTM grain size number.

Now, let us see what is meant by the ASTM grain size number. ASTM as you all know stands for American Society for Testing of Materials. Now, they have given a formula written as small n equal to 2 to the power capital N minus 1; where small n is the number

of grains per square inch at a magnification of 100 and capital N is the corresponding ASTM grain size number. So, if as a routine matter, it is necessary to find out the grain size of a polycrystalline material from time to time. One of the ways will be to take known grain size materials and find out pinhole photographs from them. Then those from those pinhole photographs we determine; what is the ASTM grain size number.

Then those we know photographs can be arranged as per the ASTM grain size number as has been shown here.

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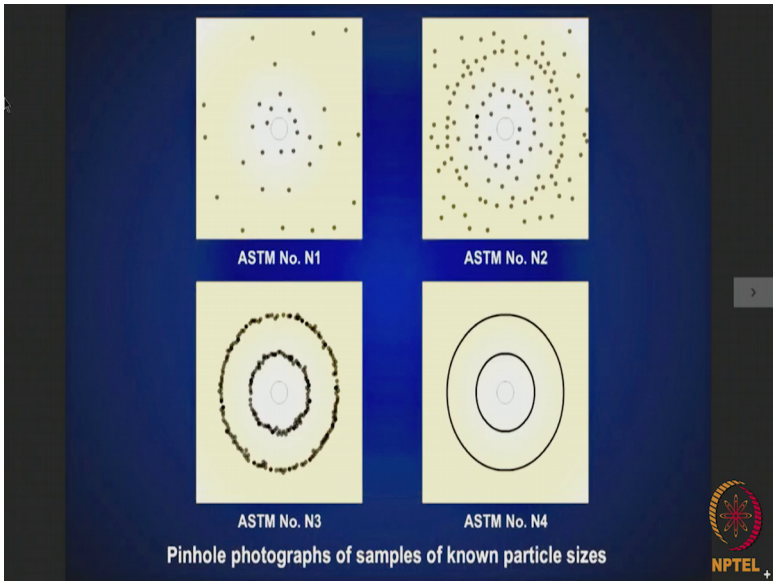

This is for the ASTM grain size number 1, this is for the ASTM number 2m this is 3, this is 4. So, whenever we have an unknown material giving to us and in develop the micro structure and also find out the pinhole photographs from them and then try to match the pinhole photograph of the unknown with the pinhole photograph of known grain sizes. In this way the grain size of a polycrystalline material can we expressed by the corresponding ASTM grain size number. When the grain size varies between 10 to the power minus 3 to 10 to the power minus 4 centimeter, we find that the Debye rings become continuous. For example, here if we can see the Debye rings are quite spotting.

Here the Debye rings have not really form here. Here the Debye rings you know we can see the outline of the Debye rings; here the Debye rings are spotting there is in is the grain size is large. In this case is Debye rings is continuous indicating that here we have a smaller grain size. So, as the grain size varies between 10 to the power minus 3 to 10 to

the power minus 4 centimeter the Debye rings become quite continuous. In fact, no change in the Debye rings is observed when the grain size varies between 10 to the power minus 4 to 10 to the power minus 5 centimeter the moment the grain size becomes 10 to the power minus 5 or less there is a broadening of the Debye rings which is observed.

So, this is a cutout value; when the grain size is 1000 and angstrom or less the lines show a broadening behavior and the individual grain size less than 1000 angstrom; we call those grains as particles.

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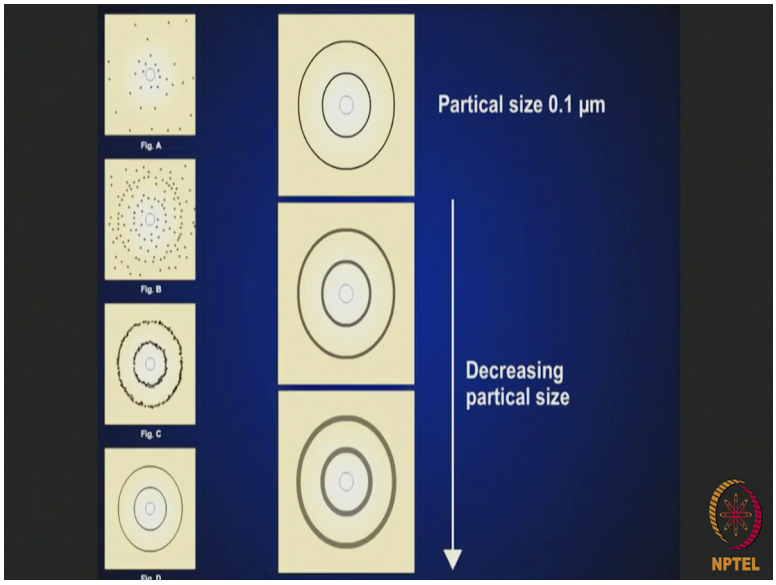

So, here we have a number of phenol photographs these are the 4 which I have already shown. So, here the particle size is 0.1 micron and then it goes down decreasing particle size. As we can see here; the Debye rings form exactly at the same locations, but the width of the Debye rings is somewhat more than in case of; this as the particle size decreases further the width of the Debye rings becomes more and more. So, there is a perceptible line broadening which is observed when a particle you know a size decreases further and further.

Now, there has been a method that is been developed to measure the particle size from the broadening of the lines of the Debye rings. So, we will discuss that particular method.

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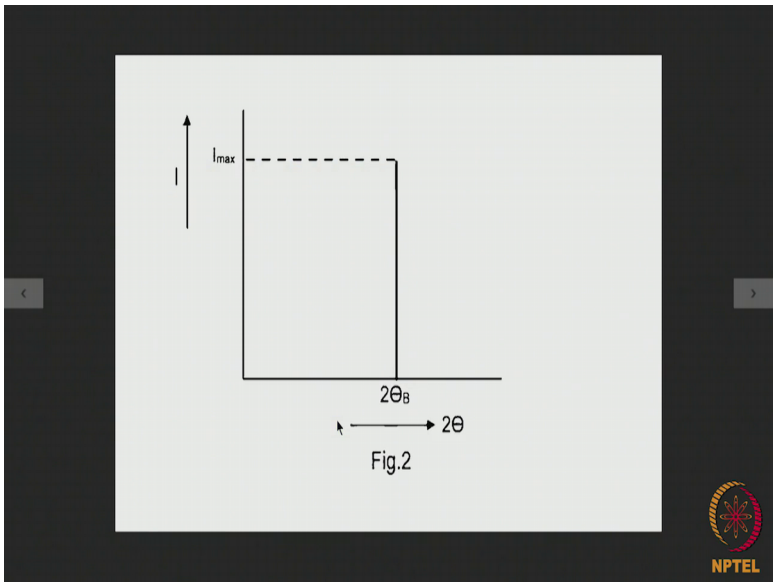

Now when we have the Bragg law perfectly satisfied, then what we expect we would expect that all the diffracted intensity will be concentrated at 2 theta B where theta B is the Bragg angle. So, this should be the shape of the diffraction line profile for when Bragg's law is perfectly satisfied, but what we observe in practice in practice you find a diffraction line has this kind of a profile.

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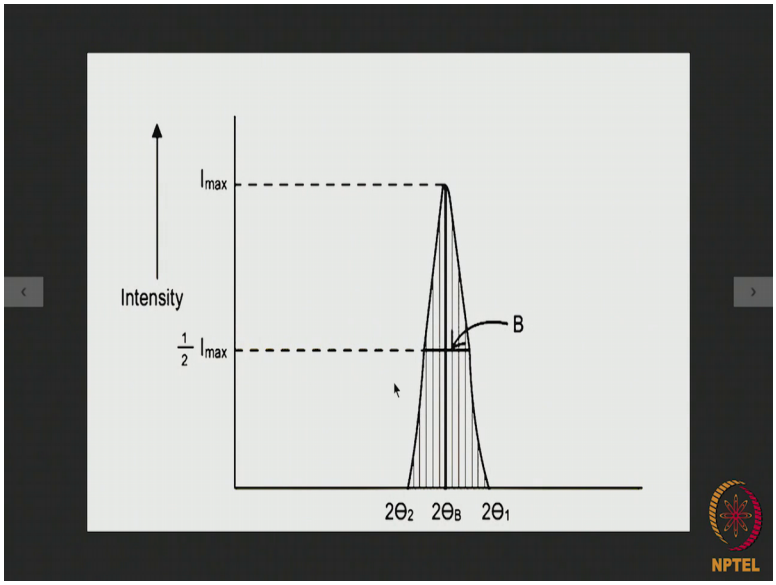

So, it has a measurable breath at half the maximum intensity. So, whenever we have a line profile, we measure the breadth of the line profile at half the maximum intensity. So,

this is the maximum intensity for the line and this is half the maximum intensity level and the breadth here is the line breadth B.

So, what we observe that this kind of a behavior is found for incident angles slightly larger than the Bragg angle and also for slightly lower the angle then the Bragg angle beyond that there is a practically no intensity obtained. So, this line profile shows that even when Braggs law is not perfectly satisfy we will find some intensity. So, this is the non ideal Bragg condition and the reason is very simple if see whenever we have diffraction occurring from a series of planes say when the incident in radiation a you know is theta B the Bragg angle necessary for diffraction.

Then there will be a diffracted intensity, but even when the Braggs law is not perfectly satisfied. That means, the angle the incident angle is slightly different from theta B then also we find some intensity the reason is very simple in order that complete destructive interference to take place we need that the diffracted wavelengths will be completely out of phase.

If the at this 2 points the diffracted radiations like x 0 and x 1, if they are completely out of phase then only their own be any diffraction, but say for example, is by some chance; we find that they are not completely out of phase even then there will be some diffracted intensity is intensity will be much less as compared to when the Bragg's law is perfectly satisfied. So, this is a very important observation that even when Braggs law is not perfectly satisfied and when the incident angle of the acceleration is slightly more or slightly less than theta B. Even then we will get some intensity as a result of which an actual diffraction line profile looks like this. So, this is practically the cut of angles beyond which their own we any diffraction possible.

Now, say for example, in this particular case we have got the Bragg equation satisfied when the incident radiation falls at the correct angle theta B. So, this is the D value; the interregnal distance. So, let us suppose that when the incident X-Rays are incident on these parallel set up plane at the correct Bragg angle then x 0 and x 1; they constructively interfere totally and giving rise to the Braggs diffraction Bragg size perfectly satisfy. Let us suppose that when theta is theta B the correct Bragg angle the path difference between the rays x 0 and x 1 is equal to 1 wavelength lambda. Now if we consider a crystal containing a series of these planes line from plane 0 up to say plane n; then what will

happen, what will the path difference between the ray x 0 and x n when the Braggs law is perfectly satisfied it will be n times lambda.

Now, suppose we increase the angle of incidence of the X-Rays to a value theta 1. So, theta 1 is slightly larger than theta b. So, in this case what we find in this case the path difference when theta is theta 1 between the 2 rays will be slightly more than the path difference between the same rays when the perfect Bragg law is satisfied. So, in this case where theta is equal to theta 1 theta 1 slightly bigger than theta B the path difference between x 0 and x 1; we know longer be one wavelength, but plus delta lambdas wavelength and what will happen when the path difference between x 0 and z n on that the condition when theta is theta 1; theta 1 is slightly larger than theta B it will be n lambda plus one more lambda it will be n plus one lambda.

Now, why this is so; the reason is very simple you see if the path difference between the ray x 0 from the 0 with plane and the x n from the n-th plane is say n plus 1 lambda then we must it is very easy to visualize that within the crystal somewhere in the middle there will be a plane the path difference between the rays from the 0 with plane and the middle plane must be equal to lambda by 2 half lambda you see that due to the increase in the incident angle from theta B to theta 1 there will be and increase in the path difference values. So, if for Bragg angle when Bragg law is satisfied completely if the path difference between the rays x 0 from the zeroth plane and x n the ray from the n-th plane is n times lambda than under this condition when we go up to a theta equal to theta 1 slightly more than theta B, but beyond which there is no diffraction possible then the path difference between those 2 rays will be one lambda extra then this.

So, it is n plus 1 lambda why this is. So, the reason is as I have already said in the whole crystal here this is suppose the whole crystal and within this crystal there must be a plane somewhere in the middle which will be such that the path difference between x 0 and the diffracted radiation from that middle plane must be equal to lambda by 2. As a result what will happen they radiation scattered from the zeroth plane and the plane somewhere in the middle they will nullify each other they will be completely out of phase in this way if we consider the scattered radiation from plane number one and scattered radiation from the plane next to the middle they will also nullify each other.

So, in this way you know in the top half of the crystal the planes the top half of the crystal the radiation started from them will be nullifying the radiation started by the bottom half of the crystal as a result of which we will find that will be no diffracted radiation possible beyond the value of theta 1 and that is what we are observing here in a similar way if we decrease the angle or incidence from theta B to say theta 2 where theta 2 is not we just slightly away from theta B.

Then we will have a similar situation that the path difference between x 0 and x l. We will again be equal to l minus 1 lambda, because here the path difference we be shorter when theta 1 is larger than theta B then the path difference between the 2 rays will be somewhat larger as compared to when it is theta B and again; when it is theta is theta 2 where theta 2 is less than theta B. It can be shown that the path difference between the rays will be somewhat lower than in case of when the Bragg's law is perfectly satisfy.

So, only in these condition; we will see that beyond a value of theta 1 or beyond a value of theta 2 for the incident radiation; they are would not be any more intensity and as a result of which the line profile we will have you know a shape of this time.

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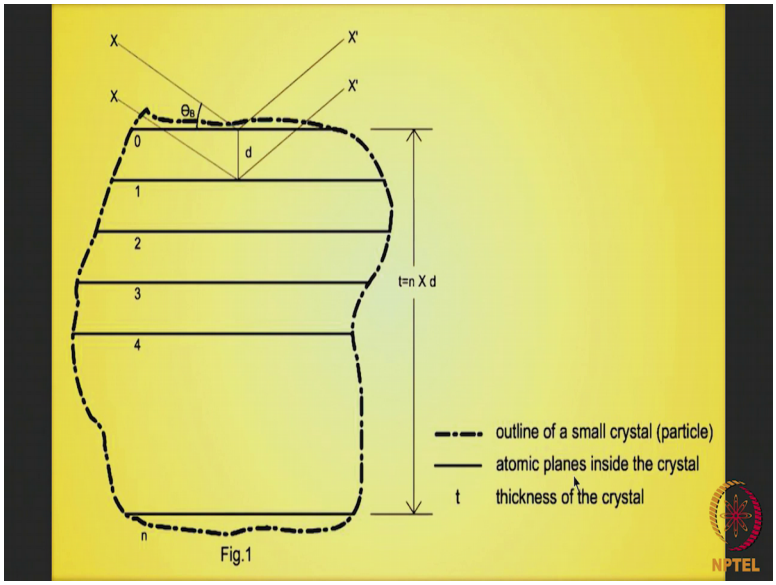

So, this is what I have already explained. So, this is say the outline of the crystal we are considering and there are planes marked as 0, 1, 2, 3, 4, etcetera up to n. So, the thickness of the crystal t we can write as n into d where d is the inter-planar this terms. So, this is the situation t is equal to n into d. Now when perfect Bragg law is satisfied for

this particular crystal we can write down 2 t sin theta B must be equal to n times lambda well between 2 consecutive planes it is 2 d sin theta B is equal to lambda.

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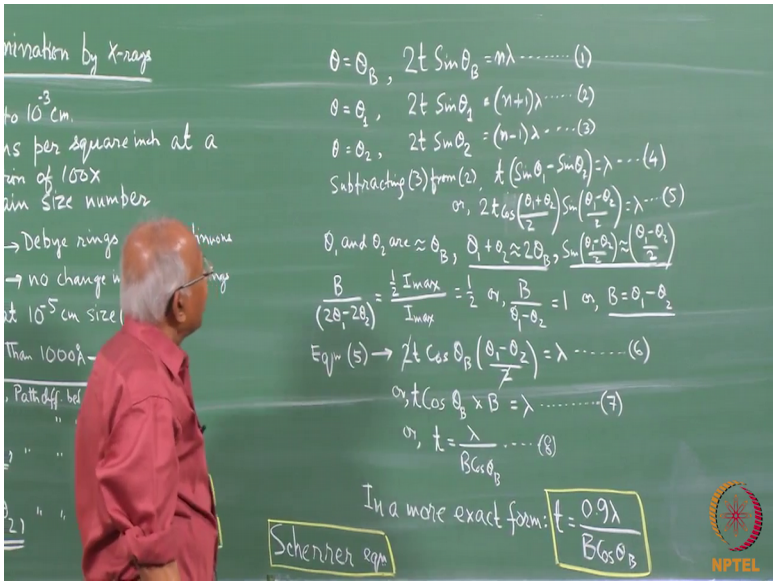

So, for the whole crystal it will be you know when we consider the radiations from the 0 with plane 0 with plane and the n-th plane we can write down when theta is equal to theta B 2 t sin theta B must be equal to n lambda and when theta is theta 1 where theta 1 is slightly larger than theta B the corresponding equation will be 2 t sin theta 1 equal to n plus 1 times lambda when theta is theta 2; where theta 2 is slightly smaller than theta B we find it can be the whole equation can be written as 2 t sin theta 2 is equal to n minus 1 lambda.

This is clear from what I have saying already. Now if we subtract equation 3 from equation 2, we can write t sin theta 1 minus sin theta 2 will be equal to lambda or 2 t cosine theta 1 plus theta 2 by 2 sin theta 1 minus theta 2 by 2 equal to lambda.

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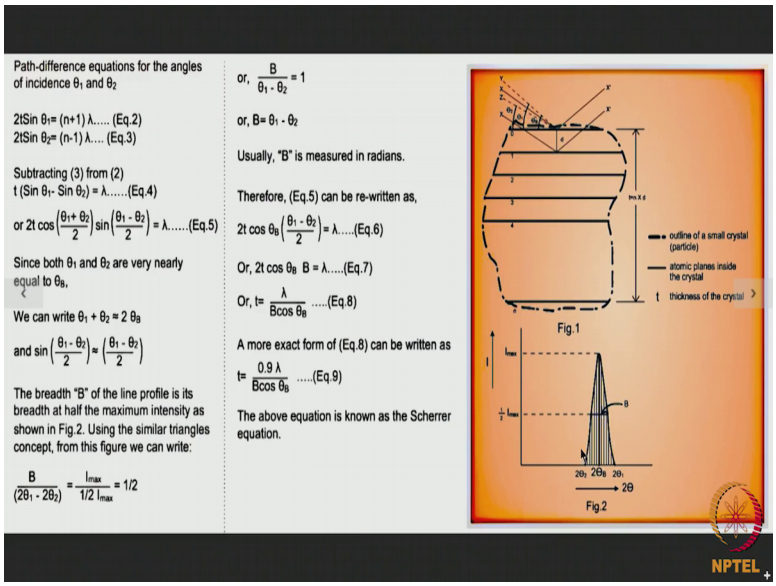

Now, you say theta 1 and theta 2 they are not very different from theta B as; we know when we talk about a diffraction line profile it is true that the intensity is obtained not only at exact 2 theta B, but also beyond 2 theta B in both the directions, but it is available only up to a certain angle you know I have shown it on a much magnified scale, but you know the angular the range within which we get reasonable amount of intensity to be very very small. So, you say that theta 1 and theta 2 or not much different from theta B and. So, each one of them can be written as almost equal to theta b. So, in that case theta 1 plus theta 2 becomes very close to 2 theta B and sin theta 1 minus theta 2 by 2 can be written as simply theta 1 minus theta 2 by 2 because this difference is very very small.

Now, from this triangle by similar triangle concept we can write B this which of the line here divided by 2 theta 1 minus 2 theta 2 is equal to half I max by the entire I max you know here it has been written the other way round there is a mistake here. So, it will be B by 2 theta 1 minus 2 theta 2 will be half I max divided by I max; that means, is equal to half. So, we write B by 2 theta 1 minus 2 theta 2 is equal to half I max by I max or it simply equal to half or we can write B by theta 1 minus theta 2 will be equal to 1 or B is equal to theta 1 minus theta 2 very important relationship. Now equation 5; now can be re-written in this form you know because of this values, if you put those values there in equation 5 may write it has 2 t cosine theta B into theta 1 minus theta 2 by 2 equal to lambda 2 and 2 will cross out and will get t cosine theta B in to B becomes equal to lambda or t is equal to lambda by B cosine theta B.

This is the very important relationship you know t the thickness of the crystal or we can call it the particle size of the crystal is equal to the lambda the wavelength that we have used for taking the phenol photograph or the Debye photograph it is divided by B the breadth of the line at half the maximum intensity multiplied by cosine of the Bragg angle now more rigorous exercise is a more exact value and that is t is equal to 0.1 lambda by B cosine theta B. This is the well known Scherrer equation. So, you see that by using the Scherrer equation and by measuring the line breadth and the value of cosine theta B where theta B is the Bragg angle. It is possible to find out the size of the particle. So, this is how particle size is determined by the X-Ray diffraction method.

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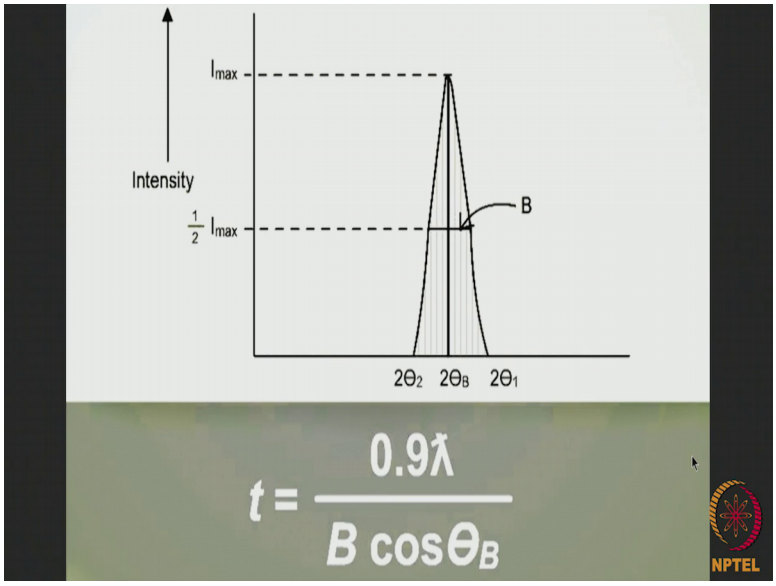

So, this is the situation if this is the breadth of the line profile we can find out t is equal to 0.9 lambda by B cosine theta be this is the well known Scherrer equation.

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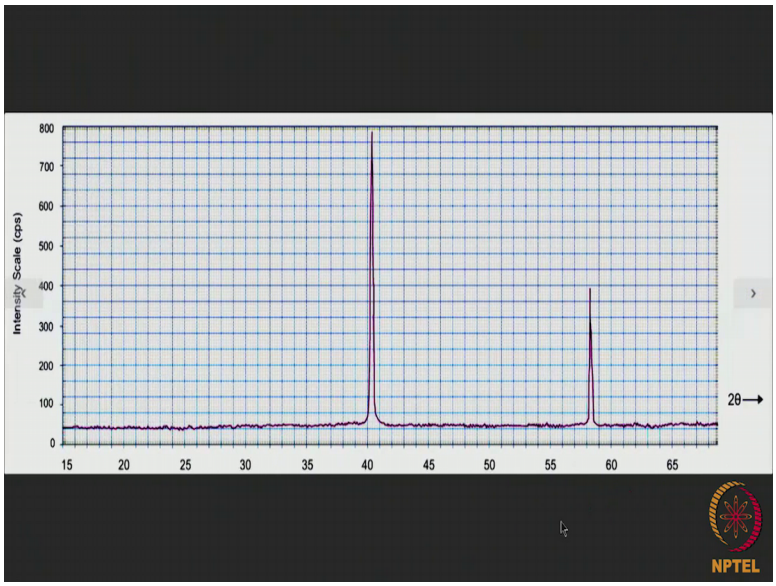

Now if we use a diffractive; it then in a defective it an output we will give the lines in this shape and from their you can find out the line breadths straight away and used in the equation now it is a when we talk about the breadth of a line how to measure the breadth of a line actually there are several ways it can be done, but we used mostly they the method given by warren you see whenever we use a Debye Scherrer camera or a diffractometer to find out the line profile of a diffraction line there is always some instrumental broadening for example, in case of Debye Scherrer method. It is because of the divergence of the incident radiation you enough due to which there will be some broadening of the diffraction lines and in case of a diffractometer, again it is because of the size of the X-Ray spot which you know causes some broadening of the diffraction line.

So, this are called instrumental broadening due to the instrument itself. So, the total width of a line total breadth of a line it is a function of 2 things one is the particle size the other is the instrumental broadening. So, whenever we want to measure the breadth of a line in order to find out the particle size we have to be careful to consider only that part of the broadening which is due to particle size alone now how to determine that. Now there is a method which was suggested by warren.

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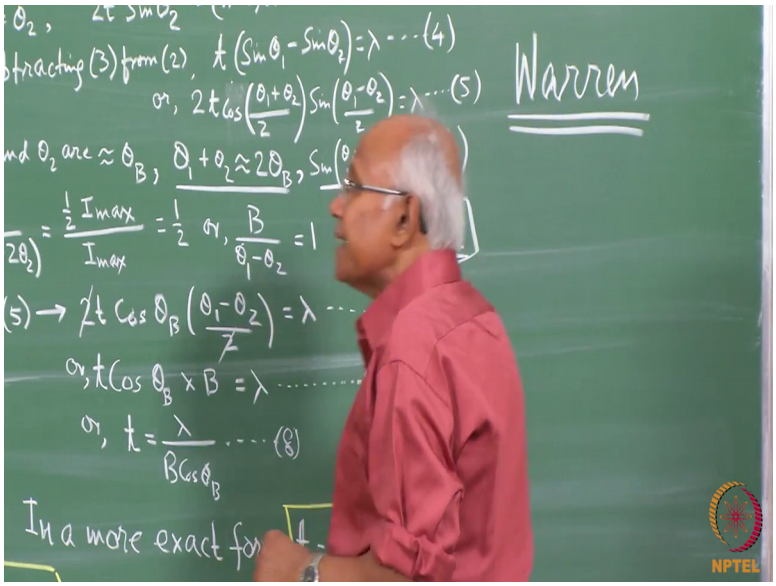

So, what is Warren's method?

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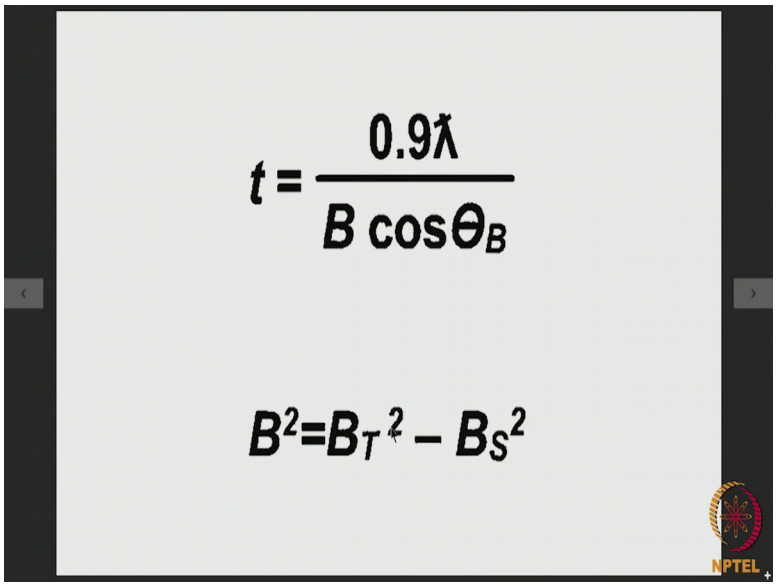

He has suggested that here suggested a formula where B square is equal to B T square minus B S square. So, what is the B square; B square is a square of the broadening due to particle size alone and B T square is this square of the total broadening measure from the diffraction line profile and this broadening is due to the instrumental broadening.

So, a square of the broadening due to the instrument; so, alone one and suggested that we determine B from this kind of an equation you know this kind of an equation is

suggested on the idea that you know the diffraction line profiles look like you know; error caps. So, that is reason why you know this kind of relationship a suggested by him now how to find out the value of B S because B T is a total measured breath and what is B S; how we find out the value of B S; well we can do it in this manner. The material which was working on we mix a standard material with it and the standard material must have a particle size greater than 1000 angstrom. So, that case what will happen the standard material if you get a diffraction line the breadth of the line will be due to the instrumental broadening alone not for particle size.

So, what we do we mix a standard material with a particle size which is larger than 1000 angstrum. So, that the any line the diffraction line from the standard we will not show any breadth due to particle size only and it will show only the instrumental broadening; then we take mix the 2 and take a diffraction pattern and we choose a line from the experimental material and the standard which are close by. And in that case what we will do we will simply measured they breadth of the standard line square it and subtracted from the measure the square of the measured breadth and from there we can find out B square and so we can find out B. So, this is the way we can find out the breadth of a diffraction line due to particle size alone. Now it may so happened that we may have a polycrystalline material containing very fine grains you know they are of the size of particles.

The problem over there is in such materials it is quite likely that there will be some non uniform strain throughout the material. So, if we measure the diffraction line profile the breadth we will also some of the breadth will be due to the strain also there will be strain broadening therefore, this method that we have described is not suitable for determining the fine particle size in polycrystalline sheet materials you know it is good only for material by the powder is in a loose condition and there is no strain in the particles now. So far as application of this method is concerned industrially this method is used for measuring particle size of carbon black industrial dust, etcetera, etcetera.