X-Ray Crystallography
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Lecture - 18
Precise Lattice Parameter Determination

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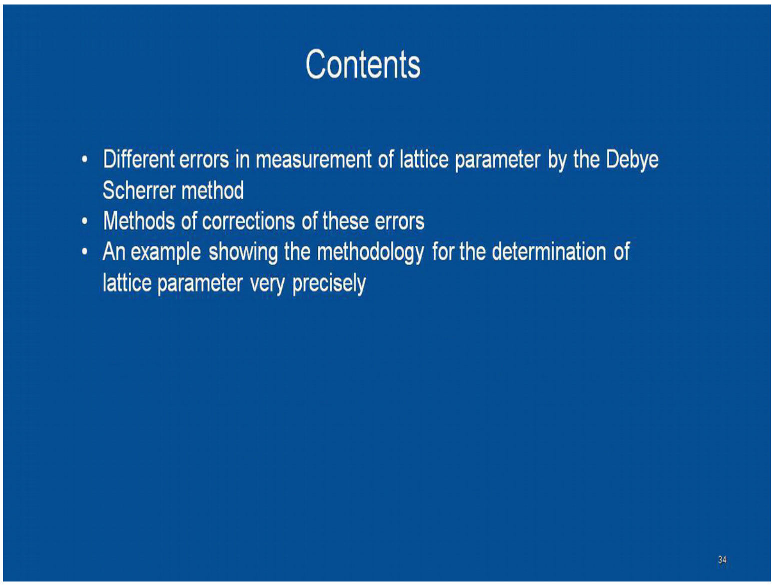

In my last lecture on the determination of crystal structure of a material by X-ray diffraction, I had mentioned that due to errors in measuring the length between a line pair in the diffraction pattern we commit some errors in the calculated value of theta, sin theta, sin square theta, etcetera. These errors ultimately get reflected in the measured or rather in the calculated values of the interplanar distances D and also in the value of the lattice parameter or parameters of the material. I have suggested that the most accurate value of lattice parameter or parameters could be obtained by considering the highest angle line in the diffraction pattern.

Today I am going to explain why I said so, at the same time I shall also describe the procedure of calculating the lattice parameter or parameters very very precisely following some method. Now to start with I would like to show a plot of sin theta versus theta. So, this is the plot of sin theta versus theta.

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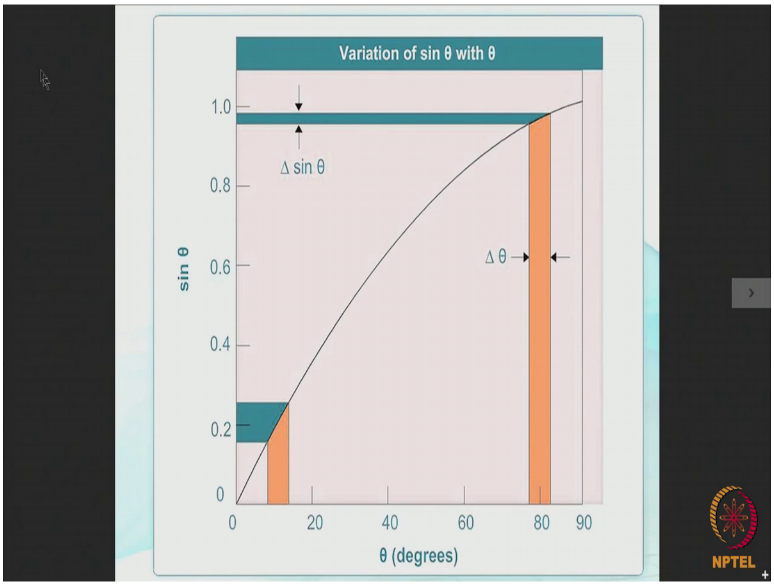

Now say while measuring the distance between the line pairs for a particular diffraction line we commit some error and that error will cause an error in the calculated value of theta. Ssay for example: this much is the error in the calculated value of theta; that means, this is the value which is the actual theta minus the measured theta. How much change this error will bring in the calculated value of sin theta? We can say that this much is the change in sin theta which will be caused by a change this much in the calculated value of theta.

Now, if we commit the same mistake for a higher angle line says over here; that means, this is the amount of error which is equal to this. And then if we figure out what will be the corresponding error in the sin theta value it will be only this much. So, we say that the same amount of error in measuring theta at the low angle side and at the high angle side in a diffraction pattern they will produce different amounts of error in the sin theta value. Not only that the error for the higher angle line will be much less as compared to the error for a low angle line. And this is the reason why when you have a diffraction pattern and when we are asked to calculate D. And therefore, the lattice parameter we always choose a high angle line.

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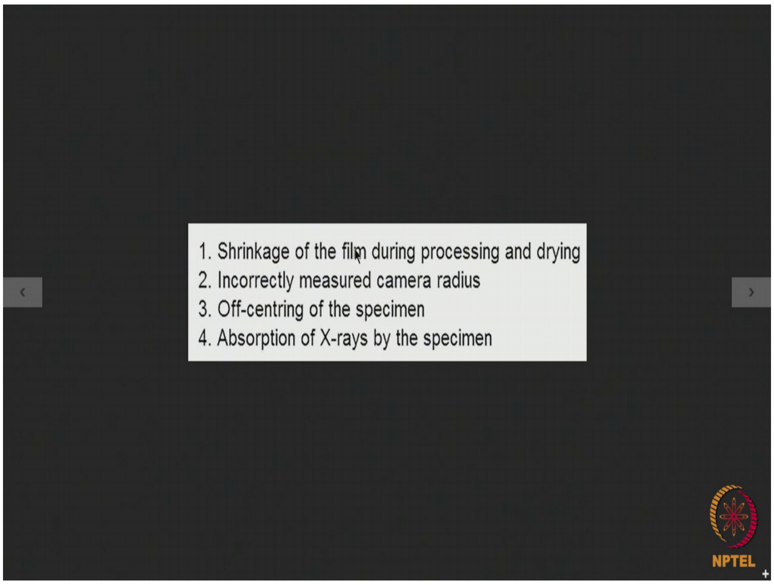

But choosing a high angle line is simply not enough. There are several sources of error for the lines obtained on a Debye-Scherrer pattern. And these errors are: number one, shrinkage of the film during processing and drying; number 2, incorrectly measured camera radius; number 3, off-centring of the specimen; and fourthly, and finally absorption of X-rays by the specimen. So, these are the causes for the errors which we commit in the measurement of line distances in a diffraction pattern. Let us consider the errors due to shrinkage and incorrect camera radius together.

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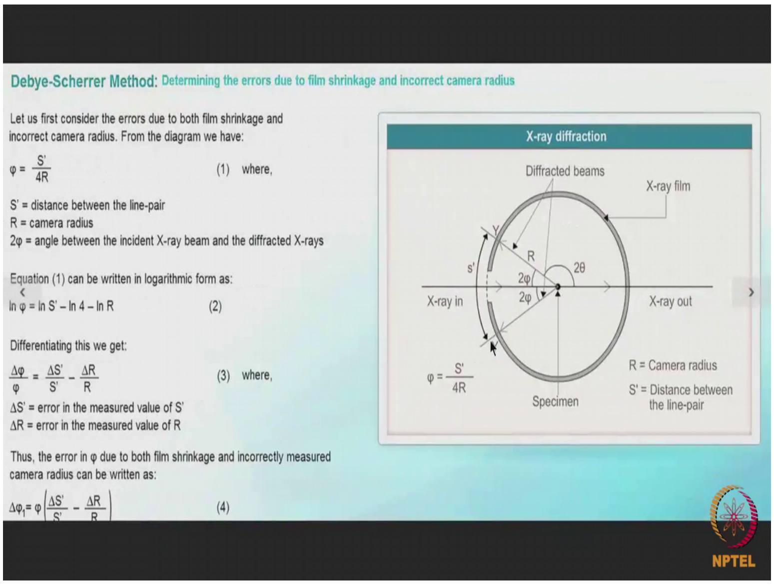

Say for example, we concentrate on a high angle line in the back reflection region of a Debye-Scherrer camera. So, this is the direction of the incident X-ray. And suppose from a particular atomic plane we find the diffracted beam intercepts on the film at y y. Now this angle 2 theta is a angle between the incident direction and the diffraction direction. Let us suppose that this angle here is 2 phi which is 180 degree minus 2 theta. Now when the film is developed and dried and we make a measurement on this particular line pair say the distance we measure as S prime. Therefore, we can write down phi or rather 4 phi into R will be equal to I am sorry 4 sorry 4 phi divided by S prime will be equal to 360 degree divided by pi D where D is a camera distance.

But straight away we can write that phi is equal to S prime by 4 R where R is the camera radius and S dash is a distance between the line pair in question. So, we can write down phi is equal to S prime by 4 R this equation can be written in logarithmic form as l and phi is equal to l and S prime minus l and 4 minus l and R differentiating this we get delta phi by phi equal to delta S dash by S dashed minus delta R by R where what is delta S dash or delta S prime this is the error in the measured value of S prime or S dash and what is delta R this is the error in the measured value of r; that means, if the camera radius is not measured very very accurately.

Therefore the error in phi due to both film shrinkage and incorrectly measured camera radius can be written as from this equation 3 delta phi 1 the error due to these 2 reasons will be equal to phi times delta S prime by S prime minus delta R by R. So, from this equation we can find out delta phi as phi into this quantity. So, if this delta phi we refer to as a error in phi due to both film shrinkage and incorrectly measured camera radius and designate it as delta phi 1 it will be simply equal to phi multiplied by delta S prime by S prime minus delta R by R.

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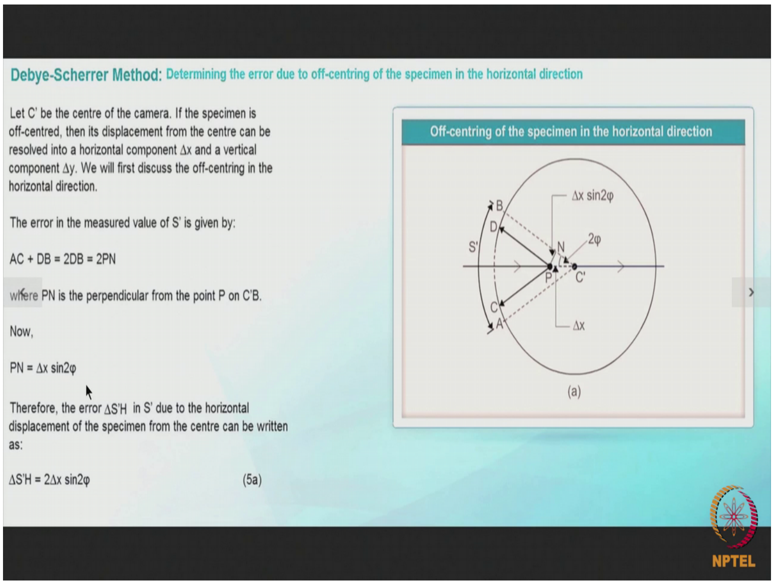

Now, we will find out how much the error is going to be due to the off-centring of the specimen in the horizontal direction. Say for example, let C prime is the centre of the camera if the specimen is off centred then its displacement from the centre can be resolved into 2 components a horizontal component delta x and a vertical component delta y.

We will first discuss the off-centring in the horizontal direction. So, if there is centring of the specimen in the horizontal direction then instead of being at the correct centre of the camera C prime the specimen is displaced along the horizontal direction to a point P. So, this distance over here is equal to delta x say if we put a perpendicular from P on this line then it is P n and this length will be equal to delta x sin 2 phi now due to diffraction the sample the diffraction to the specimen at the point P this will be the diffracted beams namely P D and P C which will intercept on the film at the points C and D, but. In fact, the specimen should have been at C prime the actual centre of the camera and in that case C dash B and C dash A would have been the correct positions of the diffracted beams on the film.

So, the actually actual measured distance for the diffracted beam for the line pair coming out of this sample should have been S prime, but there an error because of off-centring and for that reason we a measuring a distance only C B. Now the total error in the measured value of S prime due to displacement of the specimen in the horizontal direction will simply be a c plus D B, but a c and D B will be practically the same and D B can be taken to the equal to P n where is a perpendicular to the line C dash B. So, we can write the total error in the measured value of S prime only for horizontal displacement of the specimen will be equal to a c plus D B which is equal to thrice D B equal to 2 times P n, but how much is P n P n is equal to delta x sin 2 phi.

So, P n is delta x sin 2 phi therefore, if S prime h is the error in S prime due to the horizontal displacement of the specimen from the centre then S prime h can be written as 2 times delta x sin 2 phi.

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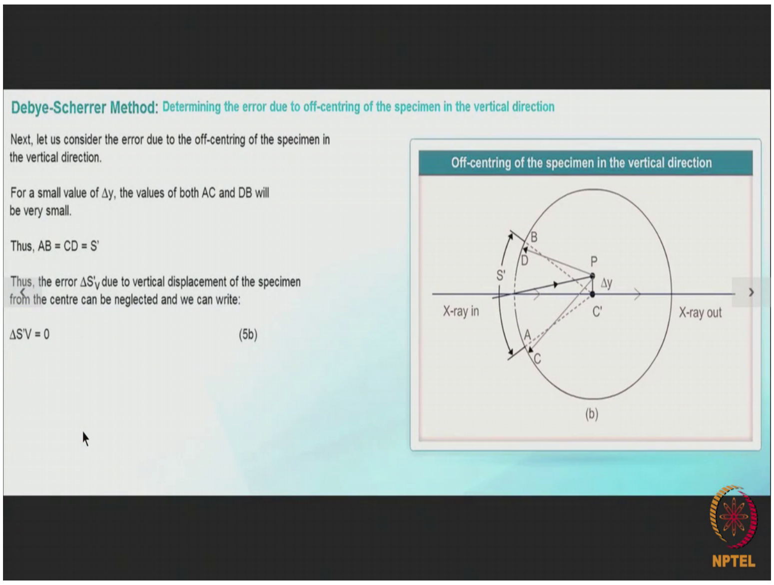

Now, if we consider the error due to off-centring of the specimen in the vertical direction the appropriate diagram is shown here you see if the specimen where at C prime the exact centre of the camera the diffracted beams would have struck the film at the point B and the point A. So, this should have been the correct value of S prime, but due to the vertical displacement of the specimen where by the specimen is placed not at C prime, but at P due to error the diffracted radiations will intercept the film along P D and A C.

Effectively if the value of delta y is very very small then what will happen we will have a situation where a c and D B can be considered very very small and as a result we can take A B is equal to C D is equal to S prime thus the error delta S prime V for vertical displacement of the specimen from the centre can be totally neglected. So, we can write delta S prime V the error in the measured value of S prime due to the vertical displacement of the specimen from the centre of the camera will be equal to 0.

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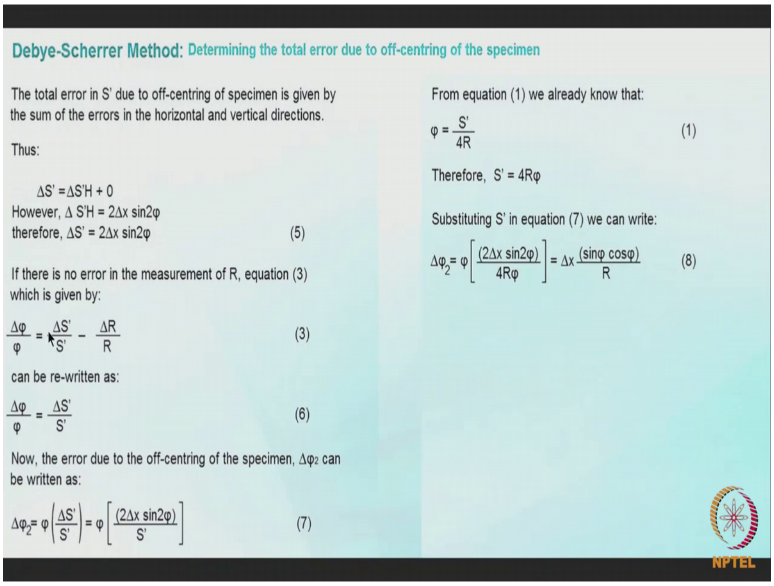

So, now what will be the total error due off-centring of the specimen the total error in the measured value of S prime which you can write as delta S prime it will have 2 components 1 is the error due to the horizontal displacement of the specimen from the centre which can be written as delta S prime h and the error due to the vertical displacement which is 0; however, we know that delta S prime h is equal to 2 delta x sin

2 phi therefore, the total error delta S prime due to the off-centring of the specimen is simply equal to 2 delta x sin 2 phi.

Now, if we consider that there is no error in the measurement of R the radius of the camera then the equation 3 which is delta phi by phi is equal to delta S prime by S prime minus delta R by R will reduce to delta phi by phi equal to delta S prime by S prime we have assumed that there is no error in the measured value of R. So, now, the error due to the off-centring of the specimen which we can write as delta phi 2 can be written as delta phi 2 is equal to phi multiplied by delta S prime by S prime. So, this is obtained from this and that will be equal to phi multiplied by 2 delta x sin 2 phi which is a value of delta S prime divided by S prime.

Now, the equation 1 already shows that phi is equal to S prime by 4 R. Therefore, S prime is equal to 4 R phi. Now if we substitute the value of S prime in equation 7 over here we can write delta phi 2 equal to phi into 2 delta x sin 2 phi and instead of S prime we write 4 R phi that gives us a value of delta x into sin phi cosine phi divided by R.

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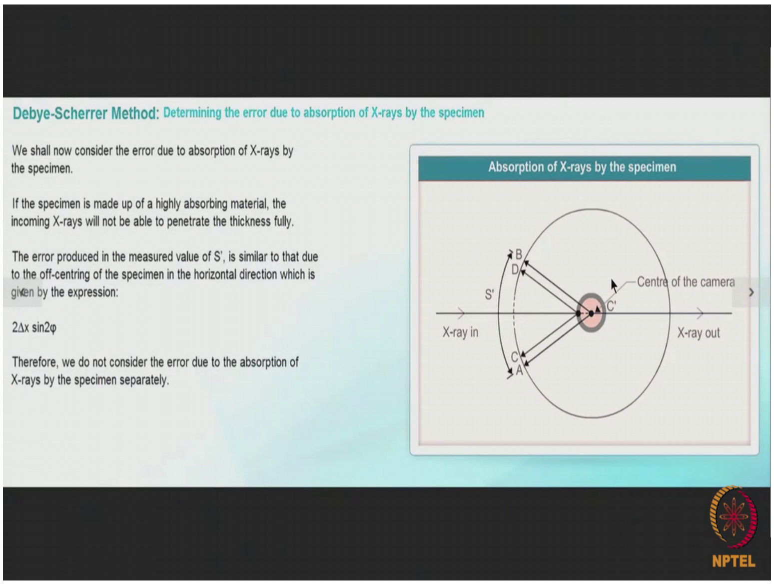

Now, we look at the error which cribs in due to the absorption of X-rays by the specimen. Say for example, this is the cross section of this specimen say and it is correctly mounted at the centre of the camera. Now if the specimen is made up of a material which is highly absorbing then it will be difficult for the X-rays to penetrate the thickness fully.

Naturally the error produced in the measured value of S prime will be quite similar to that of the off-centring of the specimen in the horizontal direction. You see if this specimen this is the cross section of the specimen the specimen is lying perpendicular to this plane. Now if it is made up of a highly absorbing material then the incident X-ray will find it very difficult to penetrate. So, as a result you know instead of the diffracted beam coming from the centre you will find the diffracted beam will emanate from a point away from the centre. So, the correct S prime should have been the length between A and B, but because of the highly absorbing material we will find that the diffracted beam will be coming along in this manner. So, that C D will be erroneously measured as the value of S prime.

Now, this error due to the highly absorbing nature of the specimen is very similar to the error due to off-centring of the specimen in a horizontal direction. So, we do not consider the error due to absorption of X-rays by the specimen separately. Since it has already been taken care of in the error due to off-centring of the specimen in the horizontal direction now what is the total error in the measured value of S prime.

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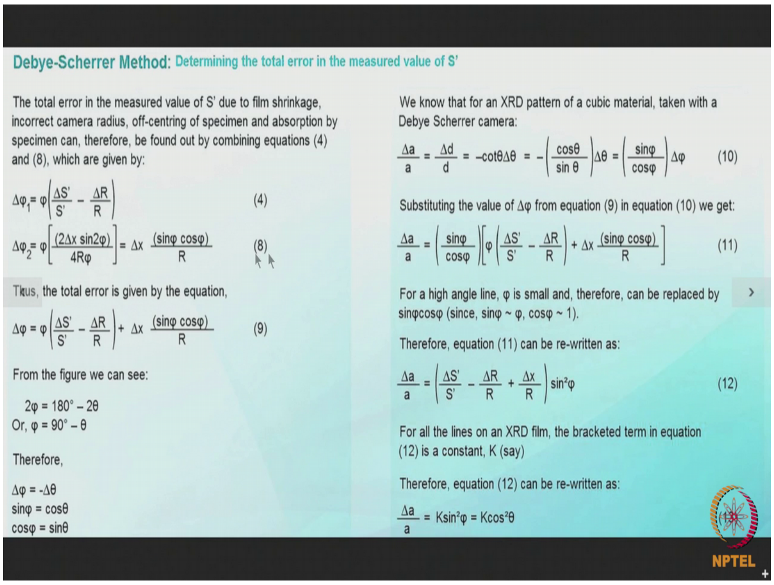

Now, we have already seen sigma phi 1 is equal to; I am sorry the delta phi 1 is equal to phi multiplied by delta S prime by S prime minus delta R by R. So, this is the error in the measured value of S prime due to both shrinkage problem and incorrectly measured camera radius.

Similarly, delta phi 2 which is due to the off-centring of the specimen plus the absorption by the specimen is simply equal to phi into 2 delta x sin 2 phi by R 4 R phi. So, it is equal to delta x sin phi cosine phi by R. Now, the total error is given by combining these 2 equations. So, we will have error in the measured value of phi is equal to phi delta S prime by S prime minus 4 R minus delta R by R plus delta x sin phi cosine phi by R. We have already seen from the previous diagram that 2 phi effectively is 180 degree minus 2 theta where 2 theta is the angle between the incident X-ray direction and the direction of the diffracted x radiation.

So, phi will be equal to ninety degree minus theta. So, in that case we can immediately write that delta phi will be equal to minus delta theta sin phi will be equal to cosine theta and cosine phi will be equal to sin theta because of this relationship now we already know that for an x R D pattern of a cubic material taken with a Debye-Scherrer camera we can write delta a by a; that means, error in the measurement of lattice parameter is equal to delta D by D error in the measurement of D the interplanar distance is equal to minus cotangent theta delta theta.

So, this will be equal to minus cosine theta by sin theta delta theta or will be equal to sin phi by cosine phi in to delta phi if we substitute the value of delta phi from equation 9 here in the equation 10 we will get delta a by a will be equal to sin phi by cosine phi multiplied by phi in to delta S prime by S prime minus delta R by R plus delta x sin phi cosine phi by R for a high angle line phi will be rather small. And therefore, can be replaced by the quantity sin phi cosine phi since sin phi when phi is very very small can be written as almost equal to phi cosine phi is almost equal to 1. Therefore, equation 11 can be rewritten as delta a by a is equal to delta S prime by S prime minus delta R by R plus delta x by R the whole multiplied by sin square phi.

Now, if we look at all the lines on an X-ray diffraction film the bracketed term in this equation is a constant for all the lines in the pattern and we can write it as the constant K. Therefore, the equation 12 can be rewritten as delta A by A is equal to K times sin square phi or it will be equal to K times cosine square theta.

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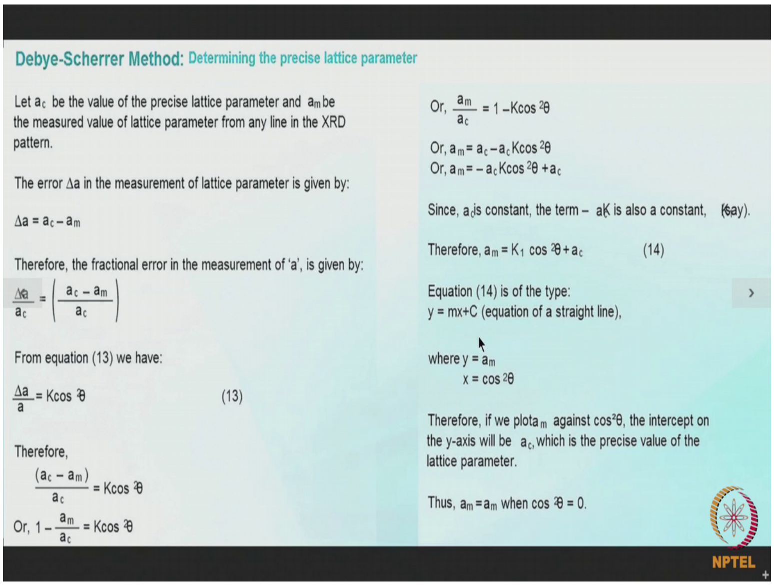

Now we can determine the lattice parameter quite precisely from by following this procedure say let A C; A subscript C be the value of the precise lattice parameter and a subscript m be the measured value of the lattice parameter from any line in the x R D pattern. So, a c is a precise lattice parameter and a m are the measured values of lattice parameter from the lines in x R D pattern.

So, what will be the error delta a in the measurement of lattice parameter it will be given by delta a is equal to a c the correct value of the lattice parameter minus the measured value written as a m therefore, the fractional error in the measurement of a is given by delta a by a c is equal to a c minus a m divided by a c, but we know that the equation that is already shown that delta a by a is equal to K cosine square theta. Therefore, we can write a c minus a m by a c is equal to K cosine square theta or dividing both the terms by a c 1 minus a m by a c is equal to K cosine square theta. In other words a m by a c will be equal to 1 minus K cosine square theta or we can write a m is equal to a c minus a c K cosine square theta or we can write it as a m is equal to minus a c K cosine square theta plus a c.

Since, a c is a constant it is the precise lattice parameter of the material the term a c K is also a constant; that means, a c is a constant quantity the actual lattice parameter the precise lattice parameter K is constant. So, the quantity a c K is also a constant say we write it as K 1. So, this quantity a c K is now a constant and we can write is as K 1 therefore, this equation can be written as a m is equal to K 1 cosine square theta plus a c, now this equation is of the type y is equal to m x plus C the equation of a straight line where y is a measured value of lattice parameter a m and x is cosine square theta.

Therefore, if we plot a m against cosine square theta the intercept on the y axis will be a c which is the precise value of the lattice parameter and a m will be equal to a c you know this has become m again it is a error here a m will become equal to a c when cosine square theta is equal to 0.

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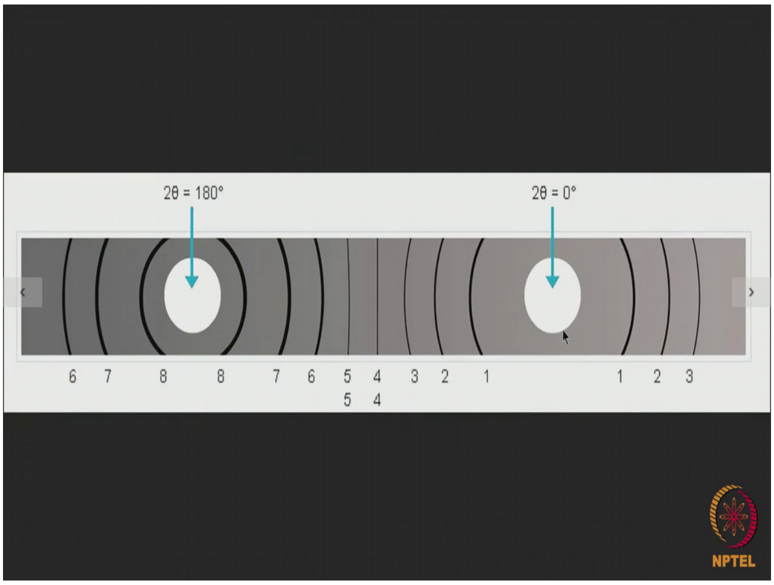

Now, let us suppose the situation where we have got the diffraction pattern of a material and this is one of the samples which we have already discussed in connection with the determination of crystal structure.

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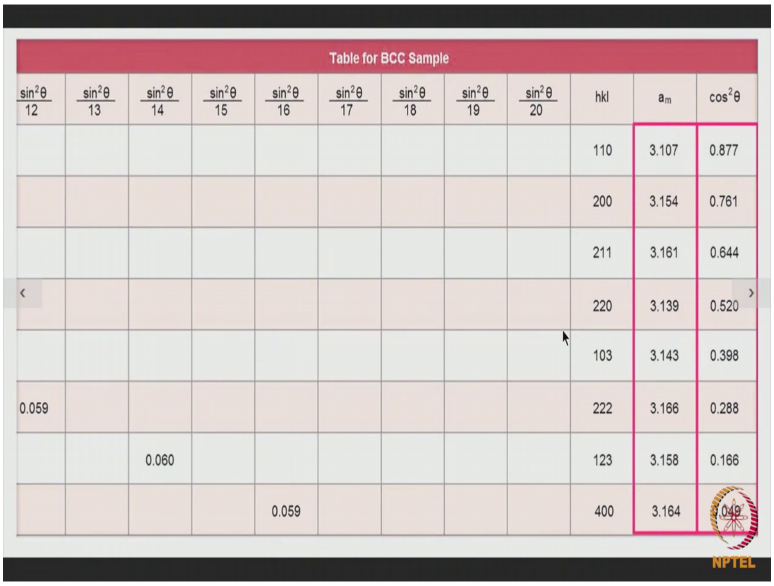

Table for BCC Sample

$\frac{\sin^2\theta}{12}$	$\frac{\sin^2\theta}{13}$	$\frac{\sin^2\theta}{14}$	$\frac{\sin^2\theta}{15}$	$\frac{\sin^2\theta}{16}$	$\frac{\sin^2\theta}{17}$	$\frac{\sin^2\theta}{18}$	$\frac{\sin^2\theta}{19}$	$\frac{\sin^2\theta}{20}$	hkl	a_m	$\cos^2\theta$
									110	3.107	0.877
									200	3.154	0.761
									211	3.161	0.644
									220	3.139	0.520
									103	3.143	0.398
0.059									222	3.166	0.288
		0.060							123	3.158	0.166
				0.059					400	3.164	0.049

Now, that material was the second sample which is studied and it is a B C c sample and if you will remember the h K l values for the lines were 8 in number are 1 1 o 2 o o 2 1 1 2 2 0 1 o 3 2 2 2 1 2 3 4 0 0. So, these are the h K l values of the 8 lines which appear in the pattern and this pattern was same as for sample number 2. In the lecture of determination of crystal structure now we also found out in that case that the measured value of the lattice parameter a n are given by these quantities this is 3.107 from the first line calculate from the first line 3.154 calculated from the second line 3.161 calculated from the third line etcetera, etcetera and 3.164 calculated from the highest angle eighth line.

Now, we know that sin square theta values we plotted the sin square theta values for the 8 lines also from there we can immediately find out what are the corresponding cosine square theta values. So, here we have got 2 tables this table which gives us the values of the measured lattice parameters from the different lines in the X-ray diffraction pattern. And these are the corresponding cosine square theta values for the different lines I had mentioned in connection with the previous lecture that the most precise value of the lattice parameter can be taken as 3.164 angstrom, because this was calculated from the highest angle line. Now we will see how using certain procedure we can come to the most correct value of the lattice parameter.

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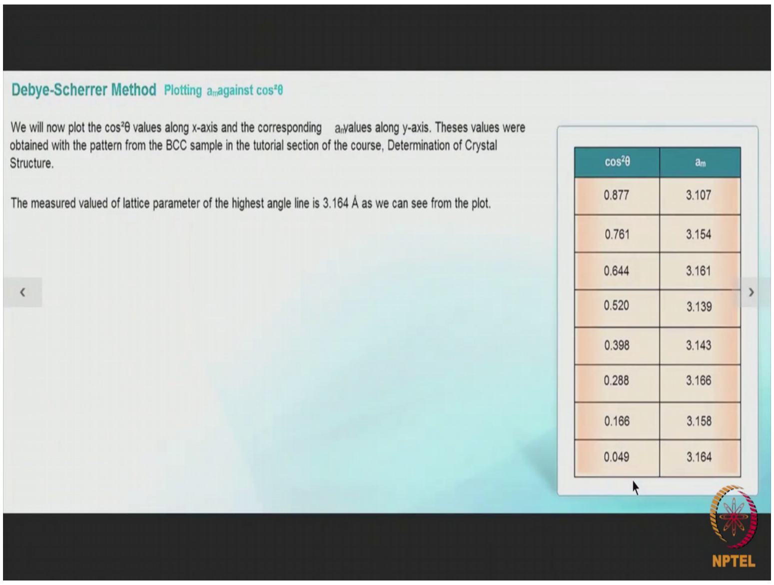

So, now we have 2 tables; 1 for the cosine square theta values and other for the measured values of lattice parameter from the 8 different lines. So, per the procedure described earlier we are going to plot these values.

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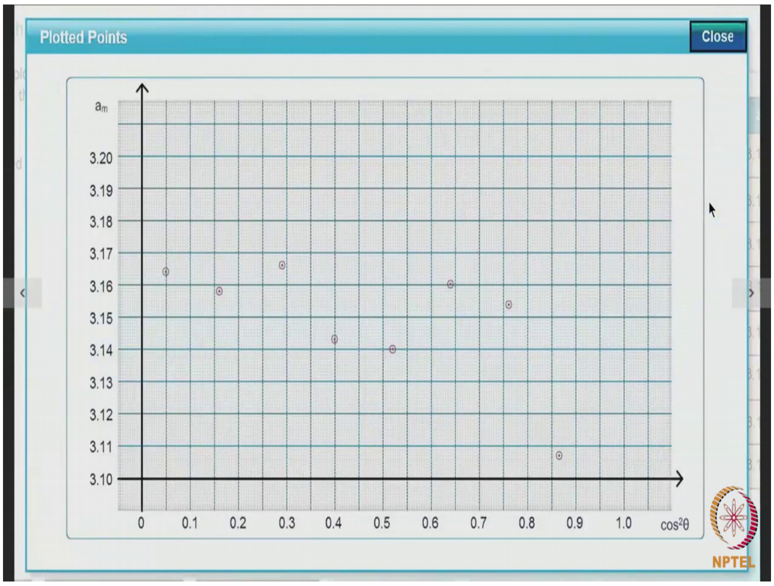

So, we plot the a m values; that means, the measure lattice parameter values along the y axis and the cosine square theta values along the x axis. So, for any particular line in the pattern we find out what is the cosine square theta value and what is the a m value and plot a point. Similarly for another line we find out; what is the cosine square theta value and what is the value of the measured lattice parameter. So, in this way for all the 8 lines 1 2 3 4 5 6 7 8 for all the 8 lines in the pattern we plot a m versus cosine square theta in this form.

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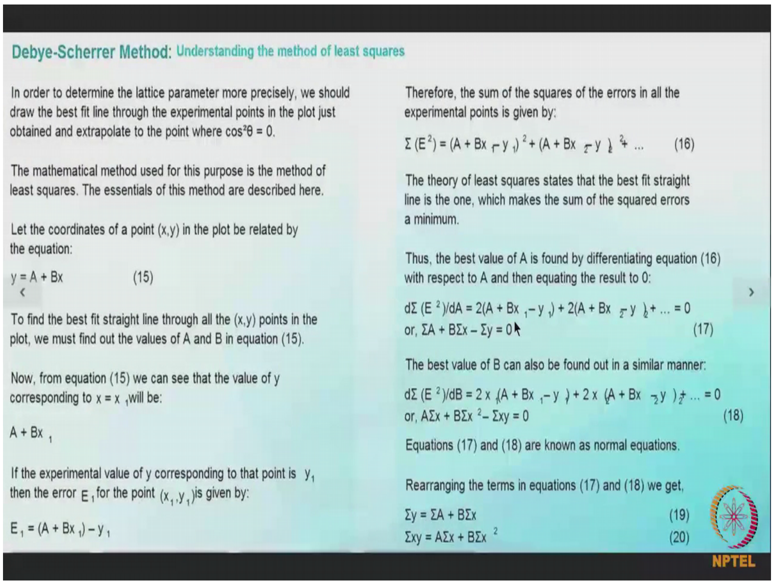

Now, what will be the next step you see the points are widely dispersed? Now in order to determine the lattice parameter precisely we must draw the best fit line though the experimental points in the plot just obtained and then extrapolate that line to the point where cosine square theta is equal to 0, because under that condition only the measured value and the correct value of the lattice parameter a c will be same now how to put a best fit line through the experimental points that is the question now.

Now, we use a mathematical method here for this purpose and that is known as the method of list squares the essentials of this method are described here let the coordinates of a point x y in the plot be related by the equation y is equal to a plus B x to find the best fit straight line through all the x y points in the plot we must find out the values of these unknown quantities a and B in equation 15. Now form equation 15 we can say that the value of y corresponding to x equal to x 1 will be a plus B x 1. So, the value of y corresponding to a point where x is x 1 will be equal to form this equation a plus B x 1.

If the experimental value of y corresponding to that point is y 1 then what will be the error in measuring the point x 1 y 1 the error e 1 will simply be equal to y minus y 1 and y is a plus B x 1 minus y 1. So, if we have a point x 1 say and if we find out that the measured value of y for x 1 is y 1 although the measured value should have been simply y then the error that is committed in the measurement e 1 can be written as y minus y 1 and y is a plus B x 1 for that particular x 1 minus y 1. Therefore, if we find out the sum of the squares of the errors in all the experimental points then you can write down summation e square will be equal to a plus B x 1 minus y 1 square for the point x 1 y 1 plus a plus B x 2 minus y 2 square plus the term for the third, fourth, fifth, sixth, and seventh, and eighth.

So, there are 8 lines. So, we will have 8 such quantities the theory of list squares states that the best fit straight line is the one which makes the sum of the squared errors a minimum thus the best fit best value of a is found out by differentiating equation 16 with respect to a and then equating the result to 0. So, we write D sigma e square D a and from this 8 quantities we can write it down as twice a plus B x 1 minus y 1 plus twice a plus B x 2 minus y 2 etcetera, etcetera must be equal to 0 which means delta or sigma a versus B sigma x minus sigma y will be equal to 0.

In a similar manner the best value of B can also be found out by differentiating e square with respect to B and if we find out the values we will see that a sigma x plus B sigma x square minus sigma x y should be equal to 0. So, these are the conditions to be fulfilled in order that the error is minimum from all the points. Now this equation 17 and 18 are known as the normal equations. So, rearranging the terms in the equation 17 and 18 we get sigma y is equal to sigma a plus B sigma x and then sigma x y is equal to a sigma x plus B sigma x square. We will now demonstrate the use of the method of list squares to find out the best fit line for our problem.

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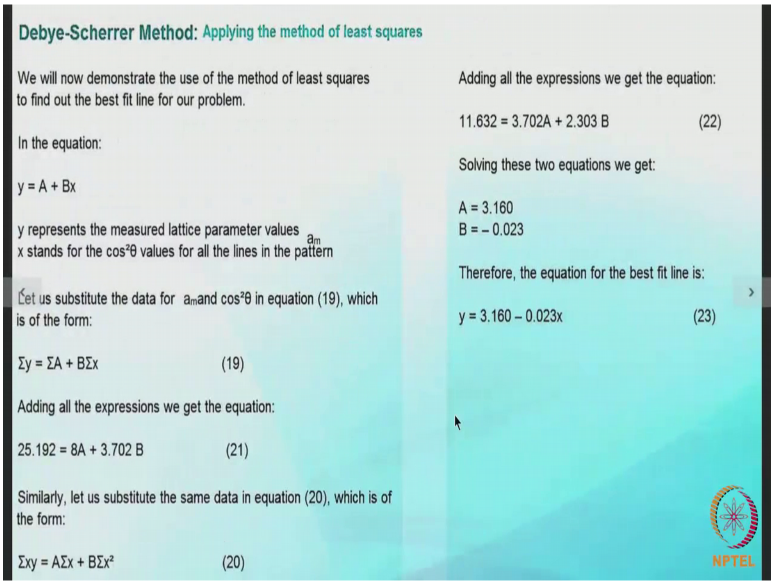

Now, in the equation a y is equal to a plus B x y represents a measured lattice parameter values a m x stands for cosine square theta values for the all the lines in the pattern let us substitute the data for a m and cosine square theta in equation 19 which is of this form. So, let us substitute the values of the data for a m and cosine square theta in this particular equation adding all the expressions we get the equation 25.192 is equal to 8 a plus 3.702 B in a similar manner let us substitute the same data in equation 20 which is of the form sigma x y is equal to a sigma x plus B sigma x square adding all the expressions here we get the equation 11.62 is equal to 3.702 a plus 2.303 B.

Now, solving equation 21 and 22 we get a is equal to 3.160 B is equal to minus 0.023. Therefore, the equation for the best fit line is y is equal to 3.160 minus 0.023 x.

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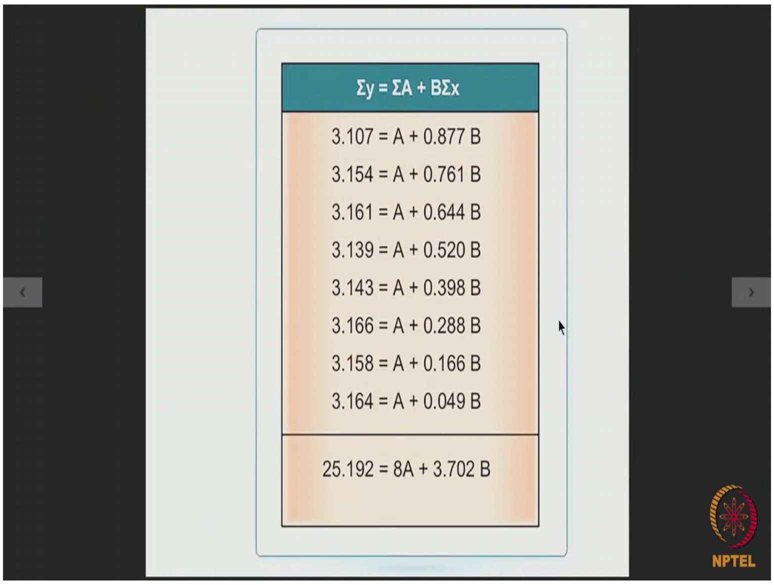

Now, here the calculations for the equations sigma y is equal to sigma A plus B sigma x are shown where for the 8 different diffraction lines in the pattern we have put the values of cosine square theta and a m at appropriate places and that gives us this equation which we have already mentioned.

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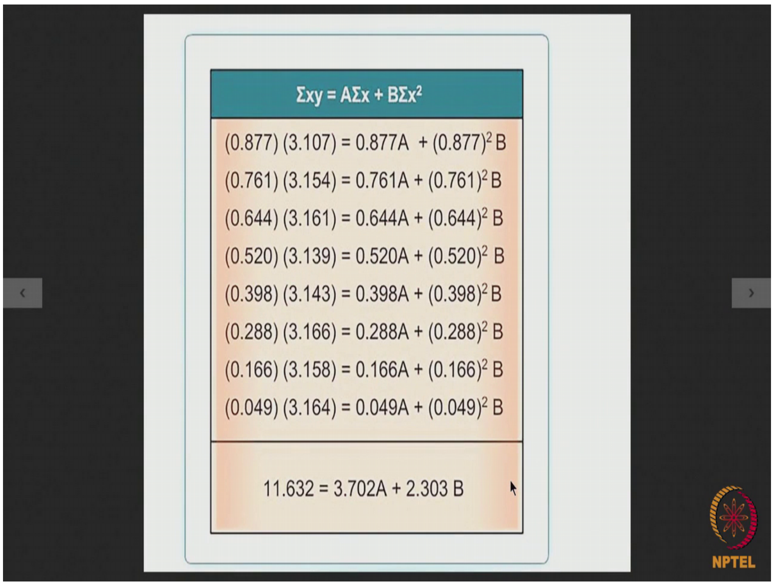

In a similar manner we have also put the appropriate values of a m and cosine square theta in this equation sigma x y is equal to a sigma x plus B sigma x square and when you put those values we get this kind of an equation which we have already used in order to find out the values of A and B.

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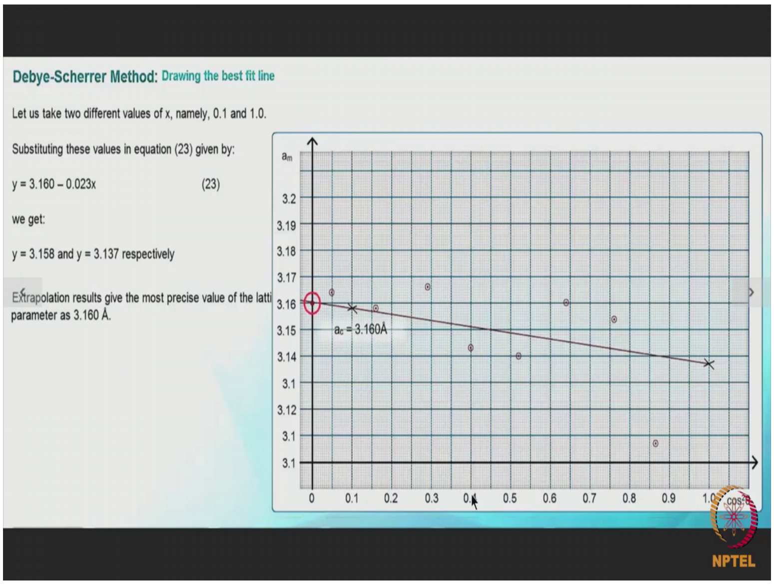

Now let us take 2 different values of x say namely 0.1 and 1.0 now if we substitute these values in equation 23 which is given by y is equal to 3.160 minus 0.023 x we get y is equal to 3.158 and y is equal to 3.137 respectively. So, for x point 0.1 the y is having this value for x equal to 1 y has got this value.

Now, we plot these 2 points and get a straight line and extrapolate it to the y axis. So, by doing, this is the best fit line passing through the 8 points and this is the point which will give us the value of the lattice parameter very very accurately because here cosine square theta has got a value 0.

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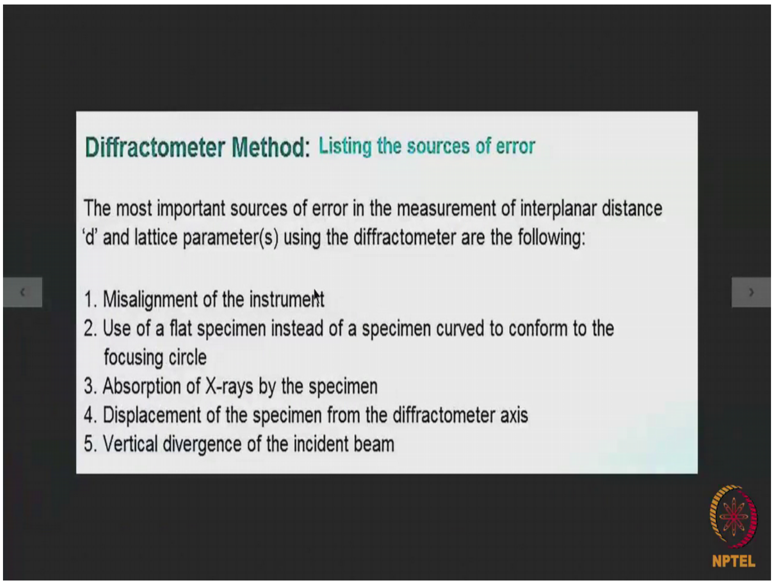

So, this is how the most precise lattice parameter can be obtained if we are given a set of measured lattice parameter values and the corresponding cosine square theta values. So, this is about the Debye-Scherrer method in which we can find out the lattice parameter or parameters very very accurately. Now when you go to the more modern diffractometer method the errors are sometimes quite different now the most important sources of error in the measurement of D. And therefore, a using the diffractometer are the following.

One is miss alignment of the instrument number 2 using a flat sample instead of a specimen which is carved to confirm to the focussing circle the third source of error is absorption of X-rays by the specimen the fourth source of error is the displacement of the specimen from the diffractometer axis and the fifth source of error is the vertical divergence of the incident X-ray beam now.

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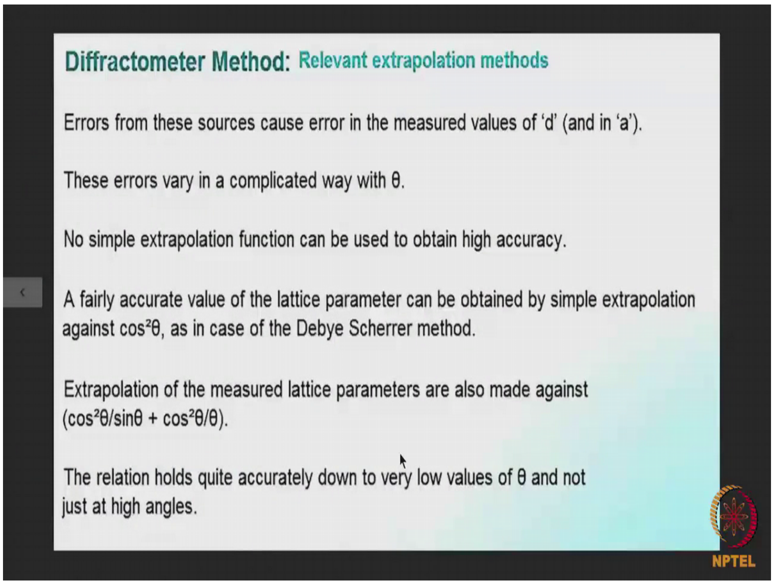

There are relevant extrapolation methods for correcting the values of D and a, but you see these errors in this particular case where in a complicated way with theta as a result no simple extrapolation function can be used to obtain high accuracy.

A fairly accurate value of the lattice parameter can be obtained by simple extrapolation against cosine square theta as we did in case of the Debye-Scherrer method sometimes extrapolation of the measured lattice parameter can also be made against these function cosine square theta by sin theta cosine square theta by theta this relationship holds quite accurately down to very low values of theta and not just at high angles.