INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
NPTEL
NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
Lecture- 14
Precise Parameter Measurements
With
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Hello, today we are going to discuss about the precise parameters of measurements. In our last lecture we have already discussed about the x rd diffractions and their applications. So in this particular lecture first we will discuss about the different types of errors generally we are freshing for doing the x rd.

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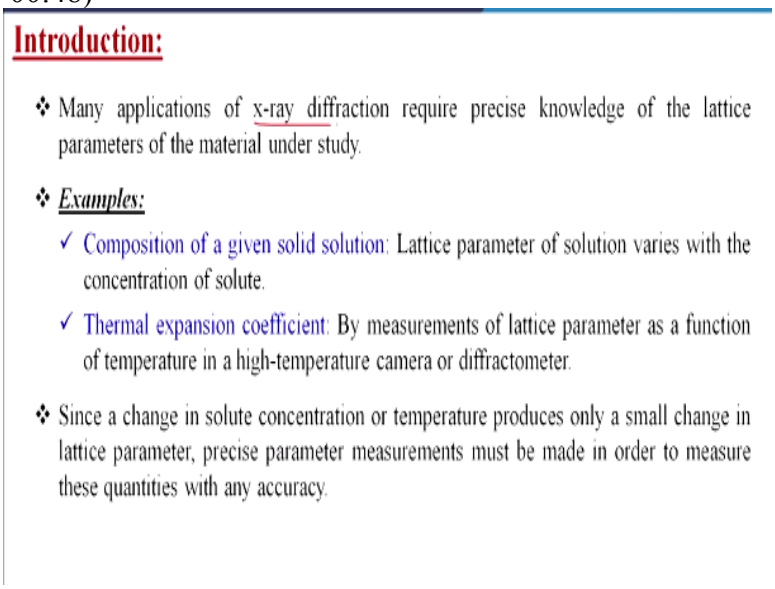

So many applications of the x-ray diffraction require precise knowledge of the lattice parameters of the materials, when we are doing the study. So what are the examples? Like competitions of a given solid solutions. Lattice parameter of solution varies with the concentration of solute and next the thermal expansion coefficient. By measurement of lattice parameters as a function of temperature in a high temperature camera or may be the diffractometer.

So since a change in solute concentrations or temperature produce only a small change in lattice parameter, precise parameter measurements must be made in order to measure these quantities with accuracy. So measurement of the Bragg angle, so generally as we know the Bragg's angle is or maybe the Bragg's law is λ is equal to $2d \sin \theta$.

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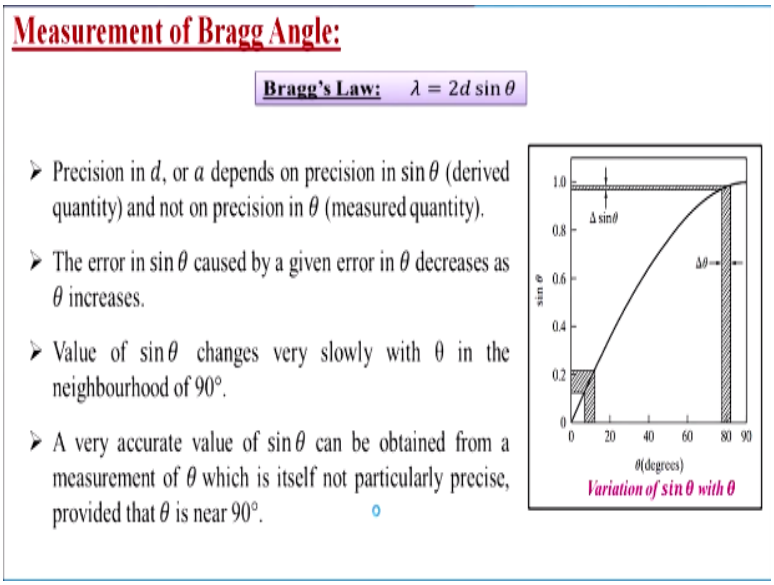

So precision in d or A depends on the precision in sin θ derived quantity and not on precision in θ that is the measured quantity. So the error in sin θ caused by a given error in θ decreases as the θ increases, so in this particular figure you can see that at low angle that θ if we increase more so automatically the sin θ will be more than that and at the higher angle ice almost 90° if we increase the θ more also but sin θ change in the sin θ is very, very less.

So value of sin θ changes various slowly with θ in the neighborhood of 90°, so hence it is going near about 90°. So a very accurate value of sin θ can be obtained from a measurement of θ which is it not particularly precise, provided that θ is near about 90°.

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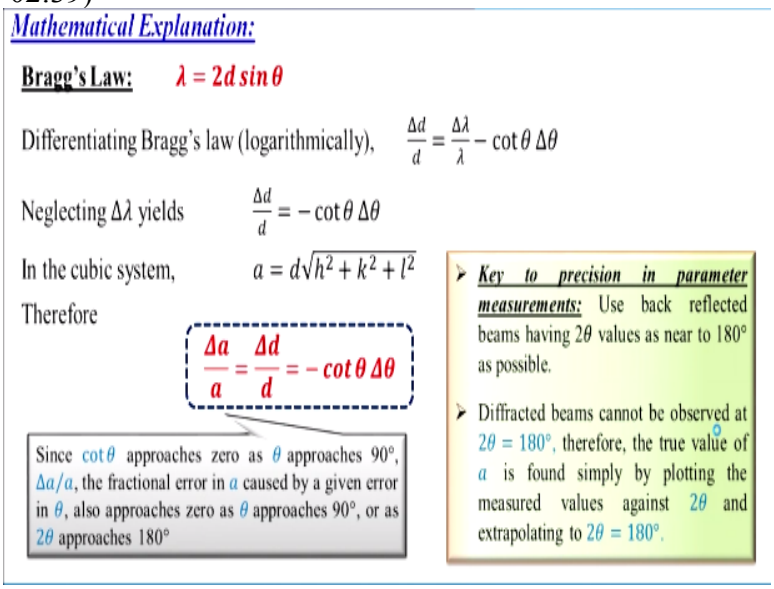

So by mathematical explanations also we can prove it, so from Bragg's angle we know λ is equal to 2df sin θ, differentiating the Bragg's law logarithmically. So Δ d by d is equal to Δ λ by λ- cot θ Δ θ. So neglecting Δ λ is Δ d by d is equal to – cot θ Δ θ and in the cubic system w already know that A is equal to D. route over $a^2 + k^2 + l^2$. In the cubic system as we know already A is equal to D into route over $a^2 + k^2 + l^2$.

Therefore Δ A by A is equal to Δ D by D is equal to – cot θ Δ θ. Since cot θ approaches 0 at 0 approaches to the 90° and Δ A by A the fractional error in A caused by a given error in θ also approaches 0 as θ approaches 90° or as 2 θ approaches 180°. So what is the key to precision in parameter measurements, use back reflected beam have 2 θ values as near to 180° as possible.
And deflected beams cannot be observed at two θ is equal to 180° therefore the true value of A is pond simply by plotting the major values against 2θ and extrapolating to 2θ is equal to 180°. Then we are going to discuss about the diffractometer. So the diffractometer is the complex apparatus and therefore subject to misalignment of its component parts.
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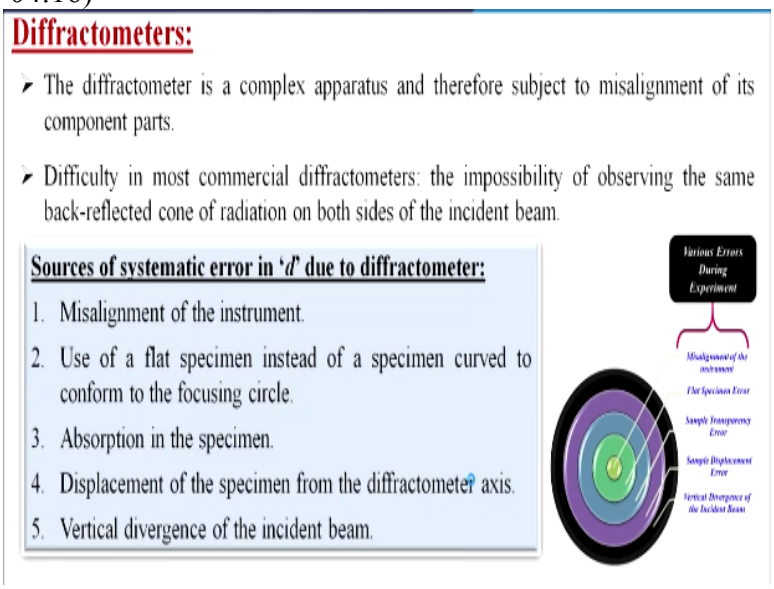

So difficulty in most commercial difrfractometers are like that the impossibility of observing the same back reflected cone of radiation on both sides of the incident beam. So there are several sources of systematic error in d due to the diffractometer. What are those? First one, misalignment of the instrument second is that use of a flat specimen instead of a specimen curved to conform to the focusing circle.
Third is the absorption in the specimens fourth is the displacement of the specimen from the diffractometer axis and the last one is the vertical divergence of the incident beam. So these all errors have been listed in this particular image.
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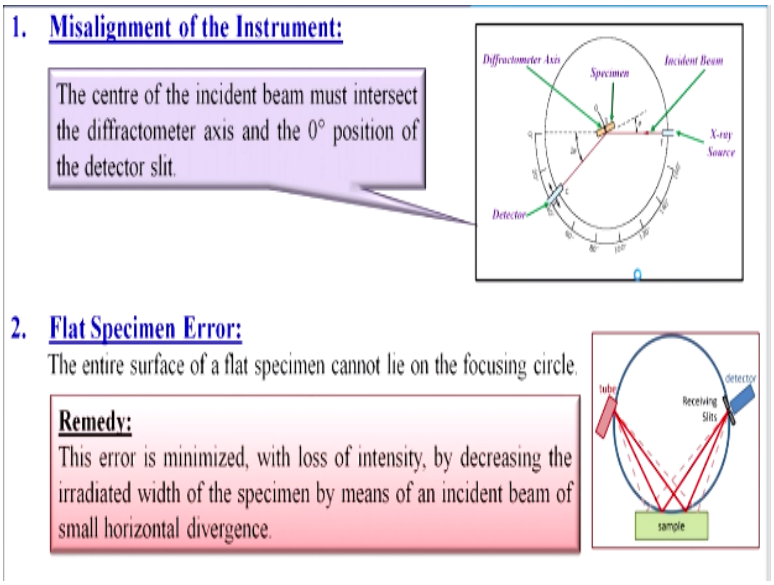

So first we are going to discuss about the misalignment of the instruments. So the centre of the incident beam must intersect the diffractometer axis and 0° position of the detector slits. So here the x-ray shows the incident beam is coming then it is falling on the specimens and then it should directly go to the detector itself through the detector slit. So in this particular case the error may occur.

Then flat specimen error as I told already the specimen surface should be flat it should not be the curved one. Then there will be error that is known as the flat specimen error. The entire surface of a flat specimen cannot lie on the focusing circle. What at the remedies this error is minimized with loss of intensity by decreasing the irradiated width of the specimen by means of an incident beam of small horizontal divergence?

So in this particular case you can see that the flat specimen here the problem is that the error may occur in this particular case or may be the join. Next hard one is the absorptions in the specimen sample transparency error. While x-rays penetrate into the sample depth of penetration depends on mass absorption coefficient of the sample and the incident angle of the x-ray beam. So this produces error.

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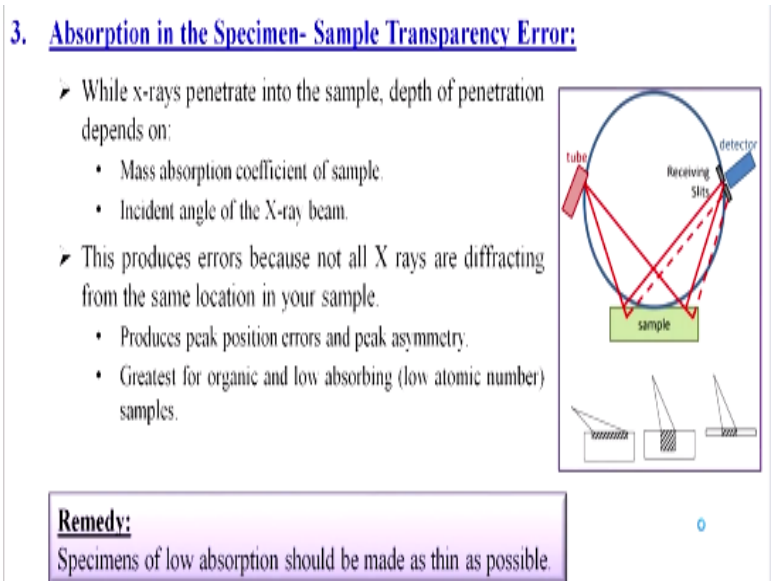

Because not all x-rays are diffracting from the same location in your sample. Yes of course because some reflection is taking place inside the samples some reflection is taking place at the surface of the sample. This produces the error because not all x-rays are diffracting from the same location in your sample that means it produces the peak position errors and the peak asymmetry.

And also the greatest for organic and low absorbing low atomic number samples. So in this particular case if you see when the incident beam we are putting on to the sample from a lower angle the area covering are is more but when the incident beam angle is too high then automatically the covering area is low but penetration is more. So what are the remedy specimens of low absorption should be made as thin as possible.

Then number four is the sample displacement error, so when the sample is not on the focusing circle x-ray beam does not converge at the correct positions to the detector itself.

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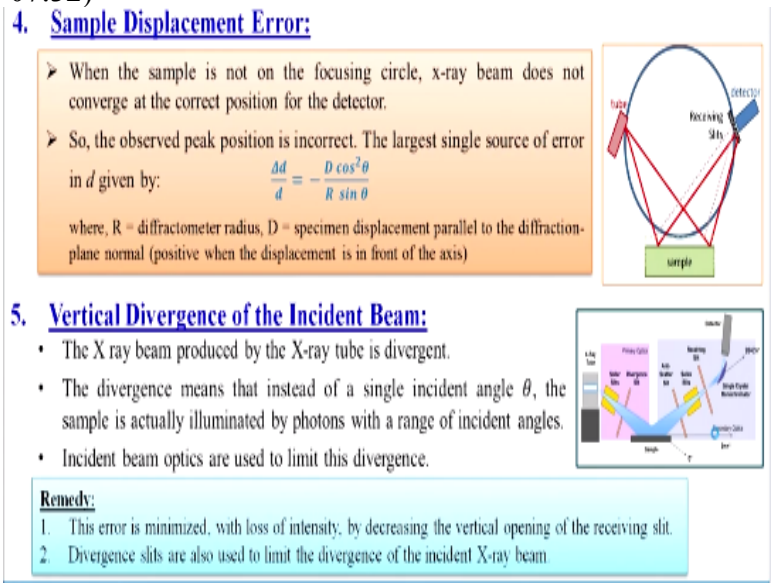

Yes! Because, it can go to outside of the samples also or maybe it can concentrate on a particular point also. It will not cover the area of the whole sample so the observe peak position is in correct. The largest single source of error in d given by Δ d by d is equal to – capital D $\cos^2 \theta$ by R sin θ. Where capital R is the diffractometer radius, d is the specimen displacement parallel to the diffraction, plane normal.

If it is positive when the displacement is in front of the access itself, the next one is called the vertical divergence of the incident beam. The x-ray beam produced by the x-ray tube is the divergent one. The divergence means that instead of a single incident angle θ the sample is actually illuminated by photons with the range of incident angles. Incident beam optics is used to limit the divergence.

So when thus incident beam is coming then we are using some divergence slits so that the whole area can be covered, then after that in we are using some kind of antis scatter slits, so that it can go through and then it can directly come to the receiving slit it can fall to the single crystal mono chromated and then from there it can directly go to the detector itself. So remedy this error is minimised with loss of intensity by decreasing the vertical openings of the receiving slit.

Divergence slits are also used to limit that divergence of the incident x-ray beam. Next we can see come kind of errors because we are using cameras due to that cameras also we can experienced some kind of errors, what are those? So first generally three are types of cameras.

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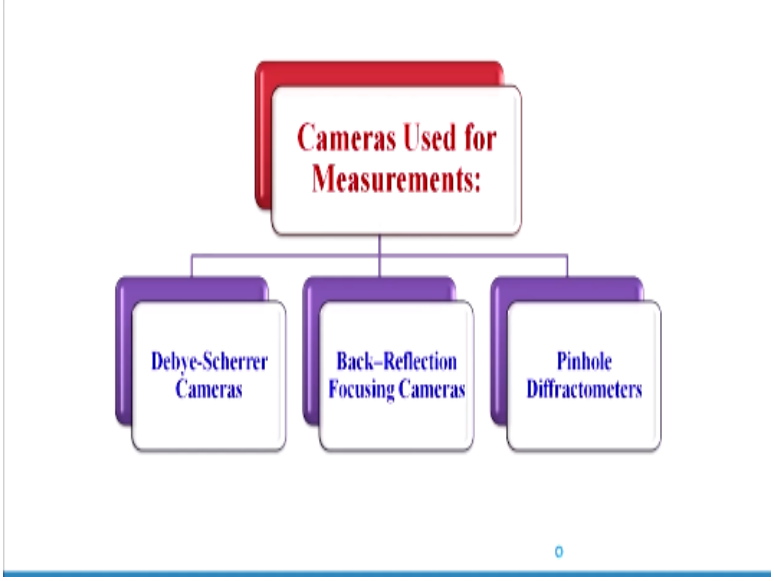

Generally we are using, first one is called the Debye-Scherrer cameras next one is called the back- reflection focusing cameras and the last one is called the pinhole difrfractometers. So when we are talking about the hull Debye-Scherrer cameras for a hull Debye-Scherrer camera the cheap sources of error in θ are as the following.

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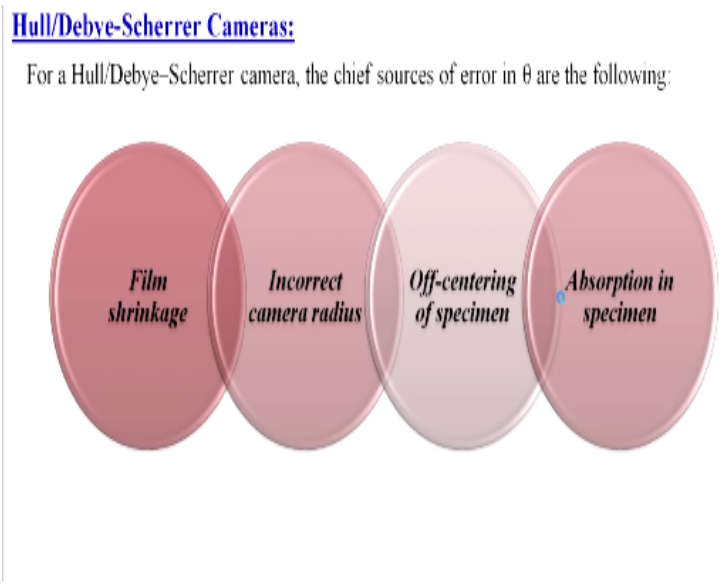

Like film shrinkage, incorrect camera radius, off-centering of specimen and the absorption in specimen itself, so first we are going to discuss about the film shrinkage and radius error. So generally it is caused by producing and drying of the photographic film due to that temperature itself.

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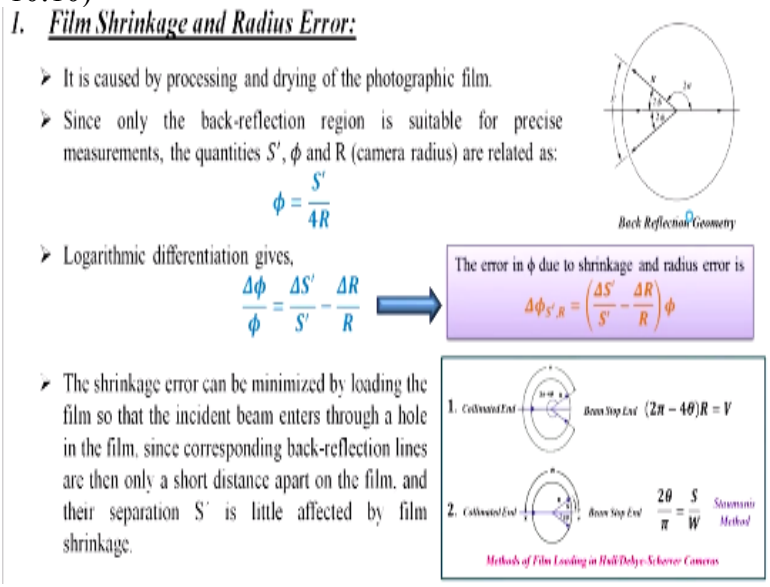

Since only the back reflection region is suitable for precise measurements, the quantities s prime φ and R are related as. In this particular case you can see that this is the join it is known as s prime and then this is R and this angle is 2φ and the 2φ. So here the incident beam is going like this and then it is diffracted and it is coming through this and this is s prime is the parameter of that particular film where the diverted beam or the diffracted beam is coming.

So φ is equal to s prime by 4R, actually it is S prime by R is equal to 4φ. so logarithmic differentiation gives Δ φ by φ is equal to Δ S prime by s prime – Δ R by R. so in this particular case the error in φ due to the shrinkage and radius error is Δ φ s prime due to the shrinkage and R

due to the radius is equal to Δ s prime by s prime – Δ R by R whole multip0lied by the φ. The shrinkage error can be minimized by loading the film.
So that the incident beam enters to a whole in the film since corresponding back reflection lines are then only a short distance a part on the film and their space separation s prime is little affected by the film shrinkage itself. So in this particular case we are seeing that the incident beam is going in this direction and then it is diffracting and it is falling onto the film itself. So if we are going to calculate the V value so generally 2 φ – 4θ which is nothing but this one.
So 2 φ- 4θ into the R which is the radius is equal to V and in this particular case when we are going to calculate this W value over there so generally 2θ by φ is equal to s by W. which is nothing by so many as methods generally we are calculating. Next we are going to discuss about the off-0centering of the specimen. So off –centre specimen is also leads to an error in φ that means we have to keep the sample in a particular location.
If the sample we still be shifting we can get some kind of off- centering error of that particular specimen.
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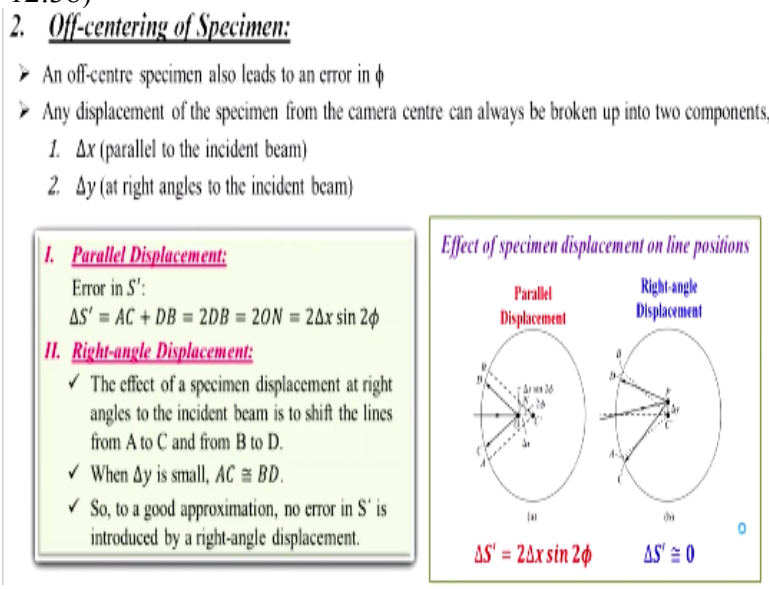

So any displacement of the specimen from the camera center can always be broken up into two components one is Δ x parallel to the incident beam, if you see in this particular image that sample should be at the C prime location but now sample is around O, so in between O to C prime is known as that Δ x in this particular case and in this particular case in the B figure number B sample should be in the C locations but it has been vertically shifted to the P positions.
So here C prime to P is known as the Δ Y. so now what is the parallel displacement over there so error in its prime this is the S prime over there so error In S prime is known as the AC + DB, which is nothing but C and DB is almost same so that is why 2 DB. 2DB is nothing but the 2 O in if we put the perpendicular on to the C prime B line. So if this angle is 2φ so automatically when will be your Δ X sin 2 φ so 2 into Δ X sin 2φ is the parallel displacement in this particular case.
And when you are talking about the right angle displacement the effect of the specimen displacement at right angles to the incident beam is to shift the lines A to C and from B to D. so

in this particular case you can see that A to C is also very, very near and B to D is very near. So Δ Y is small so automatically AC is almost equal to BD so to a good approximation no error in S prime is introduced by a right angle displacement over there.
So in this case Δ S prime is almost is equal to 0, so what is the total error? The total error in S prime is due to specimen displacement in some direction in client to the incident to the incident beam is therefore given by Δ s prime is equal to 2 Δ X sin 2φ.
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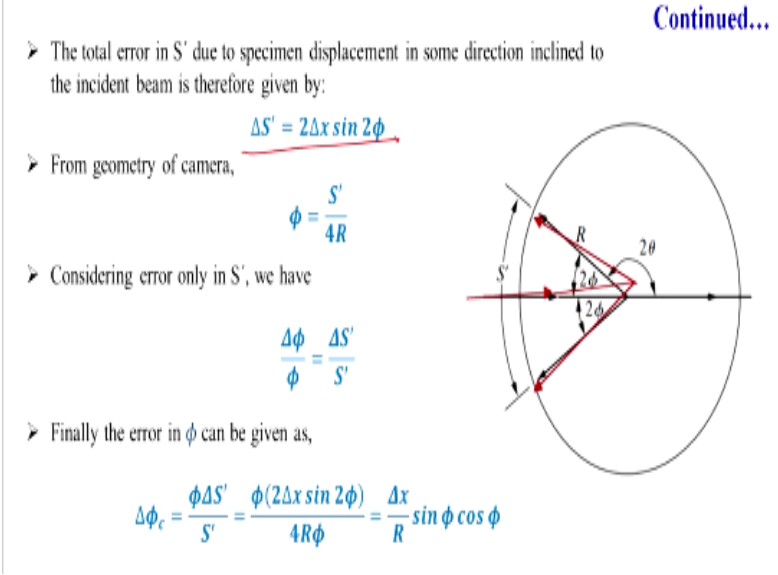

So from geometry of the camera we know that φ is equal to S prime by 4 R, so in this particular case we are going to calculate both the errors actually. So considering error in only S prime we have Δ φ by is equal to Δ S prime by S prime. So finally the error in φ can be given as Δ φ C is equal to Δ φ S prime by S prime which is nothing but is equal to φ into 2 Δ X sin 2φ by 4 or 5 is nothing but is equal to Δ X by R sin φ cos φ so this is the Δ φ C.
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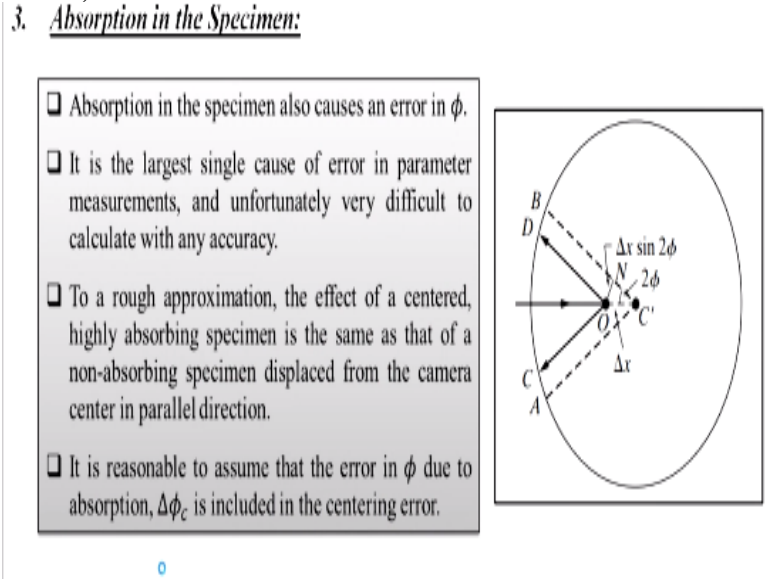

So next we are going to discuss about the absorptions in the specimen itself, so absorptions it is also one kind of mental replacement type of error. So absorption in the specimen also causes an error in φ. It is the largest single cos of error in parameter measurements and unfortunately very difficult to calculate with any accuracy to a rough approximation, the effect of a centered highly absorbing specimens is the same as that of a non absorbing specimens displaced from the camera center in parallel direction.

So it is reasonable to assume that the error in φ is all due to the absorption φ Δ C id included in the centering error. Now we are going to calculate the overall error by the hull Debye-Scherrer cameras.

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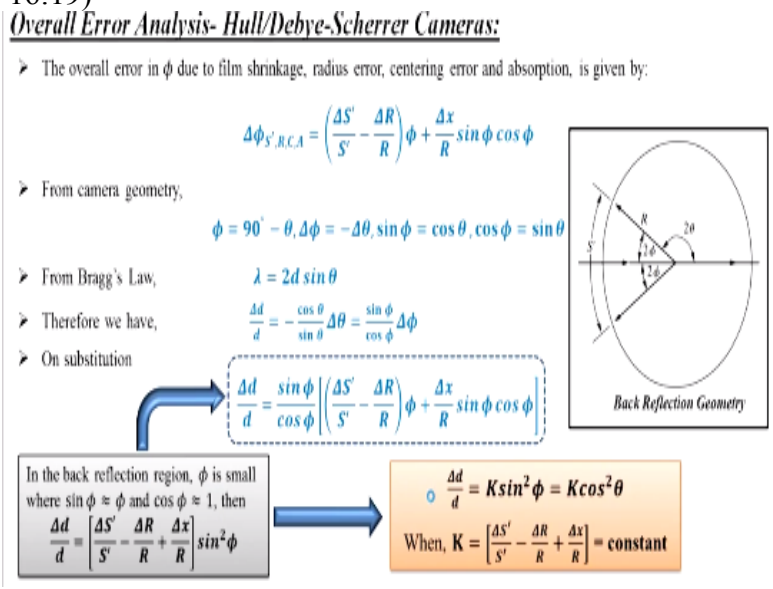

The overall error in φ due to film shrinkage radius error, centering error and absorption is given by here you can see that Δ φ S prime that is the error due to the shrinkage, then R which is the radius error C which is the centering error and absorption is E so Δ φ S prime RC is equal to Δ S prime by S prime – Δ R by R in to φ + in submission of all the errors. Δ X by R sin φ, cos φ so from camera geometry we know φ id equal to 90 – θ.

And Δ φ is equal to – Δ θ, so if we just simply change the order so we can get this value over there and then sin φ is equal to cos θ and cos φ is equal to sin θ. So from Bragg's angle we know λ is equal to 2D sin θ, so therefore we have Δ d by d is equal to – cos θ sin θ, [6 θ is equal to sin φ by cos φ Δ φ. Because cos θ we are replacing by the sin φ and then this sin θ we are replacing by the cos φ.

That is why? Sin φ by cos φ in Δ φ, so on substitutions so what we are getting actually, Δ d by d is equal to sin φ by cos φ into Δ S prime – S – Δ r by r in to φ + Δ X by R sin φ cos φ. So in this particular case you can see that in the back reflection region if φ is small whereas sin φ is almost is equal to φ and cos φ is almost is equal to 1 then Δ d by d will be Δ S prime by S prime – Δ R by R + Δ X by R into $\sin^2$ φ.

So we are getting this equation in as a final and then if we are going to make it more, shorter then Δ B by D is equal to K $\sin^2$ ↕7 which is nothing but this is equal to K $\cos^2$ θ. So where K is nothing but the constant which is Δ S prime by S prime – Δ r by r + Δ X by R. so K is the capital

K is the constant over here. So the important result is that the fractional errors in D are directly proportional to $\cos^2 \theta$.
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- The important result is that the fractional errors in d are directly proportional to $\cos^2\theta$, and therefore approach zero as $\cos^2\theta$ approaches zero or as θ approaches 90°.
- In the cubic system,

$$\frac{\Delta d}{d} = \frac{\Delta a}{a} = \frac{a - a_0}{a_0} = K\cos^2\theta$$

$$a = a_0 + a_0 K \cos^2\theta$$

- Hence, for cubic substances, if the value of a computed for each line on the pattern is plotted against $\cos^2\theta$, a straight line should result, and a_0, the true value of a, can be found by extrapolating this line to $\cos^2\theta = 0$.

And therefore approach 0 has $\cos^2 \theta$ approach is 0 or as θ approaches to the 90°. So in the cubic system as you already know that Δ d by d is equal to Δ A by A is equal to A – A0 by A0 is equal to which is nothing but the K $\cos^2$ θ, so A value is A 0 + a0 K $\cos^2$ θ. A0 hence for cubic substances if the values of A computed for each line on the pattern is plot as against $\cos^2$ θ is tripped line should be result and A0 and the true value of A can be found by extrapolating this line to $\cos^2$ θ is regard to 0. So this is also one kind of conditions.
Now we are going to discuss about the back reflection focusing cameras, so a camera of this kind is preferred over hull Debye-Scherrer cameras for work of the highest precisions.
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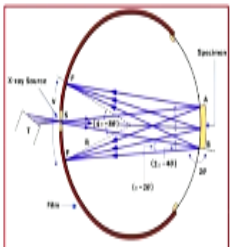
Back Reflection Focusing Cameras:

A camera of this kind is preferred over Hull/Debye–Scherrer cameras for work of the highest precision.

✓ Since the position of a diffraction line on the film is twice as sensitive to small changes in plane spacing with this camera as it is with a Hull/Debye–Scherrer camera of the same diameter.



Back Reflection Focusing Geometry

Sources of systematic error for a camera of this kind are:

1. Film shrinkage.
2. Incorrect camera radius.
3. Displacement of specimen from camera circumference.
4. Absorption in specimen.

So generally we are getting the berated error less results, so since the position of diffraction line on the film is twice as sensitive to small changes in plane spacing with this camera as it is with a

hull Debye-Scherrer camera of the same diameter. So in this case this is the film over there so generally the incident beam is coming through this line this is our sample so it falling onto the sample and then back reflection is taking place and then it is coming in this point and in this point onto to the film itself.

So there are several types of sources like four generally four types of systematic error for a camera of this kind is one is film shrinkage and one is incorrect camera radius then thirds one is this displacement of specimen from camera circumference and last one is the absorption in specimen.

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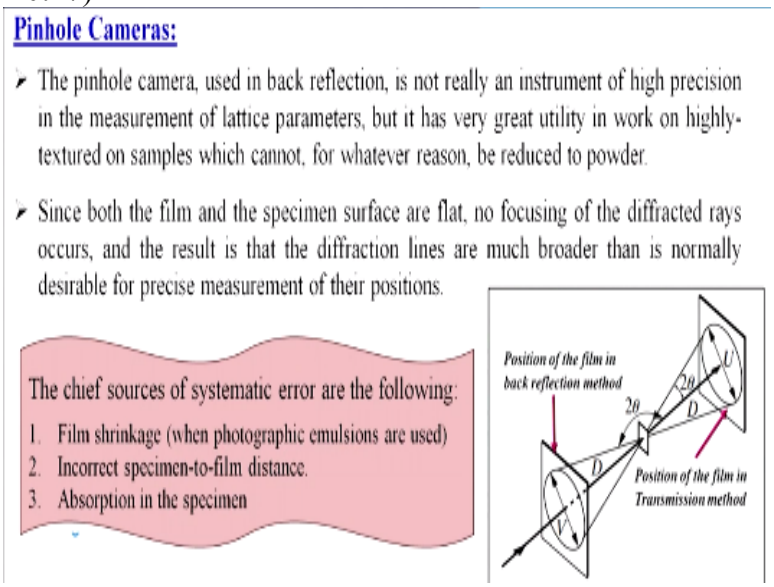

So what is pinhole camera? The third one, the pinhole camera used in back reflection is not really an instrument of the high precision in the measurement of lattice parameters but it has very great utility in work on highly textures on staples which cannot for whatever reasons be reduced to powder. Since both of the film and the specimen's surface are flat no focusing of the diffracted rays occurs and the result is that the deflection lines are much broader than is normally desirable for precise measurements of their positions itself.

So in this particular case you can see that the incident beam is going and the some incident beam is reflecting and some incident beams are transmitted through so the chief sources of estimating error are the following, film shrinkage when photographic emulsions are used and incorrect specimen to film distance and third one is the absorption in the specimen itself. So there are several types of errors when you are measuring the lattice parameter. So in any physical absorption, two kinds of errors are involved.

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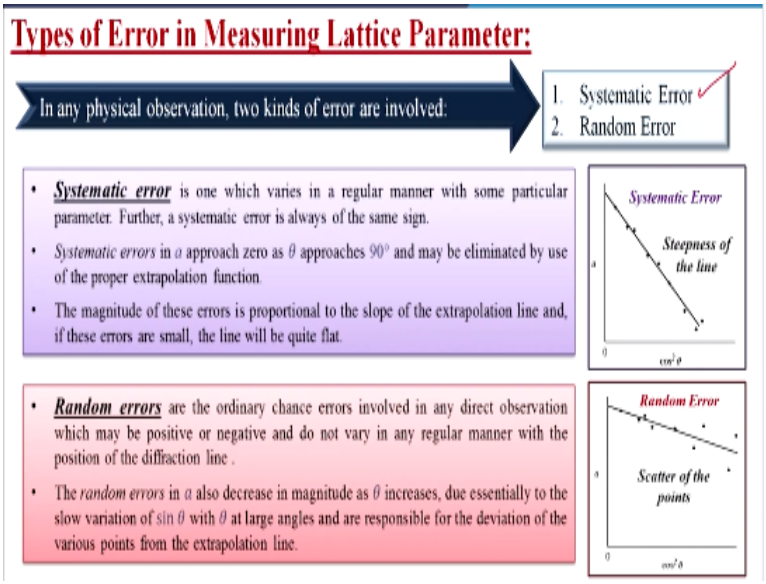

One is called the systematic error another one is called the random error, so what is systematic error? Systematic error is one which varies in a regular manner with some particular parameter further a systematic error is always of the same sign. Systematic error in, A approach 0 as θ approaches to the 90°, so almost in this particular figure we can get this one and maybe eliminated by use of the proper extrapolation function over there.

The magnitude of these errors is proportional to the slope of the extrapolation line and if these errors are small the line will be quiet flat. So in this particular case you can see that the points are nearly in to the same place they are not too much scattering over there but when you are talking about the random errors are the ordinary chance errors involved in any direct observations which may be negative or may be the positive or maybe do not vary in any regular manner with the positions of the diffraction line.

The random error in A also decreases in magnitude as θ increases due essentially to the slow variations of sin θ with θ at large angles and are responsible for that deviation on the various points from the extrapolation line. In this case you can see that the points are very, very far away to each other. So now we are going to measure or maybe the methods what are the methods to measure the error for lattice parameters.

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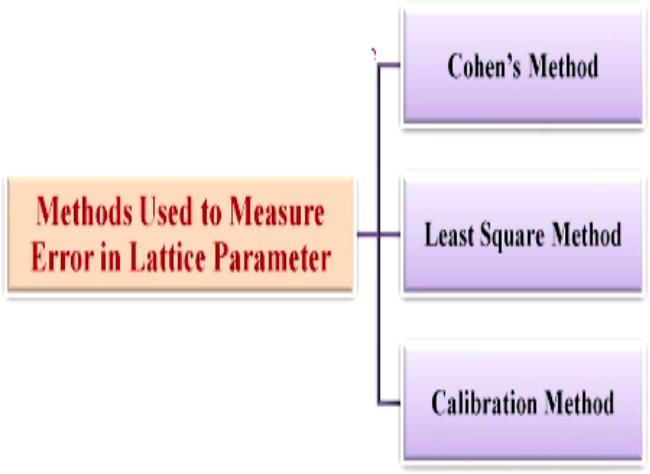

First one is the Cohen's methods second one is called the Least square method and third one is called the Calibration method. So when we are going to discuss about the Cohen's method most accurate value of the lattice parameter of cubic substance is,

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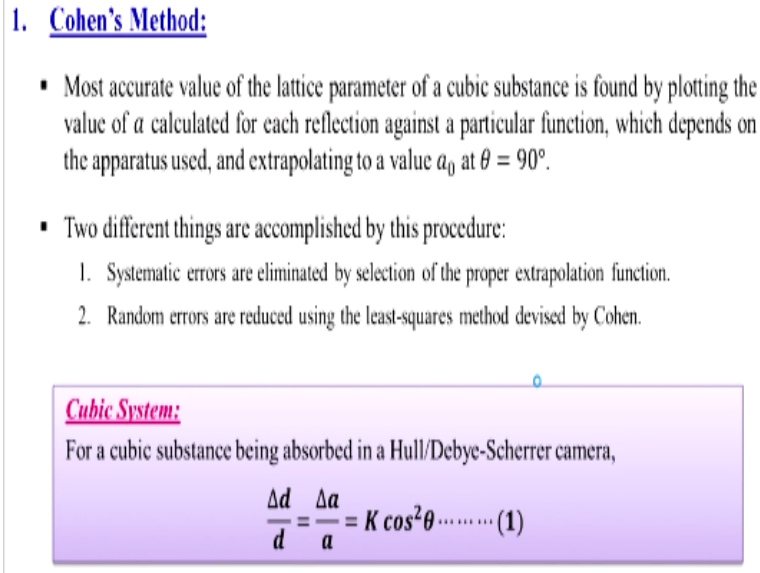

Found by plotting the value of a calculated for each reflection against a particular function, which depends on the apparatus used and extrapolating to a value at A0 at θ is equal to 90°. There are two different things are accomplished by this procedure, what are those? First one is called the systematic errors are eliminated by selection of the proper extrapolation function number one conditions.

Number two is random errors are reduced using the least square methods devised by the Cohen so that is why it is known as the Cohen's method. So generally for any cubic system that which being absorbed in a hull Debye-Scherrer camera Δ d by d is equal to Δ A by A is equal to capital K which is nothing but the constant $\cos^2 \theta$ as we have already got on through.

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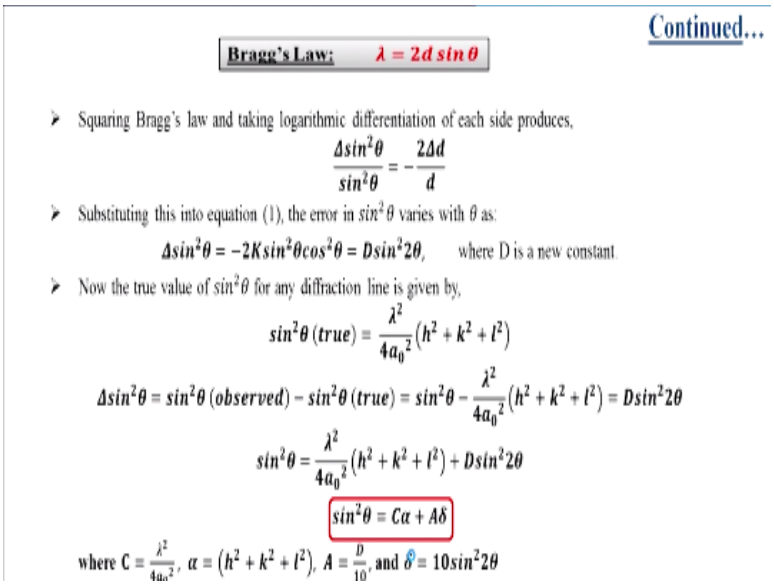

So in the Bragg's law λ is equal to 2d sin θ, so now we are going to squaring the Bragg's law and taking the logarithmic differentiation of each side produces Δ $\sin^2$ θ by $\sin^2$ θ is equal to – 2 Δ d by d. so substituting this equation into two equation 1 the error in $\sin^2$ θ varies with the θ as Δ $\sin^2$ θ is equal to – 2K $\sin^2$ θ $\cos^2$ θ which is nothing but is equal to d which is a new constant $\sin^2$ θ.

So now that true value so here is only the d is – K, so now the true value of $\sin^2$ θ for any diffraction line is given by $\sin^2$ θ true value is equal to λ^2 by 4 $A0^2$ into $A^2 + k^2 + L^2$. So if we substitute in Δ $\sin^2$ θ is equal to $\sin^2$ θ observed – $\sin^2$ θ true is equal to $\sin^2$ θ – of this one , so what we will get is equal to capital D $\sin^2$ 2 θ. So $\sin^2$ θ is equal to λ^2 by 4 $A0^2$ into $A^2 + K^2 + L^2$ class D $\sin^2$ 2 θ, so that means $\sin^2$ θ is equal to C α + a δ.

So where C is the λ^2 by $4A0^2$, α is equal to $A^2 + K^2 = L^2$ A is equal to d by 10 and δ is 10 $\sin^2$ 2 θ.

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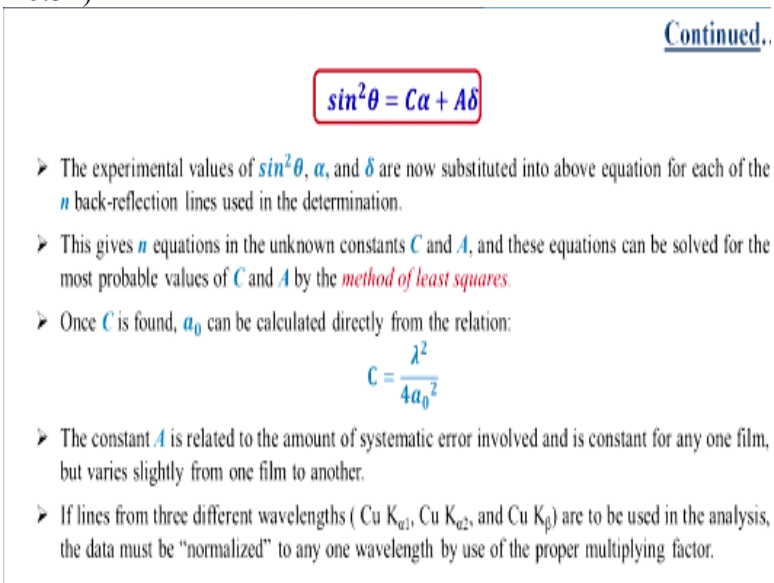

So from the last equation so we have got $\sin^2$ θ is equal to C α + A δ, so the experimental value so $\sin^2$ θ α and δ now substituted into above equations for each of the N back reflection lines in

the determination itself. This gives N equations, in the unknown constant C and A, this equations can be solved for the most probable values of C and A by the method of least squares which I' am going to discuss into the next slide.
So once C is found A0 can be calculated directly from the relations which is nothing but capital C is equal to λ^2 by $4A0^2$, so if we know the value of C then automatically easily we can calculate the value of A. so the constant A is related to the amount of systematic error involved and it is constant for any one film but very slightly from one film to another, if lines from three different wave lengths copper K α 1, copper K α 2 and copper K β are to be used in the analysis that data must be normalized to any one wave length by use of the proper multiplying factor.
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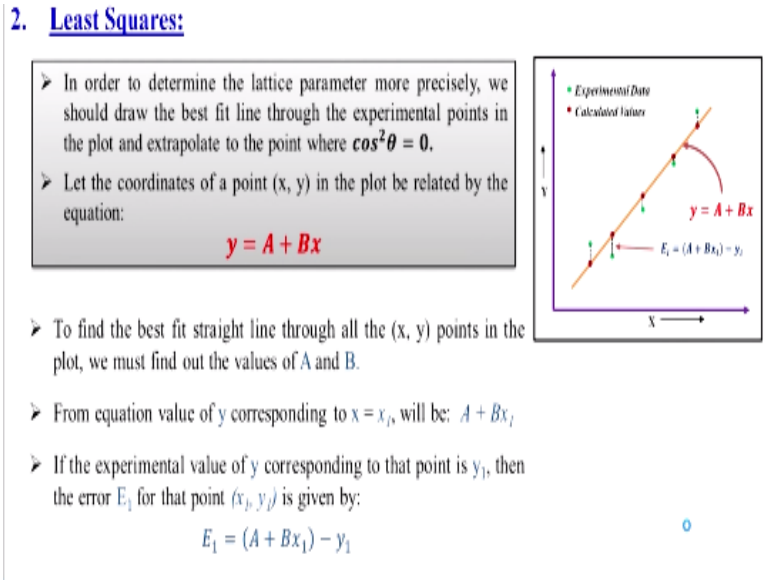

Now we are going to discuss about the least square methods. So in order to determine the lattice parameter more precisely we should draw the best fit line through the experimental points in the plot and the extrapolate to the point where the $\cos^2\theta$ is equal to 0°. So these green in color all are the experimental data and our calculated value we have plotted one line. The line should be like that, that it can satisfy all the points over there.
So let the coordinates of point X and Y in the plot be related by the equations Y is equal to A + BX, so to find the best fit straight line through all the XY points in the plot we must find out the values of A and B from equation value of Y corresponding to X is equal 6to X1 will be A + B X1. So if the experimental value of Y corresponding to that point is Y1 then the error E1 for that point X1 Y1 is given by E1 is equal to A = BX1 – Y1.
So therefore the sum of these squares because now we are up to add all this so errors in all the experimental points is given by.
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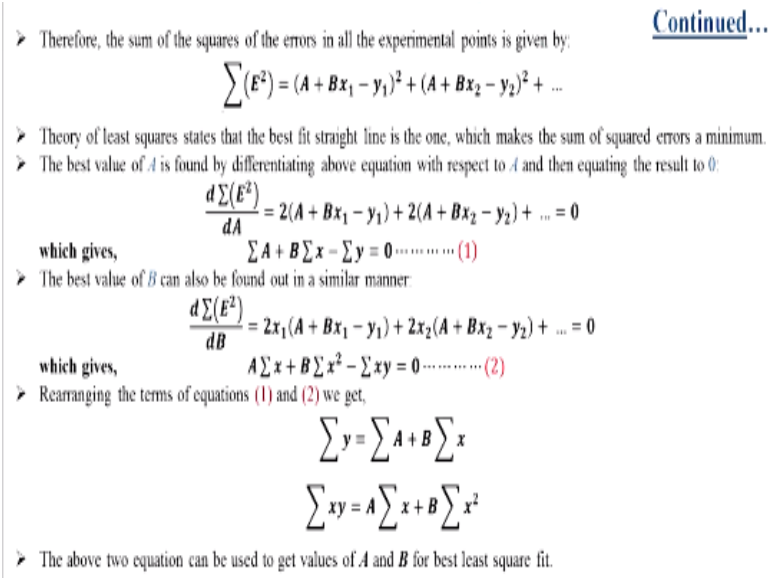

Some is sort of E^2 is equal to A + BX1 – $(Y1)^2$ + for the X2, Y2 and then up to it will continue up to XN and YN. So the theory of least squares states that the best fit straight line is the one which makes the sum of square errors a minimum. The best value of A is found by differentiating above equations with respect to A and then equating result to 0. So now we are differentiating with respect to A and then it should be is equal to 0.

So which gives salvation over A + B salvation over X – salvation over Y is equal to the 0 this is the number 1 equations and then the best value of B can also be found out in the similar manner like A salvation over X = B salvation over X^2 – salvation over XY is equal to 0. This is what second equation, so now rearranging the terms of equations 1 and 2 we get salvation over Y is equal to salvation over A + B salvation over X.

Which is nothing but salvation over XY is equal to A, salvation over X + B salvation over X^2. So the above two equations can be used to get values of A and B for the best least square method. So this is the number three and this is the number four equations. This two equations are the best fit for the least square method, so now we are going to discuss about the calibration methods those suggested process for determining the lattice parameters.

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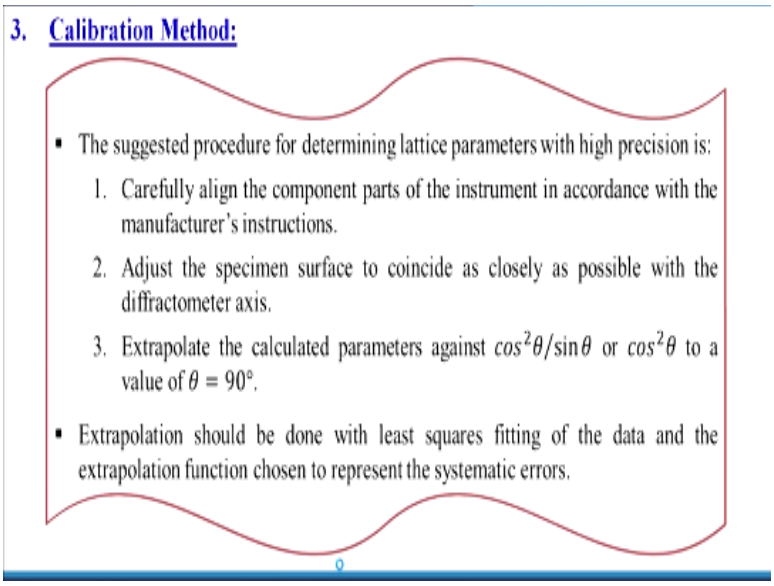

With high precision is it should be carefully align the component parts of the instrument in the accordance with the manufactures instructions. Adjust the specimen surface to coincide as closely as possible with that diffractometer axis and the third one is that extrapolate the calculated parameter against $\cos^2\theta$ by sin θ or $\cos^2\theta$ to a value up theta is equal to 90°. Extrapolation should be done least squares fitting of the data and the extrapolation function chosen to represent the systematic errors.

So now we have come to the end of this particular lecture and we have summarized the whole lecture, so in this particular lecture we have discussed about the different type of errors.

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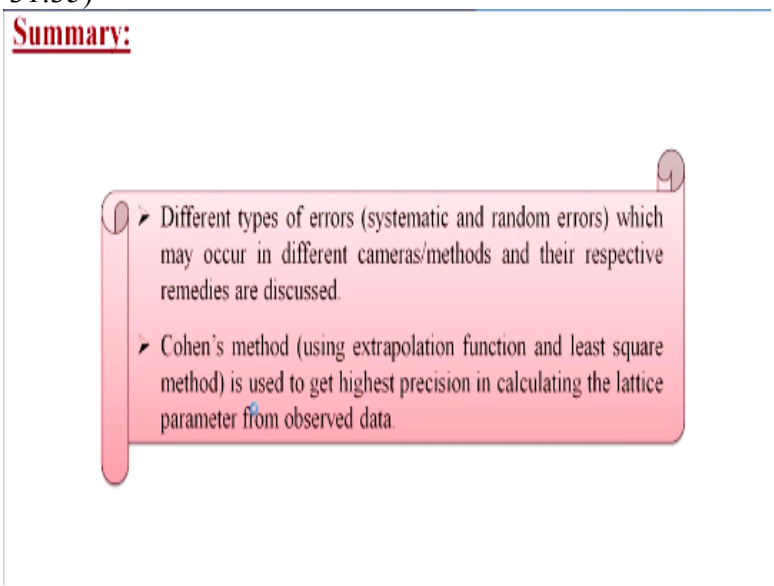

In systematic and the random errors which may occur in different cameras methods and the respective remedies also we have discussed elaborately. Cohen's method we have used which is nothing but the using the extrapolation functions and the least square methods is used to get the highest precision in calculating the lattice parameter from the observed data, Thank You.

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