An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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Lecture - 37
X-ray Diffraction

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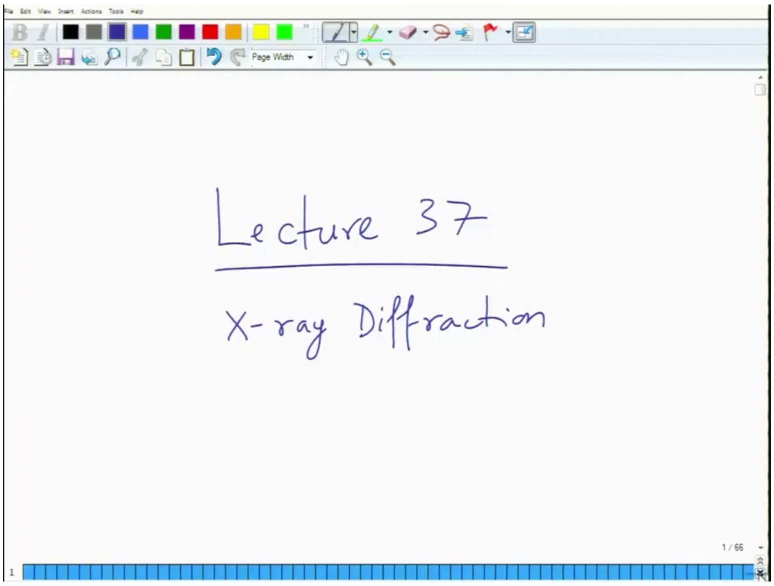

Lecture 37

X-ray Diffraction

So, we begin with the lecture 37 here. Perhaps this is the last lecture on X-ray diffraction which is a technique to characterize the crystals as we have seen in past few lectures.

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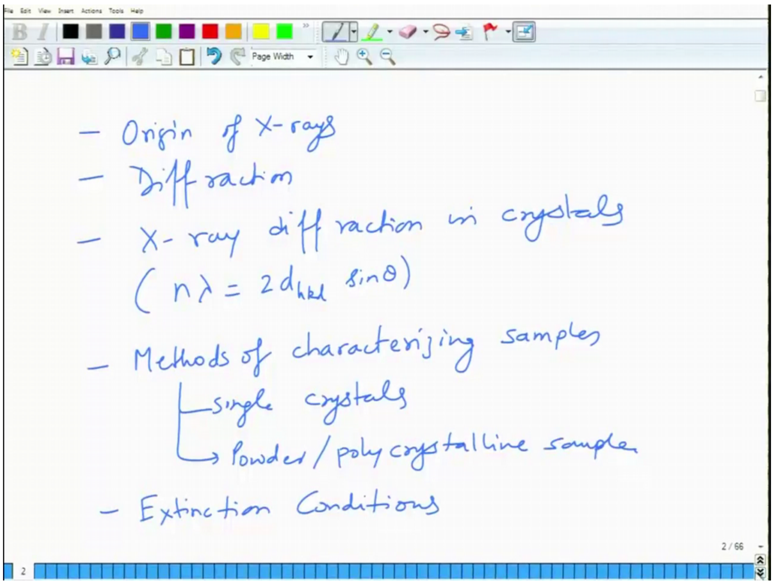

- Origin of X-rays
- Diffraction
- X-ray diffraction in crystals
  ($n\lambda = 2d_{hkl}\sin\theta$)
- Methods of characterizing samples
  - Single crystals
  - → Powder / polycrystalline sample
- Extinction Conditions

So, what we have learned so far in X-ray diffraction is the origin of x-rays, what is diffraction and then, X-ray diffraction in crystals which is characterized by, which is expressed by n lambda is equal to 2 d hkl sin theta which is Braggs law and then, we looked at the methods of diffraction, methods of characterizing samples such as we looked at single crystal and single crystals and poly crystalline samples, powder specimens, right slash poly crystalline samples and then, finally in the last class we looked at the extinction conditions which are determined by the type of crystal structure whether its FCC, BCC or simple cubic lattice.

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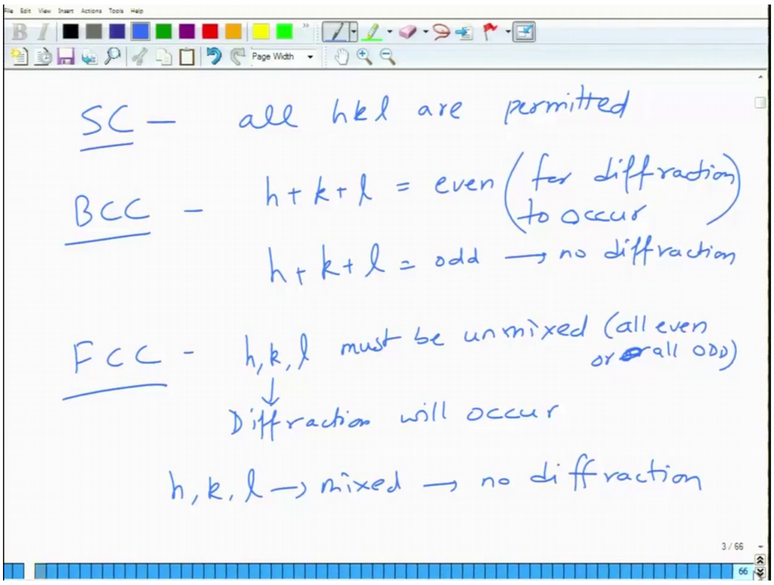

SC – all hkl are permitted

BCC – h+k+l = even (for diffraction to occur)
h+k+l = odd → no diffraction

FCC – h, k, l must be unmixed (all even or all ODD)
↓
Diffraction will occur

h, k, l → mixed → no diffraction

So, what we saw was in the last lecture that if you have if a simple cubic structure, then all hkl are permitted. If it is BCC structure, then h plus k plus l must be even for diffraction to occur and h plus k plus l odd will means no diffraction from those planes and then, we looked at FCC structured materials from which for diffraction to occur hkl must be unmixed which means all even or all odd.

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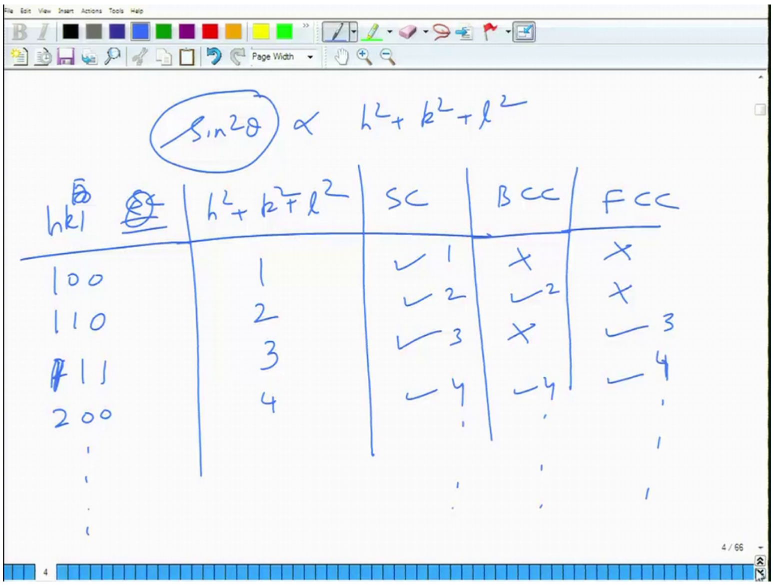

$$\boxed{\sin^2\theta} \propto h^2+k^2+l^2$$

hkl	$h^2+k^2+l^2$	SC	BCC	FCC
100	1	✓ 1	✗	✗
110	2	✓ 2	✓ 2	✗
111	3	✓ 3	✗	✓ 3
200	4	✓ 4	✓ 4	✓ 4
⋮		⋮	⋮	⋮

So, this will allow the diffraction will occur and if hkl are mixed, no diffraction will occur, and we did a simple analysis as well where we took a table of thetas. So, we took a table of Bragg angles which we converted into sin square thetas and those sin square theta were converted because we know that sin square theta is proportional to h square plus k square plus l square as a result and h square plus h square h square plus k square plus l square must be integer, right.

So, we converted the sin square theta into integers and we found that if it matches the sequence, we know that for a simple cubic simple cubic h square plus k square plus l square must go as. So, if you look at the variation of h square plus k square plus l square for simple cubic for BCC and for FCC, so if you look at hkl plane use if you start with 100 and this is 1, then simple cubic diffracts BCC. It does not diffract FCC, it does not diffract.

So, when you go to 110 h square plus k square plus l square is 2 and your simple cubic in that case will diffract, BCC will diffract, but FCC will not diffract and when you go to for example, 111 h square plus k square plus l square is 3, simple cubic will diffract, BCC will not diffract, FCC will diffract and that you keep on doing this. 200, this will be 4. This will diffract, this will diffract and this will diffract and that is how you keep on working and you will then, you convert your sin square theta in such a fashion, so that you are able to match to one of these.

So, the sequence for this would be 1 2 3 4 and so on and so forth. For this would be 2 4 6 8 and so on and so forth and for this, it would be 3 4 8 so and so forth. So, that is how you keep working on it and that is how you characterize the crystals, ok.

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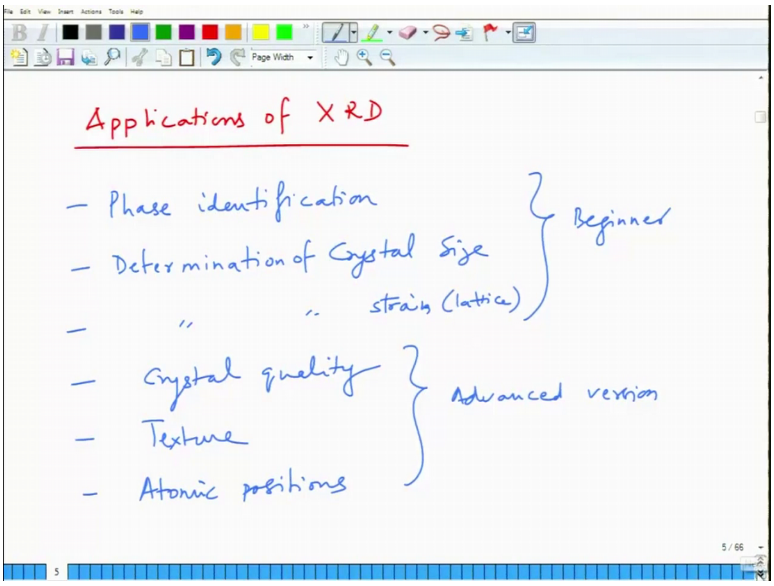

Applications of XRD

- Phase identification
- Determination of Crystal Size
- " " strain (lattice)

Beginner

- Crystal quality
- Texture
- Atomic positions

Advanced version

Now, if I will and now in this lecture what I want to talk to you about is what is the use of X-ray diffraction, what kind of a structural characterization one can do using X-ray diffraction. So, we are looking at applications of X-ray diffractions diffraction. So, X-ray diffraction can be used for first, you can use it for phase identification, then you can use it for determination of crystal size of crystal size determination of strain lattices. Strain can be determined and one can determine the crystal quality.

One can also determine the texture and one can determine there are a lot of other things you can do using X-ray diffraction. For example, one can determine what is the crystal quality texture, crystal size strain lattice is, one can also determine atomic positions for instance, but these are all advanced. So, this is I would say this is you know advanced version and these are all more you can say beginner level of expertise.

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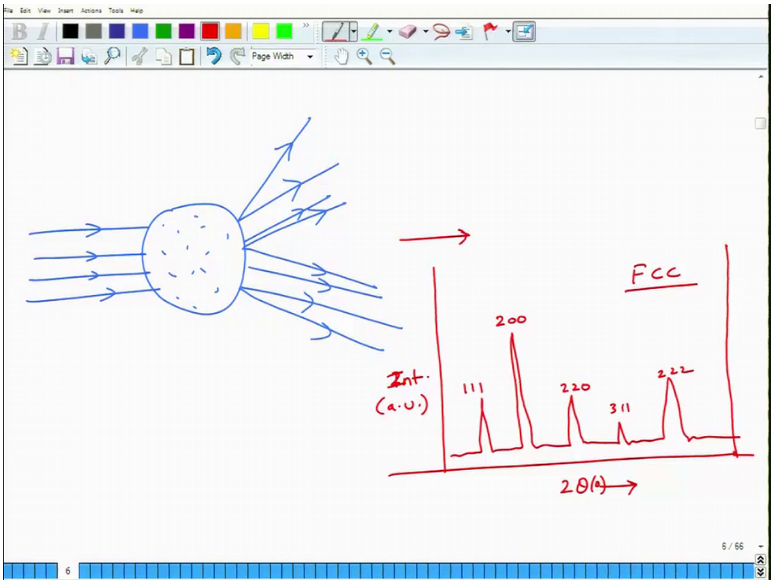

So, let me just talk to you a few things about X-ray diffraction which you might find useful for practical purposes.

So, when you have a poly crystalline let us say sample, so this is you know powder and your beams are hitting the samples in this fashion. So, this will be transmitted beam. With respect to transmitted beam, you will have something going at this tip to theta. There will be some beams going at this 2 thetas.

So, there will be beams going at all the different two thetas because it is a poly crystalline specimen. As a result the X-ray diffraction pattern that you will get is something like that. So, this will give rise to a pattern which is achieved in this fashion; So, on y axis you plot intensity which is in arbitrary units and the x axis you form 2 theta which is typically in degrees which is the angle between the transmitted beam and the diffracted beam and the pattern is something like this and so on and so forth.

For example, if it was a FCC crystal, this would be your first peak will be 111, second would be 200 and then, you will have 220. So, this would be 311, this would be 222 and so on and so forth. That is how you will get extra diffraction pattern for FCC crystal. If it was a BCC crystal, it would be different as per the extinction conditions what we observe normally in X-ray diffraction pattern of a real crystal is that and that ideal X-ray diffraction means n lambda.

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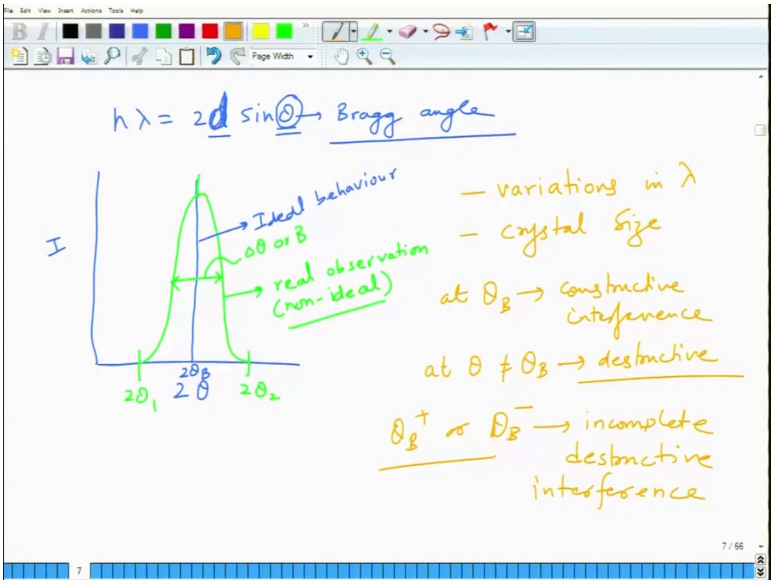

So, ideality requires n lambda is equal to 2 d sin theta which means we must have the value at fixed theta, ok. So, the ideal crystal if you plot intensity for a given peak as a function of, so this is i, this is 2 theta. For an ideal crystal I must have a single peak, a very sharp line because this angle is fixed, ok.

So, this is Bragg angle. Since, it is fixed because of this Bragg relation; there must be a single peak. So, this is 2 theta B, however in reality what we observe is behavior like this which is sort of a Gaussian or Laurentian, a mixed relation. It can be fitted to Gaussian or Laurentian, but mixed function of Gaussaian Laurentian, but this is what you observe.

So, this is you can say ideal behavior and this is your real observation. So, what this tells you is that within these two bounds of 2 theta 1 and 2 theta 2, you have a peak which shows a maxima at around 2 theta B and this peak has certain width which is called as delta or theta or B, the broadening.

Now, this is this non ideal behavior or you can say non ideal behavior. This non ideal observation is because of a non idealities in the X-ray diffraction, the deviations from idealities. So, those deviations and the idealities could be variations in lambda, very tiny variations in lambda.

Tiny variations in you can have because of crystal size. If the crystal size is very small, then the destructive interference at other theta values, so this is the theta value theta,

theta B we have constructive interference, right. If the peak is defracting and at theta not equal to theta B within the vicinity, you should have destructive interference, right.

However, if the destructive interference is not complete because of size effects because if the crystal is not thick enough to give you complete destructive interference, then what you will have is you will not have complete suppression of intensity rather you will have mild suppression of intensity. As a result you will get some finite intensity at theta values which are slightly off from theta B.

So, if you have theta B plus or theta B minus, it will have incomplete destructive interference and this incomplete indestructive interference increases as your crystal size decreases.

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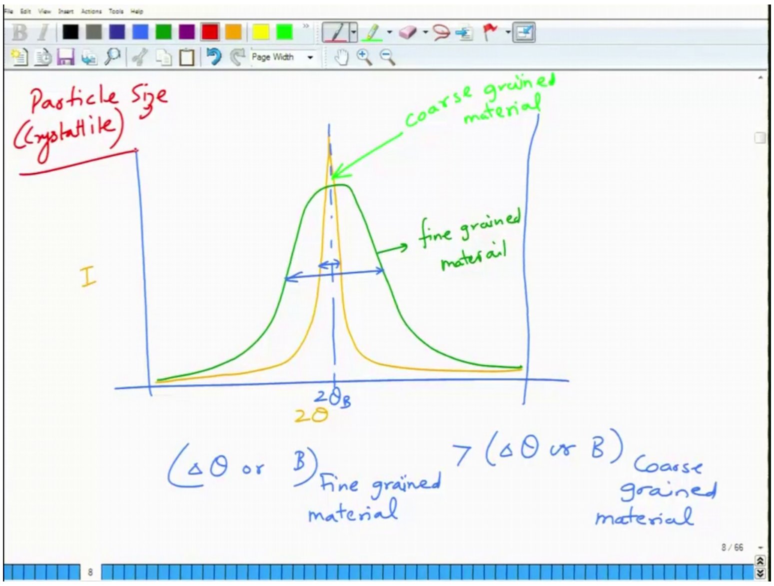

$(\Delta\theta \text{ or } B)_{\text{Fine grained material}} > (\Delta\theta \text{ or } B)_{\text{Coarse grained material}}$

So, what you will see normally is that your peak if you draw the intensity versus 2 theta, so I 2 theta peak for a very thick crystal would be something like that, but there is it for a crystal which is of small sized which has smaller grain size. So, this is for instance for a coarse grained material, whereas, the same for a.

So, this would be for a fine grained material. The peak will be centered at around theta B. So, this will be centered at theta B, however the degree of broadening, so you can say this broadening and this broadening in this case, they are different. So, delta theta or B for a fine grained material is larger than delta theta or B for a coarse grained material.

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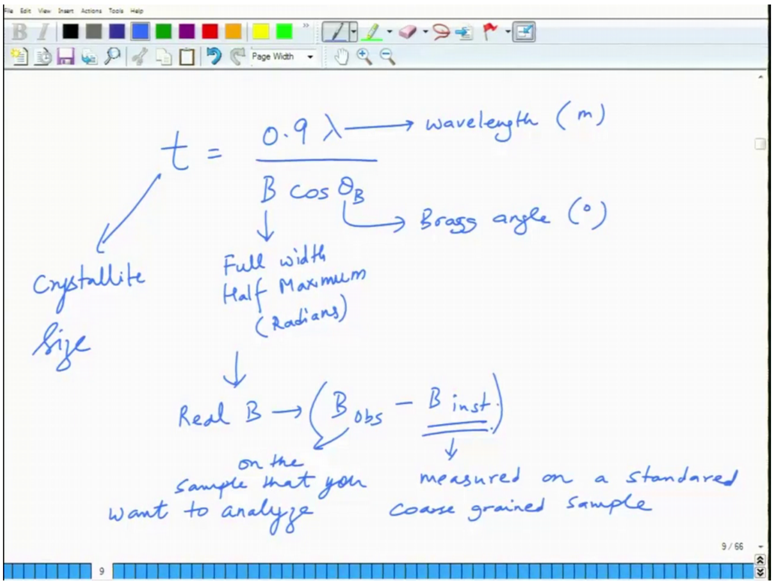

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

This is characterized by a relation called as the crystal size t is characterized by 0.9 lambda divided by B cos theta B, where lambda is the wave length, B is the full width half maximum which is in radians, and theta B is the Bragg angle in degrees, and this is your wavelength in you can say meters or whatever nanometer. So, this will give you that t which is called as crystallite size.

So, your higher broadening will mean a smaller crystallite size. So, your fine grain material will give you higher broadening and your coarse grained material will give you smaller broadening, however every instrument also has instrumental broadening. So, even if you have a single crystal, it will have some broadening which is because of the instrument, so that real B will be B observed minus B instrument.

So, one must always do an experiment with a coarse grained sample which is the reference sample which is used to measure the instrumental broadening. So, this is measured on a standard coarse grained sample and this is your on the sample that you want to measure that you want to analyze, ok. So, this is very important that you carry out the subtraction of instrumental broadening, otherwise the estimation of broadening or estimation of grain size may be wrong, ok. So, most people make a mistake in this analysis.

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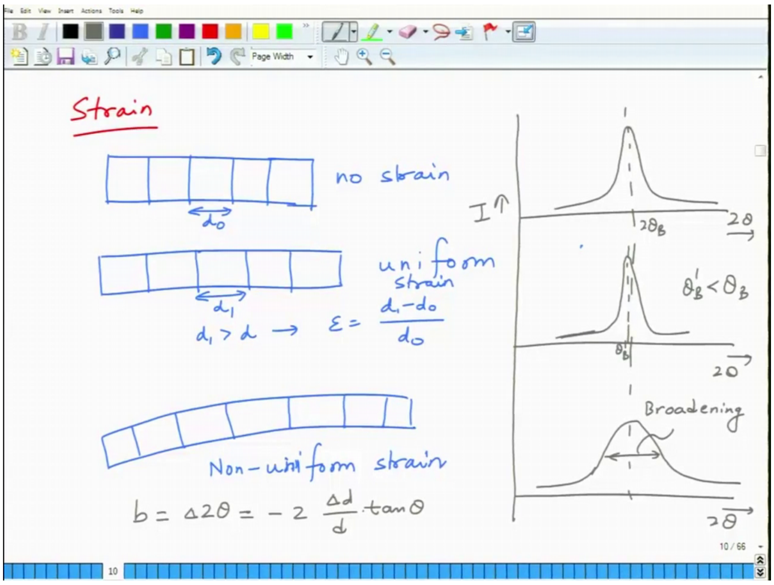

Second thing what you can do is that the strain that is when you have second thing which X-ray diffraction can give you is about the strain. So, this is about the previous thing was about the particle size. You can say particle size or you can say crystallite size. It can give you also an idea about the strain.

So, if you have a crystal which has lattice spacing like this, so this is let us say that equilibrium d, right if the crystal has a uniform strain. Let us say it has a uniform strain where d has increased a little bit. So, this is your d 1. So, this is no strain, this is uniform strain. So, this is let us say d 1 and d 1 is greater than d and correspondingly, you have a strain which is d 1 minus d naught divided by d naught, and then, you have non uniform strain.

For example, it can be bent crystal like this where you can have a smaller spacing here. Let us say it varies like this. So, this is a case of non uniform strain. What you will observe in a X-ray diffraction in this case? So, if I just remove this strain word from here and just write it here uniform strain and if I now make a plot of let say this is my 2 theta, this is the second 2 theta and this is the third 2 theta.

So, this is intensity axis and this is 2 theta for all of them, and if I choose a particular peak, the particular peak let us say this is the equilibrium 2 theta B. So, this will show you a shift. So, this will show you a peak which is something like that. If you have a uniform strain, the uniform strain will allow this peak to be shifted. So, in this case d has increased which means theta will decrease; this will be centered like this. So, this is theta B prime which is, theta B prime is lower than theta B original because the peak is slightly shifted to left because of increase in the d parameter, ok.

Now, when you have non uniform strain which means you have multiple ds now. So, what it means is that non uniform peak will lead to higher broadening. So, a non uniform peak will lead to more broadening. So, this is broadening. Let us say this is this broadening is characterized as b which is basically delta 2 theta and this is essentially equal to minus of 2 delta d divided by d into tan theta. This can be just obtained by differentiating the equation lambda is equal to 2 d sin theta, ok.

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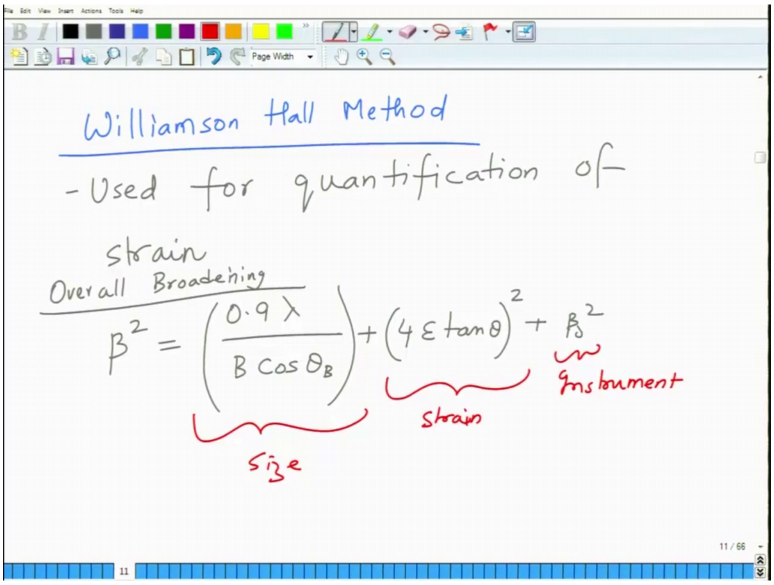

Williamson Hall Method

- Used for quantification of strain

Overall Broadening

$$\beta^2 = \underbrace{\left(\frac{0.9\lambda}{B\cos\theta_B}\right)}_{\text{Size}} + \underbrace{\left(4\varepsilon\tan\theta\right)^2}_{\text{Strain}} + \underbrace{\beta_0^2}_{\text{Instrument}}$$

So, this is the strain determination that you can do for quantification of strain. You need to use what we call as Williamson Hall method used for quantification of strain and also, since non uniform strain leads to broadening particle size effect also leads to broadening. You need to distinguish between the two, ok. So, it turns out the overall broadening beta is square.

If I express this as b or b or beta let us say beta in this case, then this overall broadening beta square is represented as 0.9 lambda divided by b cos theta b plus 4 epsilon tan theta square plus beta naught square. So, this is overall broadening. So, here this term is because of size, this term is because of strain and this is because of instrument. So, what

I need to do that is here is, basically what I need, so essentially it is what I need to do is that I need to plot in this case I can just make slight modifications.

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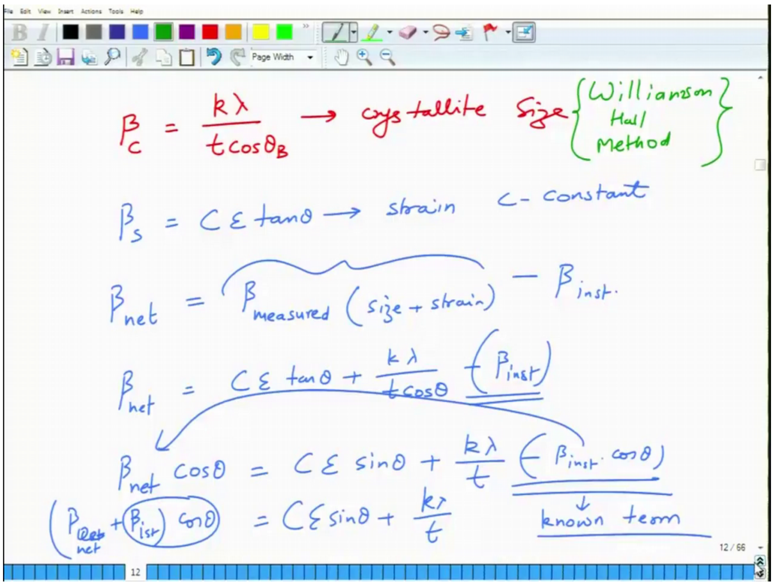

$\beta_c = \frac{k\lambda}{t\cos\theta_B} \rightarrow$ crystallite Size $\left\{ \text{Williamson Hall Method} \right\}$

$\beta_s = C\varepsilon\tan\theta \rightarrow$ strain   c - constant

$\beta_{net} = \overbrace{\beta_{measured}\,(size + strain)} - \beta_{inst.}$

$\beta_{net} = C\varepsilon\tan\theta + \frac{k\lambda}{t\cos\theta}\ \underline{\underline{-\left(\beta_{inst}\right)}}$

$\beta_{net}\cos\theta = C\varepsilon\sin\theta + \frac{k\lambda}{t}\ \underline{\underline{-\left(\beta_{inst}\cdot\cos\theta\right)}}$

$\downarrow$

known term

$\left(\beta_{net} + \boxed{(\beta_{ist})\cos\theta}\right. = C\varepsilon\sin\theta + \frac{k\lambda}{t}$

The modifications lead to beta. Because of beta let us say crystallite size is k lambda divided by t cos theta b, ok. This is because of crystallite size and the other term which is because of broadening, the beta s which is because of strain, sorry c epsilon tan theta which is a strain and here c is constant, ok. So, beta net happens to be beta measured which is because of size and minus of beta instrument.

So, it turns out that beta net is equal to c epsilon tan theta plus k lambda divided by t cos theta and if I, so this is and minus beta naught of course. So, this is beta naught if I take this. So, this value I would know, ok. Beta naught I can measure right by measuring a standard specimen.

So, what you do now here is, so this becomes beta net cos theta is equal to c epsilon, this will become sin theta plus k lambda divided by t minus beta instrument because theta which I can measure, this is a term which is a known term, ok. So, this is a known term.

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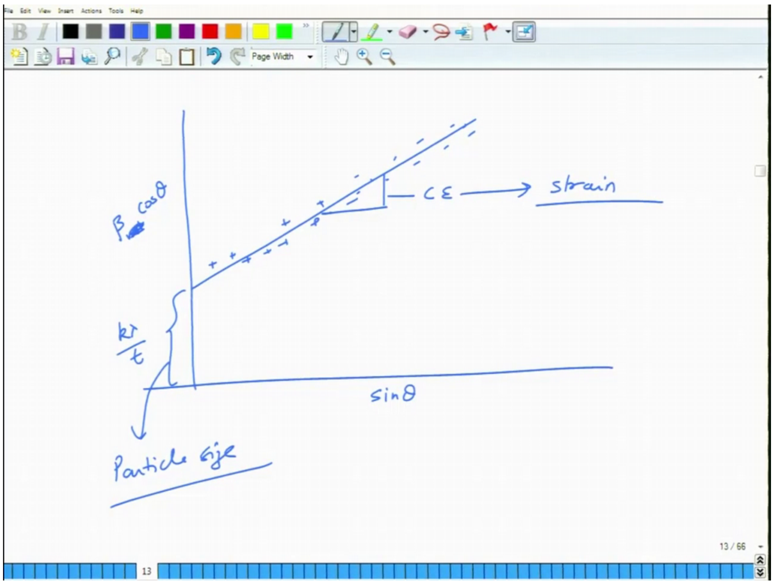

So, what I do now is that I plot basically, so this is a simple linear equation. I plot essentially beta h net cos theta as a function of sin theta. What I can do here is, I can just take this on this side. So, this will become beta observed plus beta. So, this is, sorry this is beta observed, this is beta net plus beta instrument into cos theta, right.

This will become equal to c epsilon sin theta plus k lambda divided by t and this term is known term, right instrument into cos theta. So, if I now plot beta cos theta as a function of sin theta, I should get a sort of straight line for various theta values. Let us say these are the theta values I will see, right ok.

So, the slope of this equation will be equal to c epsilon and the intercept will be equal to k lambda by d. So, this effect is particle size and this is strain. So, this method is called as Williamson. You can write it as some other color, maybe Williamson Hall method to evaluate strain and particle size in poly crystalline specimens.

The strains could be because of processing strain, it could be could be phase transformation induces strain, it could be any kind of strain. Basically it could be impurity induced strain.

No. So, for example, if you deform a crystal, heavily deformed crystal will have lot of strain, but if you anneal it, that strain will go away, ok. So, if you do for example recovery recrystallization or grain growth, depending upon what temperature to which you heat the material, it will have different levels of strain. So, this is the methodology for analyzing crystals using X-ray diffraction where we can analyze the particle size and the strain.

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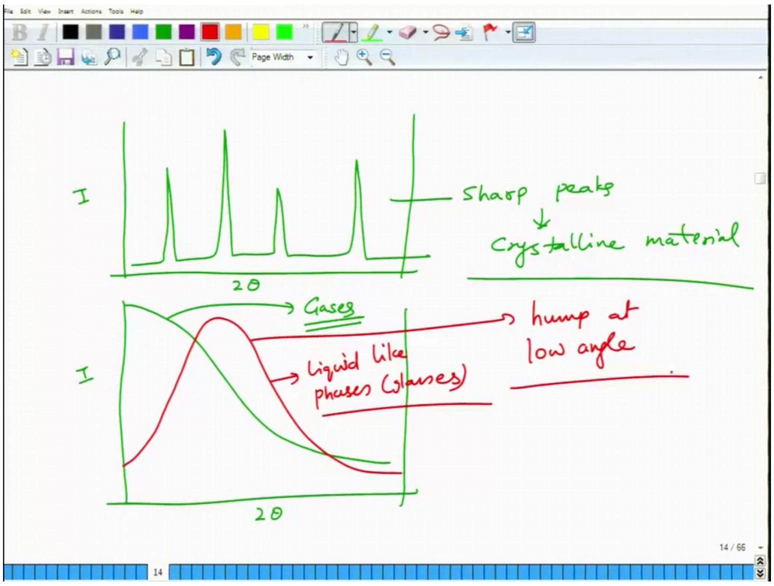

So, when you have X-ray diffraction pattern from different materials, if you plot you will see intensity to theta crystalline material will give you a structure like this, very sharp peaks. So, sharp peaks will mean crystalline material, and the peak width will give you the differences in the grain size and so on and so forth. If you have a pattern like this in which you have I versus 2 theta, you have very broad hump like that.

This will mean you have very small if you start from very low angle very broad hump like that. So, the first one corresponds to typically gases, ok. They do not diffract. They just show you broad hump and this is from a liquid like phases such as glasses, right. So, glasses will show you a structure which will show you a hump at low angles.

So, if you have bit of swelling on the low angle side in the X-ray diffraction pattern, you know that your material has amorphous content. So, you might have a X-ray diffraction pattern which has a hump on the low angle side, but it has peaks on the high angle side, then it has a mixture of crystalline and amorphous phases in the same material.

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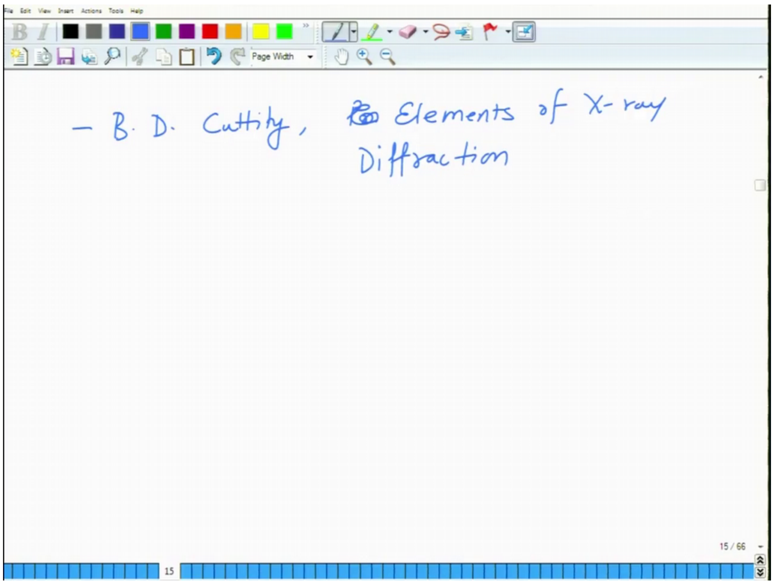

– B. D. Cullity, ~~Ele~~ Elements of X-ray Diffraction

One can also do analysis of single phase analysis of phases in the X-ray diffraction pattern. So, I will and one can also determine texture and other things which probably I will not be able to complete in this course.

If you are interested to know more about the details of X-ray diffraction, I would recommend that you go through B. D. Cullity elements of X-ray diffraction. It is a very good book on X-ray diffraction for beginners, ok. So, we can do all the reading there for understanding the advanced use of X-ray diffraction. Let me show you one picture of modern X-ray diffractometers how they look like.

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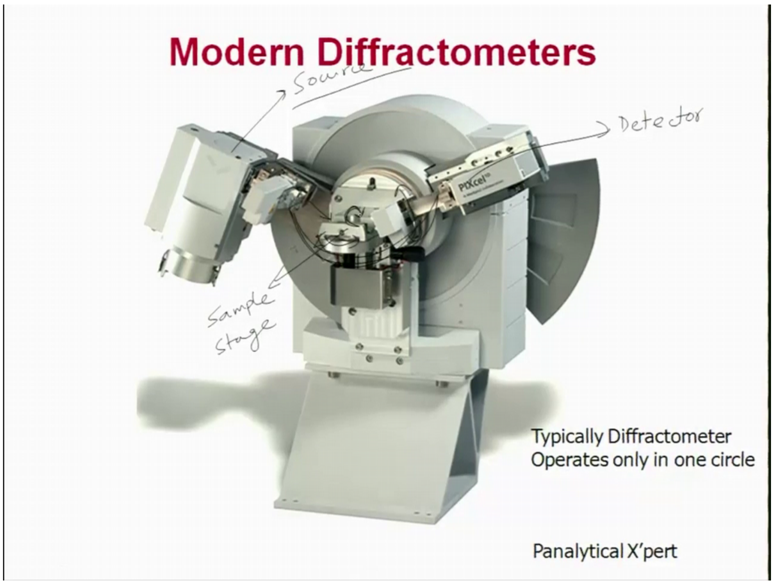

Modern Diffractometers

Typically Diffractometer
Operates only in one circle

Panalytical X'pert

So, your modern X-ray diffractometers look like this. So, this is for example, a panalytical X-ray diffractometer where this is a sample holder. So, let me just use a pen. So, this is the sample stage, this is the source and this is detector. So, your beam, so in this case what might be happening is that your beam may be coming at a fixed angle and this might be rotating and this might be rotating, ok.

These two and the sample may also rotate within the plane. So, it may also rotate within the plane. So, these are typically one circle or two circles diffractometers, ok. So, there is only one circle of rotation which is this. In this circle sample as well as diffractometer rotate, there could be second rotation in this plane, but that could be absent in more advanced diffractometer.

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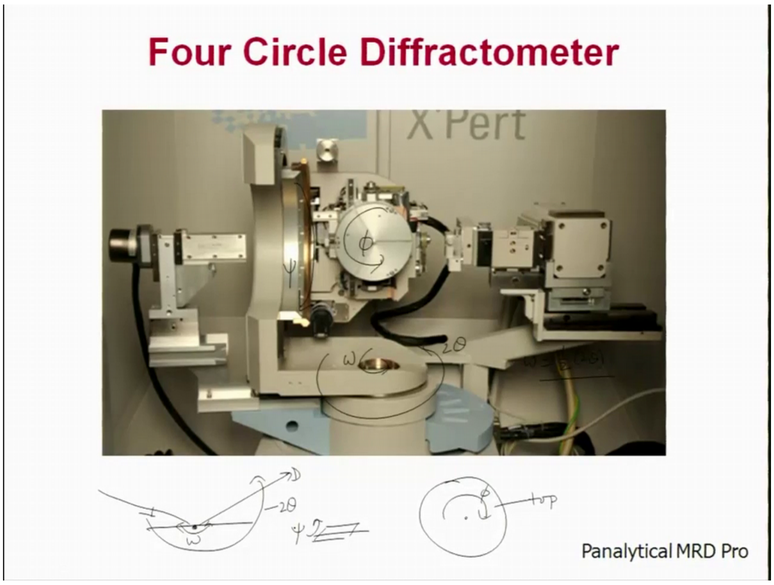

Four Circle Diffractometer

Panalytical MRD Pro

You have a diffractometer like this which has four circle diffractometers. So, you have sample rotating within, this plane you have the cradle rotating within. So, this is phi, this is psi and then, your machine can 2 theta rotates in this and this is 2 theta and then, your sample and then, the sample itself can rotate within this plane. So, this is 2 theta plane. Sample can also rotate along its own axis where, so this is omega.

So, you can have omega, you can have 2 theta. So, omega is used for rocking. Curve omega is basically half of 2 theta, ok. So, this is used for rocking curve analysis. So, if you want to do texture analysis for example, you need to use all these four angles, 2 theta omega phi n psi. This is sample rotation within, but sample may be tilted in some direction, but it is rotating along its sample normal.

So, if it rotates around its sample normal, then it is phi, but if your sample is like this and if it goes like this, this is omega. If it goes like this, then this is psi and 2 theta is and just this is omega, but 2 theta is mean the detected rotating like this, this is 2 theta. So, if your sample is, so this is your sample. So, if sample is rocking around its own axis, this is omega, but you have a detector which is here and detector and this is your X-ray beam. So, if these two rotate together, then this is 2 theta.

So, we can see that omega into theta are coplanar ok, but you have phi and psi which are different, alright. So, phi if you look at the sample from top and sample rotates, so this is the top view, this is phi and psi would be if you look at the sample on the other direction, this is my sample.

So, if I tilt it around this axis, then it is psi, ok. These are the four angles of rotation that you might have an diffractometer.

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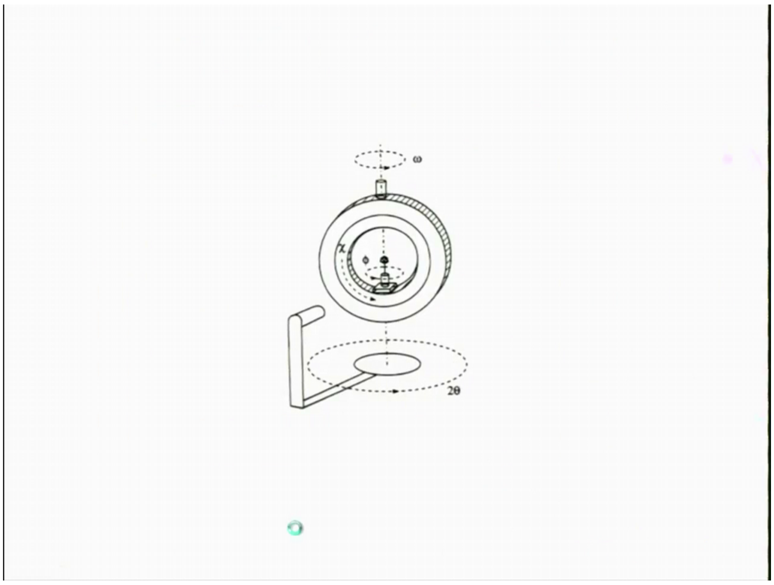

So, basically X-ray diffraction is a useful technique for structure determination phase identification which I have not done.

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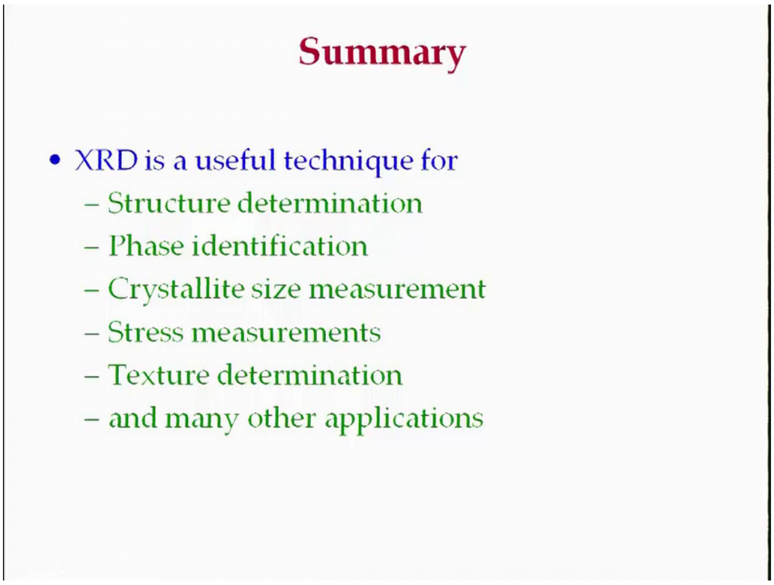

Summary

- XRD is a useful technique for
  - Structure determination
  - Phase identification
  - Crystallite size measurement
  - Stress measurements
  - Texture determination
  - and many other applications

Phase identification is done by peak matching, with respect to standard files and you can also use a lot of software's using this. It can also do crystallite size measurement, you can do strain and stress measurement, texture determination, many other applications you can do which are advanced application for which you need advanced understanding of X-ray diffraction, ok.

So, we will close this lecture here with which we closed X-ray diffraction and in the next lecture, we will start about the defects in the solids which will come to and next three lectures will complete the course all together.