X-Ray Crystallography

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Lecture - 39
Tutorial 10
Factors contributing to peak broadening

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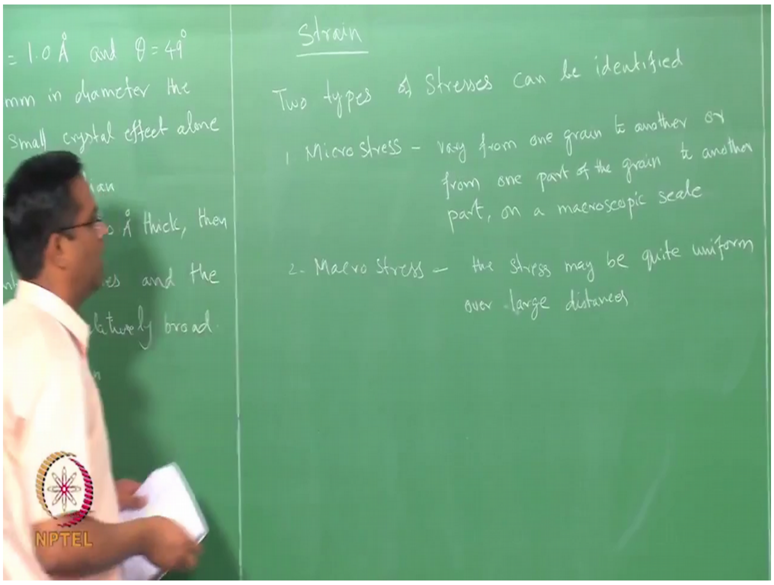

Strain

Two types of Stresses can be identified

1. Micro Stress – vary from one grain to another or from one part of the grain to another part, on a macroscopic scale

2. Macro Stress – the stress may be quite uniform over large distances

So, before we talk about the effect of strain on the peak broadening, you have to bring certain things in mind especially when we talk about crystal and crystal size and grain size and so on. Suppose if you take any poly crystalline material which will have I mean which will contain small units called grains, multiple grains of single crystals, right. So, each grain or a single crystal will orient with respect to the neighboring grain with some degree. It could be a low angle boundary or high angle boundary.

So, whatever we discuss just previously about Bragg theta, here also it will come into effect because if your neighboring grain is oriented to with respect to a given single crystal, the angle is if it is very extremely small. So, that orientation also is going to contribute to the X-ray diffraction. So, of course, if you say that an X grain or X single crystal in a poly crystalline material diffracts with theta B if the neighboring grain is oriented for example, theta 1, then the diffraction is going to be from theta B plus theta.

So, that effect we are going to consider similar to what we have seen before. So, you have to visualize that we are now talking about a diffraction coming from a poly crystalline material, where it contains units of single crystal or grains and then, we are now considering a diffraction being coming from 2-3 different grains altogether.

So, this is with this background we can discuss the effect of strain also. So, first we will define type of stresses because what we measure is actually a stress and then, we convert that into strain or vice versa. If you are able to measure strain and then, we can convert that into stress, we will see that there are two types. So, there are two types of stresses which can be identified through X-ray diffraction. One is micro stress which will vary from one grain to another or from one part of the grain to another part and the macroscopic scale. On the other hand, the macroscopic stress is may be quite uniform over large distances. So, these are the two types of a stresses which we are talking about here.

So, similarly we will talk about the strain, also a uniform strain and as well as a non-uniform strain to illustrate that again I have to draw one schematic and then, we will talk about it.

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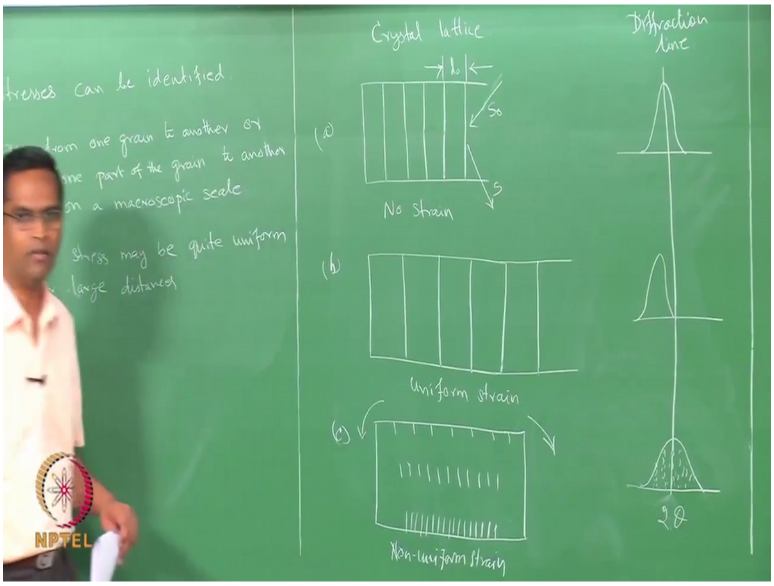

So, I have drawn here is a three schematic. Suppose this is a crystal lattice with D planes distance from D naught that is equilibrium distance and then, this is the incoming X-ray and this is a diffracted X-ray.

So, what we are now seeing is D naught is equally space. So, we describe this as a no strain and then, if you assume this plane is being pulled in this direction and then, we say that all D is stretching into a distance away from D naught, that is more than D naught, then it is called uniform strain. In third case, what we do is we try to bend the crystal like this towards this direction. So, in that case what happens is with respect to the equilibrium position that D naught is going to increase on the top which is going to get compressed on the bottom and somewhere in between it will be equal into D naught.

So, there are three situations. One is under tension, where D is more than D naught and the bottom it is D is less than D naught and somewhere in between. It will be equal to D naught. Then, we say that the specimen is subjected to or the crystal lattice is subjected to non-uniform strain. So, we will now see what the corresponding peak, diffraction peak line is. So, you see that a typical X-ray diffraction line, this is for D no strain state. You will have a peak like this and if it is a uniform stretching, then your peak is shifted to the left hand side and when you have the non-uniform state, you have bit of broadening with little bit of complexity inside. We will see why it is so.

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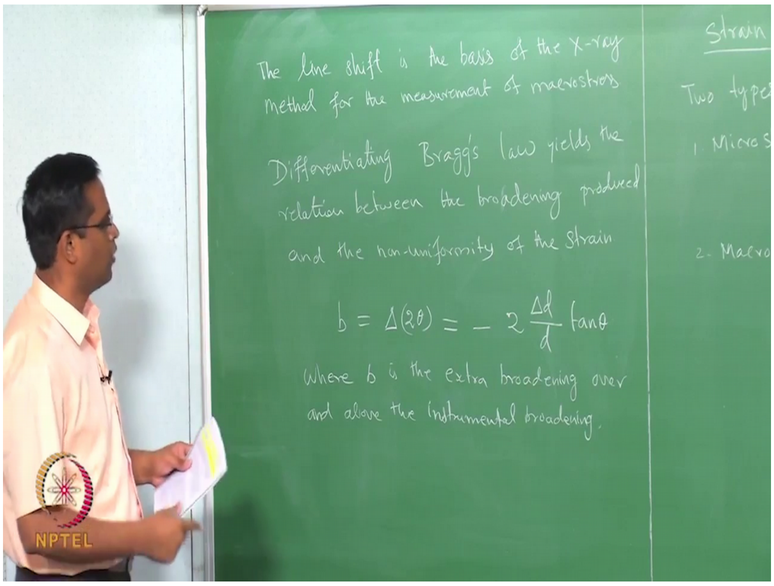

The line shift is the basis of the X-ray method for the measurement of macrostress

Differentiating Bragg's law yields the relation between the broadening produced and the non-uniformity of the Strain

$$b = \Delta(2\theta) = -2\frac{\Delta d}{d}\tan\theta$$

Where b is the extra broadening over and above the instrumental broadening.

So, the first point to note down here is the shifting of the line is the basis of the X-ray method for the measurement of macro stress. So, that is the fundamental information one you should keep in mind because these X-ray methods are used for measuring the macro stress and then, like I said this particular case where you have D is more than D naught and here D is less than D naught and somewhere in between, it is equal to D naught. Because of that you will have with a region in a grain, where D spacing is constant for some region with respect to the neighboring region with the grain itself. So, because of that kind of a situation, each one of this peak will produce a small sharp peak inside which eventually be observed or record as a a broad intensity peak. That is why you see this as a very broad intensity spectrum and we will now see that how do we measure this.

So, we can say that diffracting or I would say that let me write that equation directly. If we are directly differentiating each, the relation between the broadening and the non uniformity of the strain, so how to differentiate the Bragg law you will get a relations like this. So, you differentiate n lambda, I mean lambda is equal to 2d sin theta u v dash is equal to u v dash plus v u dash kind of formula can apply and then, you will be able to drive a relation between delta theta is equal to 2d. I mean 2delta b by d tan theta, but what we measure is theta 2 theta naught theta.

So, delta theta can be written like delta 2t is equal to minus 2 delta d by d tan theta. So, this is the expression, where b is extra broadening over and above instrumental broadening. So, the question is we are talking about a big broadening because of a crystal size. Now, we talk about broadening because of the instrument error and also broadening due to the strain.

So, how to separate these two? How do we know that a particular amount of broadening is because of the strain or because of the crystal size and before we get into further details, I would like to show you little bit about the intensity big details because we always say that whether it is effect of crystal size as well as strain or instrumental broadening, everything we account for the breath of the peak.

So, how to understand this and how to correct this peak for the required intensity from which you either calculate the crystalline size or characterize the strain in the material? So, look at the slide.

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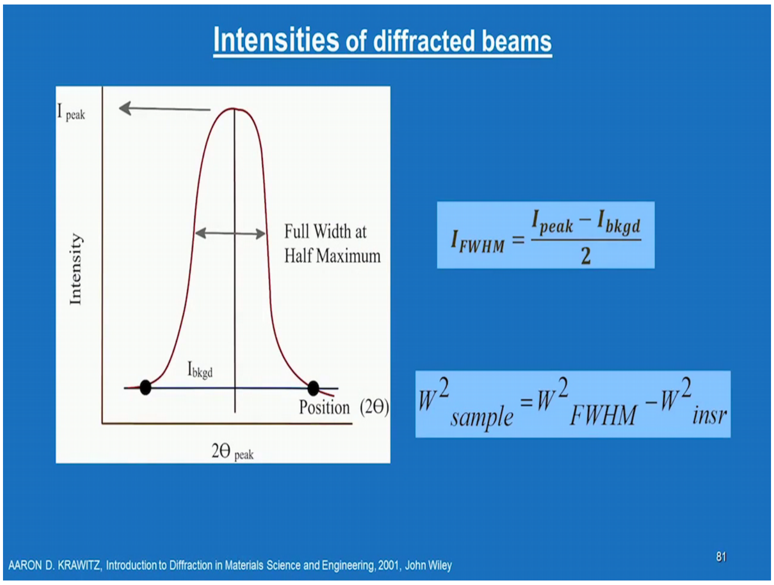

Intensities of diffracted beams

$$I_{FWHM} = \frac{I_{peak} - I_{bkgd}}{2}$$

$$W^2_{sample} = W^2_{FWHM} - W^2_{insr}$$

AARON D. KRAWITZ, Introduction to Diffraction in Materials Science and Engineering, 2001, John Wiley

This is a typical X-ray diffraction peak, where you have a peak intensity as well as the the integrated intensity which is on area on to the peak and then, you have typically we always measure the full width at half maximum and then, this is the background we have to subtract and you have the intensity at full width of maximum is equal to i. That means, intensity peak minus intensity background divided by 2 and we also discuss about this peak broadening is due to a sample as well as the instrumentation reasons. So, that can be represented by this w square sample is equal to w square full width at half maximum minus w square instrumentation.

So, this is a typical peak representation of X-ray diffraction. So, from their how I mean separate all these effects that exactly we want to see. Before that we would like to see some of the models.

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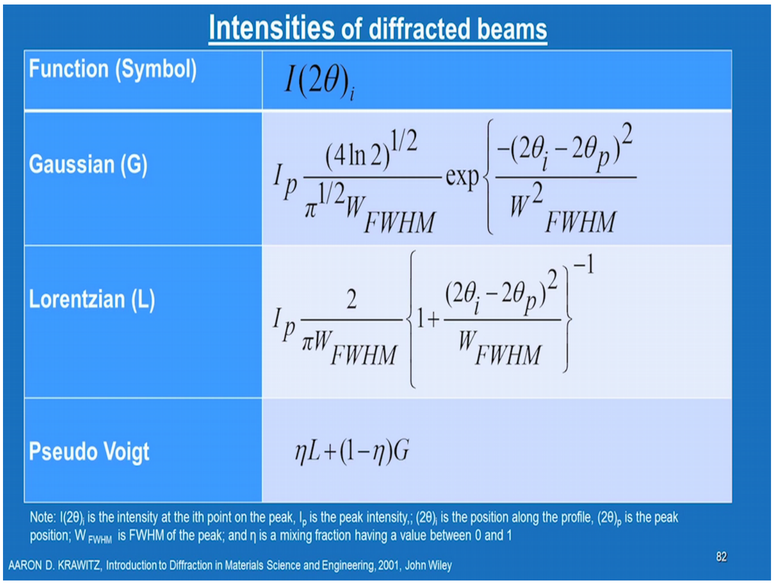

Intensities of diffracted beams

Function (Symbol)	$I(2\theta)_i$
Gaussian (G)	$I_p \frac{(4\ln 2)^{1/2}}{\pi^{1/2} W_{FWHM}} \exp\left\{ \frac{-(2\theta_i - 2\theta_p)^2}{W^2_{FWHM}} \right\}$
Lorentzian (L)	$I_p \frac{2}{\pi W_{FWHM}} \left\{ 1 + \frac{(2\theta_i - 2\theta_p)^2}{W_{FWHM}} \right\}^{-1}$
Pseudo Voigt	$\eta L + (1-\eta) G$

Note: $I(2\theta)_i$ is the intensity at the ith point on the peak, I_p is the peak intensity,; $(2\theta)_i$ is the position along the profile, $(2\theta)_p$ is the peak position; W_{FWHM} is FWHM of the peak; and η is a mixing fraction having a value between 0 and 1

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82

Typical models for X-ray diffraction, it is very clear that if you want to quantify some of these effects, you need to model them first and then, some of the models which are represented in this table for an X-ray diffraction. You see that the first column is a function, second column is the intensity

So, you see the first is Gaussian. If your peak can be fitted into a Gaussian, this model based upon this expression then we can do certain type of calculations. Secondly, if your peak can be modeled with a Lorentzian function like this, then that has got some advantage. We will see and then, you also have a Pseudo Voigt model which is represented by this equation. I will not get into the details of this, but you should know the the basic idea of the fitting the X-ray diffraction and then, how it can be utilized.

So, let us look at the meaning of the details of the terms which is given in this equation I2 theta I is the intensity at i-th point on the peak. That means, any point on the peak IP is peak intensity; 2 theta I is the position along the profile 2 theta P is the peak position, WFWHM is the full width half maximum of the peak and ETA is the mixing fraction having a value between 0 and 1. So, if you have this kind of an expression, then we have some advantage of using this mathematical model to separate some of the effects, namely instrumentation or crystal size effect or the strain in the lattice and so on.

So, we will have a look at those aspects today and before we really look into the separation of these effects from an X-ray diffraction, I would like to go back to little more fundamental aspects of X-ray diffraction itself. I would like to draw some of the typical X-ray diffraction pattern for a crystalline material as well as for liquid and amorphous material and then, you will have to guess how the X-ray diffraction peak will look like and how do we understand them.

So, let me draw some of the typical X-ray diffraction peak and then, we will continue our discussion.

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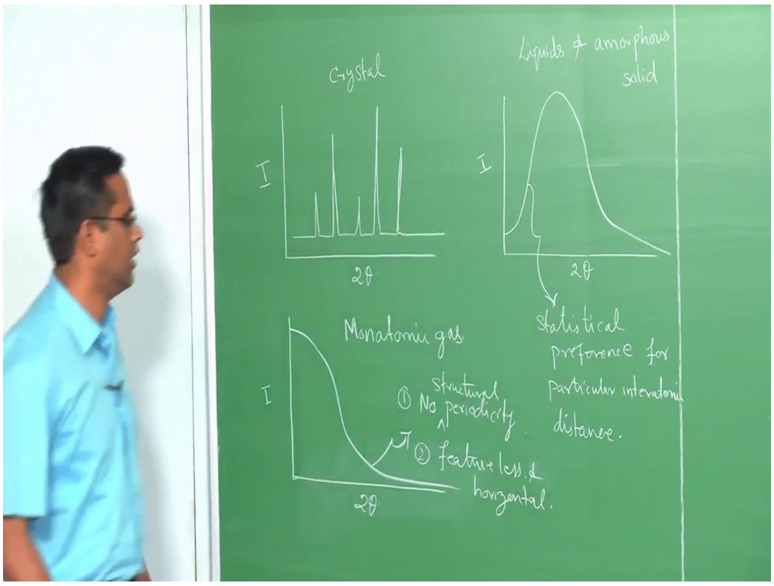

So, what I have drawn is a typical X-ray diffraction pattern from three different kind of materials. One is a crystal, the other is for the liquid and amorphous solid and then, you have a monatomic gas. So, what do we understand from this? This is now well known to us. The intensity is 0, almost 0 except at particular 2 theta value typically known as Bragg angle. So, one thing we have to understand from this is very important.

You see you take a single atom, then you assume that X-rays are interacting with this atom, that atom scatters the X-rays in all directions and in a periodic lattice, you would just assume that you get only with certain 2 theta angle. This intensity you see means rest of all directions. The intensity is canceled by the destructive interference which is also very important aspect of diffraction.

As much as the constructive interference, we have to appreciate that. So, the destructive interference plays a crucial role in appreciating this. The constructive interference that happens only at particular angle of I mean Bragg law that is Bragg angle. Rest all the other direction is completely canceled by all the atoms which is arranged in a period three dimensional periodic lattice. So, that is point number 1.

If you look at the the intensity verses 2 theta peak for a liquid and an amorphous solid, it is quite interesting. Note that you do not have a very a sharp peak for a given 2 theta. So, it is quite random you saw it is something called you know it s a lack of order. You see that here is now a concrete order or a three dimensional periodicity. What you see the peak is 1 naught 2 peak statistically chosen by the system and then, what you really observe is a very broad peak, ok.

So, it is only a statistical preference of particular interatomic distances which will give a two preferential angle peak and then, eventually you see only a broad peak which is true for amorphous solid and liquids which really lacks the order, the crystal order orderliness and if you look at the monatomic gas, it is much more interesting. You do not even see that any kind of a peak broadening because of a complete randomness.

So, you can write that the features no periodicity at all. I would say no structural periodicity and this is point number 1. Point number 2 is, it is feature less horizontal and since, it does not have any structural periodicity, you will have a featureless curve or a peak like this. You will obtain for monatomic type of a gas.

So, now let us look at, let us come back to X-ray diffraction peak, where you have the contribution from a crystal size as well as the strain effect of the lattice; so how to separate them; that we will see now.

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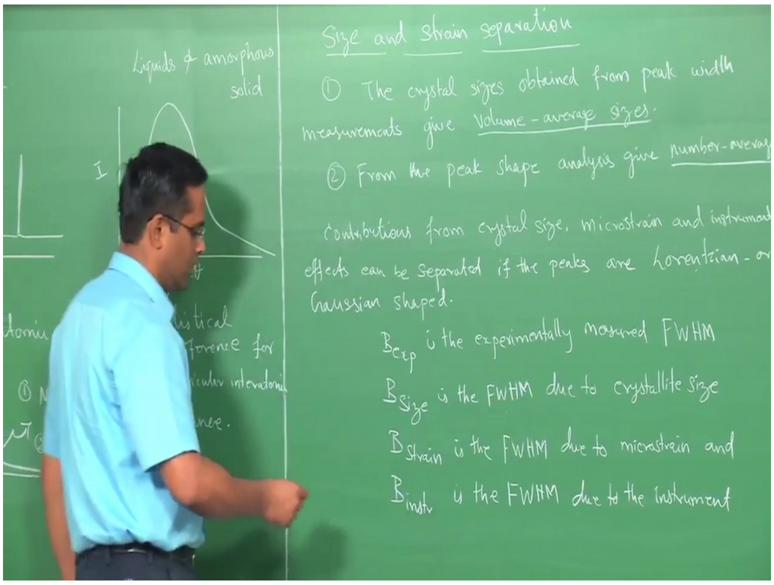

Size and strain separation

① The crystal sizes obtained from peak width measurements give Volume - average sizes.

② From the peak shape analysis give number-averag

Contributions from crystal size, microstrain and instrumen effects can be separated if the peaks are Lorentzian - or Gaussian shaped.

B_{exp} is the experimentally measured FWHM

B_{size} is the FWHM due to crystallite size

B_{strain} is the FWHM due to microstrain and

B_{instr} is the FWHM due to the instrument

So, the first point to note down here is when we talk about the crystal size which we obtain from the X-ray diffraction experiments, if you are the crystal sizes obtained from a peak width measures give volume average sizes, whereas from the peak shape analyses give a number averages. So, these two certain things you have to appreciate whether it is a peak shape analysis or from peak width analysis.

So, now let us look at the contribution from crystal size microstrain and instrumental effects can be separated if the peaks or Lorentzian or Gaussian shape. So, like just before we have seen in these slides where we have seen how theae peaks are model and if your peak is close to these models, then separating effects are straightforward.

So, we will see suppose your b experiment is the experimentally measured B experiment that is full width half maximum B size, so you have a different contribution to the peak width B. B experiment is the experimentally measured full width half maximum B size is FWHM due to the crystallite size B strain is FWHM due to microstrain and B instrument is FWHM due to the instrument effect.

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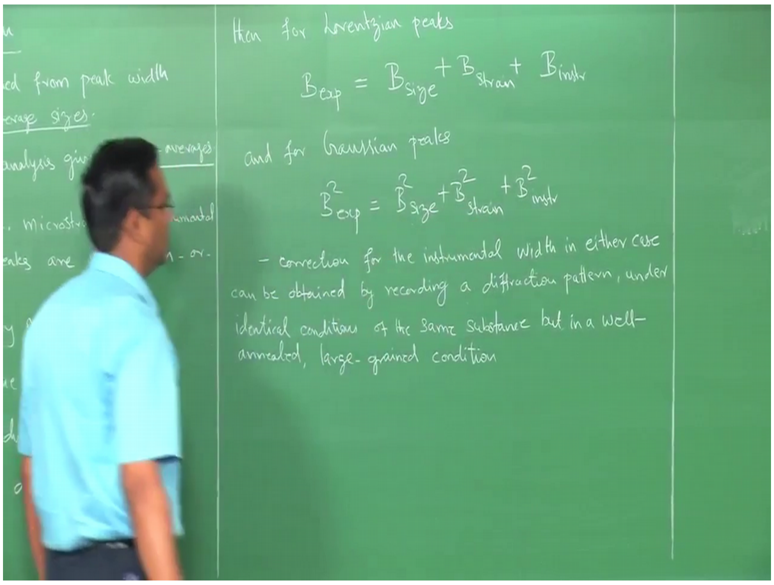

then for Lorentzian peaks

$$B_{exp} = B_{size} + B_{strain} + B_{instr}$$

and for Gaussian peaks

$$B^2_{exp} = B^2_{size} + B^2_{strain} + B^2_{instr}$$

– correction for the instrumental width in either case can be obtained by recording a diffraction pattern, under identical conditions of the same substance but in a well-annealed, large-grained condition

Now, if it is for lorentzian, for lorentzian peaks, B experiments equal to B size plus B strain plus B instrument and for Gaussian peaks. So, for Gaussian peaks, it has a square of these terms that is B square experiment equal to B square size plus B square strain plus B square instrument. So, now correction for the instrument is done. You can write that also as a point.

So, how to get this instrumental width contribution, the correction for the instrumental width in either case that is both these cases can be obtained by recording a diffraction pattern under identical conditions of the same substances, but in a well annealed large grained conditions, so that you do not have a contribution from the crystallite size itself. That is why it is emphasized a large grain condition.

That means you obtain that by complete annealing treatment. You relieve all the strain and then, record this peak that is considered as the instrumentation contribution and then, we will have these two alone size and strain.

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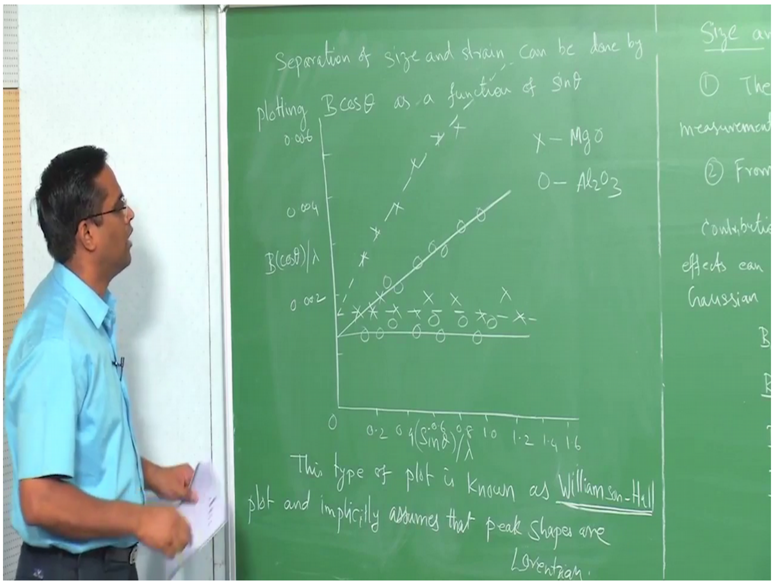

Separation of size and strain can be done by plotting $B\cos\theta$ as a function of $\sin\theta$

This type of plot is known as Williamson-Hall plot and implicitly assumes that peak shapes are Lorentzian.

So, what I have drawn here is a plot of B cos theta by lambda verses sin theta by lambda, that is B cos theta verses sin theta. That is what I have written here. Separation of size and strain can be done by plotting B cos theta as a function of sin theta.

So, let us write. So, this type of plot that is B cos theta verses sin theta is known as Williamson-Hall plot. Willianson-Hall plot implicitly assumes that the peak shapes are Lorentzian. So, let us now try to understand how this separates the size and strain.

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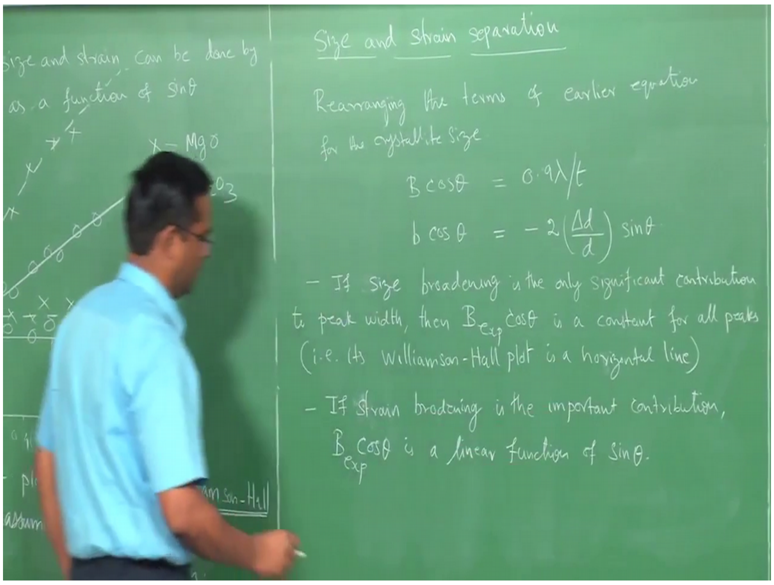

Size and strain separation

Rearranging the terms of earlier equation for the crystallite size

$$B\cos\theta = 0.9\lambda/t$$

$$b\cos\theta = -2\left(\frac{\Delta d}{d}\right)\sin\theta$$

- If size broadening is the only significant contribution to peak width, then $B_{exp}\cos\theta$ is a constant for all peaks (i.e. its Williamson-Hall plot is a horizontal line)
- If strain broadening is the important contribution, $B_{exp}\cos\theta$ is a linear function of $\sin\theta$.

Terms of that are why equation I am saying here in the terms of earlier equation for crystallite size that is Scherrer formula. We can write B cos theta is equal to 0.9 lambda divided by T and this one equation we know and we also done the other equation that is strain equation minus 2 delta D by D sin theta.

So, these two equations are quite familiar to us. This one is a Scherrer formula. I have just rearranged and this one is again rearranged. If you differentiate Bragg’s law with respect to theta and D, you get this expression that we have seen in the last class. So, combined these two we can now explain this plot as how this separates the first remark. So, let us look at what that detail of this using these two equations are if the size broadening is the only significant contribution to the peak width, then B cos theta is the constant for all peaks. That means, it is Williamson-Hall plot is a horizontal line. So, like this you have a straight line and if the strain broadening is the important contribution, then B cos theta is the linear function of sin theta.

So, what you have the data points here plotted for magnesium oxide as well as aluminum oxide magnesia and bring this is for alumina. So, now we can see that this portion, erase this.

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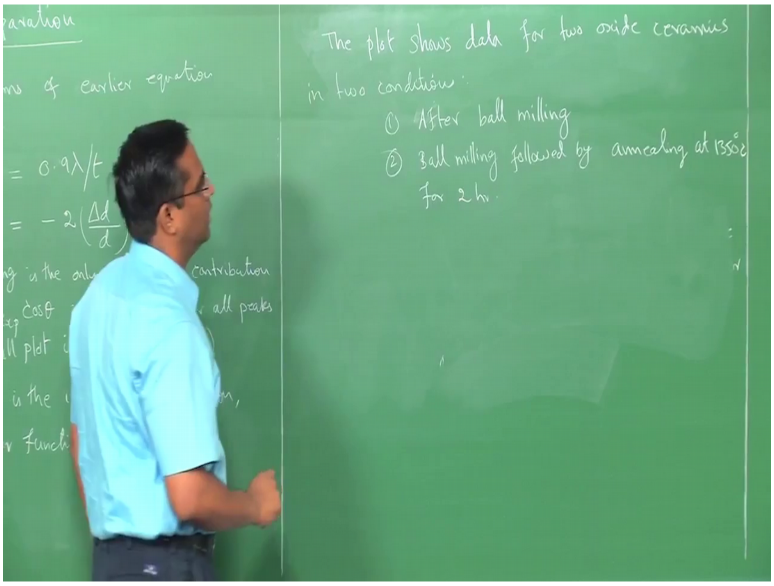

The plot shows data for two oxide ceramics in two condition:

① After ball milling

② Ball milling followed by annealing at 1350°C for 2 hr.

So, now let us complete that discussion. This plot as I mentioned belong to two materials; magnesia and alumina after two conditions i.e. after ball milling followed by annealing at 1350 degree centigrade for 2 hours.

So, when you say ball milling, that means you are basically trying to make the powders more fine. That means, you are straining this system or straining this lattice. So, you have the strain accumulation, then after this annealing the complete strain is revealed. So, you will have only the size contribution or the strain contribution and that is how these two effects are separated in these two examples. So, if you look at the complete procedure, it is first you have to measure the instrumental broadening, subtract them and then, use these two equations; one for size and one for strain and then, plot this B cos theta versus sin theta. Then, you will be able to separate these two effects.

So, this is one typical example of application of X-ray diffraction, where we have demonstrated how this size effect as well as strain effect can be measured and then, other typical applications of X-ray diffraction is a crystal structure determination which everybody commonly use this technique and also, the X-ray diffraction is primarily used for the phase identification. Suppose if you have a mixture of two or three phases in you know substances and then, how to identify each phase that is again a primary application of this technique.

And then, finally people use this technique quite often for stress measurements that is residual stress measurements of all the engineering compounds. That is one of the vital industrial applications and also, X-ray diffraction is used for crystal orientation determination namely a texture analysis.