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Lecture - 29
Materials Characterization

Fundamentals of X – ray diffraction

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Hello everyone welcome to this material characterization course in the last class we discussed about the x-ray diffraction intensity and the factors which are influencing this intensity and its consequences and one of the factors which we talked about is about two kinds of intensity that is I max that maximum intensity as well as the integrated intensity most of the time we are interested in the integrated intensity and we try to interpret this integrated intensity to arrive at the possible crystal structure determination or the estimate the residual stress or the crystal orientation and so on.

So in order to understand the factors which cause the peak broadening which is also very important aspect of understanding this intensity of the x-ray diffraction so we will continue our discussion in this lecture also about the same thing and we will try to derive some of the expressions which will relate the peak broadening with the crystal structure and crystal size and, so on so I will continue this discussion from there and if you recall I just talked about to kind of theta effect one is the x-rays exactly obeying the Bragg's law that means they the tabbing dragged angle that is the diffract exactly at the back Bragg θ.

Or a slightly away from this Bragg angle the diffraction takes place slightly away from Bragg angle so these two things are going to give large more effect on the final I mean expression or

even the amount of intensity which we are going to get. So when we talk about exact Bragg angle and then slightly away from the Bragg angle so what is the meaning of this we have already discussed.

So when you say that the crystal planes if you consider a poly crystalline material the crystal planes which are going to diffract slightly away from the θ B then their path difference also will be slightly different from the integral multiple of λ, so what draggle states if the path difference is in the range of integral multiple of λ then the diffraction takes place, and then we also talked about the destructive interference okay where you have this path differences exactly one half of the wavelength then they will cancel out each other.

So this also has some influence I mean the because of the slightly different from the θ B the diffraction will also have a significant influence on the amount of out of phaseness and its relation to the crystal structure okay, so we will look at this concept once again with a simple schematic and then we will get into this derivation of intensity with the effect of crystallite size and so on. So let me draw the schematic.

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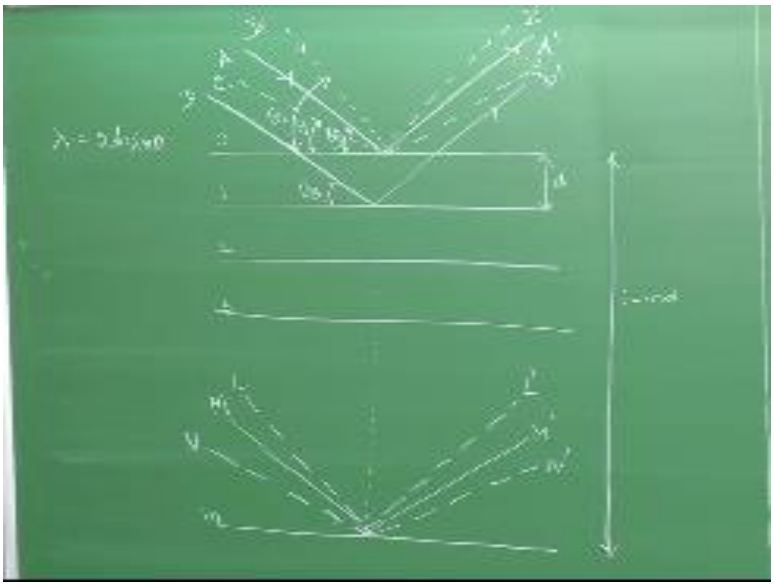

Let us assume this spacing between the planes is D and this is the total crystal we are interested with the thickness t which is equal to M D and this is m plane. So this diagram we have already though we have already seen for the sake of completion let me start describing this, so now what we understand is that the scattered being a' will have the I mean we will have the path difference from this D' by one wavelength that is what we have seen if you assume that λ is equal to 2 d sine-θ and that is what we said so that means what these two scattered beam will have fall in the same phase all of them will be in the same phase.

So similarly when you have this ray m' will have will be M wavelengths out of phase because it is coming from the M plane so this is one wavelength out of plane this is M wavelengths out of plane again M' D' and a' will all have the same phase that means they all will contribute to the diffraction intensity, so that is very clear that is brag glass states.

So now the question is suppose if I have a beam which is slightly away from the back Bragg angle like this let us call it as B' be and c' and similarly here we can have here l l' n'this is incident beam and this is a scattered beam or diffracted beam again so why we do this is for EM case this is for a particular given case that is why we are comparing this these two.

So now if you apply the similar rule suppose since this theta is slightly different from θ B it could be slightly XS are slightly lower in this case it is slightly excess θ 1 and this case it is slightly lower θ 2 you since it is slightly different from the θ B as I mentioned the path difference also will be very a very small fraction of integral multiple of λ not exactly integral multiple of λ the consequences is this is not going to cause the destructive interference.

So the plane which is going to have the atoms which are scattered the scattered beam will have exactly half the wavelength out of phase will be somewhere inside the deep of the crystal which we are not seeing because this θ is only fractionally varying only the atoms which is scattered from the plane which is at least have half the wavelength only will cancel the scattered beam from this a a', so that plane will somewhere lying in between we do not know okay.

But if you talk about this beam b & b' it will have the phase difference between l and l' m plus one wavelength and similarly ever c and c' will have a phase difference of M minus one wavelength with respect to n and n', so these are the wavelength at which the integrate I mean the intensity of the diffraction will be zero. So what are we trying to say here since you have the crystal planes which exist or which diffracts slightly away from the tab there exist at two limiting angles.

Because we are talking about 2 θ here because that is what we measure 2 θ 1 and 2 θ 2 so that we are talking about a range of angles which find this that means at least within the range only your intensity will be very and then these are two limiting θ where the intensity diffraction intensity will become zero that we will see. So that is the idea of doing all this, so let us now try to write few points.

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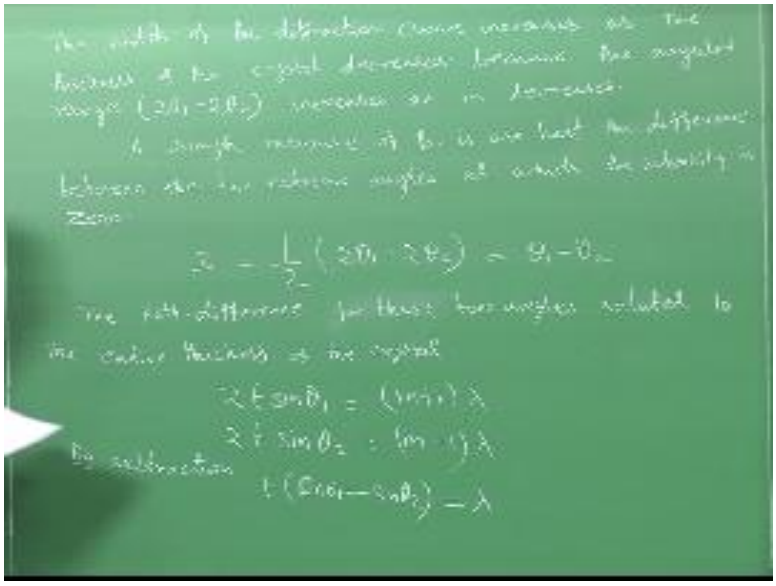

You so the width of the diffraction curve increases as the thickness of the crystal decreases because the angular range θ 2 θ 1 minus 2 θ 2increases as M decreases as the M decreases and your range is going to increase that means it is going to cause peak broadening. So one more point you have to recall we have already discussed in the last class the as the crystal size

becomes smaller and smaller and if we consider this θ 1 and θ 2 that is they are slightly away from the θ B then there is that the plane which is going to diffract off a length of phase difference may not exist okay.

So that is another reason why we will see their peak broadening so that is the bottom line that is that is the bottom line, so there is a connection between the amount of out of phaseness and that crystal size exist so this you have to keep in mind before I mean when we talk about the peak broadening and one of the primary reason the physical basis for the peak broadening is this there may not be a plane which will completely make the post difference out of phase.

So now let us write the error of measure of a angular width, so which is nothing but the B is equal to 1/2 to θ 1 - 2 θ 2 so your B is measured in the angular range in the diffracted peak, so now you write the path difference of these two extreme angles with respect to the schematic what we have drawn. So the path difference for the two limiting angles related to the entire thickness of the crystal is 2 T sine θ 1 equal to M plus 1 λ. So that means we are talking about this way be B' with respect to el L' they will differ in their path by M +1 λ wavelength or M + 1 λ and then the second ray which is a less than θ B CC' will have the path difference with respect to n n' tot sine θ 2 is equal to minus 1λ.

So now we will manipulate this by subtraction, so we can use some de Garamond regulations to replace this so we can write to t cos θ 1 + θ 2 / 2 which is equal to λ.

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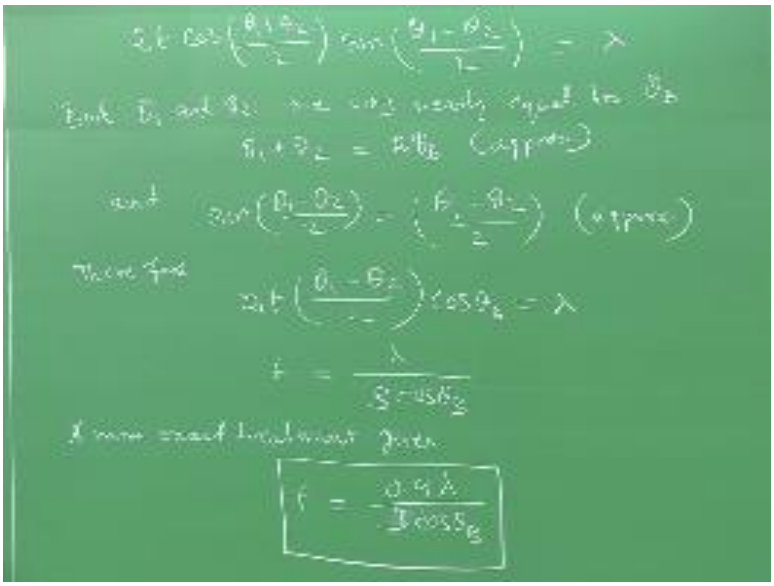

So what we have done is we have subtracting these two equations and we are replacing this with this expression trigonometric equation, and now we see that some assumption θ 1 and θ 2 are very small or very nearly equal to θ B then we can assume this θ 1+ θ 2 = 2 θ B this is an approximation to arrive at some relations, and you can also assume one more thing that is sine θ 1 / θ 2 is nothing but θ 1 - θ 2 / 2 this is also an assumption from this therefore, so we can substitute all this assumption here. So what you get is 2 T θ 1- θ 2 / 2 cos θ B = λ, R T is equal to λ / B cos θ B and more exact treatment gives this as T is equal to 0.9 λ / B cos θ B.

So which is known as a sheriff's formula we will write it here which is known as popularly known as sharers formula and most of our scholars use this especially when we are interested in the fine grain material to find out the crystallite size they use this relation quite often so we will see what all the precautions we have to take before we explicitly use this but this is a basic relationship between a crystallite size and the peak broadening effect are in the x-ray diffraction these are one of the fundamental aspects of x-ray diffraction. So now we will just illustrate this relation with some numerical example course you have.

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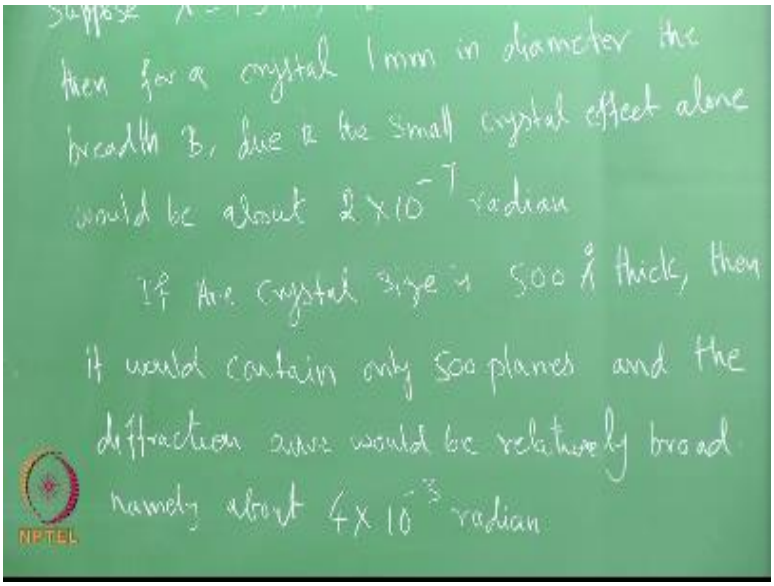

λ is equal to 1.5 angstrom t is equal to 1 angstrom and p equal to 49 degree then for a crystal 1 mm in diameter are breath, so what I am trying to say is what is the crystal size effect which will be having some visible effect on this week gardening suppose if you assume that λ = 1.5 angstrom DS that is one angstrom and the theta is 49^0 then went for a crystal one mm in diameter the be due to the small crystal effect alone would be about 2 into 10 to the power minus 7 Radian it is going to be extremely small.

So what is the size we will be able to see appreciably there is a some example for example we can say that suppose if the crystal size is about five hundred angstrom click then too it would contain it would contain. So if you have a crystal size in the order of five hundred angstrom thick then it would contain only 500 planes and the diffraction curve would be relatively broad namely about 4 into 10to the power minus 3 Radian which is easily measurable so that is one a simple example how to realize the effect of this relation and now we will move onto the strain effect whatever we have. Now seen is a size effect now we talk about a strain effect on the peak broadening.

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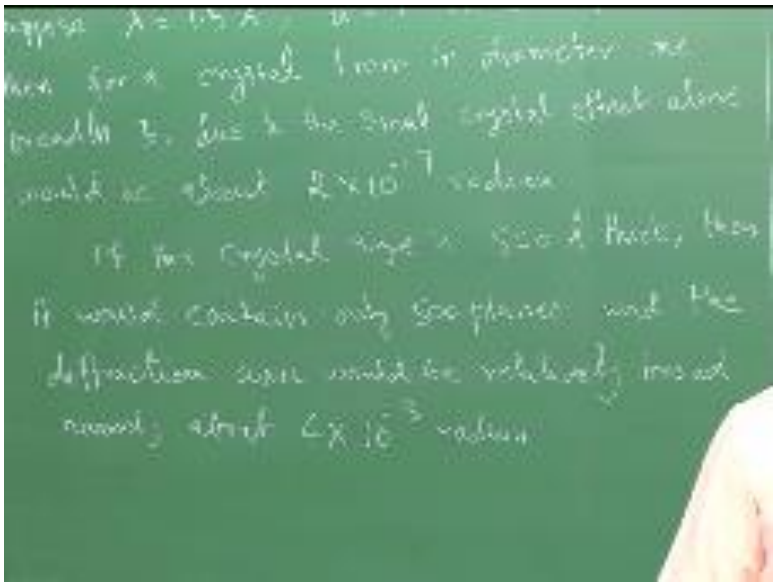

So before we talk about the effect of strain on the peak broadening you have to bring certain things in mind especially when we talk about crystal and crystal size and grain size and soon suppose if you were suppose if you take any polycrystalline material which will have I mean which will contain a 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 just discussed just previously about the Bragg theta here also it will come into the effect because if your neighboring grain is oriented with respect to a given signal crystal the angle is if it is very extremely small, so that orientation also is going to contribute to the x-ray diffraction so suppose if you say that any X grain or an X sinking crystal in a poly crystalline material defects with the θ B if the neighboring grain is oriented for example θ 1 then the diffraction is going to be from θ B + θ.

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 polycrystalline material where it contains units of single crystals or grains and then we are now considering a diffraction

being coming from at 23 different grains together all together. So this is with this background we can discuss the effect of strain also.

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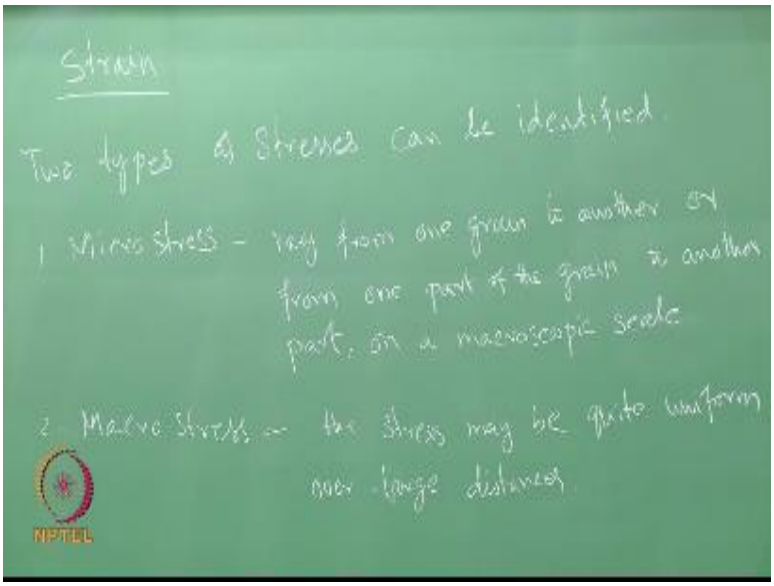

So first we define type of stresses because we had what we measure is actually a stress and then we convert that into stream or vice versa if you measure if you are able to measure strain and then we can convert that into stress we will see that there are two types, so there are two types of stresses 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 on the macroscopic scale on the other hand the macroscopic stress which may be quite uniform over a large distances.

So these are the two types of stresses which we are talking about here, so similarly we will talk about the strained also a uniform strain and as well as a non-uniform strain to illustrate that again I have to draw one schematic then we talked about it.

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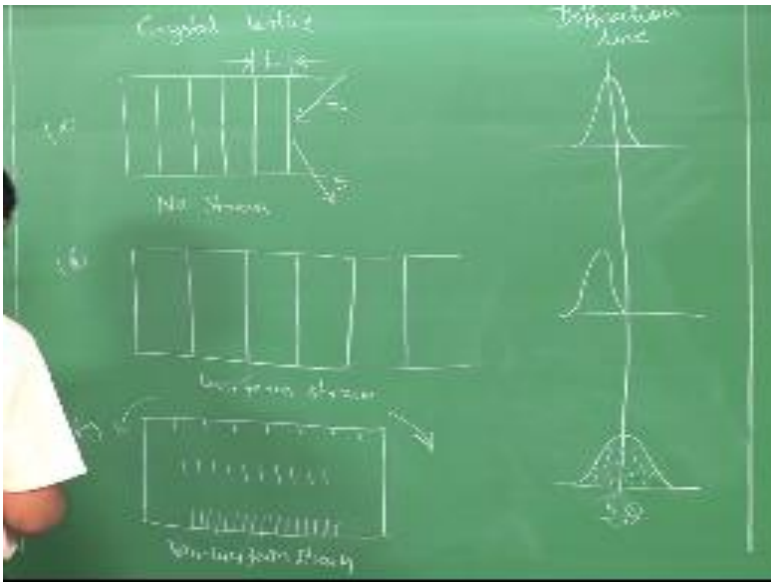

So what I have drawn here is a 3schematic suppose this is a crystal lattice with the deep planes distance from D_0 there is an equilibrium distance and then this is the incoming x-ray and this is a dye factor X a, so what we are now seeing is the D_0 is equally spaced so we describe this as a no strain and then if you assume that these this plane is being pulled in this direction and then we say that all the D is stretching into a distance away from D_0 that is more than V_0 then it is called a uniform strain and in the 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_0 is going to increase on the top and which is going to get compressed and the bottom and somewhere in between it will be equal to D_0. So there are three situation one is another attention where the D is more than D_0 and on the bottom it is d is less than D_0 and somewhere in between it will be equal to V_0 then we say that the specimen is subjected to or the crystal lattice is subjected to learning new form string.

So we will now see what is the corresponding peak refraction peak line so you see that a typical x-ray diffraction line this is for the no strain state you will have the peak like this and if it is a

uniform stretching then you are a peak is shifted to the left hand side and when you have the non-uniform state you have a bit of broadening with little bit of complete complexity inside we will see why it is so.

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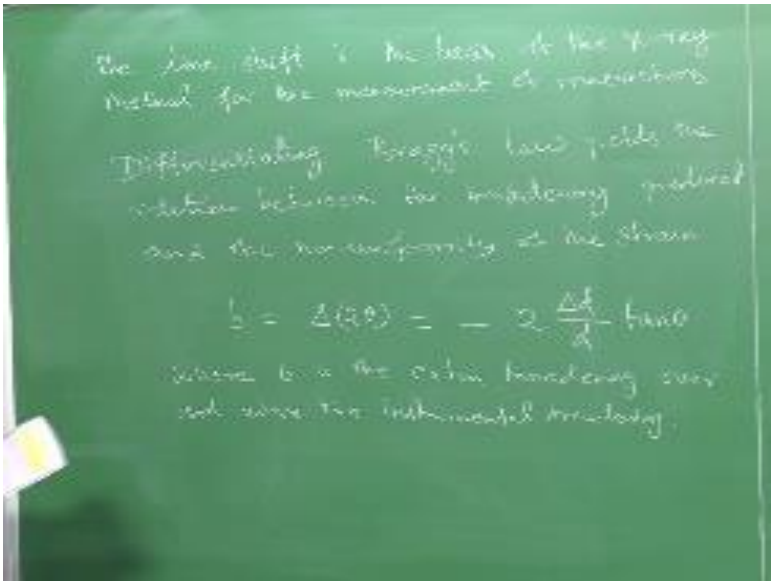

So the first point to note down here is so they shifting the shifting of the line is the basis of the x-ray method for the measurement of macro stress, so that is the fundamental information one you should keep in mind because of this x-ray methods are used for measuring the macro stress and then like I said this particular case where you have d is more than D_0 and here the b is less than V_0 and somewhere between it is equal to D_0 because of that you will have a region in a grain where the D spacing is constant for some region with respect to the neighboring region within the grain itself.

So because of that kind of a situation each one of the speed will produce a small sharp peak inside and which eventually we observe or a record have a broad intensity peak that is why you see this as a very broad intensity p spectrum and we will now see that how do we measure this. So we can say that type racking or I would say that let me write that equation directly if we can

directly differentiating yields the relation between the broadening and the non-uniformity of the stream.

So how to differentiate the drag la you will get relations like this so you are as you differentiate n λ I mean λ is equal to 2 d sine-θ u v dash is equal to u v dash plus b u dash kind of formula can apply and then you will be able to derive a relation between δ θ is equal to 2 d I mean to δ d by d tan theta but what we measure is theta 2 theta naught θ, so δ θ can be written like δ 2 θ is equal to minus 2 δ d by d and θ.

So this is the expression where b is extra broadening over and above where the instrumental burdens. So now the question is we are talking about peak broadening because of crystal size now we talk about broadening because of the instrument error and also broadening b due to the strain, so how to separate these two how we know that a particular amount of broadening is because of the strain or because of the crystal size. So that aspects we will discuss in the next class. Thank you.

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