X-Ray Crystallography

Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 33
Tutorial 08
Effect of crystallite size on diffracted X-Ray intensity

In the last class we discussed about the X-ray diffraction intensity and the factors which are influencing this intensity and it is consequences. And one of the factors which we talked about is about 2 kinds of intensity, that is iMax 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 to 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 2 kind of theta effect. One is the X-rays exactly obeying the Braggs law.

That means they the theta being Bragg angle, that is they diffract exactly at the Bragg theta, or a slightly away from this Bragg angle, the diffraction takes place slightly away from Bragg angle. So, these 2 things are going to give lot 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 crystal in material, the crystal planes which are going to diffract slightly away from the theta B then their path difference also will be slightly different from the integral multiple of lambda. So, what Bragg law states if the path difference is in the range of integral multiple of lambda then the diffraction takes place. And then we also talk about the distractive interference where you have this path differences exactly one half of the wave length then they will cancel out each other.

So, this also has some influence, I mean the because of the slightly different from the theta B, the diffraction will also have a significant influence on the amount of out of phaseness, and it is relation to the crystal structure. So, we will look at this concepts 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 that schematic.

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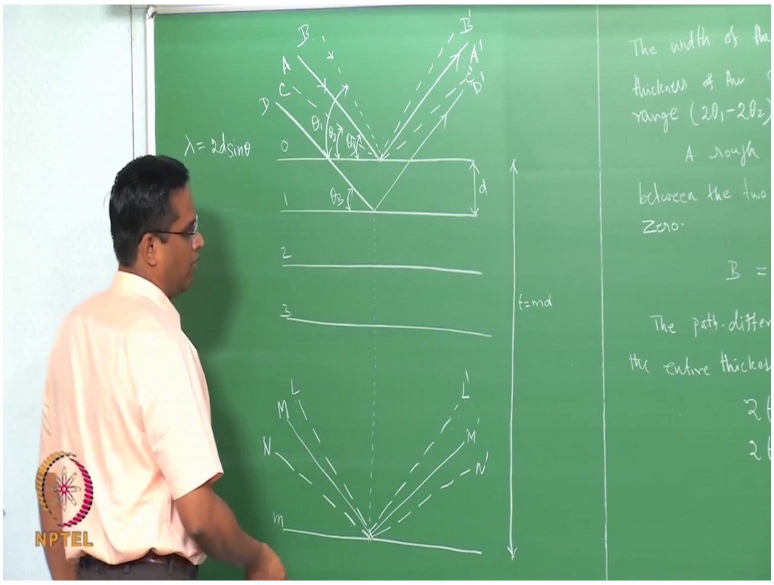

Let us assume this spacing between the planes this d, and this is the total crystal we are interested with the thickness t which is equal to md and this is m plane.

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 this scattered being A prime will have the, I mean will have the path difference from this d prime by one wavelength, that is what we have seen. If you assume that lambda is equal to 2 d sin theta, and that is what we said. So that means what? These 2 scattered beam will have all in the same phase; all of them will be in the same phase.

So, similarly when you have this ray m, M prime will have will be M wavelength out of phase because it is coming from the M plane. So, this is one wavelength out of plane this is M wavelength out of plane. Again M prime d prime and A prime will all have the same phase; that means, they all will contribute to the a diffraction intensity. So, that is very clear that is Bragg law states. So, now, the question is suppose if I have a beam which is slightly away from the Bragg angle, like this let us call it as B B prime.

And C C prime, and similarly here we can have here, L L prime, N N prime. This is incident beam and this is scattered beam or diffracted beam. So, why we do this? This is for M case this is for a particular given case that is why we are comparing these 2. So, now, if you apply the similar rule suppose since these theta is slightly different from theta B, it could be slightly excess or slightly lower. In this case it is slightly excess theta 1, and this case it is slightly lower theta 2. Since it is slightly different from the theta B, as I mentioned the path difference also will be very, as very small fraction of integral multiple of lambda.

Not exactly integral multiple of lambda the consequences 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 their wavelength out of phase will be somewhere inside, the deep of the crystal which we are not seeing because this theta 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 prime. So, that plane will somewhere line in between, we do not know ok.

But if you talk about this beam B and B prime it will have the phase difference between L and L prime M plus 1 wavelength. And similarly your C and C prime will have a phase difference of M minus 1 wavelength with respect to N and N prime. So, these are the wavelengths at which the integrated, I mean the intensity of the diffraction will be 0. So, what are we trying to say here since you have the crystal planes which exist or which diffracts slightly away from the theta B there exist a 2 limiting angles, because we are talking about 2 theta here.

Because that is what we measure 2 theta 1 and 2 theta 2. So, the there we are talking about a range of angles which define this; that means, at these 2 within the range only your intensity will be varying. And then these are 2 limiting theta where the intensity diffraction intensity will become 0, that we will see. So, that is the idea of doing all this.

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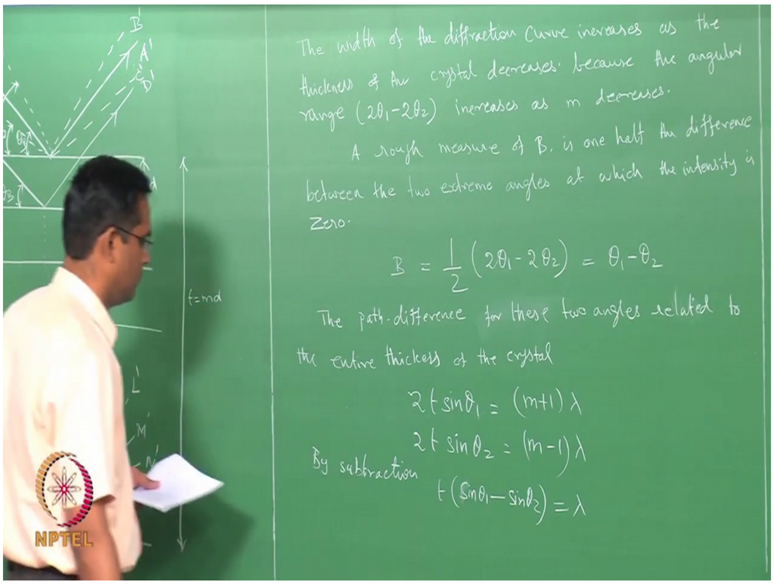

So, let us now try to write few points. So, the width of the diffraction curve increases as the thickness of the crystal decreases, because the angular range theta 2 theta 1 minus 2 theta 2 increases as M decreases, as the M decreases And your range is going to increase; that means, it is going to cause peak broadening.

So, one more point we have to recall, we have already discussed in the last class the as a crystal size becomes smaller and smaller and if we consider this theta 1 and theta 2 that is they are slightly away from the theta B, then there is that the plane which is going to diffract half a length of phase difference may not exist. So, that is another reason, why we will see their peak broadening. So, that is the bottom line that is the bottom line. So, there is a connection between the amount of out of phaseness and the crystal size exists.

So, this we 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 path difference out of it is. So, now, let us write the a rough measure of a angular width. So, which is nothing but the B is equal to half 2 theta 1 minus 2 theta 2.

So, your B is measured in the angular range in the diffracted p. So now, you write the path difference of this 2 extreme angles, with respect to the schematic what we have drawn. So, the path difference for their 2 limiting angles related to the entire thickness of the crystal is 2 t sin theta 1 equal to M plus 1 lambda. So that means, we are talking about this ray B B prime with respect to L L prime they will differ in their path by M plus 1 lambda wavelength, or M plus 1 lambda.

And then the second ray which is a less than theta B, C C prime will have the path difference with respect to N N prime 2 t sin theta 2 is equal to M minus 1 lambda. So now, we will manipulate this by subtraction. So, we can use some trigonometric relations to replace this.

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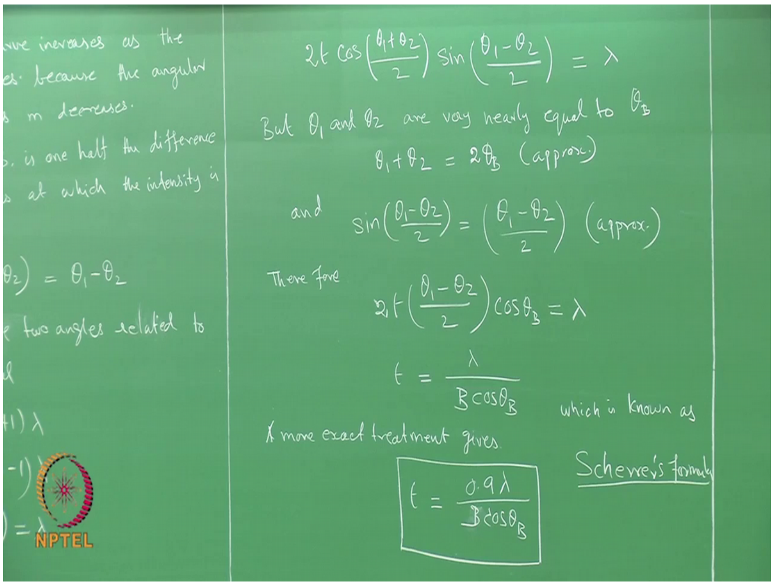

So, we can write 2 t cos theta 1 plus theta 2 by 2, which is equal to lambda. So, what we have done is, we have subtracting these 2 equations, and we are replacing this with this expression trigonometric relation.

And now we see that some assumption theta 1 and theta 2 are very small or very nearly equal to theta B. Then we can assume this theta 1 plus theta 2 is equal to 2 theta B this is an approximation to arrive at some relations. And you can also assume one more thing that is an sin theta 1 by theta 2 is nothing but theta 1 minus theta 2 by 2. This is also an assumption from this. Therefore so, we can substitute all this assumption here.

So, what you get is 2 t theta 1 minus theta 2 by 2 cos theta B is equal to lambda. Or t is equal to lambda by B cos theta B, and more exact treatment, treatment gives this as t is equal to 0.9 lambda divided by B cos theta B; so which is known as a scherrers formula. We will write it here, which is known as popularly known as scherrers 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 the expectedly use this, but this is a basic relationship between crystallite size and the peak broadening effect in the X-ray diffraction. This is one of the fundamental aspects of X-ray diffraction. So, now, we will just illustrate this relation with some numerical example.

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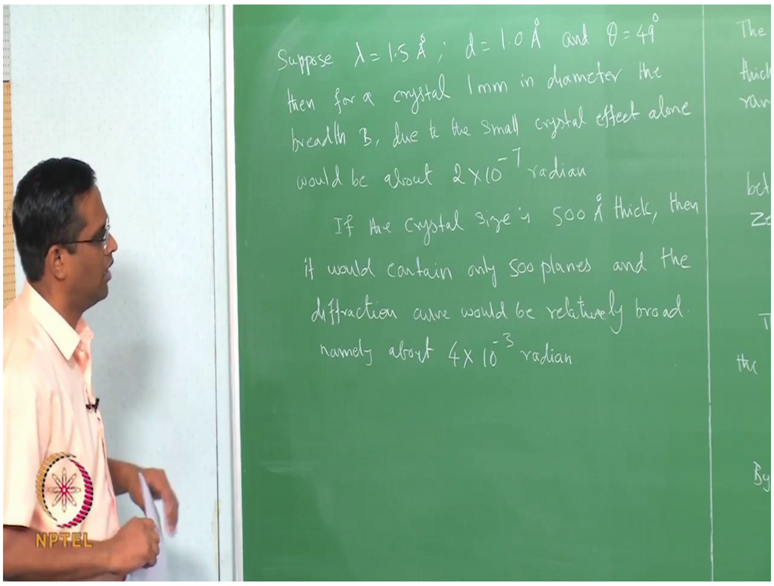

Suppose you have lambda is equal to 1.5 angstrom d is equal to 1 angstrom.

And theta equal to 49 degree then for a crystal 1 mm in diameter the breadth. So, what I am trying to say is; what is the crystal size effect which will be having some visible effect on this peak broadening. Suppose if we assume that lambda is equal to 1.5 angstrom d is that is 1 angstrom and theta is 49 degree then for a crystal 1 mm in diameter, the B 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 able to see appreciably? There is some example for example, we can say that suppose, if the crystal size is about 500 angstrom thick then to it would contain so if you have a crystal size in the order of 500 angstrom thick. Then it would contain only 500 planes and the diffraction curve would be relatively broad namely about 4 into 10 to the power minus 3 radian which is easily measurable.

So, that is one a simple example how to realize the effect of this relation.

Thank you.