Techniques in Materials Characterization

Prof. Shibayan Roy
Department of Material Science Center
Indian Institute of Technology - Kharagpur

Module No # 14
Lecture No # 57
X-ray Diffraction Profile and Analysis

Welcome everyone to this NPTEL online certification course on techniques on material characterization. And we are in module 12 this is last module and we are discussing about X-ray diffraction this is lecture 2 and now until up to now we have discussed about various factors that basically modifies or that effects the intensity of an X-ray diffraction beam. And we have seen starting from structure factor starting from atomic scattering factor we did not build up structure factor.

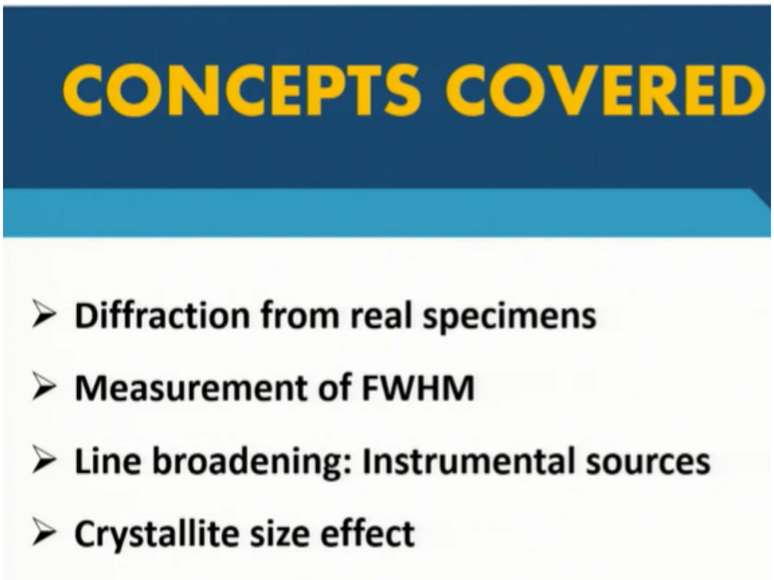
We discussed about the multiplicity factor we discussed about the temperature factor absorption factor lots of other different factors we discussed about them. That how the intensity can get modified certain deflection certain diffraction beams will be present certain other factors will be present. And then we have obviously before that we discussed about the extra source and we discussed about Bragg's law required conditions for diffraction and all of these things.

Now onwards so the remaining 4 lectures we will be concentrated on understanding the X-ray diffraction peak or X-ray diffraction profile from a real specimen I mean real specimen. Mostly we concentrate on powder specimen or solid specimen but mostly on a normal regular X-ray machine that possibly you will be seeing Braag-Beneto geometry kind of X-ray diffraction machine that you will be seeing.

And the X-ray diffraction profile that we will be getting we are not discussion as I last lecture if you remember that I told that there can be many difference geometry of X-ray diffraction, Laue diffraction, Debye-Scherer diffraction and so and so forth. We do not go into all of this very regular and if sounds familiar to you the powder diffraction method. You can use the solid specimen instead of powder but basically it is the same powder diffraction a kind of X-ray diffraction profile that you get.

So will try to understand various aspects of this X-ray diffraction profile from a real specimen and why we are getting that what we can understand out of it so on and so forth.

(Refer Slide Time: 02:34)



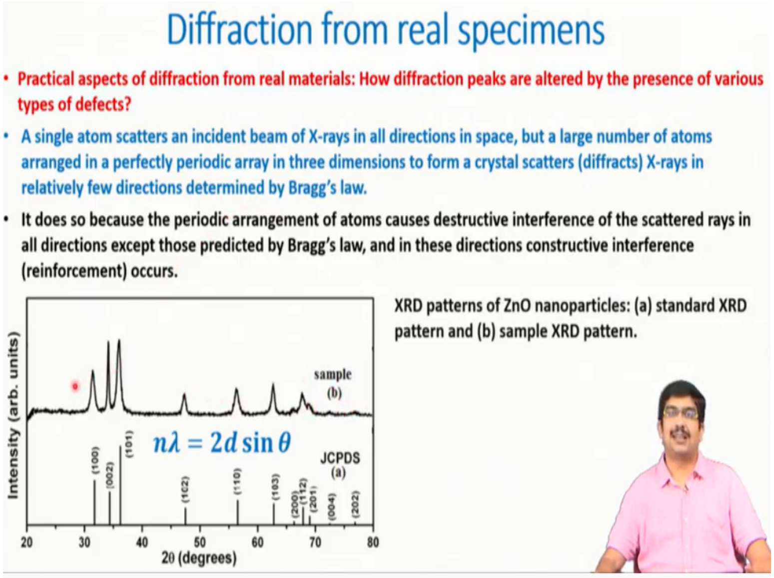
CONCEPTS COVERED

- Diffraction from real specimens
- Measurement of FWHM
- Line broadening: Instrumental sources
- Crystallite size effect

So here first we will try to understand various aspects of diffraction from a real specimen then measurement of FWHM what does that mean? Full width half maxima that we will discuss and then we will discuss about something called line broadening. First and various sources of line broadening first one we will discuss about the instrumental sources and then we will discuss about certain sources which are inherent to the specimen itself.

And that we will reveal possibly many information more than just identity of crystal more than such a solving the crystals structure we will be able to understand many more aspects about the material.

(Refer Slide Time: 03:11)



Diffraction from real specimens

- Practical aspects of diffraction from real materials: How diffraction peaks are altered by the presence of various types of defects?
- A single atom scatters an incident beam of X-rays in all directions in space, but a large number of atoms arranged in a perfectly periodic array in three dimensions to form a crystal scatters (diffracts) X-rays in relatively few directions determined by Bragg's law.
- It does so because the periodic arrangement of atoms causes destructive interference of the scattered rays in all directions except those predicted by Bragg's law, and in these directions constructive interference (reinforcement) occurs.

$$n\lambda = 2d\sin\theta$$

XRD patterns of ZnO nanoparticles: (a) standard XRD pattern and (b) sample XRD pattern.

So we will discuss all of these things but let us first see the diffraction from a real specimen how does it look like. And I am I assume that many of you possibly particularly the research students many of you have particularly have possibly seen a real X-ray diffraction profile you may be having a powder sample. You may have taken a piece of solid specimen and you put it in a X-ray diffraction machine and that machine finally give you this kind of a graph which is basically an arbitrary unit.

With this side it is intensity and this side you will see the theta and the heart of this is definitely the Bragg's condition in lambda is 2dsinΘ. And of course the intensity part is determined by this various factors we will discuss so far. Fine that is there now the point is that why I am saying diffraction from real specimen why I am stressing on this fact that real specimen. What is real specimen and what exactly happens for a real specimen.

So if you compare these 2 X-ray diffraction profile and this is also possibly you have seen in if you try to solve this X-ray diffraction profile if you want to identify the phase you want to know the lattice spacing and so on. If you want to do that what you try to do is to do first you bring something called JCPDS various other names are there. This is basically crystallography database which gives you the X-ray diffraction profile of corresponding phase or element that you want to.

You are interested you can bring out that but basically this X-ray diffraction profile you yourself can generate what you get from the data is actually, a real specimen again. A real specimen under idealized condition and all real specimen we should try to match with your specimen. But you can generate this one how you can generate this? The idea or the way you can generate this is very simple you just use the Bragg's law that is it.

You do not need to do anything else you can generate and X-ray diffraction profile for any material how is it so? All you have to do is to know the crystallography of the material any particular material you know that is the BCC structure or a FCC structure simple cubic structure whatever it is. You know the structure you know the symmetry you know the lattice parameter abc and so on that is it.

That means in this $n\lambda=2d\sin\Theta$ Bragg's law you know the λ that is from the instrument you know what is λ you are operating on and we will see there are even this λ is not a constant that brings another kind of an error. But for that moment you assume that λ is purely monochromatic excellent monochromatic X-ray beam and one single λ value you are getting that is it.

Then what you know is d value of course you know the symmetry of the material you know the unit cell you know the lattice parameter everything you know. So, you know the d spacing for different lattice planes. If you are interested for say 100 plane you know the d value and let us assume again let standard unit cell you are using BCC you are using a FCC you know the relationship how to calculate this d spacing from the lattice parameter.

Fine you know the d value all you have to calculate you know lambda you know d you have to calculate the $\sin\Theta$ value. So you know exactly at what $\sin\Theta$ you can expect the diffraction to happen and then there you mark that here fine then you know the exactly which position you will be getting this peaks first thing. Next thing what you can do is that you can find out even the intensity of this theoretically if you know the structure factor.

So structure factor and multiplicity factor if you remember I said structure factor and multiplicity factor these 2 are related to the crystallography of material. So, you know the crystallography and you can find out the intensity of say 100, 002, 101 that is 110 type all of this peaks you basically know their peak intensity also in the lative unit. You know the peak intensity what should be the peak intensity of say 100 peak what should be the intensity of 002, 110 type or 111 peak and so on and so forth.

So you can ideally generate this entire diffraction pattern when I say ideally generate what you assume is an ideal material. Ideal material means a material which does not have imperfection or in other words the material does not have any kind of defects into it complete ideal material where only Bragg's law is determining the diffraction. Where exactly which direction diffraction should happen means sin2ϴ and only structure factor multiplicity factor this are determining what should be their intensity that is it.

Then you can very well generate this entire thing and if you notice this is giving you as a line that means at a particular 2-theta value you are getting this diffraction and that as a particular intensity fine. So this is completely generated by you can do you can take a excel sheet and generate this entire diffraction profile then you plot it. Problem is if you try to see for a same material this is shown for a ZnO, zinc oxide nanoparticles.

If you want to see this what you will be seeing is a complete difference picture alltogether you will see that your peaks are not a single line. If you are fortunate, you will be getting a maxima of those peak at least in this exact position that also is not guaranteed because that depends on any other thing. But let us say you are very lucky you get you maximum exactly at sin 2-theta position at this one is showing fine.

Even with that you will see that this is not line function this has a certain width this is some other kind of function this is some other shape all together the peak as a certain width or finite width number 1. Second thing what you can notice is that the structure factor and other factor the intensity that you calculated is not matching here. Here according to these 100 peaks should have a higher intensity then 002 peak right.

But you can see here that is exactly reverse so you are getting completely different intensity now the intensity part is now getting modified over and above structure factor and multiplicity factor the intensity is getting modified by other factors. We discussed that temperature factor absorption factor so on and so forth. May be other factors are there is something that we even discussed if time permits I will try to discuss something called texture factor that is also there.

And that is invariably that is used to be there for solid specimen texture factor but all of this practical factor will modify the intensity mostly plus there are many other factor related to materials itself. The defects in the material because ideal material or this one is derived for an ideal material which does not have any kind of defect any kind of diffraction which is absolutely completely a defect free.

Now if you remember our discussion about the temperature factor there we said that the entire this intensity calculation is done or even the Bragg's law derivation is done with the assumption that all the atoms are fixed at the mean position. But the temperature itself will cause this sort of something vibration at then mean amplitude position. And that itself we have seen how we can modify the intensity so same way it can modify peak position and all.

That also we have seen that we can do so these are the kind of defects or these are the kind of scenarios which are taking the diffraction phenomena from a perfect idealized condition to real condition. In a real material where the diffraction material is possibly carrying out at a higher temperature where you cannot neglect the temperature factor. It is carrying out on a real some certain thickness of the material.

So you cannot neglect the absorption factor it as carrying out on a specimen which has a finite size so that also is kind of imperfection for an ideal material it has to be infinite just like a definition of a lattice which says that it is an infinite way of points when you make this break this infinity the lattice is not expanded up to infinity that itself is a defect or imperfection in the real specimen.

Then many other imperfections any other defects can come and that will basically modify this entire diffraction profile that you theoretically modify generated for an ideal material. And what you will be really getting is something like this which is close to your ideal condition. But deviated because of certain factors which are related to the real specimen some of them and those factors will be discussing one by one will try to understand what basically gives us this kind of a X-ray diffraction profile instead of this one.

So intensity part as I said mostly it is because of those factors we are already discussed temperature absorption polarization factors all of these things are related to this diffraction this one. The modifying this intensity of this peak so that we will not discuss in great detail but we will be discussing mostly about this position where this peak and why the finite thickness of the position comes.

Because that will tell us more story about this entire real specimen that can help us to tell us some more about this specimen itself. Now the first thing is if we look at this Bragg's condition itself. So Bragg's condition as it says if it is followed the Bragg's condition is completely through for an ideal specimen then you are getting only intensity at a specimen position right that is one key you should not get.

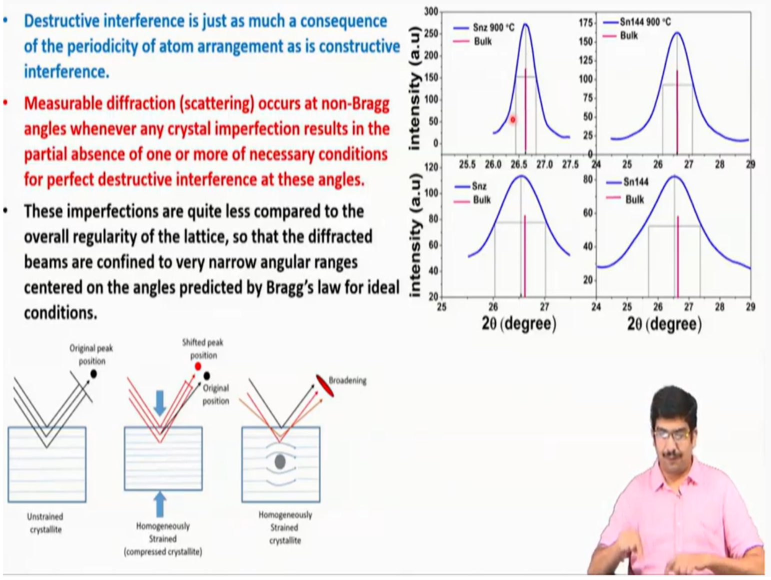
But what Bragg's law says is that an atom we discussed about that if it is an isolated atom that atoms scatter extra beam in all possible directions. But that atom is a part of an unit cell because of the crystalline periodicity because of the crystalline arrangement what happens is that the X-ray beams are getting constructively reinforced along certain direction. Very specified directions and all other directions there is a imperfection certain direction.

There is a destructive interference complete destructive interference most of the other direction there is an imperfect one or partially interference that is happened. So that means in a ideal conditions the Bragg's law is valid only in an ideal condition the Bragg's law is valid and there only we are getting intensity along certain directions. And that is related that the Bragg's law as to be valid is related to this periodicity of this crystals itself in the first position.

So anything that disturbs this periodicity of crystalline structure or this periodic arrangement of atoms regular intervals atoms are arranged in symmetry with specific distance and all. Anything that changes that periodicity anything that takes it away from this periodic structure will cause an imperfection will cause a defect and that will take you from an idealized specimen where Bragg's law is exactly to an conditions is Bragg's law is somehow relaxed.

So now we have to see what could be this different type of defects in the real specimen will make the real specimen. And which is taking it away from an idealized condition that will be that will help us to understand as I said why are getting this kind of an extra diffraction profile.

(Refer Slide Time: 15:07)



- Destructive interference is just as much a consequence of the periodicity of atom arrangement as is constructive interference.
- Measurable diffraction (scattering) occurs at non-Bragg angles whenever any crystal imperfection results in the partial absence of one or more of necessary conditions for perfect destructive interference at these angles.
- These imperfections are quite less compared to the overall regularity of the lattice, so that the diffracted beams are confined to very narrow angular ranges centered on the angles predicted by Bragg's law for ideal conditions.

Now as I said constructive interference is a consequence of this periodic arrangement of atom. Same way destructive interference is also a consequence of this period arrangement because just like if you remember when there is this path difference is exactly an integral multiple of λ we are getting a periodic we are getting a constructive interference. And remember the base centre versus body centre example when we are deriving the Bragg's law.

That time we saw that if same thing can happen if the path difference in half of or ½ of λ then there is a complete constructive destructive interference. So basically, destructive interference is as much a consequence of periodicity of atomic arrangements as the constructive interference these are the 2 extremes and in between there is partial interference. So that means when we are having this defects inside the material.

We are basically going from perfect constructive interference case to an more imperfect one and closing towards the destructive interference. But again perfect destructive interference also is consequence of periodic arrangements. So defects and imperfections will not take us there also it will be somewhere in between this constructive interference and destructive interference and then what we will have is?

We will have some diffraction of scattering or intensity at non-Bragg's angle when a crystal imperfect friction is present within the material. So something like this what we try to tell here this is an crystallite where the case all the atomic planes are perfectly placed and d-spacing between them also perfect this is constant through out the material. And in this case now we are getting this peak exactly are the same position something like this we are getting the peaks exactly at the middle at the same position.

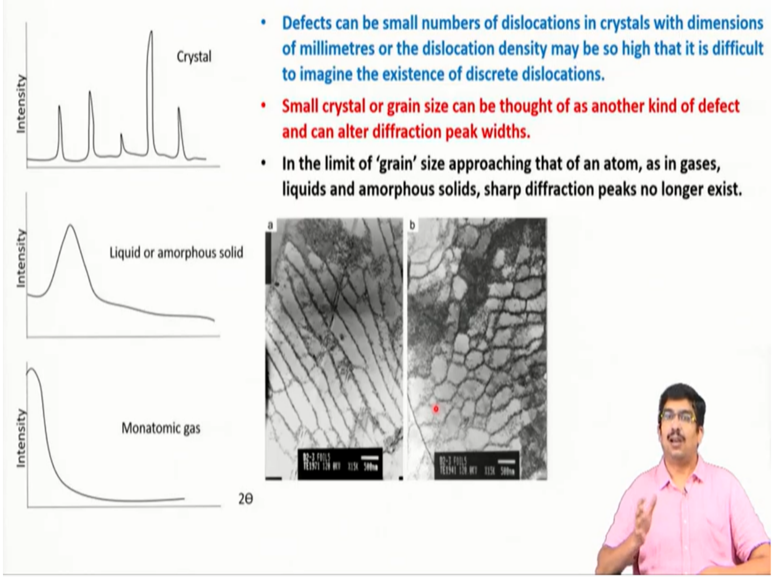
But when we have some kind of defect present in the material the atomic planes are any longer continuous they are not having the same d-spacing having that results is that. Now you started getting this peak to be boarded this peaks are not as narrow as this line function they are now getting bigger and bigger that means diffraction satisfied from non-Bragg's angle. So this point or this line is showing you exact Bragg's condition and you are trying to started getting certain intensity at non-Bragg's angle also.

So that means you are getting basically partial interference you are from complete destructive interference you are going away to partial interference conditions. Now the point is compared to this ideal condition the imperfection within a real specimen is order of magnitude lower. Usually the imperfection amount of imperfection in a material is order of magnitude lower than the perfect nature somewhere else.

That is why more or less you get this kind of intensity maxima more or less lies at exact Bragg's angle and what you afterwards what you get basically is non-Bragg's angle conditions diffraction certain intensity that occurs due to the partial interference. And you get basically the broadening the peak gets broadened the peak becomes from a line function the peaks become other kind of Gaussian function many other functions will briefly discuss about that.

But you are getting this little bit broadening peaks are getting broader in the 2 theta axis so that is what is mostly the effect of imperfections on a material and this real diffraction pattern from a real specimen is all about the presence of this imperfections fine.

(Refer Slide Time: 19:06)



- Defects can be small numbers of dislocations in crystals with dimensions of millimetres or the dislocation density may be so high that it is difficult to imagine the existence of discrete dislocations.
- Small crystal or grain size can be thought of as another kind of defect and can alter diffraction peak widths.
- In the limit of 'grain' size approaching that of an atom, as in gases, liquids and amorphous solids, sharp diffraction peaks no longer exist.

So the defects what kind of defects we are talking about we will be there can be various type of defects that you can just name as many as possible point defects 1d defect, 2d defect, 3d defect all can be defects will have a on the diffraction profile. So here the main few defects there will be talking here so for example one of the most important defect of the material or in the real specimen is basically the grains, the size of the finite size of the material s there.

As we discussed the Bragg's law if it is an idealized material it has to be an infinite array of this points just in order to have exactly like an line function. But our crystal are of finite size that means they have interfaces if it is a single crystal you will have interface with let us say air or other material there will be this interfaces. And if it is poly crystalline material we will be having this grains which are essentially single crystal and then separated with others from by this grain sizes.

So basically this size of the crystal itself that this it has a finite size itself is an imperfection in within itself. So the size effect this finite size of the material that itself is a defect and will effect the peak the extra diffraction profile from real crystal. And this best way we can imagine this or best way we can understand this if we compare the X-ray diffraction profile from a crystalline material and with that of a liquid or amorphous material which we can think of is a another extreme or a mono atonic which is another extreme there is no perfection.

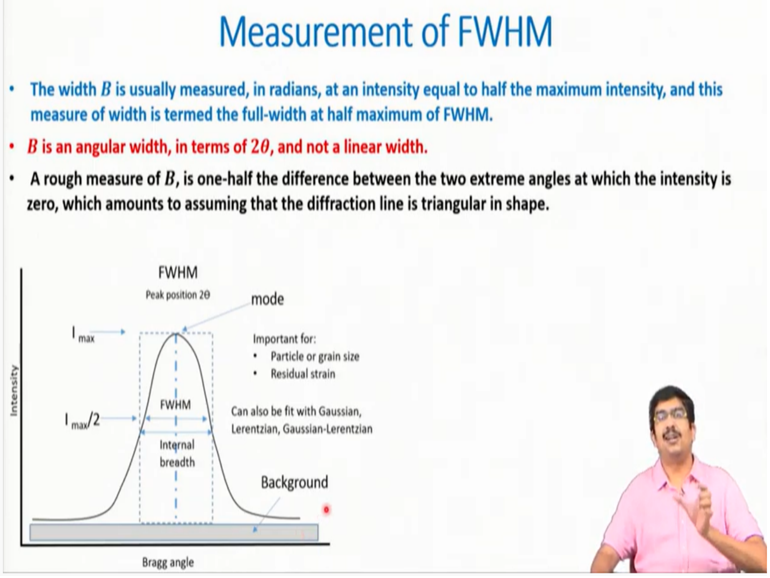
And there is no order itself so from a complete order condition to an disorder condition and that itself that show us that effect of this size the finite size or the effect of order present in the material. Another kind of defects that we can think of mostly happens for metallic materials is the dislocations. The dislocations are the stream in broader context we can talk about this stream or in other context we can talk about the dislocations.

So dislocations is the line defect that all of you know the dislocations is a line defect and mostly within the material they are present the dislocations are present wherever they are present they are associated with stream fields and so on and so forth. So there could be strain associated within that material within that material if it is a crystalline material within the material there are strain associated with it.

So and this dislocations when the dislocations are too many number they form their structure and they further divide the material into smaller unit. So even within the grain they form this kind of structure this is thermo mechanical process and thermo mechanically processed iron. And this material you can see that this has typical dislocation structure which we called substrate we will discuss about that maybe in the next lecture.

We will discuss about this dislocation of structure but this kind of a just because of the presence of dislocations high amount of dislocations we are getting a structure within the materials. So the grains are even more sub divided into smaller crystallites. So size is getting decrease so all are these are defects all of these are an imperfection within that materials which are basically taking the real specimen away from the ideal or idealized condition.

(Refer Slide Time: 22:43)



Measurement of FWHM

- The width B is usually measured, in radians, at an intensity equal to half the maximum intensity, and this measure of width is termed the full-width at half maximum of FWHM.
- B is an angular width, in terms of 2θ, and not a linear width.
- A rough measure of B, is one-half the difference between the two extreme angles at which the intensity is zero, which amounts to assuming that the diffraction line is triangular in shape.

As I said most of this effect of defects are seen in the broadening of this peaks so instead of the line function the peaks becomes like a different or peaks becomes different shapes and can be fitted with different functions and usually they becomes broadened their size increases in the 2 theta axis. So the way this is measured is called FWHM full width at half maxima.

So this is measured usually this is in measured in radians so you must remember that this is an angular width the FWHM. So if you take this real diffraction profile and you try to measure there FWHM basically what you are measuring is this axis along this axis which given in terms of 2-theta. So the angular width you are measuring for a peak is basically the angular width which is normally given in a radiant or you can express it in degrees as well.

And this is definitely not a linear bit many people I have seen even the students I deal with many of them they do this mistake they measure along the scale. Of course they measure it they come back to me with the FWHM which is they are reported in terms of sum unit of length. But actually they should be measured in terms of the width or this measured in terms of the 2 theta angle here.

So the way this FWHM is measured is actually basically is half the maximum intensity where the intensity drops the maximum intensity drops to half the value there the width measure the width of a peak. And that is why it is called the full max width full width means from this to this angle where the intensity drops exactly to half from this angle to this angle this is the full width at half maxima.

Also what we will be seeing at we can also measure this width of the peak by measuring these 2 angles by taking the difference of this 2 angles where this one becomes the intensity becomes basically 0. So this intensity where the intensity becomes 0 are very small that 2 points the difference between these 2 angles that also is giving us the full width of maxima B. So this is the way of measuring the width of a peak and as just now we understand that ideal condition in ideal Bragg's condition this is a line function.

So anything that increases the width of this is the broadening basically and what we are interested now onwards is what cause the broadening. So the FWHM is basically the measurement of this broadening how much broadening as happened? And now we will be trying to understand what causes this broadening what takes this away from a line function which is here and making it some other kind of a shape other kind of a function.

Now this itself this understanding this broadening phenomena itself is a real big area of result and this is known by many names one few of the names that you may be here heard of here is something called Reitveld refinement where you basically try to understand this peak broadening from different sources you consider and you try to match this peak all of these processes basically involve matching this peak by suitable function it something like examples in this given lie Gaussian the peaks are Gaussian sometimes they are Lerentzian you can fit it with Gaussian-Lerentzian.

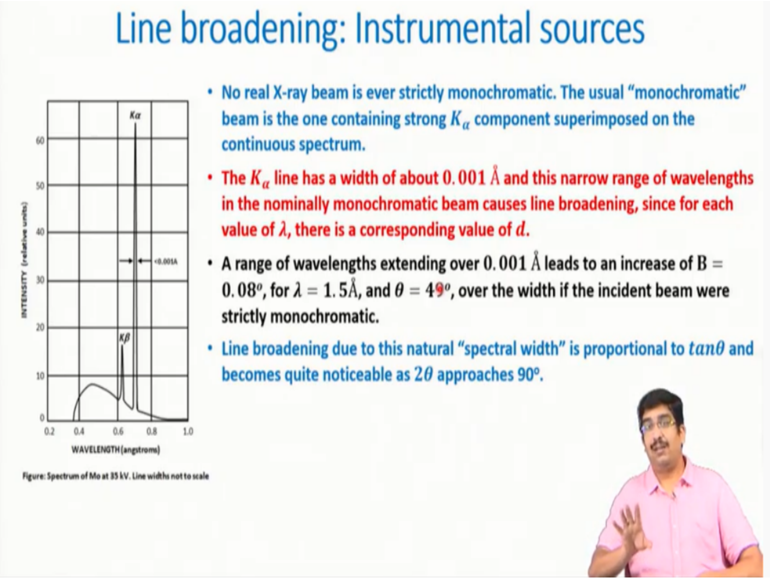
There are many other different functions that you can pseudo-void various type of functions you can bring and try to match these peaks and in the process of matching you imagine different type of sources of this peak broadening and the relative contributions of that. From there you can find out that what exactly is causing this broadening?

And you can extrapolate that and understanding many other things many this about with one example is you can understand the type of dislocations present there or the dislocations density that is present within that material the time of even. Sometimes even the people are trying to understand the type of dislocations where the edge dislocation or screw dislocation and what is the relative portion.

All of these things you can try understand just by fitting this curve in the different kind of functions and then understand various sources which are causing this broadening and which helps you to fit this curves basically. And this process as I said this peak fitting is called many a times it is called extra LPA extra diffraction line profile analysis or Reitveld refinement various other names are available.

But all of them basically tries to understand what causes this broadening so that is the importance of this peak broadening here.

(Refer Slide Time: 27:36)



Line broadening: Instrumental sources

- No real X-ray beam is ever strictly monochromatic. The usual "monochromatic" beam is the one containing strong K_α component superimposed on the continuous spectrum.
- The K_α line has a width of about 0.001 Å and this narrow range of wavelengths in the nominally monochromatic beam causes line broadening, since for each value of λ, there is a corresponding value of d.
- A range of wavelengths extending over 0.001 Å leads to an increase of $B = 0.08^o$, for $\lambda = 1.5$Å, and $\theta = 49^o$, over the width if the incident beam were strictly monochromatic.
- Line broadening due to this natural "spectral width" is proportional to $tan\theta$ and becomes quite noticeable as 2θ approaches 90°.

Figure: Spectrum of Mo at 35 kV. Line widths not to scale

So the first source of broadening before we go into the material itself we must discuss and understand one of the sources which is basically coming from the instrument itself the entire instrument the instrumentation itself. So the first source as we can already understand is basically in the entire Bragg's condition we have taken $n\lambda=2d\sin\Theta$. And we said that $\lambda$is fixed what if the lambda is not fixed because this is what happens in the real X-ray diffraction conditions the beam is never monochromatic.

The monochromatic beam usually the monochromatic beam we try to capture is a strong k alpha component basically this if we imagine this is the Mo k alpha at 35 kv. So this strong k alpha component and it passes through filter even with that. Even if we pass it through the filter what we will be finally getting is a range of lambda in the monochromatic it will not be a perfect monochromatic beam it will have a range of this angle.

And that is related to basically this width of k alpha itself in the 2 theta in the wave length axis the k alpha peak will have or the k alpha radiation will have some finite width. That means in the X-ray beam which is finally falling on the specimen will have lambda or with that kind of a range in class minus direction it will have little bit of deviation from the exact monochromatic condition.

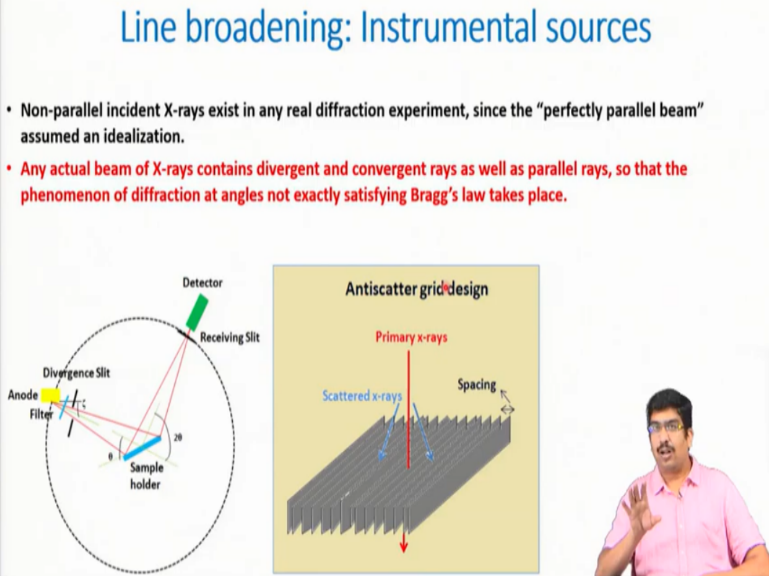
So this will definitely then from Bragg's condition what it will do is the λ will change within a range d if we or if we take that the d is constant for certain region the material is perfect no imperfection nothing. Even with a perfect material just because λ is different in the source itself then we will have different sin theta values. And the peak itself will get broadened by a certain amount little bit of amount.

Just because lambda is getting within a range we are not getting a perfectly monochromatic beam we are getting it in a range or X-ray diffraction peaks will also get slightly broadened because of this instrumental source. Now if we put some values and try to understand that how much broadening we can expect from this we put something like 0.001 angstrom for this perfectly monochromatic beam that the wave length range.

Which is very typical for most of the X-ray sources that we use moly copper chromium most of the beams k alpha. Usually have a wavelength range of 0.001 λ so if we put that the kind of width increase in width we can expect it 0.08° for lambda. If λ value if we take 1.5 angstrom and theta value we take it around 49 that means 2 theta is around 100°. So at this kind of a 2-theta level what we can get a width increase of around 0.08 which is for most of the practical purpose which is very small compared to other sources.

If we take other sources of line broadening usually is very less and people uses various other kind of filters so that the line broadening, they could putting it down even to that kind of a level even less than 0.1° and that is really small for most of the practical purposes.

(Refer Slide Time: 31:04)



Line broadening: Instrumental sources

- Non-parallel incident X-rays exist in any real diffraction experiment, since the "perfectly parallel beam" assumed an idealization.
- Any actual beam of X-rays contains divergent and convergent rays as well as parallel rays, so that the phenomenon of diffraction at angles not exactly satisfying Bragg's law takes place.

Another problem other than the monochromatic beam from instrumental sources another problem that happens is that what we use is not a parallel X-ray is not a polarized X-ray beam perfectly polarized X-ray beam. So that itself will we are seen in the polarization factor it causes the problem. Moreover, if it is a not a parallel incident beam it is not a parallel X-ray beam if it is combination of divergent and convergent X-ray beams that itself cause more broadening.

Because then the exact Bragg's condition will not be satisfied for the parallel diverging it will be only satisfied for a parallel beam with a particular lambda value but for other kinds of beam. Like divergent or convergent beams that will show certain intensity for non-Bragg's angle condition. And it will finally result in some width increase of to width of the X-ray diffraction peaks.

Normally this again we rectify this by using some kind of this kind of special attachment which are known as anti-scattered grid we are not going to that. Basically these are kind of grid through which the X-ray beam goes through it and it becomes a parallel X-ray beam divergent convergent X-ray beam goes through this anti-scatter slits and this anti-scatters finally they will become plain polarized beams.

So this way we can even reduce the line broadening to a much more X-ray so we will so from this we understand that the broadening of the peak can also happen. Because of the instrumentation aspect of it fortunately modern days the X-ray diffraction machines that we use are corrected in such a fine way that you tend to get very little line broadening. And line broadening remember one thing if you as we said when we are trying to fit this curve and trying to understand various sources of broadening.

We do not expect the line broadening to come over here because if that is present in huge broadening is present we have no ways to identify that or to take care in most of the refinement methods that we use we do not have corrections. Or it does not there is no formulation path the correcting the line broadening. So we must correct it online we must correct it using the hardware part and those are the hardware parts as I said we used different types of filter anti-scattering grid and all.

And usually after using this line broadening comes down to very low value, we can safely neglect that on most of the diffraction kind of refinement experiments or X-ray diffraction experiment. So with this we stop it here and we discuss about the crystallite size effect in the next class.