Lecture 18
X Ray Diffraction Diffractogram Calculations

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Now we'll focus on X-Ray diffractometer. So far, we focussed on how to get the diffraction, and how to analyse the diffraction pattern. It is important to know how do you collect, where do you collect the pattern. So X-ray diffractometer is used to collect the x-ray diffraction pattern. What is it? What does it consists of, X-Ray tube?

- Obviously you need X-rays, so we need source of X rays.

- Then you have some incident beam optics. So you have to condition your x-ray beam before it hits the sample. You may use some slits, you may use some solids slits, divergence slits, just to condition the X-ray beam.

- Then you have a goniometer, which is the platform that holds and moves the sample, optics, detector, and/or tube. The whole arrangement where you have the sample, detector, tube; that is called goniometer.

- Sample and sample holder.

- Receiving-side optics: Now when X-rays are on the receiving side after diffraction, you have to condition the X-ray beam again after it has encountered the sample. So, you have another set of optics.

- Then you finally need a detector because we need to count the numbers of X-rays, to get the intensity. These are the elements of X-Ray diffractometer.

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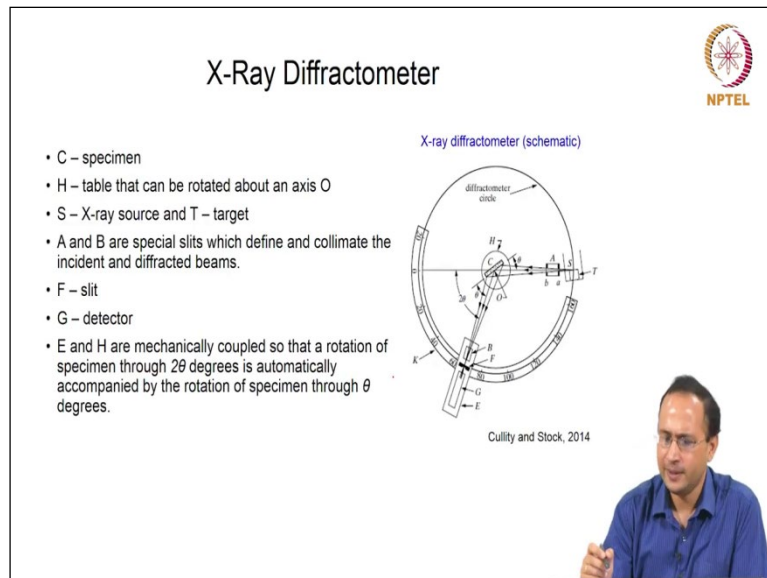
Again let us look at the schematic. This is the schematic of X-Ray diffractometer. It has the diffractometer circle, where you have the tube, detector, and it can rotate. The sample (C) is here in the middle. A table that can rotate about; you have this table here and X-Ray source (S) and target (T). A and B are slits, as we talked earlier about the incident beam slits, optics, because; we are not going in detail, but you can think of it as to condition the X-rays which are coming out, so that you stop, part of it, simple example of slits. So you condition your x-rays, and sometimes you want to make them parallel. We use divergence slits to do that.

Then once the X-rays hit the sample then you have to take care of the X-rays which are coming out, which are diffracted beams.

So again you have some optics here, which helps to focus. And now, this whole assembly moves, so E and H are mechanically coupled. E and H are mechanically coupled, so that the rotation of specimen through 2θ degrees is automatically accompanied by the rotation of specimen through θ degree. You know from Bragg's condition, this whole angle is 2θ; this is diffracted beam and incident beam (Figure 1).

Figure 1 Incident and Diffracted beam

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The detector moves in circle around the sample, so you have an x-ray tube here, you have the sample and $\omega = \frac{1}{2} * 2\theta = \theta$ where ω is the incident angle. So the detector position is recorded as 2θ, and the detector records the number of X-rays observed at each angle. Usually the X-ray intensity is recorded as 'counts' or 'counts per second'.

Many powder diffractometers use Bragg-Brentano parafocusing geometry. What does that mean? To keep X-ray properly focused, the incident angle 'ω' changes in conjunction of 2θ, as it change the θ, your 2θ it will also change. So this can be accomplished either by rotating the sample or you can rotate the x-ray tube. See you can keep your sample stationary and then let your x-rays and detector move around the circle. Otherwise, you can also have your X-ray tube fixed and then just let sample and detector move.

So in Bragg-Brentano geometry, the diffraction vector (s), which is nothing but the vector which bisects your incident and diffracted beam, is always normal to the surface of the sample.
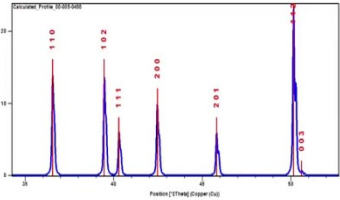
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So why do we use X-rays? X rays are used to understand the crystalline materials. So you see crystalline materials have long range order, and so you get sharp peaks. Wherever the Bragg's condition is satisfied, you will get the peak and you will have the difference in the intensity and that is very characteristic of crystal. In amorphous solids or liquids, you do not see such pattern. Notice the difference, this (figure at top in slide) is the crystal; this (figure in middle in slide) is liquid or amorphous solid.

So, almost lack of periodicity, because you do not have the periodicity. You need the periodicity to get the diffraction. But you see some tendency to "order", only in a sense that the atoms are fairly tightly packed together. Let's think of an amorphous solid. The atoms are fairly tightly packed together and show a statistical preference for a particular interatomic distance. So, they are packed such a way that they have some tendency to show a statistical preference for a particular interatomic distance. That is why you are seeing some peak (nature of graph); but it is not like what you see in crystals.

And in monoatomic gases - no structure periodicity; that is, you don't see anything. Basically what it tells you, you can probe crystal, any material (it could be mixture of amorphous and crystalline phases), as long as there is crystalline phase, you will be able to use this technique.

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Diffraction Pattern

- Each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms.
- Miller indices (hkl) are used to identify the different planes of atoms.
- Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample.
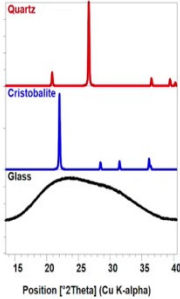
http://prism.mit.edu/xray/

So what does diffraction pattern look like? So the typical pattern looks like; you have intensity on Y-axis and you plot 2θ on X-axis. And you see these peaks; they are associated with these planes. So, each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms. Miller Indices are used to identify the different planes of atoms. We all know how to get that. Observed diffraction peaks can be related to the planes of atoms to assist in analysing the atomic structure and microstructure of sample. So this can provide lot of information.

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X-Ray Diffraction Pattern: A Fingerprint

- A phase has a specific chemistry and atomic arrangement.

- The X-ray diffraction pattern is a fingerprint that enables the phase identification in the sample.

- Quartz, cristobalite and glass are all different phases of SiO_2.

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So basically X-ray diffraction is nothing but a fingerprint; each of us have a very unique fingerprint, so once you know the fingerprint, you know where it has come from and we have a very good database where these fingerprints are stored. The information is kept, and we can

always refer to the database where we can get this information. That is because a phase has a specific chemistry and atomic arrangement and that's the basis for this.

Each phase has a specific chemistry and also atomic arrangement - chemistry may be same, we will see in this case, quartz, crystobalite, glass all are different forms of silica only SiO_2. So, chemically they look same, SiO_2, but if you do X-ray diffraction you find big difference; that is because the atomic arrangement is different. So, specific chemistry and atomic arrangement, it will be able to pick it up.

Basically X-ray diffraction is a fingerprint, which enables the phase identification. So once you know the fingerprint, we know each phase has a unique fingerprint, we can use that to understand what we have in our sample or unknown sample. So, here you in see quartz, crystobalite, crystalline phases, you see sharp peaks and in case of glass, since it is amorphous, you do not see sharp peaks.

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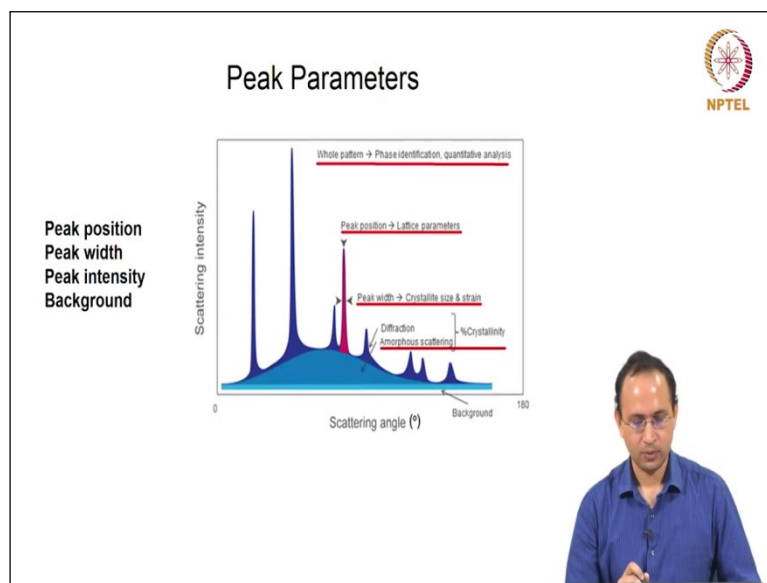
So, let us look at some peak parameters. What are the various things which we get from the pattern? So, typical pattern will be like this (see figure in slide), you are always going to have some background because of some instruments or sample. This is the background (marked in figure in slide). Then you are going to have some level of, suppose amorphous content is there in your samples, you have some contribution because of that.

And then you see these peaks, 1, 2, 3, 4, 5, 6, 7, 8 peaks, for example, so in a typical diffraction pattern will get the 'peak position'. 'Peak width' is another thing you have to check; so, what

does peak position give you? Lattice parameters, as we discussed. The peak position means you know the Bragg's angle θ, and it will tell you about the lattice parameters. Peak width tells you about the crystallite size and strain. What is the size of your crystallites? Is there any microstrain? We can use that information to examine this.

Then you will have this diffraction, you are getting these peaks, and amorphous scattering. Basically you can get some information about degree of crystallinity. What is the degree of crystallinity? Is it 100% or 80% or 70%? That will depend on this contribution of the amorphous and diffraction pattern. This whole pattern can be used for phase identification and phase quantification.

You can tell what are the phases present what contributes to peak 2, peak 4, peak 6, and how much? Suppose it is a mixture of (A + B), how much of A you have and how much of B you have? So, qualitative and quantitative analysis can be done.

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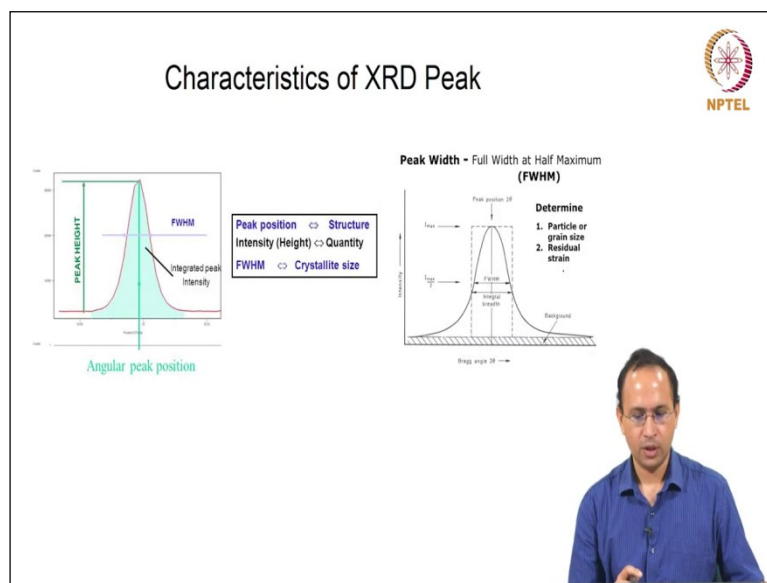
 Let's look at the characteristics of XRD peak. In a typical XRD peak, we have this peak, we have angular position, and we often talk about the peak width which is FWHM - full width at half maximum. Take half of the intensity, draw a line and you measure this (width), it is called FWHM - full width at half maximum. So, peak position gives you the structure, intensity tells you about the quantity. We'll see how peak intensity can be used to get the quantity.

And FWHM can be related to crystallite size. So I$_{max}$ is the maximum intensity. You draw a line $\frac{I_{max}}{2}$, so it is half maximum full width, that is the characteristic of XRD peak. And this is peak height (Figure in left in slide). Obviously, we have to remove the contribution of background, if you are talking about the peak height, because you always get some contribution from background. In the last slide, you see that you have some background, when you talk about the peak height, you have to exclude that.
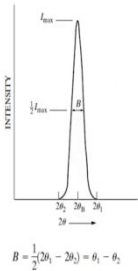
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So, we discussed that peak width can give us some information about the crystallite size. So what happens is, it turns out that very small crystals, we are talking about smaller than 120 nanometres (nm), cause broadening of diffracted beam, means the XRD peak will tend to broaden, at angles near to, but not equal to exact Bragg angle. So you have a Bragg angle, where you are getting diffraction, but if you go little bit left and right, you will see the peaks are broader, if your size gets smaller, small enough,

So this can be used to get the size of crystallites. So, this is a simple relation, which relates this crystallite size 't' and Bragg angle 'θ_B', called the Scherrer's equation, which gives an estimate of the size of very small crystals. So, what do you need to know? You need to know the B, which is FWHM. How do you calculate it? Using the formula: $B = \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$. You know B, you know θ_B, you know λ, and hence you can calculate the crystallite size.
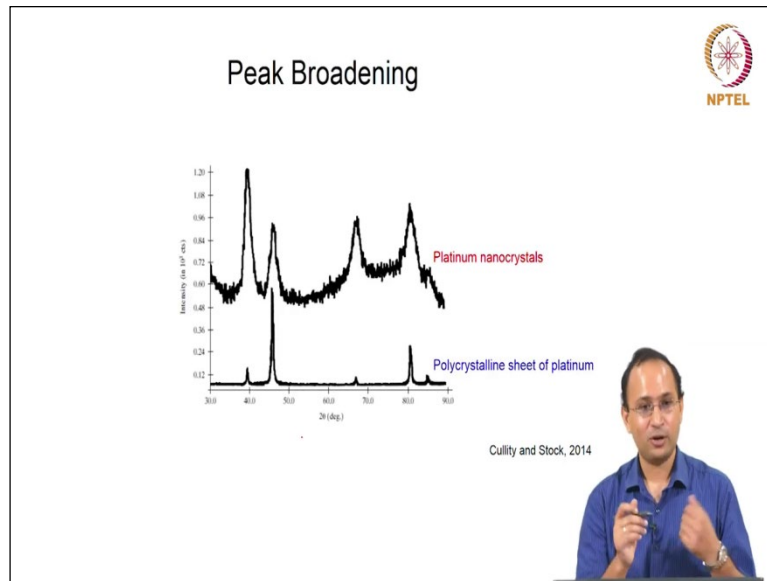
Why is it important? It is important because there is an effect. So it's the same material platinum, here is the X-ray diffraction of nanocrystals. And here is X-ray diffraction from polycrystalline sheet of platinum. See the difference, peak positions are same because the material is same; so, peak position will depend on your lattice parameter. But you are seeing broadening in the case of nanocrystals. So, we can calculate based on this broadening what the size will be.
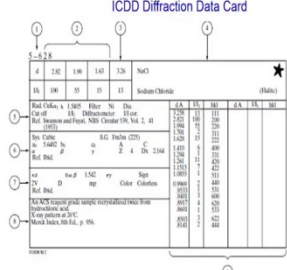
If you are asked question what the size of nanocrystals will be, you can calculate based on the peak broadening, once you know B and θ_B Bragg's angle you can calculate crystallite size. This effect is more pronounced when we are talking about crystallites of size less than 120 nanometres.

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So, now we know that X-ray diffraction is like a pattern like a fingerprint. So, obviously people thought about developing a database, as that will be important if you want to probe unknown samples, which may have already known sample. So, these people Hanavalt, Rinn and Frevel started building up a collection of known pattern. You need simply a diffraction pattern. Based on diffraction pattern, you will have all parameters, you know the crystal structure and you relate it to X-ray diffraction file.

So, lot of work was started by Hanavalt, and from 1941 to 1969, ASTM published more and more data was published. Since 1969 JCPDS (Joint Committee on Powder Diffraction) has been carrying out this activity. This was renamed as ICDD (International Centre for Diffraction Data), that is the term we use currently.

So, what does the ICDD file have? Typically, you have this data card ICDD; in this case you have for halite, which is sodium chloride. You see there are a lot of things, there's a diffraction file number (labelled 1), which is a unique file number.

Number 2 is, three strongest lines, strongest line means - you have a diffraction pattern and then you can get relative intensity, for strongest one you can define it is 100% then you can normalise it. So, these are the three strongest lines.

Number 3 is, lowest angle line. So it has lot of information, you can check.

Also you will have inter planar spacing for hkl (d) versus intensity (I).If you are talking about d then you have to talk about hkl. it will tell you d_{hkl}, for example, d_{111} is 3.258 Å, and the intensity is 13% and also, 100% intensity is for 200 plane. The inter planar spacing is 2.821 Å

the intensity is 100%. Then obviously you will get the relative intensities based on atomic position.

This is a typical ICDD diffraction data card. Also, one more thing, if you have a star, that means it's a good quality data as lot of people will be doing test at different places, so that if you have published data, if someone else does the same experiment and find similarity, that means your data is good because the quality is good and it can be repeated. It depends on the conditions also.

So, anyway this tells you about the data quality, so it is good to rely on star quality data. There is other information, you see literature information also who did this? You can see the reference. It also gives you information about where this data was taken from. Space group and other information are also there. So, this is the typical ICDD deflection data card.

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Then next is, we have to find way to identify phases. Now you have diffraction pattern, now you have this database, now how do you search? You did the experiment and you got the pattern, and what have we got? We are talking about a single phase. You got d (Å), and you have relative intensities and this information you have from diffraction pattern. Now you want to find out what is it? And we are talking about single phase now.

And you know that already someone has done the experiment. There has to be a way, because we are talking about more than 300000 PDFs power diffraction files being available, so how do you search? Now you have computers but I am just saying. So Hanawalt in 1936 laid out a

procedure for classifying the known patterns, there has to be a systematic procedure, and what did he say? He described each pattern by listing the 'd' and 'I' values of its diffraction lines and to arrange the known pattern in decreasing values of 'd' for the strongest line in the pattern.

And, the values of d_1, d_2, d_3 together, which are the three strongest lines with the relative intensities, are usually sufficient to characterize the pattern. So how do you search? So, these are different chemicals, you can see the chemical formula (right side table in slide)? You have in the first line, 2.82, 1.99, 3.99, these are 3 strongest lines for this space.

So, now look at the intensity here. So you see here that your 100% intensity is for 2.82, when you have a 'd' of 2.82 Å, you have100% intensity, the next one is 1.99Å, 60%. Now if you look at this file, the way it has been arranged, you have taken the strongest lines, then arranged as per the 'd'. These are the 3 strongest lines. But if you can just look at just one, 2.82Å, a lot of phases are there, which have the same 'd' value, so you cannot just decide based on that, that is the point, because you are talking about the 'd' which is calculated based on hkl and a lot of things are there, you may get the same 'd'.

Now if you come to the second one, we are looking at this 3 strongest line for this (I, II, III, marked in table in slide). If you look at one (I), you can't tell which one is what, because there are multiple ones with the same 'd' value, that is, multiple ones which have the strongest line at 2.82Å. Now if you come back to second one, 1.99Å, again it is hard to tell, but if you come back to the third one, 1.63Å, we can say that third one is NaCl. So, 2.82, 1.99, 1.63 tells you this is Sodium chloride.

So typically in most cases, if you check for three strongest lines, you will be able to identify the phase. So, this is the procedure. So, 3 strongest lines will be able to help you with the identification of the phase.
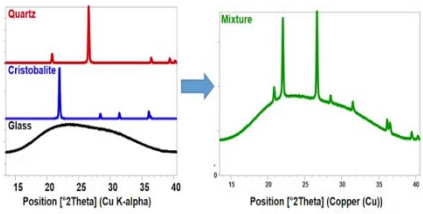
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So, this is what it looks like if you use any commercial software or any software you use. Till now, what we saw was manual searching. People used to do that long time ago, but these days you do not do manual searching. We can rely on available software. This is from Highscore Plus and we will come back to it. So, powder diffraction file database, you can also pull data, that is, the files from this. So, lot of files are there, more than 300000 diffraction patterns are available. This number keeps increasing this may not be up-to-date.

Modern computer programs can help you determine the phases present in your sample by quickly comparing the diffraction data to all the patterns. Again this PDF card for entry contains a lot of useful information including literature references. Same thing, you have literature information, you have whether it is a star quality data. What is it about? Rutile, space group, etc. crystal structure, and you have finally this diffraction 2θ (Bragg angle), d, I (intensity). So, everything is available.

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What is the usefulness of a diffraction pattern? So we saw this, you may have a mixture of crystalline and amorphous phases. So, in this case, when you mix quartz, crystobalite and glass, you will get this type of X-Ray diffraction pattern, because it will have a contribution from amorphous phase, also it will have contribution from crystalline phases. Now, from XRD pattern one can determine what crystalline phases are in the mixture? What are the phases, because that you can do through peak search, you can find which phase corresponding to which peaks.

How much of each crystalline phase is in the mixture? We can do quantitative phase analysis, how much of it, if you know A, B, C constitute the X-ray diffraction pattern and all are crystalline phases, we can calculate that. There are ways; we'll go over that, it is called quantitative phase analysis. If any amorphous material is present or not - we can also tell if the material sample has amorphous phase. So, in this case, we can clearly see that you have contribution from amorphous phase. A lot of things we can get out of it and other things also, but we'll focus on this one.

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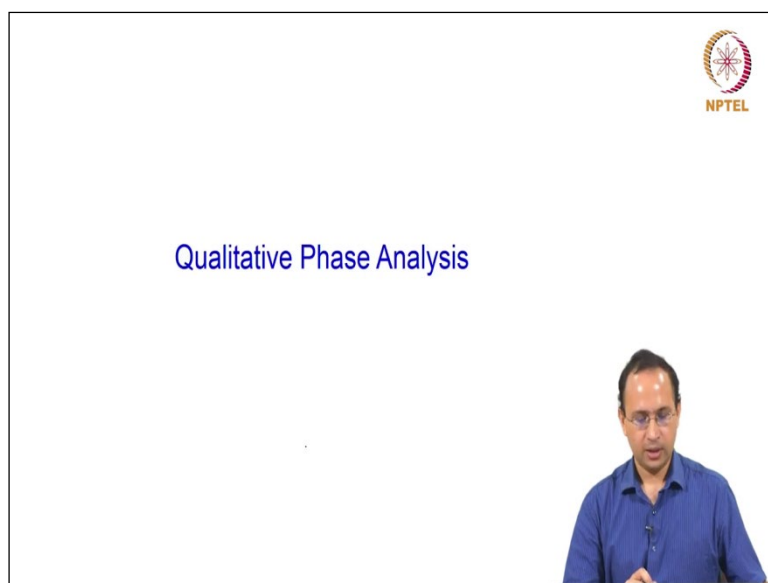
Let us go over the qualitative analysis now. Now we know that we have this database of different PDFs (powder diffraction files) and if we have to probe any unknown sample, we have to just go to this database and see, but there has to be some way. So we'll see how to do this qualitative analysis.
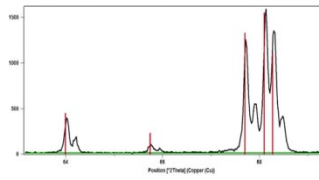
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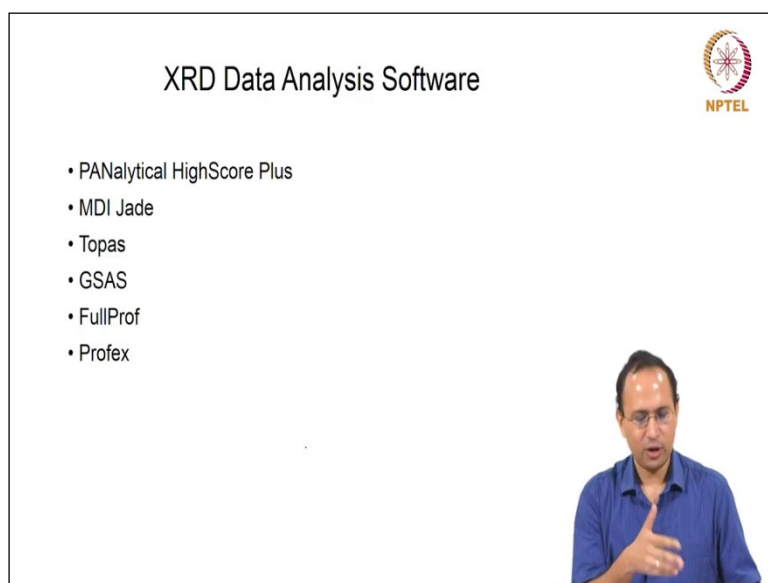
We can use various softwares, these are again some commonly used softwares. Those of you, who are interested in quantitative X-ray diffraction or qualitative X-ray diffraction, will have to use one of these - HighScore Plus, MDI Jade, Topas, GSAS, FullProf, Profex - few of these software's are free. Few are not free. But these are commonly used when you refer to any paper you'll see people have analysed the data using one of these.

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So, you have a pattern, now first thing is to identify peak position. So you have a pattern, now you want to see whether the phase you are interested in, how do you make sure, that phase has the peak, in this case, for example, you got this pattern (see figure in slide) you get from an experiment. Now you pick one phase, these lines will tell you about the intensity, and also location, so this phase will tell you the strongest peak should be here. So this is the strongest one, (red one) because you can see from the height.

Then the next one is here, second highest. You can see, if you are picking one phase, it will show you these are the peaks, because where is it getting that information from? It's just pulling the PDF. PDF has your 2θ values and intensity, we are just plotting it. Now how do you make sure it (peak intensity) is a good match? So position and intensity of the reference pattern should match the data.

Obviously, if you are saying about good match, it has to match the data. A small amount of mismatch in the peak position and intensity is acceptable, small amount experimental error, but you can see here, it is not that bad. You have this pattern and these red sticks, kind of match what you have, that is what we do. When you do profile fitting what we do is, suppose, this is a mixture of two; you have a contribution.
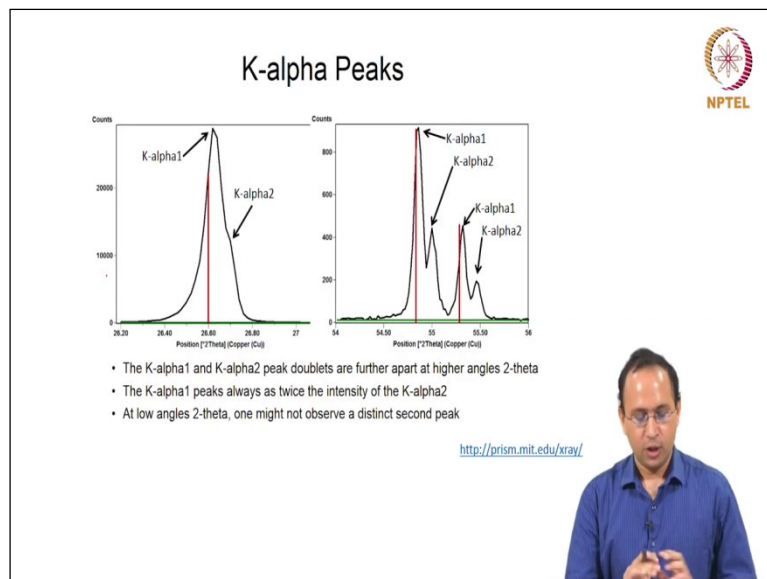
If I have to draw it like this, there could be something like this (Figure 2); it is a superposition is not that straight forward. I am just giving an example. So, you have these two peaks, neighbouring peaks, so you have take that also into account.

Figure 2 Two neighbouring peaks

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So we know that for characteristic spectrum, we talked about K-alpha, L-alpha. So, we can use filters to get rid of, for an example, L-alpha, if you go to the lecture one, where we talked about using filters, because we want monochromatic X-rays. Monochromatic is nothing but single wavelength. But it is very hard to separate K-alpha 1 and K-alpha 2; still you will get these two peaks. So K-alpha 1 and K-alpha 2 peak doublets are further apart, so you can see in some cases, will you be able to see these K-alpha 1 and K-alpha 2.

Here, at higher angles you can see the difference; the two peaks are quite apart. Here, it's a contribution, they are mixed and you cannot see K-alpha 2 separately, but typically you can see

the K-alpha 1 and intensity is twice as much of K-alpha 2, so it is good to keep in mind. So K-alpha 1 always has twice as intensity of K-alpha 2. These are K-alpha peaks you'll often notice.

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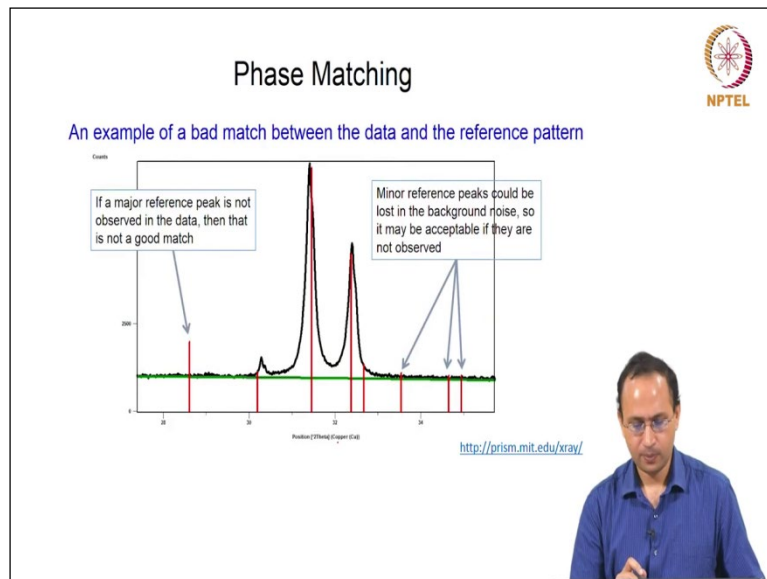
The phase matching, now this is an example of a bad match between the data and the reference pattern, you have to know when the match is bad also. So your main peak matches, but see here you have this intensity, but there is no peak. So, you have to make sure not only one peak matches, but you know whole pattern at least three four strongest peaks should match.

So if a major reference peak is not observed in the data, then that is not a good match. This is like the third most strong. So these are also important things to keep in mind when you are matching, do not just rely on one. So, that means this pattern does not belong to this phase, otherwise there would have been a peak here. Minor reference peaks could be lost in background noise.

So it may be acceptable if they are not observed. So at least major peaks you will be able to see.
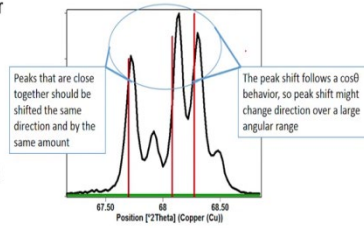
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And one thing also is simple displacement, we will stop here.