Materials Chemistry
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Module - 3
Lecture -1
Application of X-Ray Diffraction

In the first 2 modules, we have looked at the synthetic approaches to materials, in the first module we have extensively seen all the chemical synthetic routes, which are potential for making materials. And module 2, we have worked on the various aspects of thin films, how different materials, inorganic materials can be made. In the third module, we will be discussing some of very crucial characterization tools that are inevitable for materials chemistry, and materials chemistry and materials synthesis is never adventure without use of proper characterization tools.

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X-ray Diffraction

"A tool to track your synthesis"

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http://prism.mit.edu/xray

And therefore in this module, I am going to highlight about diffraction methods, microscopic methods, spectroscopic methods and thermal analysis methods, which can be used as a tool to characterize materials. And I have specially singled out X-ray diffraction measurements as a very important tool, which stands very different to other characterization tools. Main reason, there are other characterization methods which are post synthetic approaches, you make a material and then you try to characterize after you have processed it.

But X-ray diffraction is a material, not just to characterize what you have synthesized, but during the synthesis itself, it is used as a characterization tool much to the tune of infrared spectroscopy or enema spectroscopy, which is actually used in any chemistry lab to map your synthetic strategy. So, even before you complete your synthesis, you use certain characterization tools to analyze, whether you have really made the right measurements.

And therefore, I have coined this X-ray diffraction method as a tool to track your synthesis, rather than even characterizing the material. And as you would see here, there are different cartoons I have given in this opening slide, any material which is crystalline will actually give very beautiful diffraction spots. And this is a particular SEM image, which shows a well ordered crystal lattice and each spot in this, gives you an idea about how the atoms are arranged in a crystal lattice.

As you can see here very clearly, this is nothing but a fcc pattern, each spot in this diffraction pattern talks about a definite arrangement of atoms in a lattice. And that is what you see in this cartoon that, there are different planes, which has a preferential occupation of a particular atom and they are periodic in fashion. And how do we go about analyzing and getting different informations about this atomic arrangement or order in a lattice.

We have X-ray diffraction as a tool, not just in terms of pattern like this, but we can also try to map it as a wave, because X-ray diffraction is nothing but bending of waves. And therefore, when X-ray hits a particular lattice and if it is order, there will be bending of waves and this bending of waves can be either constructive or destructive. If it is a constructive interference then you will see a X-ray peak and if it is a destructive interference, you will see no peak.

Therefore, a constructive interference will give you a X-ray diffraction pattern, not necessarily a spot pattern, but a diffraction pattern which is more like a wave. So, you can easily understand, which material or which element gives what sort of pattern. So, this cartoon shows here one of the latest versions of a diffractometer, which can be used for getting a X-ray pattern of a particular material, so let us go progressively.

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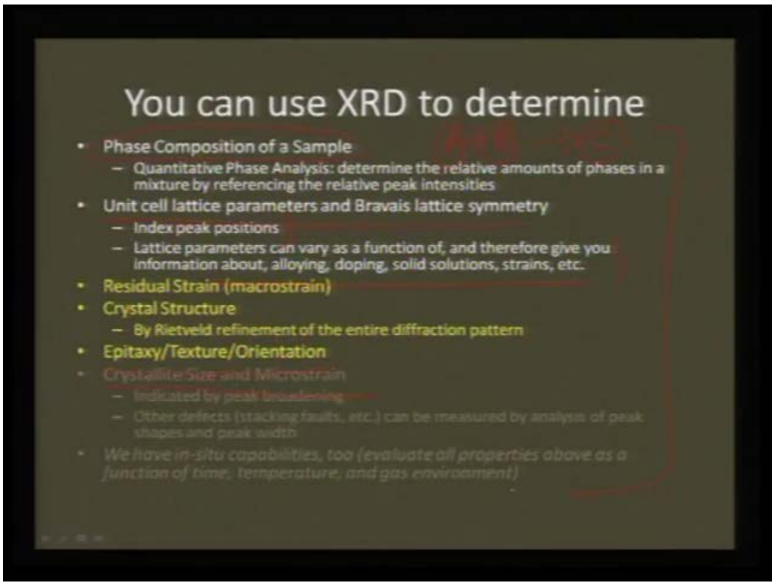

You can use XRD to determine

A+B → C

- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern
- Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width
- *We have in-situ capabilities, too (evaluate all properties above as a function of time, temperature, and gas environment)*

In this talk to understand, what sort of information I can get about a lattice or about a material that I am synthesizing. So, XRD, when I say that means, powder X-ray diffraction principally, because we are going more with the powder patterns and XRD can be used first for phase composition of a samples. So, when I am starting with say, A plus B giving C then your A and B will actually have a characteristic pattern. And as you are heating during the thermal process, C is getting formed and we do not know, whether Cc is complete or still some remnant of A and B is present.

Therefore, you can talk about phase composition and this can also be quantified, so it is a quantitative phase analysis, which determines the relative amounts of phases. Sometimes, we might start with A plus B, we are expecting C, but actually it can give C prime or C double prime, which are some secondary phases which are not needed. And therefore, it is easy for us to map even those phases and then more importantly, when we want to analyze and understand, what sort of crystal pattern that comes when two samples are heated together.

What is the nature of crystal symmetry of the third pattern that is, the product then you talk in terms of unit cell parameters and what is the lattice symmetry. And we can quantify all this, indexing the peak position and we can also look at the lattice parameters that can vary as a function of the substituent ions compositions. So, different things we can try to harvest from this simple X-ray pattern, alloying, doping, solid solutions, strains, etcetera.

And this is big list and not only we look at the cell symmetry, we also look at the macro strain in a lattice and how we can correlate the strain induced by the crystallites or induced by this poly crystals. And we can correlate that to physical property like resistivity or magnetism or so on. And then we can also look at epitaxy texture or orientation, if we are going to make the material in thin film form, suppose I have a sol gel route we have seen in earlier.

And then I am going to make a thin film, how can I look at the texture, whether it is growing epitaxially or whether it is going in a orientated way. As I had shown you in the previous modules, a chemical approach to thin film is quite different from a physical route to make thin films. And we are talking about a very high degree of epitaxy or order growth and in such case, how we can use X-ray for mapping that. And also other informations like peak broadening, that can tell us about crystallized size, micro strain and so on. So, we will try to revisit some of these aspects, as we go through this lecture and I am going to show atleast one example of each of this that we are trying to discuss in this talk.

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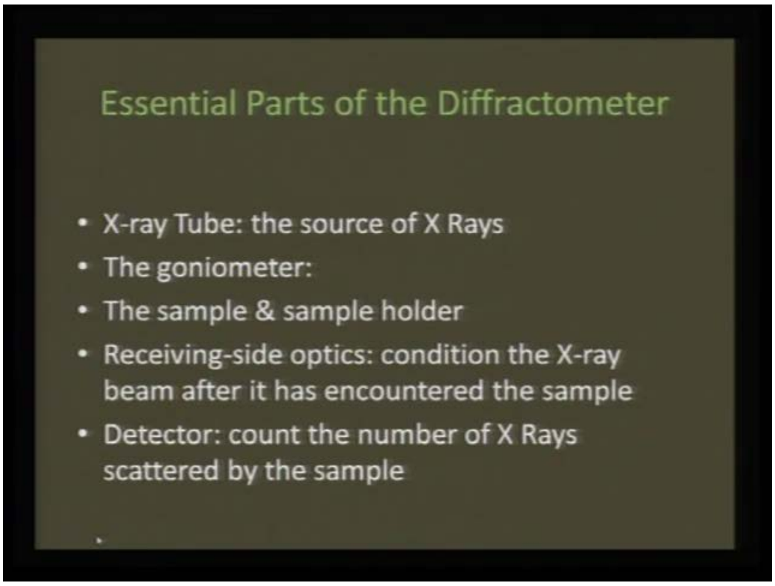

Essential Parts of the Diffractometer

- X-ray Tube: the source of X Rays
- The goniometer:
- The sample & sample holder
- Receiving-side optics: condition the X-ray beam after it has encountered the sample
- Detector: count the number of X Rays scattered by the sample

Now, let us look at the diffractometer in the first place and see, what are all the crucial elements in a diffractometer, because all these are going to affect our extra studies, one

X-ray tube and the source of rays. So, what is that to do with my X-ray analysis, because the target that you are going to choose will also change the pattern that you are getting. Suppose, I use a particular target for producing X-rays and you shift the target then the X-ray pattern will totally be different.

So, I need to know the goniometer that is the assembly to get this X-rays and then the sample and the sample holder, because that are very essential. Sometimes, I will mount the sample, but not get any pattern at all, principally because the alignment is not correct. And then receiving side optics, because when you try to use some X-rays then sometimes the target can also show some reflections, therefore you need to filter off stray radiation to get the right pattern. So, we are talking about receiving side of optics and then the detector that counts the number of rays scattered by the sample, which gives you a pattern; so all these are essential components.

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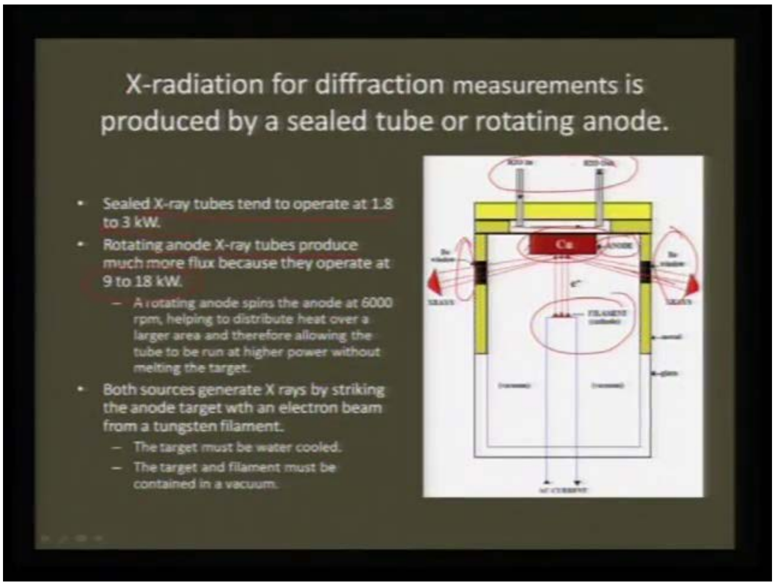

X-radiation for diffraction measurements is produced by a sealed tube or rotating anode.

- Sealed X-ray tubes tend to operate at 1.8 to 3 kW.
- Rotating anode X-ray tubes produce much more flux because they operate at 9 to 18 kW.
    - A rotating anode spins the anode at 6000 rpm, helping to distribute heat over a larger area and therefore allowing the tube to be run at higher power without melting the target.
- Both sources generate X rays by striking the anode target wth an electron beam from a tungsten filament.
    - The target must be water cooled.
    - The target and filament must be contained in a vacuum.

And this is a assembly of target and this is how it is schematically defined, suppose you have a X-ray tube which is sealed tube then you can operate the source between 1.8 to 3 kilo watt. But, if you are going to have a tube or the target which has rotating anode that is, X-ray tube then you can improve on the flux by increasing the operating voltage to 9 to 18 kilo watts. Why is that so because when you look here, cathode rays are generated from a filament, usually it is a tungsten filament that is actually striking on an anode.

In this case, we are talking about copper and X-ray is produced and X-ray is actually taken through these windows, which are beryllium windows and this is the way X-ray is stabbed out. Now, when you are heating it continuously X-ray is produced, as a result, the whole of your target can melt, because of continuous bombardment. As a result, at the rear side, you actually have a cooling system and without this cooling system, your target will melt down.

Therefore, you need a very good chilling unit to cool your anode, that is your source for the target. But, to bring down this melting effects or heating effect, apart from using a cooler, you can also rotate the target, so that it does not really gets localized. So, if you are going to do that then you can improve on the wattage, so you can play around between 9 to 18 kilo watts, so this is a perfect assembly.

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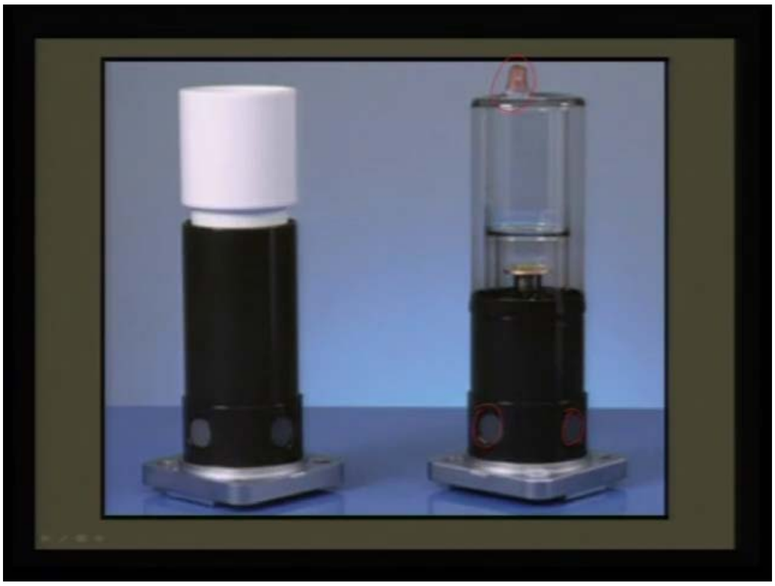

And we can also see that, in a real picture, this how a target looks like and these are your windows and this is a evacuation, as you see this is vacuum sealed. Therefore, this is typically the X-ray target, that you are using in a typical diffractometer.

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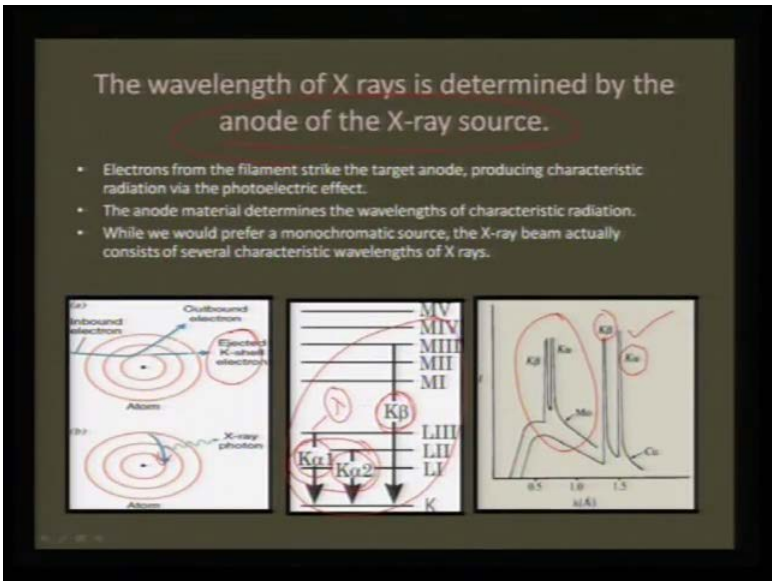

The wavelength of X rays is determined by the anode of the X-ray source.

- Electrons from the filament strike the target anode, producing characteristic radiation via the photoelectric effect.
- The anode material determines the wavelengths of characteristic radiation.
- While we would prefer a monochromatic source, the X-ray beam actually consists of several characteristic wavelengths of X rays.

Now, when you are using a target, there are several things that are happening, therefore you need to know which X-ray you are trying to use. So, the wave length of X-ray is determined by the anode of the X-ray source and the typical chemical process that is happening, inbound electron is actually knocking out and this is K shell that is ejected. And therefore, some of the outer electrons are actually coming back to the K shell and that is where, the X-ray is produced, because X-ray photon is coming out.

So, the process is actually listed in this cartoon, you can actually have a K beta radiation coming from a X-ray source and that is nothing but the transition from M level to K level or you can have K alpha radiation, which is from L to K. And within K alpha also, you have K alpha 1, K alpha 2 and that is actually seen in the typical X-ray mapping. As you would see here, for molybdenum of a copper, you can single out the K alpha and K beta. Beta always comes on the left side of the K alpha peak that is, high energy radiation.

But, if you look at the intensity, K beta will be slightly lesser compared to K alpha, therefore K alpha is the most preferred radiation that you would you use. So, in any X-ray analysis, you would say, you have to specify what is your target, you can mention this as copper K alpha. That means, you are talking about copper as source and this is the radiation that you are using to analyze your material, which has a specific lambda and this lambda is unique of the particular target. But, what happens is that, you also get K alpha 2 and K beta or the stray radiations that keep coming, therefore you need a required optics and other alignment to block all these extra stuff, so that you get a monochromatic source that is called K alpha.

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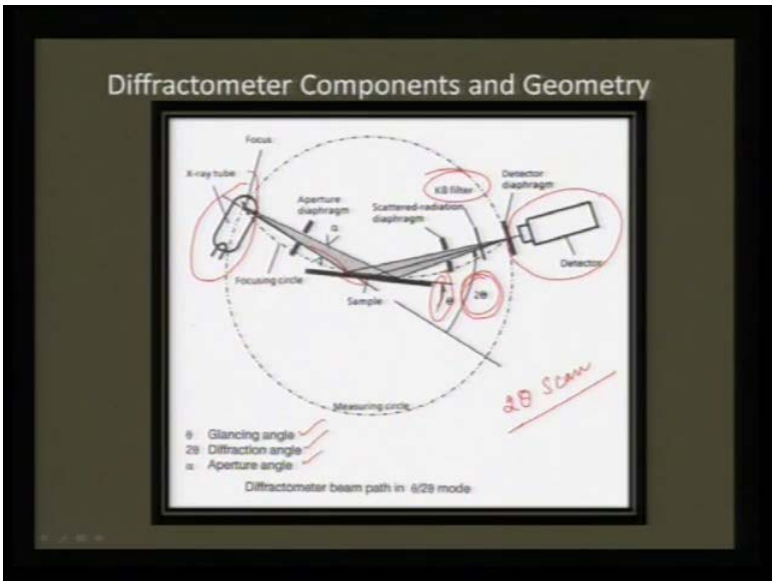

Diffractometer Components and Geometry

So, those are essentially part of the assembly of your X-ray diffractometer, as you see here, this is your X-ray and from X-ray, you are actually getting the monochromatic X-ray beam to your sample. And then these are the scattered radiation diaphragm, which will filter all the unnecessary ones then you have the K beta filter and this is your detector, which will finally sends the reflection that is coming.

And what is the principle here, you have this measuring circle which will actually go 120 degrees. And as the sample angle is changing at different atomic planes, you will have the diffraction coming and therefore, the measuring angle is typically a theta 2 theta combination. So, your X-ray is incident over the sample at a distance theta or an angle theta and then you are getting the diffraction at an angle 2 theta, so that is why, it is properly called in powder X-ray diffraction as 2 theta scan. So, when you say 2 theta scan, we are talking about this incident beam, which is making an angle theta and then this is measured at 2 theta. Therefore, we measure always as 2 theta scans and that is what we see here.

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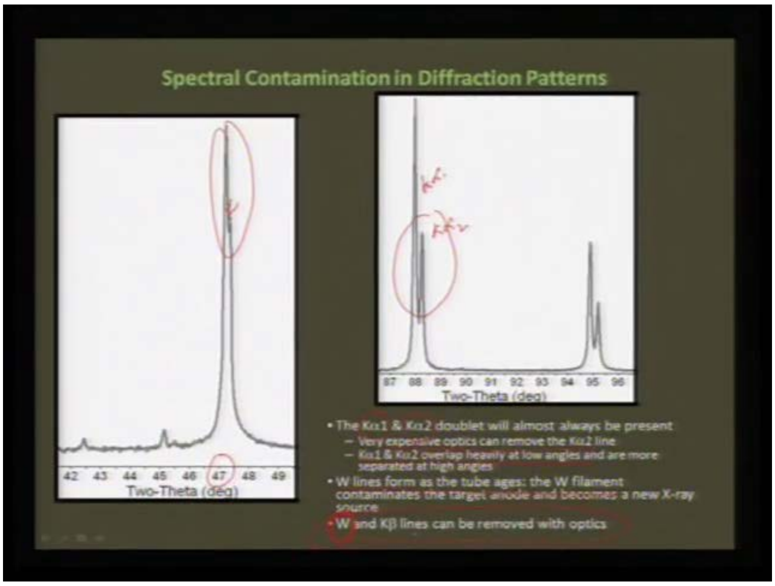

Spectral Contamination in Diffraction Patterns

- The Kα1 & Kα2 doublet will almost always be present
  - Very expensive optics can remove the Kα2 line
  - Kα1 & Kα2 overlap heavily at low angles and are more separated at high angles
- W lines form as the tube ages: the W filament contaminates the target anode and becomes a new X-ray source
- W and Kβ lines can be removed with optics

Now, as you see here, there are spectral contamination in the diffraction patterns, so one need to be very careful about those peaks, which will actually merged with your peaks. So, if you are using this X-ray diffractometer, you have to be very careful mainly with this K alpha 1, K alpha 2, this is a doublet almost always present and it is very expensive to filter this K alpha 2. But, actually K alpha 2 and K alpha 1, they will not be split very much in the lower angles as you can see here.

This is the split here, but at 47 degrees you do not see the splitting much, but when you go to higher angles, you see the splitting much more clearly for K alpha 1 and K alpha 2, so you got to be careful about the contribution, that is coming from the k alpha. Why this is also coming, since we are using tungsten filament as the source, sometimes on over burning, the tungsten lines can also come in the diffractometer. Therefore, we should be very careful to filter off the contributions coming from both K beta of that of the target and also the contribution coming from tungsten filament. So, this can come as a spectral contaminant in your diffraction patterns.

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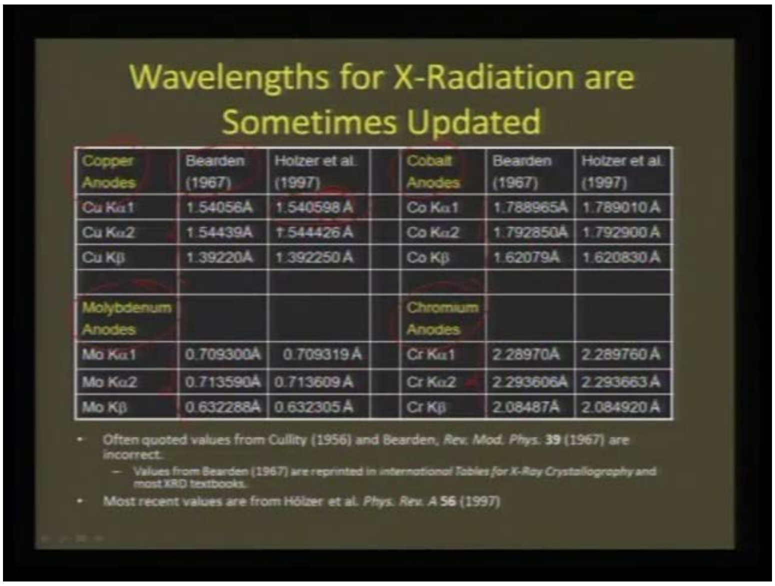

Wavelengths for X-Radiation are Sometimes Updated

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

- Often quoted values from Cullity (1956) and Bearden, *Rev. Mod. Phys.* **39** (1967) are incorrect.
  - Values from Bearden (1967) are reprinted in *International Tables for X-Ray Crystallography* and most XRD textbooks.
- Most recent values are from Hölzer et al. *Phys. Rev. A* **56** (1997)

And before we go more into the details or the basics of X-ray diffraction, I want to tell that, in today’s diffractometers, different targets can be used or X-ray source can be used. More popular is copper anode and then we have cobalt anode, chromium anode and molybdenum anodes, and each of this have a particular K alpha, which is to be used in our calculations. And we have, so far in most of our characterization have used beardens data, which gives you the K alpha value.

But, in 1997 we have Holzer, who has brought about refinements in this data with the much better optics and much better analytical tools that are available, therefore these are the refinement data. So, typically when we talk about copper K alpha 1, we usually say 1.5405, but you can see here in the 4 th and 5 th decimal places, they do change. These are all needed for redual analysis or for more precise analysis of measurements, so we need to have this in mind that, there are different sources which can be used. And I will also tell in one of the slides, which anode or which target we need to use, copper or cobalt depending on the nature of the sample. So, it is not always required that, you should use only copper, we can gamble with other targets.

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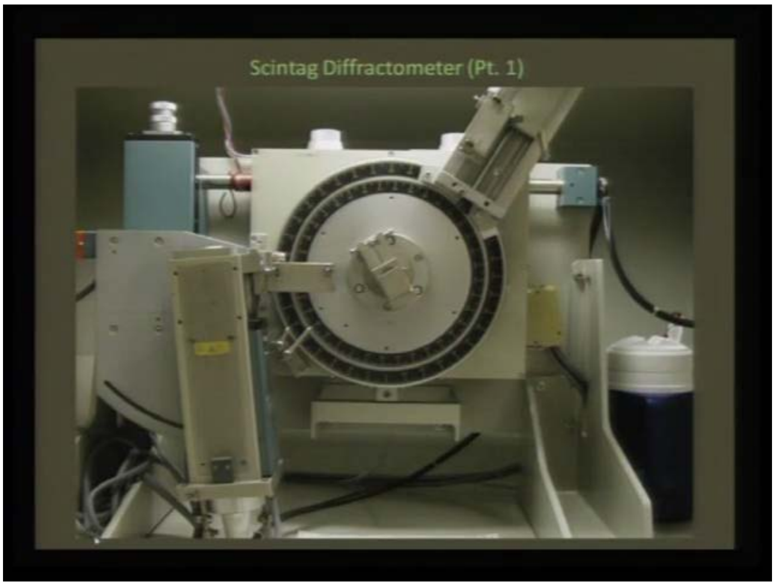

Scintag Diffractometer (Pt. 1)

Typically, diffractometer looks like this, this is one of the older version of the diffractometers. There are more than 6 companies, which are producing such X-ray diffractometers, this is just to give you an idea, how involved this procedure can be. And I will also show some of the other ones present generation ones, which are much more simpler, but with different facilities that are available in a single diffractometer.

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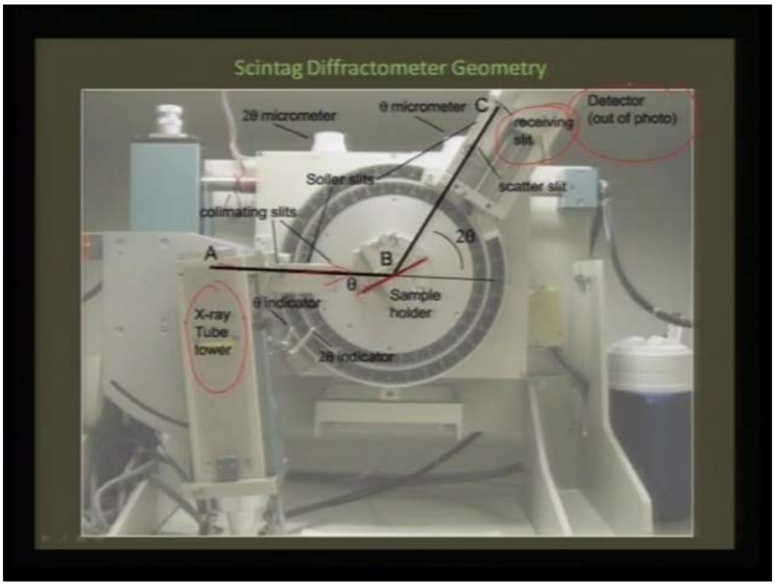

Scintag Diffractometer Geometry

So, as you see here, this is your X-ray tube that is, tower through which X-ray is produced and your sample holder is mounted here. And then you have the receiving slit and your detector, and this is all connected to a X Y recorder. Therefore, you can actually get present generation diffractometers, not only have a X Y machine, but also they have computer to record your data, so this is the assembly of a diffractometer.

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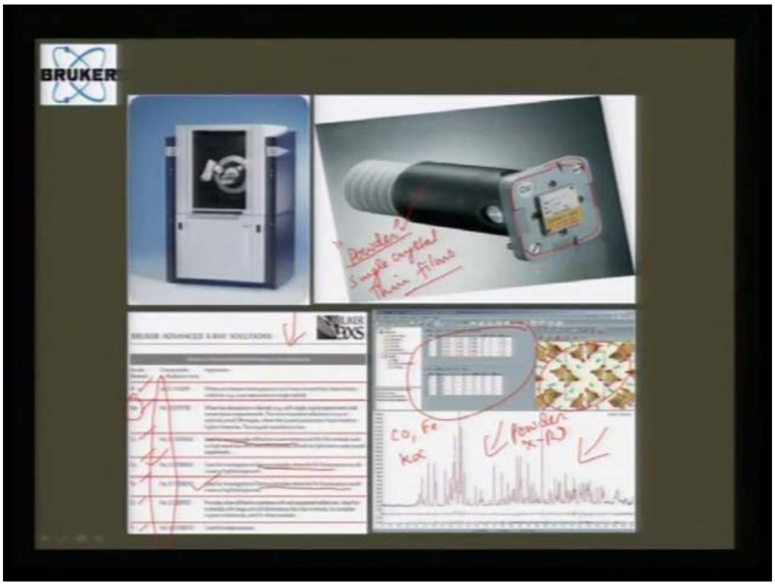

And Bruker is another company, which brings different versions of this X-ray diffractometer. There are several versions of diffractometers that are available, we have powder, we have single crystal, only for starting single crystals. And presently, we also have those, which are dedicated used for thin films, because the settings for starting thin film patterns are different from powder, therefore you need such precise assembly. So, these are some of the different versions and I will be mostly talking to you about powder diffraction.

And as you see in this cartoon here, you can have tungsten, molybdenum, copper, cobalt, iron, chromium, titanium, all these K alphas or L alpha is listed here. But, what I want to stress here is that, if you have iron for example, iron K alpha is used for ferrous samples where, the iron florescence would cause a very high background or you can also use cobalt for ferrous compound. So, if I am working with iron oxide or if I am working with ferrite based samples, the florescence will be very high, therefore it is not advisable to use copper K alpha in those conditions.

For ferrous samples, you always use only cobalt or iron K alpha, which is highly recommended, but copper is ideal for most diffraction examinations and for thin film analysis also. So therefore, copper is almost used in the many of the laboratories and then you also have molybdenum. When low absorption is desired that is, with single crystal experiments, it is always molybdenum, that is usually used. And this is again the rear view image of the target that I have been mentioning to you, this is copper K alpha target, which is used in the instrument.

And today, the version of X-ray diffractometer is much much different from the earlier ones, as you can see here, this is the output that you would get for a typical powder XRD pattern for a complex material. And you can see so many peaks are there and it could be as simple as 3 or 4 peaks in this whole spectra, if it is highly crystalline and cubic pattern. So, just by looking at a typical 2 theta scan, you can guess what sort of crystal symmetry that you are looking for.

More the patterns, more complex the symmetry and therefore, just looking at this, you can say this should be a monoclinic or a triclinic symmetry. So, number of peaks can also give a quantitative information about, what sort of system you are working with and you see, there are several menu driven interactive softwares available, which can generate the atomic procession. It can give you the lattice parameter, lattice dimension, everything can be mapped in situ, because such softwares are also available. So, it is very fascinating to use a X-ray diffractometer principally to understand, what is the system that you are working with.

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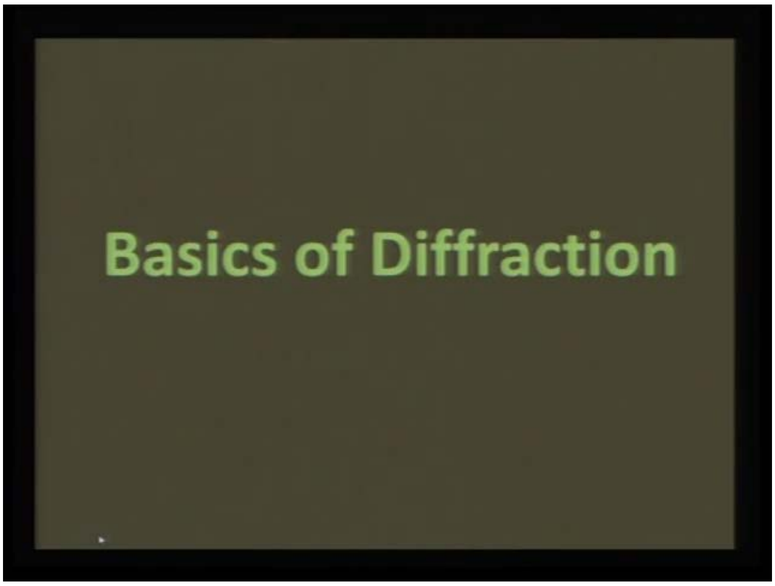

Basics of Diffraction

Now, let us go into some of the basics of diffraction and see, if I am going to use a X-ray machine, what are all the informations that I can look for…

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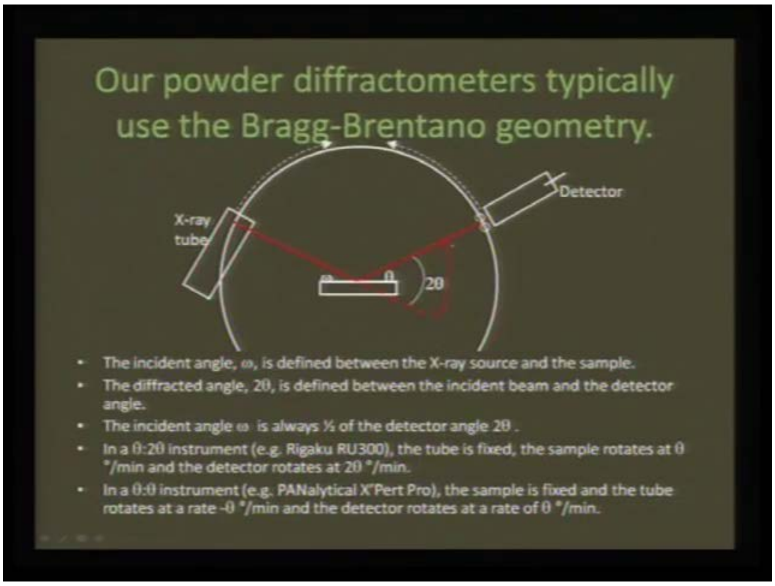

Our powder diffractometers typically use the Bragg-Brentano geometry.

- The incident angle, ω, is defined between the X-ray source and the sample.
- The diffracted angle, 2θ, is defined between the incident beam and the detector angle.
- The incident angle ω is always ½ of the detector angle 2θ .
- In a θ:2θ instrument (e.g. Rigaku RU300), the tube is fixed, the sample rotates at θ °/min and the detector rotates at 2θ °/min.
- In a θ:θ instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate -θ °/min and the detector rotates at a rate of θ °/min.

Number 1, as you know, we are now looking at a theta 2 theta scan, so this is what I mean by a 2 theta scan. So, once I get 2 theta values, what do I do, how do I go from there.

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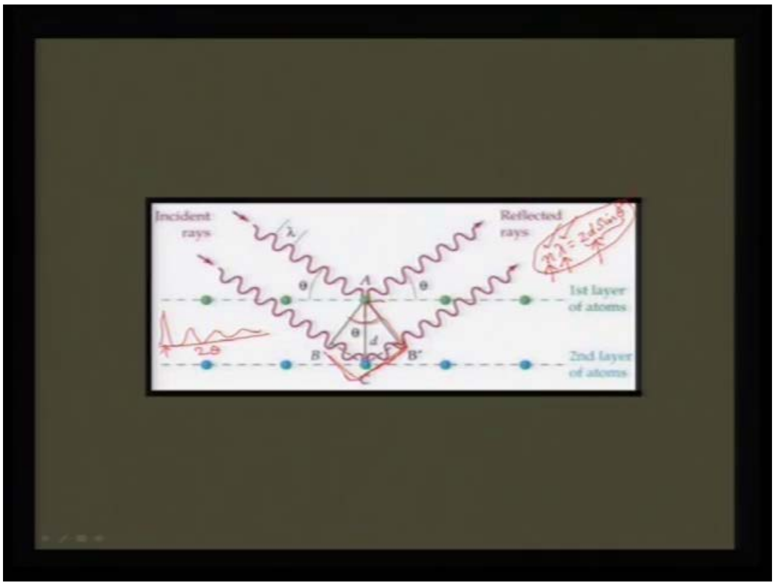

So, we have to first understand the basic expression that governs our analysis, is nothing but Bragg's law, which is n lambda is equal to 2 d sine theta. Now, what is this n lambda is equal to 2 d sine theta, n in powder X-ray diffraction experiments, we always take n to be integer which is 1, because we are looking at the first order reflection. N is 1 and lambda is nothing but your wavelength of your target and this is 2 d sine theta, that is actually coming from here, this is d and this is your sine theta.

So, this is actually 2 d two d sine theta, so this is what we are measuring, so n lambda is equal to 2 d sine theta and using this expression, we can try to find the inter planer placing, that is nothing but your d. This inter planer spacing between two adjacent atomic arrangements can be mapped, because I know n and I know lambda and I can also know theta from the 2 theta value. So, if I have a peak like this and I have some patterns like this and this is your 2 theta scan, this will give me 2 theta value and from there, I can find out theta.

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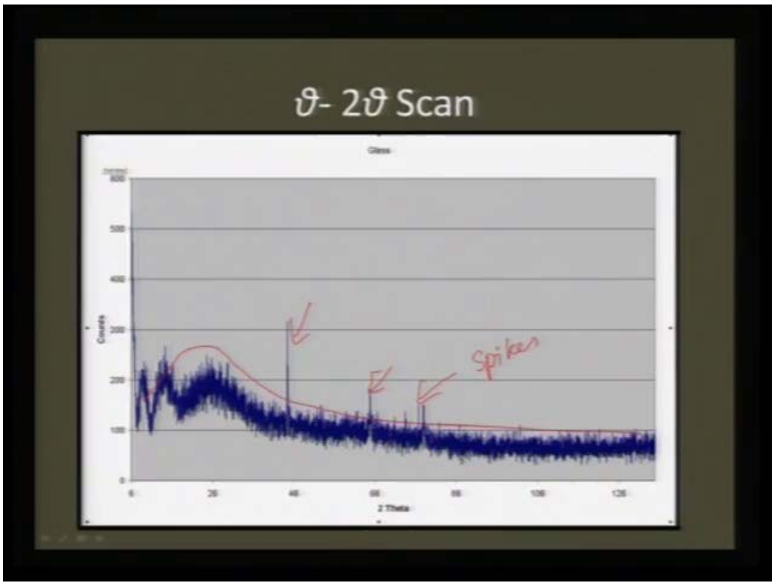

ϑ- 2ϑ Scan

So, this is how we go about it and first let me start with a featureless curve, because in reality, this is how it is, because this is nothing but a X-ray diffraction pattern of glass. Glass is amorphous, therefore there is no long range ordering and if you see only big hump at low angles then that is the very clear indication that, it is amorphous in nature. You would not see anything, these are all spikes, these are not peaks, these are spikes, therefore what you see here is a featureless noisy curve and that says that it is, the material is amorphous or glassy.

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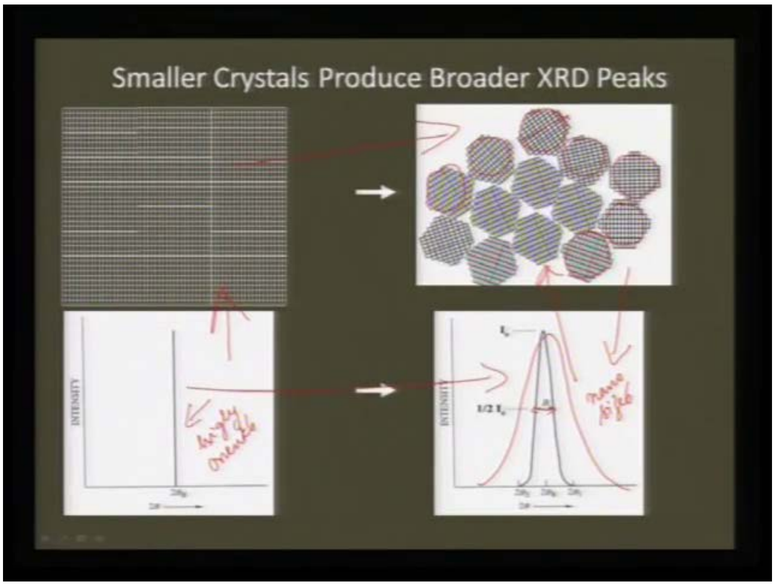

Smaller Crystals Produce Broader XRD Peaks

Now, if you go for single crystal or poly crystals, this is how it is, if it is a ordered lattice like this then I would get a very sharp pattern, as sharp as this and this is for a highly oriented system. So, the peak with or the crystallinity of a particular pattern will be reflected by the shape and size of the X-ray peak. Now, if these lattices are broken into poly crystals as small small crystals then we are actually breaking the long range order. And therefore, this peak now splits or broadens into this fashion and this B is nothing but your full width at half maxima, which gives you idea about the peak broadening.

And therefore, peak broadening has a consequence directly to the size and also shape of your poly crystals. If they are very fine then broadening will become more, so we are talking about going from a bulk to a very small dimension. And typically for that matter, nano sized powders will either be amorphous in nature or it will have a very broad peak like this.

And when there is a broadening, you should understand, broadening necessarily does not mean it has to be very low sized crystallized or nano size, broadening can also come from several other instrumental problems also. Therefore, we need to be careful, where is origin for this peak broadening, suppose one peak shows a broad one and the other peak in the same spectra is showing a thin one then it is not due to the sample, but it is due to some alignment problem. But, if the sample is truly a amorphous or nano in size then all the peaks that are appearing in the pattern will have same broadening. Then you can be sure that, this is the truly coming from a nano sized powder.

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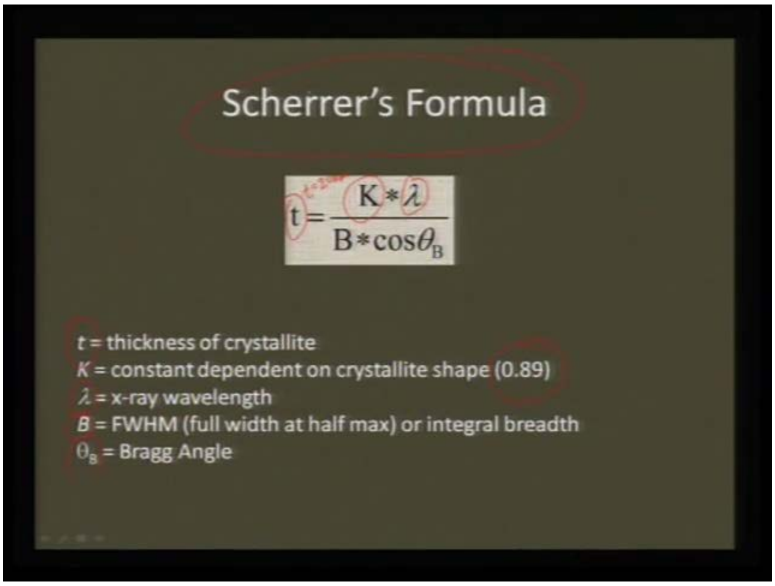

Scherrer's Formula

t=20nm

$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

t = thickness of crystallite
K = constant dependent on crystallite shape (0.89)
λ = x-ray wavelength
B = FWHM (full width at half max) or integral breadth
θ_B = Bragg Angle

Now, what informations we can get, number 1, we can get information about t, t is nothing but the thickness of your crystallite. This is the crystallite that I am talking about and what is the dimension of this crystallite, because crystallites are made of very small lattices. And therefore, I can map what is t, t is given by K into lambda by B cos theta B where, K is nothing but a constant that depends on crystallite shape. This is actually taken to be 0.89 and the contribution comes from both broadening and from other factors relative to the shape of the crystallite.

Lambda we know, b is nothing but full width at half maxima, so you can actually map your broadening and you can also measure the height and take the full width at the half maxima then that becomes your B, and theta B you know, that is your Bragg angle, so you can get t. If t is equal to 20 nanometer then you are saying that, your crystallite size is as small as 20 nanometer. So, peak broadening is defined by Scherrer's formula, which is a very potential information that you can achieve.

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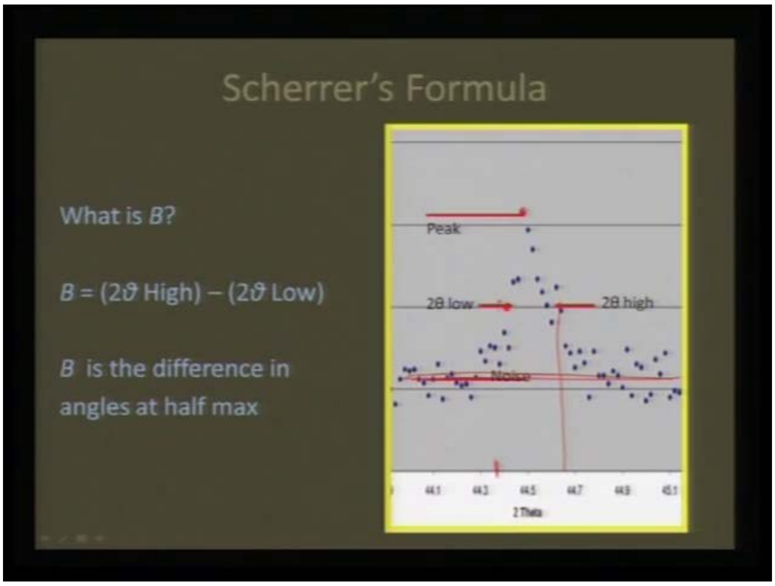

Scherrer's Formula

What is *B*?

B = (2ϑ High) – (2ϑ Low)

B is the difference in angles at half max

Now, this is how we go about, so draw, if it is not a very symmetric peak then you need to draw a base line and then fix your peak. And then you look at your 2 theta low that is, your B here and then your 2 theta B and then you can look at the full width at half maxima.

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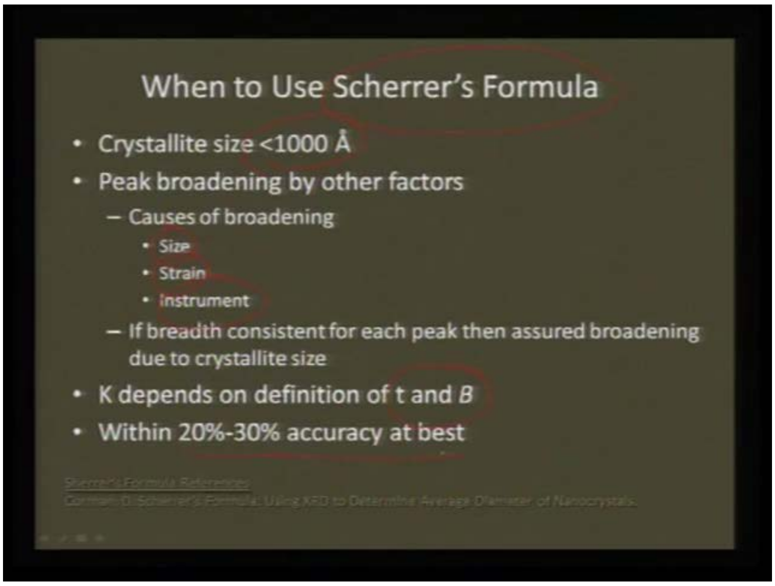

When to Use Scherrer's Formula

- Crystallite size <1000 Å
- Peak broadening by other factors
  - Causes of broadening
    - Size
    - Strain
    - Instrument
  - If breadth consistent for each peak then assured broadening due to crystallite size
- K depends on definition of t and *B*
- Within 20%-30% accuracy at best

Scherrer's Formula References

Connor, D. Scherrer's Formula: Using XRD to Determine Average Diameter of Nanocrystals.

So, this is how you go about doing this, but word of caution, you can resort to Scherrer's formula only if, your crystallite size is less than 100 nanometers or 1000 angstrom. If it is more, it is not good to correlate your X-ray broadening to crystallite size, which is not needed. Because, broadening as I told you, can come from strain, can come from the instrument and also come from size, therefore peak broadening can be very, very deceptive. Therefore, we should know, what we are looking for, so K depends on t and B, and this can be evaluated within 20 to 30 percent accuracy at the best.

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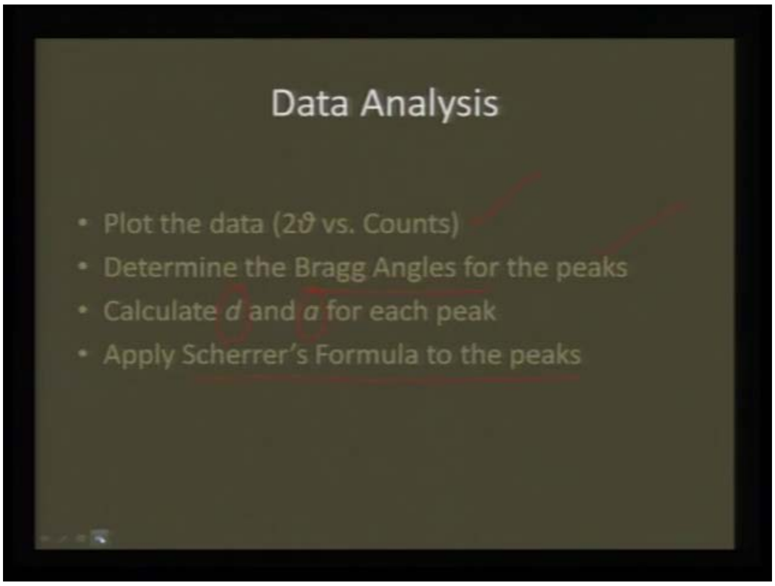

Data Analysis

- Plot the data (2ϑ vs. Counts)
- Determine the Bragg Angles for the peaks
- Calculate *d* and *a* for each peak
- Apply Scherrer's Formula to the peaks

Now, when we look at the data analysis, we are looking at the plot data that is, 2 theta versus counts, that is the principle data that you will get. And from there, you would define what is the Bragg angle that is, 2 theta, so you can get theta. Then you can calculate d and from d, you can calculate a and also you can apply Scherrer's formula to the peaks. So, these are the basic steps that you would choose, when you are handling any data.

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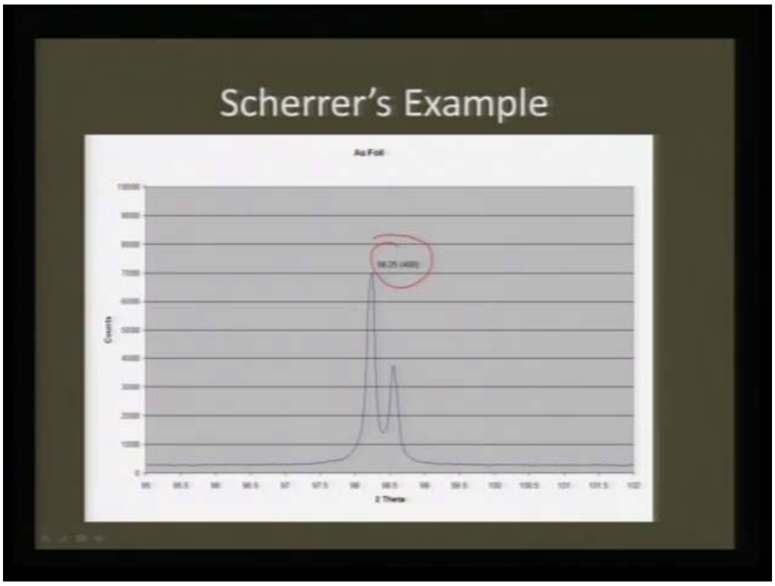

Scherrer’s Example

Now, Scherrer’s example, let us take the case of this 4 0 0 refraction that is coming from gold foil, which appears at 98.25 degrees.

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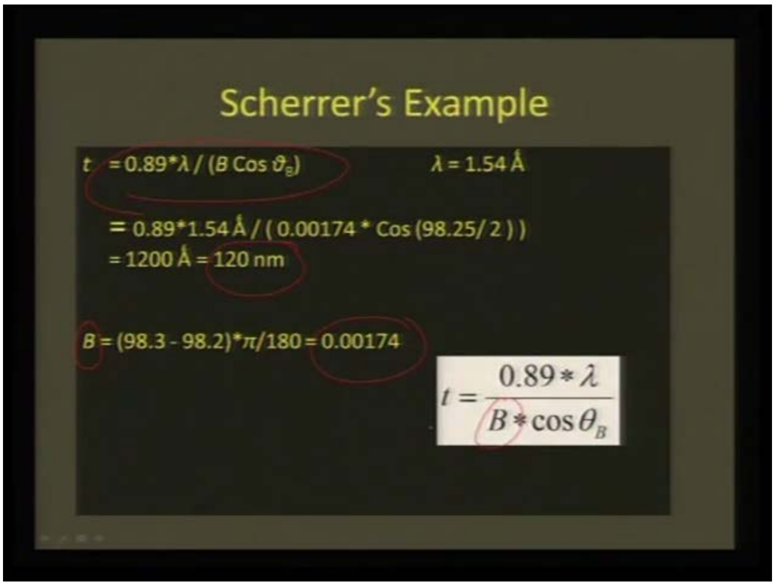

Scherrer’s Example

t = 0.89*λ / (B Cos ϑ_B) λ = 1.54 Å

= 0.89*1.54 Å / (0.00174 * Cos (98.25/ 2))
= 1200 Å = 120 nm

B = (98.3 - 98.2)*π/180 = 0.00174

$$t = \frac{0.89 * \lambda}{B * \cos\theta_B}$$

Then, we can calculate the crystallite size, in that case, using the formula which gives you approximately the dimension of your crystallite size to be 120 nanometer. And from there, you can actually also calculate your B, if you know the crystallite size, we can try to see the peak broadening, but peak broadening is a direct measure of the peak distance itself.

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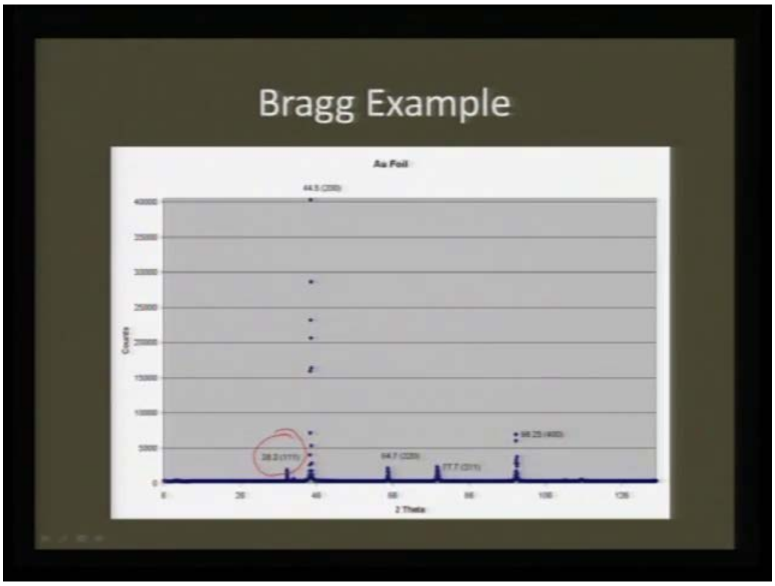

Bragg Example

We can also take the other example of calculating your inter planer spacing and this is the Bragg example that we can talk about. Let us take the small peak that is, 38.3 which is index to 1 1 1 reflection for gold foil.

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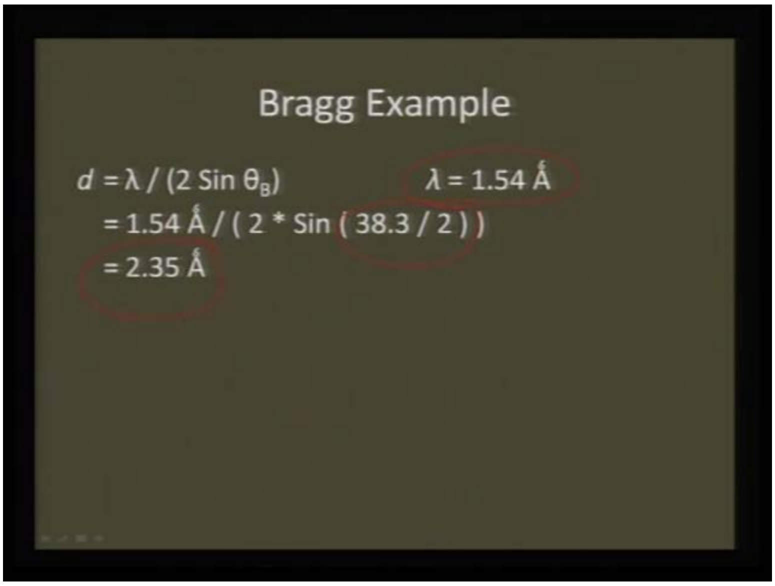

Bragg Example

$d = \lambda / (2 \text{ Sin } \theta_B)$ $\lambda = 1.54$ Å

$= 1.54$ Å $/ (2 * \text{Sin} (38.3 / 2))$

$= 2.35$ Å

And how do we go about, your lambda is known, that is from copper and theta is known, so your theta will be 38.3 over 2, so your inter planer spacing for your 38.3 will be 2.35 angstrom. So, this is how you assign the peak, similarly we can do it for 44.5 degrees, 64.7 degrees and you can index a pattern.

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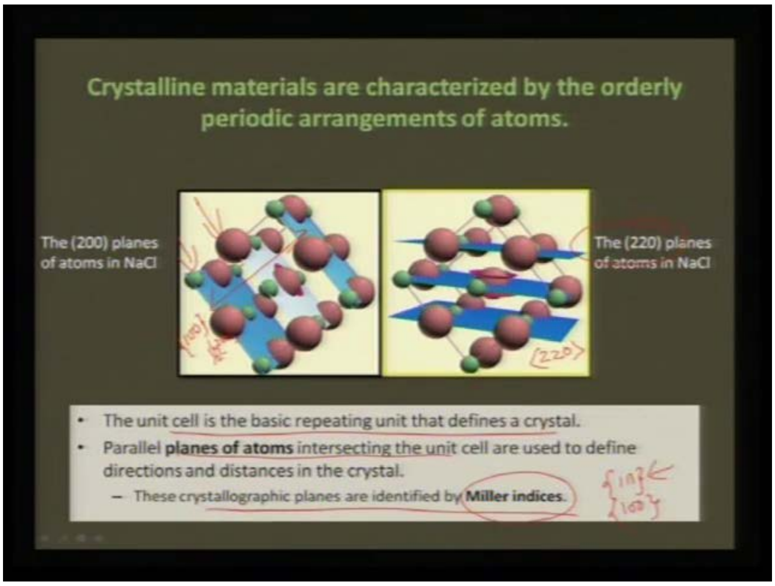

Crystalline materials are characterized by the orderly periodic arrangements of atoms.

The (200) planes of atoms in NaCl

The (220) planes of atoms in NaCl

- The unit cell is the basic repeating unit that defines a crystal.
- Parallel **planes of atoms** intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by **Miller indices**.

{111}
{100}

Now, crystalline materials are characterized by the orderly periodic arrangement of atoms, therefore when the sample is actually rotating, you can see that, several planes will come into diffraction. So, this is one plane and this is one plane, specially these two planes are characterized as 2 0 0 planes, this will have exactly half the inter planers placing, as that of your 1 1 0. So, if you have 1 0 0 plane, it will be exactly, half of that will be your 2 0 0 plane.

Similarly, when the lattice rotates, you can bring other planes also into focus for example, this is the way you can visualize a 2 2 0 plane and this can also give you a particular reflection. So, the unit cell is basic repeating unit and parallel planes of atoms intersect the unit cell and are used to define the directions and distances. And how do we map this, by knowing the lattice parameter, we can actually index this to some Miller indices a as 1 1 1 or 1 0 0 and so on. So, these are called Miller indices, which we can try to index based on the minimum details that we get from your X-ray diffraction pattern.

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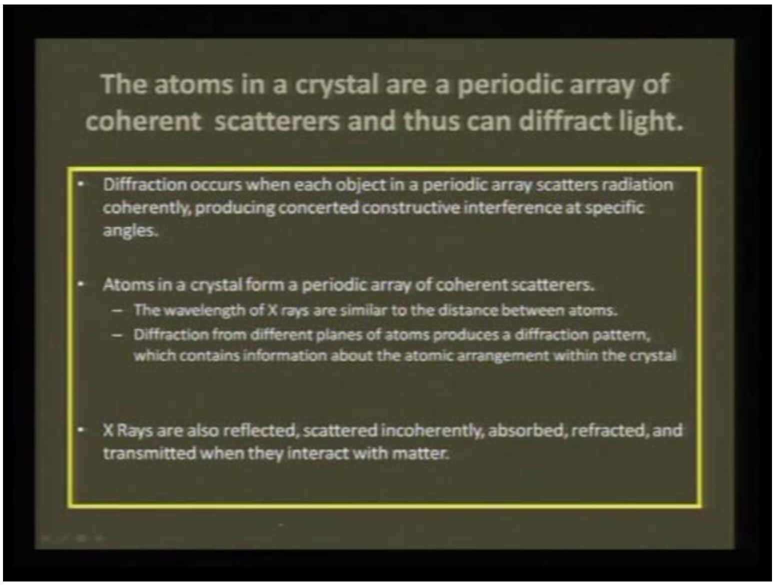

The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract light.

- Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.
- Atoms in a crystal form a periodic array of coherent scatterers.
  - The wavelength of X rays are similar to the distance between atoms.
  - Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- X Rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.

So, the atoms in a crystal are in a periodic array and therefore, we can try to use this diffraction to understand the long range ordering or the short range ordering that is available or that is present in the crystal lattice.

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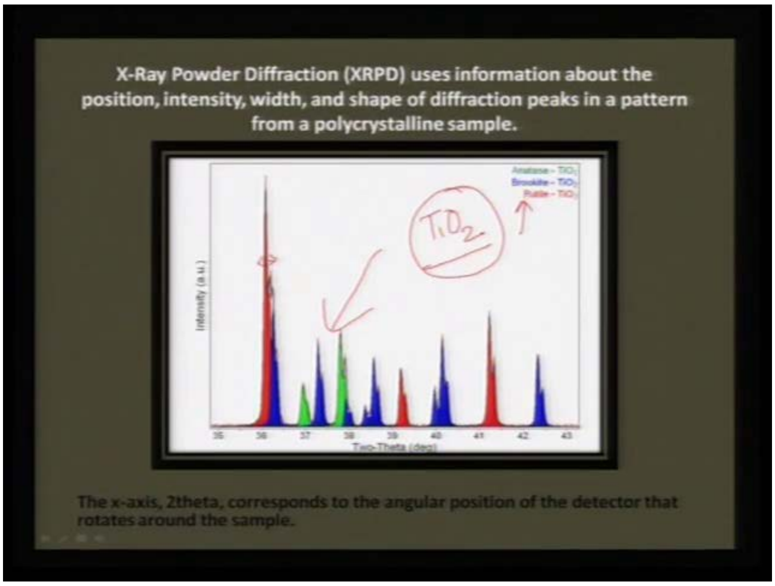

X-Ray Powder Diffraction (XRPD) uses information about the position, intensity, width, and shape of diffraction peaks in a pattern from a polycrystalline sample.

The x-axis, 2theta, corresponds to the angular position of the detector that rotates around the sample.

Here is a cartoon that I want to highlight to you, this is a X-ray diffraction pattern, which gives you idea about the different phases of a single material that is present. For example, you take the case of TiO 2 and TiO 2 can actually be present in three different phases, anatase and rutile, which is more predominate and you also have a brookite phase. Now, if you take a X-ray map, you would see, depending on the phases that are present, you can also see different patterns that are emerging.

And the red ones are predominately the rutile pattern and anatase pattern comes out as green and then the blue ones are indicative of brookite phase. What you should be careful here is that, within short range all these phases are overlapping, so if you are not precisely measuring then you might confuse one phase for the other. So, you need to have some idea about all the phases that are possible, which will help you in identifying what sort of phases are present.

For example, even today, the greatest challenge for you to understand is the challenge in TiO 2 crystallize in a preferred symmetry. For example, rutile, but what happens, anatase comes as a major impurity phase, so chemical approaches are there, which are used to stabilize only the rutile phase. So, the complex can become more confusing, if we do not know what are all the different phases that can be present in your given sample.

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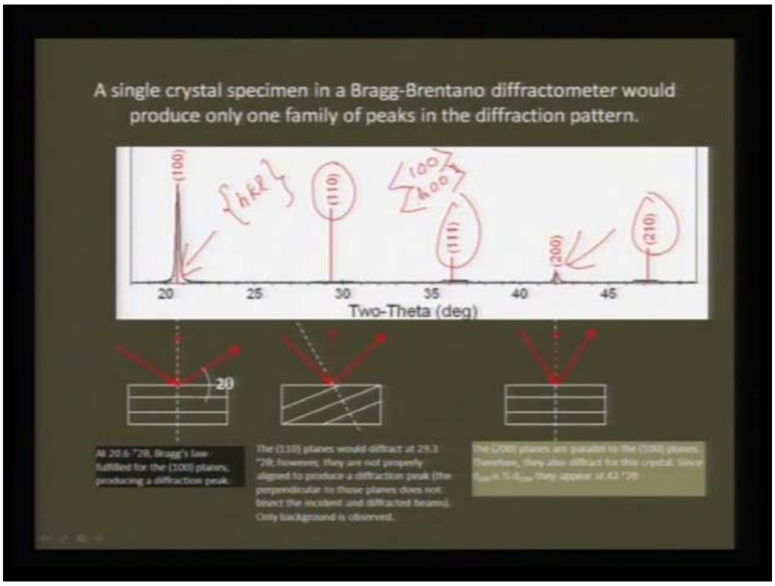

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

Now, we will look in the other few slides, how to index or understand, what is the repeating X-ray peak and from that, what sort of information that I can get. We will see this in the next two slides, take for example, this X-ray pattern where, you only see two patterns that are present. In such case, what information you can achieve is important, as you would see here, this particular peak refers to 1 0 0 and this particular peak refers to 2 0 0.

So, in that case, only those repeating peaks you will get, whereas the other miller indices or other crystal planes like 1 1 0, 1 1 1 and 2 1 0, these are all absent in this particular reflections. So, just by looking at it, you can easily trace that, when the several peaks are missing, only few peaks are represented in your X-ray scan, you can say, those belong to a particular class of h k l reflections. So, you call this as 1 0 0, when you put within this inverted brackets, then you say that, this belongs to h 0 0 type of planes. So, you will get only 1 0 0, 2 0 0, 3 0 0, this also talks about the orientation or the texture of your growth.

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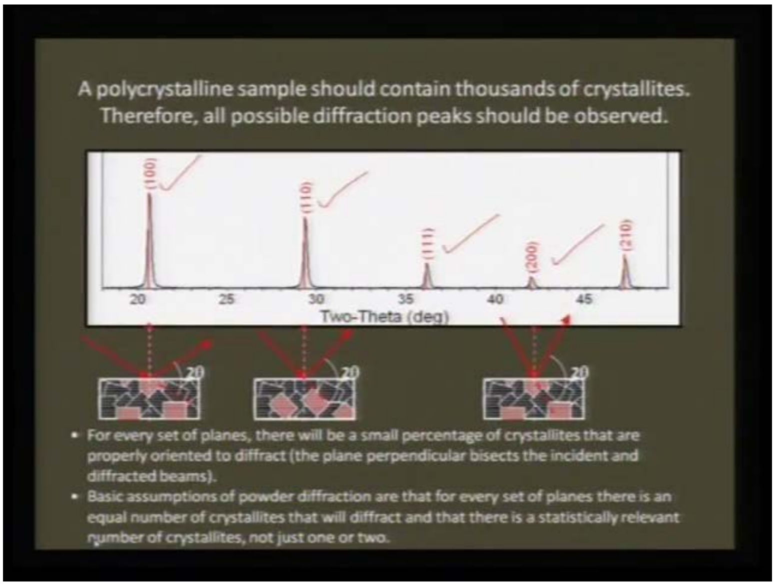

A polycrystalline sample should contain thousands of crystallites.
Therefore, all possible diffraction peaks should be observed.

- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Now, if you look for polycrystals for example, then in polycrystalline patterns, you would get all the reflections. So, 1 0 0 and as you see here, 1 1 0, 1 1 1, 2 0 0, all the peaks of different crystal planes are present, which you can get in a polycrystalline sample against a single crystal. So, in single crystal, you would get only a preferred Miller indices reflection, whereas in polycrystalline sample, you will get all the patterns emerging in picture.

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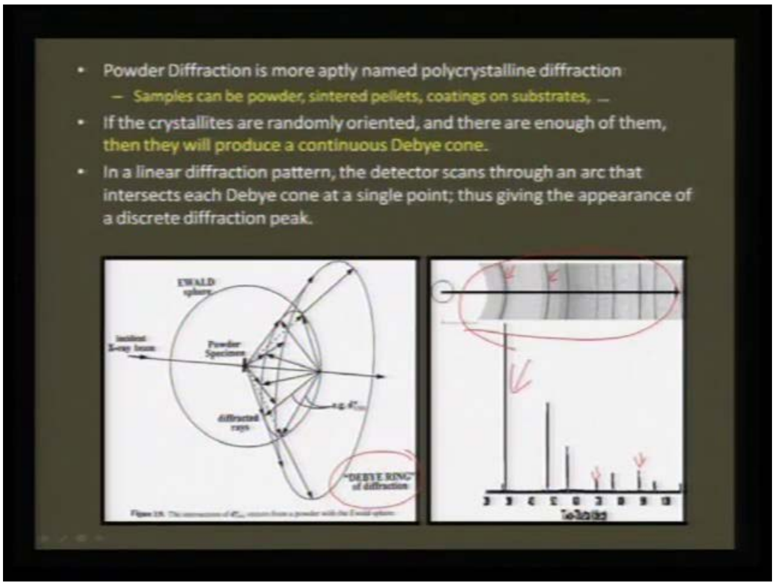

- Powder Diffraction is more aptly named polycrystalline diffraction
  - Samples can be powder, sintered pellets, coatings on substrates, …
- If the crystallites are randomly oriented, and there are enough of them, then they will produce a continuous Debye cone.
- In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.

Now, in the earlier days, before we got this X-ray recorder or as you see in present generation, everything is appearing on a computer screen. In earlier days, it was mostly obtained as a photography, so you would see X-ray patterns coming out as a pattern like this. And these are nothing but these lines represent the Debye ring or Debye cone, which is coming out as a intersection of your detector on this cone, which is appearing as this sort of rings.

So, with respect to the sample, these rings can be measured and each of this ring will give you a particular d value, inter planer spacing and if you see here, the intensity of this also tells, which reflection is going to be at it is maximum. For example, this is a darker shade compared to these peaks, therefore we can say that, these peaks are highly intense compared to the other ones. So, these peaks for example, is intense, but this peak is less intense, so it comes out like this, so this is the way it was mapped.

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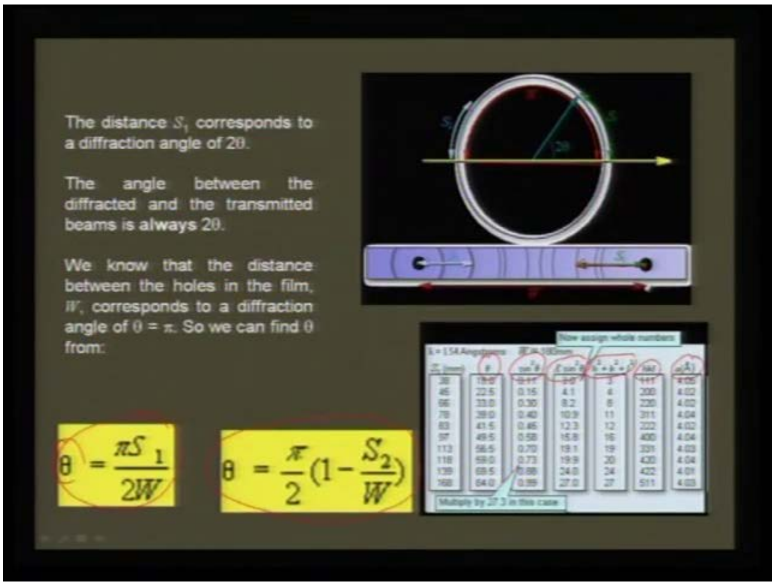

The distance S_1 corresponds to a diffraction angle of 2θ.

The angle between the diffracted and the transmitted beams is always 2θ.

We know that the distance between the holes in the film, W, corresponds to a diffraction angle of $\theta = \pi$. So we can find θ from:

$$\theta = \frac{\pi S_1}{2W}$$

$$\theta = \frac{\pi}{2}\left(1 - \frac{S_2}{W}\right)$$

λ = 1.54 Angstroms W = 180mm

Now assign whole numbers

S_1 (mm)	θ	$\sin^2\theta$	$k\sin^2\theta$	$h^2+k^2+l^2$	hkl	a(Å)
38	19.0	0.11	3.0	3	111	4.05
46	22.5	0.15	4.1	4	200	4.02
66	33.0	0.30	8.2	8	220	4.02
78	39.0	0.40	10.9	11	311	4.04
83	41.5	0.45	12.3	12	222	4.02
97	49.5	0.58	15.8	16	400	4.04
113	56.5	0.70	19.1	19	331	4.03
118	59.0	0.73	19.9	20	420	4.04
139	69.5	0.88	24.0	24	422	4.01
168	84.0	0.99	27.0	27	511	4.03

Multiply by 27.3 in this case

And we can also try to measure that distance from the dark spot, so each of this distance can be evaluated using this formula as S 1 or S 2, S 1 S 2 is nothing but the turn it makes with respect to the incoming X-ray. So, if you can measure S 1 based on the distance then you can generate the value theta and if you now value theta then you can calculate for sine square. Then you can calculate for K sine square theta and from there, you can get your Miller indices and also your lattice parameter.

So, this is the earlier version, by which X-ray diffractions were made and those were available only as a photographic film. So, you need to take X-ray photograph and then you should develop and calculate the distance from the central spot and that is how, you measure the inter planer spacing’s.

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Sample Preparation

But today, this is all simplified and you can get everything in a single fashion.

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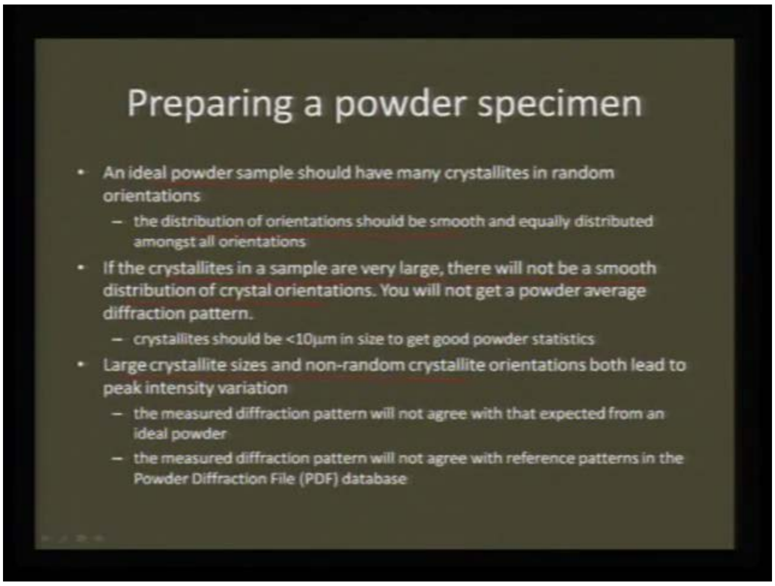

Preparing a powder specimen

- An ideal powder sample should have many crystallites in random orientations
  - the distribution of orientations should be smooth and equally distributed amongst all orientations
- If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern.
  - crystallites should be <10μm in size to get good powder statistics
- Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation
  - the measured diffraction pattern will not agree with that expected from an ideal powder
  - the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database

Just one or two comments about sampled preparation, it is not always the problem of the X-ray diffractometer when you do not see anything. Therefore, powder preparation is a very very important protocol, when you try to look for a very decent X-ray diffraction pattern. Therefore, an ideal powder sample preparation means, it has the different orientations should be smooth and equally distributed.

If the crystallites in the sample are the very large, there will not be a smooth distribution of crystal, therefore there will be too much of noise coming into picture. And larger crystallite size and non random crystallite, they can also affect the peak intensity to a larger fashion.

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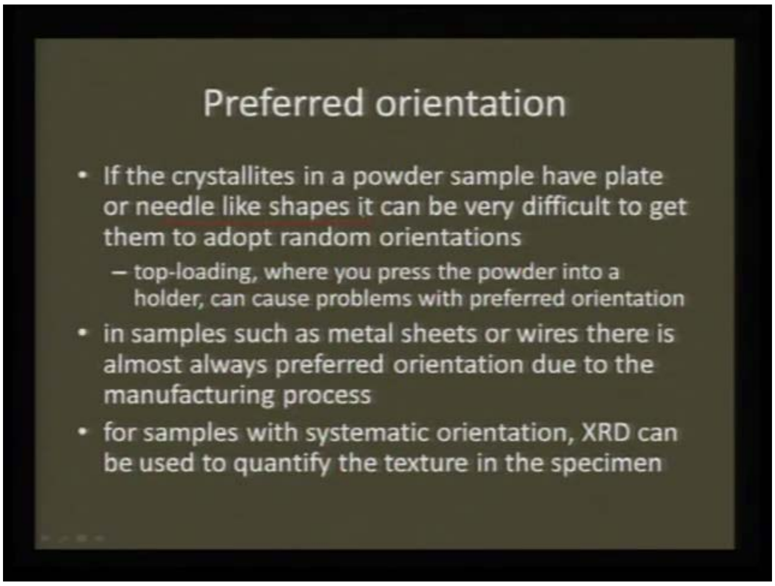

Preferred orientation

- If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations
  - top-loading, where you press the powder into a holder, can cause problems with preferred orientation
- in samples such as metal sheets or wires there is almost always preferred orientation due to the manufacturing process
- for samples with systematic orientation, XRD can be used to quantify the texture in the specimen

So, we need to be very careful about, how we orient the sample, how we prepare the sample. If the crystallites in the powder sample have plate or needle shape for example, if those are the morphology then you assure to get a very confusing X-ray pattern and it can be very difficult to get them, adopt to random orientations. So, you need to look for a top loading where, you can press the powder into a holder and somehow, try to make a very continuous spread so that, you do not miss out on the reflection. So, when we have particles with different morphology, it becomes increasingly important how you prepare the sample.

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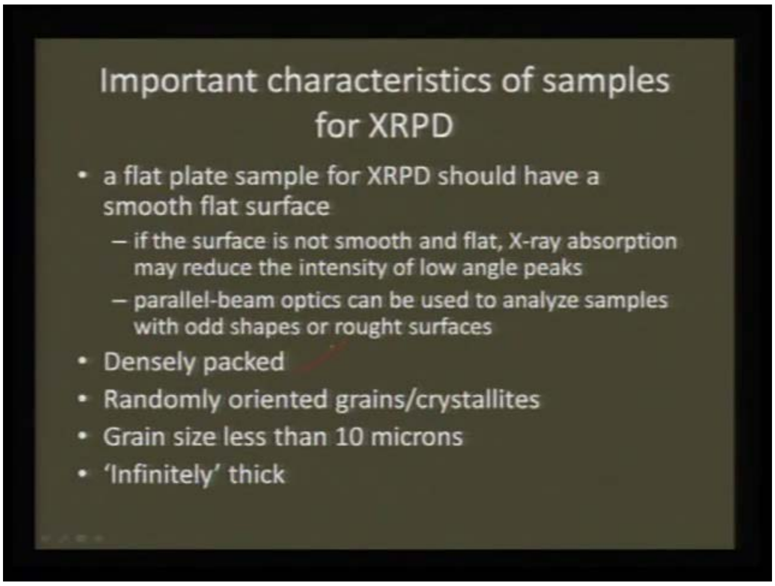

Important characteristics of samples for XRPD

- a flat plate sample for XRPD should have a smooth flat surface
  - if the surface is not smooth and flat, X-ray absorption may reduce the intensity of low angle peaks
  - parallel-beam optics can be used to analyze samples with odd shapes or rought surfaces
- Densely packed
- Randomly oriented grains/crystallites
- Grain size less than 10 microns
- 'Infinitely' thick

So, we need to go through that and it should also be densely packed, therefore care should be taken how you pack the sample. And we should also make sure that, the samples are ground nicely if you are looking for a polycrystalline one, you cannot take just from the furnace and mount it. Because, when you heat any sample at 900 degree, you are actually looking at samples with 100 micron or so. So, you got to bring it down so that, it is somewhere in the 10 micron range, so the diffraction can be uniform.

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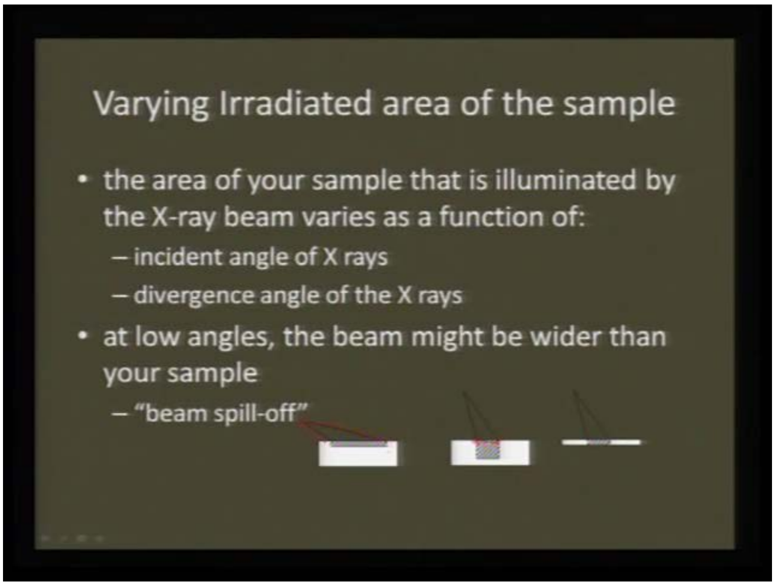

Varying Irradiated area of the sample

- the area of your sample that is illuminated by the X-ray beam varies as a function of:
  - incident angle of X rays
  - divergence angle of the X rays
- at low angles, the beam might be wider than your sample
  - "beam spill-off"

And also, you should understand that, the spread of your beam has to be this big at very low angles, whereas at very high angles, it can be very small. Therefore, when you spread the sample, we should make sure that, at all angles, the incident radiation is falling exactly on the sample and not elsewhere. So, these things we need to bear in mind.

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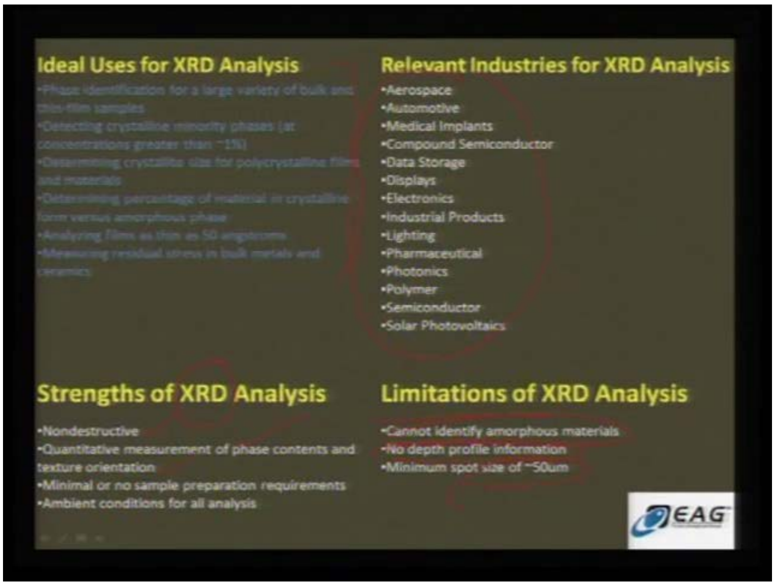

Ideal Uses for XRD Analysis

- Phase identification for a large variety of bulk and thin-film samples
- Detecting crystalline minority phases (at concentrations greater than ~1%)
- Determining crystallite size for polycrystalline films and materials
- Determining percentage of material in crystalline form versus amorphous phase
- Analyzing films as thin as 50 angstroms
- Measuring residual stress in bulk metals and ceramics

Relevant Industries for XRD Analysis

- Aerospace
- Automotive
- Medical Implants
- Compound Semiconductor
- Data Storage
- Displays
- Electronics
- Industrial Products
- Lighting
- Pharmaceutical
- Photonics
- Polymer
- Semiconductor
- Solar Photovoltaics

Strengths of XRD Analysis

- Nondestructive
- Quantitative measurement of phase contents and texture orientation
- Minimal or no sample preparation requirements
- Ambient conditions for all analysis

Limitations of XRD Analysis

- Cannot identify amorphous materials
- No depth profile information
- Minimum spot size of ~50um

And just want to mention to you some of the relevance of this XRD analysis, as I am progressively mentioning in this lecture, there are different ways of using X-rays for characterizing your sample. Strength of the XRD is, it is non destructive, quantitative measurements can be made, texture can be used, limitation is that it cannot identify amorphous materials. So, it goes really blank, therefore we do not have potential way to characterize amorphous material and your spot size has to be of the order of 50 micron.

And you do not get any information on the depth profile, so you just get whatever is on the surface, you get that. Now, there are also several areas where, X-ray diffraction has come into prominence, relevant industries who use this analysis are from medical to electronic, to several range of industries, which are using this as a fundamental tool to characterize the sample.

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SOME SPECIFIC EXAMPLES

I am going talk in the next few minutes about some specific examples, how we can understand X-ray. And always X-ray goes in combination with some physical property where, you can try map some reasonable conclusions.

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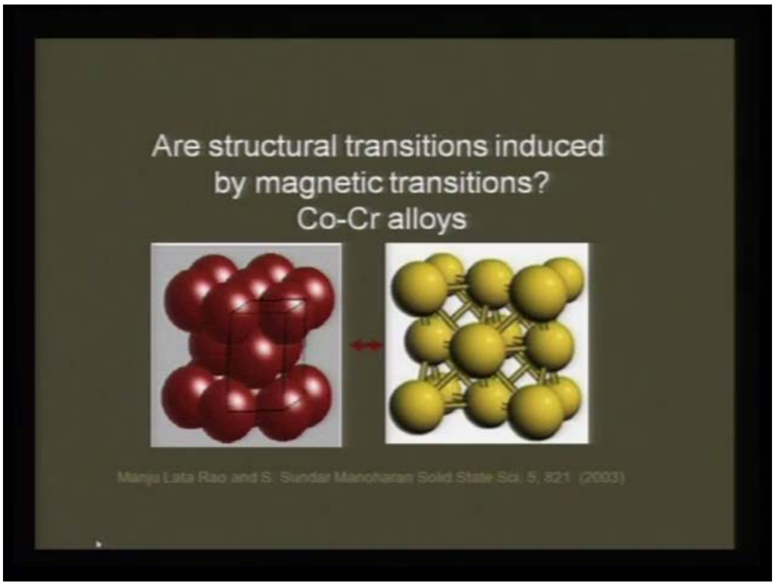

Are structural transitions induced by magnetic transitions?
Co-Cr alloys

Manju Lata Rao and S. Sundar Manoharan Solid State Sci. 5, 821 (2003)

For example, take the case of cobalt chromium alloy, this is a alloy which is a shape memory alloy and this is used in variety of applications including biomedical applications. Question is, are structural transitions induced by magnetic transitions, because magnetic transition and structural transition can go hand in hand.

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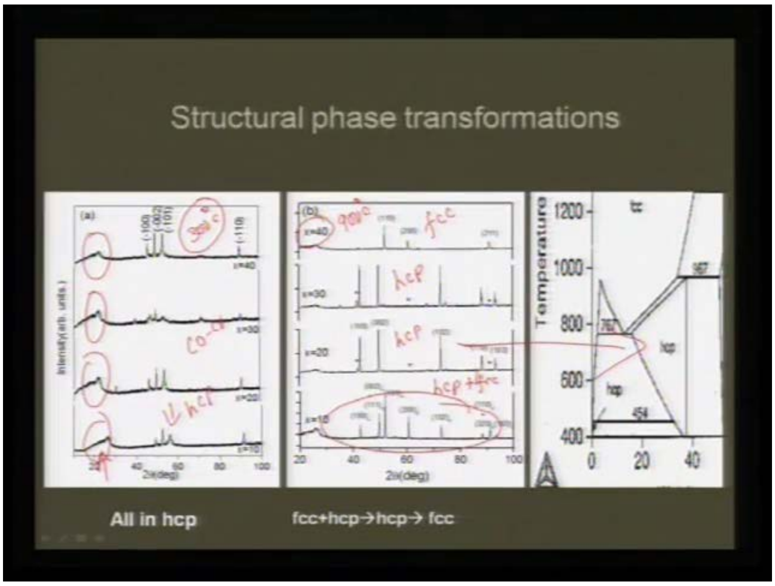

Structural phase transformations

All in hcp

fcc+hcp→hcp→ fcc

And we can see, if you try to prepare cobalt chromium compounds and this is for 300 degree c anneal, because the as prepare compound shows X-ray amorphous nature. And because of X-ray amorphous nature, you see this low angle peak broadening or hump and if this hump is present at low angles, you can be sure that, this it is just crystallizing. And when you heat it only to 300, you can see this hcp phase is crystallizing out in your cobalt chromium sample. And if you heat it at 900 degree C, you can see different phases coming into picture, in this case it is hcp plus fcc that is coming. And in this case, it is purely hcp, hcp and at chromium 40 percent, you are getting a fcc phase and then this seems to be going hand in hand with the phase diagram that is predicated.

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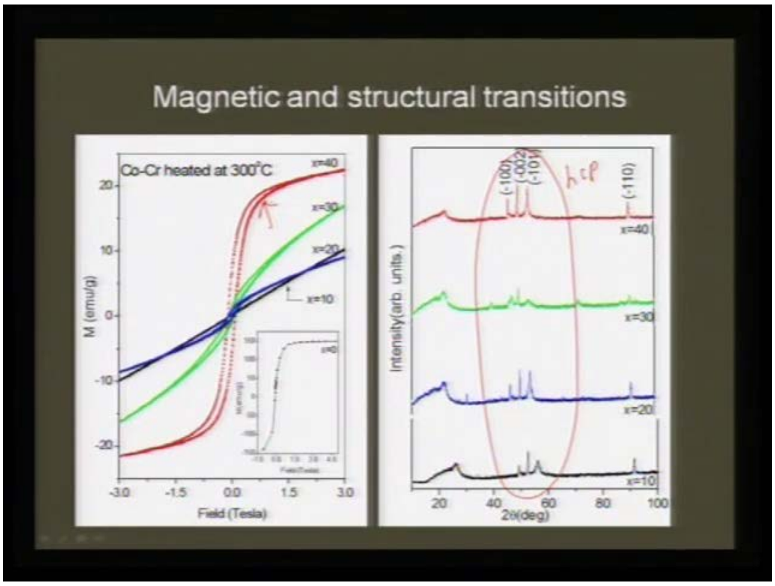

Magnetic and structural transitions

But, what we see here is that, for all the 300 degree sintered samples, which is hcp, there are certain peaks which are showing a nearly anti ferromagnetic interactions or computing anti ferromagnetic interactions, for example this 20 and 30 percent, compared to a clear ferromagnetic loop, but in this case, all are hcp.

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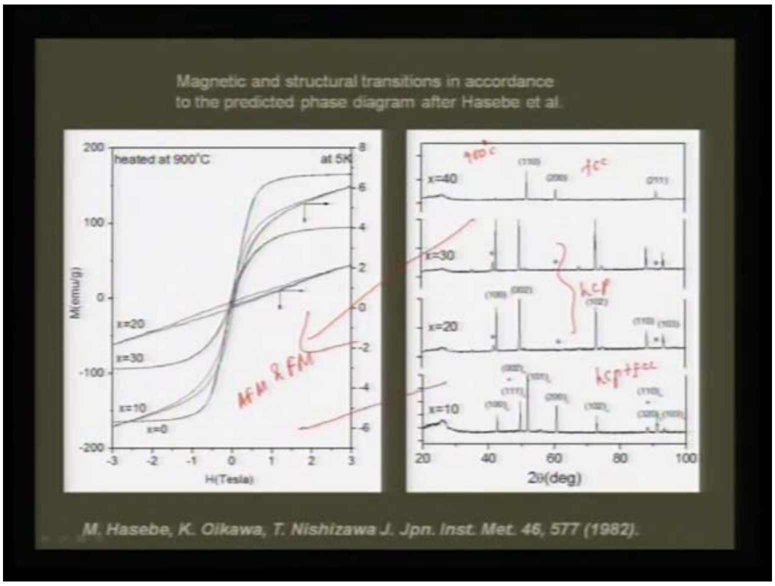

Magnetic and structural transitions in accordance to the predicted phase diagram after Hasebe et al.

M. Hasebe, K. Oikawa, T. Nishizawa J. Jpn. Inst. Met. 46, 577 (1982).

But, when you try to heat this to 900 degree C, when in this case if it is fcc, here hcp plus fcc and in both these cases, this h c p you can see that, there is a different change in the magnetization. And so we can directly correlate, which phase is responsible for the anti ferromagnetic coupling, which phase is giving you a ferromagnetic signal, all this can go hand in hand when you try to map your X-ray diffraction pattern. So, this becomes very useful to understand, how the magnetic transformations affect the structural disorders and how the structural impurities can alter the magnetic signature. So, a computing interaction between AFM and ferromagnetism, in this cobalt chromium is actually linked to the structural changes that are happening.

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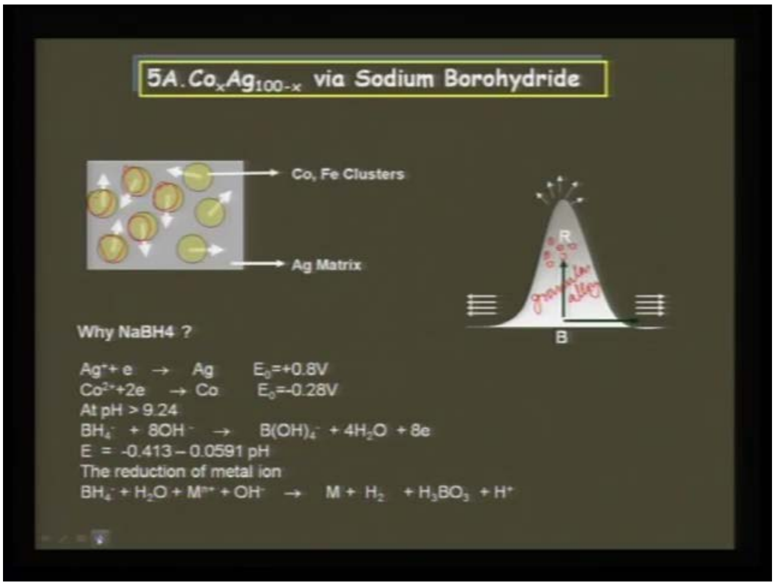

5A. Co_xAg_{100-x} via Sodium Borohydride

Why NaBH4 ?

$Ag^+ + e \rightarrow Ag \quad E_0 = +0.8V$

$Co^{2+} + 2e \rightarrow Co \quad E_0 = -0.28V$

At pH > 9.24

$BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e$

$E = -0.413 - 0.0591\, pH$

The reduction of metal ion

$BH_4^- + H_2O + M^{n+} + OH^- \rightarrow M + H_2 + H_3BO_3 + H^+$

This is another example that I want to quote, which is a cobalt silver and this is nothing but a granular alloy, because if you try to put silver into cobalt or cobalt into silver, silver is crystallizing in fcc, cobalt will not actually form a alloy, rather it is a immiscible alloy. And in this what happens, cobalt actually forms a cluster like this and therefore, it is called a granular magneto resistance system where, cobalt does not spread and get mixed with silver, rather it isolates into cobalt nano particles. So, there can be correlation between the cobalt clusters and the way they orient, can affect the electrical conductivity also, so this is actually used as granular MR system or magneto resistance system.

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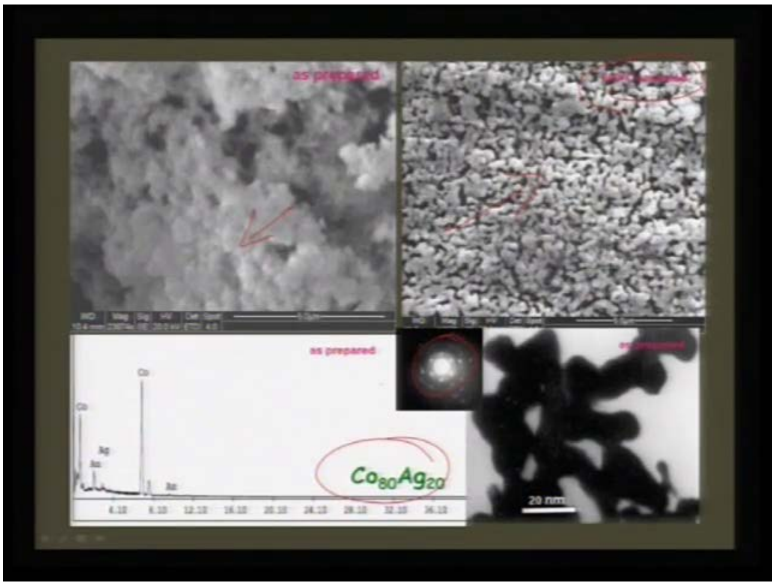

This is the as prepared alloy, this is a alloy that is annealed, at 600 you can see that it is getting crystallized. And the as prepared alloy clearly shows the presence of both cobalt and silver, and it when you anneal it, it is actually transforming into a polycrystal.

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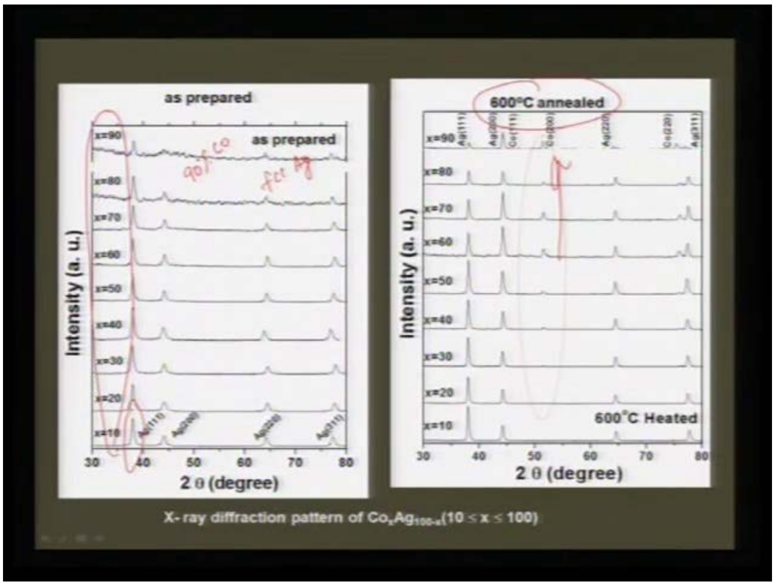

X-ray diffraction pattern of Co_xAg_{100-x} ($10 \le x \le 100$)

Now, what you see here is, this is silver and in silver, when you try to put cobalt as of, this is the X-ray pattern as a function of the atom percent of cobalt. And you can clearly see, even upto 90 percent atom percent of cobalt that is doped, only fcc silver phase is present. What it means is that, cobalt even though you dump it with 10 percent, the crystallites grow, but they are remaining in a amorphous form. And all that you can see is, only the fcc phase, the hcp phase of cobalt does not come into picture.

But, when you anneal the sample of the as prepared compound then you can see that, the cobalt phase is emerging out of it which means, cobalt is crystallizing from a amorphous phase to this one. So, you can directly make a correlation between the sort of crystallization process that is going on with any other physical properties. And if you actually map this peak, which is true for silver and this peak, which you are seeing for cobalt.

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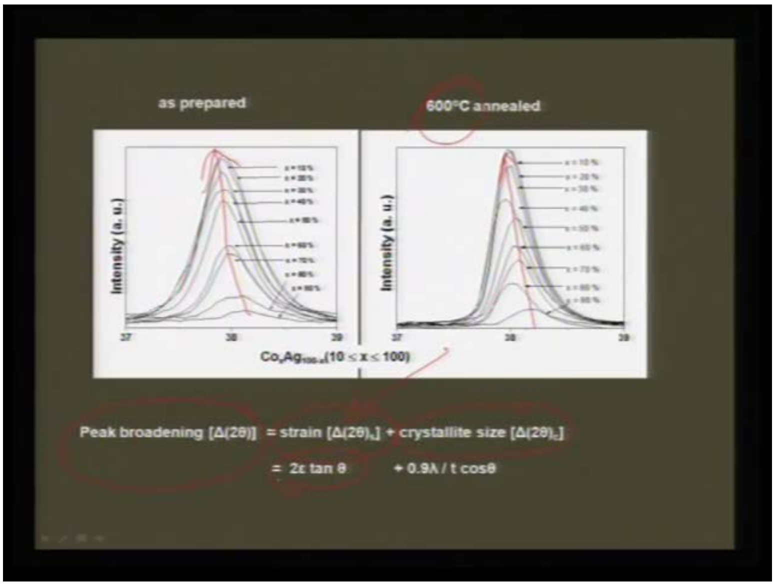

Peak broadening $[\Delta(2\theta)]$ = strain $[\Delta(2\theta)_s]$ + crystallite size $[\Delta(2\theta)_c]$

$= 2\varepsilon \tan\theta$ $+ 0.9\lambda / t \cos\theta$

Now, as you see here, this 38 peak clearly shows a change in the full width at half maxima and the position, as a function of cobalt and this can have a tremendous influence on the properties of this silver cobalt nano alloys. Here again you see, for the 600 annealed sample, the peak position changes and the full width at a half maxima also changes. And therefore, there is a way to actually interpret the peak broadening, so in this case, the peak broadening can come from two situation, one is due to strain induced broadening or one is due to crystallite size.

Crystallite size is what we get from Scherrer’s formula where, you calculate the peak broadening. But, one should also understand, the peak broadening comes from strain, which is nothing but delta 2 theta, which is given as 2 epsilon tan theta where, epsilon is nothing but your micro strain.

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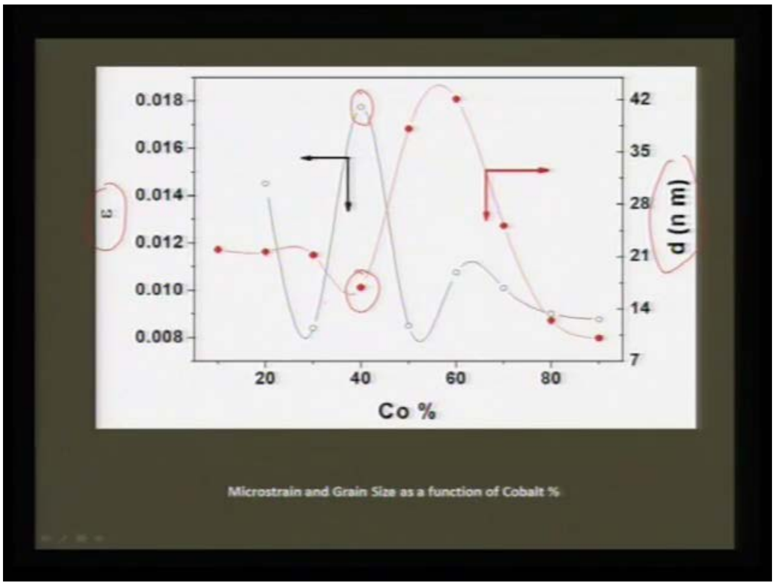

Microstrain and Grain Size as a function of Cobalt %

And therefore, you can actually correlate that strain to the grain size and you see here very clearly that, with maximum strain is there when the crystallite size is at it is minimum. So, when you go down in the nanometer range, what you are inducing is a macro strain, which will also affect your MR property.

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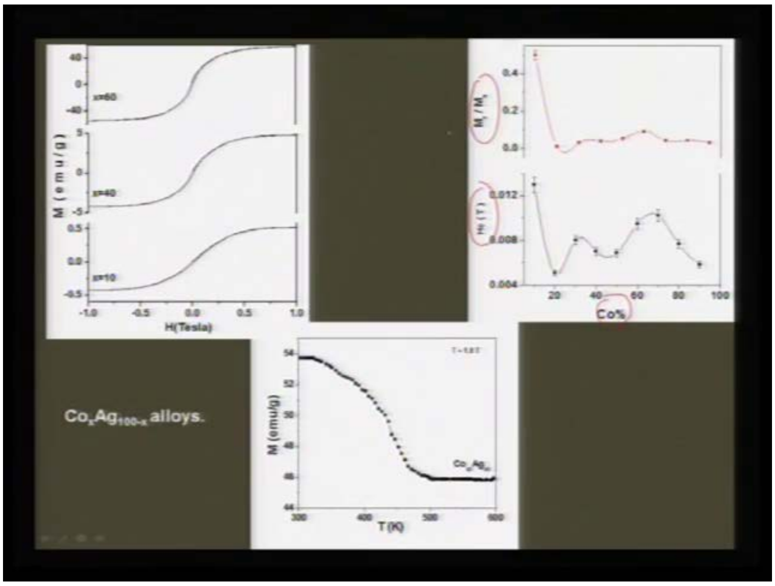

Co_xAg_{100-x} alloys.

And that is what, we try to see from these measurements, we can actually try to map the dependence of these micro strains to coercivity and to MR also.

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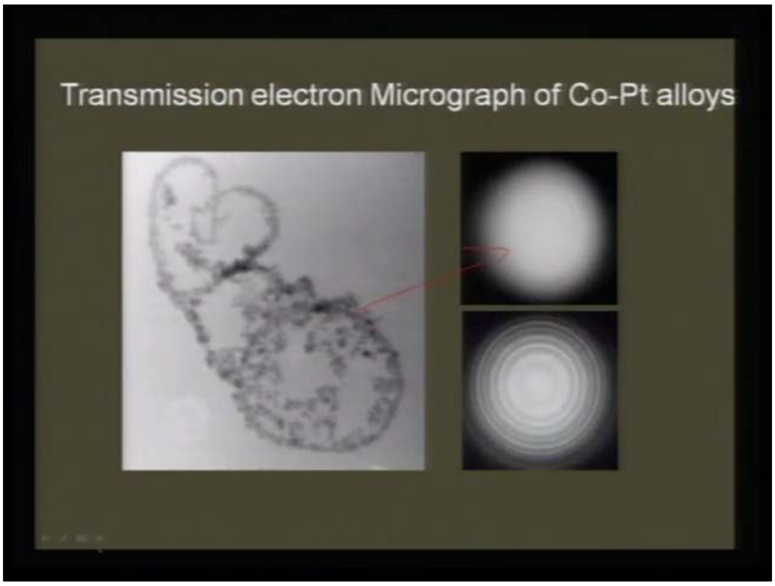

Transmission electron Micrograph of Co-Pt alloys

Another example of cobalt platinum alloy, which actually shows this sort of decorations, when you try to synthesize. As you see, the as prepared one shows TEM pattern like this, but as you show the TEM beam it gets crystallized in no time.

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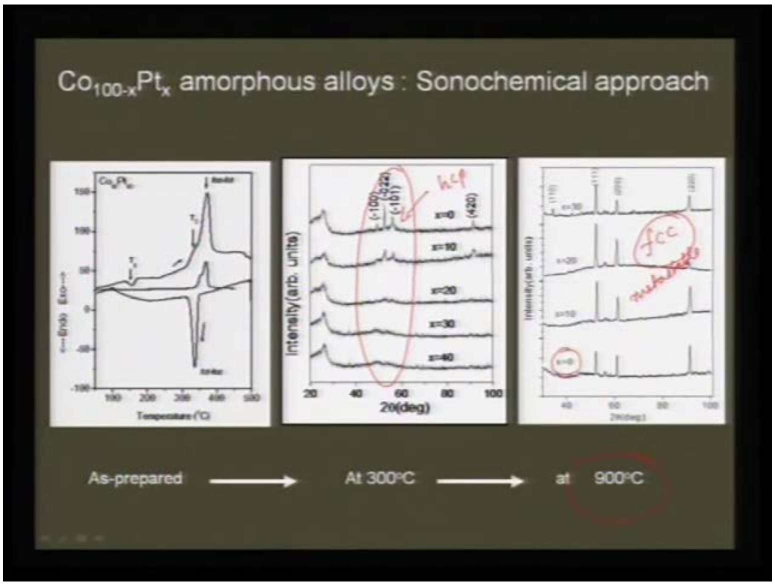

$Co_{100-x}Pt_x$ amorphous alloys : Sonochemical approach

As-prepared → At 300°C → at 900°C

And the as prepared compounds are clearly showing a amorphous phase, but with increasing amount of platinum, you can see this hexagonal phase coming for the as prepared alloy. But, when you try to heat it at 900 degree C, you can see a fcc phase that is forming. What you would expect this to be a hcp, is actually getting into a fcc phase even for a platinum 0 percent composition which means, metastable phases can be stabilized when they are nano in size.

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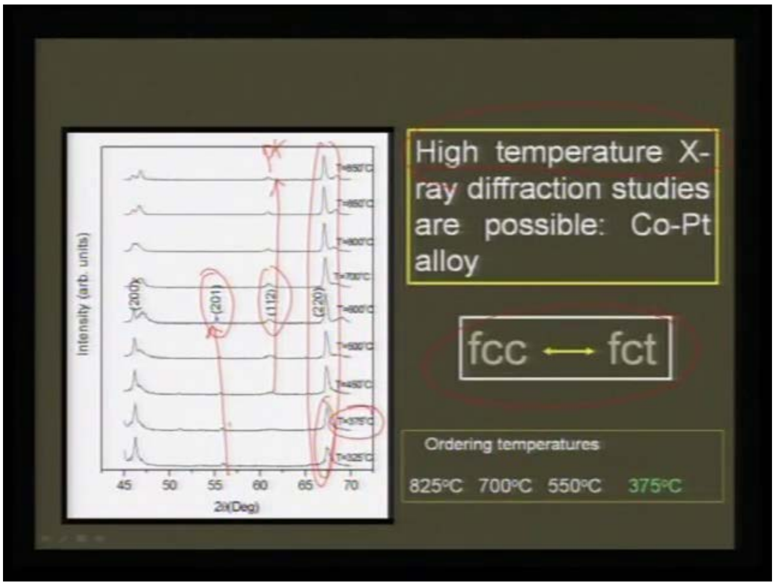

High temperature X-ray diffraction studies are possible: Co-Pt alloy

fcc ⟷ fct

Ordering temperatures

825°C 700°C 550°C 375°C

And this can be easily mapped through a high temperature X-ray diffraction, so this is a very unique facility that is available. The X-ray diffractometer has a platform, which can be used for sintering and where, you can easily map a fcc to fct transformation that is happening. This you can clearly see in this peak, which is building up as your heating in situ, this is not taken out and then recorded. As you are heating, you can do a isothermal X-ray and you can see, how the phase transformations are occurring and you can see how clearly these fct peaks are coming. These peaks are nothing but the peaks of platinum foil, which is used for spreading your stuff. But, the regions that are of interest is, the peak that is growing along this 2 0 1 and 1 1 2, which clearly shows that, a fcc to fct transformation is occurring.

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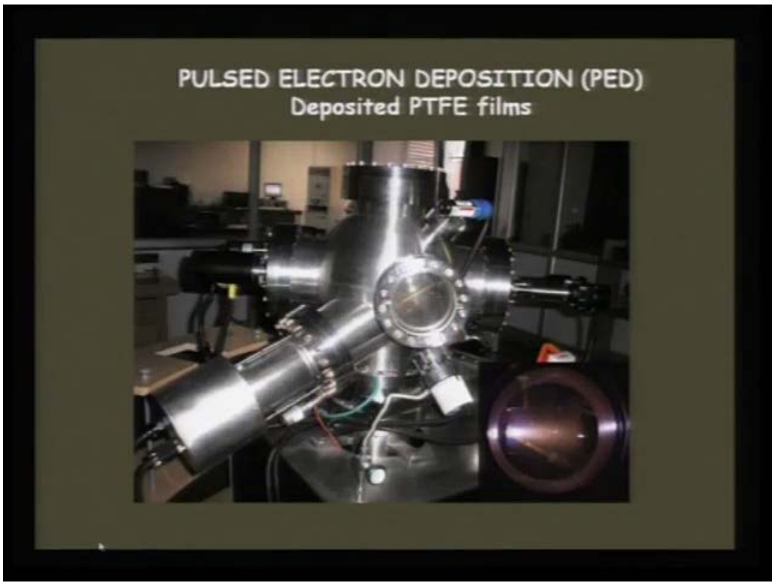

PULSED ELECTRON DEPOSITION (PED)

Deposited PTFE films

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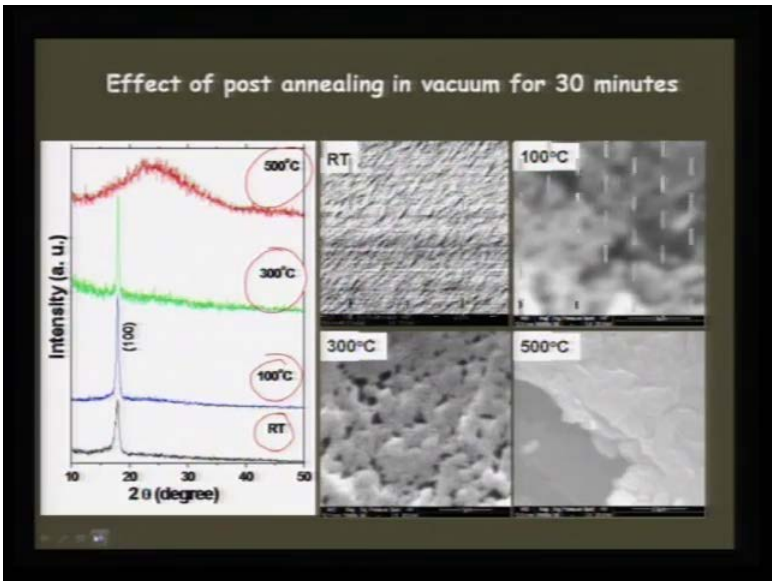

Effect of post annealing in vacuum for 30 minutes

And also, we can use this for mapping the teflon or PTFE polymeric films, which you can deposit using PED. And as you can see here, this is for a room temperature deposited film and this is for a 100 degree deposited film, 300 degree deposited and at 500 degree annealed film, you can see that, the peak is lost. And we can also make correlations with the SEM pattern, which I will skip for now.

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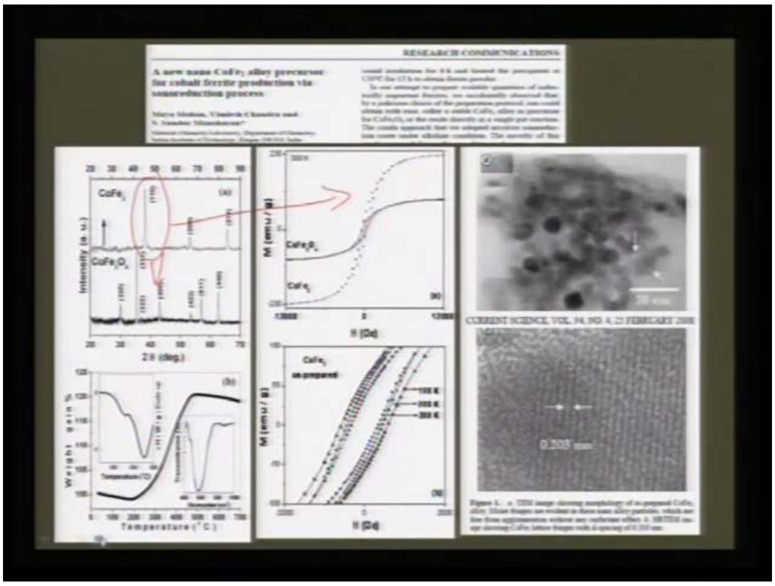

RESEARCH COMMUNICATIONS

A new nano $CoFe_2$ alloy precursor for cobalt ferrite production via sonoreduction process

CURRENT SCIENCE, VOL. 94, NO. 4, 25 FEBRUARY 2008

And then I will also show another example where, you can try to see, how you can track different things that are happening. This is a alloy where, if you take starting materials like cobalt and iron, you can end up in a sono chemical process, a alloy which is stable even at room temperature on oxidation gives a cobalt ferrite. So, this can go hand in hand with other experimental techniques, which clearly gives you idea about the alloy formation, which is actually reported for the first time.

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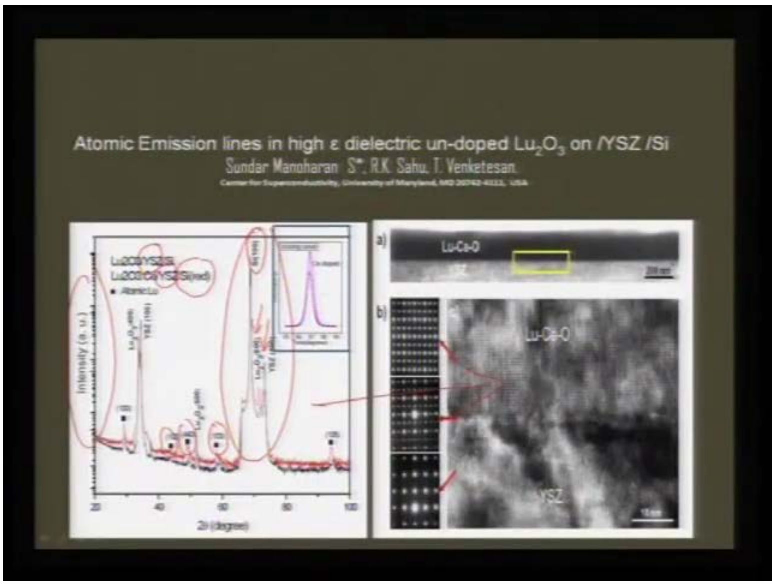

Atomic Emission lines in high ε dielectric un-doped Lu_2O_3 on /YSZ /Si

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Another point that I want to emphasize before I close is that, we need to be very careful about the X-ray patterns that we are producing. I have rounded it here in this cartoon as a log plot, because when you try do single studies, if you do it at linear intensity, you would see only the peak of silicon being very huge and the system peak will almost be absent. Therefore, if you want to really map the epitaxy then you need to plot it in log scale, instead of linear intensity only then you will see the comparable values.

For example, here is a situation I have, deposited a lutetium oxide on silicon or on YSZ, so in that case, very close to the silicon substrate reflection, you would see lutetium oxide and YSZ reflections coming. If this is the way it shows then you can say that, it is epitaxially growing but then that is not enough. Because, you also see in the log scale, several small peaks which are coming, these are not commensurate to your 1 0 0 peak, which are showing 1 0 3, 4 4 0.

Therefore, we can, although a very impressive TEM is there then you have to understand that, it is showing some polycrystalline feature and it is not totally a epitaxy. Therefore, this is very important and the other thing that will also tell, whether it is a real epitaxy is nothing but your rocking curve. Each of this curve, we can try to do a rocking curve more, which will give you idea about, the width of this rocking curve will tell how good the texture or growth of these films are. So, rocking curve is one important accessory in thin films for you to map, whether you are growing a textured film.

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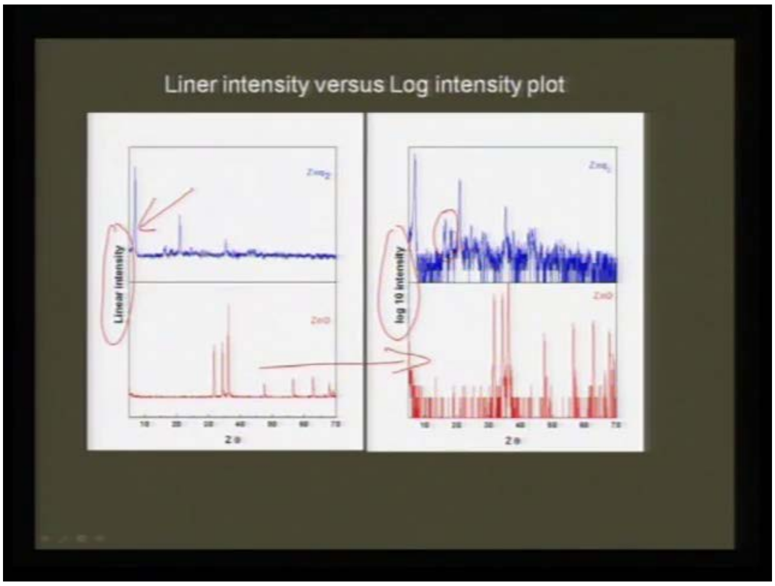

Liner intensity versus Log intensity plot

And also, this is another example where, I am trying to quote for a organic molecule, how these patterns can give useful information. In linear intensity versus log intensity scale, you can see, how the same pattern changes, but what is the advantage, you can easily map whether any purity ion is there. Therefore, when we record any X-ray pattern, we should always look at the log intensity scale, to see whether any minute impurities are there. For example, in this case, these are very small peaks does not come into the prominence, but in a log intensity, these are projected much easier, therefore we can see whether any secondary phase can come out.

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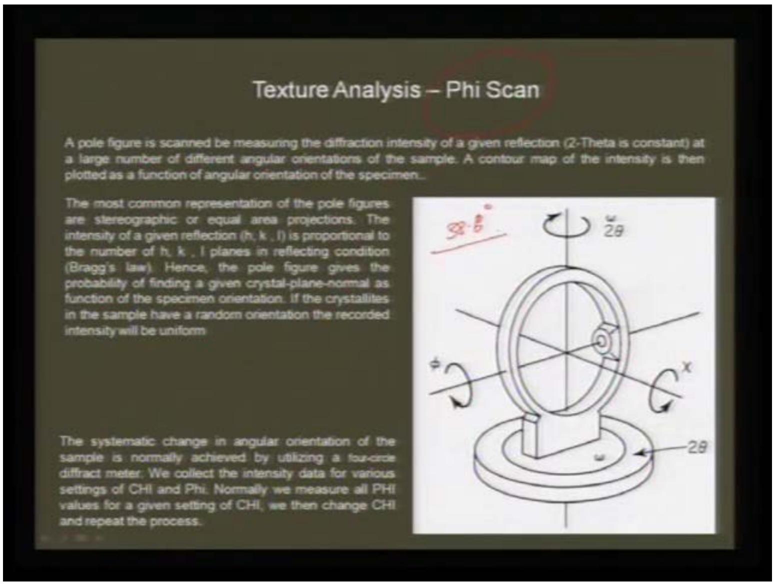

Texture Analysis – Phi Scan

A pole figure is scanned be measuring the diffraction intensity of a given reflection (2-Theta is constant) at a large number of different angular orientations of the sample. A contour map of the intensity is then plotted as a function of angular orientation of the specimen..

The most common representation of the pole figures are stereographic or equal area projections. The intensity of a given reflection (h, k , l) is proportional to the number of h, k , l planes in reflecting condition (Bragg's law). Hence, the pole figure gives the probability of finding a given crystal-plane-normal as function of the specimen orientation. If the crystallites in the sample have a random orientation the recorded intensity will be uniform

The systematic change in angular orientation of the sample is normally achieved by utilizing a four-circle diffract meter. We collect the intensity data for various settings of CHI and Phi. Normally we measure all PHI values for a given setting of CHI, we then change CHI and repeat the process.

Another important one, I may not able to cover in this lecture but then certainly I will be able to cover in future lectures is the phi scan, which is used for mapping the orientation or textured growth of your thin film samples. Suppose, I have a peak at 38.6 degrees then I can try to see, whether it is texturally growing in a single crystal substrate for which phi scan issues.

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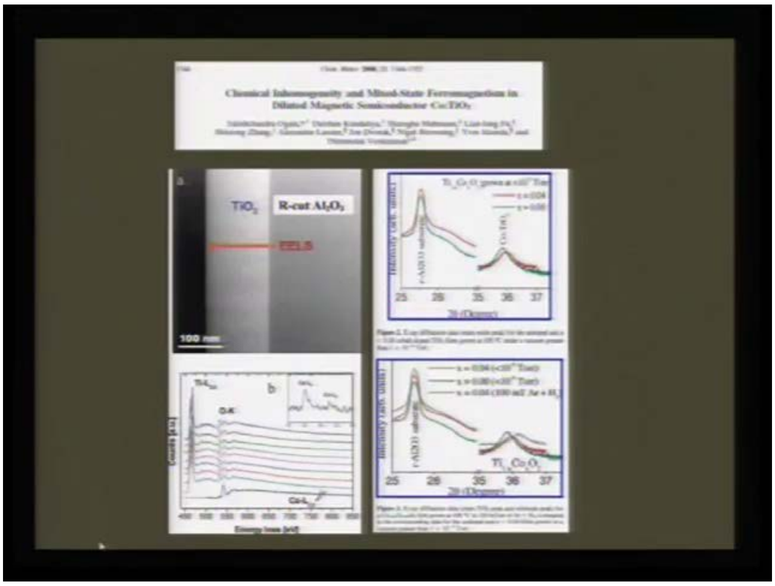

Chemical Inhomogeneity and Mixed-State Ferromagnetism in Diluted Magnetic Semiconductor Co:TiO$_2$

I will come to this in the subsequent one.

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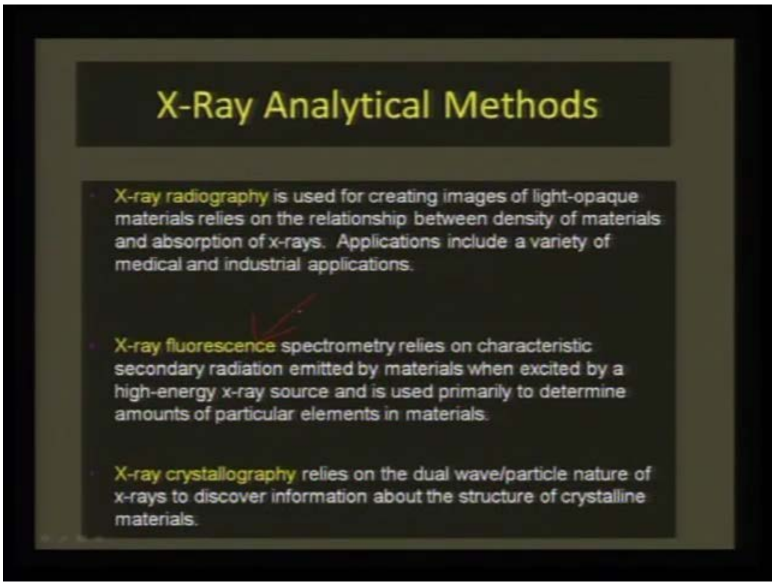

X-Ray Analytical Methods

- X-ray radiography is used for creating images of light-opaque materials relies on the relationship between density of materials and absorption of x-rays. Applications include a variety of medical and industrial applications.
- X-ray fluorescence spectrometry relies on characteristic secondary radiation emitted by materials when excited by a high-energy x-ray source and is used primarily to determine amounts of particular elements in materials.
- X-ray crystallography relies on the dual wave/particle nature of x-rays to discover information about the structure of crystalline materials.

And there are other examples also, which I may have to skip for want of time in this lecture. But, just want to tell you that, there are three things that are fundamentally used using X-rays, one is X-ray radiography in medical applications. But, X-ray fluorescence is also another avenue where, you can quantitatively get to know, how many metals are there or what is the composition of the metal using the same X-ray technique, apart from the X-ray crystallography.

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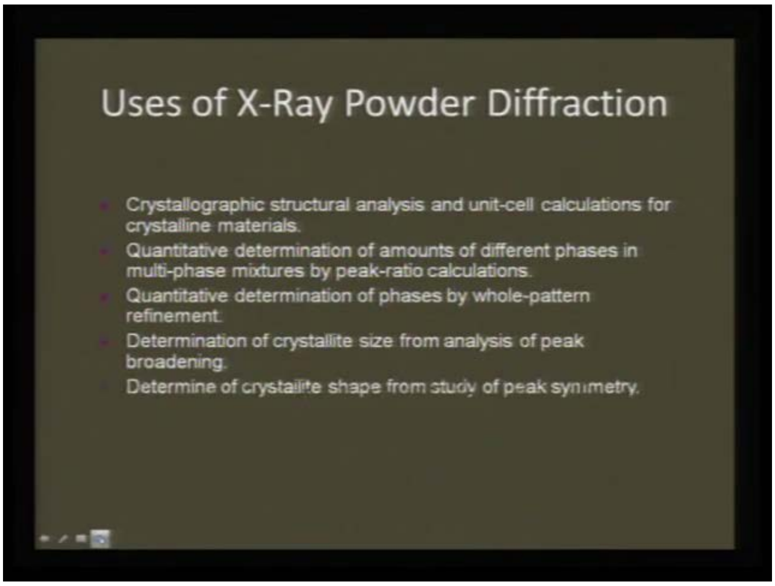

Uses of X-Ray Powder Diffraction

- Crystallographic structural analysis and unit-cell calculations for crystalline materials.
- Quantitative determination of amounts of different phases in multi-phase mixtures by peak-ratio calculations.
- Quantitative determination of phases by whole-pattern refinement.
- Determination of crystallite size from analysis of peak broadening.
- Determine of crystallite shape from study of peak symmetry.

So, as I pointed out to you, there are several X-ray powder diffraction features that becomes useful.

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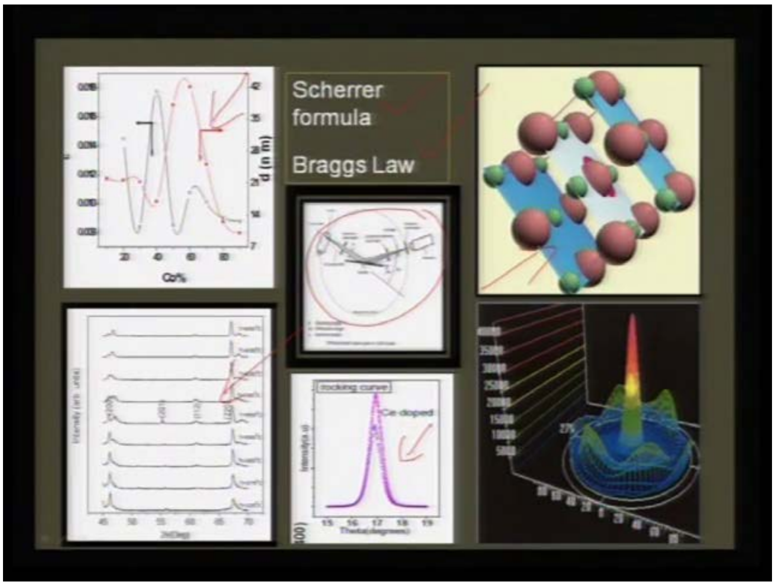

Scherrer formula

Braggs Law

And in this lecture, I have basically covered few things to bring it to your focus, one is about, how this whole thing works and the two important laws that can be verified that is, Scherrer formula and Bragg’s law, the information that you get out of it. And try to understand, how your crystals are growing and I have told you about, how we can use in situ high temperature diffraction. Measurements can be made to understand the phase transition and also the strain effects that can be correlated to other properties. And in thin films, I also try to show one passing example of, how we can map the epitaxial growth. So, in the next few lectures, we will also look the applications of this X-ray in perspective with other case studies. And not only that, we will be looking at other spectroscopic tools in this particular module.