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On
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-26

by…
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Hello everyone.

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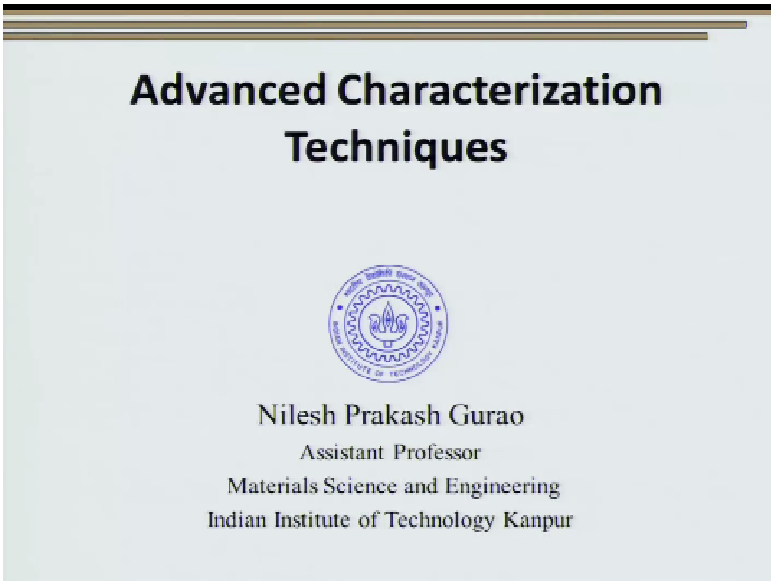

Advanced Characterization Techniques

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Welcome to the second class on the advance characterization techniques module compressing with X-ray diffraction. In the last class we had understood how x-ray is can be used to study this structure of materials and what exactly constitutes diffraction.

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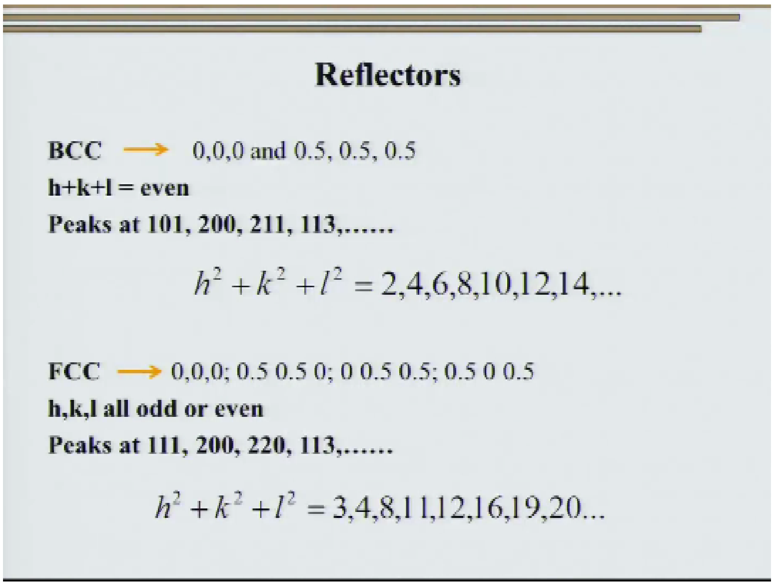

Reflectors

BCC → 0,0,0 and 0.5, 0.5, 0.5

h+k+l = even

Peaks at 101, 200, 211, 113,……

$$h^2 + k^2 + l^2 = 2,4,6,8,10,12,14,...$$

FCC → 0,0,0; 0.5 0.5 0; 0 0.5 0.5; 0.5 0 0.5

h,k,l all odd or even

Peaks at 111, 200, 220, 113,……

$$h^2 + k^2 + l^2 = 3,4,8,11,12,16,19,20...$$

We had ended up calculating the reflection condition for various test line structure and figured out that for BCC the condition for diffraction is that h + k + l = even and for FCC we need h, k, l all even or all odd. Having understood the theoretical basis of X - ray diffraction in terms of the white sphere and reciprocal space, in the present lecture, we are going focus on different experimental techniques for doing X - ray diffraction.

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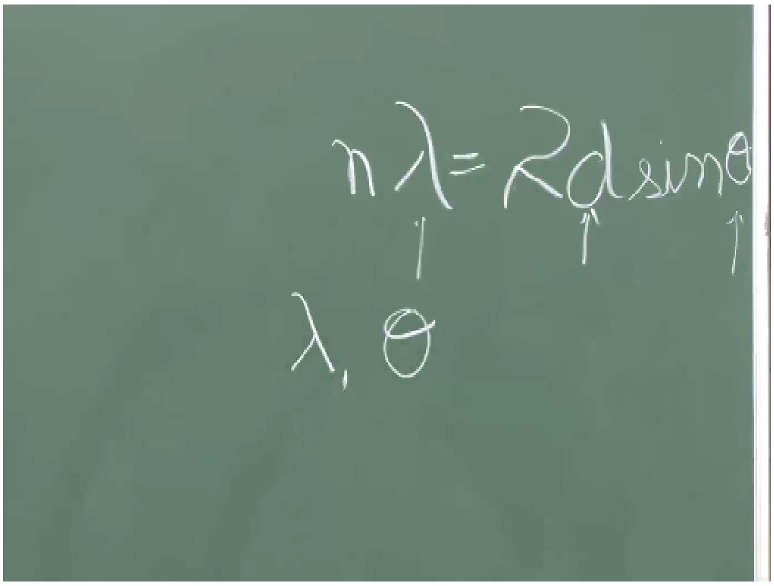

We know that the entire technique all the techniques compressing of X - ray diffraction have one thing in common and that is essentially the Bragg’s law which goes as. So we know that for a given crystalline material the d is related to the lattice parameter. At the same time, the wave length λ and the angle θ are the two variables. So all the diffraction techniques essentially deals with either varying λ or θ. In order to have a look at those diffraction techniques let us look at this table.

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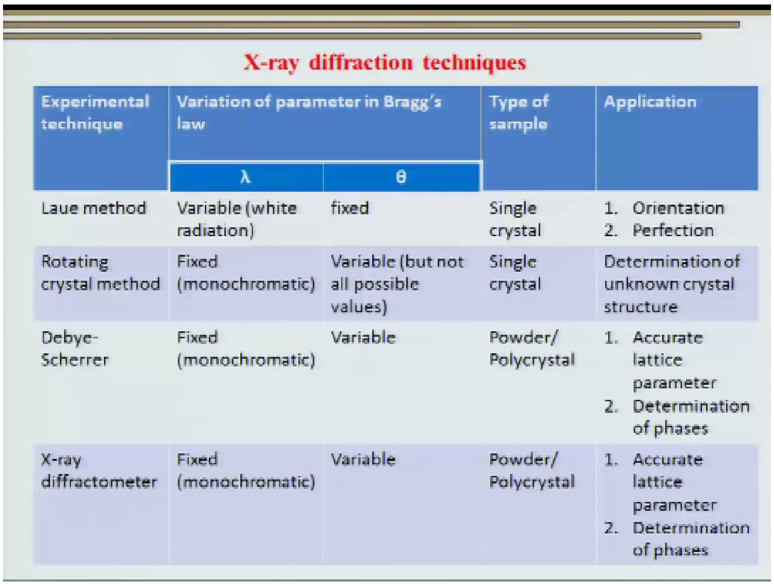

X-ray diffraction techniques

Experimental technique	Variation of parameter in Bragg's law		Type of sample	Application
	λ	θ		
Laue method	Variable (white radiation)	fixed	Single crystal	1. Orientation 2. Perfection
Rotating crystal method	Fixed (monochromatic)	Variable (but not all possible values)	Single crystal	Determination of unknown crystal structure
Debye-Scherrer	Fixed (monochromatic)	Variable	Powder/ Polycrystal	1. Accurate lattice parameter 2. Determination of phases
X-ray diffractometer	Fixed (monochromatic)	Variable	Powder/ Polycrystal	1. Accurate lattice parameter 2. Determination of phases

The first and foremost that was developed was the Laue method which is essentially used to characterized single crystalline material. As you can understand that is single crystalline material has a fixed reciprocal space and to get diffraction is much more difficult compared to a polycrystalline material where in you would expect that all different grains will have corresponding reciprocal space which is of all different orientations. Therefore, we need to use of variable or white radiation.

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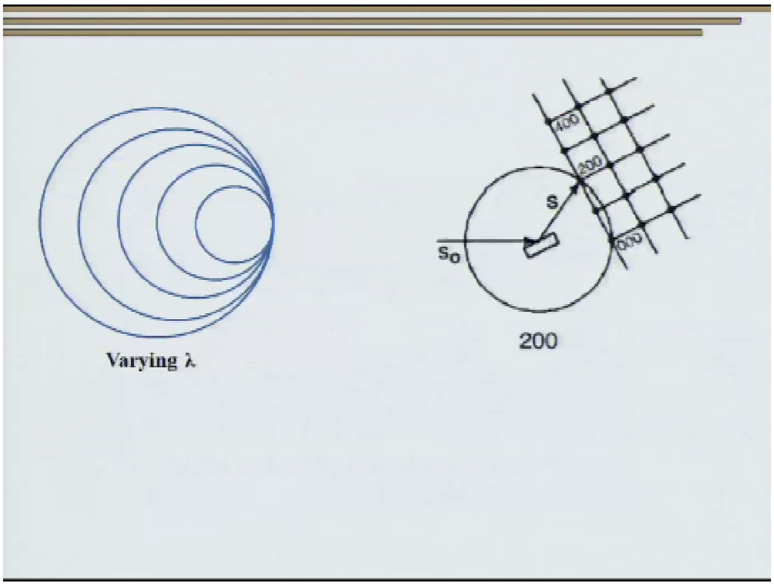

Now the white radiation essentially ensures that we have a white sphere with varying radius. This essentially ensures that the changes of the white sphere meeting some part of the reciprocal space or reciprocal point is much, much higher, and hence the probability of diffraction increases. Particularly this is very important for single crystalline materials where in diffraction condition is very stringent.

Having said that, even more challenging case is varying we do not have any idea about the existing crystal structure of the material. In that case, not only the reciprocal space orientation is unknown, the reciprocal space itself is unknown, or other the reciprocal space vectors are unknown. In order to map this reciprocal space generally we use what is known as a rotating crystal method.

Wherein we use a fixed wave length and the sample is angle or θ is varied in two most of the values. This is essentially used to determine the unknown crystal structure. I would like to mention that though it is much easier for me to write it here that rotating crystal method give us information about determination of unknown crystal fixed wavelength λ and by varying angle θ it is quite complicated and field in itself altogether.

What most of the time we end up using in a laboratory scale X - ray diffraction is essentially the device error or normal powder diffractometer, in which case the wavelength is fixed and the θ is varied. Now this technique we use routine need to characterized powders as well as polycrystalline materials. This kind of technique provides a wealth of information about the lattice parameter, the faces present and various other things which I will demonstrate in the later few slides.

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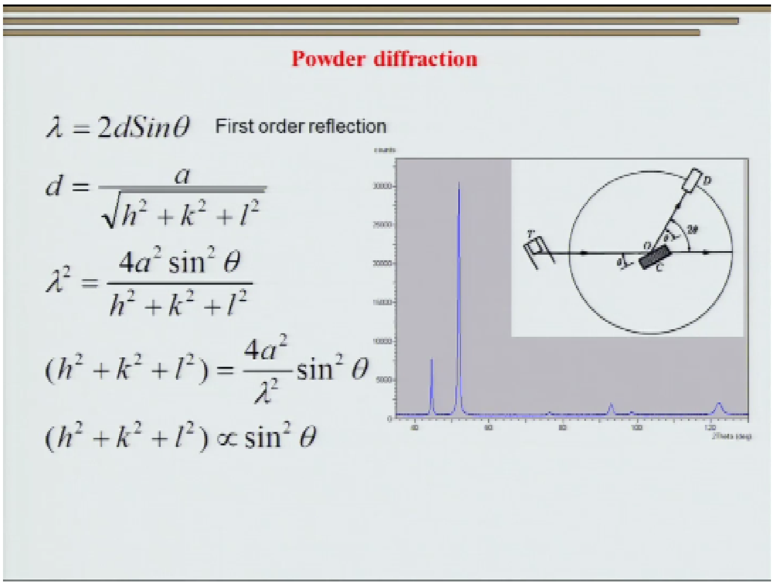

Powder diffraction

$\lambda = 2dSin\theta$ First order reflection

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\lambda^2 = \frac{4a^2 \sin^2\theta}{h^2 + k^2 + l^2}$$

$$(h^2 + k^2 + l^2) = \frac{4a^2}{\lambda^2}\sin^2\theta$$

$$(h^2 + k^2 + l^2) \propto \sin^2\theta$$

So we know that a normal X - ray powder diffractometer that we use in our laboratories gives us output in the form of intensity versus 2θ. Another question that arises and is very important is we talked about Bragg’s law, and we all have recollected by now that Bragg’s law deals with nλ= 2d sinθ. So the obvious question arise is from where does we get this value of 2θ.

So I would again like to drawback your attention to the first figure that we have seen in the last class. Here in we see that the detector makes an angle of 2θ with the incident beam. Therefore, if the sample is moving at an angle of θ the detector is essentially moving at an angle of 2θ. Therefore, whenever we do normal powder diffraction we essentially end up the team or I versus 2θ plot from this plot we have to calculate θ and use it in the Bragg’s law.

However, in order to understand which peaks are present in the diffractive graph which is shown over here we can do simple calculations, again we go back to the Bragg’s law and if we rewrite it considering first order reflection we do get λ = 2d sinθ, and then substituting D for cubic crystals it is $a/h^2 + k^2 + l^2$, and then substituting and rearranging the terms we do get that our $h^2 + k^2 + l^2$ is proportional to $\sin^2\theta$.

So once you obtain a diffractogram essentially we calculate the θ at which the peaks are present, and then calculate the ratio of $\sin^2\theta$. However, I would like question you that this is applicable only for single face materials, in case of multi-face materials one needs to use software that can take care of all the peaks which are present in the diffractogram. Having said that I hope you have noticed that the diffractogram is characterized by a couple of things.

We see a various intensity of the peaks as well as the peak broadening and all this gives us a lot of information about the structure of the material.

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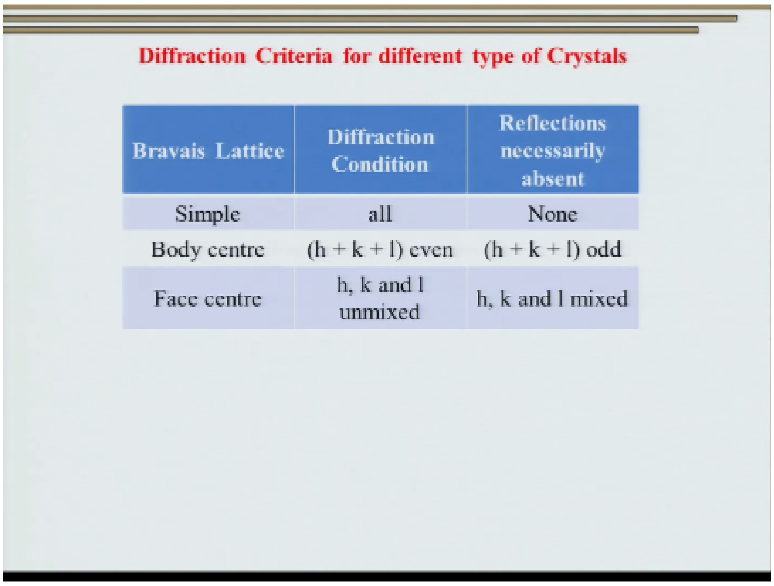

Diffraction Criteria for different type of Crystals

Bravais Lattice	Diffraction Condition	Reflections necessarily absent
Simple	all	None
Body centre	(h + k + l) even	(h + k + l) odd
Face centre	h, k and l unmixed	h, k and l mixed

So let us go back and concentrate on powder diffraction. So depending on the Bravais lattice various diffraction conditions can easily be calculated, and we find out that for simple cubic all diffractions are possible while for body centred h + k + l = even are necessary present while h + k + l odd are necessarily absent while for face centre cubic h, k, l unmixed are always present while h, k, l mixed are always absent.

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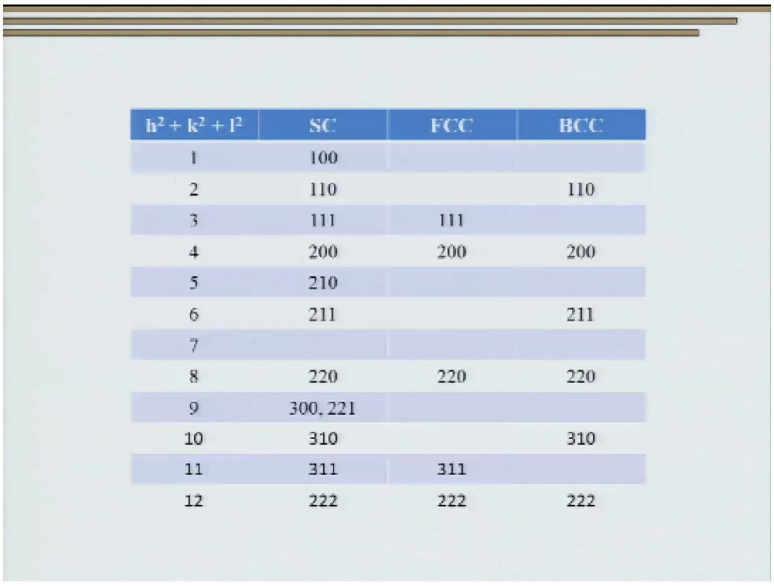

$h^2 + k^2 + l^2$	SC	FCC	BCC
1	100		
2	110		110
3	111	111	
4	200	200	200
5	210		
6	211		211
7			
8	220	220	220
9	300, 221		
10	310		310
11	311	311	
12	222	222	222

I have just noted down different values of $h^2 + k^2 + l^2$ and the kind of peaks that we get in the simple cubic, face centre cubic, and the body centre cubic crystal. Here in we see that the simple cubic material shows a peak rich diffractogram meaning that we have plenty of peaks in the diffractogram of a material that has simple cubic crystal structure. However, when we go to the face centre cubic structure we see that the diffractogram is not that heavily populated.

Another important thing that we notice is that we do have two peaks which are closed and the third the peak is far of this is essentially because of the diffraction condition or the reflector set are present in a FCC, wherein we do get reflection from 3, 4, 8, 11, 12 and 16. However, when we look at BCC we do see that the reflection condition is essentially 2, 4, 6, 8, 10 which essentially indicates that the peaks equidistant in the diffractogram for BCC materials.

Having said that the point that I want to emphasize is that just looking at the diffractogram of single face material we can make a guess about the crystal structure of the material. Another important thing that I would like to bring to your notice on which is generally missed in most of text books is that we do not get a peak, even in simple cubic case for $h^2 + k^2 + l^2 = 7$. And this is essentially because the sum of more three squares adds up to 7. So that is nothing so special about this number.

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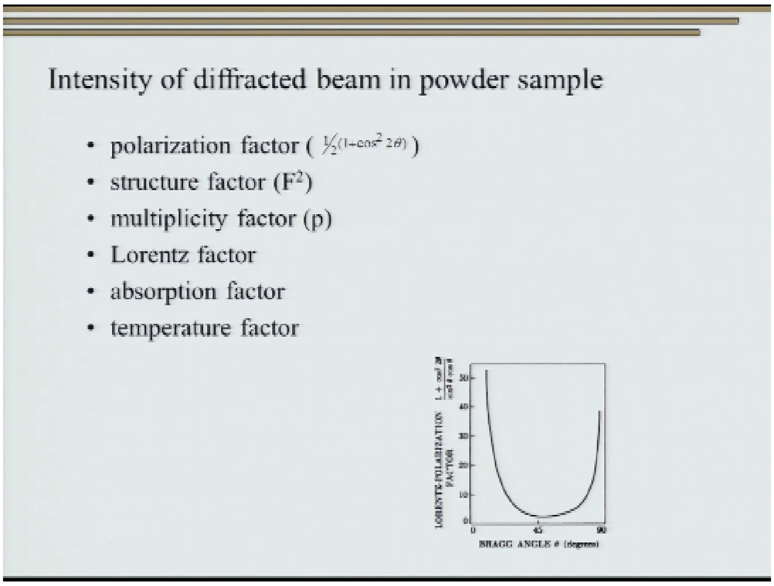

Intensity of diffracted beam in powder sample

- polarization factor ($\frac{1}{2}(1+\cos^2 2\theta)$)
- structure factor (F^2)
- multiplicity factor (p)
- Lorentz factor
- absorption factor
- temperature factor

Having said that you must have noticed the intensity of the peaks which I had shown in the earlier slide. Here in after gaining knowledge about the kind of reflections and the crystal and Bravais lattice, I hope you can make a guess that this material showing two peaks very close separated by a third peak, and again two peaks close separated by another peak corresponds to a FCC crystal structure with reflections at 3, 4, 8, 11, 12, 16 and corresponding to 111, 200, 220, 113 and so on.

Having said that this is the peak of nanocrystalline nickel which we will see in some time. So as I had already mentioned if you look at the intensity of the diffracted beam for a powder sample it gets affected by the polarization factor which we had considered in the last class. At the same time we also looked at the structure factor which essentially determines what is going to be the intensity of your diffracted peak.

Another important parameter which we had not touched upon by now is the multiplicity factor. In this regard, I would like to point your attention to the 100 peak, and the 111 peak in cubic crystals. So if you look at 100 peak the multiplicity of 100 peak is 6 while that of 111 peak is 8. Therefore, we can believe that if we consider only the multiplicity factor the ratio of intensity of the 111 peak will be 8/6 times that of 100 peak.

Another important parameter that affects the diffraction condition is the Lorentz factor which is essentially due to the fact that diffraction occurs not only exactly at the Bragg angle, but at angle slightly away from the Bragg angle, the kind of polarization because of Lorentz contribution as well as the original polarization factor is generally combined together and when plotted together shows this kind of a variation.

So whenever we compare different diffractogram or different peaks in the same diffractogram we have to account for the Lorentz factor. Another important parameter that generally affects diffraction and we tend to in which is generally ignored is the absorption factor. We all know that whenever X-rays are incident on a material part of it gets absorbed and therefore, there is an additional path length that is to be considered.

However, in most materials the absorption of X-rays is not significant and it can be easily neglected. One important parameter that is not really valid for room temperature deformation or rather room temperature X-ray diffraction, but becomes very important at high temperature is the temperature factor. We all know that all the calculation for structure factor and X-ray intensity is placed on atom s sitting at a particular point in the crystal structure.

However, we all know that the atoms are not actually sitting at a particular point in the lattice, but they are constantly vibrating. Now this vibration of atoms is directly proportional to the temperature and hence with increasing temperature there is a decrease in the intensity of the diffraction pattern. And this becomes particularly important for knowing high temperature study involving these transformations.

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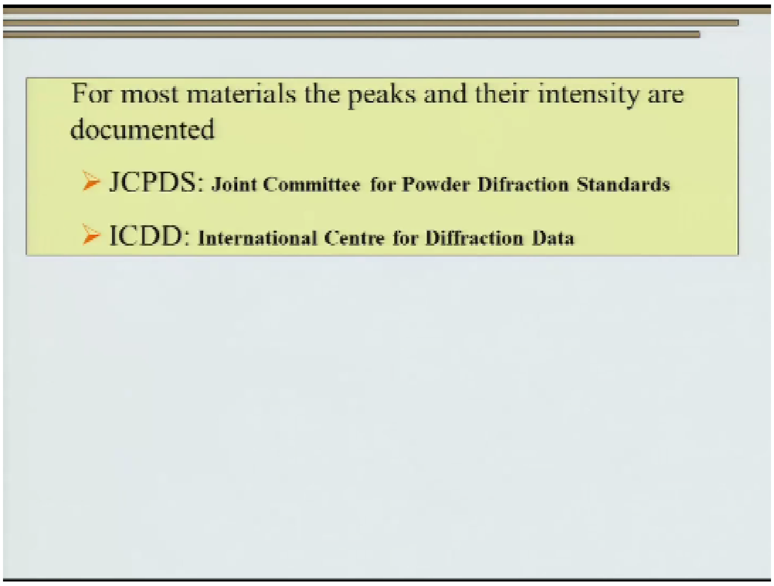

For most materials the peaks and their intensity are documented

- JCPDS: **Joint Committee for Powder Difraction Standards**
- ICDD: **International Centre for Diffraction Data**

Having understood the various factors which govern the intensity of the diffracted beam will now shift our focus and have a look at the actual way we go about indexing. So all the peaks in the diffractogram can be indexed manually and then we can go back and compare them with a look of table. So the earlier look of tables which comprised of all the database was maintained by the joint committee for powder diffraction standards.

So these are like standard charged wherein for specific materials all the diffraction information is tabulated. This committee has now being renamed or recrystalled into the international centre for a diffraction data. So this database contains all the data pertaining to all the available material which have been identified till date.

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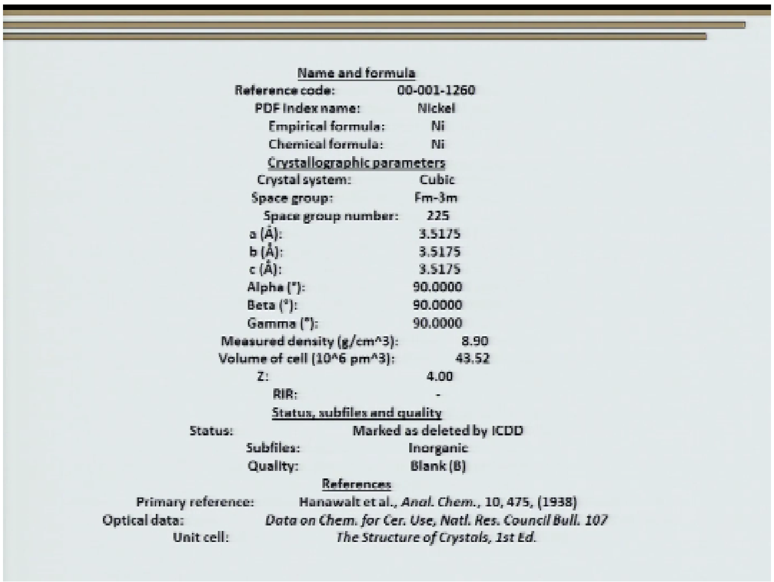

Name and formula

Reference code:	00-001-1260
PDF Index name:	Nickel
Empirical formula:	Ni
Chemical formula:	Ni

Crystallographic parameters

Crystal system:	Cubic
Space group:	Fm-3m
Space group number:	225
a (Å):	3.5175
b (Å):	3.5175
c (Å):	3.5175
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Measured density (g/cm^3):	8.90
Volume of cell (10^6 pm^3):	43.52
Z:	4.00
RIR:	-

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic
Quality:	Blank (B)

References

Primary reference:	Hanawalt et al., *Anal. Chem.*, 10, 475, (1938)
Optical data:	*Data on Chem. for Cer. Use, Natl. Res. Council Bull. 107*
Unit cell:	*The Structure of Crystals, 1st Ed.*

Having said that I will now give you a glimpse of how does one of the file looks in the database. Since, we are discussing on nickel I have chosen the file for nickel, and herein you can see all the information contained in the file. So in addition to the lattice parameter and the angles we also see that other important information like the density, volume of the unit cell are also mentioned.

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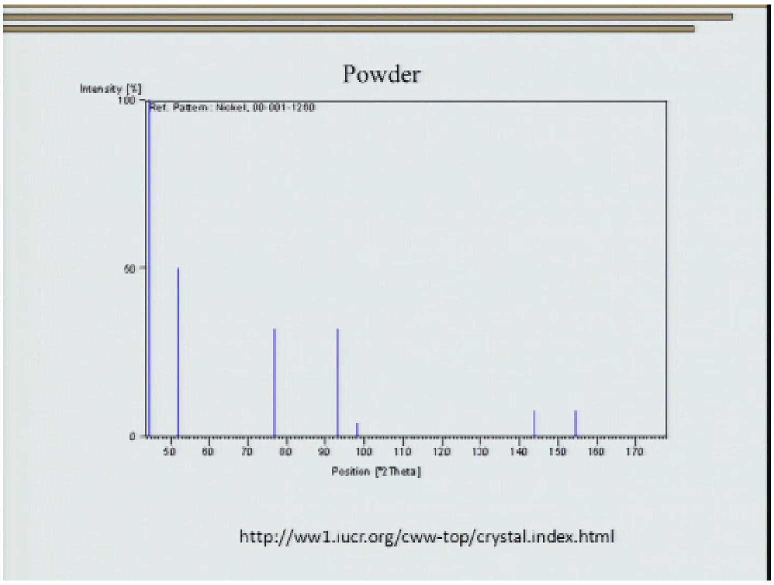

Powder

http://ww1.iucr.org/cww-top/crystal.index.html

Having said that the most important parameter that we get from this database is what is known as the stick pattern. So this essentially shows the theoretical variation of intensity with respect to the θ value for indeed diffractogram. Herein we can see that the different peaks shows different intensity. Now the variation of intensity is directly proportional to the structure factor of the corresponding orientations.

Since, we are talking about FCC nickel we can see that the one on one peak which is the highest structure factor and multiplicity shows the highest peak. And the other peaks namely the 200, 220, 113 and the remaining peaks also show intensity in accordance with the structure factor and multiplicity calculations. Now these are theoretical intensity variation shows a nice match with the theoretical calculations, because they are obtained on random powder samples.

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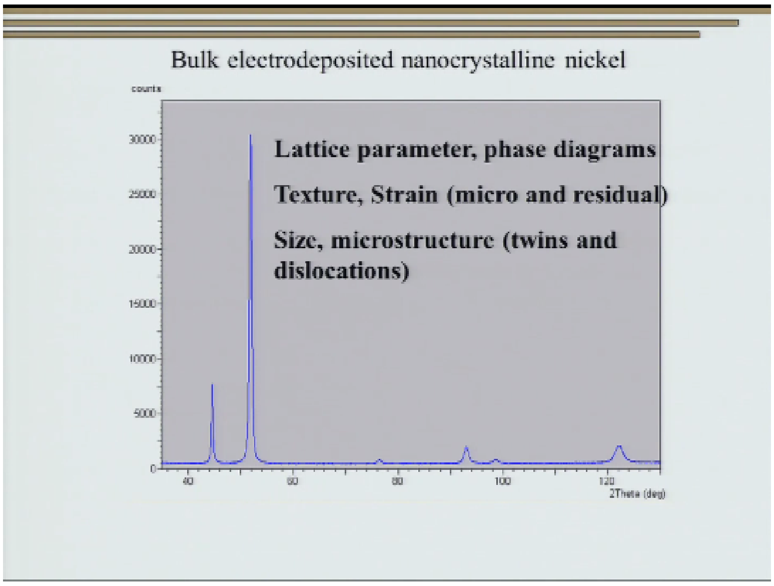

Bulk electrodeposited nanocrystalline nickel

Lattice parameter, phase diagrams

Texture, Strain (micro and residual)

Size, microstructure (twins and dislocations)

However, we know that most of the materials that we use are hardly anything but random and this is what is shown in our nickel slide. So this nickel which I was showing in the last few slides essentially is a bulk electro deposited nanocrystalline nickel. So we see a quite of few important things in the diffractogram. The first and foremost important thing that we see in the diffractogram is that the peaks are reflected the strong peaks that we saw in the earlier stick pattern are replaced with broaden peaks.

Therefore, we do get diffraction at not just the Bragg angle, but at a angle slightly away from the Bragg angle. This essentially is due to the mosaic structure of the crystals. In this particular case, this is essentially due to the nanocrystalline structure of the nickel sample under consideration. Another important observation that we make is the change in intensity level of the different peaks.

In the stick pattern we do see the first peak namely the one and one peak is the strongest peak followed by the other peaks. However where we look at this diffractogram we do see that the one on one peak is no longer the strongest peak, however the 200 peak shows the highest intensity this essentially indicates that the sample under consideration shows preferred crystographic orientation which is also known as texture.

Another important point that is to be mentioned is that the exact lattice parameter of the nickel obtained from this diffractogram is slightly different from the one that was expected in the stick pattern. In addition, we see that the intensity ratio is also different. All these indicate towards the presents of texture, strain, as well as broadening due to size and micro structure.

In addition, there are techniques which claim that they can get an estimate of operation of training, stacking faults, and even dislocations using the diffractogram. We are not going to discussed all these techniques in details in the present lecture, but I do want to emphasize that X - ray diffraction which is generally taken as a normal meandering tool is a very powerful tool, and when complimented with other microscopic stools can provide you wealth of information regarding the microstructure of the material.

Another we must remember that encounter is powder diffraction, but we see that we end up using the material mostly all polycrystalline material bulk materials for doing X - Ray diffraction, and it gives us the same kind of information as we do get in fact much more than what we get in case of power diffraction.

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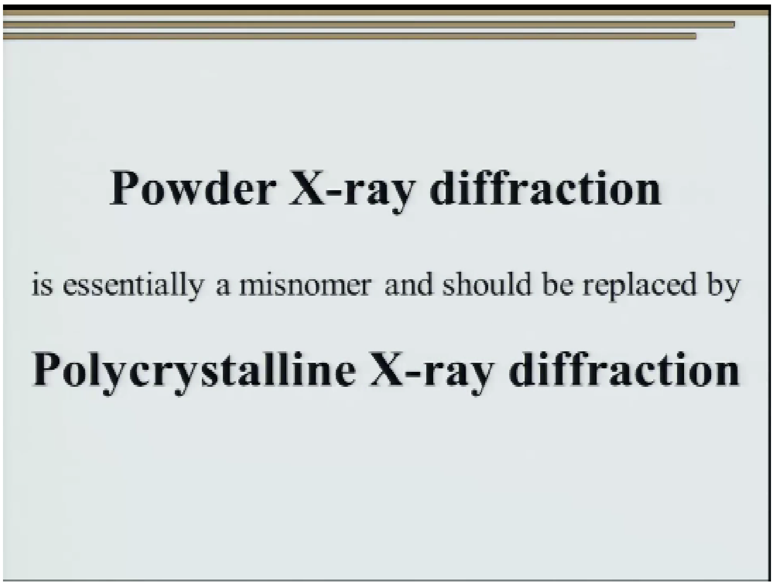

Powder X-ray diffraction

is essentially a misnomer and should be replaced by

Polycrystalline X-ray diffraction

And hence I personally believe that power X - Ray diffraction is essentially misnomer and it should be replaced by polycrystalline X - Ray diffraction. Since polycrystalline X - Ray diffraction encompasses all the information pertaining to the size, strain and crystographic texture which is relevant to a given microstructure. Having seen and covered a broad spectrum of X - Ray diffraction and what all capabilities that X - Ray diffraction normal laboratory scale X - Ray diffraction study.

Then do we will now focus and try to understand what are the actual hardware or the instrumentation that makes it possible. So we will go very slowly in this part and try to understand how actually it works. So when we go to a normal X - Ray diffraction facility we come across what is known as a diffractometer. A diffractometer comprises as we all know we need a source which on the X – Rays.

Having said that we just cannot to take this. We knew to massage them, kind of modify them, to get them in a particular shape, particular size, and particular coherence so that we get proper Bragg's diffraction. Having said that once our X - Rays interact with the matter we also need to collect the signal, and then use the signal to analyze of results.

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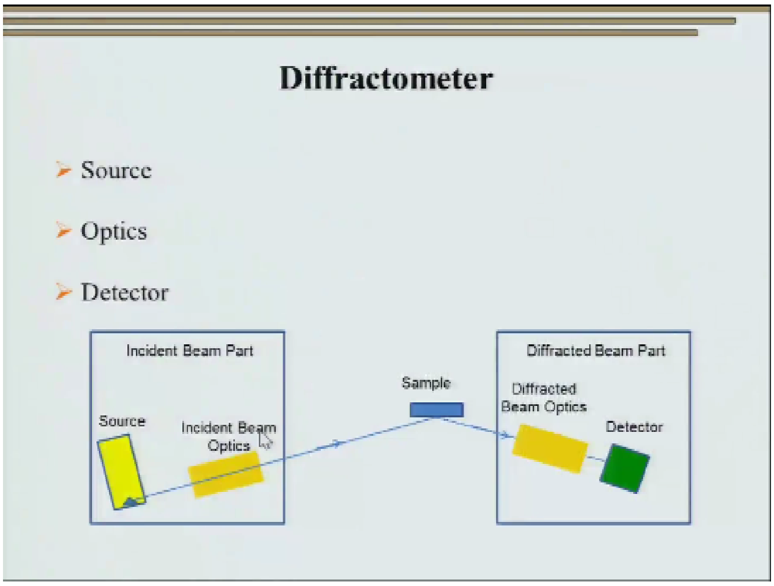

Diffractometer

- Source
- Optics
- Detector

This is what is shown here in a small schematic. So we see we need a source which are the rate X – Ray, we need what is known as the incident beam optics to massage the X - Rays and produce X - Rays in the proper format in which we want then the X - Ray is made to interact with the sample, and then what all signal we get essentially passed through the diffracted beam optics again to ensure that we are looking at a particular wavelength, and then finally it goes to the detector.

I would like to again and again mention that the entire exercise of going for incident and diffracted beam optics is to ensure one that we are looking at the wavelength of interest, because most of the studies said we are looking at the wavelength has to be constant. And second we are ensuring that the profile of the beam remains the same, therefore, the need of the optics in X-ray diffraction.

Before we move ahead let us look at the diffractometer itself, so I hope you have appreciated the diffractometer is nothing but an assembly which comprises of a source, the detector, the optics and the sample.

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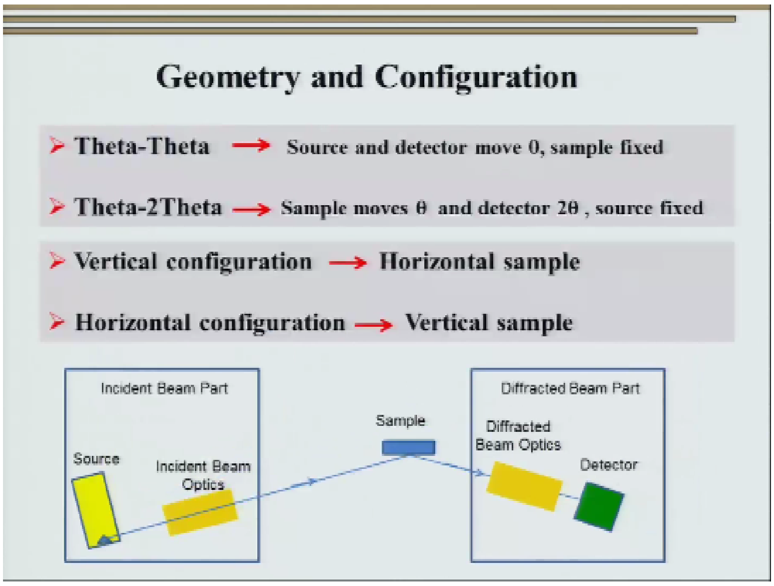

Geometry and Configuration

- **Theta-Theta** → Source and detector move θ, sample fixed
- **Theta-2Theta** → Sample moves θ and detector 2θ , source fixed
- **Vertical configuration** → **Horizontal sample**
- **Horizontal configuration** → **Vertical sample**

So a diffractometer can be obtained essentially in what is known as a θ –θ geometry. Now what is θ-θ geometry, we have gone and we have looked at the diffraction condition time and again. So let me just go back and let us have a look at the diagram which we have seen for hump ting times. So let us focus on this diagram, and herein we can see that as I had mentioned that our detector is moving at through θ and the sample is fixed over here.

So there are two ways of doing it, so one is you move your sample which is over here at θ and the detector also by θ. This will essentially ensure that your detector is still maintaining 2θ with the incident beam. So this is known as the θ-θ geometry, so essentially this can be done by keeping your sample fixed and moving the tube, and the detector both at θ-θ. So this is known as θ-θ geometry.

In the other case what we do is, we fix the tube and move the sample at θ and the detector at 2θ. So this is essentially known as the θ-θ geometry which is shown over here. Now another configuration that we use on a routing scale is the vertical configuration and the horizontal configuration. The vertical configuration as the name suggest includes all your source and detector on a vertical circuit.

This essentially ensures that your sample is on a horizontal sample holder. This essentially ensures that you can study powders very easily. However, if you are studying thin films or carrying out texture analysis, you may like to use a horizontal configuration which essentially ensures that your sample is vertical. Having said that the diffractometer essentially has to ensure that the diffraction condition is satisfied.

Not only that the diffraction condition has to be satisfied at not just the Bragg's angle, but at the Bragg angle as well as at different inclinations of the sample, as well as the rotation of the sample to improve the statistics. Therefore, a diffractometer consist of a sample which consist of a sample holder that can give different kind of rotations to the sample and their consideration. So we have what is known as a three circle and a four circle diffractometer.

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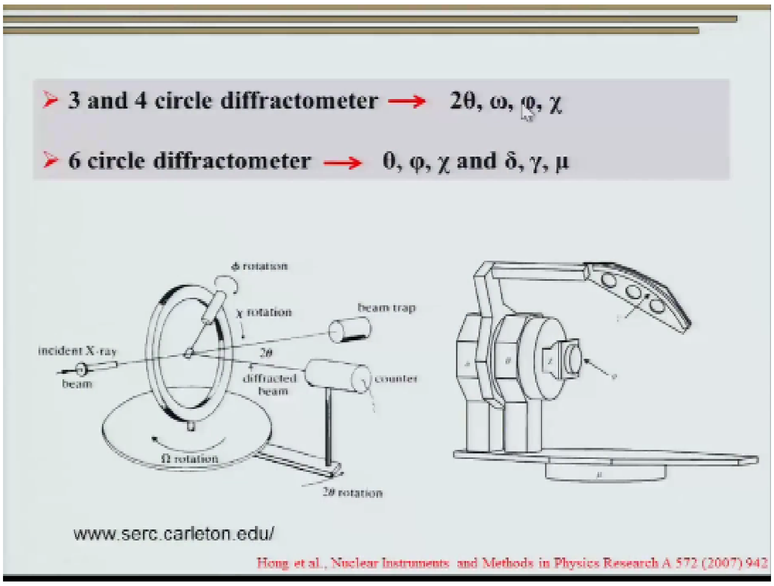

- 3 and 4 circle diffractometer → 2θ, ω, φ, χ
- 6 circle diffractometer → θ, φ, χ and δ, γ, μ

www.serc.carleton.edu/

Hong et al., Nuclear Instruments and Methods in Physics Research A 572 (2007) 942

In a three circle diffractometer the 2θ and ω, ω corresponds to the θ which essentially ensures that the two angles are corresponding to the moment of the detector and the moment of the sample. While the angle φ and χ correspond to the rotation of the sample about the normal axis and the rotation of the sample about an axis which is perpendicular, which is going through the sample which is known as χ.

This is what is shown in the figure over here. So we see that in the case if 2θ and ω are c it will be a three circle diffractometer, while in case they are uncoupled it will be a four circle diffractometer. Having said that state of the at synchrotron sources which we are going to talk about in the next few slides and the neutron sources which we are again going to talk in the last class later can use as complicated as six circle diffractometers which comprise of θ, φ and χ for the sample Δ and γ rotations for the detector.

As well as the μ rotation for the entire assembly. Let us not go into the details of six circle diffractometer, but the point that I want to pass on is that the diffraction condition is not just simple θ-θ which we θ-θ or θ2θ two circle diffractometer. But in order to do advanced studies and do proper sample alignment we do need this flexibility of rotating the sample in different ways. And therefore, the need of three circle and four circle diffractometers.

I am sure that you can find out course on crystographic texture in NPTEL courses wherein this will be covered in details. At the same time in a course compressing of thin film diffraction we will also find the great use of using a four circle diffractometer.

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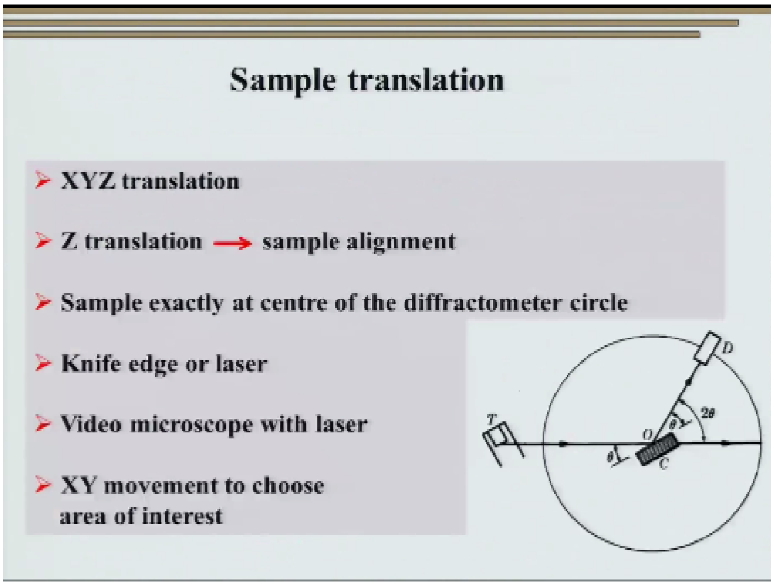

Sample translation

- XYZ translation
- Z translation → sample alignment
- Sample exactly at centre of the diffractometer circle
- Knife edge or laser
- Video microscope with laser
- XY movement to choose area of interest

Having said that about we talked a lot about kind of rotation of the sample and all, but the most important thing in my opinion or further matter for diffraction to occur is the alignment of the sample. At the same time the ability to look at the region of interest. Many times we may find some particular region of interest in the given sample and therefore, the XYZ translation is very important.

The XY translation helps us to move and focus of X - Rays to the point of interest, while the Z translation essentially ensures that the sample follows the alignment exactly. So if the sample is exactly at the centre of the diffractometer as seen what here, we see that diffraction condition is satisfied. If it is not there at the centre and slightly above or below it, we may see that all the peaks in the diffractogram may be shifted.

And this may be just an artefact of sample with alignment. Now the sample miss alignment can be taken care of by using a knife edge or a laser. State of the diffractometers use a video microscope with laser to align the sample in a particular, align the sample perfectly.

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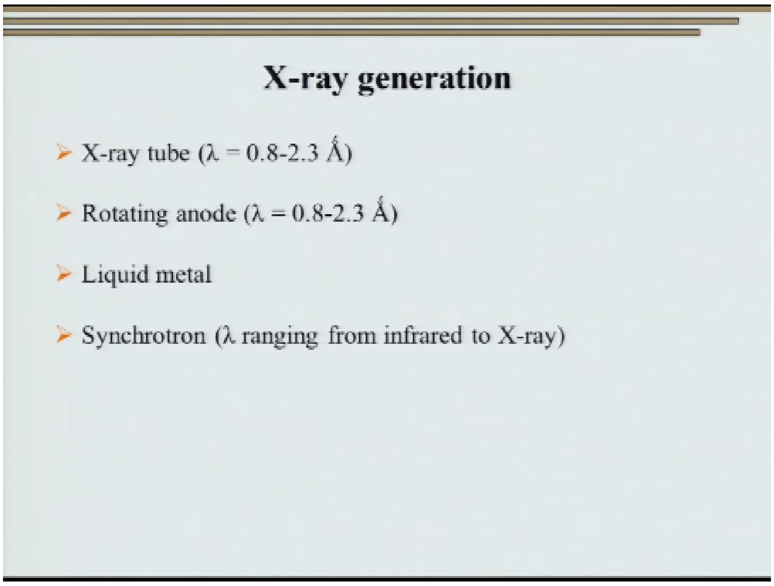

X-ray generation

- X-ray tube ($\lambda = 0.8$-2.3 Å)
- Rotating anode ($\lambda = 0.8$-2.3 Å)
- Liquid metal
- Synchrotron (λ ranging from infrared to X-ray)

Now let us go back and look at part by part what constitutes actually a diffractometer. So we know that an X - Ray diffractometer compresses of a source, the beam of the optics, and the detector. So let us first look at the source, for this we need to understand x-ray generation in details. So we know that for x-ray generation conventionally we use x-ray tube at the same time, if we need more intensity we use what is known as rotating anode x-ray tube which compresses of a rotating anode.

Recently that has been development of liquid metal x-ray sources which provide high intensity x-ray at with very small special size. Another important source of x-ray which as captured imagination of researcher over the last couple of years is the synchrotron which essentially provides wavelength ranging from infrared to x-rays.

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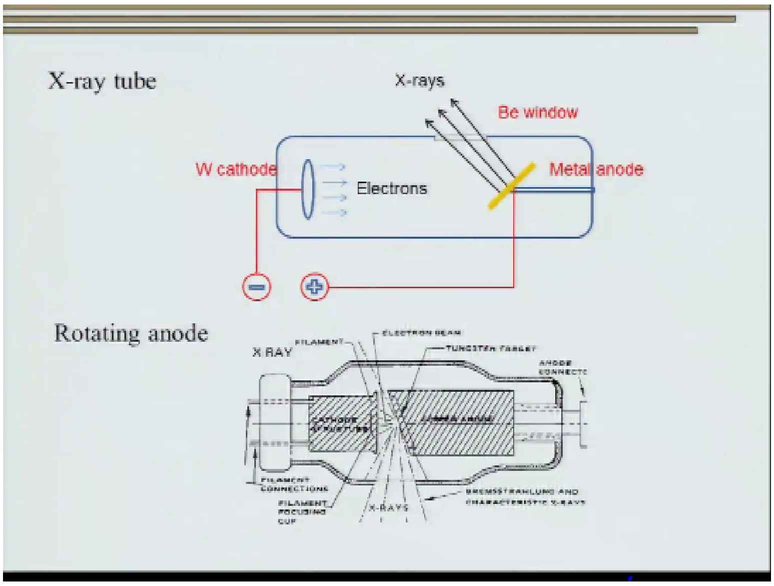

X-ray tube

Rotating anode

So x-ray tube essentially compresses of electrons which are accelerated towards a metal anode the all of us know that electrons which are emitted, because of thermionic emission travel and hit the metal target and produce x-rays. I am not going to go in details of x-ray generation in details, but I will touch upon it in a later slide. However, I hope you can appreciate that if all the electrons are hitting the metal target, there is going to be a temperature raise.

And therefore water cooling which is not shown over here is essential. However, I hope you appreciate that the electrons are hitting the metal anode at the same particular point, and hence it can the flux of electrons can only be to an extent which can sustain, so that the metal can sustain this flux of electrons without getting evaporated or melting. Therefore, in order to avoid this efficiency there has been a development of what is know as rotating anode.

In case of rotating anode source we have rotating anode compressing of a metal with high melting point like tungsten and moly. This rotating around which is physically rotating at the same time which is cool essentially ensures that the electrons which are hitting the anode or hitting in different regions ensuring that the flux of electron that are heating the anode and producing x-rays can be much, much higher.

The rotation of the anode essentially ensures that the sample, the flux of electron and therefore, the flux of x-ray can be higher without overheating the anode. This essentially ensures that the x-ray intensity obtain from a rotating anode is much higher than that of obtain from a normal x-ray tube. Another important observation is that the x-ray tube compresses of metal anode which can be different element like copper, chromium, moly, etc...

However, for rotating anode we do need a high melting point element, so that it can endure the flux that is incident on the anode and release x-rays of very high intensity.

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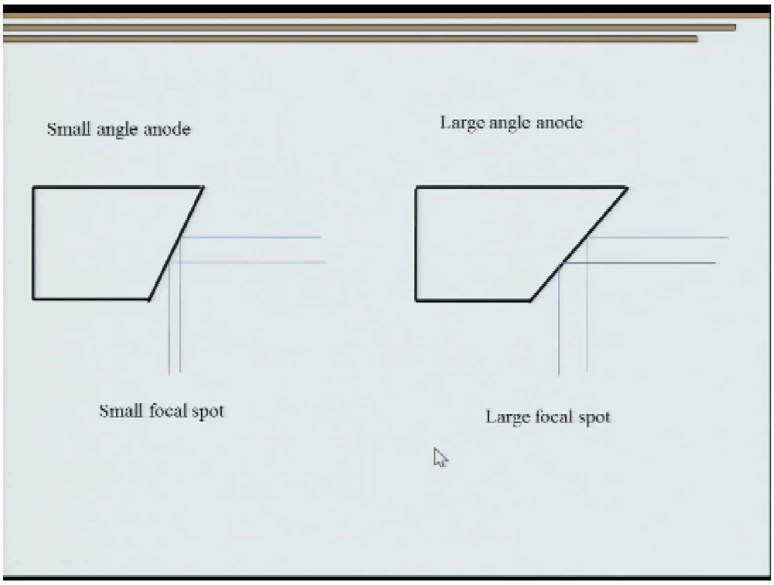

Just to show you the different kind of rotating anodes that are available.

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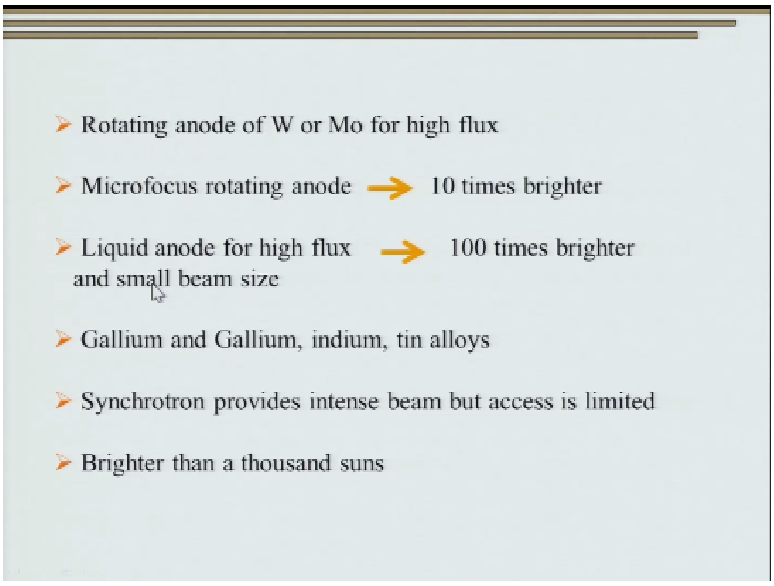

- Rotating anode of W or Mo for high flux
- Microfocus rotating anode → 10 times brighter
- Liquid anode for high flux → 100 times brighter
  and small beam size
- Gallium and Gallium, indium, tin alloys
- Synchrotron provides intense beam but access is limited
- Brighter than a thousand suns

We do have a small angle anode which were essentially you see that this angle over here is essentially quite and it gives small focal spot while in case the angle is large we do see that we get a large focal spot. Now depending on our requirement we can go for a large or small focal spot. Having said that as I mentioned rotating anode of tungsten or moly gives you high flex.

This micro focus rotating anode is at the best 10 times brighter a conventional x-ray tube. Another recent development in the area of x-ray source has been the evaluation are the development of what is know as liquid anode x-ray tubes. I would like to mention that the most important problem that is essentially the peak is healed in getting high x-ray intensity in x-ray tubes as well as rotating anodes is the heat or the removal of hea t from the anode.

Now this becomes the biggest problem, and therefore we cannot heat the material or we cannot bombard the anode with electrons as the material tends to melt or evaporate if it is increased. However, with liquid anode we do have a constant flow of liquid. And the electrons are always hitting a new interface compressing of liquid therefore, there is no problem of overheating and we can obtain very high intensity as good as hundred times weight than the x-ray tube.

Another important advantage is the beam size that we can obtain with a liquid anode x-ray tube which essentially ensures that we get a very high intensity and small focus x-ray beam. The metals like gallium and gallium, indium, and tin alloys are used for generation of liquid anode x-ray tubes. A lot of literature is available recently and I request you to go through what all existing literature on the liquid anode technique.

Another important parameter, thing that I have mentioned which can provide a very good source of x-rays is synchrotron which provides intense beam, alliances which I have borrowed from the radial light source essentially says that it is brighter than thousand suns.

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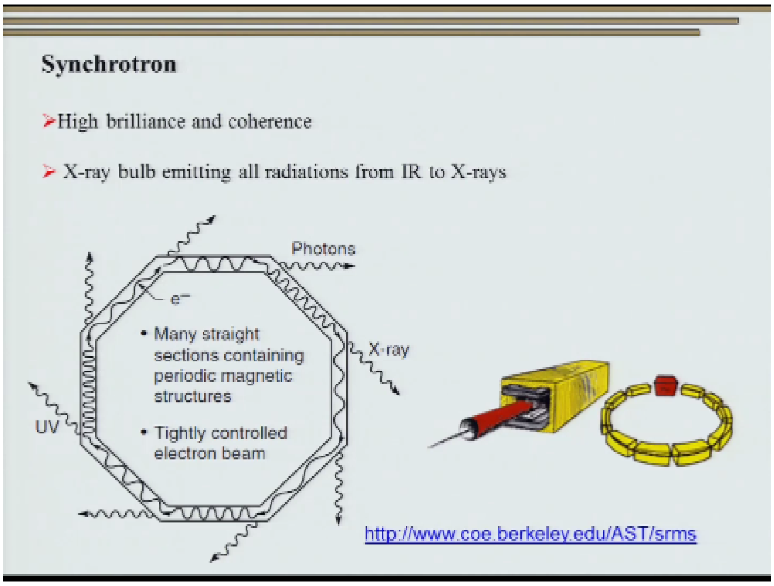

Synchrotron

- High brilliance and coherence
- X-ray bulb emitting all radiations from IR to X-rays

- Many straight sections containing periodic magnetic structures
- Tightly controlled electron beam

http://www.coe.berkeley.edu/AST/srms

However, as we all know the access to synchrotron radiation is many times limited. So I would just like to mention of few things about synchrotron would not going much details, but we know that synchrotron is a very high brilliance provides x-ray source with very high brilliance and coherence. It provides a x-ray bulb emitting all radiations from IR to x-ray and it can be as high as 10^{10} times brighter than a normal x-ray source.

So here you see that essentially it comprises of a large ring comprising of straight and code sections. A very good collection of synchrotron notes is available on this both side and I request you to go through those a truth lecture on synchrotron, and wherein he covers the details of synchrotron generation, as well as various techniques that can be used using synchrotron.

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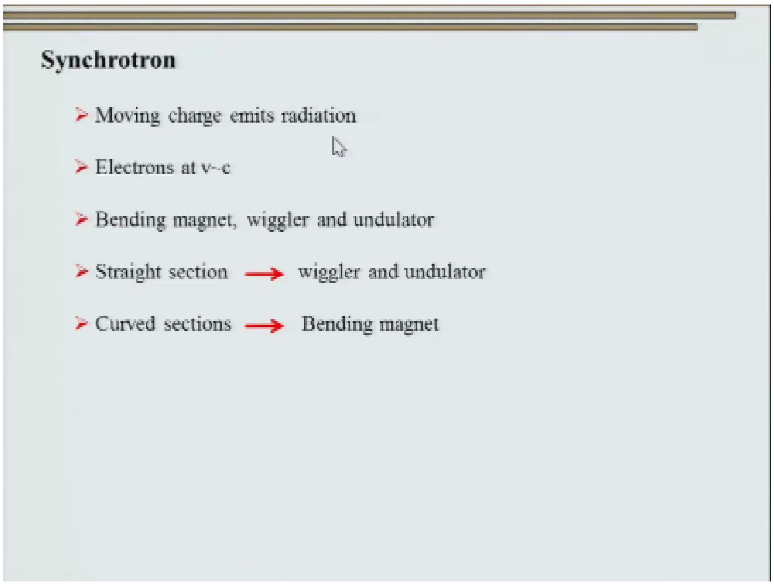

Synchrotron

- Moving charge emits radiation
- Electrons at v~c
- Bending magnet, wiggler and undulator
- Straight section ⟶ wiggler and undulator
- Curved sections ⟶ Bending magnet

So we know that the essence of synchrotron lies in the fact that moving charge essentially emits radiation. And we have electrons which are travelling at velocity close that of light in a synchrotron. These electrons which are travelling at the speed of light are focused using electromagnets which are used in different geometry mainly the bending magnet in the code sections as well as the wiggler and the undulator in this straight sections. I will just show you how the profile of these thing look like.

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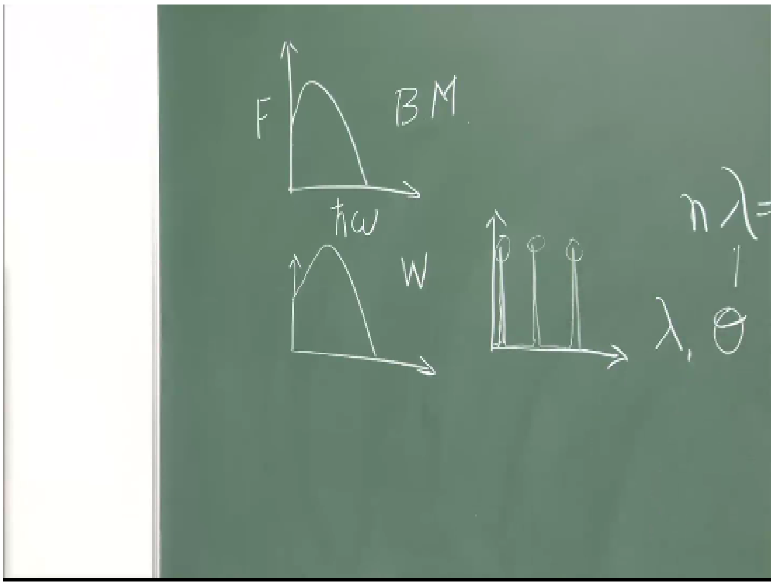

So if look at the bending magnet and if you look at the lets call it hω versus diffraction we see that this is how we get for the distribution of energy. This is how we get for what is known as bending magnet. When we go to the access are the same, when we go to wiggler we get something like this. So this is just likely shifted. So this is my wiggler. However, then I go to an undulator which again comprise as only the difference between all these things is the vary electromagnets are arranged.

If we do get high intensity. So we can understand that using a combination of these bending magnet wigglers and undulator we can get something perspector which is similar to very high intensity as shown in this case. So now coming back to our normal x-ray diffraction all of us know that as we increase the voltage. Initially we get no intensity at all which is essentially known as the short wavelength limit. So if you look at this again I am sure must be covered in your course on x-ray diffraction.

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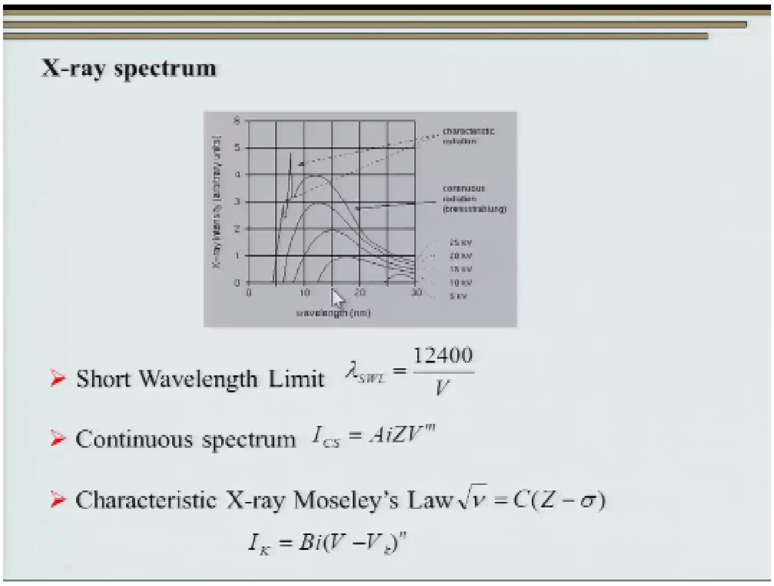

X-ray spectrum

- Short Wavelength Limit $\lambda_{SWL} = \frac{12400}{V}$
- Continuous spectrum $I_{CS} = AiZV^m$
- Characteristic X-ray Moseley's Law $\sqrt{\nu} = C(Z - \sigma)$

$$I_K = Bi(V - V_k)^n$$

But since this is advance course, I thought we will go through it again we see that for a particular wave length that is no intensity. So this essentially is the sided wave what is known as the short wavelength limit and if this is given by 12400 /v where v is your voltage, and you will see that if the voltage is lower than a particular for a given voltage that λ short wavelength limit there is no radiation.

I hope you remember that this formula is obtain by just doing the energy balance for the encompassing the kinetic energy of your electrons and the energy or rather the energy of the x-ray that is expected to be limited. Another important thing is as we increased the voltage we see that we do get a continuous spectrum. Now the intensity of the continuous spectrum is given by $AIZV^m$ where m is generally equal to 2 and Z is your atomic number.

And A is a constant, and I is the current, so we see there is a continuous spectrum. However, when the voltage is further increase we do see a characteristic peaks in the spectrum. Now this characteristic peak essentially occurs according Mosley's law which essentially says the frequency the square root of the frequency is essentially = constant z- σ which is another constant.

So depending on the atomic number we do see that different metals will give two different peaks. Now the intensity of the peak or the characteristic peak I_k is given by $Bi(V-Vk)^n$, where n is a constant is equal to generally 1.5, and VK is the characteristic voltage that is needed for getting characteristic radiation. I hope all of you remember that a characteristic radiation is essentially obtain than a high energy electron and inner cell electron from the atom and when an outer cell electron essentially replaces or jumps to this inner cell electron.

The difference in the energy level is essentially emitted in terms of a characteristic x-ray. Having refreshed our knowledge of conventional x-ray diffraction let us know go back to the instrumentation part. We have seen that how we can get a peak in the normal x-ray source which comprises of as we see here two peaks which are essentially obtain because of K_α and K_β radiation.

I would also like to mention that these characteristic peak K_α essentially comprises of two peaks which are known as $K_{\alpha1}$, and $K_{\alpha2}$, and the K_β comprises of $K_{\beta1}$ and $K_{\beta2}$. I am not going in details of these things considering that you have gone through it in your basic course on x-ray diffraction.

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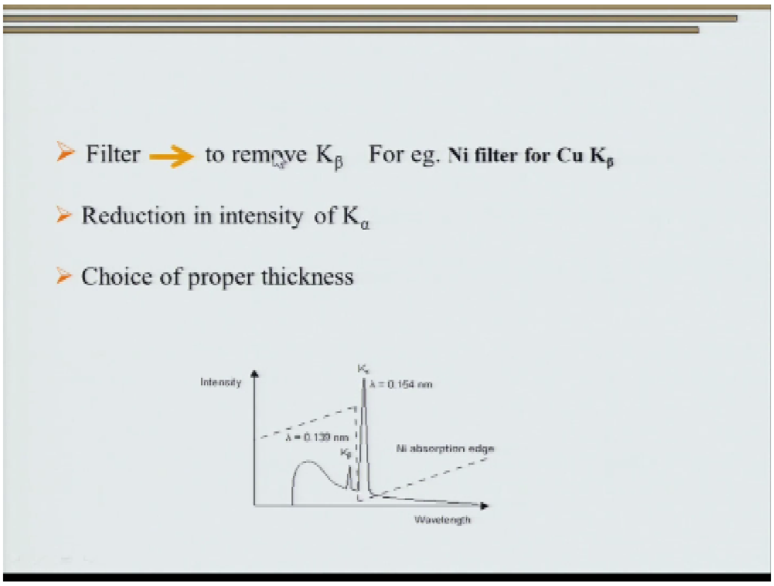

- Filter → to remove K_β For eg. **Ni filter for Cu K_β**
- Reduction in intensity of K_α
- Choice of proper thickness

So having seen this characteristic peak. The first in the foremost important job at our hand is to separate the two peaks and for this we use what is known as the filter. All of you must be aware of the absorption H phenomena in which we know that material can absorb x-rays of a particular wavelength, and this is characteristic of the atomic number of that element. Having said that we know that generally for copper to remove copper K_β nickel filter is essentially used.

However, when use a filter we see that there is an direction in intensity of $K_{\alpha2}$. Therefore, the choice of proper thickness of the filter is a very essential to ensure that we do get a high intensity Kα beam. So this filter compress of nothing but the thin foil of the metal, which is inserted in the path of the x-ray beam. Having said that the x-ray beam as you all aware 10 to diverge in order to kind of the limit the divergent of the beam we use what are known as slits.

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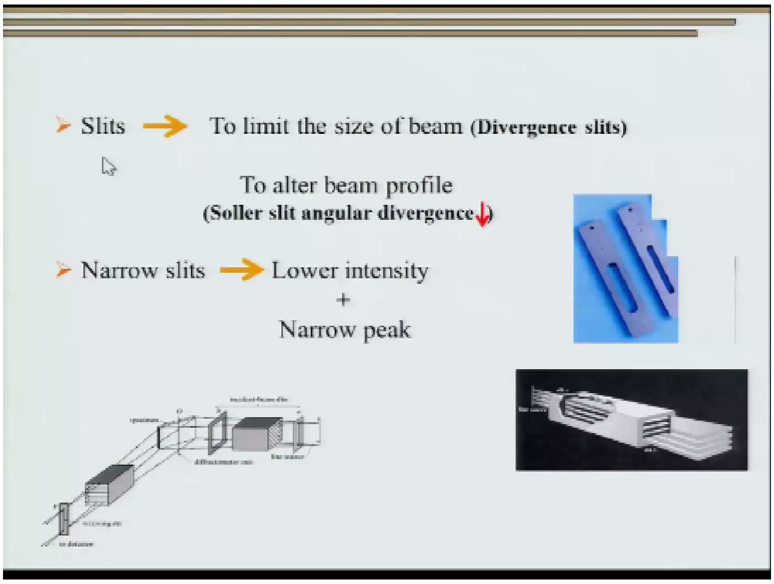

- Slits → To limit the size of beam **(Divergence slits)**

To alter beam profile
(Soller slit angular divergence ↓)

- Narrow slits → Lower intensity
+
Narrow peak

So the slits are used to limit the size of the beam, at the same time we can use the slits to alter the beam profile, and the so called solar slits show know what is here can essentially reduce the divergent of the x-ray beam and provide parallel or rather semi parallel coherent x-ray it can be appreciated that narrow slits can lead to low intensity and can give us can lead to a narrow peak and lower intensity.

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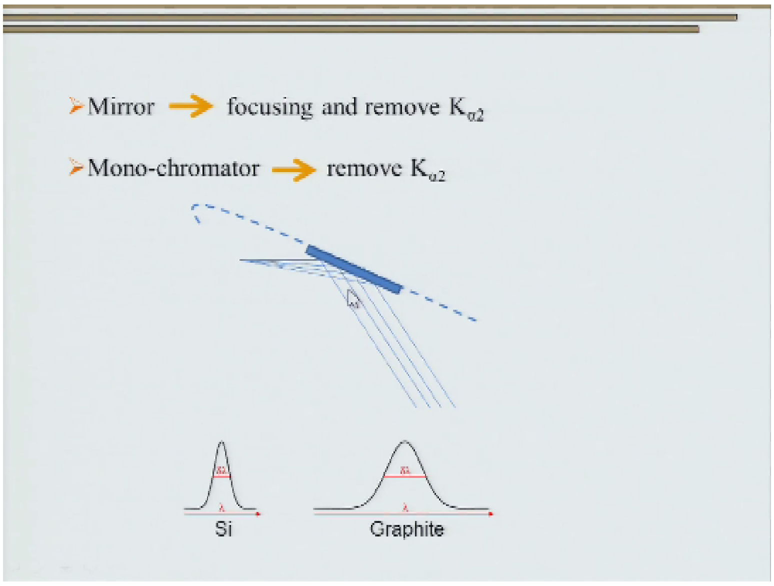

- Mirror → focusing and remove $K_{\alpha 2}$
- Mono-chromator → remove $K_{\alpha 2}$

Another important hardware that we used is essentially the mirror. Now the mirror comprised of multi layers of heavy elements on silicon which essentially acts as a diffraction greeting, and can be used to separate $K_{\alpha 1}$ and $K_{\alpha 2}$ which are very close to each other. At the same time we can also use what is known as a mono-chromator for that means consist of a particular crystal like the one shown over here namely the silicon and graphite crystal.

The silicon beam are much better mono-chromator that a graphite to separate the $K_{\alpha 2}$. Another important thing that I would like to mention about the mirror which I missed out is that all of us are aware that x-rays cannot be focused. However, having said that the mirrors that ensure that the divergence of the x-rays is limited and therefore we do get nice covariant x-ray beam which can be result rather limited in terms of spacial dimensions.

So now let us look at the different profiles that we can obtain, so we know that a normal defect now is going to or the normal source is going to give us x-rays which are tending to diverge, using slits are now limited passing through solar slits we have ensured that most of them are parallel. Now using a particular way we have ensured that the Bragg's law in the mirror is satisfied and all the planes are rather, all the lines or x-ray beams are diffracted only in one particular direction.

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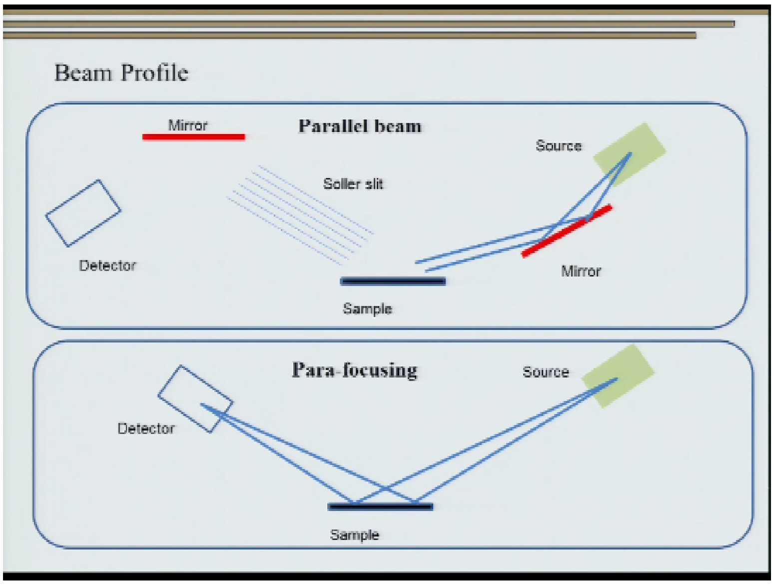

So this essentially ensures that we are getting a parallel set of or rather a parallel x-ray beam. And this time we use, we notice known as essentially a parallel beam geometry. Now not only that what we can do is, we can also put what is known as the soller slit which we had used in earlier case at the received inside, and then a mirror. So that we will ensure that our detector is only seeing parallel x-ray that are getting diffracted from the sample.

So this is essentially known as the parallel in geometry. However, normally what we use in normal x-ray diffractometer for powder and polycrystalline bulk materials is a para focusing geometry which comprises of filters and all, but not much of mirrors and soller slits. All we have is a few or other few divergent slits and the source side and the detector side. Having said that there are certain applications like what I mentioned like texture measurement or received texture measurement.

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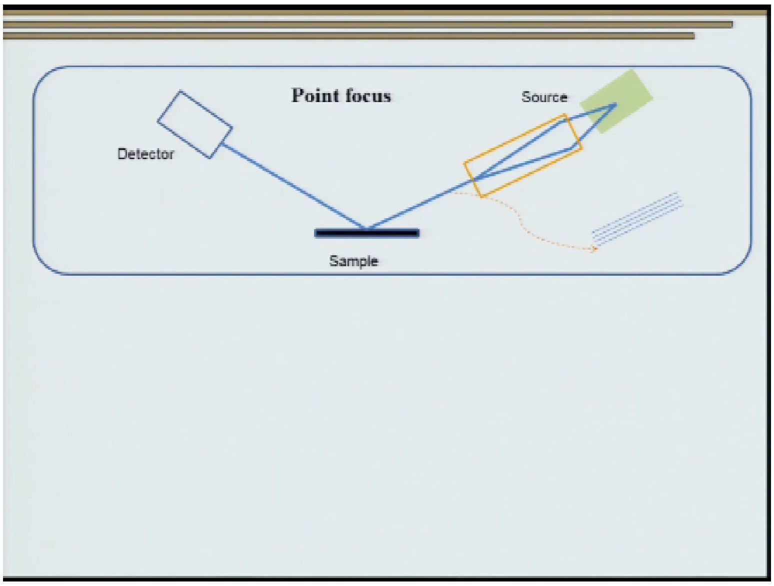
Point focus

Where we need a point focus here in we can see that the x-ray is focused into a point a good observation or other good option is to use a rotating anode source which provides a very small, but coherent source of x-rays. However, those sources are very rare and pretty costly. So normal point source can be obtain using what is known as a poly capillary.

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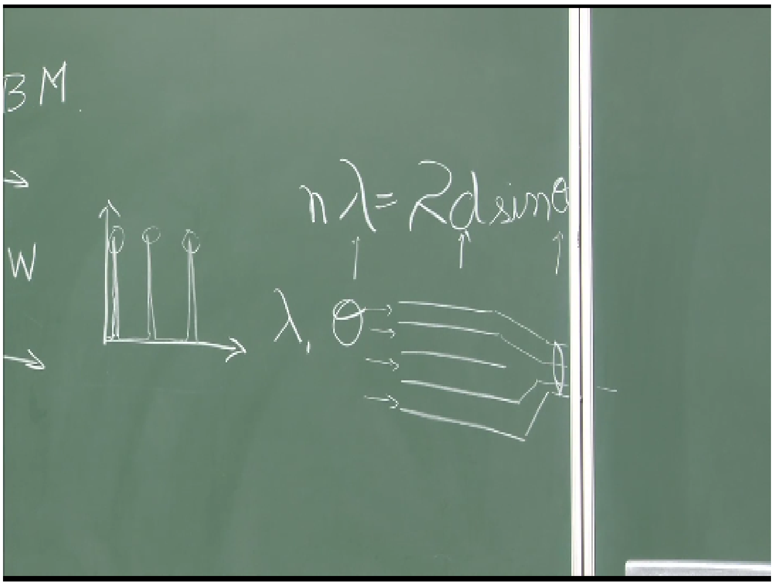

A poly capillary essentially comprises of a lot of optical fibres and x-ray being which is incident essentially undergoes complete internal reflection ensuring that we do get a high intensity of x-ray beam with smaller special size. So this can be used essentially for characterising texture and residual stress while the normal parallel beam which I had shown over here can be used mostly for characterizing thin film samples.

So I would just like to give you a comparison of the parallel beam and para-focusing geometry. But before I do that I would like to mention that even in the point focus we do have a nice parallel beam geometry. Only thing is the spatial size of this particular geometry is reduced by an order of magnitude.

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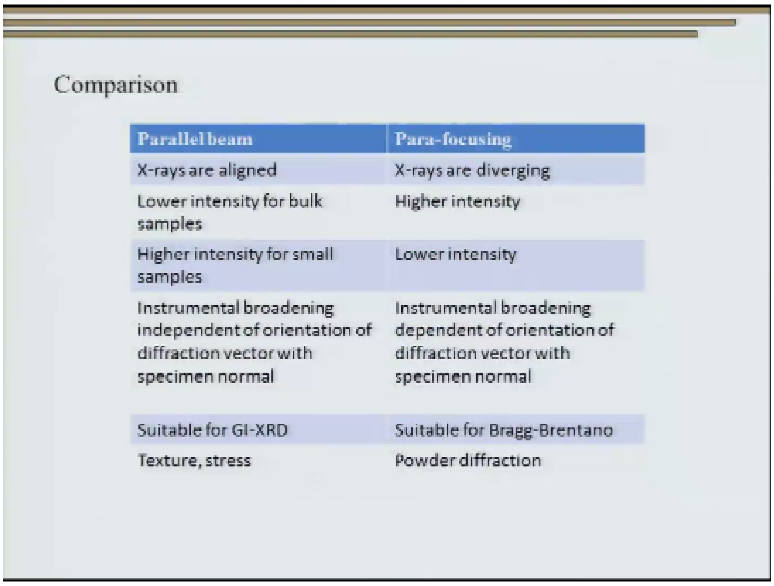

Comparison

Parallel beam	Para-focusing
X-rays are aligned	X-rays are diverging
Lower intensity for bulk samples	Higher intensity
Higher intensity for small samples	Lower intensity
Instrumental broadening independent of orientation of diffraction vector with specimen normal	Instrumental broadening dependent of orientation of diffraction vector with specimen normal
Suitable for GI-XRD	Suitable for Bragg-Brentano
Texture, stress	Powder diffraction

So to compare the parallel beam and para-focusing geometry, I would say that the X-rays are allied for the parallel beam while the X-rays are diverging for the para-focusing geometry. The parallel beam geometry, this lower intensity for bulk samples and that is why we do not use it regularly while for normal bulk and powder samples we use the normal para-focusing geometry which gives higher intensity.

However, whenever we come to smaller samples or thin film samples, we go and use a parallel beam geometry, because para-focusing geometry gives us a lower intensity. Now another important thing is that the instrumental broadening is independent of orientation of diffraction vector with specimen normal. Now remember we had talked a lot about these angles which tend to rotate the sample as well as rotate your detector namely the φ, the χ which essentially rotate your sample along the access which is perpendicular to the surface of the sample, at the same time along axis which is passing through the sample.

So this which is known as the χ rotation gets the pin. This is the χ rotation, and this is the φ rotation. So you can imagine then in order to get good diffraction data in such a case, the most important thing is to use a parallel source or parallel beam geometry. And therefore, almost all thin film measurements, crystallographic texture, and residual stress measurement are carried out using parallel beam geometry and this is what is mentioned in the last slide.

At the same time, we know that the para-focusing geometry is very suitable for normal Bragg Brentano geometry. This is something that we go to the normal X-ray diffractometer take in our sample, put it in a diffractometer and this is what we get. However the parallel beam geometry as I mentioned is useful for stress, texture and also for gracing incidence X-ray diffraction.

We will cover this GI-XRD part in the next to next lecture, but keep this in mind that the entire spectrum of diffraction can be covered just by playing with the optics and the source used in a normal diffractometer. So having said that, now let us look at what exactly happens once the X-rays has interacted with the sample. After this interaction, we do get a signal. Now once we get this signal, we can again pass it through the optics part which I had shown earlier to ensure that we are getting a particular wavelength.

I would repeat that the entire thing that we are talking about, the powder diffraction or poly crystalline diffraction and its various sub domains essentially deals with only a single wavelength. And therefore, it is important to get information from a particular wavelength. Having said that, this is probably the only reason why we need a lot of optics in the kind of source side which essentially ensures that you are producing only one particular wavelength to interact with your sample.

However, I hope you remember that the interaction of X-rays with material can also lead to what is known as fluorescence and produce X-rays with a different frequency or wavelength. Though if that happens, you do not want that noise to come and interfere with your detector signal. And therefore, you have to again put the same optics or similar optics rather from your source side to your detector side to ensure that you are looking at one particular wavelength of your interest.

Once the X-ray beam passes through all this optics it then encounters the detector which essentially reads the intensity of the X-rays and the angular dependence.

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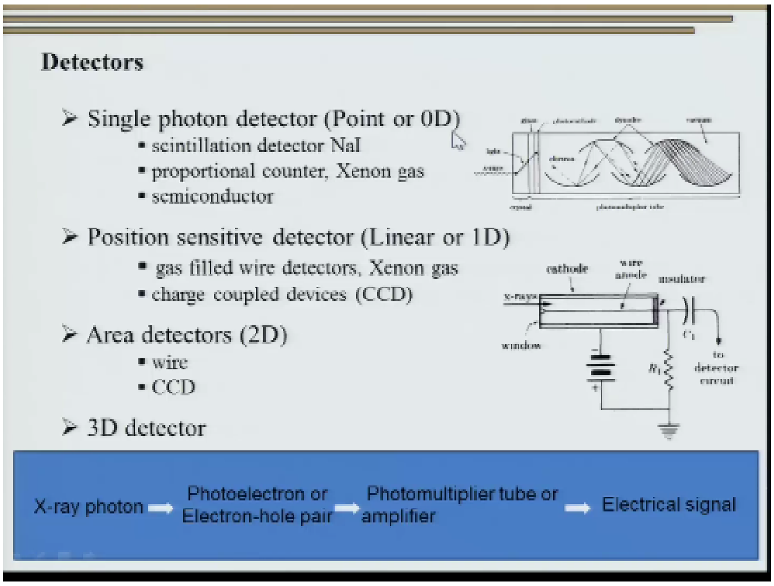

Detectors

- Single photon detector (Point or 0D)
  - scintillation detector NaI
  - proportional counter, Xenon gas
  - semiconductor
- Position sensitive detector (Linear or 1D)
  - gas filled wire detectors, Xenon gas
  - charge coupled devices (CCD)
- Area detectors (2D)
  - wire
  - CCD
- 3D detector

X-ray photon ➡ Photoelectron or Electron-hole pair ➡ Photomultiplier tube or amplifier ➡ Electrical signal

So detector comprised and be classified depending on dimensions as 0D, 1D, and 2D. So let me first talk about the concept of dimensionality of detectors. So all of us know that the Bragg’s Law is not simple as simple as it sounds, and it is anything but just a reflection of X-rays from.

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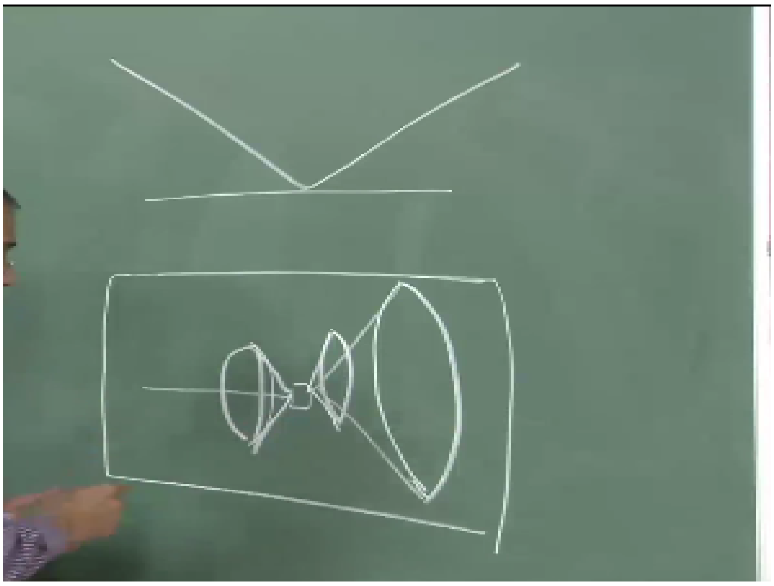

So this is how generally we draw Bragg's law, incident beam and this is the diffracted beam. But all of us know that this is not exactly what happens. In fact, what gives us a much better picture is ensuring that all this is essentially we have a cone of diffraction. If you remember the more genetic picture is the x-rays coming over here and this getting diffracted at a particular angle forming a cone.

So, this is the actual, this is a simplified version and this is just a schematic for understanding what is diffraction. A more realistic view is like this where in we see not only one, but a multiple number of diffraction peaks occur.

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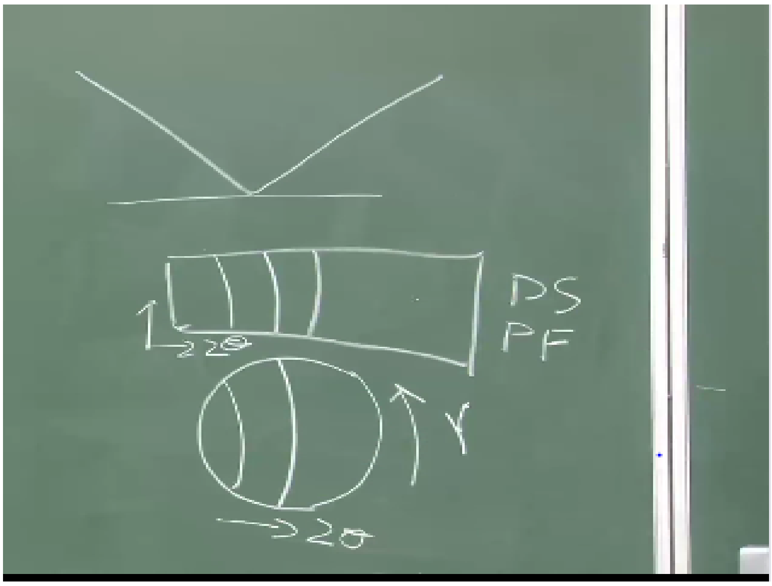

Now having appreciated that diffraction comprises of diffraction cones rather than diffraction lines, I would like to mention that the detector essentially has to see part of this thing. So we can imagine that if we take something like a normal film, a photographic film, which we do generally in the diffraction of method. We know that we do see the intersection of these cones in terms of these arcs, right.

So this is probably the oldest detector that has been used or the oldest two dimensional detector that has been used to study x-ray diffraction. Now, I will go back and show you the state of the detectors which can do the counting the x-ray signal and convert it to electronic signal. So we have what is known as a single photon detector which reads only 1θ or one angle at a particular time.

So, this comprises of the normal scintillation detector comprising of sodium iodide, which essentially on hitting the x-ray, we do get the emission of a photo electron. And this photo electron is then passed through a photo multiplier tube to generate an electrical signal. And this electrical signal is proportional to the number of x-ray photons hitting the sodium iodide crystal.

We can also use what are known as proportional counters and xenon gas, which again lead to the interaction of the x-ray with the gas, leads to the formation of photo electron and which can be amplified to obtain current. Another important thing is semiconductors. So, in case of semiconductor detector, what we have is once the x-ray interacts with the semiconductor, we do get an electron-hole pair and therefore a current, which is directly professional to the number of x-ray photons, you know, hitting your detector.

So, the detector can give us information in single dimension or what is known as 1 detector. If we take the detector and place it with a wire, which can give us information, not at a particular value of θ or 2θ for that matter, but over a range of 2θ, it is known as a position sensitive detector. The state of the detector, the old fashion what I showed here with the debaser ring of a photographic plate, what we do get essentially is a two dimensional CCD detector.

So the two dimensional CCD detector is not just giving me information, so this is the old debaser photographic film, instead what we have is a nice area detector, which covers a large area and shows me patterns like this, which are nothing but the intersection of my diffractions cones. So, these peaks essentially gives us information not only in 2θ which is shown over here.

But also you see there is another angle over here which information you are getting, so this information corresponds to what is known as the γ or χ angle, which we had talked and corresponds to orientation of the crystal of the sample. So essentially, we talked about only diffraction which comprises of this particular thing where you know, the x-rays are getting diffracted, but the sample can also be tilted accordingly.

And therefore, you see this is what corresponds to this diffraction from not only the place which are directly aligned this way, but also the plains which are aligned at an angle corresponding to χ. So we can, I hope you appreciate that in a normal two dimensional detector, you get a lot of information or a much better view of reciprocal space. Having said that, we know that the entire concept of x-ray detectors is based on converting the x-ray photon into a photoelectron or electron-hole pair.

Then, you use a photo multiplier tube or amplifier to increase the intensity of the signal and essentially get an electrical signal, which can be correlated with the θ or rather 2θ value and the intensity. Having said that what is important for the choice of a particular detector, we need to focus on the resolution which is essentially the ability to distinguish between two energies.

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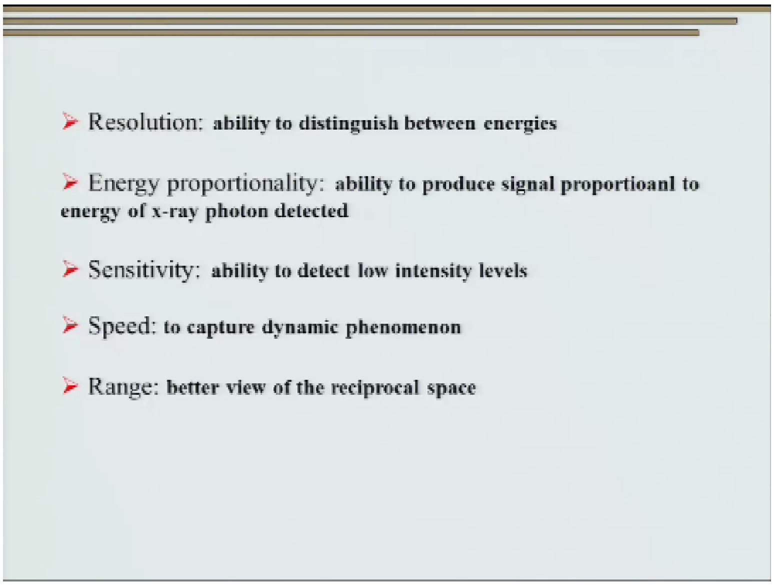

- Resolution: **ability to distinguish between energies**
- Energy proportionality: **ability to produce signal proportioanl to energy of x-ray photon detected**
- Sensitivity: **ability to detect low intensity levels**
- Speed: **to capture dynamic phenomenon**
- Range: **better view of the reciprocal space**

At the same time what is more important is look at the energy proportionality, which is the ability to produce signal, which is proportional to the exact energy of the x-ray photon. Another important parameter is the sensitivity, which ensures that we can detect low intensity levels. The state of that x-ray diffractometers that we are talking about, we talk about the speed, is very important, because we need to capture dynamic phenomena occurring during the process like heating or face transformation.

At the same time, we have to get a better view of the reciprocal space, as I showed for the 2D detector, which essentially ensures that we get a better view of the reciprocal space and get more information about the x-ray diffraction pattern. I hope by the end of this lecture, you have got a rough idea about the instrumentation part of x-ray diffractometer.

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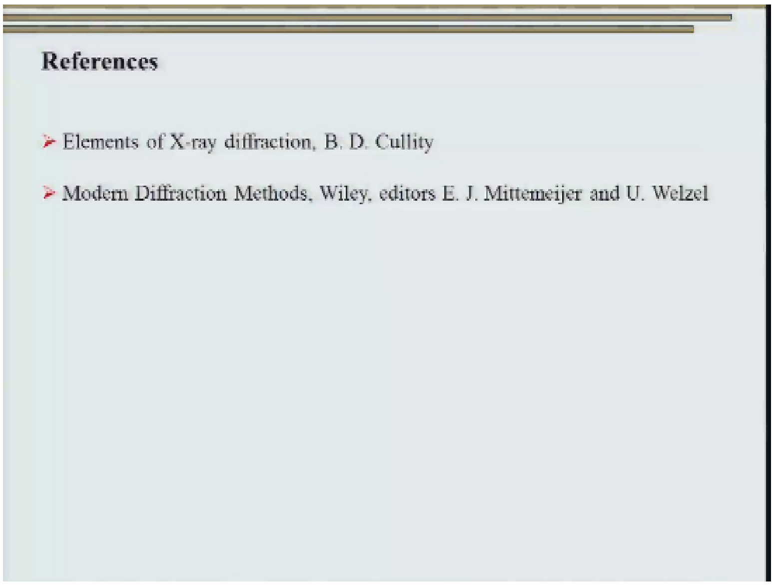

References

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In the next couple of lectures, we are going to talk about two of the most important diffraction techniques, namely the small angle x-rays scattering, and grazing incidence small angle x-ray scattering. So, see you after the next class.

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