An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

Prof. Ashish Garg
Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture- 33
X-ray Diffraction

So, today again be we begin a new lecture and will continue on X-ray diffraction, which we started in the last class.

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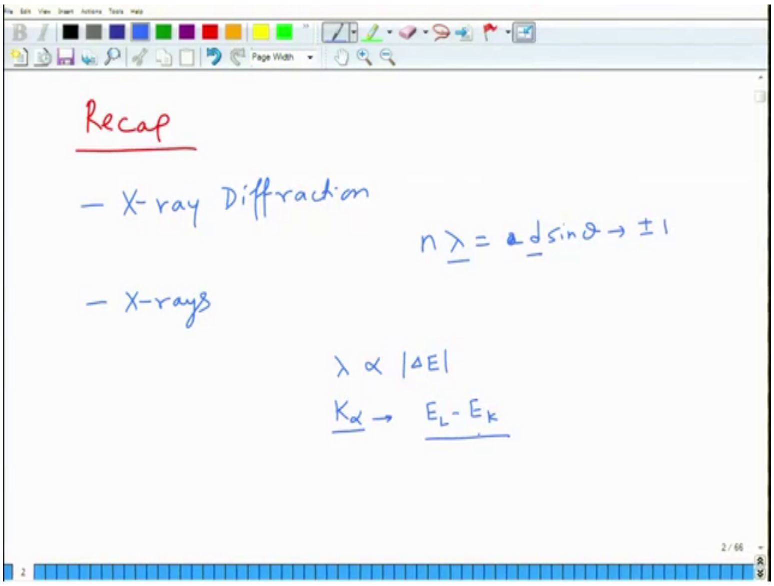

Recap

– X-ray Diffraction

$$n\underline{\lambda} = a\underline{d}\sin\theta \rightarrow \pm 1$$

– X-rays

$$\lambda \propto |\Delta E|$$

$$\underline{K_\alpha} \rightarrow \underline{E_L - E_K}$$

Let me just begin with a bit of recap of the last lecture. We were talking about so, we finished discussing the structure of materials with concluding with the structure of polymers.

So, in this lecture we started talking about X-ray diffraction and basically diffraction effects were discovered earlier by Thomas young young's double slit experiment and very concluded that, you know d and lambdas glow d sine theta is a is a condition to be met for diffraction to occur with and being an integer.

So, he following that there was a concept of constructive and destructive interference. So, when waves when they pass through a obstacle they undergo diffraction and when they when the amplitudes of the wave add up constructively, then there is maxima observed in the diffraction pattern and when at at other angles when they do not add up constructively there is a destructive interference as a result there is no diffraction that takes place.

So, following this you know the experiments, which were conducted by young were on slit spacing, which were of the order of a visible light wavelength. Now atoms in crystals if they are arranged periodically they can be considered as slits.

However, the spacing between those slits is as small as you know 2 to 3 angstrom something like that 2 to 4 angstrom 5 is to angstrom is the typical lattice parameter of materials. Which requires you to so, the condition n lambda is will 2 d sine theta or d sine theta in young’s experiment, it allows it tells you that lambda and d should be comparable because sine theta cannot be more than plus or minus 1.

So, if you want to get the diffraction effects from crystals you need to have a radiation whose wavelength is comparable to the lattice spacing in the crystals and that is where X- rays were useful after they were discovered. So, X-ray s so, we talked about X-ray s how they are generated. So, basically we looked at when you have when you reject a cation electron, when a high energy electron beam bombards a target let us say copper in this case then high energy electron beam ejects a k electron if it is high energy, if it is high enough in energy.

Then this k electron which has been ejected it leaves a vacant place there, now this becomes excited state as a result is it becomes unstable configuration. As a result the electron from the higher energy level has to go down and it can make a transition from l level, it can make a transition from m level, it can make a transition from n level, and there is a probability of transition and it is it turns out that the probability of transition highest from the l level than, if the transition has to happen to k level, then it is more probable that electron will come from the next level rather than from the further levels.

So, that is how these transitions occur and they give rise to an electron from higher to lower energy transition undergo the transition it emits a X-ray X-ray photon. And this X-ray wavelength with that X-ray corresponds to the energy difference between the 2 energy levels. So, if it is if it is k alpha and then for k alpha it is going to be the energy difference between the E L minus E K ok.

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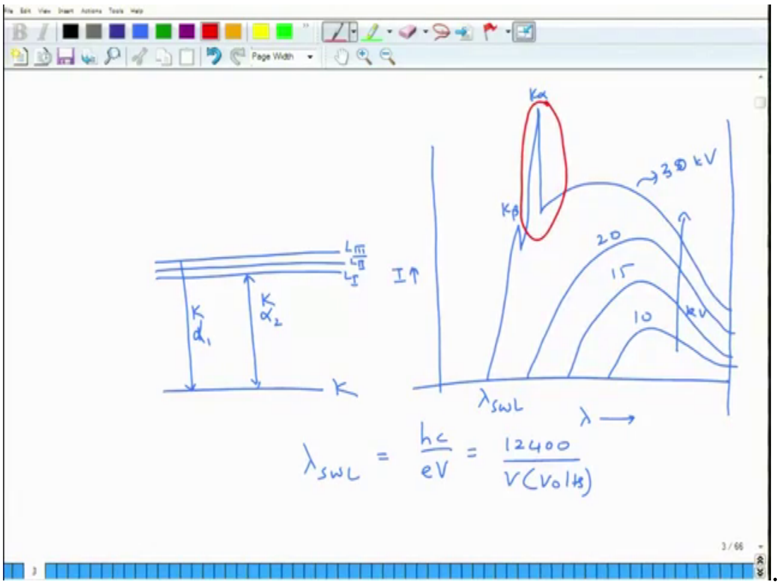

$$\lambda_{SWL} = \frac{hc}{eV} = \frac{12400}{V(\text{Volts})}$$

So, this is what is going to be the so, we looked at so, you can have so, if you if this is your k shell and this is your L shell, then L shell has 3 shells ok. So, this is l one this is L 2 this is L 3. So, typically the transition which is made from L 3 level that is alpha 1 transition and transition from L 1 L 1 and L 2 applied quite close to each other, they are designated at alpha 2 transitions this is the signature.

So, this in this case it will become k alpha one in this case it will become and accordingly you will have l alpha m alpha and so on and so forth. Now we then looked at the spectra after bombarding a spectra is sort of it varies in this fashion. So, as the as the kv increases and so, this is lambda this is intensity of radiation and this is kv increasing ok.

So, this could be let us say at 25 or 30 kv and this could be let us say at 20 kv and so on and so forth. So, what you have here is 15 10 and if you have 5 it will now what happens is that you get a at lower voltages you get a radiation of wide wavelengths, which is called as continuous radiation. At higher k vs you start getting characteristic radiation which is in this case it could be k beta this could be k alpha and this is what is very useful for X-ray diffraction to occurred, because it provides you high intensity.

And the limit of wavelength is called as lambda as SWL, which I showed you last in the last class this is equal to hc divided by e v, which turns out to 12 400 divided by v in volts.

Student: (Refer Time: 06:45) k.

Sorry.

Student: (Refer Time: 06:47).

So, that k electrons gets emitted it goes out of the material and as a result you have transition from the higher level. So, so the whole idea in X-ray diffraction is to use these characteristic radiations for so, typically we use k alpha radiation for X-ray diffraction analysis, because k alpha radiation has a wavelength, which is comparable to lattice parameters and it has a intensity, which is very high intensity.

So, you do not have to go to very high k vs to achieve good signal to noise ratio. So, it provides you very good signal to noise ratio as well. And most of the X-ray diffraction is carried out using monochromatic radiation unless you are dealing with single crystals, if you are dealing with single crystals then typically you use white radiation or continuous radiation whereas, in case of polycrystalline materials, typically we use monochromatic radiation and that is where we choose k alpha in most cases. And this k alpha choice of k alpha radiation typically k alpha 1 is the 1, which is chosen.

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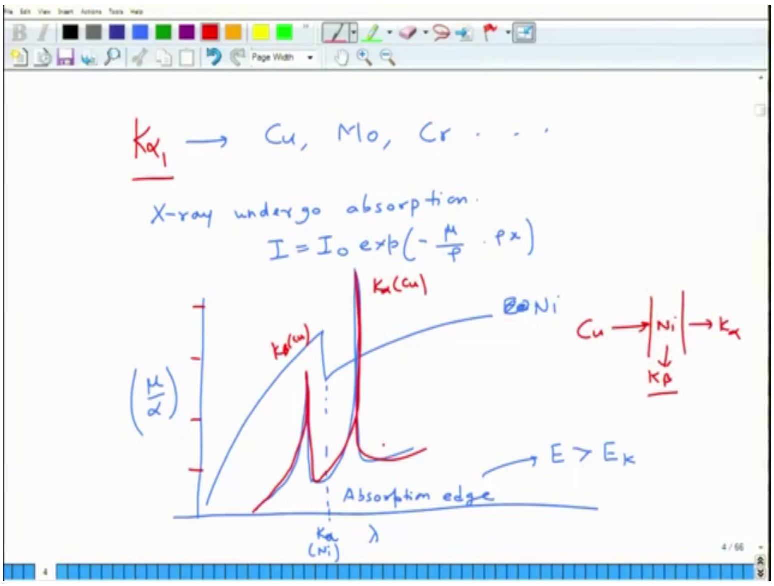

$K_{\alpha_1} \rightarrow$ Cu, Mo, Cr . . .

X-ray undergo absorption.

$I = I_0 \exp\left(-\frac{\mu}{\rho} \cdot \rho x\right)$

So, we can use copper if we can use moly we can use chromium these are some targets which are typically used in X-ray diffraction. So, another thing which happens is that when X-ray s undergo the X-ray is a strike of material then X-ray s undergo absorption ok. When X-ray s undergo absorption of course, the intensity changes as a function of I is equal to I 0 exponential of minus mu by rho into rho x this is my mass observation coefficient mu mu rho.

So, the to accu plot the math observation coefficient as a function of wavelength then typically it shows behavior which is like this. So, this basically is the point where absorption sudden or suddenly decreases, depending upon how you look at it this is called as absorption edge.

This can be basically this is this is the absorption edge corresponds to the energy, when the energy becomes E is greater than E k, when energy of the incident photon is higher than the k binding energy. So, the moment it starts it is energy is higher than the k binding energy, which means it can eject k let k electron, but at the same time which means that the energy is absorbed, because now energy is spent in ejecting the k electrons.

So, which means the incident radiation will lose it is energy if. So, basically let us say if this is the this is a certain material in this case let us say iron, if it is the case of iron and you are bombarding iron with something then or you can use this let us say this in this material is let us say nickel ok. It turns out you can use this absorption is to suppress certain radiation and to allow certain radiation to go through. So, for example, in case of copper the k beta radiation is somewhere here and k alpha is somewhere here ok.

So, it turns out that if you want to use k alpha predominantly you let the X-ray s pass through a nickel filter ok. Because nickel has a k absorption edge this is k alpha k k a of nickel. Nickel has a k absorption edge which falls between so, this is let us say k beta peak of copper and this is k alpha peak of copper ok, k alpha c u and this is k beta c u.

So, if you want to use copper radiation if you want to use copper radiation and you want to use k alpha component, then you let copper radiation pass through a nickel filter what nickel filter will do nic and this is by the way a logarithmic axis ok. So, this is these scales are logarithmic in nature log plot.

So, which means the decrease or change is substantial. So, when nickel when copper radiation Cu passes through a nickel filter. The nickel absorbs k beta component and it allows k alpha to pass through, because k alpha gets absorbed lesser than k beta as a result what you get out of the system is predominant predominantly k alpha.

So, this absorption edge properties of materials can be used in using you it it one use of this absorption is property is to choose a material, which can be used as a filter to give you the wavelength that you want for the incoming radiation ok.

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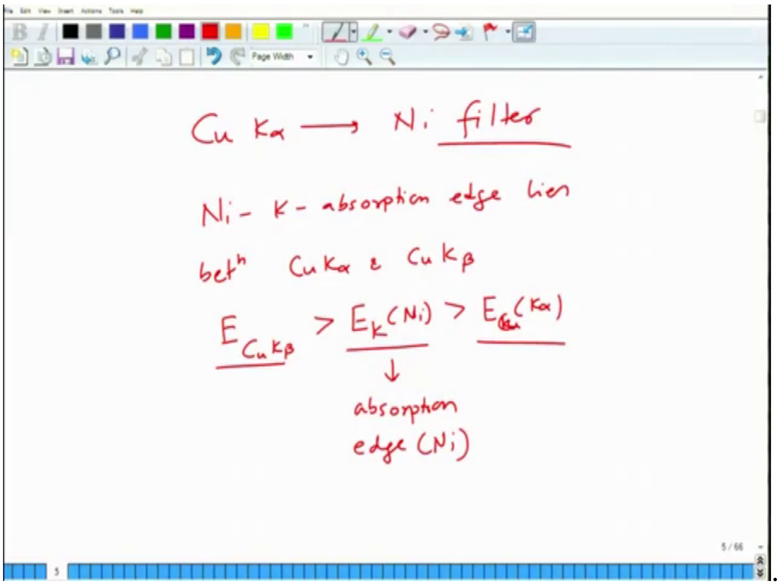

$Cu\ K\alpha \longrightarrow Ni\ \underline{\text{filter}}$

Ni - K - absorption edge lies

bet^n Cu Kα & Cu Kβ

$$\underline{E_{CuK\beta}} > \underset{\substack{\downarrow \\ \text{absorption} \\ \text{edge (Ni)}}}{\underline{E_K(Ni)}} > \underline{E_{Cu}(K\alpha)}$$

In case of copper radiation Cu k alpha we typically use nickel filter, because nickel has a absorption edge, which lies between a nickel k absorption edge lies between Cu k alpha and Cu k beta.

So, is such that that e Cu k beta is higher than E k of a nickel higher than E k E Cu k alpha. So, basically it will absorb this, but not that alright ok. Because you see the lambda has a different relation the lambda is on the higher side. So, which means lambda of Cu k alpha is higher than the lambda corresponding corresponding to the absorption edge, which means the energy of the absorption edge, has to be higher than the energy of the Cu k alpha.

So, energy of the absorption edge this is the absorption edge of nickel this energy is higher than the Cu (Refer Time: 13:21), but it is lower than cu k beta which is where it has high absorptivity, high absorption for this thing. Another thing that you need to now since this absorption takes place since this absorption takes place, the X-ray s which come out of material the X-ray s, which are emitted those X-ray s also have X-ray s which are incident on the material.

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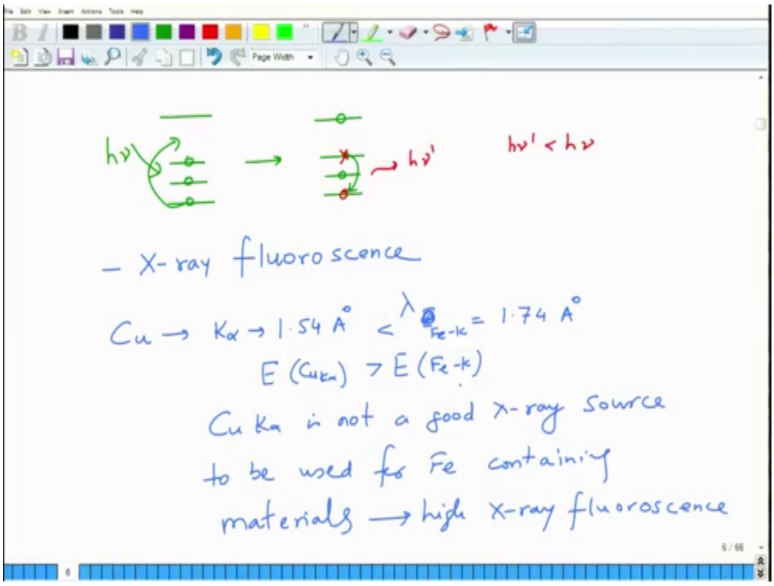

$h\nu' < h\nu$

- X-ray fluoroscence

Cu → $K_\alpha \rightarrow 1.54$ Å $< \lambda_{Fe\text{-}K} = 1.74$ Å

$E(Cu_{K\alpha}) > E(Fe\text{-}K)$

Cu Kα is not a good X-ray source to be used for Fe containing materials → high X-ray fluoroscence

So, when you have X-ray s incident on the material in such a fashion. So, that let us say if you have energy levels like this ok. And these X-ray s then you have when you have X-ray incident on a material it can excite electron from the lower energy levels.

As a result this electron goes there and the energy levels here. So, this was filled this electron now makes a transition to this level. So, this becomes empty and this gets filled which means it will emit a wavelength which is you know h nu prime where h nu prime is lower than h nu alright the energy of this is lower than the energy of incoming be it has to be lower right, but what it has done is if secondary X-rays come out of the material then this leads to a phenomena which is called as X-ray fluorescence. So, this is called as X-ray fluorescence.

And this fluorescence is basically they create lot of noise in the system, because they you have lot more lot many photons coming out, they go to the detector, they get detected and as a result they create lot a background in the system. So, when you this is typically important for so, to minimize the absorption of incident beam, you choose an X-ray which has lower absorption in the material ok.

So, for example, in case of copper copper k alpha edges 1.54 and strom and iron turns out iron E F e k is nearly lambda E F e k in lambda F ek is nearly 1.7 4 and strom. So, which means energy of Cu k alpha is higher than energy of Fe k. Because this lambda is lower.

Student: lower.

Which means when you bombard iron with copper; copper has capacity to excite the k electrons in the iron k alpha, which means it will create a lot of secondary X-rays. So, this is secondary X-ray right. So, iron so, copper k alpha is not a good X-ray source to be used for iron containing materials.

Because it gives rise to high X-ray fluorescence, because energy of Cu k alpha radiation is higher than k absorption edge of iron, as a result that X-rays get absorbed in emitting secondary X-rays and they lead to higher noise in the data and hence weak signal of the X-ray pattern. So, if you want to use. So, you have to choose a radiation for iron containing materials whose wavelength is whose wavelength is higher than the wavelength of iron.

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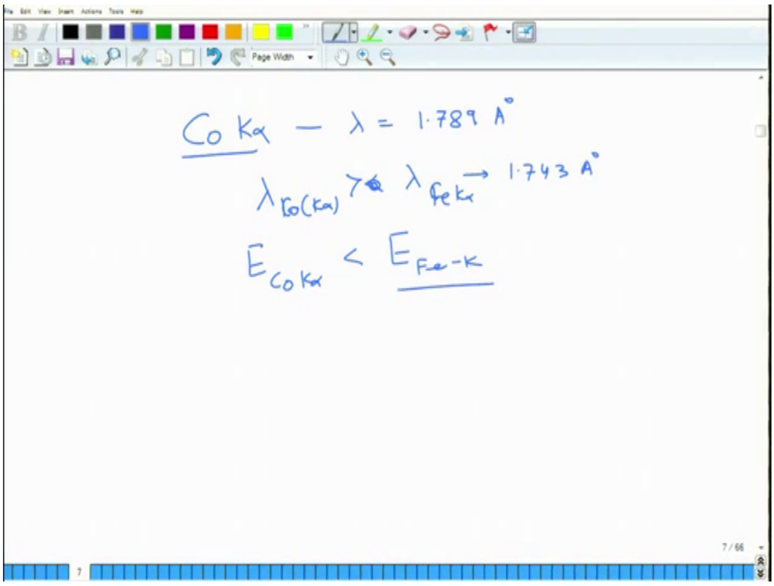

$\underline{Co\ K\alpha} - \lambda = 1.789\ \mathring{A}$

$\lambda_{Co(K\alpha)} > \lambda_{Fe\,K\alpha} \rightarrow 1.743\ \mathring{A}$

$E_{Co\,K\alpha} < \underline{E_{Fe-K}}$

So, for these we choose for example, cobalt k alpha cobalt k alpha has a lambda which is 1.7 8 9 angstrom. So, this lambda is lower than is higher than the lambda of iron, which is a Fe k alpha, which is as I said 1.74 3 angstrom. So, which means the energy of Co k alpha is lower than energy of Fe k. So, there will be no absorption ok.

So, basically a same concept of the absorption edge so, you can use this knowledge of absorption edge with respect to the incident radiation in different ways you can choose appropriate filter to filter out k beta, but at the same time you can choose an appropriate radiation which will not lead to background radiation in the form of secondary X-ray s out of the incident material out of the material which you are using for analysis.

So, basically these are two uses of knowledge of absorption edge. So, for nickel as I said we you for copper xu k alpha we use nickel filters and there are other materials for which we use different filters.

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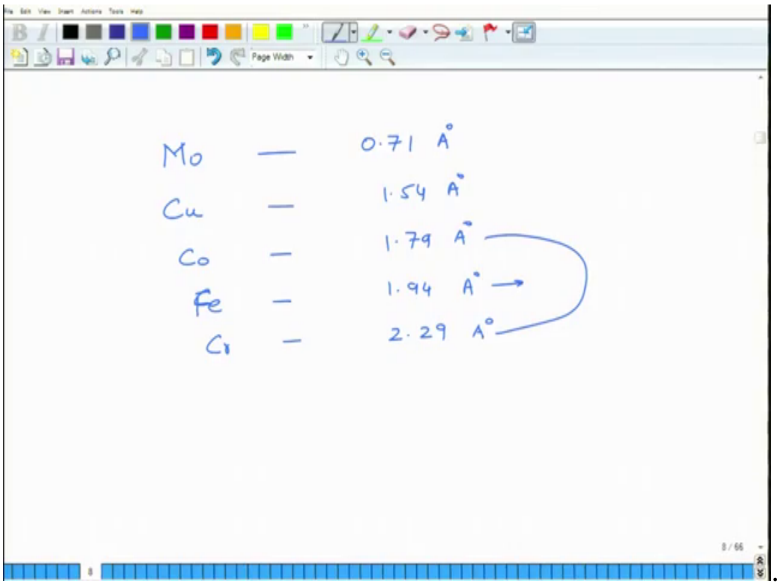

Mo — 0.71 Å

Cu — 1.54 Å

Co — 1.79 Å

Fe — 1.94 Å →

Cr — 2.29 Å

So, now, let me give you the wavelength of various radiation that we use the wavelength that we get is about 0.7 1 angstrom, see you we have about 1.5 4 angstrom, copper we have cobalt we have 1.7 9 angstrom, ira we have about 1.9 4 angstrom and chromium is about 2.2 9 angstrom.

So, if you have iron containing material if you have iron containing material we typically use cobalt or chromium you do not use copper. So, that is how you choose so, but what it requires is operator needs to change the source of X-ray s. So, there is a gun which has a filament is fixed.

So, the filament and the target is fixed either it is copper target or chromium target or smalley target, which means you need to change the gun every time you make this measurement. So, some system hours I think system some systems have both iron and copper and chromium targets some systems have only copper targets. So, you have to live with that appropriately ok. So, this is about the X-rays.

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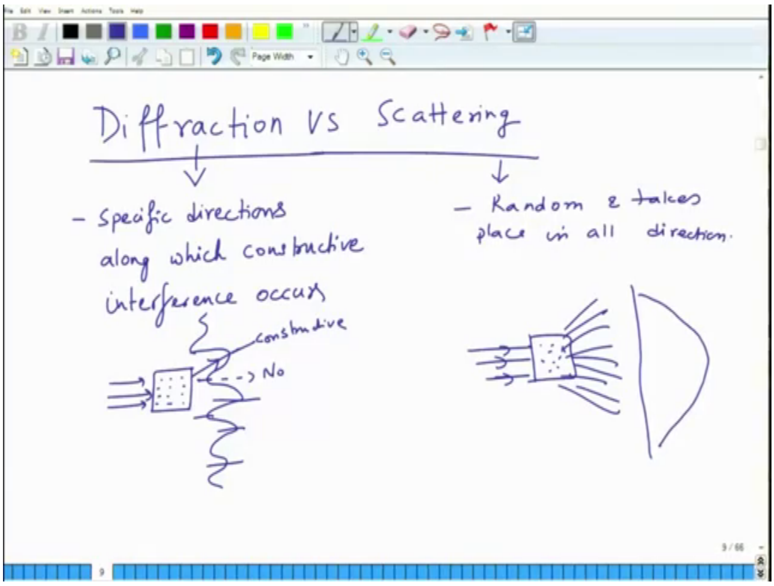

Diffraction VS Scattering

- Specific directions along which constructive interference occurs

- Random & takes place in all direction.

Now, let us move on to the diffraction. So, now diffraction when light encounters any obstacle well it is an obstacle atoms or obstacles. Now depending upon whether they have periodicity or not light will get scattered or refracted.

So, there is difference between diffraction and scattering diffraction leads to effect. So, when you have a periodic. So, diffraction let us say versus scattering diffraction happens in specific directions along, which constructive interference takes place ok. Along which constructive interference occurs whereas, catering on the other hand is it is random it takes place in all the directions right.

So, in what happens here is when up when the x rays encounter when a light when a radiation encounters a material, which is periodic in nature and the diffraction leads to for example, this is constructive interference certain angle in this there is no diffraction.

So, you will have sort of maxima minima maxima minima this kind of thing ok. So, you will have this kind of thing. So, wherever you have peaks you have constructive interference, wherever you have valleys you have destructive interference and this is as a function of spacing or angle ok. Whereas, in this case when radiation encounters an object, which may be non-periodic then you have a scattering in all the directions very weak effective observed ok. So, you will have a sort of broad hump kind of thing as a function of spacing or angle you will not have a particular constructive or destructive interference.

Student: are they different from the basis of the size of the object.

So, size of the object is going to determine side though. So, whether the diffraction will take place or not size of the object will determine the wavelength. So, if you choose appropriate wavelength depending upon the size of the slit spacing; then potentially it will diffraction, but if slits are randomly placed all over the place then they do not reinforce they just cancel it they just they interfere in such a manner. So, that there is no constructive interference.

Student: (Refer Time: 23:23) size of the (Refer Time: 23:25).

Size of the object mean size of the material.

Student: The object.

The Atoms.

Student: The Atoms ok.

I mean atoms have a spacing right.

Student: (Refer Time: 23:34) we can talk about the atom.

Yeah, every atom so, if you if you just have single atom a single atom will scatter a single atom will scatter, but the effect will be weaker, but it is only when the you have it is only you have multiple effects. So, if you if you if you want to talk about the number of slit, that you can have then the system.

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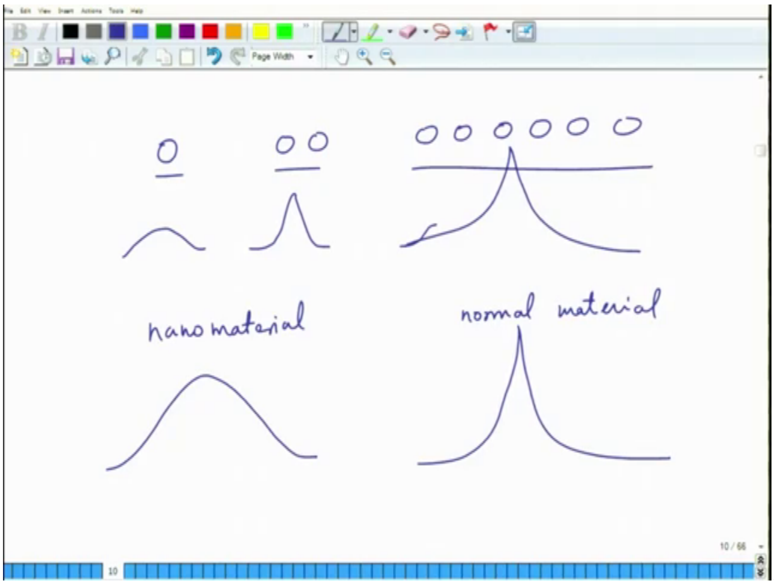

So, you can have 1 slit you can have 2 atoms you can have multiple number of atoms. And this is basically changing the number of slits, when you change the number of slits or you change the number of atoms in a material, then the diffraction effects become stronger.

So, this will give you one broad peak this will give you a sharp peak this will give you even more sharp peak, to a sharpness of X-ray diffraction pattern there is a whole analysis on the intensity as a function of number of slits. So, as the number of slits increase the X-ray envelope that the envelope of reinforced beams becomes sharper as a function of number of slits. So, when the number of let us go up it becomes very sharp.

So, size of the atom does not matter size of the atom does not matter the size of the atom is same as nearly same as the wavelength of diffraction, but so, that is what you see? So, if you have a nano-material and if you have a normal material and nano-material gives you a diffraction pattern, which has a broad peak, but if you look at the normal material it gives you a sharp peak.

So, this is what is the different number of so, this is basically number of slits number of slits are increasing as the number of slits increase with the same spacing the peaks get sharper and there is a whole physics behind this. So, basically the it says that your X-ray envelope gets more and more sharper as your number of slits increase I unfortunately cannot go into details of that, but there is whole analysis behind that.

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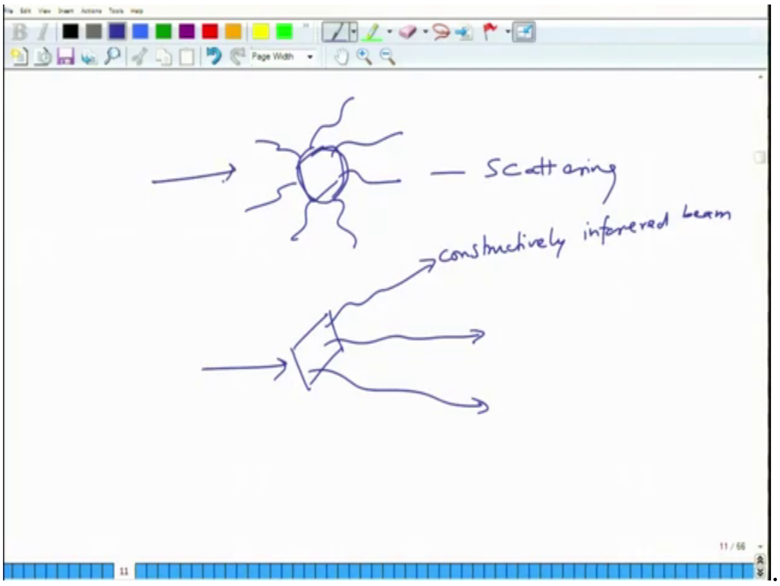

So, basically when you have a scattering you have beams going in all over the directions this is scattering and if you have a crystal, which is diffracting. So, let us say this is the a periodic crystal or or just scattering over a particle and when you have so, you have specific directions along which so, this is constructively interfered beams.

So, only at these positions you will have diffraction which is occurring ok. Constructive destructive interference I am sure you know from basic physics. So, let us not get into that. So, the diffraction there is a whole lot of physics of diffraction as far as crystals are concerned, one can talk about diffraction from crystals in a using a reciprocal lattice model.

So, where you need to talk about the reciprocal lattice vectors because reciprocal, because lambda is just a scalar property, but diffraction phenomena itself is a directional phenomena. So, if you want. So, it is it is appropriate to represent the X-ray s in the form of vectors, and that is where we use a quantity which is called as wave vector wave vector is a reciprocal of wavelength, but if you want to use the wave vector then even for the lattice you cannot use a normal lattice vector you have to use the reciprocal lattice vector.

And that is where one deals with (Refer Time: 27:25) equations and Ewald sphere we will not get into details one neat way of evaluating X-ray diffraction, through crystals is via Braggs law which put it very which puts it very simply using without you without the use of vectors as such.

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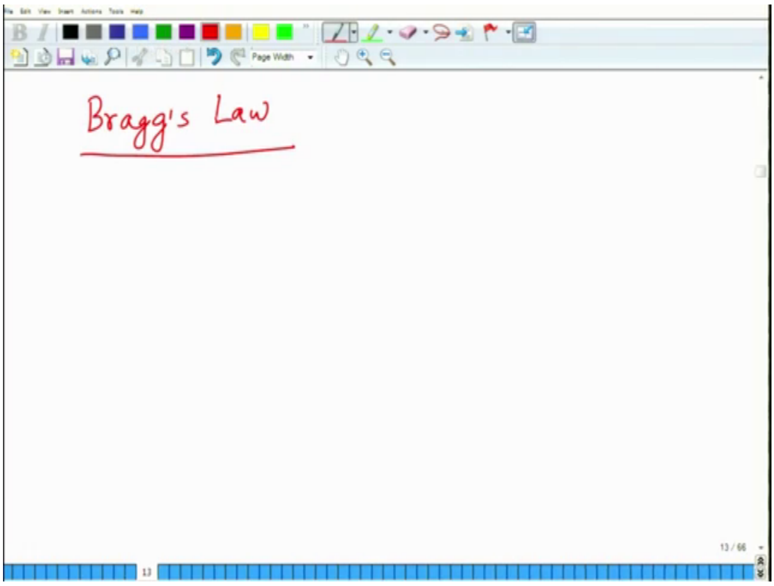

Bragg's Law

So, let us now look at what is a Bragg's Law. So, we perhaps take this up in the next class, because we have the time running out. So, we will start with the Braggs law in the next class and then we will look at the diffraction intricacies through the crystals.