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

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Lecture- 32
Structure Determination (X-ray Diffraction)

So, we start a new lecture, again we will start the new topic.

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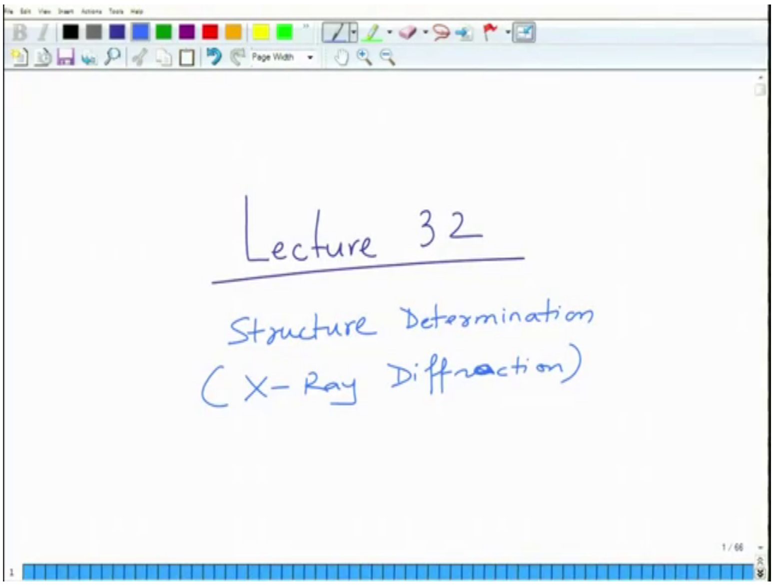

Lecture 32

Structure Determination
(X- Ray Diffraction)

In this lecture which is so, now, having studied the structure of various solids, we started metals, we then, we moved on to ionic solids and covalent materials, which are basically ceramic materials and then we moved on to non crystalline materials, such as glasses and polymers. So, now, the question arises is how do we evaluate their structure experimentally and, and how do we distinguish between various materials having same in structure or having crystalline in structure.

So, one technique, which is very useful and powerful is X-Ray diffraction, which is the most fundamental technique to characterize the structure of crystalline materials ah. So, what we will do in this lecture and henceforth, in subsequent few lectures is, we will study the basics of X-Ray diffraction and it is usefulness to characterize the structure of materials. So, all of you are aware of physics of diffraction.

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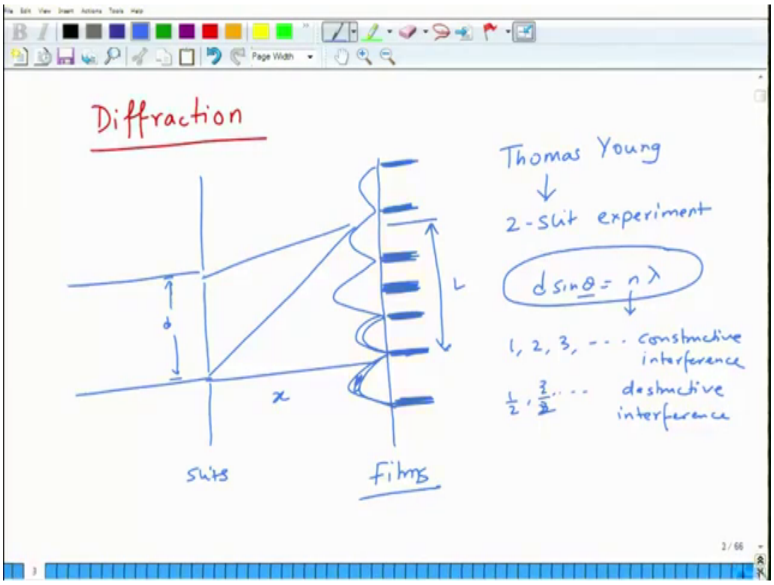

So, diffraction, it was initially studied by people like you know it, the effect was discovered, observed in 1600s in 1665 by some Italian scientists, but proper understanding of diffraction came only after Thomas Young conducted his two slit experiments. So, Thomas Young conducted his two slits experiment, where he had these two slits and he had a screen here. So, these are two slits, which are spaced by spacing d and when the light strucked them at certain angle, whatever angle it was. He observed the pattern on the screen, which was basically something like that; it was fringe kind of structure.

So, not very nicely made, but nevertheless, you understand what I need. So, he, he observed dark and basically, series of you can say dark fringes followed by light fringes, on a photographic film ok. So, this was a, you can say film the light hit, the film and wherever it had, wherever it had maxima and minima correspondingly, you had bright and dark fringes, depending upon the exposure of light with the. So, basically, the word so, this was started by Thomas Young, who is famous for his two slit experiment, who said that? So, you had certain angle of diffraction.

Let us say and if the screen, this distance was x this was L then and the slit spacing was d then what he found out was d sine theta was equal to n lambda and what he said was sine theta was the angle of diffraction and was the integer. So, when n, n was 1 2 3, then you had, then he had constructive interference and when n was equal to half 3 by 2. So, on and. So, forth then it was destructive interference, which means when the port; so the angle, the corresponding angle and d there was a slit spacing and the angles of diffraction and a lambda was the wavelength.

So, basically what he said was, that there is a, this condition, which needs to be fulfilled for diffraction to occur, where n is an integer, the moment it ceases, ceases to be an integer. There is no diffraction at least. So, destructive interference; so basically a Thomas Young's experiment laid the foundation of modern diffraction analysis and basically what it meant was, if you can observe diffraction phenomena using visible light in and using two slits materials crystalline materials, which have atoms, which are periodically arranged that spacing d equal to a.

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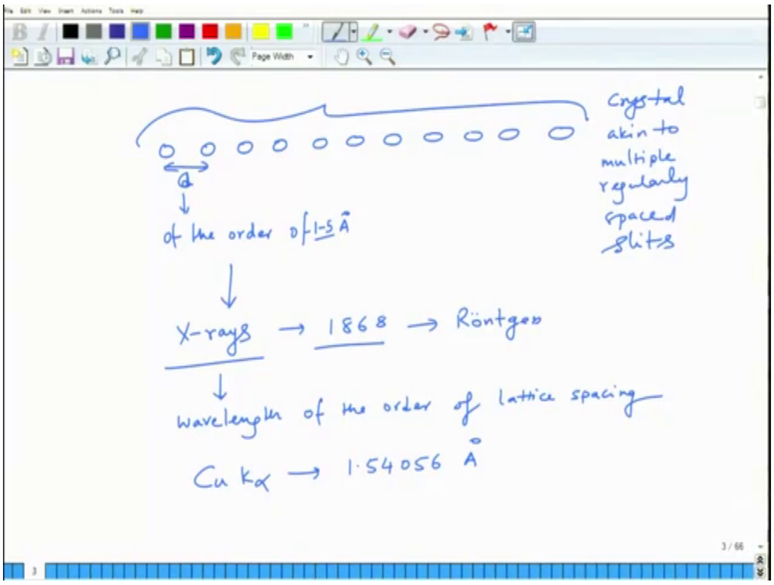

Let us say lattice parameter, they can be considered as if these are multiple number of slits. So, in Thomas Young's experiment, he conducted the experiment with visible light. The slit dimension was same as that of a light, because you can see from this relation d sine theta is equal to n lambda ok. So,, sine theta, since sine theta cannot be beyond plus and minus 1 and that d and lambda should be comparable to each other ok. So, in this case the slit spacing was comparable to the, to the wavelength of light how.

So, the question now, in case of materials is that if we consider materials as made up of millions of slits, which are equally played, which are regularly spaced in space as at a spacing, a this a happens to be of the order of angstrom or, so maybe 3 angstrom, 3 angstrom, 3 angstrom, 4 angstrom. We need, radiation, which is of equivalent wavelength. So, it cannot happen. So, you cannot get diffraction effects from metals or materials, using visible light.

Visible light wavelength is far higher, it lies, visible light lies between 300 to 700 or 800 nanometer right whereas, the spacing here that we see in case of materials is of the order of few angstroms. Let us say 1 to 5 angstrom. So, the question was what is that radiation and this happened only when X-rays were discovered. So, this let us lead to X-rays, which were discovered in 19th 1868 by a German scientist called as Rontgen. He was the one, who discovered X-rays, first in 1868 and X-rayed; X-rays had the wavelength of the order of lattice spacing.

So, for example, copper k alpha, x-ray it has a wavelength of I am strong, which is nearly of the same order of magnitude as you have the lattice spacing. So, this was a major turning point in, in, in terms of characterization of crystals post Thomas Young's two slit experiments. So, these are basically you can consider a crystal akin to multiple regular, regularly spaced slits. So, basically they should also behave like slits, it is just that we need to find a right wavelength, which can fulfill the diffraction condition. So, so lot of work was done in 1912 1900s or 1900s.

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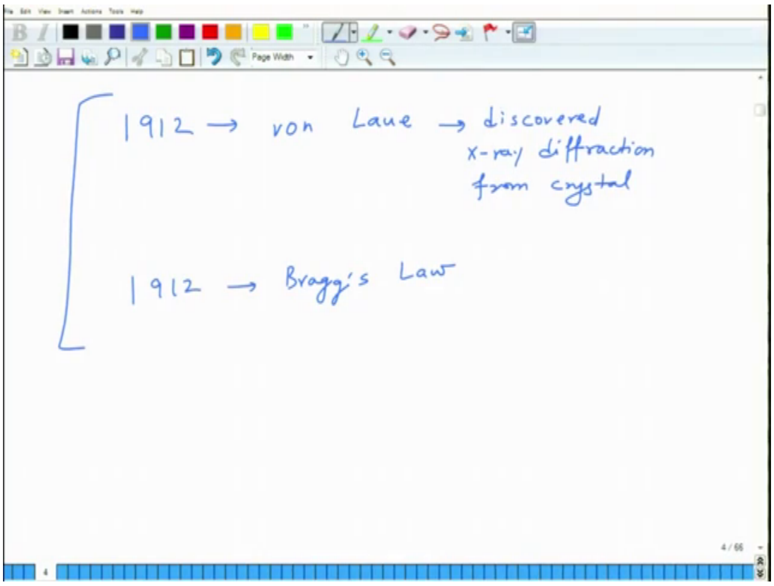

1912 → von Laue → discovered
x-ray diffraction
from crystal

1912 → Bragg's Law

So, 1900 and 12 Von Laue, he discovered X-ray diffraction from crystals and then in 1912 Lorenz and William Bragg father and son. They gave rise to Bragg’s law. So, that was again a remarkable discovery. These were two landmarks in crystal characterization using X-ray diffraction. So, we will not get into history of it, we just stop here, but this is basically the, the message was that you needed to found, find a radiation, whose wavelength was comparable to the lattice spacing, because lattice can be considered as an array of slits and it happened only when X-rays were discovered, because X- rayed had a wavelength, which was of the order of which had the same order of magnitude as the lattice spacing. So, where do X-rays lie. Well let me show you a picture.

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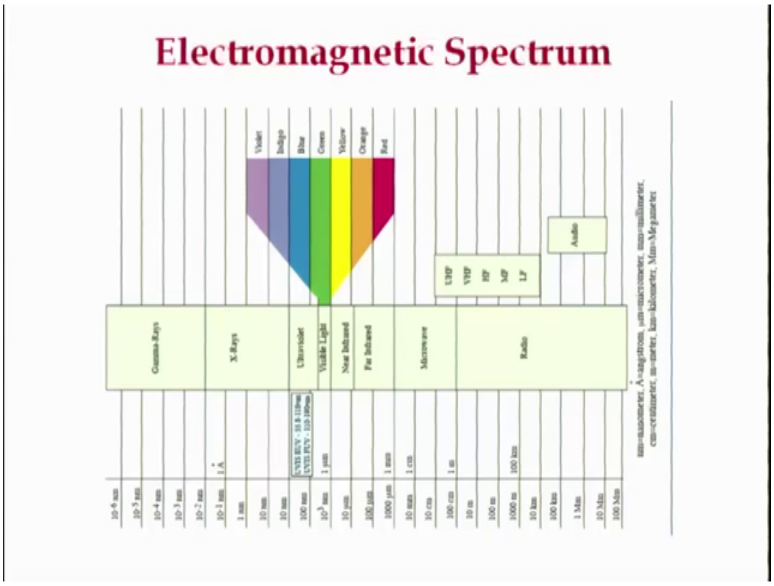

Electromagnetic Spectrum

So, X-rays lie somewhere here. So, you can see, this is the electromagnetic spectrum, we have, this is a visible region, visible region lies between, nearly 300 to 700 or 800 nanometers on the right of visible, which means at higher wavelengths. We have near infrared, far infrared microwave, radio waves, which are of very long wavelength and they are useful as far as, diffraction from crystals is concerned for diffraction to happen from crystals, you need to have shorter wavelengths. So, UV is nearly 100 nanometer, which is not very useful.

So, that is where we jump bump into X-rays and these X-rays, the one on the left of the wavelength of the order of 1 angstrom to 2 angstrom are useful for us. We have, you can have excess of 1 nanometer wavelength as well, but that is not useful, because most materials have lattice parameters, which is far smaller than 1 nanometer.

So, we need to be in the far extreme of X-rays to have wavelengths, which satisfy our criteria of diffraction, if you further deduce the wavelength, you get into gamma rays, but we do not want gamma rays for diffraction, they are also very dangerous to deal with x is also dangerous, we need to use them properly, but ah. So, this is where we are, we are in this regime of wavelength of the order of one and strong. So, how does X-ray get produced?

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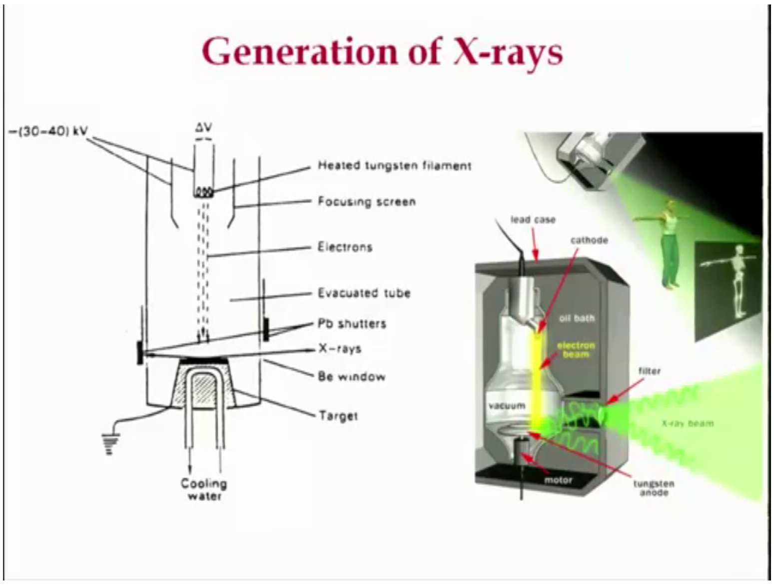

Generation of X-rays

So, this is a picture which shows you the production of X-rays. So, what happens in this case is you, you have a heated tungsten filament, which is kept at a very high bias 30 to 40s kilo volt, which is the mid large amount of voltage. Under this high voltage, the filament emits electrons high energy electrons are emitted from the filament and they leave in an evacuated tube. So, this whole thing is kept inside evacuated tube. So, that you have no scattering, no by the air molecules ok.

So, there are no air molecules and these electrons are focused onto a, target and this target is made up of a material from which, you want to generate X-rays. So, if you want to generate copper X-rays, it could be copper target, if you want to generate iron X-rays. It could be iron target, if you want to generate molybdenum X-rays, it could be molybdenum target and this hits the target and target generate X-rays at certain angles and these X-rays are then taken through windows, which are typically made up of beryllium to, to wherever you want to use them.

So, this is how you produce X-ray. Now, since a very large voltage since the energy of an impinging electron is very high target gets heated. So, this target has to be consistently cooled with the cooling water, otherwise is a chance of melting and evaporation. So, this is how you produce X-rays all right and X-rays are also used for lot of other applications such as; medical applications, but we will restrict ourself to the use of diffraction in crystals. So, now. So, basically how X-rays are generated are, you have these atomic, you have these electronic crystals. So, let us electronic orbitals.

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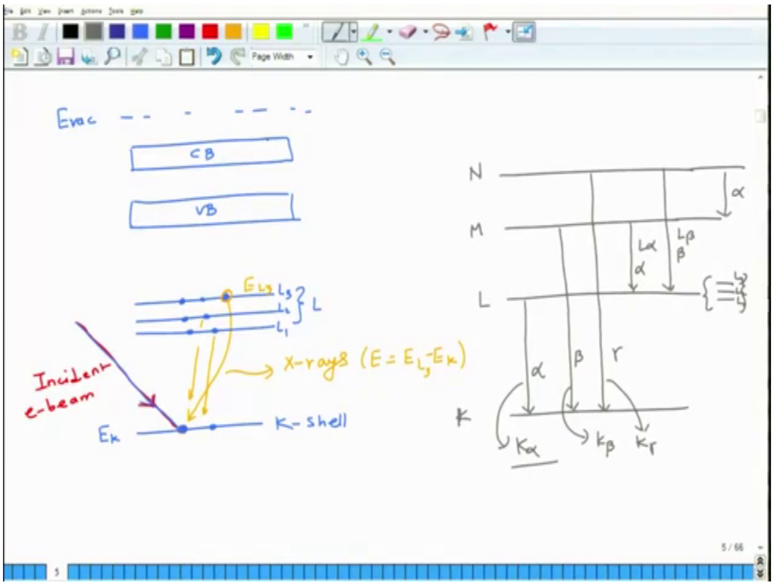

You have K shell and then we have L shell, L shell can have three sub levels ok. So, this is K shell, which is corresponding energy E K right and then you have L shells, you can have L 1 L 2 and L 3. So, and then you have of course, have you know something called as valence band and then you have something called as conduction band, you have these energy bands and then of course, you have vacuum level ok, this is evac all right. So, this is how energy levels are falling. So, when you. So, these you have, these electrons here, some electrons will be sitting somewhere ok.

So, these electrons are there. Now, when a high energy, when high energy electron comes in. So, this is high energy electron that comes in ok. This high energy electron gets knocked off. So, this is incident electron beam. So, this knocks off this electron. So, this electron has, has been knocked off. Now, what happens is that you have created, now a vacant state here, this is vacant state. So, which means something from the top level has to fall to make sure that there are no excite. So, this becomes excited state right. So, this electron will now, come and occupy this place. So, this will the, the release of this from higher energy.

So, this is higher energy electron. This higher energy electron will come and occupy this place leaving this as empty and this gives rise to emission of X-rays. So, basically the X-ray energy is this energy. Let us say this energy is E 1. This energy is E K. So, X-ray energy will be; so, energy of X-ray will be equal to even minus or let us say EL 3 in this case EL 3 minus EK. So, this is how the X-rays are produced. So, depending upon that, depending upon from where the transition has happened the X-ray will have certain energy, if the electron comes from higher levels, it will have even more higher energy.

So, there is a probability of transition electron come, come from here, it can come from here, it can come from even higher levels KLMM. You have all sorts of levels there. So, there is a probability of transition and not know and there are certain transitions, which have higher, intensity as compared to other, they may not have same energy, they will have different energies, if they are coming from different levels, but the probability of transition from certain levels is higher as compared to others. So, you can say now, you can draw this as KA K edge and then we can have L, then we can have M and then we can have N.

So, transition from L to K, this is L M N the transition from K L to K is referred as alpha transition, transition from M to K is referred as beta transition and transition from M N to K is referred as gamma transition. Similarly, in this case, this will be alpha, this will be beta. Similarly, in this case it will be alpha. So, transition from the next level to the level below is called as alpha, if you are going to one above transition from there to the bottom level is called as beta an so on and so forth. So, this is why we say, when we say K alpha, this becomes K alpha, because the transition has taken place from L to K K beta will mean transition from M to K, this is K gamma, which is very rare. Similarly, this will be L alpha, this will be L beta.

So, these are all X-rays, you will see if you, if you, if you go to a CM room, you see that chart right, where different energies are there. You will see for some elements, you see K alpha, for some elements you see K L alpha and so on and so forth. These are what those lines are basically transition from, it is if it is L line, it is basically transition from M to L, if it is K line, it is transition from L to K K alpha, if it is K beta line, it is M to K and they have different energies as you can see, because energy is that, that the energy difference between, different transitions, different lines is different ok. So, now, let me show you sample, in this I could just draw it.

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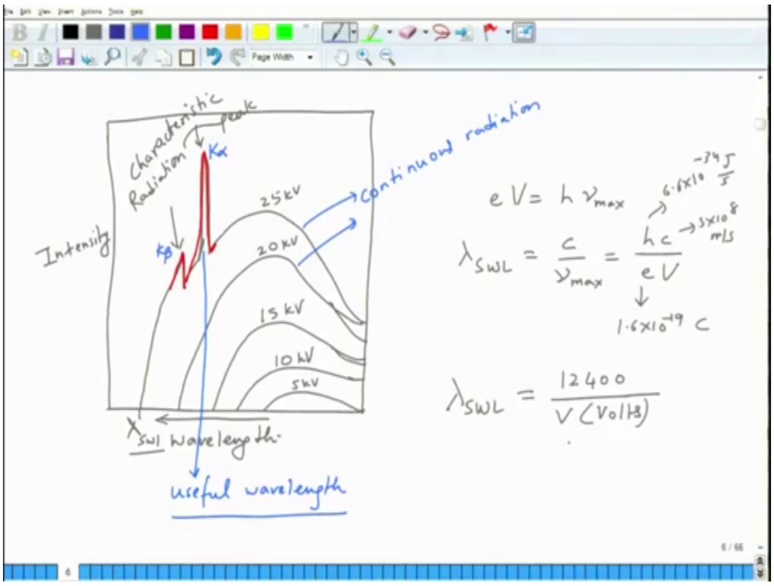

$$eV = h\nu_{max}$$

$$\lambda_{SWL} = \frac{c}{\nu_{max}} = \frac{hc}{eV}$$

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

So, when you know (Refer Time: 19:29) ok. So, I written this alpha also, you can have alpha 1, alpha 2, alpha 3. So, because L is made up of three sub levels ok, L 1, L 2, L 3. So, from here, you can have the transition from the lowest 1 will be alpha 1, the lowest 2 will be alpha 2 and so on and so forth; so, ah. So, you can have this various transitions alpha 1 and alpha 2. Now, let me show you the diagram of how X-rays spectrum looks like. So, if, when the X-rays are produced on the bottom axis, I plot wavelength on the top axis, I plot intensity y axis and the, as a function of voltage.

The X-ray spectrum, because you, because there is a possibility of all sort of transitions happening, you do not produce just 1 wavelength, you produce multiple wavelengths, when you produce multiple wavelength is called a continuous radiation or you know white radiation. So, we tend to produce these lines like that ok. So, these are lines and then suddenly at certain you have these, actually, they go, they go more steeply here far more steep drop. So, these are ah. So, this is basically as a function of voltage, this is 10, let us say 15 and this is 20 and this is let us say 25 KV ok. So, this is KV, KV, KV and you will have 5 somewhere here. Let us say 5 KV ok.

So, as you are accelerating voltage, changes your spectrum shifts to left and this is, this limit is called as lambda SWL short wavelength limit. How do we work this out? We know that e V can be equated to h nu. So, corresponding to the voltage, you will have maximum frequency. So, lambda SWL is basically C divided by nu max which is equal to h c divided by eV nu max is equal to e V divided by h it goes up. So, if you work this out h is 6.6 planks constant 6.6 into 10 into 20 minus 34 joule per second C is 3 into 10 to power 8 meter per second, electron charge is 1.6 into 2 by 10 to power minus 19 coulomb.

So, lambda SWL works out to 12, 12400 divided by V in volts. This is how lambda will. So, this is how. So, at a given KV you can see, now as the voltage increases the lambda as will decrease. So, that is what we see the lambda SWL decreases, as we increase the voltage and this is also useful, because at higher lower voltages, you get a radiation, but you do not have any characteristic radiation, you have all sorts of wavelength, you do not know which one to pick from suddenly, at about to 25 30 KV, what happens is that there are some very intense peaks, which is start developing, these are called as characteristic peaks, that is just a radiation peaks.

Let us say these are, this kind of peaks, these are characteristic radiation peaks, typically they are referred as this could be K beta. This could be K alpha. So, you can see K alpha is a transition form L to K, K beta is a transition from m to K. So; obviously, m to K will have higher energy correspondingly lower wavelength. So, K beta will always occur at lower wavelength as compared to K alpha, but intensity of K alpha is far higher as compared to K beta and that is a reason, why we use K alpha radiation and X-ray diffraction, because it is a very intense peak, it gives you high intensity x-rays of wavelength. So, this K alpha wavelength is the useful wavelength.

So, this gives you a very intense peak, there could be other peaks as well and there could be other minor like L alpha, L beta and all that, but they, they are not, intense as compared to and they will probably be lower in energy as well, because it is a L would be transition from, klmn, m to l right. So, m to L transition will be far lower in energy as compared to transition from let us say from m to K. So, it works out. So, this is all depend upon probability of transition and what is the yeah. So, lot of factors, it is determined by, but nevertheless, what we get is, K alpha radiation with very high intensity, corresponding to a wavelength, which is useful in nature and the, this, these plots are called as continuous radiation, because they are basically continuous contours.

So, they give you the overall, what you get out of a material at a given voltage. So, they have all sorts of X-rays and the intensity changes of course, as a function of, wavelength, but there is no very sharp peak at lower voltages. It is only at high voltages, you start getting these sharp peaks, because you are then able to excite the electrons form K alpha.

Remember, if you want to excite the electron from K alpha, you also need higher energy, because K alpha is the bottom most shelf, when you, when you bombard material with, at higher, at lower voltages. You are only exciting electrons from the top orbital, because they are loosely bound as compared to the, the one inside the one, which are close to the nucleus ok. So, this is what the X-ray spectrum looks like and if you for example, look for various materials.

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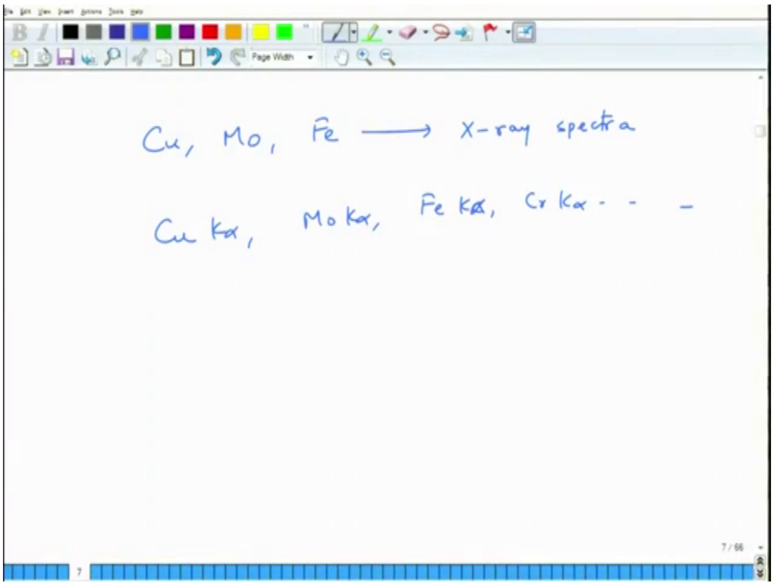

Cu, Mo, Fe $\longrightarrow$ X-ray spectra

Cu $K\alpha$, Mo $K\alpha$, Fe $K\alpha$, Cr $K\alpha$ - - -

So, various materials, which are used are copper molybdenum, iron to give you this X-ray spectra. So,. So, we use copper K alpha, we use moly K alpha, Fe K alpha chromium K alpha and so on and so forth, these radiations are used and they will have different wavelength.

Student: what is the criteria (Refer Time: 27:06) material (Refer Time: 27:08) target materiall.

Most of these are metals, because they emit X-rays, which are useful to you. So, you can, the radiation that you use, depends upon type of materials that you want to examine ok. So, for example, copper gives you a wavelength, which is useful in most circumstances, but copper wavelength is not very useful in case of iron containing materials that is where you choose chromium target. So, the criteria and I will come to that in a little while.

So, probably we do not have enough time. Today, we will probably wind up here, what we have seen basically is how X-rays are generated, what do you mean by K alpha and K beta and so on and so forth. In the next lecture, we will see some of these intricacies as to which, X-rays to choose, which is dependent upon the absorption of X-rays by the material, what is because X- rays also create radiation of out of materials. So, whether it leads, when your fluorescence or not. So, we will discuss that in the next lecture.