## Indian Institute of technology Madras Presents

## NPTEL NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture-22 <u>Materials Characterization</u> <u>Fundamentals of X-ray diffraction</u>

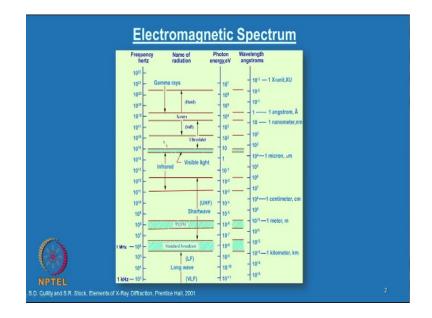
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Hello everyone. Welcome to this material characterization course. So far we have seen the scanning electron microscopy as an instrument and its principal, application and so on and from this class onwards we will look at the X-ray diffraction in much more details as we have already discussed in the fundamentals of this, this course we have gone through the basic aspects of electromagnetic radiation and in that respects, we have also looked at the indirectly the properties of X-ray to some extent.

And this lecture we will just look at the properties of X-ray in specific and then how they are generated and how this X-ray diffraction technique is exploited in understanding the crystallography, phase identification and quantification of phases and texture etc during the next ten lectures.

So if you look at the, the fundamental ideas what we have generated so far X-rays also falls into the category of electromagnetic radiation and then all this you know the wave properties what we have just discussed in terms of electrons as well as the other electromagnetic radiation will holds good and I also assume that before we get into the actual syllabus content, I assume that you have enough or a basic crystallographic knowledge to observe this ideas whatever we are going to discuss and I am not going to spend exclusively some time on the crystallography. But then I will just discuss the concepts then and there wherever it is necessary. So in this class I would like to just talk about the general properties of X-rays and how is the X-ray spectrum is going to look like and what are the characteristic X-rays a little more detail about that and from next lecture onwards we will talk about production and then how they are actually used in the practical application and so on.

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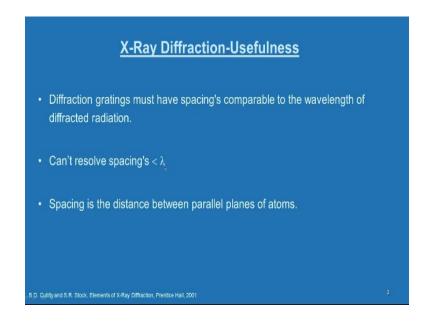


So yeah now look at this electromagnetic spectrum which you are already familiar with. We are now going to concentrate only on this X-rays where you see that the range here is around  $10^{-2}$  to here about  $10^2$  here and then you have the corresponding photon, photon energy in electron volts and you have this classification here or the X-rays depending upon its wavelength, whether it is hard X-rays or a soft X-rays depending upon the, the penetrating capability and then the wavelength.

It is all classified. We will look at the details much more in the due course. So just to give you an idea where these X-rays or falling in the electromagnetic spectrum and as I just have been mentioning all these lectures like when you choose an electromagnetic radiation for the material characterization you have to be sure that you are the, the probing dimension is equivalent to the

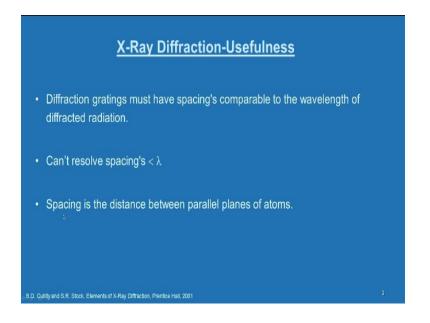
wavelength of probing radiation. So same thing is applicable in X-ray of X-rays also. So in order to use X-rays as a probe in determining the crystal structure or any phase identification,

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you have to make sure that even that material which you are examining or the crystal system which we are examining we have the similar d-spacing as I mean the  $\lambda$  should match with the probing dimension as well. So that is what we are just recollecting again. For example diffraction gratings must have the spacing comparable to the wavelength of the diffraction diffracted radiation, can't resolve any, any structure which is less than this range of X-rays, spacing is the distance between the parallel lines of the atoms.

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So that is how the grating experiments are I mean with these assumptions the grating experiments are done. And we will now just see what is the continuous spectrum there is basic characteristic of electro I mean X-ray spectrum is called continuous spectrum. We will see why the word continuous. X-rays are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated. As we have already seen that how these characteristic X-rays are produced in, in one of the lectures in SEM where we, we have taken up the energy dispersive spectrometry.

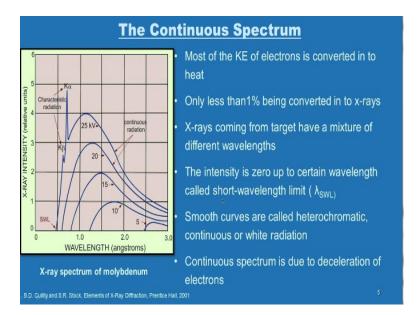
So the character, characteristic X-rays are produced fundamentally in the similar manner. The electrically charged particle of sufficient kinetic energy how this is achieved that means you should have an electron source and then to accelerate its path or the moment you have applied voltage which keeps that acceleration and then these accelerated electrons are made to impact on a target. These we have seen already the same thing X-rays are generated and their energy is rapidly decelerated.

So that is what the same thing here. We will see in an in a systematic manner in a X-ray diffraction meter as well. Electrons are normally used for this purpose. X-rays are produced at a

point of impact and radiate in all direction. You see the, the X-ray production what, what we are going to see in a in a laboratory X-ray diffraction, X-ray tube it is based on the a point impact but we will also see that whether we are only going to create X-rays by a point impact or is there something else that is that, that details we will see but, the characteristic X-rays what we talk about is produced at the point of impact and when it, I mean went it radiates in the all direction

The kinetic energy of the electrons on impact is given by the equation that is  $\mathbf{KE} = \mathbf{eV} = (\frac{1}{2})$ **m.v**<sup>2</sup>, e is the charge on the electron 1.6 X 10<sup>-19</sup> coulombs, m is the mass of the electron 9.11 X 10<sup>-31</sup> kilogram, V is the voltage across the electrodes and v is the velocity in meter per second. So this is how the, the kinetic energy of the electron in the X-ray tube is described and what, what now you are seeing is a continuous spectrum.

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A typical X-ray spectrum what, what is plotted here is is an X-ray intensity and in the x axis it is the wavelength in angstroms. So what you have to now look at is, these curves are plotted as a function of different applied voltage you see that 5, 10, 15, 20 and 25. So you have so many things to observe from this graph we will look at one by one. What you have to see here is you see that the, the wavelength what you are seeing in each of this curve is not just a single wavelength it is a range of wavelength. So what happens is in an X-ray tube when, when they the electron source which is accelerated and then made in rap I mean rapidly impact on the target the X-rays are generated.

These X-rays are not having a particular wavelength. They will have a range of wavelengths that is why it is coming like this. So this is a typical X-ray signal which is coming out of the X-ray generation tube. So you will have a spectrum of wavelengths which is associated with the kind of signals you get from the target. So the first point is most of the kinetic energy of the electrons is converted into heat. Only less than 1% being converted into X-rays. Please understand this that is why the X-ray tubes are critically cooled by the water.

It is for most important thing that this tube is cooled continuously during its operation because you are seeing that only 1% is being converted into X-rays rest of them are being converted into heat. So X-rays coming from the target have a mixture of different wavelengths that is what you are seeing here it is a mixture of different wavelengths. The intensity is zero up to certain wave length called short wavelength limit  $\lambda_{swl}$ .

This is what it is. Up to certain wavelength you do not have any intensity. Smooth curves are called heterochromatic or continuous or white radiation the whole spectrum this continuous line is called white radiation as well as heterochromatic or polychromatic radiation which is having a mixture of wavelengths and continuous spectrum is due to deceleration of electrons.

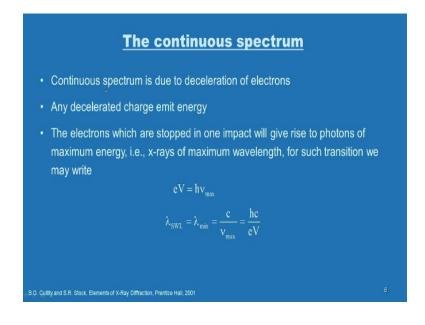
You see I just said that the electrons are accelerated and then made to impact rapidly on the target and then it produces an X-ray. In that process it is not going to give you a radiation with the single wavelength or energy it is going to give a mixture of wave lengths that is what we have seen. Now it is not that every impact which is being made on the target is giving signal with one impact there is something like you know you will get an X-ray characteristic X-ray with the one impact of maximum energy that may produce a characteristic signal.

We will see what is a characteristic signal in a new course. But you will also have an electron which will not make one impact which will deflect somewhere and then finally impact the target and then produce a signal which may have a less energy or a range of energy like that you get signals that is why you get a kind of a disperse wavelength signal here and that is very important. So the one which makes the signal with one impact which will for example produce a maximum energy that you make call it I mean call it as a characteristic signal as well.

So what you are seeing here is a characteristic radiation which is  $K\alpha$  and  $K\beta$  we will talk about it little I mean in due course but before that it is important to note that these curves are plotted as a function of applied voltage. What you have to appreciate here is it is not that you know if you, you get the characteristic signal at all the given voltage but there is a particular threshold voltage which only trigger the release of characteristic X-rays that is very clear.

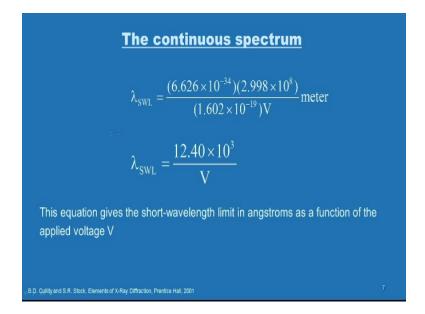
So as the voltage increases the intensity of the X-ray coming out is also increases and you can also appreciate that as the voltage increases the wavelength of the peak intensity also reduces. You can see that the peak is here, peak is here, peak is here and peak is here. As the voltage increases the peak intensity, the wavelength correspond to the peak intensity also moves to the left and then at particular wave I mean applied voltage you see that the maximum intensity with a very narrow wavelength.

So called a characteristic wave I mean radiation of a particular target is known. So we should also think about what will happen if I keep on increasing this radiation further, what will happen that we will see. You may increase the intensity and what will happen to this characteristic wavelength, will it move left or right that we will see in next few slides. So these are all some of the important characteristic see how do we have to observe and then and I this schematic plot clearly shows what is continuous spectrum. (Refer Slide Time: 16:04)



And what is characteristic line and why do you get a range of wavelengths all this aspects one can understand from this X-ray spectrum of a molybdenum here this is a molybdenum spectrum. So continuous spectrum is due to deceleration of electrons. Any decelerated charge emit energy. The electrons which are stopped in one impact will give rise to photons of maximum energy that is X-rays of maximum wavelength for such transition we may write  $eV = hv_{max}$  which can be written like this  $\lambda_{swl} = \lambda \min = (c/v_{max}) = hc/eV$ .

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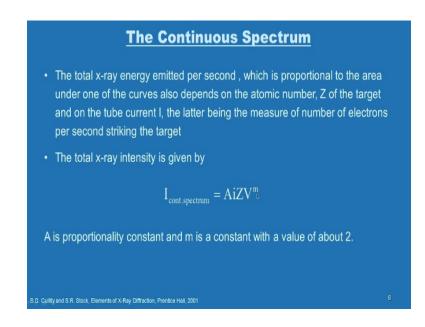
So what you are trying to see here is the electrons which are stopped in one impact how that is being visualized in terms of energy and then indirectly the  $\lambda$ . What is that short wavelength limit and how to find out that, this is the simple expression. And if you put all this units in it I mean and its values constants in place and then you get a final expressions like this as a function of applied voltage  $\lambda_{SWL} = (12.40 \times 10^3)/V$ . This equation gives the short wave length limit in angstroms as a function of applied voltage.

So this is about continuous spectrum. Few more marks, the total X-ray energy emitted per second which is proportional to the area under one of the curves also depends on the atomic number Z of the target and on the tube current I, the later being the measure of number of electrons per second striking the target. So we are now talking about the energy of the characteristic X-rays or the X-rays which is coming out of their target in X-ray tube and what is the kind of energy we are interested in.

So the total X-ray intensity is given by  $I_{cont.spectrum} = A^*i^*Z^* V^m$ . A is proportionality constant and m is a constant with the value of about 2. So you get a kind of value for a continuous spectrum in

terms of intensity using this expression which mainly depends upon the atomic number and the voltage.

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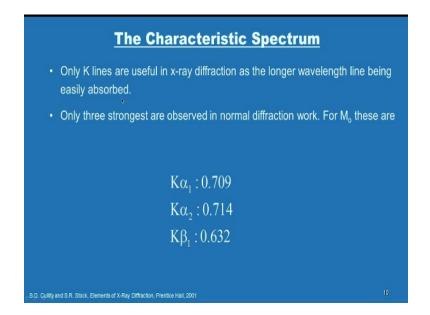


So another important aspect of this continuous spectrum is characteristic spectrum as I said. You can look at the schematic which is again plotted versus intensity of the X-rays versus wavelength in angstrom. When the voltage is raised above a certain critical value characteristic of the target metal, sharp intensity maxima appear at certain wavelengths superimposed on the continuous spectrum. So this is a continuous spectrum and it is being superimposed on it and it has got a very sharp intensity signal with a narrow wave length.

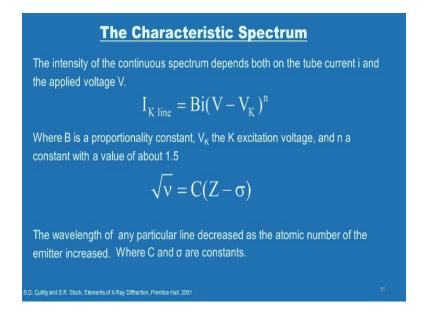
These lines are narrow and since their wavelengths are characteristic of a target metal used they are called characteristic lines. So now you have a basic explanation for what is characteristic lines and you have to appreciate one more thing here. If you for example this spectrum of molybdenum is obtained at 35 KV and with that we have the normally the K $\alpha$  is resolved, if it is not that it may appear as a single line.

The another important thing is the as the voltage is increased then the you may get the, the intensity of the continuous spectrum also will go up and also you will have the higher intensity of your characteristic peak however the wavelength will not change. You have to understand that. If the voltage is increased you may get higher intensity in the continuous spectrum as well as the characteristic lines but the wavelength is always a constant very narrow range. So that is the characteristic spectrum we talk about. Only K lines are useful in X-ray diffraction as the longer wavelength line being easily absorbed.

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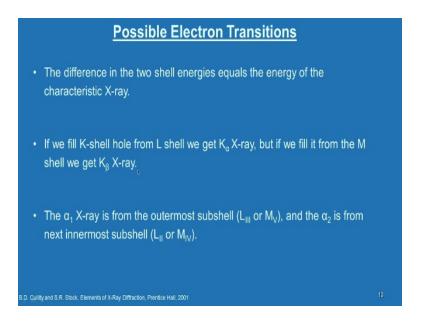


You see you have a range of signals and out of this range of signals only K lines are useful and you may get other signals like you know L M and N shell so on but they will have a very high wavelength and since they are getting easily absorbed they typically they are not being used in X-ray diffraction. So only the typically only K lines are being used we will see how this K lines are defined and produced and typical K lines are given here only three strongest are observed in normal diffraction work. So you see that K $\alpha$ 1, K $\alpha$ 2 and K $\alpha$ 3 these are the typical signals you get from the K shell which is being used for the X-ray diffraction in a normal diffraction work. (Refer Slide Time: 22:48)

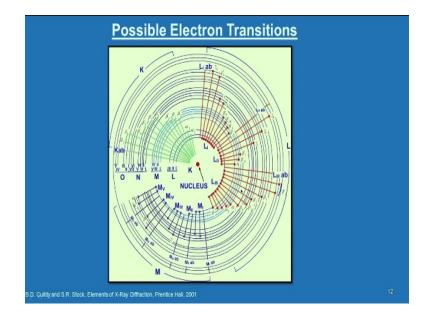


The some more marks on the characteristic spectrum, the intensity of the continuous spectrum depends both on the tube current and the applied voltage. So we can write  $I_K = Bi(V - V_k)^n$ , where B is the proportionality constant,  $V_k$  the K excitation voltage and n a constant with a value of about 1.5. And you have another relation called Mosley relation  $\sqrt{v} = C(Z - \sigma)$ . The wavelength of any particular line decreased as the atomic number of the emitted increased.

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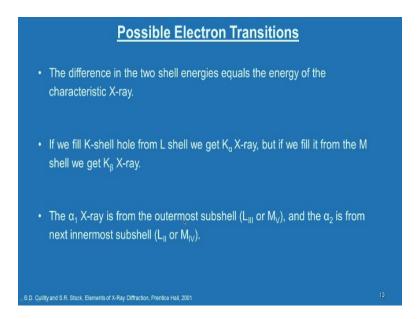


Where C and  $\sigma$  are the constants. And if you want to just appreciate this the continuous spectrum and its origin of this continuous spectrum you can look at the basic all the possible electronic transitions and this is just brought back to you again we have already gone through this. Just for your reference you see the all K shell, L shell, M shell, N shell and so on with different different possibilities and various possibilities of this electronic transitions and which forms the basis for this continuous spectrum. (Refer Slide Time: 24:37)



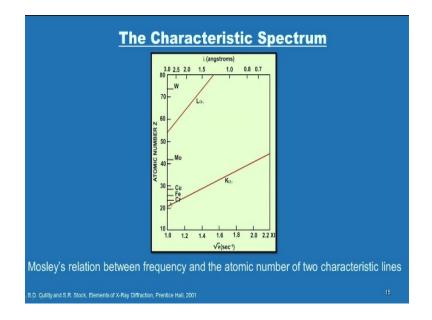
The difference in two shell energies equals the energy of the characteristic X-ray. This point we have already seen we all know if we fill a K shell hole from an L shall we get K $\alpha$  X-ray but if we fill it from the M shell we get K $\beta$  X-ray. The  $\alpha$ 1 X-ray is from the outermost shell that is L<sub>III</sub> or M<sub>V</sub> and the  $\alpha$ 2 is from the next innermost shall L<sub>II</sub> or M<sub>IV</sub> and so on so that is how the, the energy is being defined based upon which kind of shell and which level it is coming from and they the difference of the two shell energy is the energy of the characteristic X-ray.

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K excitation voltage is necessary to excite K characteristic radiation. You see from the very beginning we have seen we are seeing that in the continuous spectrum only at particular value of the voltage the characteristic signals are appearing otherwise you get only a continuous spectrum or white radiation only we are seeing. So that clearly tells that there is a excitation critical voltage which only can excite the for a given shell in this case since we are using only K shell electrons or K shell lines we talk about K excitation voltage.

So your critical voltage is necessary to excite K characteristic radiation and increasing the voltage above the critical voltage increases the intensities of the characteristic lines relative to the continuous spectrum but does not change their wavelengths. This also we have just seen. You have the characteristic lines at a critical or I would say the excitation voltage of K shell.



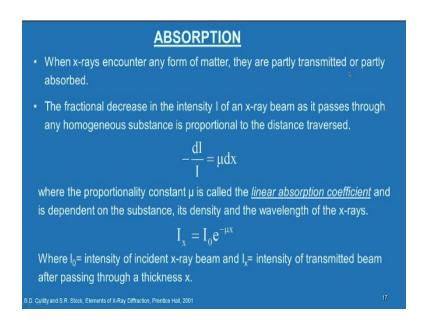
As the voltage increases the intensity will increase but not the wavelength. And these are all the, some of the application of this mostly relation between the frequency and the atomic number of two characteristic lines where K  $\alpha$ 1 and L  $\alpha$ 1 are shown, how this frequency and atomic numbers are related with respect to these two levels and also the wavelength. These curve shows that L lines are not always of longer wave lengths. The L  $\alpha$ 1 line of a heavy metal like tungsten they have the same wavelength like K  $\alpha$ 1.

Critical excitation voltage is required for a characteristic radiation that we have seen. For example K radiation cannot be excited unless the tube voltage is such that the bombarding electrons have enough energy to knock an electron out of the K shell of the atom. So we will not talk about the work. The work required to remove a K electron then the necessary kinetic energy of the electrons is given by  $W_K = (\frac{1}{2}) mv^2$ . So  $W_K$  will determine the energy required to knock out an electron from the K shell of the atom.

So similarly you will have  $W_L$ ,  $W_M$  and so on depending upon the amount of energy required. So you can guess that since K is K shell is very close to the nucleus which will require highest energy to remove the electron as compared to M, N, L and so on because they are further away

from the nucleus so you will me you may require less work as compared to, to remove an electron from K shell as compared I mean compared to other M, N and L shell and so on.

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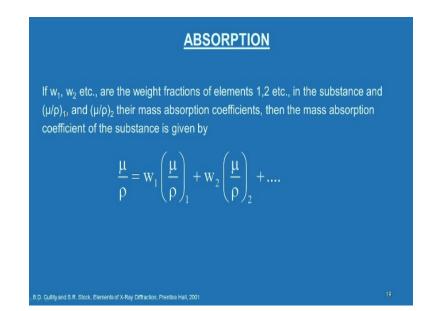
So that is the idea one should get from this. So when X-rays encounter any form of matter they are partly transmitted or partly absorbed. See now we talk about the properties of X-rays and its interaction with matter. So in order to appreciate this characteristic spectrum it is not only important to understand the interaction of electrons and, and matter and you, you have to understand the interaction of X-rays with the matter has well. So in that context we, we talk about little bit about this absorption of the X-rays.

And the first point is this. So when the X-rays are in when the X-rays encounter any form of matter they are partly transmitted or partly absorbed. The fractional decrease in the intensity I of an X-ray beam as it passes through any homogeneous substance is proportional to the distance traversed, that is  $-dI/I = \mu dx$ , where the proportionality constant  $\mu$  is called linear absorption coefficient and is dependent on the substance, its density and the wavelength of the X-rays, where if you can integrate this equation you can write  $I_x = I_0 e^{-\mu x}$ , where  $I_0$  is the intensity of the incident X-ray beam and  $I_x$  is the intensity of transmitted beam after passing through a thickness

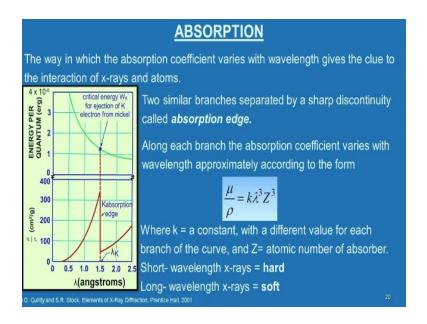
x of the material. The linear absorption coefficient  $\mu$  is proportional to the density  $\rho$  which means that  $\mu/\rho$  is a constant of a material and it is independent of physical state whether it is a liquid solid or a gas.  $\mu/\rho$  is called mass absorption coefficient.

So if you consider this into account the above equation and can be rewritten as  $I_x = I_0 e^{-(\mu/\rho).\rho x}$ . Whether the substance is a mechanical mixture a solution or a chemical compound and whether it is a solid liquid or gaseous state it's the absorption coefficient is simply the weighted average of the mass absorption coefficients of its constituent elements. Suppose w<sub>1</sub>, w<sub>2</sub> etc are the weight fractions of the elements 1, 2 etc in the substance,

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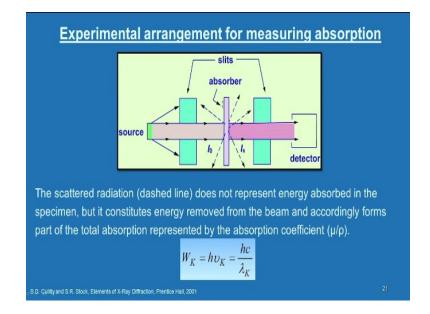


And  $(\mu/\rho)_1$ ,  $(\mu/\rho)_1$  and  $(\mu/\rho)_2$  is the most absorbent coefficients then the mass absorption coefficient of the substance is given by  $\mu/\rho = w_1(\mu/\rho)_1 + w_2(\mu/\rho)_2 + \dots$  and whatever the number of constituents there in the substance depending upon that this entity also will continue like this. So this particular slide shows the, the way in which the absorption coefficient varies with the wavelength gives a clue to the interaction of X-rays and the atoms. You see this schematic plot where you have the energy per quantum versus wavelength, as well as  $\mu/\rho$ , this mass absorption coefficient versus  $\lambda$ . So you have this two similar branches separated by a sharp (Refer Slide Time: 33:06)



discontinuity called absorption edge. This is one branch and this is another branch which is being separated by a sharp discontinuity called absorption edge. Here it is belong to K shell so it is called K absorption edge and you can see the corresponding critical energy to eject the electron from the K shell of the nickel here which is clearly shown here. So along each branch the absorption coefficient varies with the wave length approximately according to the form expressed as  $\mu/\rho = k \lambda^3 Z^3$ , where k is a constant with a different value for each branch of the curve and Z equal to atomic number of the absorber.

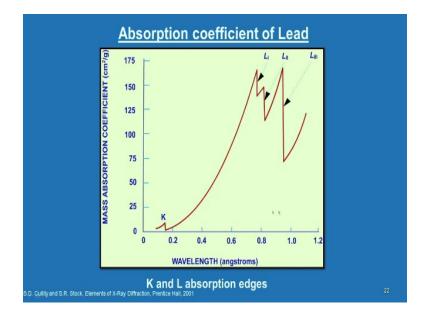
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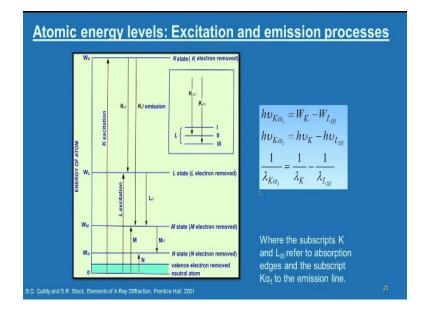
So where you have the shortwave length X-rays they are characterized as a hard X-rays where the long-wavelength X-rays they are called soft X-rays. So these two classifications in fact even in the very first slide which was marked on the electromagnetic spectrum how these X-rays are classified as a hard as well as a soft X-rays. So you see that the mass absorption coefficient clearly shows to characterize this I mean the  $\mu/\rho - \lambda$  plot clearly characterizes the, the edge absorption edge of a given element. So this is the experimental arrangement for measuring absorption where you have the source and you have the detector and you have slits and this is a absorber and then you see that intensity before reaching the sample and I<sub>x</sub> is the after the transmission.

So the scattered radiation that the dashed line does not represent energy absorbed in the specimen but it constitutes energy removed from the beam and accordingly forms part of the total absorption represented by the absorption coefficient  $\mu/\rho$ . So we will now just rewrite this the work that is energy required to remove an electron from the K shell,  $W_K = hv_K = hc/\lambda_K$ .

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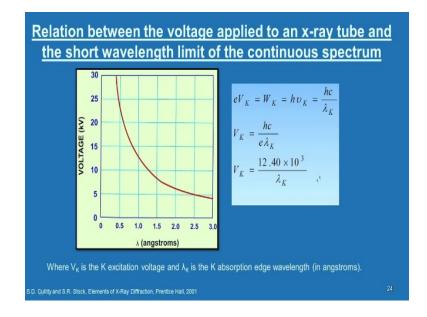


So you now arrive at you can get the characteristic wavelength which correspond to a K shell can be obtained from this relation. So you see that another typical example for absorption coefficient of lead where you have the K edge and L edge,  $L_I$  edge  $L_{II}$  edge and  $L_{III}$  edge they are all shown having a sufficiently higher wavelength. You can see that the kind of range of wavelengths has as compared to the K absorption edge in this sample. (Refer Slide Time: 37:39)



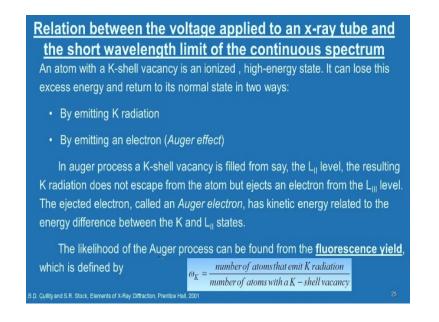
So in order to again appreciate this characteristic spectrum, we will just talk about a little bit of the, the emission process that is the energy of the atom vs the transition between different shells here you can talk we can just look at it to appreciate the, the characteristic wavelength which is arises because of the electron being removed from the particular shell. So you see that you have this energy of the atom where you have different shell  $W_K$ ,  $W_L$ ,  $W_M$ ,  $W_N$  and you have the K excitation, L excitation and you have K $\alpha$  emission K  $\beta$  emission and then L $\alpha$  emission and so on.

And then you see that the, the valence electron removed from the neutral atom then you, you also see the corresponding the other states of energy like M and N and so on. So for all each of these transitions all possible transition we can write the corresponding the W that is work required to knock out that particular electron from the same given shell where the subscripts K and L<sub>III</sub> refers to the absorption edges and the subscript K $\alpha$ 1 to the emission line. So this is all summarized in one graph and this is how the, the energy being worked out and then the  $\lambda$  is being calculated using these simple relations:  $hv_{K\alpha 1} = W_K - W_{LIII}$  and  $hv_{K\alpha 1} = hv_K - hv_{LIII}$ , then  $(1/\lambda_{K\alpha 1}) = (1/\lambda_K) - (1/\lambda_{LIII})$ .



So this is a schematic plot where one can just characterizes the the, the wavelength corresponding to shortwave length limit, you can find out for a given voltage, you can characterize this plot where you have this for example if you take  $eV = W_K = hv_K = (hc / \lambda_K) \& V_K = (hc/e\lambda_K)$  and this also we have already seen where voltage required to remove the electron from the K shell,  $V_K = (12.40 \times 10^3)/\lambda_K$ . So for a given voltage you will find the  $\lambda$  which is the absorption edge wavelength or I would say the short wavelength limit or absorption edge wavelength. In this particular case  $V_K$  is the K excitation voltage  $\lambda_K$  is the K absorption edge wavelength in angstrom. So similarly you can find the, the absorption edge for the given shell from this a plot.

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So we will see a few more remarks. An atom with the K shell vacancy is an ionized state where high energy state. It can lose this excess energy and return to its normal state in two ways. By emitting K radiation or by emitting an electron which is called Auger effect. In the Auger process a K shell vacancy is filled from say the  $L_{II}$  level and the resulting K radiation does not escape from the atom but ejects an electron from L level, the ejected electron called Auger electron has kinetic energy related to the energy difference between K and  $L_{II}$  states.

The likelihood of the Auger process can be found from the fluorescence yield which is defined by  $\omega_{K}$  = (number of atoms that emit k radiation) / (number of atoms with a K shell vacancy). See you have to remember the Auger electron again every surface phenomenon this is also a part of a characteristic emission that is why it has come under this category of you know whether when the electron is removed from the K shell it can either it can remove a characteristic X-rays or it can further remove an electron from the outermost shell like an L<sub>III</sub> or L<sub>II</sub>, then the electron which is coming out of that process is called if Auger electron and this is again a characteristic I mean characteristic signal which is also being used to characterize the material that we will see it in a separate lecture. But you should know this kind of signals also associated with when we talk about characteristic radiation that is all I want to mention here and then that Auger process can be found from this fluorescence shield which is given by this relation. So next we will talk about the production of X-rays and its equipment details and then how exactly the instrument are operated those details we will start our lectures in the next class. Thank you for listening.

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