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Lecture-22
Materials Characterization
Fundamentals of X-ray diffraction

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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 slow graphic face identification and quantification of faces and texture etc during the next ten lectures so if you look at the, the fundamental ideas what we have generated so far excel as us 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 is assume that you have enough are 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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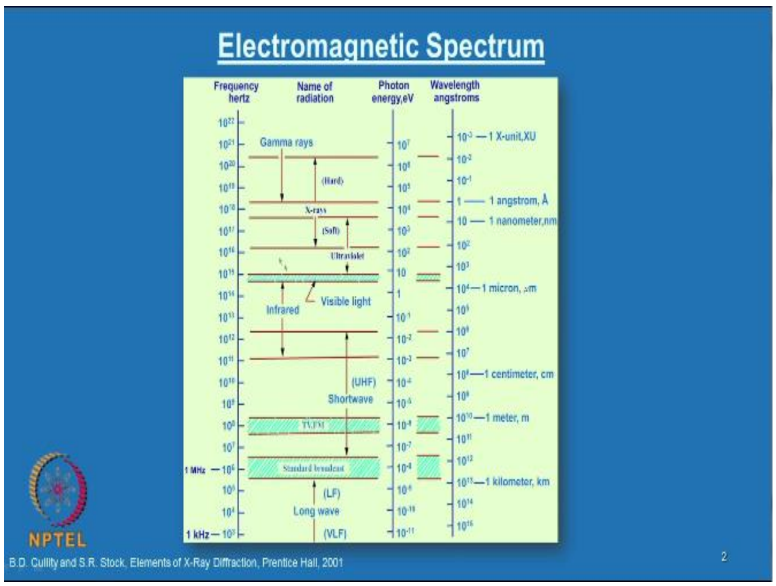

So yeah now look at this electromagnetic spectrum which you are already familiar with we are now going to concentrate only on this x rays where you see that the range here is around 10^2 - 2 to hear about 10^2 - 2 here and then you have the corresponding photon photon energy in electron volts and you 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 this 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 face identification.

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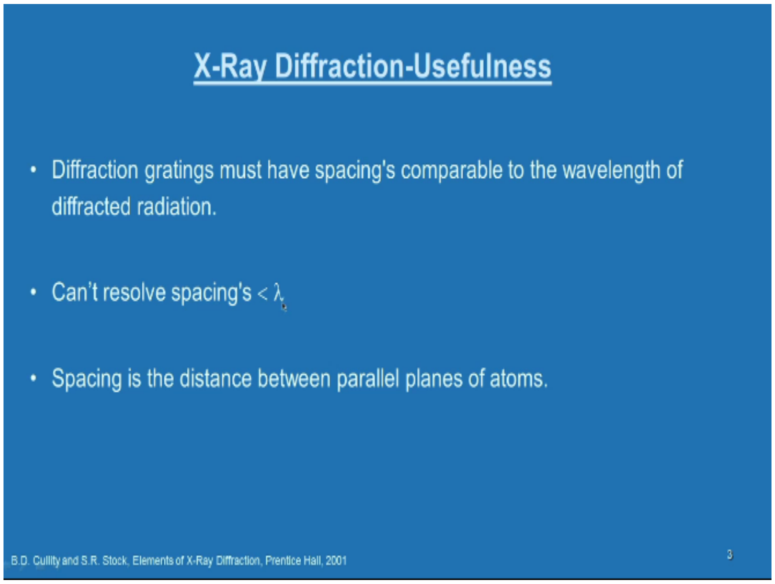

You have to make sure that even that material which you are examining or the crystal system which we are examining we have the similar D-spacing as I mean the λ should match with the probing dimension as well so that is what we are just recollecting again for example diffraction gratings must have the spacing comparable to the wavelength of the diffraction reflected radiation cannot 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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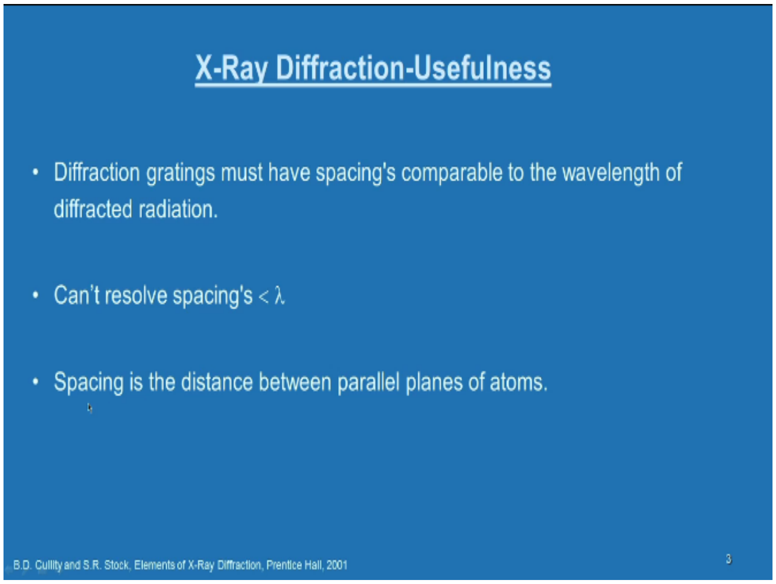

So that is how the spacing experiments are I mean with this assumptions and rating experiments are done and we will now just see what is the continuous spectrum there is basic characteristic of electro I mean x-ray spectrum is called continuous spectrum we will see what is the continuous spectrum are produced when any electrically charged particle of sufficient kinetic energy is rapidly decelerated as we have already seen that how this characteristic x-rays are produced in, in one of the lectures in SCM where we, we have taken of the energy dispersive spectrometry.

So the character characteristic x-rays are produced fundamentally 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 this what we have seen already the same thing next days are generated and their energy is rapidly decelerated.

So that is what the same thing here we will see in an a in a systematic manner in a x-ray diffraction meter as well electrons are normally used for this purpose XS 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 is what we talk about is produced.

At the point of impact and when it I mean went in radiates in the all direction the kinetic energy of the electrons on impact is given by the equation that is ke is equal to which is in electron volts which is equal to 1/2 m-v square e is the charge on the electron $1.6*10^{2}$ - 19 coulomb m is the mass of the electron 9.11* 10 -31 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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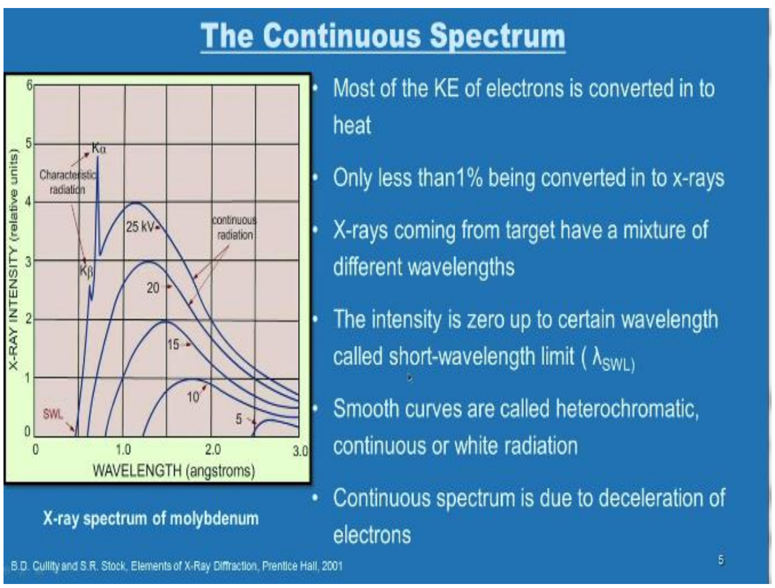

A typical x-ray spectrum what ,what is plotted here is is an x-ray intensity and in the x axis it is the wavelength in angstroms so what you have to know that is these curves are plotted as a function of different applied voltage you see that 5 10 15 20 in 25 so you have so many things to observe from 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 wavelengths so what happens is in an x-ray tube when, when they the electron source r 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 atypical 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 XS 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 wavelengths 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 or 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 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 correct.

I mean call it as a characteristic signal as well so what you are seeing here is a characteristic radiation which is Kα and Kβ we will talk about it little I mean in due course but before that it is important o 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 one lee 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 it 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 it 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 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.

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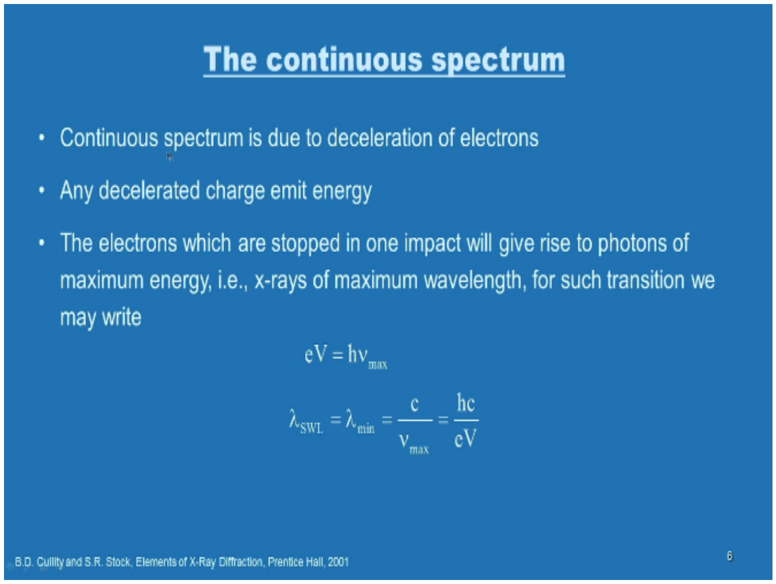

And what is characteristic line and why do you get a range of wavelengths all this aspects one can understand from this x-ray spectrum of amolybdenum here this is a molybdenum spectrum so continuous spectrum is due to deceleration of electrons any decelerated charge emit energy the electrons which are 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 equal to H nu max which can be written like this $\lambda_{swl} = \lambda$ minimum which is nothing but C by mu max which is equal to HC by EV.

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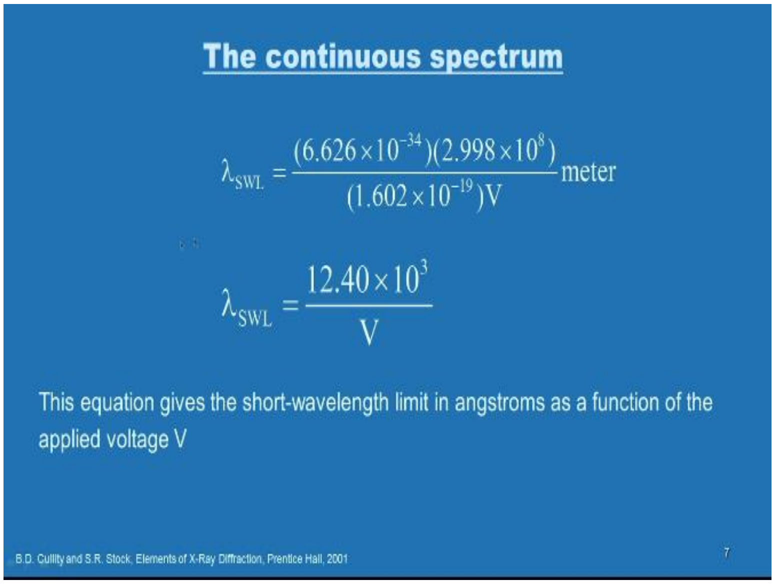

So what you are trying to see here is the electrons which are stopped in one impact how that is being visualized in terms of energy and then indirectly the λ what is that short wavelength limit how to find out that this is the simple expression and if you put all this units in it I mean and its values constants in place and then you get a final expressions like this as a function of applied voltage lambda short wave length is equal to 12.40 into tens of over three divided by 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 under the tube current 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 continuum spectrum which is equal to a* xi multiplied by Z times B^2M is proportionality constant and M is a constant with the value of both to 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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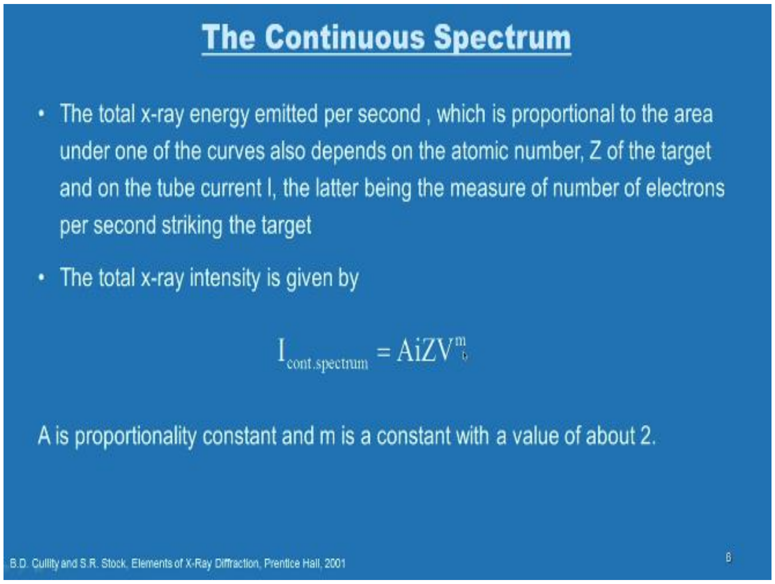

So another important aspect of this continuous spectrum is characteristic spectrum as I said you can look at the schematic which is again plotted versus intensity of the x-rays versus wavelength in angstrom when the voltage is raised above a certain critical value characteristic of the target metal sharp 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 they are 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 organim obtained at 35 k v and with that we have the normally the kα 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 their 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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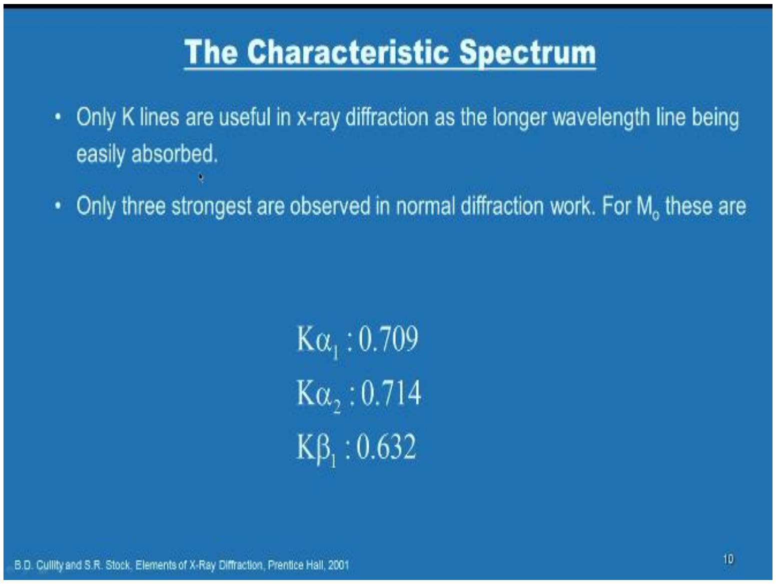

You see you have a range of signals and out of this range of signals only k lines are useful and you may get other signals like you know L M and n shell so on but they will have a very high wavelength and since they are getting easily absorbed they typically they are not being used in x-ray diffraction 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 kα1 kα2 and Kα3 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 the some more marks on the characteristic spectrum.

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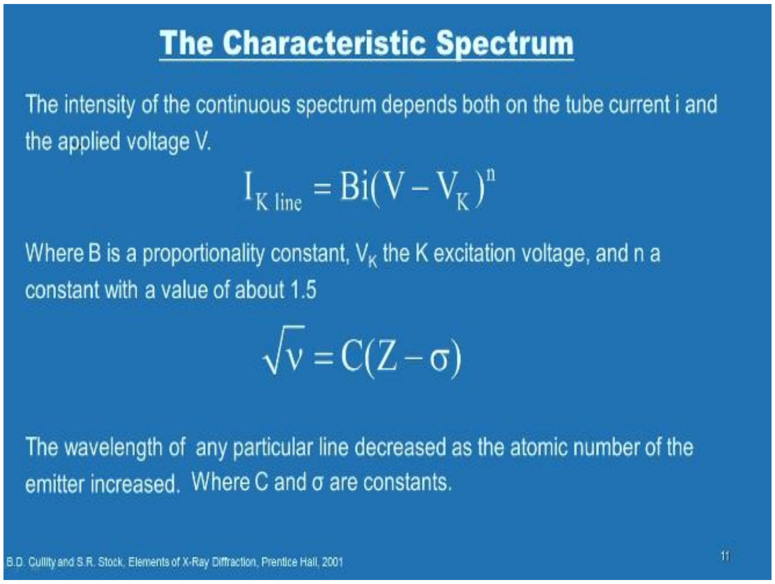

The intensity of the continuous spectrum depends both on the tube current and the applied voltage so we can write I K line this is equal to B times I into V minus v k to the power M where B is the proportionality constant V k the voltage and n a constant with a value of both 1.5 and you have another relation called mostly relation where the square root of U is equal to C into Z minus € the wavelength of any particular line decreased as the atomic number of the emitted increased.

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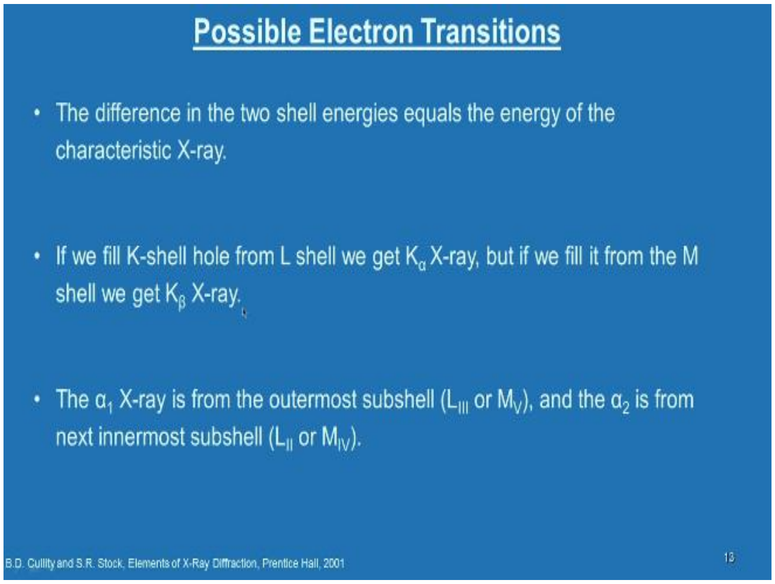

Where C and € are the constants and if you want to just appreciate this the continuous spectrum and its origin of this continuous spectrum you can look at the basic all the possible electronic transitions and this is just brought back to you again we have already gone through this just for your reference you see the K shell N shell and so on with different, different possibilities and various possibilities office electronic transitions and which forms the basis for this continuous spectrum.

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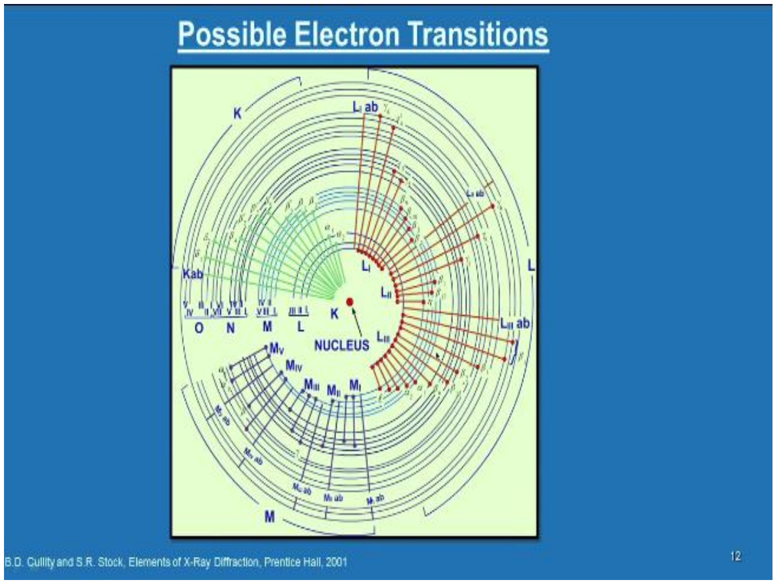

The difference into shell energies equals the energy of the characteristic x-ray this point we have already seen we all know if we fill AK shell hole from an L shall we get Kα X ray but if we fill it from the m shell we get K β X ray the α1 x rays from the outermost shell that is l3 rm5 and the α 2 is from the next innermost shall L to R m4 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.

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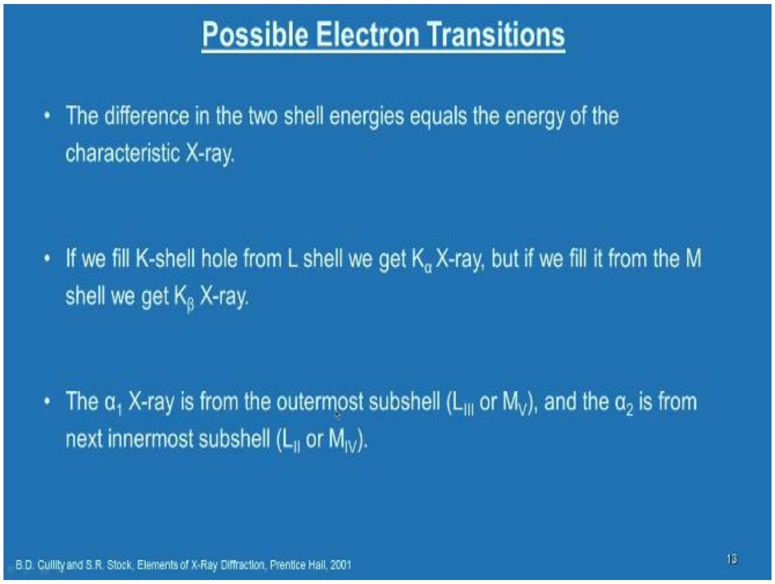

Is the energy of the characteristic x ray k excitation voltage is necessary to excite k characteristic radiation you see from the very beginning we have seen we are seeing that in the continuous spectrum only at particular value of the voltage the characteristic signals are appearing otherwise you get 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 thee for a given shell in this case since we are using only K shell electrons are casual 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.

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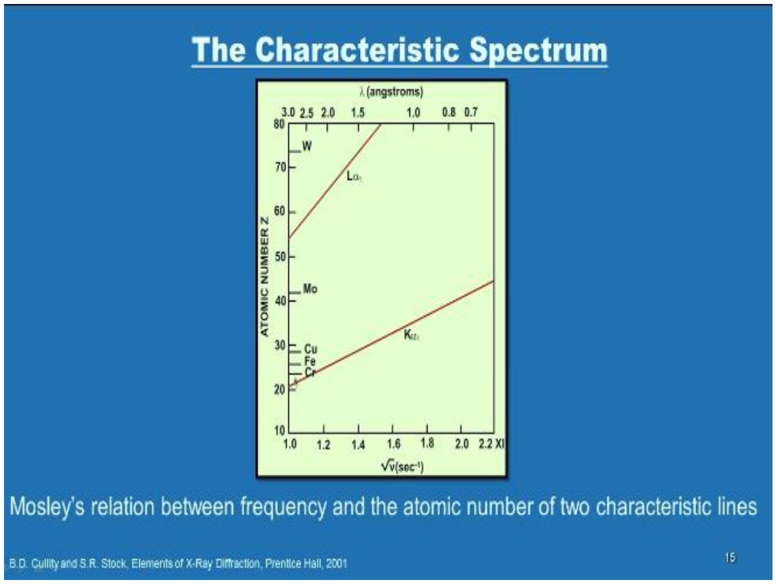

The intensity will increase but not the wavelength and these are the some of the application of this mostly relation between the frequency and the atomic number of two characteristic lines where K α1 and L α1 are shown how this frequency and atomic numbers are related with respect to these two levels and also the wavelength these curve shows that lines are not always of longer wave lengths the l alpha one line of a heavy metal like tungsten they have the same wavelength like K alpha one 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 case 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=1by 2 m-v^2 so WK will determine the energy required to knock out an electron from the K shell of the atom.

So similarly you will have 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 MNL and so on because they are further away from the nucleus so you will me you may require less work as compared to two to remove an electron from k shell as compared I mean compared to other m l and l shell and so on.

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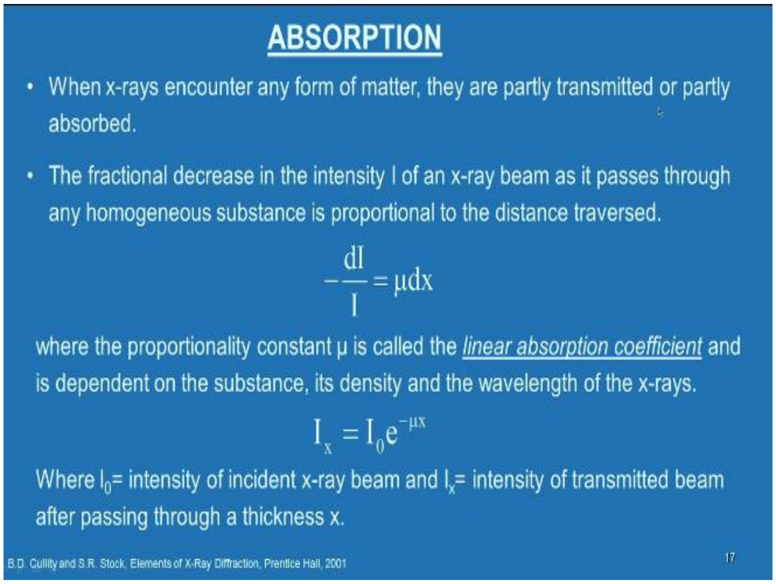

So that is the idea one should get from this so when x rays encounter any form of matter they are partly transmitted or partly absorb see now we talk about the properties of x-rays and E and its interaction with matter so in order to appreciate this characteristic spectrum it is not only important to understand the interaction of electrons and, and matter and you, you have to understand the interaction of x-rays with the matter has 12 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 absorb the fractional decrease in the intensity I of an x-ray beam as it passes through any homogeneous substance is proportional to the distance traverse that is minus - D/I =μdx 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 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 μ is proportional to the density Rho which means that μ/Rho is a constant of a material and it is independent of physical state whether it is a liquid solid or a gas μ/Rho is called mass absorption coefficient.

So if you consider this into account the above equation and miri written like this I X equal to i naught into e to the power minus μ / Rho into 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 1 W 2etcetera are the weight fractions of the elements 1 2 etcetera in the substance.

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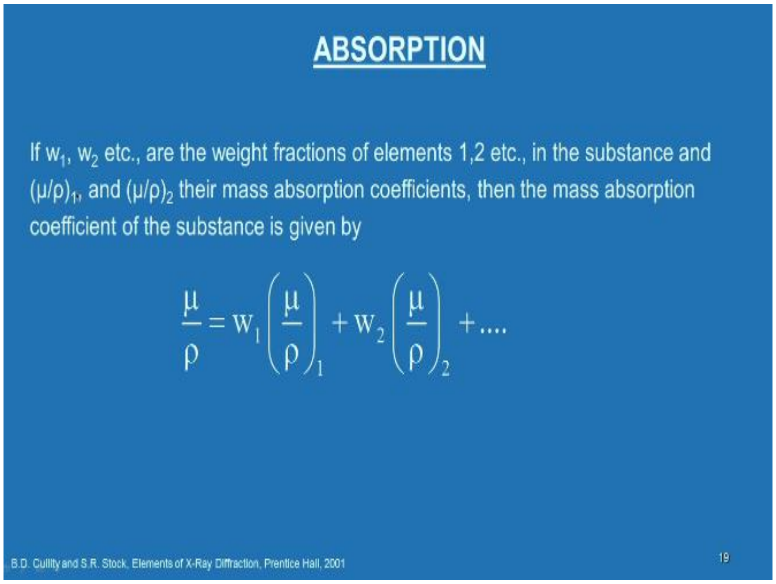

And view by Rho 1 μ/Rho 1 and μ/Rho 2 is the most absorbent coefficients then the mass absorption coefficient of the substance is given by view by Rho = w1 into μ/Rho 1 + w2into μ/Rho 2+ and whatever the number of constituents there in the substance depending upon that this dentity also will continue 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.

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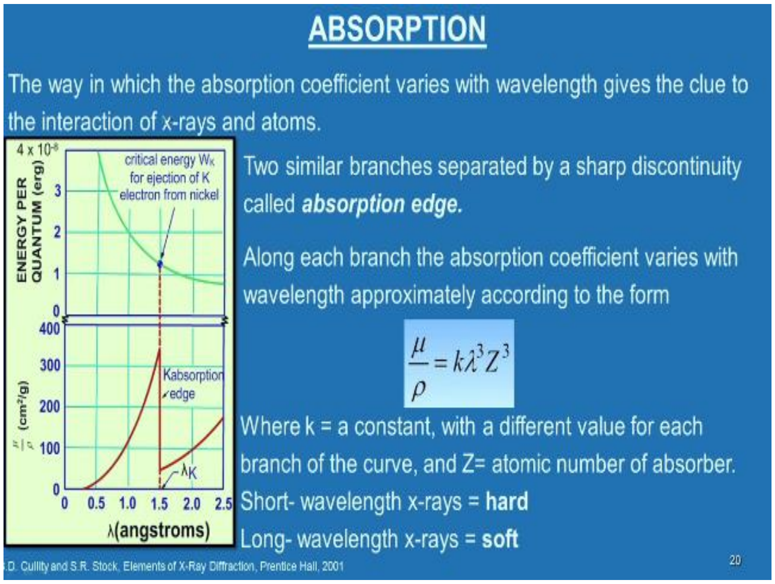

As well as you by Rho this mass absorption coefficient versus λ so you have this too similar branches separated by a sharp discontinuity called absorption edge this is one branch and this is an another branch which is being separated by the sharp discontinuity called absorption edge here it is belong 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 a long each branch the absorption coefficient varies with the wave length approximately according to the form μ/Rho equal to K λ^3 Z^3 where K is a constant with a different value for each branch of the curve and easy equal to atomic number of the absorber.

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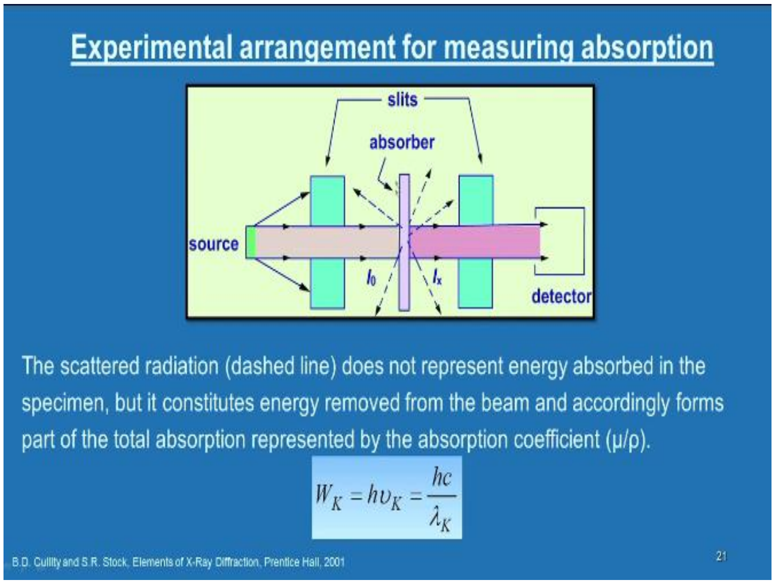

So where you have the shortwave length x-rays they are characterized as a hard x-rays where the long-wavelength x-rays they are called soft x-rays so these two classification in fact even in the very first slide which was marked on the electromagnetic spectrum how these x-rays are classified as a hard as well as a soft x-rays so you see that the mass absorption coefficient clearly shows to characterize this I mean the μ/ Rho λ 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 XC 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 you by Rho so we will now just rewrite this the work that is energy required.

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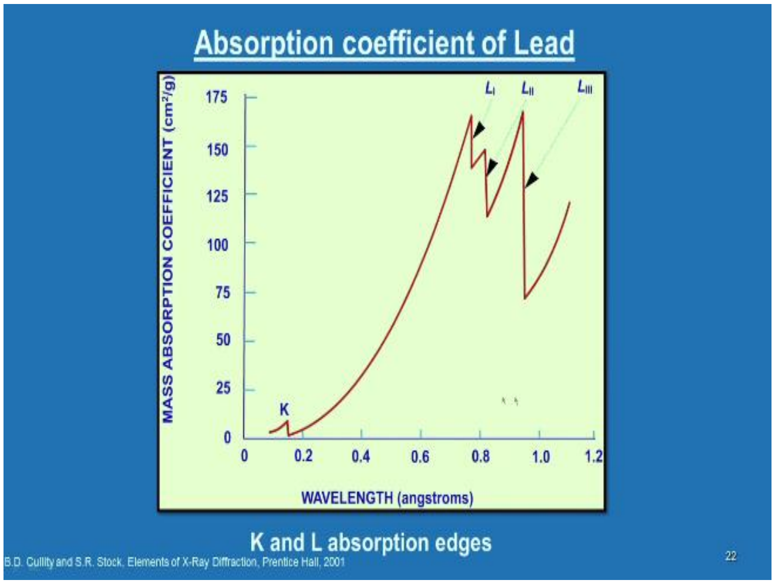

To remove a electron from the K shell WK in terms of photon Hμ K which can be written as H/λK so you now arrived at you can get the characteristic wavelength which correspond to AK shell can be obtained from this relation so you see that another typical example for absorption coefficient of lead where you have the Kedge and allege l1 edge l2 edge and l3inch 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 the sample.

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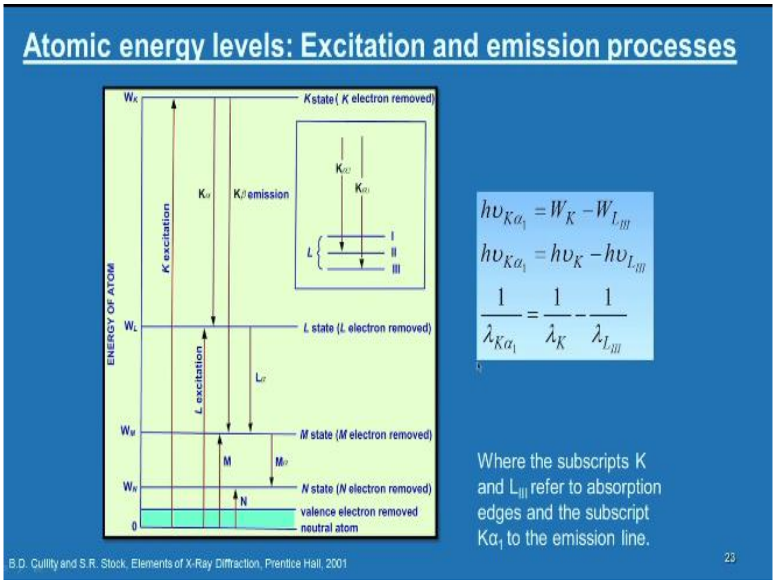

So in order to again appreciate this characteristic spectrum we will just talk about a little bit of the, the emission process that is the energy of the atom vs the transition between different shells here you can talk we can just look at it to appreciate the, the characteristic wavelength which is arises 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 WKWL wmw yen and you have the K excitation L excitation and you have Kα emission k β emission and then Lα 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 3 refers to the absorption edges and the subscript kα1 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 λ is being calculated using this simple relation.

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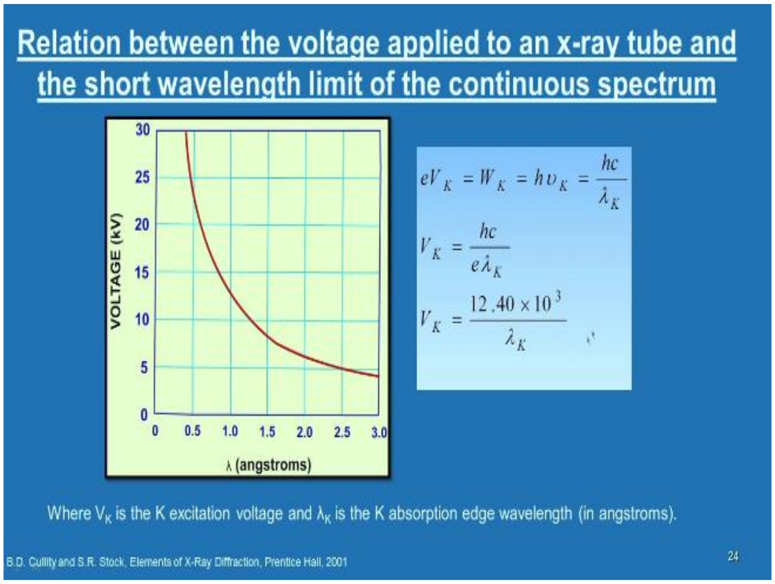

So this is a schematic plot where one can just characterizes the the, the wavelength corresponding to shortwave length limit we can find out for a given voltage you can characterize this plot where you have this for example if you take electron volts for a case shell which is w case H nu k is equal to HC /λ k & B K is equal to HC by λK and this also we have already seen where voltage required to remove the electron from the K shell is equal to12.40 into 10 to power 3 by λ K so for a given voltage you will find the λ which is the absorption edge wavelength.

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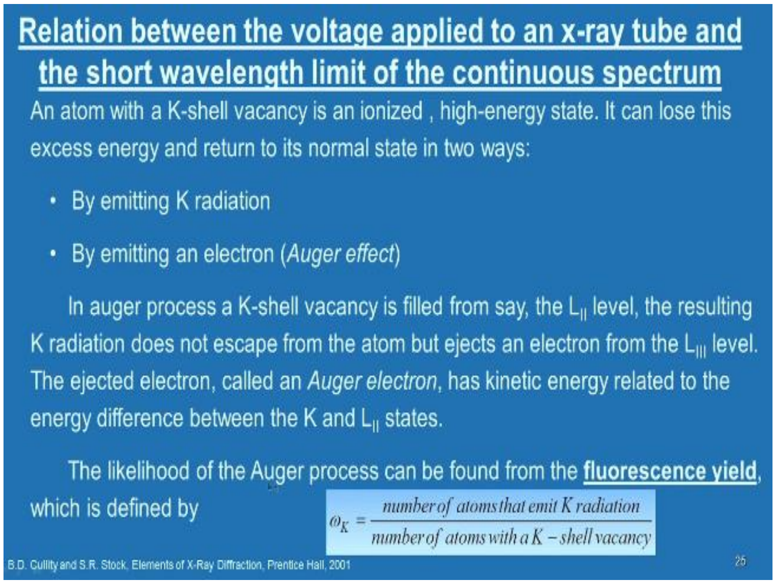

I would say the short wavelength limit or absorption in wavelength in this particular case VK is the K excitation voltage λK is the K absorption edge wavelength in angstrom so similarly you can find the, the absorption edge for the given shell from this a plot so we will see a few more remarks an atom with the K shell vacancy is an ionized an estate 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 oj affect the in wo J process a casual vacancy is filled from say the l2 level and the resulting k radiation does not escape from the atom but ejects an electron from l3 level the ejected electron called oj electron has kinetic energy related to the energy difference between K and L two states.

The likelihood of the og process can be found from the fluorescence heat which is defined by Omega K is equal to number of atoms that emit k radiation / number of atoms with AK shell vacancy see you have to remember the oj 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 case 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-3 or l2 then the electron which is coming out of that process is called if aj 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 oj 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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