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NP-TEL
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on
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-22

by…
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So today we are going to discuss a new advanced surface cavitations technique the name of the technique is RGR electron spectroscopy.

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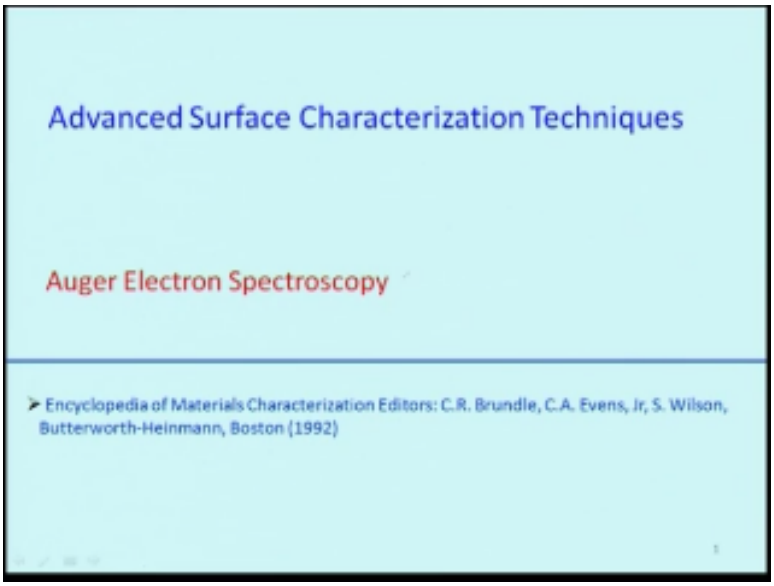

Are in short it is known as a yes we have discussed about the SPS or x-ray photo electron spectroscopy in details so how the concepts I will borrow from the XPS today es but I will have to discuss many other new things in the advanced spectroscopic technique so therefore I need to

constrain myself so that time does not come go out of order so in audio spectroscopy the basically the materials which I am going to use here are taken from different sources.

But most notably this book is the source of the material for all the spectroscopic techniques in the encyclopedia of materials calculation edited by bundle Levin's Wilson published by butter washenman was done in 1992.

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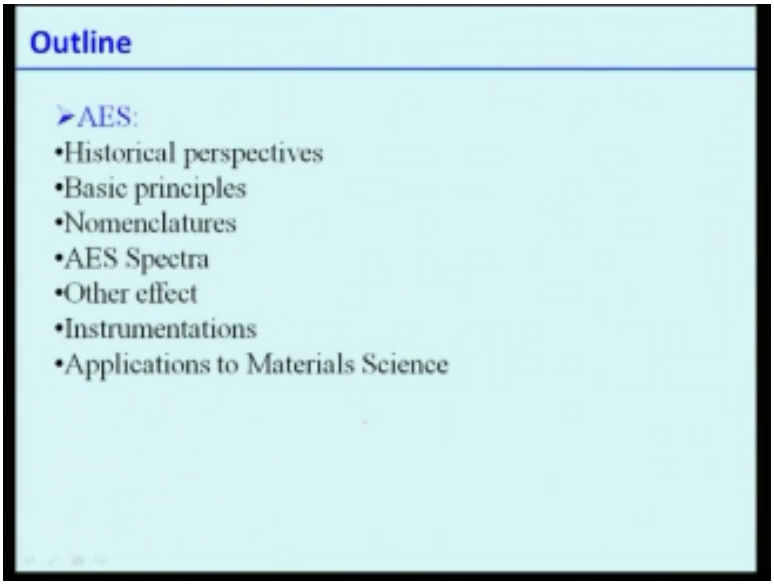

The schematic representation or the outline of the particular lecture series of on AES is as follows first I will talk about some historical perspectives of RG electron spectroscopy how it has come about it then I need to discuss in detail about the basic principles and you must know very well that then there are certain nomenclatures which are used in AES like any other techniques then I will go to a spectra what is out any spectra of AES.

How does it look like what are the information we can obtain from there this will be followed by discussion on the other effects there are many other effects and obviously some amount of instrumentations we need to discuss any all this many examples will be given to show you how relevant this technique is for different applications in material science.

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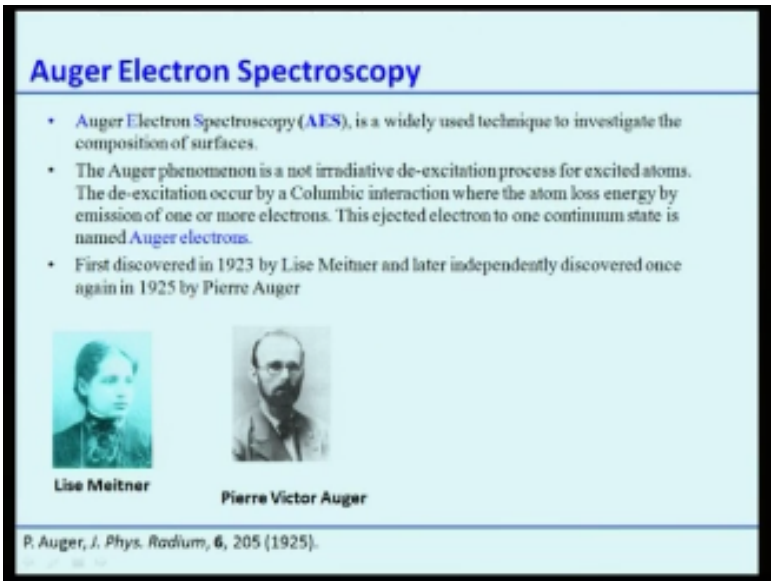

So let me just start with the historical perspectives as you know RG electron spectroscopy is a very widely used technique for surface characterization of materials it is used to know the electronic states of different elements present in the surface it can be used to measure compositions of the different elements on the surface this is a non radioactive oxidation process unlike XPS where you are using and x-ray source to eject out a code level electron from an atom and thus sow

And then say the electrons comes out from the material and measure the kinetic energy of the coal electron and do remaining other things this is not like that this is a non reality tip the acceleration process name but this is not exit a specific d Exeter's process but this is also non radioactive that is you are not irritating we are not getting this phenomena because of the radiation like an XPS this excitation occurs obviously by Coulomb interaction where an atom loses energy by omission of one or more electrons.

And then exactly electron 21 continuum state is what is known as OGIA obviously at the beginning definition will not be clear to you it needs to be discussed and needs to be you know up with talked about it I am going to do that in the basic principle stuff but first you are discovered at 19 23 by lady named Lee ice met normally mina basically her picture is shown here this all taken from different books.

And after two years in 9025 this was independently discovered it seems this was independent discovered by Pierreogia and after his name prospectus copies Kwan this is pure Victoria jeer

picture you can see there this paper bog was published in a journal of physics radium into 1925 and he even this process is named after him to give you even how the developments took place later on let me just talk little detail.

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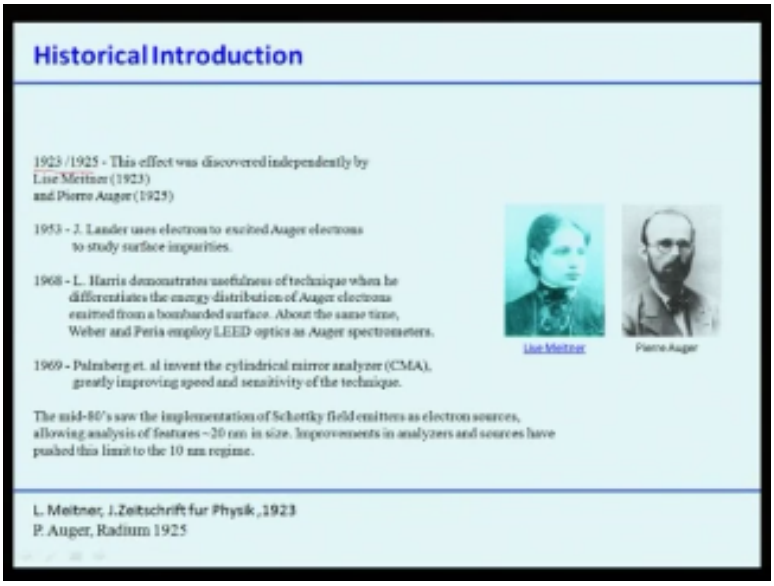

So that for 1923 25 defect was discovered independently by Madonna and archaic a miners publishes paper eternal of Jack skip through physics and audio published in Journal of radium their pictures are so near but then they are also be loved nothing happened because of obviously because of instrumentation problem 1953 Jens lender uses electrons too excited to create excited or the electrons.

And those are the electrons who are used to study the surface impurities the problem of basically they are tracking system because you know these electrons which are created by the RJ possess are very low energy so therefore vacuum has two very good to detect now and also obviously detection system needs to be developed then 19 628 so that is 1953 by Lander and landing6 28 l Harish demonstrates the usefulness of this technique.

When he differentiates the energy distribution of OJ electrons emitted from a bombarded surface at the same time however imperia employed lead optics as audio spectrometers lead I have taught actually low-energy electron diffraction this will be taught by Michael a colleague so lead actually is us call lead can optics can be used for aussie ER for detection system that was done by a waiver and Pieria.

Then 1969 plumber's at all invent the cylindrical mirror analyzer was known as CMA which greatly improved the speed of sensibility of the technique so you can see from 1925 1970 almost like 35 years took to develop this technique to useful and then it meant 80's saw the real implementation of the this technique because of the Scotty free limiters as electron source what Knifing limiters has a very high brightness this we discussed in the electron microscopy.

So these allow is actually turn on lights remember surface features size of 20nanometers very small size and then in fact afterwards 1990s even beginning of1990s lot of implement happened in analyzing analyzers actually and sources this limit is now pushed to 10 nanometer regime in fact to be frank this limits has pushed below 10 nanometer regime assembly.

So that is so actually the whole the technique has been so nicely developed but we must give credit to this manner and Pierre olio for disk wine is technique because this was a very fundamental technique which is used extensively in material science even till today before I actually talked about audio spectroscopy in detail.

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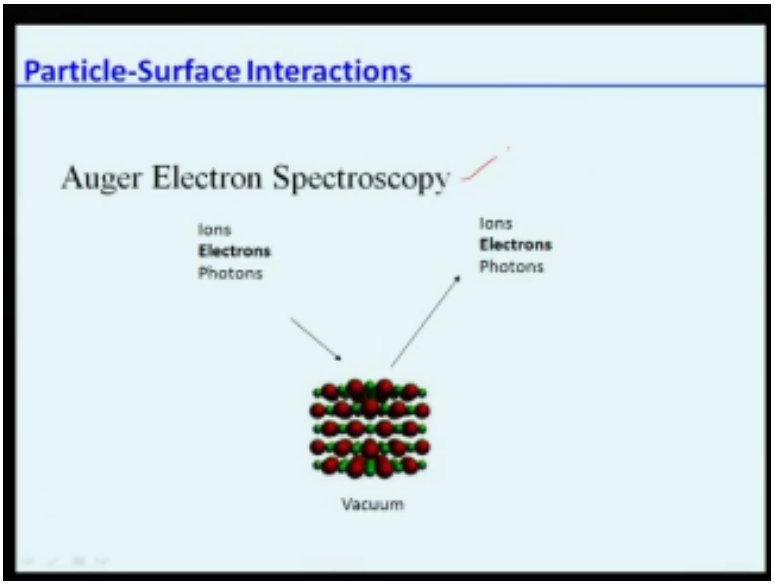

Let me just tell you, you know we know that any spectroscopic technique with its electron spectroscopy or excess spectroscopy or audio spectroscopy it actually basically depends on the

interaction of the radiation or the or the electron of x-ray or any other radiation with the material and material means atoms Adam means nucleus and the nuke electrons.

So anions electrons of photons they are all actually source of radiation this falls on a surface material any atom actually in the sense which is kept inside a vacuum it can cannot generate ions electrons and photons and if we analyze this which generated.

The cross of this interaction process we can get a lot of information about the atom that is the basic principle of any spectroscopic technique whether it is a electron energy loss spectroscopy or XPS RGR so that means the an interaction between the surfaces of a material with the incoming high-energy radiation source generating other radiation like ions electrons or photons is

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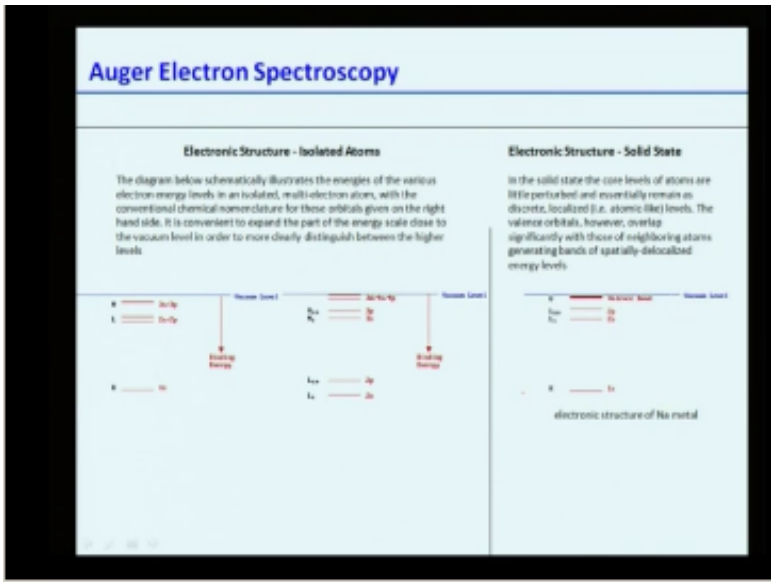

What is the basic thing of spectroscopy well to you know talk about the audio spectroscopy we need to know a little bit about the electronic structure as you know electrons rotates around the nucleus in Adam in an atom so and this electrons have different energy levels and all we know that the energy level depends on their quantum numbers the principal quantum numbers the that is SPDF then you have magnetic quantum number L then you have azimuthally quantum number say a lubricant fill magnetic number m a spin quantum number s.

So depending on the energy levels we can actually split the electronic levels in different cells like this one is shown k ln m k cell has1s electrons that is the inner self a core electrons EL, EL cell has 2s 2pelectrons m cell has 3s 3p electrons so the binding energy of electron will increase as you go closer and closer to the coal level so that means skill level case electrons will have more binding energies 10 m and.

So forth and then you have basically we have a basically at the above they occupied cells you have what is known as Fermi level and then you have happened now we can actually the market this energy levels in 2s as you know in the x-ray nomenclature this one in basically k is k so k scale is one sl1 is known as two sl2 p is known as el 23 m one is known as a 3 x 2 3 as corresponds to m23 correspond to 3p and then you have 3d 384 s and 4p levels and above that is so actually x-ray I know people use the nomenclature.

And this is atomic normal culture expiry have used ml kind of normal ketchup now if I consider the electronic structure of a metal like sodium what it has sodium has two electrons in one is level two left on scene in the to his level then you have six electrons in to pee levels correct so that means k l 1 l 2 3 these are the energy levels created so in a solid state the coal levels of atoms are little / trapped and essentially remain as a discrete localized levels that we know.

And this is this the balance orbital cyber overlap sometimes significantly with those of the neighboring atoms chanting bands of special ED collides delocalized energy levels so after knowing this.

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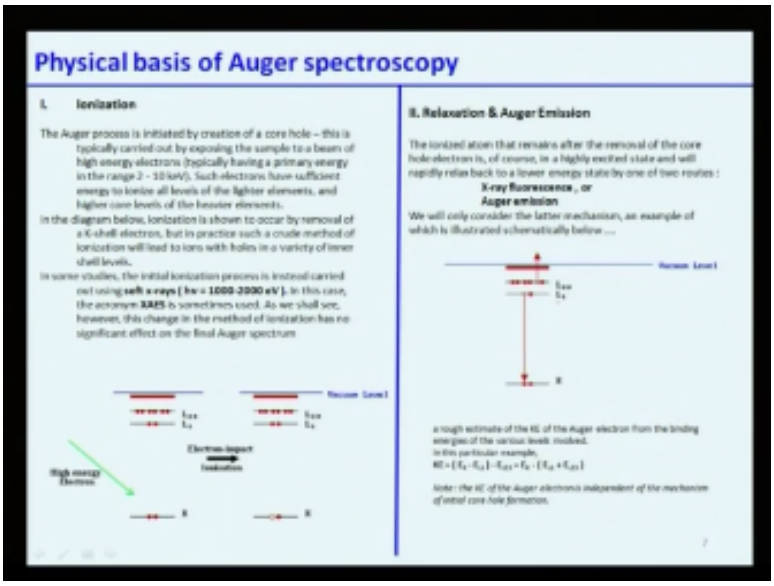

Now let us talk about the physical basis of audio spectroscopy what is the physical basis of this structure technique well I think I talked about XPS let me just bring in the XPS concept and what happens in XPS concept is we have x-ray source which is high-energy x-ray source it is allowed to follow the sample and this is x-rays then basically interact with the electrons for electrons of the atom.

And eject the core electrons of the atoms living behind hole there so then once it leaves behind the hole and the ejected electron goes out and that we have analyzed the injecting electron energy levels were kind and that is how we actually are do their analysis so if I have to show it very nicely I can just sew it on the board.

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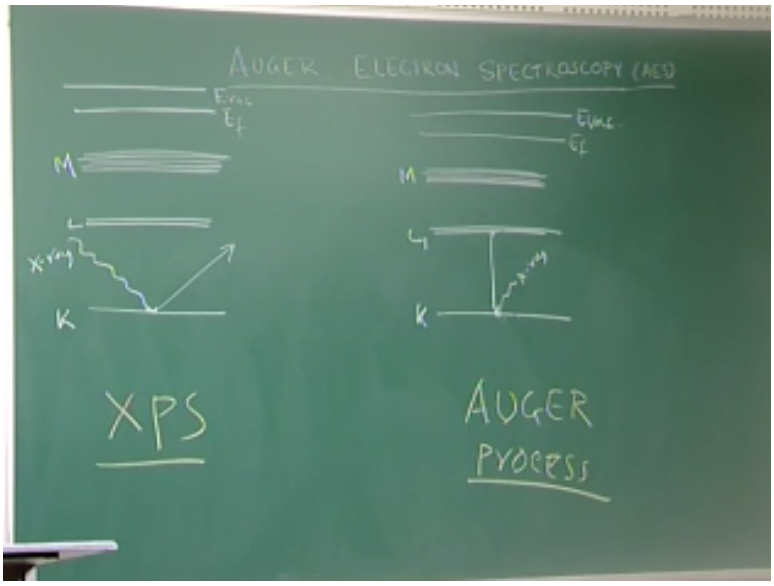

Let us suppose we have K level this is k say this is l and this is M right and then you have EF there is a Fermi level and you have then vacuum back that is how the energy diagram of a atom can be represented now if I have certain radiation like XL photon falls on this k level electrons and what will happen these because of this, this electrons some amount of this electron because of this x-ray photon.

This electronic a level will be ejected out and then these passes through because this is a very high kinetic energy normally the incident we will have very high energy, energy higher than almost 10times higher than the kind of the binding energy of this electron in the key level because of this excess energy of the incident x-ray the ejected electron will have lot of kinetic energy and because of this high kinetic energy this electron will go out and that is what we do measure in the XPS.

So this is what is used in the XPS as you know I have discussed that this is creative process and this is also kind of leads to create a hole in the key level now let us discuss what happens in orgies so I draw the same thing here again so I have K level electrons L cells and then you have EM cells and then you have K L M and then he back right so now have already created a hole in the key level electron.

Because of this radiation so what will happen this an atom is now in excited state because ionized basically is an ionized Adam because one electron has gone out so because of that it has one you know because of this high energy state so what is what this atom can do to come you

know to a lower is energy some higher-level electrons can jump suppose this level electron l one here can jump into the this whole or can jump to the k level hole.

And fill this space and if it does so what will happen if it does so this electron has jam and filled space so now what will happen because of the difference energy between the L&K simonies of X'S will be coming out as these x-rays which will come out can eject out another electrons from the higher level like MR l m level or whatever or maybe higher level and this is what is called OGI electrons and this is what is known as or the earth process.

So that means basically what is done here is as follows which can be seen from this picture very carefully what I have drawn here and what I am showing in the slide is similar so because you have a hole created in the K level as the electron has gone out so one electron from the l1 level will jump and fill the hole and because of this there will be some energy released and this energy can then eject out electron from suppose l23cell and this is what is known as OJ electrons.

So in a nutshell I can say ionized Adam that remains after the removal of the core hole electron is of course a highly excited state and will therefore we like to rapidly relax back to the lower energy state and it can do by two roots as you say one is known as x-ray flow sense root other words OG remission route let us consider because we are not talking about XA flows and shared as a separate thing will consider only RGR.

So as you say here the this is what is the audio source so that way rough estimate of the kinetic energy of the Sari electron can be done by knowing the binding, binding energies of the various levels so kind again is basically EK minus l1 that is what is the jump minus l two three this is what the difference which is created the energy and then this is the binding energy of the electron al 2 through CL so therefore basically k - e yellow 1plus C 2 C the kind again jaws electrons the independent of the mechanism of initial whole creation.

This is very important initial whole creation can be anything particularly Osier process uses electrons electron beams to create the whole not the x-rays so basically it is very clear that the kinetic energy of this assize electron is independent of whatever the processes used to create the hole in inertia or the core level ourselves.

So normally XPS normally what is done is that you know they took in practice we use a very high energy incident beam and the electrons like of the order of five million five to ten kilo

electron volts so holes will be produced by this electrons armed it can produce my own back story eloquent also so that how I, I hope now that these two processes the difference between these two processes are clear to you.

So because of the creation of the Sari electrons a totally different from the XPS synergy of the OJ electron is also very small because it is very small energy is much small gas compared to the space electrons so the information which you can gather will be very small depth of the surface of the material so did to give you in mass little perspectives.

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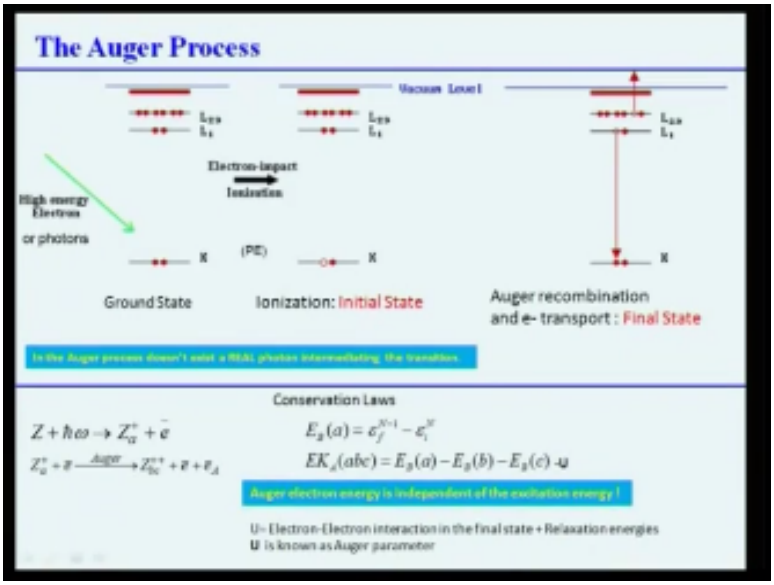

Let us do it again so how do the electron beam comes suppose this is the ground state of electron k level l 1 l 2 3 and then emu higher the electrons it can be also photons but normally you do not use any photon so use electrons and he rejects the electrons from the core level of care level leaves behind a hole this is what is ionized electron so one electrons then falls form the l1 level to fill this k1 level.

Because of this some energy released a this energy then eject out l23 level electrons and the electron gets transported this is what is in inertial hoorah GIA process and this is what is shown

here j+h μ this is JED is the at minimum of the material suppose h omega is the energy of the electron j plus electron level and JADA plus electron level produces whenever RJ electron it will be jail BC plus electron plus electron a that is what is the electron a that is RJ electron see.

If I use a conservation law EBA EV is energy of the material is basically n 1 - n of the two final state in the initial state n 1 is n is number of electrons EK a that is the RGR ABC, ABC is a three processes a is the beginning process actually midterm in across and C -u is basically the energy to remove the electrolysis there so electron energy is independent of the excitation a yes I have told you, you is known as the orgy a parameter or j parameter is the machine given a parameter.

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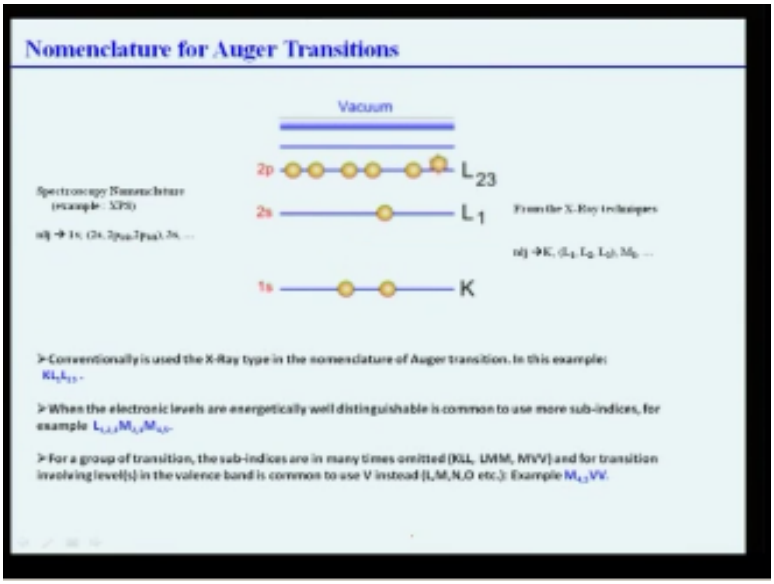

So what are the nomenclatures this is what is shown here and the whole process well nomenclatures are very complex in a spears I I need to discuss in detail our dad the XPS known pictures are basically like 2s 2p half 2p 3 by 2 you know half is basically 1minus half and 3 by 2 is 1 plus half and one transport stands for p SS now these basically stands for 0 and then if you use el L will be customer 2 so 2 – 1/2 3 / 2 to + i was 5/ 2 this we have seen.

So what happens in espionage ER as you see here in this case source comes keeps a hole this comes down and then electron goes out that is what is shown so in XA in India we use X a nomenclature so what is this x + 1 pitch I conventionally used DHOLKI that is x-ray type in awe GIA sub suppose for example KLO 1 l 2 3 that is what is here happened k L 1 l 2 3 this is a

whole transition when electronic levels are analytically well distinguishable it is common to use most subs are businesses like l 123 m 2 3 m 45.

This also one can use very well distinguish atoms can be turned up for a group of transition sub-indices are when many times orbited like KLL KMM MVB are for technicians involving levels in the valence band commonly used V instead LMNOP for example m4 x 5 V V so but normally we use this or this other things are not extensively use let me have discuss in detail about a table and to show you so that you do not forget so basic nomenclature which is used in SPS camera turn like this.

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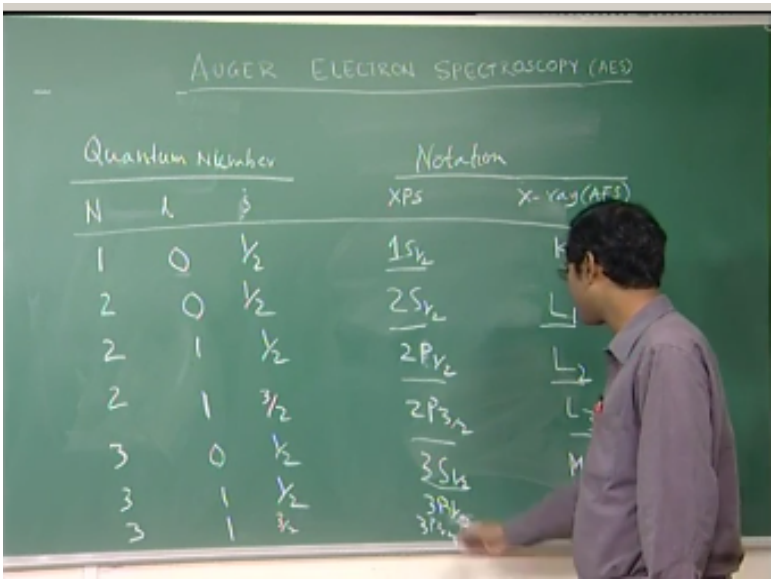

So this is quantum number this is quantum number and this is suppose notation so we are going to notations both XPS and x-ray and that is what is used in n yes right so quantum all means n l and yeah right so this is what we are going to do so let us suppose for point number n = 1 l = 0 and j = 1/2 L is the azimuthally quantum number and j is the spin quantum number here you can use it set up j let us use s speed one or.

So and then we use basically what we use one s half this is just one s there is no need of writing in x-ray we use this is a key so if it is too cu and o number this becomes 0 and this become half then what is this XPS you use is we use to s half right and this is corresponding length x rays l1 so if you suppose to again one and number two and one and half here so this will be 2 s 2 s not top half basically.

Because 2l is 12 p 1/2 and this will be L too I guess sl2 and then if we use to 11 3 / 2 3 /2 is 1plus half 3 / 2 this will be 2 p 3 / 2 this is what we have discussed how to pee hop and 2 p 3 by 2 comes in XPS I have discussed and this will be L 3right now let us do something for three actually when pencil corner my cum 3this is zero this is 1/2 this will be what so with three p3s sorry 3s half and this will be m1 so if it is become three one and half.

So this will be 3 p π/2 1/2 653 1/2so 3p 1/2 and this will be mm2 last one let me see 3 1 3 /2 c1 3 / 2 lee p 3 / 2 3 p 3 / 2 this will be m3 right and so on so as you see here k tens for one is ½ l one stands for to SF l two stands for 2p 1/2 LT transferred to p 3 / 2 m 1 stands for3s 1/2 m 2 stands for three feet to y2+ mt transport 3p three by three t / 2at this three by two basically comes because of spin JPAS el L is suppose one here.

So it becomes 1 + ½ is 3/ 2 okay so that is how it comes basically in XPS we use these notations to demarcate different pick on the other hand in assize are we use this notation this is funny because these two techniques are sin spectroscopic stem is actually but to use different, different notations for this week's robe and our transitions.

So that means if there is a transition from suppose like this one k l 1 l 2 3 l 2 3is 2 3 levels so it will be k l 1 l 2 3or kll both are possible if the transition from k suppose L 1 m 1 this will be k l 1 m 1or k l m RK mm is also possible okay all these things are possible different kinds of commissions are possible.

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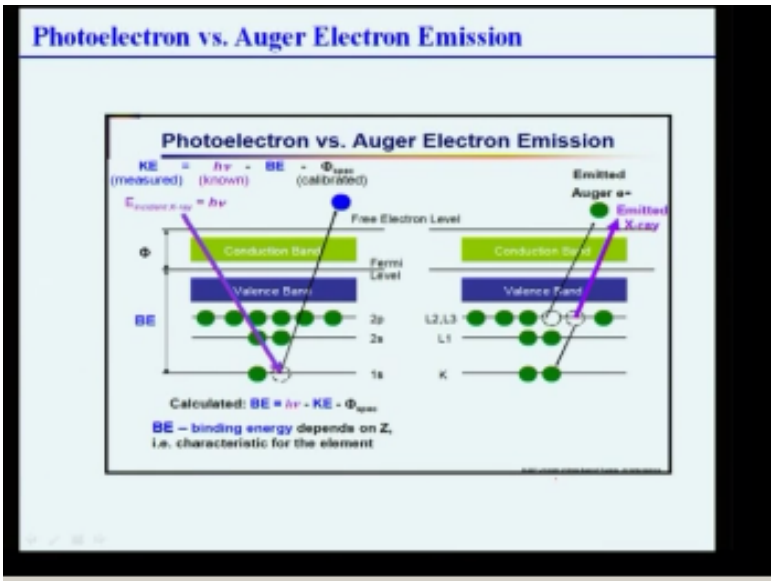

Well to give you in a better perspective so what is the difference between this photo electron Raja spectroscope I will be clear from here well as you see her one is to is to pee this is energy level of an atom at the different electron and Dubcek basically than a way Fermi level quantum band quantum bands and the vacuum and the free electrons so we are instead an x-ray with energy k nu falls on it, it creates it removes and cool level electrons.

The score level electron goes out so that means the kinetic energy of electron will be H nu minus binding energy of this electron minus five specification is basically specification basically because of the machine but in a as y what is happening you are created a whole because of this whole the electrons from the l two three jumps.

And then emitted x-ray comes out this x-rays then generate or ejects acuter the electron from these l2 l3cells and this electrons is known anarchies a so are the kinetic energies obviously is will be depending on K L 1and L 2 3 and that is all we have calculated in the early also.

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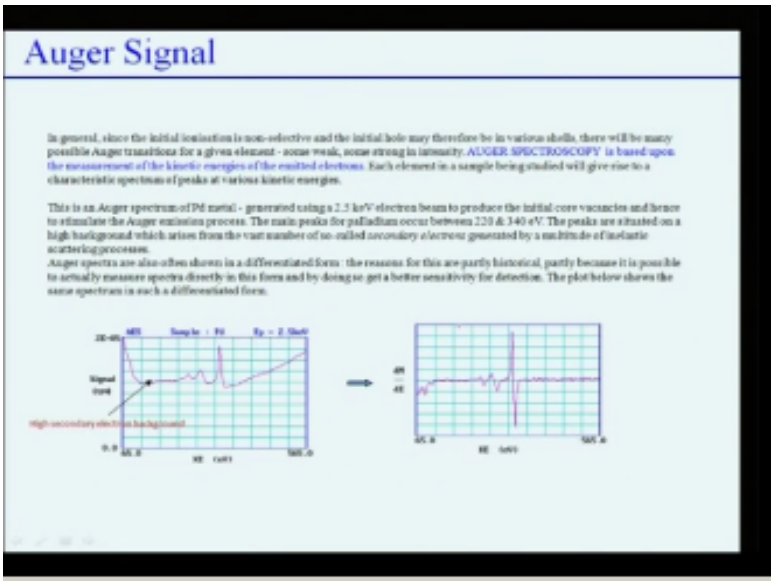

Now next thing you so discuss is what is the audio signal on what is basically audience how does the audio spectral loop spectrum look like in general initial or animation is non selective because insulin is it means how the hole in the key level is created is non selected an initial hole may therefore be in various shells like case LLL seller sell any shells because the depends on the how the initialization has taken place.

And then there will be many, many OGS tension possible for a given element Somali very weak shall be strong so RG respective could be basically based upon the measurement of the kinetic energy of the emitted electrons of the olio was a electrons so easy element sample being studied will give rise to characteristic Backstop pica of various kinetic energies so that is the audio spectrum is basically will contain large number of peaks.

And now that creates many times a problem to give an example let us suppose let us take the audio spectrum of tedium metal palladium have a line number of electrons in this in the Sydney let out ourselves I within ourselves and this is generated by 2.5 KAV electron beam to produce initial core electron reckon sees and hence to stimulate DA GR emission process the main peaks of the Palladium occurs between 222 340 electron volts the peaks are situated.

Between you know between basically on a high background that is what is the problem in fajita this mainly because of the Trinity electrons are generated by a multitude of English tea scattering processes so are they spectral often shown in differentiate from that is why and the reason for

this is partially historical partially because it is possible to actually measure the spectra directly in this form and doing so get a better sense a bit of a detector text in actually the plot actually.

So say a son spectrum this is the signal versus KE you can see how they say hi background because of the secondary electron and these are the pics which are coming out which is between 220 and 340 but whenever we take a different set of the selectively a signal with respect to our the energy level DN by D we get a smoother background and the pics can be seen very nicely that is what is normally used in nausea this one is not used in Nadia.

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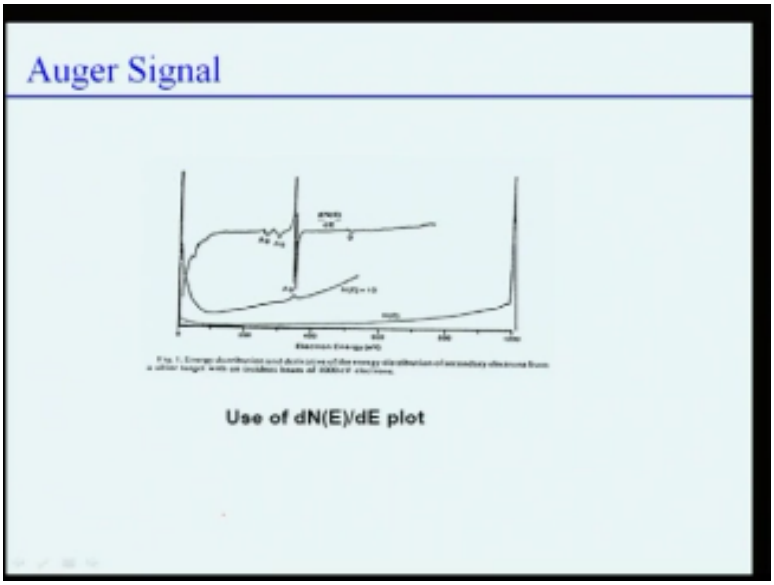

Well to give you a much better idea this is a plot between D and E but says d with respect electron and this is basically from the silver as you see here this is any of silver this is energy level electrons this is the any for 10 and then this is d NE ye signals od much stronger when he plot DNA by D passes energy levels that is why we use all this.
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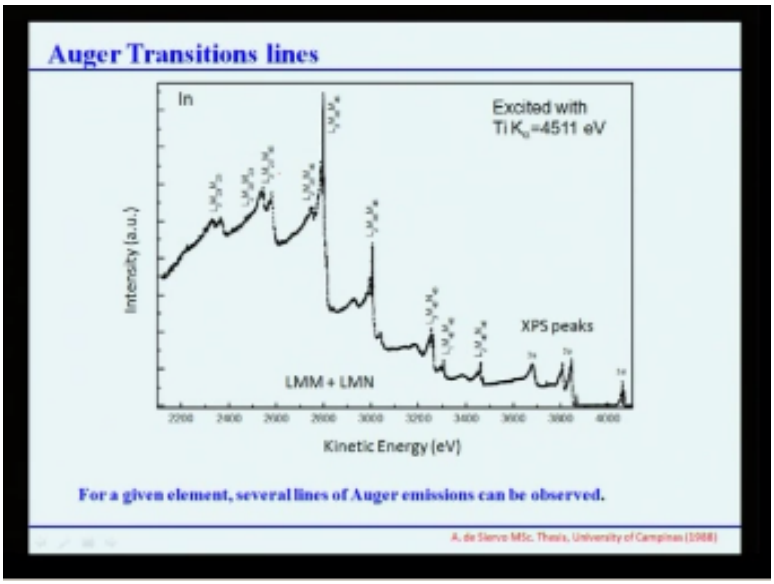

Now to tell let you give you some examples of these audios transition lines I have already discussed you different transitions let us do it for I think sudden example this is taken from IM Texas MSC thesis of university of camping us long back if you look at that on this plot you have intensity versus kinetic energy of indium element helium indium you have both your XPS pics which are here.

And audio pica which are here audience will have less energy than the XPS less than3,400 or less than 3,500 actually EV is the energies of the of this audio and higher than 3600 basically from TS 3pand 3d electron levels of tea this was done with the excitation we take titanium QRK alpha which is energy of 45 11 electron volts so what do you see we see all the tension like LMM ll MN transition indium as a line of electrons so therefore there will be large number of audio transitions possible.

So the once which are basically very when our routine is l 1 m 45 m 45 m 45 is m 45 4545 and all others l2m 45 m 45 again l3lthree also they are from l 32 m transitions mm transition then this actually call all LMN transitions there are different, different element a nationl12 l4m 45 in 45 and then l 1 10 45 m 45l3l 2 and so on so basically these are all LM mm transitions as you see here.

And there are many and there is only two this is the one LMN this is another one11 this is also L mm conditions and these transitions actually can be detected very nicely in ampere spectrum here although it is plotting DNA intensity of whatever energy coming out from the electrons but

many times if you plot DNA vs t plus kinetic energy DNA by DA is what is plot the slope of the scar basically that will give you much better pics so for a given elements several lines of all years will be observers in that is what is observed.

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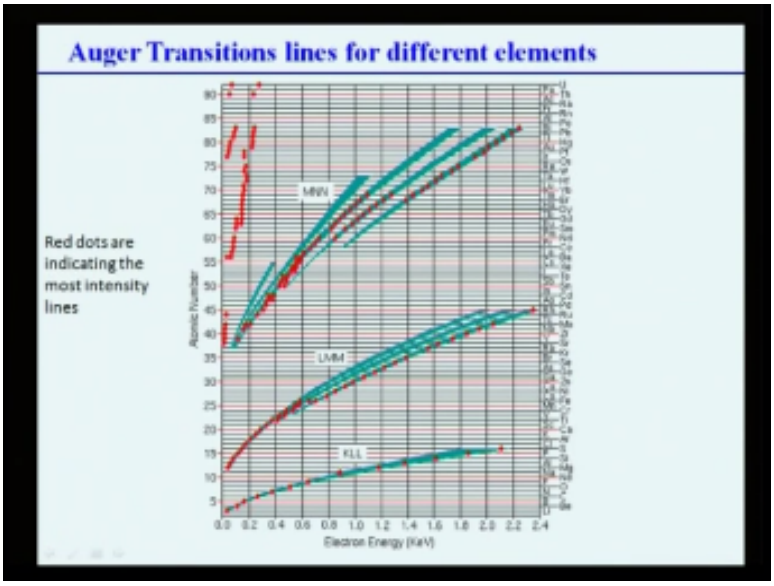

So all the transition lines for different elements can be plotted like this, this is at my number buses electron energy and the different elements starting form lithium to uranium correct so what you see are basically KLL Tennyson k 11 Tennyson MMM transitions and so on red dots actually indicates the most intense lines which is seen in the spectrum.

So I could see here we can observe KLL transition till sulfur as you can see here because energy levels are small the atomic numbers are small so that put this in as you go on we can observe seeing LMM transitions form a tube number about 12to 18 number about 40 and then MMN transitions since at hierarchy number starting from 37 to over 84 85 and.

Then so on you can observe actually m and higher level positions like this one is for very high at minimal elements so this is this is very important because this tables tells you what all transition you can expect when you are doing the XPO GR measurements.

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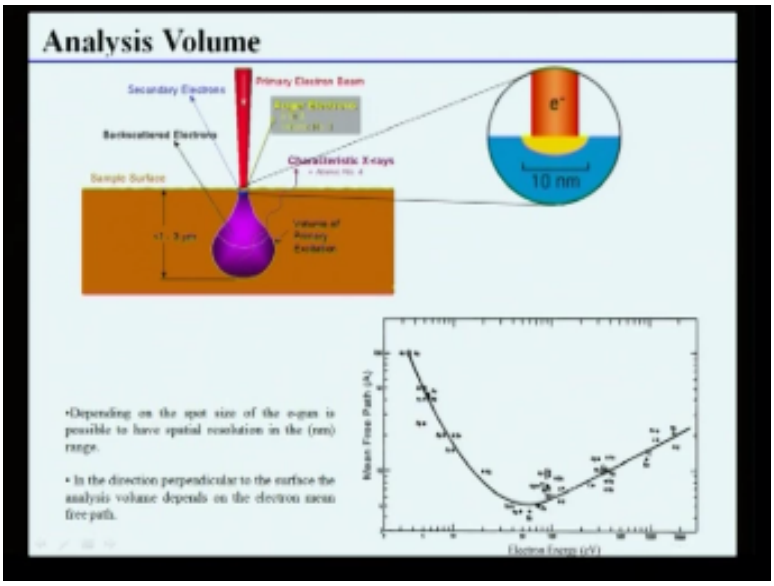

I think last one today's class today is lecture I am going to show you is the analysis volume as you know that when the certain energy source is falling in the simple material it interacts with the material and it creates a volume of interaction or interaction volume rather so the excess comes out from a large volume thence comes out the d is actually cattery exist as you see here which higher than a twin number for a backslide electron also comes out secondary.

Let in comes out to a Mars level awes electrons comes out only form for 25 50 Armstrong this is the depth from which it can come out very small depending the sports the electron gun it is possible to have special resolution by a small pressurized listen in the direction perpendicular face the analysis volume depends on electron mean free path some an people was electrons.

If you plot if you see a mean free path basically first it decreases from gold to a no bottom to beryllium then increases steel sodium so this is what is the destroy the main factor was the beam size as August a mean free path so if you use a perpendicular measurement system here like that then a mean free path becomes very important.

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