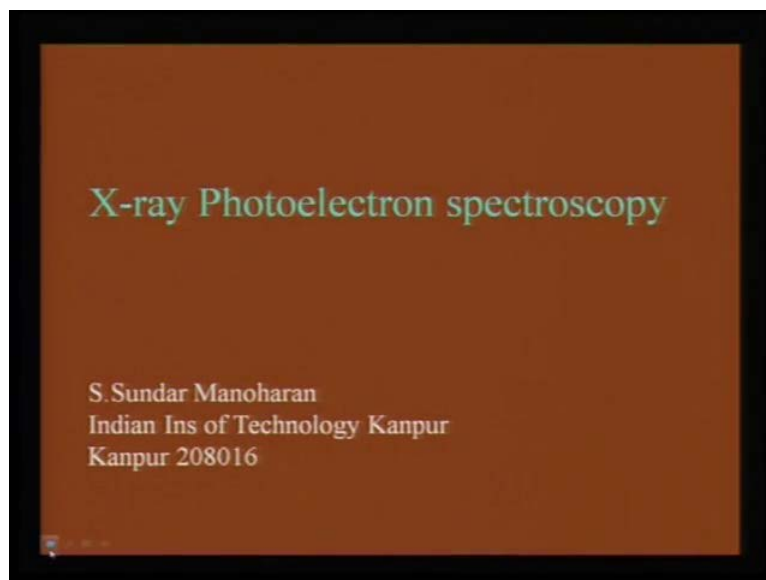


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**Module - 3**  
**Lecture -2**  
**Applications of X-Ray Photoelectron Spectroscopy**

In this lecture, we will be looking at a specific spectroscopic tool, which has been widely used in materials chemistry. And as the title suggests, there are two issues that are involved in this spectroscopy, the name suggest that it is a X ray photoelectron spectroscopy.

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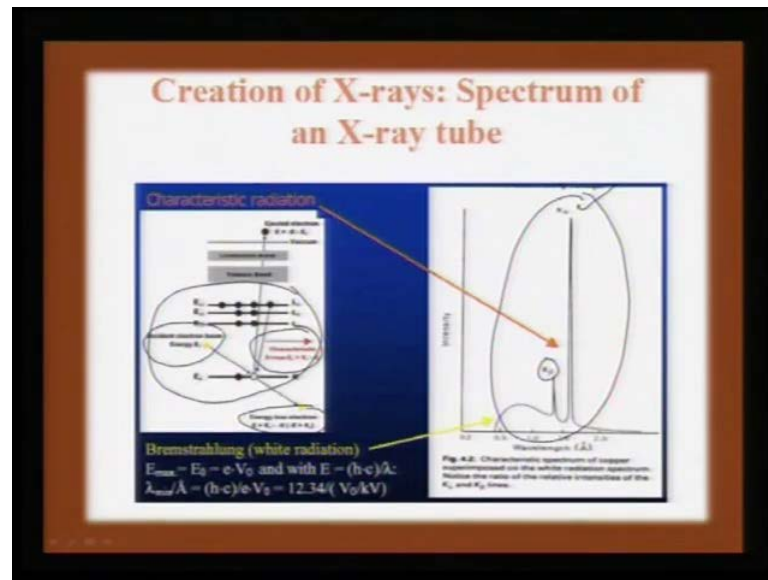


Therefore, there is a X ray that is produced when a photoelectron is ejected, so a combination of two processes that are happening, brings about a very rich chemistry that one can learn. Material scientists, physicists and chemists have used this technique extensively and this is now a very established tool for characterization materials in the last three decades. Improvised and very sophisticated instruments have come, in the last two decades the machine could actually occupy a very big room.

But, today this sophistication of this instrumentation has moved such a way that even a bench top X ray photoelectrons spectrophotometer can be used. So, we will look into this issue of, what is principle behind this spectroscopic tool is and if there is something very

highly complementary to X ray diffraction, it is the spectroscopic tools. And as you would see in this lecture, there are several spectroscopic issues that are manifested when X rays are emitted. And how this can be mapped and how we can translate this into quantifying some results, we will see in the next few slides.

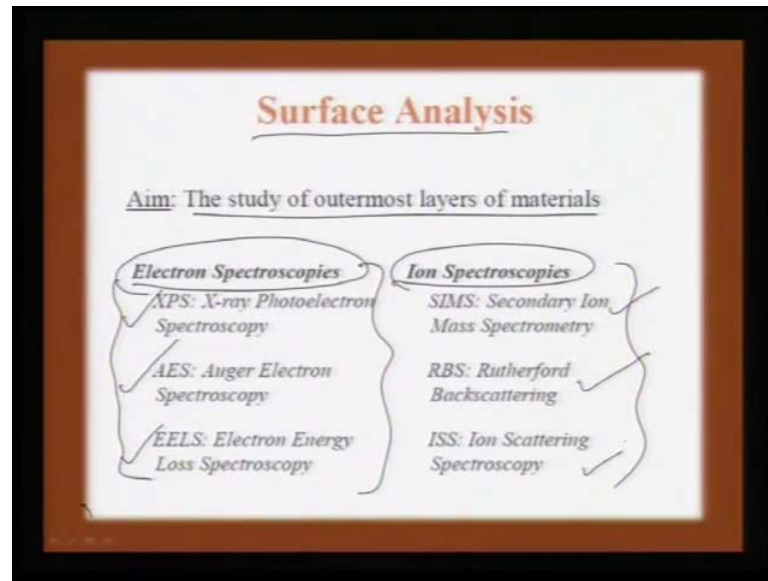
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And to start with, let us see how we create X rays and how this spectrum of a X ray tube is generated. Now, when a incident electron beam is incident on a core electron that is, in the K shell then there are several things that can happen. Electron can be ejected out to the vacuum level which means, it is totally out of the binding force or binding energy of the metal or it can actually have a electron loss energy situation that is involved or X rays can be produced from one of the L shells to a K shell when a electron jumps from one to the other.

So, we can actually look at the particular X ray that is produced during this transfer of this electron from L shell to K and that can be a characteristically mapped for a particular element. And this is the characteristic radiation that once observes, which has 2 components K alpha and K beta, but usually we try to use K alpha, because the intensity of K alpha is much higher than K beta. So, we will now look at the process that involves generation of X rays, which is typical of a material. And this has to do with the core shell electrons, instead of the valence band electrons, therefore this is particularly called as X ray photoelectron spectroscopy.

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Now, when we look at this analysis tool, it is mainly classified or generally referred to a surface analysis and the study of the outer most layers of materials can be studied. Therefore, in thin film may be through the bulk, but in the bulk materials you can only penetrate to very few nanometres. Therefore, it is mostly a surface phenomena rather than a bulk phenomena that we can look for, but generally this can bring about a rich chemistry. Because, all the impurities that are occluded to a given bulk material can be analysed, because the depth that it can go is only for few nanometres.

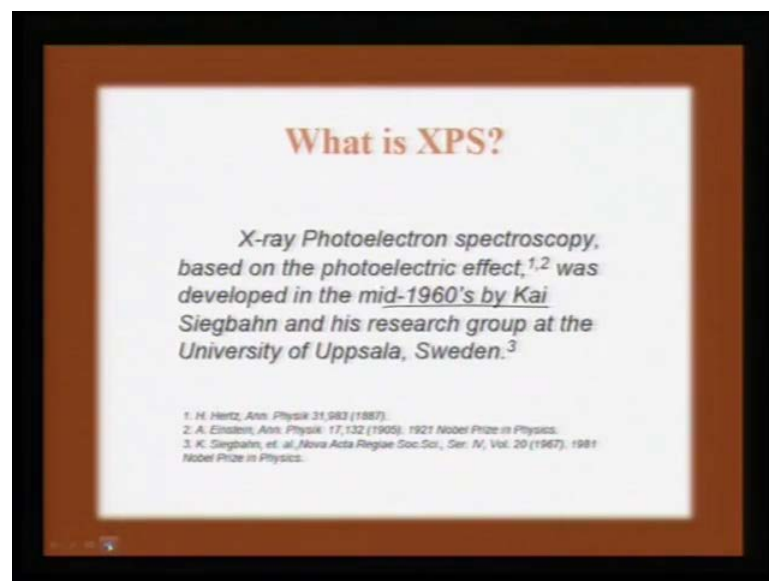
Now, depending on the manifestation of the interaction of the beam with the sample, there are several things that can happen, one is based on electron spectroscopy and another one is based on ion spectroscopy. So, a series of characterization tools can emerge out of the approach that we take, if you are going to use a electron beam to interact then the manifestations are XPS that is, X ray photoelectron spectroscopy.

Or another secondary process that happens during the XPS, which is auger electron spectroscopy or there could be a another secondary effect, which is a electron energy loss spectroscopy. All this when a electron beam is interacting with the core shell electrons, we can also have ion interaction with the matter and as a result, we can come across several spectroscopic tools, which can carry useful information. One is your SIMS that is, Secondary Ion Mass Spectrometry can give you very refined information into all the corresponding elements or impurities that are present in the surface.

Or the Rutherford backscattering, which is another very sophisticated tool where, helium ion is sent into the lattice and if the lattice is actually ordered then you have a good channelling that is happening. But, if it is a disordered material, the helium ion will get scattered back and therefore, you can look at the length of this ordering of the lattice or how orderly the lattices are developed during the process can be mapped.

And specially, those who are involved in thin film technology, use RBS as a very, very sophisticated tool, which can give you a clear insight into the epitaxial growth of the film, whether the film is growing along a particular axis or not, can be mapped using RBS and then you also have ion scattering spectroscopy. So, a range of spectroscopic tools are categorised in the form of surface analysis and today, we will look little bit more deeper into the XPS technique.

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So, what is XPS, X ray Photoelectron Spectroscopy is actually based on the photoelectric effect, that is why it is called X ray photo electron spectroscopy. And this was developed in mid 1960 by Kai Siegbahn and his research group at the University of Uppsala in Sweden and since then this has been a pioneering probe tool.

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### What is XPS? – Historical Development

1887 Discovery of the Photoelectric Effect (Hertz) ✓  
1905 Einstein explains the Photoelectric Effect ✓  
1914 First Formulation of basic XPS Theory (Rutherford) ✓  
1920 Photoelectron spectra of different elements were recorded ✓  
1954 Further Development of the Method (K. Siegbahn) ✓  
1970 First commercial XPS machines available

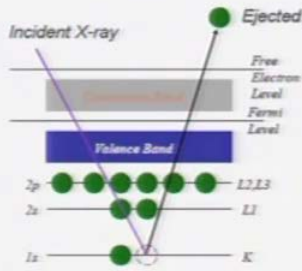


H. Hertz      A. Einstein      P. Rutherford      K. Siegbahn

So, what is XPS and how historically we can identify this, 1887 it was actually the discovery of photoelectric effect and this was not explained based on classical physics, because what we saw from the photoelectric effect was not commensurate to the theory that was existing about light. So, in 1905, it was Einstein who used the issue of a quantization proposed by Max Planck and he explained, what this photoelectric effect means. And the first formulation of basic XPS theory by Rutherford in 1914 and then photoelectron spectra of different elements were recorded in 1920 and then on, it has been a major effort as a surface probe tool.

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### The photoelectric process



Incident X-ray

Ejected Photoelectron

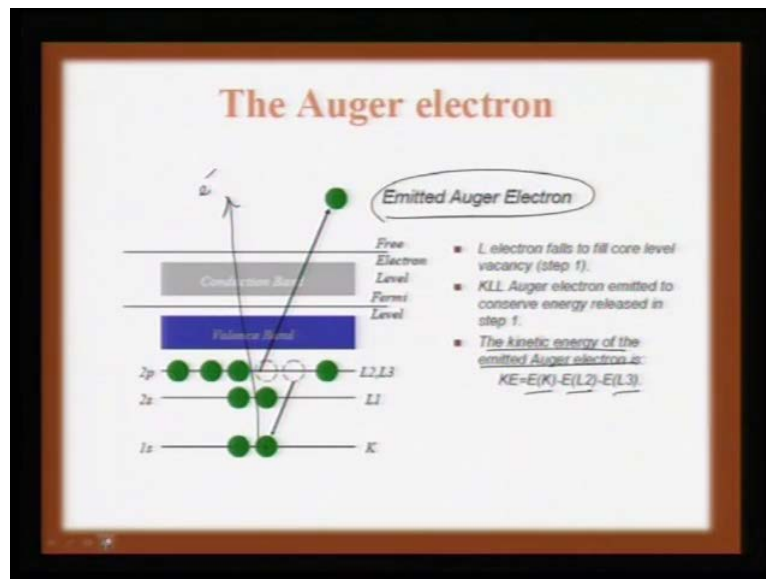
Free Electron Level  
Fermi Level  
Valence Band  
2p  
2s  
1s  
L2, L3  
L1  
K

- XPS spectral lines are identified by the shell from which the electrons were ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:  
 $KE = h\nu - BE(\phi)$
- Following this process, the atom will release energy by the emission of an Auger Electron.  
 $h\nu = \bar{\Phi} + \frac{1}{2}mv^2$

Now, what really happens in the photoelectric process, as you would see, the incident X ray actually falls on the core shell electron that is, K shell and this is immediately ejected as a photoelectron. So, this is the photoelectron that we are trying to map, but in the process, there are several things that can happen. Once the hole is created here then the neighbouring shells that is, in the L 1, L 2 or L 3 will quickly translate one of the electrons to the lower shell that is, K shell and thereby, secondary processes do emerge.

So, XPS spectral lines are identified by the shell, from which the electron was ejected, it could be from K shell or l or m and so on. The ejected photoelectron has a kinetic energy, which is  $h\nu$  minus binding energy minus  $\phi$  and this is actually from the instrument. We will look at this equation, because we are familiar with this expression from photoelectric effect, which is a work function plus half  $m v$  square. This is your basic expression from photoelectric effect, but what you would see here is an extra parameter that is coming, which we will try to understand, as to why we do that. Following this process, the atom will release energy by emission of an auger electron.

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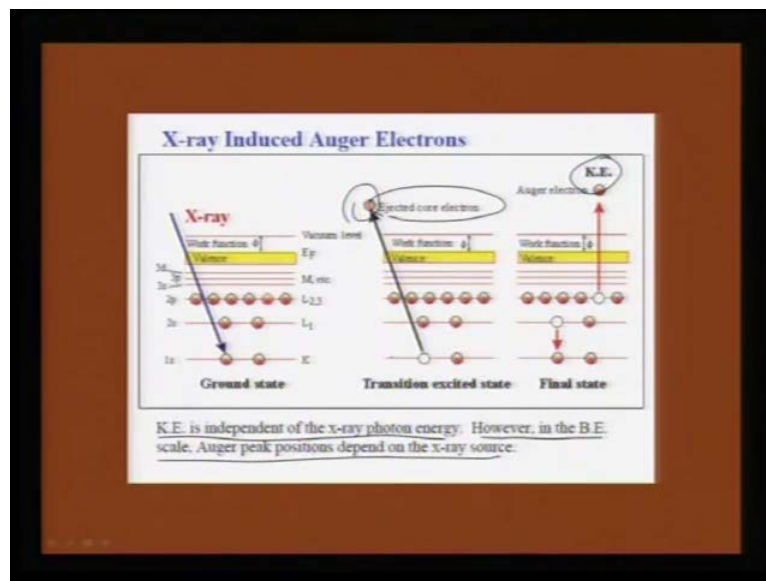


So, where this auger electron is coming into picture, the l electron falls to fill the vacancy, which is step 1. So, once the photoelectron is ejected out which was from here, the photoelectron was ejected and in that place, one of the L 2 or L 3 electrons will actually come and fill this place and to conserve energy, one of the other electron will be

emitted. As a result, you are actually getting a auger electron, which is actually not the photoelectron, which was ejected in the first step.

Therefore, 2 different processes do occur, one is auger electron which is coming and the other one is the photoelectron, X ray photoelectron. So, the kinetic energy of the auger electron is actually different from the kinetic energy of the photoelectron. In photoelectron, we are bringing another phi, this binding energy is also a work function of the sample. This is typical of the sample and this is typical of the machine or the electron gun, which will come to it. Therefore, there are two work functions that are related when we talk about a XPS, we are talking about the kinetic energy of the auger electron, which is linked to the energy of the electrons in different levels. So, both are different the information that you get is different.

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So, the X ray induced auger electrons can be actually mapped in this way, so when we have this X ray photoelectron then the electron actually is ejected from the core shell and this core shell a electron which has gone. So that means, the binding energy is the energy that we go from here to the valence band and from valence band to the vacuum level. So, that is your energy that is associated with the kinetic energy of the ejected electron and when we think of the auger electron, it is the energy that is translated from one of these shells to the vacuum level.

So, the kinetic energy of the auger electron, therefore is going to be completely different or will be less than the kinetic energy of the photoelectron. However, the kinetic energy is actually independent of the X ray photon energy as far as the auger electron is concerned. However, in the binding energy scale, auger peak positions depend on the X ray source, we will also look at it shortly from now.

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**X-ray photoelectron spectroscopy**

X-ray spectroscopic notation

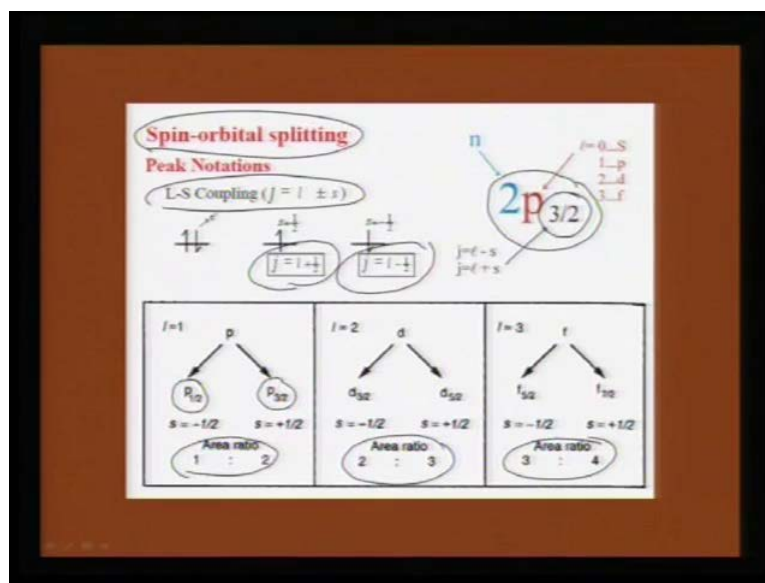
Quantum numbers		X-ray suffix	X-ray level	Spectroscopic level
$n$	$l$			
1	0	1	K	1s <sub>1/2</sub>
2	0	1	L <sub>1</sub>	2s <sub>1/2</sub>
2	1	2	L <sub>2</sub>	2p <sub>1/2</sub>
2	1	3	L <sub>3</sub>	2p <sub>3/2</sub>
3	0	1	M <sub>1</sub>	3s <sub>1/2</sub>
3	1	2	M <sub>2</sub>	3p <sub>1/2</sub>
3	1	3	M <sub>3</sub>	3p <sub>3/2</sub>
3	2	4	M <sub>4</sub>	3d <sub>3/2</sub>
3	2	5	M <sub>5</sub>	3d <sub>5/2</sub>
etc.	etc.	etc.	etc.	etc.

When we look at a typical X ray photoelectron spectra then there are some spectroscopic notations, which are included and they are actually summed up either as K, L 1, L 2, L 3 or it is actually abbreviated as 1 s half 2 s half 2 p half 2 p 3 by 2. So, we need to understand in perspective, what this exactly means, the suffix that we are looking at is mainly coming from the j and j is nothing but spin orbit coupling. So, where, L is your orbital momentum or orbital angular momentum number, quantum number, therefore the L and the spin of the electron will couple together and give half.

For example, if your spin is half then 0 plus half will give you half, if it is 0 in this case, if this going to be 1 then 1 minus half will give you half or 1 plus half will give 3 by 2. So, this suffix is actually a product of both L plus s, which is denoted as j, so depending on the shell, we can abbreviate this as L 1. If you say L 1 then we talk about 2 s half, L 2 is 2 p half, L 3 is 2 p 3 by 2. So, by this way, we can actually map all the shells or the electrons related to that particular shell. And these are having very characteristic binding energy, which we will see shortly from now.



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So, this is the spin orbit coupling that we picked from the earlier slide, so L s coupling is nothing but your j coupling, which is L plus or minus half. So, if L plus half is there then we talk about half or 3 by 2 or L minus half will be half. So, this is the way, it is denoted, your 2 is nothing but your principle quantum number, that determines which shell the electron is involved in this spectra and this is to do with the coupling. So, if you are actually looking at a 2 p half or 2 p 3 by 2 spectra then there will be certainly a ratio of the area for this peak.

So, if we talk about 2 p 3 by 2 then the area under the curve will be approximately 2 times more than the 2 p half. And similarly, between 3 d 3 by 2 and 3 d 5 by 2, you will have a intensity ratio of 3 is to 2 and same is the case for 4 f electrons, 4 f 5 by 2 and 4 f 7 by 2 will have a ratio of 3 is to 4. So, looking at this, we can easily map even without a notation, looking at the area under the peak, we will be able to immediately say what is the sort of peak that we are looking at, so typically a peak will look like this.

And this is the case for gold 4 d 5 by 2 and gold 4 d 3 by 2, as I told you in that previous case that, if it is a d electron then the ratio would be somewhere between 2 is to 3 and you can see that very well here and the area under this curve will be the measure. So, the separation between the two peaks are named as spin orbit coupling and the values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

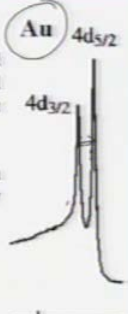
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For p, d and f peaks, two peaks are observed.

The separation between the two peaks are named **spin orbital splitting**. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

The **peak area ratios** of a core level of an element in different compounds are also nearly the same.

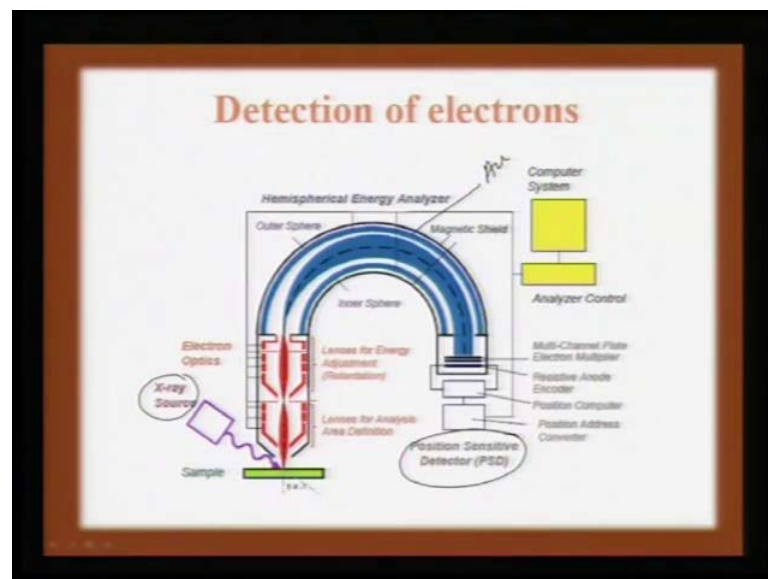
Spin orbital splitting and peak area ratios assist in element identifications.



The diagram shows a plot of intensity versus binding energy for the Au 4d core level. Two distinct peaks are visible, labeled 4d<sub>5/2</sub> and 4d<sub>3/2</sub>, representing the spin-orbit splitting of the 4d level. The 4d<sub>5/2</sub> peak is higher and occurs at a lower binding energy compared to the 4d<sub>3/2</sub> peak.

So, this splitting will nearly be the same for almost all the elements and the peak ratios of the core level of an element in different compounds are also nearly the same. Because, it does not depend on the material, but it depends on the spin orbit coupling. So, this are very unique to the quantum states, so what we can identify is, in spin orbit splitting, the peak area will assist in the element identifications.

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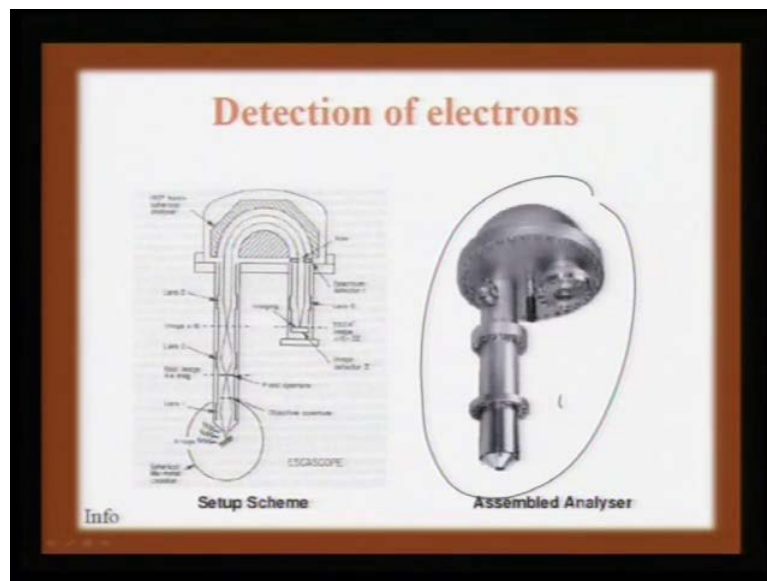


Now, how will a X ray photoelectron spectra chamber look like, the analyzer which will actually analyze the X ray photoelectron, will actually be a semi hemispherical chamber.

And this is how it goes, if you have a X ray source which is heating the target that is, your sample. Now, electron is ejected out beyond the vacuum level and this is actually translated through a semi hemispherical chamber, which is the inner layer is actually coated with gold.

So, outer chamber might look metallic but then it is actually plated with gold, so gold is your analyzer and this is actually channelized, so as to get the stuff directly to the detector through a photomultiplier tube. So, this is in essence, a simple set up of a X ray photoelectron spectra spectrophotometer, so because we are actually using an analyzer which is gold in this case. Now, since the gold is acting as a reference detector where, all the photoelectrons are collected, the work function of the gold is also to be equated or grounded to the sample. Therefore, the Fermi level of both the sample and the analyzer has to be same and as a result, we need to include the work function of gold electrode also.

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And this is a typical picture of a assembled analyzer that we are talking about, so you would have the sample fitted here. And then it will go through the detector and the photoelectron will be mapped. So, this is a cartoon that tells how simple or how intricate the assembly is made.

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**XPS Energy Scale – Kinetic Energy**

$KE = hv - BE - \Phi_{spc}$

Where: BE= Electron Binding Energy  
KE= Electron Kinetic Energy  
 $\Phi_{spc}$  = Spectrometer Work Function

Photoelectron line energies: *Dependent* on photon energy.  
Auger electron line energies: *Not Dependent* on photon energy.

Why spectrometer work function?  
Electrons are detected when reaching the detector's Fermi level.  
Kinetic energy measured relative to the detector's zero point

In addition: Sample may be on a different potential (e.g. charged)

Now, when we talk about XPS energy scale, there are two things that we need to understand, one is the XPS energy with respect to kinetic energy and the XPS energy scale with respect to binding energy, two things are there. So, when we talk about kinetic energy, the expression that we follow is kinetic energy, is equal to the incident energy of the electron beam and the binding energy of your sample minus the work function of your spectrophotometer, which is nothing but gold.

So, we usually take the gold work function and we minus that, because that is also involved in the analyzing process. Photoelectron line energy is therefore, are dependent on photon energy whereas, the auger electron line energies are not dependent on photon energy, this is a very important principle. So, only the XPS lines are dependent on the photon energy, which we are talking about this and the binding energy is not dependent on this  $h\nu$ . So, why we use spectrophotometer work function, because electrons are detected when reaching the detector's Fermi level. Kinetic energy is therefore measured, relative to the detectors 0 point, that is why we use the work function and in addition, sample may be on a different potential that is, it can be charged.

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**XPS Energy Scale - Binding Energy**

$$BE = h\nu - KE - \Phi_{\text{spec}}$$

Where: BE= Electron Binding Energy  
KE= Electron Kinetic Energy  
 $\Phi_{\text{spec}}$  = Spectrometer Work Function

Photoelectron line energies: *Not Dependent* on photon energy.  
Auger electron line energies: *Dependent* on photon energy.

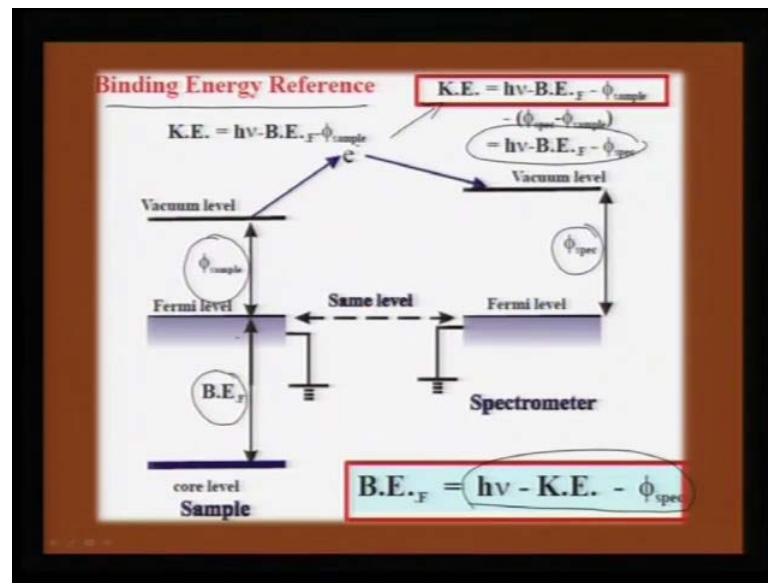
*The binding energy can be calibrated by standards, typically*

- ✓ C1s at 285.0 eV
- ✓ Au4f<sub>7/2</sub> at 84.0 eV

When we talk about the energy scale in terms of binding energy then you will easily find out that, we are talking now about binding energy, which is equal to  $h\nu$  minus kinetic energy minus  $\phi$  spectrometer. So, in this case, the photoelectron line energy is not dependent on photon energy whereas, Auger electron is dependent on photon energy, when we think about binding energy. So, the binding energy can be calibrated by standards, typically we always use carbon 1 s standard.

Because, when we are running the vacuum system, there will be some amount of carbon in the vacuum, which will get deposited on the surface of the sample, therefore carbon impurity will always be there. However, you treat your sample and therefore, carbon 1 s which is coming from the vacuum chamber will actually serve as an internal standard. How much ever we try to flush out this sample, yet we will see a very clear carbon 1 s spectra and that is typically 285 electron volt and that is used as a reference point. And then we also have gold, gold 4 s 7, that is 7 by 2 which appears at 84 as a reference point. If suppose, this binding energies are differing by 1 electron volt or 2 electron volt then we need to use this as a correction factor when we are analyzing our sample, so that is the way we do.

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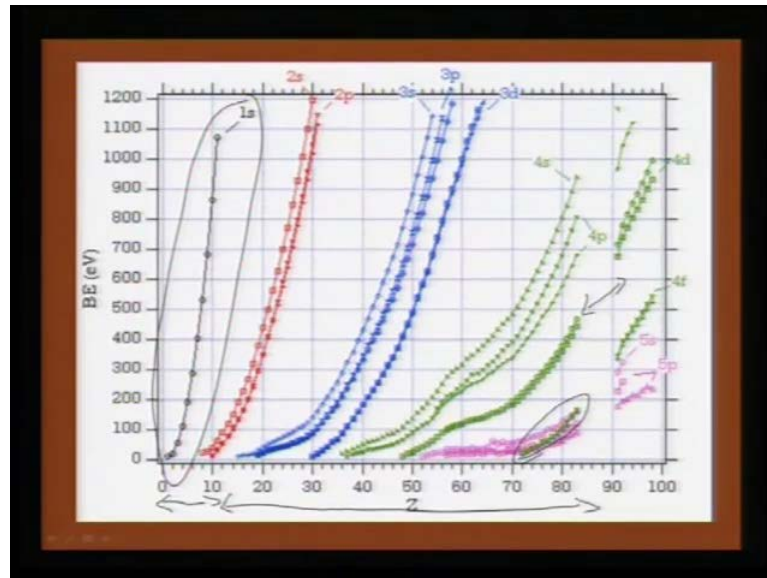
There are two things that we saw is the binding energy reference or the kinetic energy reference. Now, this is the process that we talked about, taking the electron from the core level to the Fermi level, which is the binding energy plus the work function of the sample where, you take the electron from the Fermi level to the vacuum level. And then this electron is actually put into the vacuum level of the analyzer, therefore we are talking about the work function of the spectrophotometer.

So, when we look at the kinetic energy of the photoelectron then we are talking about  $h\nu$  minus  $BE$  minus the sample. And similarly, we have to take into consideration the work function of the sample minus the spectrophotometer. Therefore if we merge all these four parameters,  $h\nu$  minus  $BE$  minus  $\phi_{sample}$  minus the difference of sample and spectrophotometer then we boil down to this expression. And similarly, for binding energy we have this equation,  $h\nu$  minus kinetic energy minus  $\phi_{spec}$ , that is the reason, why we have two different ways of evaluating the ejected electrons.

And this is a map, which tells us the relative binding energy of different elements and the 1 s electrons usually have a range between 0 to 1100 electron volt and this is for the atoms with atomic number 0 to 10. And as you progressively increase then you can see all the binding energies can be mapped, the 2 s and 2 p and these are all very specific to the core shell of different elements. So, each number will have a very precise count, so

there would not be any change and therefore, we can easily try to analyze the local state of each of this metal or elements.

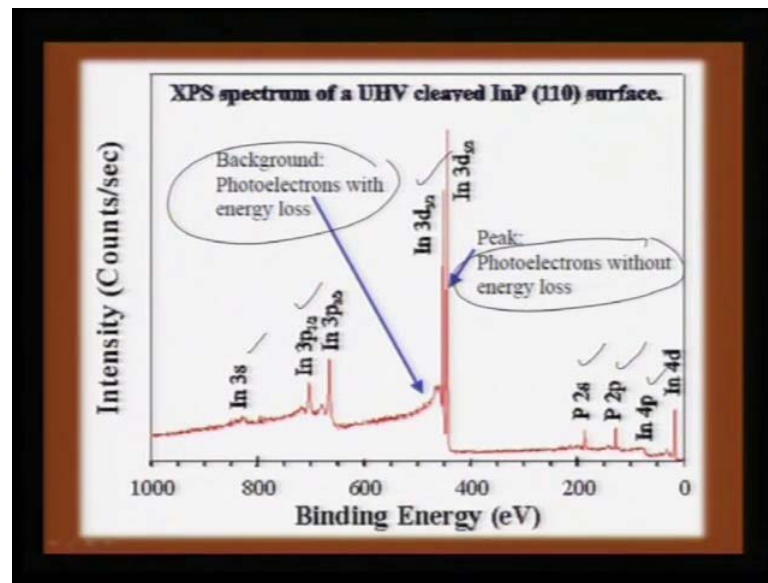
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But, when you go to higher energies, as you can see here, there are some gaps for 4 f and for 4 d electrons, mainly coming because of the heavier electrons. And the screening and the penetration effect, which will actually distort the way, the Aufbau principle describes. Therefore, there are some gaps here, for which we can see, how we can account for those regions. Mainly those are heavier metals, therefore you would see those missing data's present here. So, bulkier the atoms then you have this Aufbau principle dictating the binding energy.

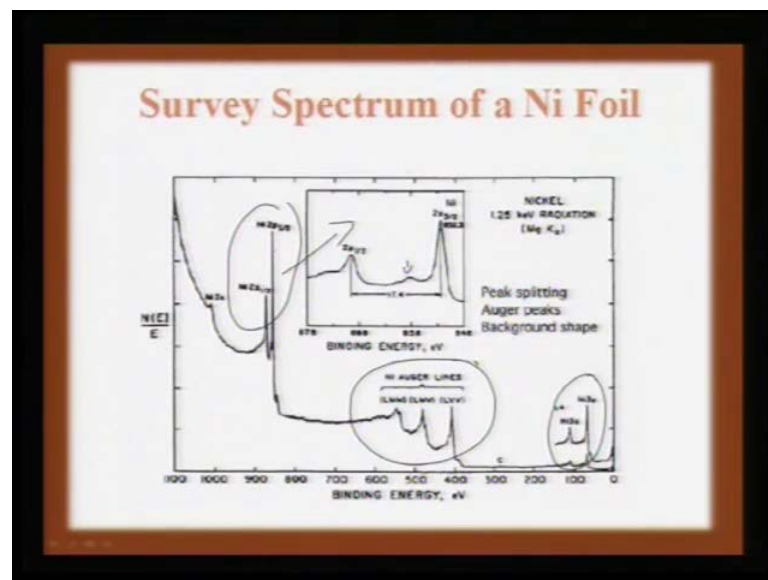
When we have a survey spectrum taken for indium phosphide for example then these are the different peaks, that one would see and each peak and every hump that is shown here, has some message to convey. For example, if you look at indium 3 d phi by 2 and indium 3 d 3 by 2, these two peaks are coming because of the photoelectrons without energy loss. Whereas, there will be a broadening or a small satellite feature that is coming, which is actually a background effect, coming because of the photoelectrons energy loss.

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And as you would see here, you can pin point each of this peaks, which is characteristic for indium 3 s 3 p 3 d and phosphorous 2 s 2 p and indium 4 d, so each of this peak can be monitored precisely.

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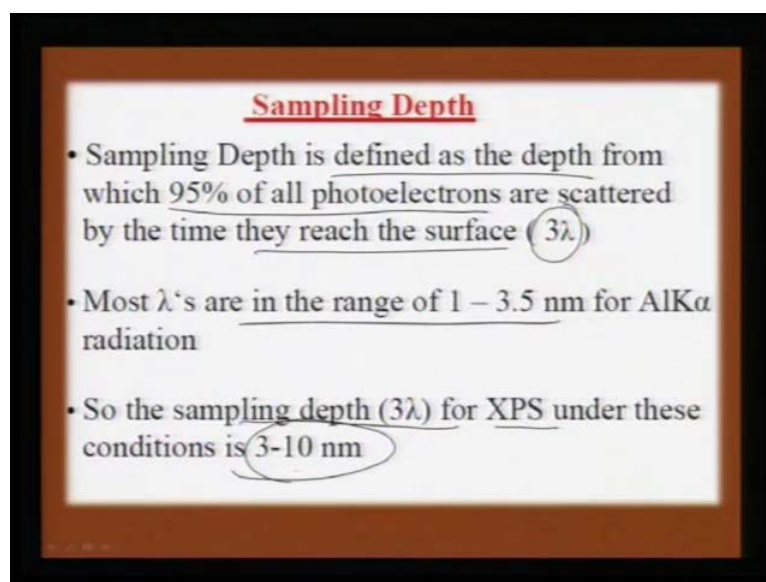
And this is a survey spectrum of a nickel foil, which clearly gives you the peak for 2 p and also for 3 s and 3 p electrons. And in between, you also see the auger lines, which are coming and typically, you cannot avoid the auger lines in a survey spectrum. But, you can easily make out, which is coming from auger spectra, mainly because they will



be asymmetric and it will be broad. So, those peaks which are asymmetric and broad, are coming due to the auger effect whereas, the sharp ones are due to the photoelectron.

So, in a survey spectrum, you can easily pinpoint on those features and if you try to expand or enlarge this portion, you can see this in the inset. You can clearly get the nature of the peak, whether it is symmetric or asymmetric and what is the broadening and is there any other extra features that are coming, all these can be seen when we try to expand this scale. So, every satellite feature that you see to the primary feature, will give some idea about the local state and the oxidation state of those elements.

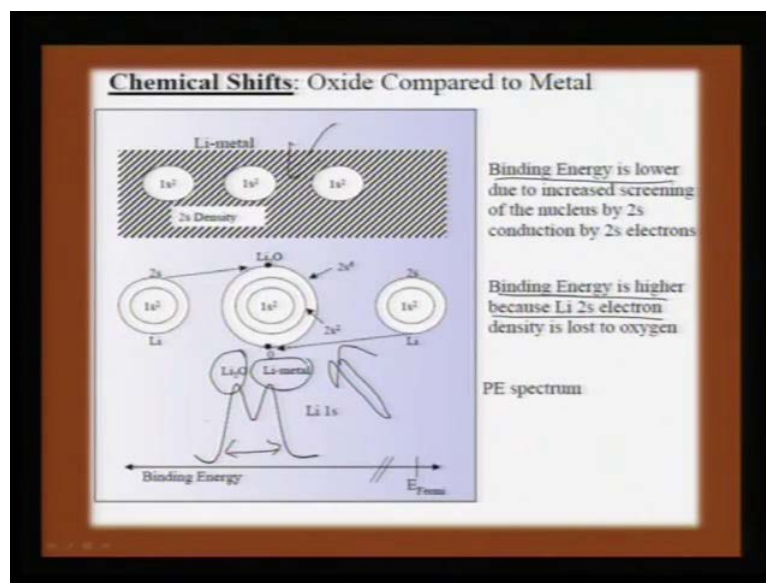
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One more thing that we need to understand, why this is a surface technique is, because of the sampling depth that is involved. The sampling depth is actually defined as the depth, from which 95 percent of all photoelectrons are scattered by the time they reach the surface. So, when electrons are ejected, the time taken or the distance it travels by the time, 95 percent of the photoelectrons can be scattered, is the sampling depth and that is of the order of 3 lambda.

Most lambda wave lengths are in the range of 1.1 to 3.5 nanometre for aluminium K alpha radiation, usually we use aluminium K alpha or magnesium K alpha as the radiation for XPS. So, the sampling depth is approximately 3 lambda for XPS under this condition, therefore your sampling depth can be ascertained to be anywhere between 3 to 10 nanometres and that is all we can probe.

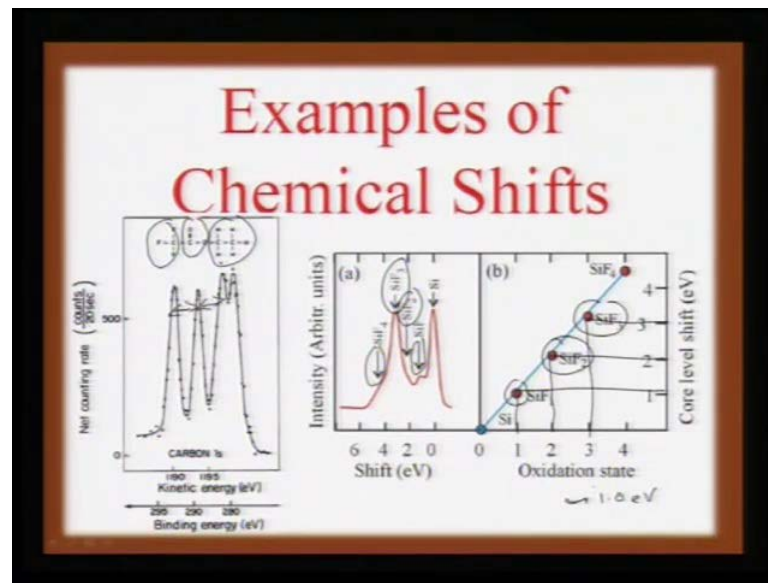
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One of the very useful information that you get from XPS is the oxidation state, we will see several examples in the next few slides where we can understand, what are the intricacies as we study those numbers. This is the case for lithium metal and this is the case for lithium oxide, as you see here, the binding energy is actually lower for lithium metal, because of the increase screening of the 2 s electrons. And therefore, the binding energy will always be on the lower side and that is what you see here in the two peak spectrum.

If you have lithium oxide and lithium metal together then you see two peaks coming one corresponding to lithium metal and the higher binding energy peak is actually corresponding to lithium oxide. And that is because the lithium 2 s electron has been given to oxygen in the bonding, and therefore the binding energy is much more stronger for lithium oxide. So, you would get two peak spectra which clearly tells, what is the centre and what is the coordination site that is involved in this compounds.

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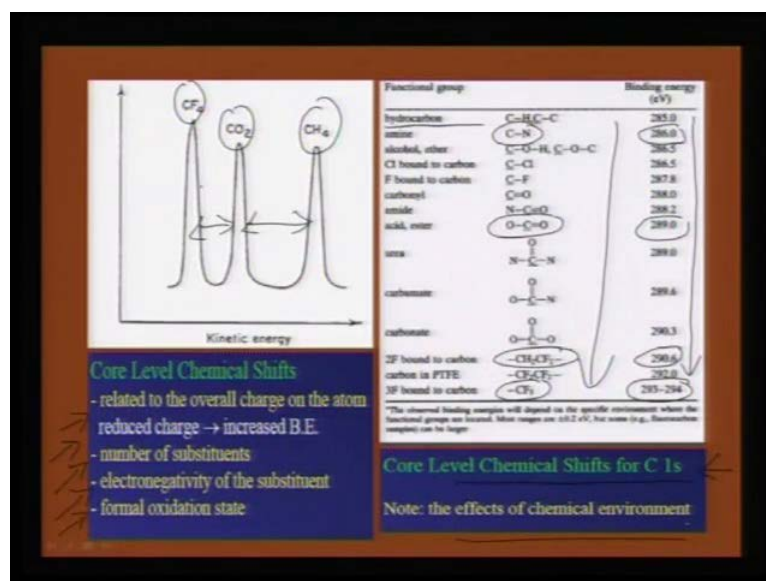
So, examples of other chemical shifts we can see here, this is a compound with the fluorine as substituted groups and then you have a carbon hydrogen bonds, carbon oxygen bonds. So, clearly we have three different range of substitutions in this polymer and if you take a XPS spectra, you can clearly find out that, carbon 1 s spectra will have 3 peaks. And all these three peaks correspond to different bonding CF will give at a very higher binding energy than CO than CH.

So, clearly the peak separation suggests that, there are three different sets of carbon that is present. And similarly, you take a spectra of silicon in comparison with silicon fluoride of different fluorine substitutions SiF or SiF<sub>2</sub>, SiF<sub>3</sub>, SiF<sub>4</sub> then you can clearly see, the silicon spectra gives different features and this is what we call as satellite feature, these two are called as satellite features. And if we properly deconvolute then we can quantify what is actually present in this sample.

So, if you map this in each case, for example silicon, the oxidation state is 0 and then silicon fluoride oxidation state is 1, silicon F<sub>2</sub> is actually 2 plus, silicon F<sub>3</sub> here 3 plus. So, if you make a comparison between the core shell shift here versus the oxidation state, it is actually linear. And as you would see here, for each oxidation state, the increase in the core shell shift is by the order of 1 electron volt. So, roughly we can take this to heart that, for every oxidation state, the jump would be approximately 1 electron volt.

So, if carbon or any other element for example, oxygen is 2 minus, if you are looking for oxygen 1 minus then you would only see a difference of around 1 electron volt or less than 1 electron volt. It cannot be 2 then there is something else which is happening, therefore this calibration clearly gives you an idea that, it has to be somewhere around 1 electron volt for a change in oxidation state by plus 1 or minus 1.

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This is another case, if you have  $CF_4$  or  $CO_2$  or  $CH_4$  as we saw from the previous graph, we can clearly see the carbon 1s peaks are shifted core level. Chemical shifts, these are related to the overall change on the atom and reduced charge which means, increased binding energy, there are number of substituent, which can be evident from the number of peaks. The electron negativity of the substitution also is magnified between oxygen, fluorine and hydrogen, so the shift is a very clear and the formal oxidation state can also be traced.

In fact, for many of the organic compounds or material with organic substitutions, just like IR, which gives finger print region, so is the case for these functional groups. In the case of carbon nitrogen single bond, you can see 286, in the case of keto group or ester group it is 289 and when we go for fluorocarbons it is 290 when we go for complete substitution of  $CF_3$ , you can go to 293. As you see here, the range of shift in the binding energy for carbon 1s, can vary up to 285 to 293, which is nearly 12 electron volt and that totally depends on the substitution that is going along with the carbon atoms.

So, this can become a very useful tool, because as I told you carbon 1 s 285 is a very good calibrant, which is the hydrocarbon. So, compared to that, any other functional groups that are there, you can easily pick out selectively, which particular carbon atom is there. For example, if you take a compound which is hygroscopic, it will also absorb carbon dioxide, so it will form carbonates. So, easily you can map based on the position of your carbon 1 s, whether it is a carbonate impurities present. So, the core level chemical shift for carbon 1 s can be easily found out, and therefore the chemical environment can easily be assigned ascertained in our materials.

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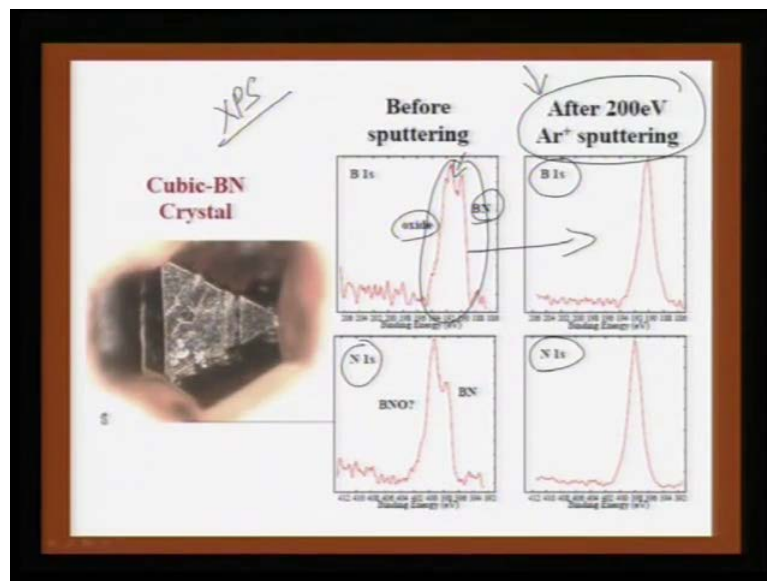
In the next example, we will take example of metal oxide in comparison with pure metal and try to see, what is the approximate shift and what is the nature of shift that you can expect. As you can see here, this is a iron 2 p spectra and in this case, you can see metallic iron actually shows a much sharper peak, but once we talk about oxides or iron oxide then we see a more broader peak.

And the difference between the iron oxide peak, Fe to be peak, from that of the pure metal is approximately of 3 electron volt and this 3 electron volt suggests that, the oxidation state of iron actually has shifted from 0 to plus 3. And similarly, let us take the case of a partially oxidized magnetite and if you map the Fe 2 p lines spectra of this magnetite, you would find out, apart from the Fe 3 peak, which is visible here very clearly, you also see a small inflection and there is asymmetry in the XPS peak.

The moment we see asymmetry in the peak then we got to be cautious, the base line shift here can actually come from many issues, which we will also see. But, one of the things that, we need to find out is, the sort of a satellite feature that is bent here. And if we try to deconvolute, we would see a proportion of this peak and a smaller proportion of this peak coming into picture, which suggests that, it is partially converted to Fe 2 plus.

So, the nature of the XPS peak will clearly tell us not only about the proportion, but also about the mixed valence states. Take for example, the case of oxygen 1 s spectrum, in the case of metal of metal oxide you would see a very clear oxygen 1 s whereas, because of surface hydration, you will also see a satellite peak which is coming. So, we can easily map, whether the iron oxide is pure or it is having some water of hydration associated with it.

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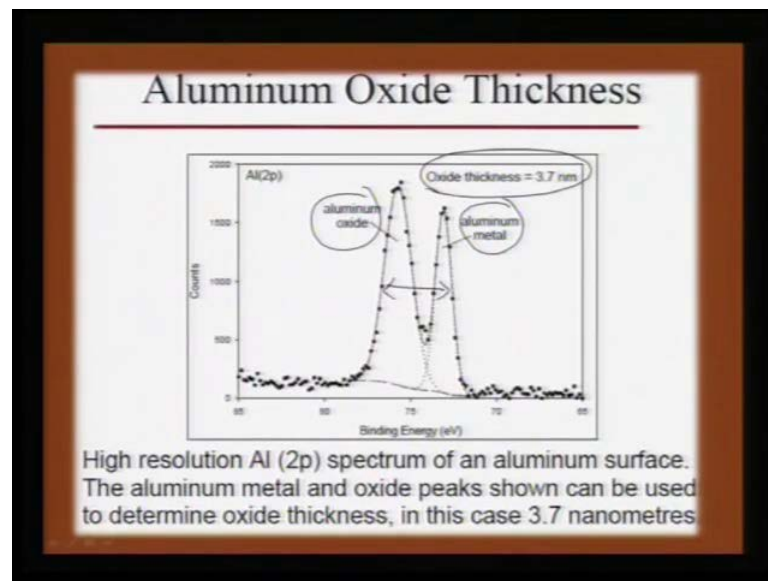
Similarly, in the case of cubic boron nitride crystal, if we try take this crystal and look at the boron 1 s or nitrogen 1 s, you would be confused with the sort of spectra that you are seeing here. Mainly, such a unsymmetric broad spectrum is coming, because of the surface impurity and in the case of boron nitride, you would actually have a oxide impurity, which brings about this broadening and this multi plate feature. And similarly, in the case of nitrogen, you can see that, there is a ambiguity there.

What you do here is, as a protocol in XPS, before we map the 1 s or 2 s or 2 p spectra, as a regular protocol it is suggested to sputter the sample with 200 electron volt argon ions.

And this sputtering actually is bound to remove all the surface occlusions or absorbed molecules, therefore after sputtering you can clearly see that, the boron 1 s is giving a very sharp Gaussian peak, similarly nitrogen 1 s gives a very resolved peak. Therefore, it is very important when we study XPS that, we just do not map your spectra, rather you do the surface treatment on the first place.

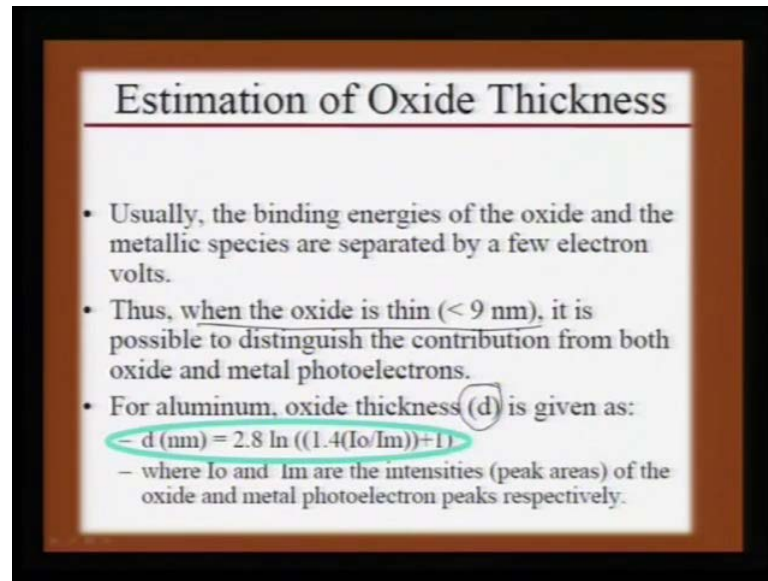
But, one should also understand, this argon sputtering can modify the oxidation states of the elements, which are already present. Therefore, we need to be very careful to have a rough idea about such a impact of the sputtering ions on the sample. Therefore, if we look for a mixed valency then we need to be doing this in a much more careful way. But, generally the argon sputtering will try to take out all the surface impurities, which are settled on the sample.

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Let us take the case of aluminium oxide, aluminium oxide actually we can not only map the trivalent state of the zero valency. In this case, the metal and aluminium oxide clearly shows a two peak spectra, so we know that, both aluminium oxide and aluminium is there. But, apart from that, we also get to see that, the oxide thickness can be mapped which is of the order of 3.7 nanometre, how do we do that.

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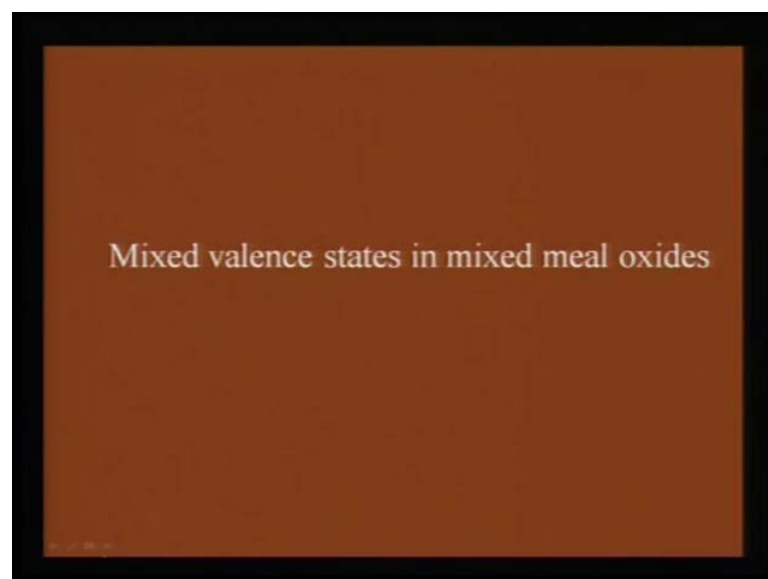


**Estimation of Oxide Thickness**

- Usually, the binding energies of the oxide and the metallic species are separated by a few electron volts.
- Thus, when the oxide is thin (< 9 nm), it is possible to distinguish the contribution from both oxide and metal photoelectrons.
- For aluminum, oxide thickness (d) is given as:  
 $d \text{ (nm)} = 2.8 \ln ((1.4(I_o/I_m))+1)$   
– where  $I_o$  and  $I_m$  are the intensities (peak areas) of the oxide and metal photoelectron peaks respectively.

We have already seen, what is the length depth that we can scan, which is ranging up to 10 nanometre. based on that when the oxide is actually 9 nanometres, it is possible to distinguish the contribution from both the oxide and metal photoelectrons. And the expression that is given here is d, which is the depth or the thickness of the oxide layer, which is given by  $2.8 \ln 1.4$  and this is the ratio of your oxide versus the metal photoelectron peaks. Therefore, we can actually quantify, what is the amount of surface oxidation that has occurred on a aluminium foil.

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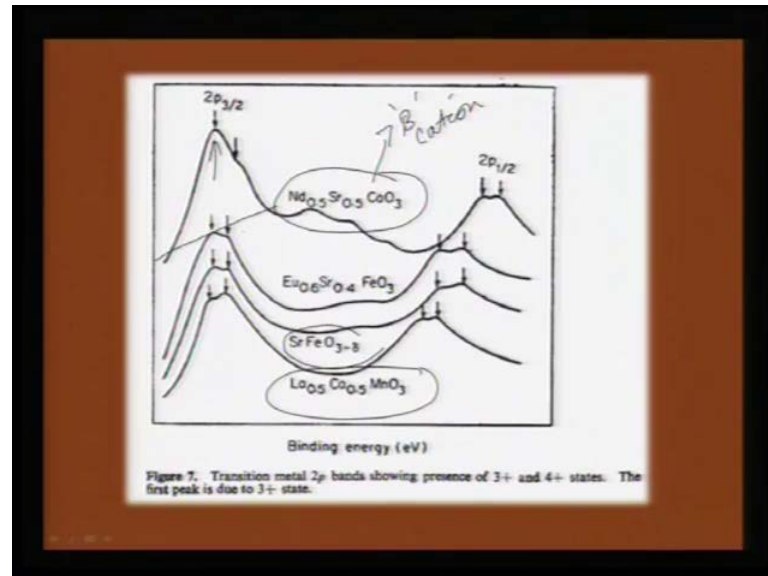


Mixed valence states in mixed metal oxides



So, a XPS can actually give you a quantize picture of that situation, we will also look at some more examples of mixed valence states in mixed metal, it is actually metal oxides.

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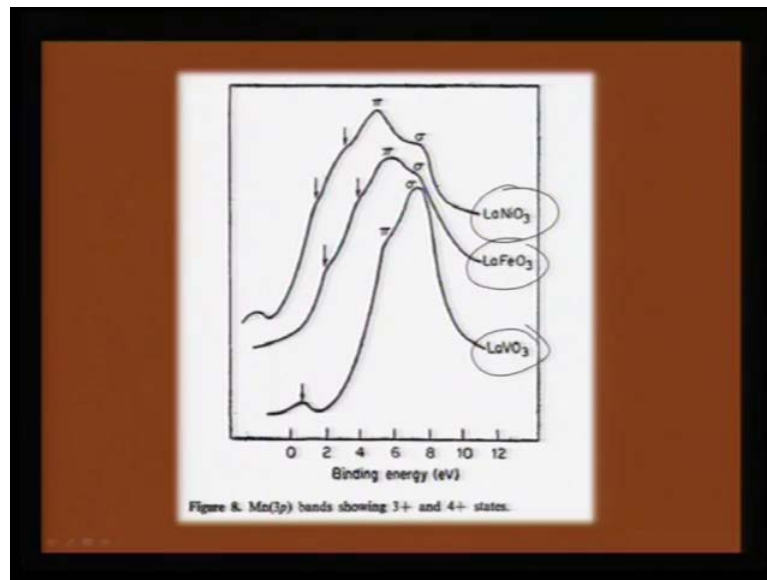


Take for example, the perovskites, the transition metal 2 p bands showing both plus 3 and plus 4 states, the first peak what we see here in this case, is actually coming from the plus 3 state and then we also see a satellite feature. So, for all compounds, whether it is ferrites or manganites or cobaltites, we can always look at the mixed valence states of the B cation. And therefore, this can become a very useful way to analyze it and as you see here, when we have mixed valency, the 2 p 3 by 2 is asymmetric with the satellite feature. Therefore, one has to deconvolute this spectra in order to quantify how much of 3 plus and how much of 4 plus ions are there. And similarly, in this case, all the perovskite compounds like lanthanum nickelate, lanthanum ferrite, lanthanum vanadate, all this show asymmetry related to the 3 plus and 4 plus states.

Here is another cartoon, which gives us a range of oxides starting from  $\text{LaMnO}_3$ , cobaltites, ferrites, everything can be mapped. For example, these two compounds can serve as a standard when we are specially analyzing mixed compounds or substituted ones. As you know here, a pure  $\text{LaMnO}_3$  actually should have Mn in 3 plus, but when you substitute calcium in the lanthanum site, Mn 3 and Mn 4 ratio will be present. So, how do we map that, we can take the individual spectra of  $\text{Mn}_2\text{O}_3$ , which is predominantly 3 plus and  $\text{MnO}_2$ , which is predominantly 4. And therefore, these two

can act as a standard to find out, how much of 3 and 4 is present and looking at the peak positions we can clearly map, whether the 3 4 combination exists. Similarly, in the case of ferrites, we can use Fe 2 O 3 as a standard to see, how much of reduction in the oxidation state or oxidation has happened from Fe 3 to Fe 4.

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Table 7. Core level binding energies (eV) of Mn, Fe and Co in mixed valence oxides

Compound	$2p_{1/2}$	$2p_{3/2}$	3p
LaMnO <sub>3</sub>	Mn <sup>3+</sup> 640.9	652.9	48.3
	Mn <sup>4+</sup> 642.1	654.1	49.4
La <sub>1-x</sub> Ca <sub>x</sub> MnO <sub>3</sub>	Mn <sup>3+</sup> 640.8	652.7	48.2
	Mn <sup>4+</sup> 641.8	653.8	49.2
La <sub>1-x</sub> Ca <sub>x</sub> MnO <sub>3</sub>	Mn <sup>3+</sup> 641.1	652.6	48.4
	Mn <sup>4+</sup> 642.0	653.7	49.4
Mn <sub>2</sub> O <sub>3</sub>	641.2	652.9	48.3
MnO <sub>2</sub>	641.9	653.5	49.5
SrFeO <sub>3-x</sub>	Fe <sup>3+</sup> 710.0	723.2	55.4
	Fe <sup>4+</sup> 711.0	724.2	56.2
Eu <sub>1-x</sub> Sr <sub>x</sub> FeO <sub>3</sub>	Fe <sup>3+</sup> 709.6	723.1	54.9
	Fe <sup>4+</sup> 710.8	724.0	56.0
Fe <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup> 710.3	723.6	55.2
SrCoO <sub>3-x</sub>	Co <sup>3+</sup> 779.8	795.3	60.4
	Co <sup>4+</sup> 780.6	795.8	61.2
Nd <sub>1-x</sub> Sr <sub>x</sub> CoO <sub>3</sub>	Co <sup>3+</sup> 780.0	795.0	60.6
	Co <sup>4+</sup> 781.0	796.0	61.6
NdCoO <sub>3</sub>	Co <sup>3+</sup> 780.1	795.5	60.5

\*15% Mn<sup>4+</sup> was present in the sample.

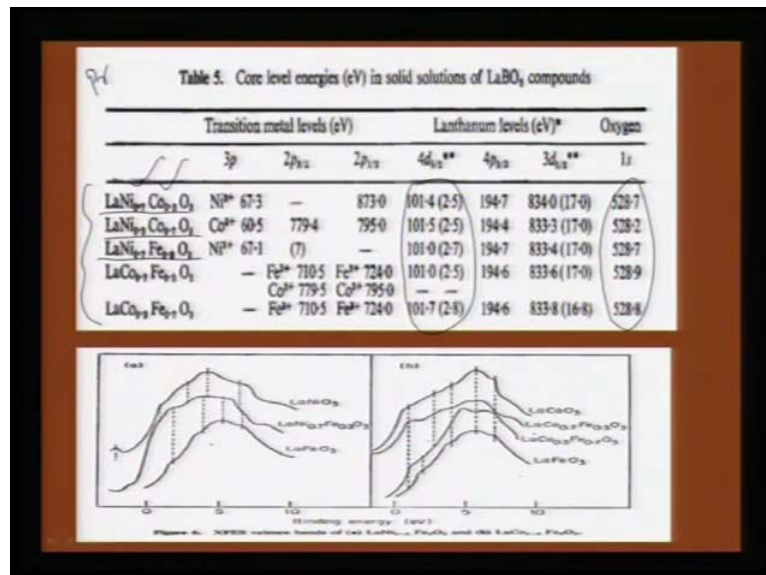
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Table 6. Chemical shifts of K-absorption edges of nickel, cobalt and iron in LaBO<sub>3</sub> compounds

Compound	Chemical shifts (eV)		
	Nickel	Cobalt	Iron
LaNiO <sub>3</sub>	11.0	—	—
LaNi <sub>0.7</sub> Co <sub>0.3</sub> O <sub>3</sub>	11.1	10.7	—
LaNi <sub>0.2</sub> Co <sub>0.7</sub> O <sub>3</sub>	11.1	10.7	—
LaCoO <sub>3</sub>	—	10.8	—
LaNi <sub>0.7</sub> Fe <sub>0.3</sub> O <sub>3</sub>	10.7	—	10.8
LaFeO <sub>3</sub>	—	—	11.0
LaFe <sub>0.7</sub> Co <sub>0.3</sub> O <sub>3</sub>	—	10.8	11.0
LaFe <sub>0.2</sub> Co <sub>0.7</sub> O <sub>3</sub>	—	10.7	10.8

And here, again there are other examples given, only thing in this case it is about K absorption edge. Therefore, you can see the values are much less, because we are talking about K shell. So, this can the K absorption edge can also serve as a useful number, when we try to map between substituted ones and the parent perovskite oxides.

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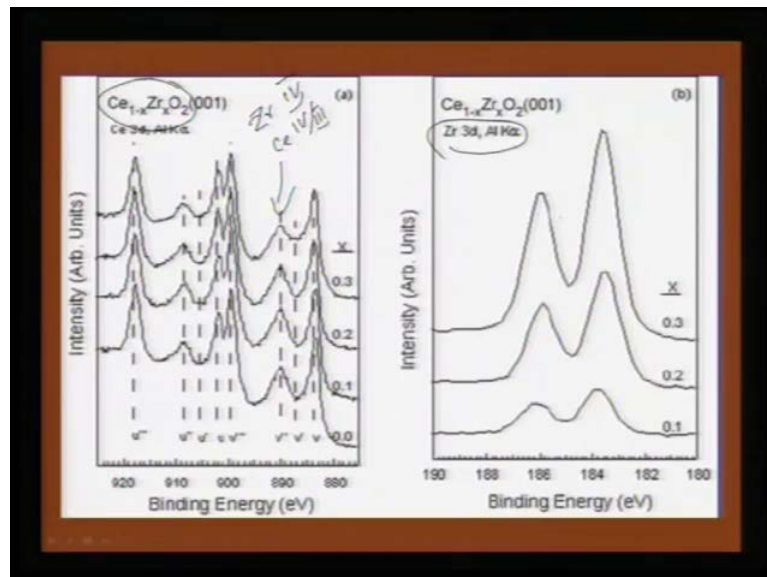


When we look at the XPS, there are other advantages that we have for example, if we look at lanthanum nickelite and substituted with more than two metal ions, all that we can observe from the lanthanum 4 d 5 by 2 and 4 d 3 by 2, you can see here hardly there

is any change. In other words, the lanthanum valency is not affected in the process when substitution is going on, therefore rather the peak positions, can also serve as an internal standard. Because they do not exhibit mixed valency except for praseodymium, which shows 2 plus, 6 plus and 4 plus oxidation state.

Lanthanum in general, can show a very precise number, and so is the case for oxygen 1s, you would hardly see any change happening, unless or otherwise a perovskite species is present. So, when we have these perovskite compounds taking a look at lanthanum and oxygen position itself, can be a useful calibrant to see, whether the effect is predominantly coming from the mixed valence states. So, the features of such XPS spectra are given here.

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And this can also be used for a methodical study for example, if we are going to make a systematic substitution of zirconium into ceria then this technique can be a very successful one. As you would see here, with substitution of zirconium, you can see this 90 eV peak is actually decreasing in intensity, why because zirconium is in 4 plus and cerium can actually exist in both 4 as well as 3.

So, when you substitute zirconium then there is a fallout of one of the oxidation states of cerium, as a result you can clearly see a systematic trend. And so is the case for zirconium, you can see the position or the peak intensity varying, as we substitute in

ceria. So, we can clearly map or make a very detailed study, specially when we are looking at solid solutions of two dissimilar metals.

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**Spectroscopic evidence for strongly correlated electronic states in La-Sr-Cu and Y-Ba-Cu oxides**

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TABLE I. Properties of the samples, the relative intensities  $I_j/I_0$ , and positions  $\Delta E_m$  of the satellites to the main lines for the Cu  $2p_{3/2}$  core level, and the electronic structure parameters (defined in the text).

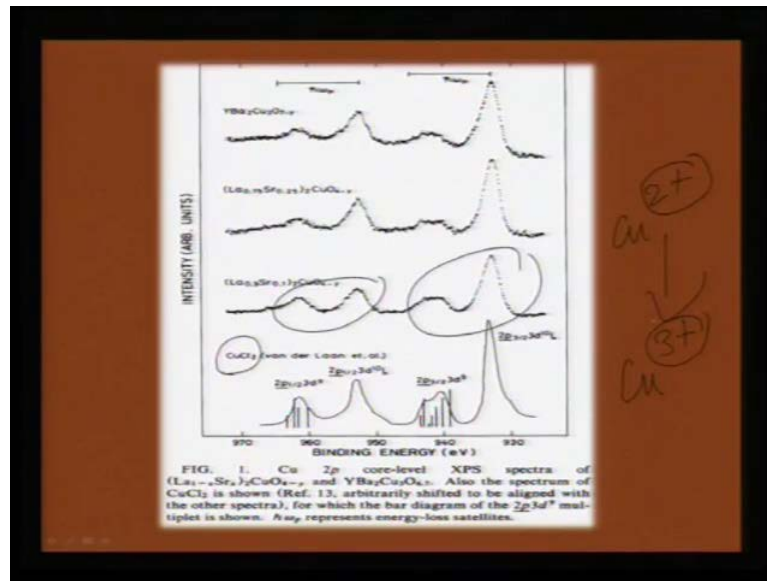
Sample	$T_c$ (K) <sup>a</sup>	Conductivity type above $T_c$	Formal valence of Cu	$\Delta E_m$ (eV)	$I_j/I_0$	V (eV)	$\Delta$ (eV)	$n_0$
$(\text{La}_{0.8}\text{Sr}_{0.2})_x\text{CuO}_{x-\gamma}$	34	Metallic	2.18	8.5	0.33	1.9	0.4	9.45
$(\text{La}_{0.7}\text{Sr}_{0.3})_x\text{CuO}_{x-\gamma}$	...	Semicond.	2.20 <sup>b</sup>	8.8	0.21	2.4	0.7	9.49
$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$	90	Metallic	2.13	8.8	0.24	2.3	0.5	9.45

<sup>a</sup>Defined as the middle points. <sup>b</sup>Reference 14.

And similarly, XPS has been used almost to crack the chemistry behind the superconductors. And I will be dealing with the superconducting oxides in one of the lectures in module 5, but here quickly I want to bring out the usefulness of X ray photoelectron spectra in elucidating the electronic states of the copper valency for example. In the case of the 34 K superconductor, which is lanthanum strontium cuprate compared with the 90 K superconductor, the conductivity as we see, the both are metallic. But, if you look at the formal valence of both the 34 K and 90 K superconductor, this is actually nearly the same compared to a semiconductor and the formal valence also goes beyond to suggest that, copper is not exactly in copper 2 plus, but it is in a higher valence state.

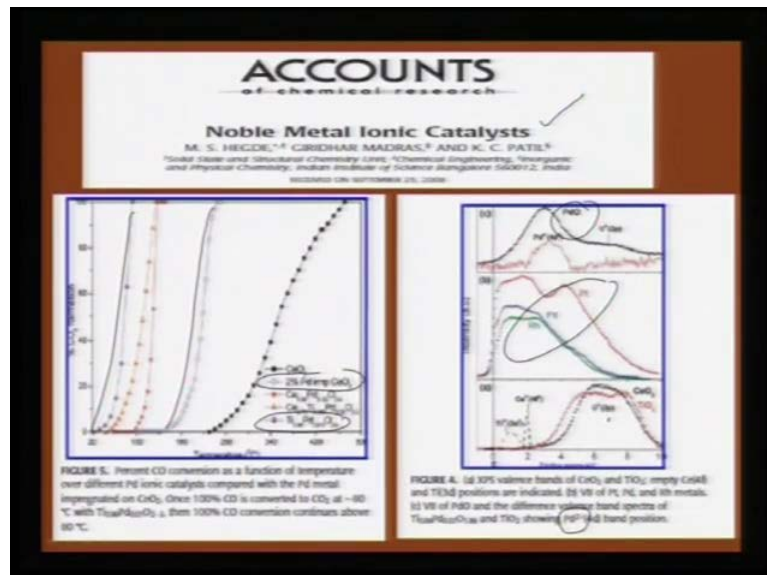
So, if you make a comparison with a standard compound, which is cupric chloride which is a well studied system. And if you try to reposition this to match with the copper 2 p core level spectra, you can clearly see that, there is the copper 2 p 3 by 2 and 2 p half spectras, they are both divided. In other words, they show a split in each peak, so this split in each peak clearly shows that, copper is not remaining totally in copper 2 plus, but a part of copper 2 plus is oxidized to copper 3 plus and that is happening in order to bring the charge neutrality into this lattice.

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And therefore, this valence state of copper 2 plus and copper 3 plus has really helped the community to ascertain, what is the conduction mechanism, which actually drives this super conducting oxides, to show absolute zero resistance. So, XPS is a very useful tool, therefore to provide the mechanism in a much more elegant way.

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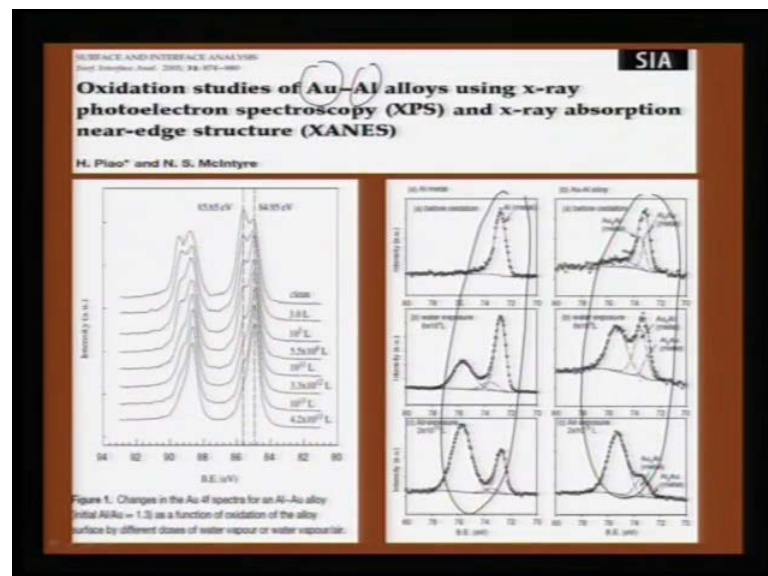
And this is another example, which I will be talking about in module 1 under combustion synthesis where, noble metal ionic catalyst has been proved to be existing. Because, if you think of any catalyst with noble metals like platinum on silica, platinum and ceria or

platinum or alumina, it is always recognized that, these noble metals are in zero valence state. And that is why, they show very high efficiency in converting the affluent gases in automobile exhaust.

So, till today, most of the companies are using this platinum coated solid supports for catalytic conversion. But, what has been found recently that, if you take platinum and actually treat it with ceria in a combustion mode, platinum is not actually sitting on the surface, but it is actually getting precisely doped in the cerium site. And as you would see here very clearly, these are the valence bands spectra for platinum palladium and other noble metals.

Whereas, when palladium is actually doped into ceria, you can see the spectra is completely different from the noble metals. What it suggest that, platinum is actually getting doped and it is in 2 plus state and because of that, one can see that 2 percent and 1 percent platinum doped in titania shows a tremendous increase in the conversion compared to the undoped ceria state. So, a mechanism has been very clearly elucidated based on XPS spectra where, the substitution of this noble metal precisely into ceria and the valence state has been ascertained using XPS spectra.

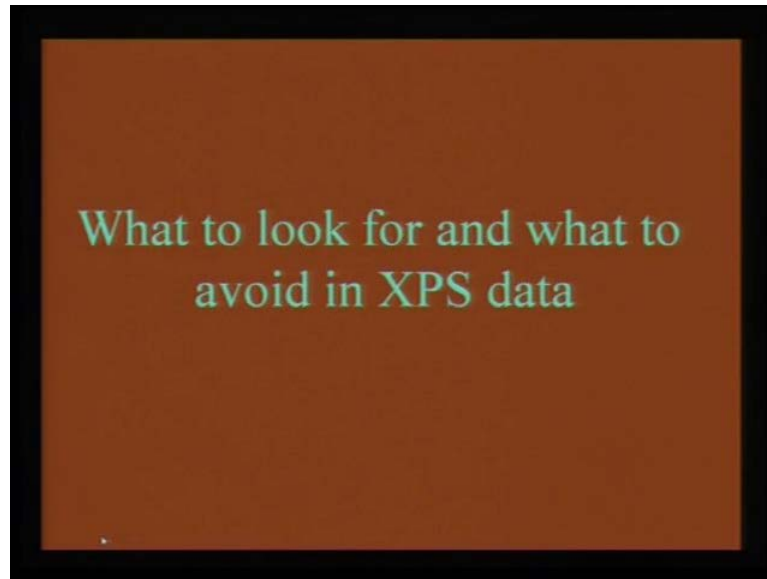
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And similarly, if you take alloy and then try to see, what is the influence of doping gold along with aluminium. We can clearly find out that, if you have gold then the oxidation of aluminium to aluminium hydroxide or aluminium oxide can be inhibited largely,

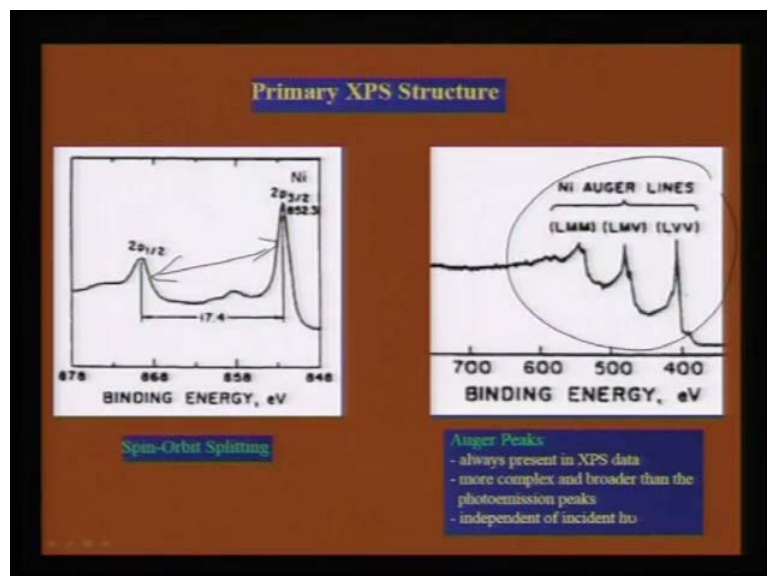
because of this alloy formation with gold. So, if you take the XPS spectra of aluminium and you do a comparison with aluminium gold alloy, you can clearly see that the conversion rate is much faster in this case compared to gold alloyed aluminium. So, when we try to look at the degradation process of alloys, XPS again can prove very useful.

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So, in next few slides, I would just leave with some parameters, which we need to bear in mind, what to look for and what not to look for or what to avoid in XPS data.

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Number 1, as we know that we are looking at the splitting and as a result, we are mapping the unusual oxidation states. And we will also be observing the auger lines in the XPS spectra.

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**Secondary XPS Structure**

- 1) **X-ray Satellites**  
caused by poor X-ray source and X-ray fluorescence
- 2) **Surface Charging**
- 3) **Intrinsic Satellites**  
caused by atomic relaxation →
  - (1) excitation of electron to bound state (shake-up satellite)
  - (2) excitation of electron to continuum state (shake-off satellite)
  - (3) excitation of hole (shake-down satellite)
- 4) **Multiplet Splitting**  
splitting of 1s orbital
- 5) **Excitonic Satellites**  
caused by energy loss in electrons as it travels towards the surface (i.e., plasmon)

But, apart from that, we will also get X ray satellites and surface charging effects, intrinsic satellite effects, all these can come into picture. So, one has to be careful while trying to analyze the nature of XPS spectra.

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**Secondary XPS Structure**

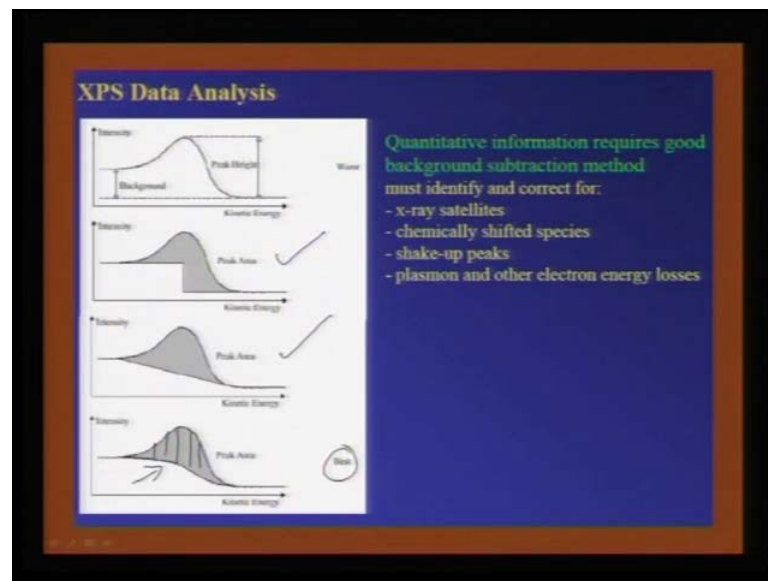
- 2) **Surface Charging**  
caused by accumulation of positive charges due to photoemission of electrons → results in peak shift to higher B.E.

Neutralized using a flux of low energy electron

Al 2p

For example, surface charging can become a very important issue when a specimen neutralizer is actually on, you can see this is the peak due to  $\text{Al}_2\text{O}_3$  and this is due to aluminium metal. But, once you remove this specimen neutralizer because of the surface charging, this peak actually gets shifted here. But, the aluminium peak will remain the same, but this peak has actually moved here. So, we need to be very careful about the charging effects, which can totally mislead our analysis.

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And also, the XPS data analysis has to be viewed carefully, now we can try to use the peak area analysis in this way or we can just draw a base line this way and try to analyze, but what is actually expected is a optimization of your base line, which has to be in this form. Now, there are several soft ways, which can help us in adjusting the base line corrections. So, that the area under this peak can be mapped to quantify the amount of this oxidation state that is present.

Therefore, the peak analysis or the deconvoluted peaks need to be analyzed with proper position. So, this can prove to be a very useful technique, specially when you play with the heavier metals. So, more than organic samples, the inorganic samples have taken a much better attention as far as XPS is concerned and lot more informations can be drawn with the XPS and this can be quantified. So, this is one of the spectroscopy where, it is not only qualitative, but it is also a quantitative picture. In the next few lectures, we will also look at other spectroscopic tools, which can be used for surface analysis.