Materials Chemistry
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Module - 3
Lecture - 3
Applications of X-ray Absorption Spectroscopy

Today I will be dealing with another interesting topic on spectroscopy. And this is one of the spectroscopic tool widely used in many research labs.

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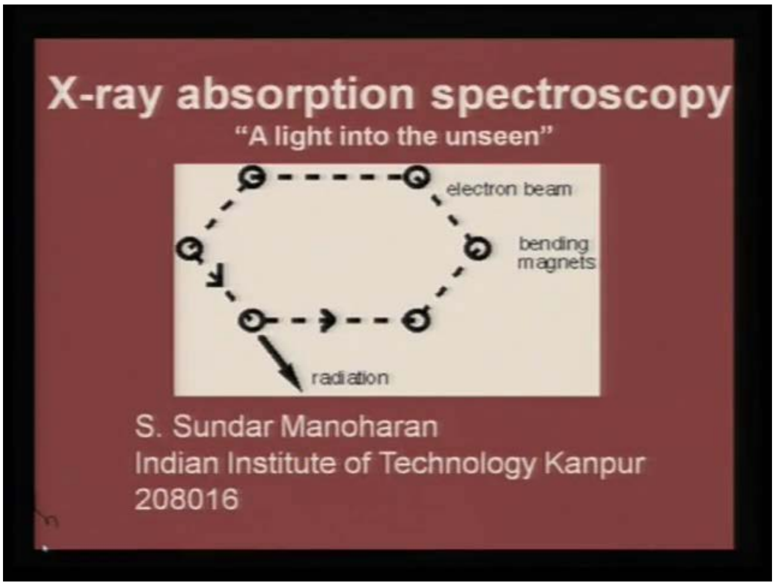

X-ray absorption spectroscopy

"A light into the unseen"

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However, considering our own limitations for getting such a sophisticated spectroscopic tool, in our country we have not really majored on this spectroscopy. And therefore, I would like to singly emphasize more about the usefulness of this spectroscopic tool, which has come into the study of materials in a bigger way. This is popularly called as x-ray absorption spectroscopy and this is also complimentary to whatever information that we are getting from x-ray photoelectron spectroscopy which we have seen in the previous lecture, where we have highlighted that XPS spectroscopy is or XPS spectra is a very good surface analysis tool, where up to 10 nanometre thick surfaces can be studied in greater detail, talks about the impurities that can happen in the surface.

And then how we can probe the different metal ions that are present and also on, the characteristic x-ray that is coming out. Therefore, XPS is a very good analytical tool, but today what we are going to see is a absorption phenomena, which has been used very nicely to explore unusual oxidation states. So, in this lecture I will give you some principles about how x-ray absorption spectroscopy can be understood, and then little bit on the instrumentation and I will take one particular group of oxide and do a thorough study on how we can use excess information for analyzing a particular perovskite compound.

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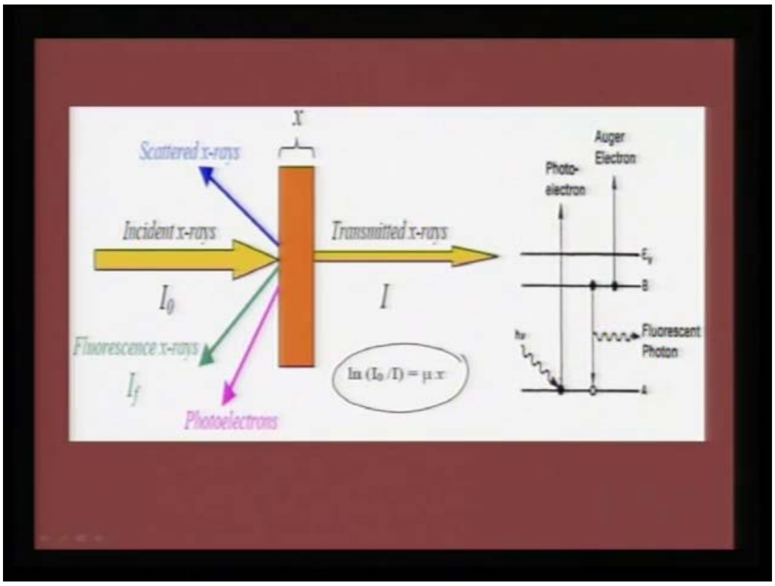

As you would see, the incident rays that are falling on a sample. Actually is undergoing lot of change, one is you can get scattered x-rays from the sample or we can get a fluorescence x-rays, which are used for a x-ray fluorescence spectroscopy or we can get photoelectrons. The light can also be transmitted, but not in the same magnitude of that of the incident ray and therefore, we can try to map the intensity ratio as a function of mu x and x is your thickness and mu is here absorption coefficient.

So, if your sample is sufficiently thin it is possible even to map the transmitted x-rays, and the phenomena that is happening when x-rays are absorbed by the sample, it can either come out as a photoelectron or as a auger electron and then a fluorescent photon. So, from the way we harvest the secondary processes that happened due to the interaction between the material and the incident x-rays, we can categorize different sort of spectroscopies.

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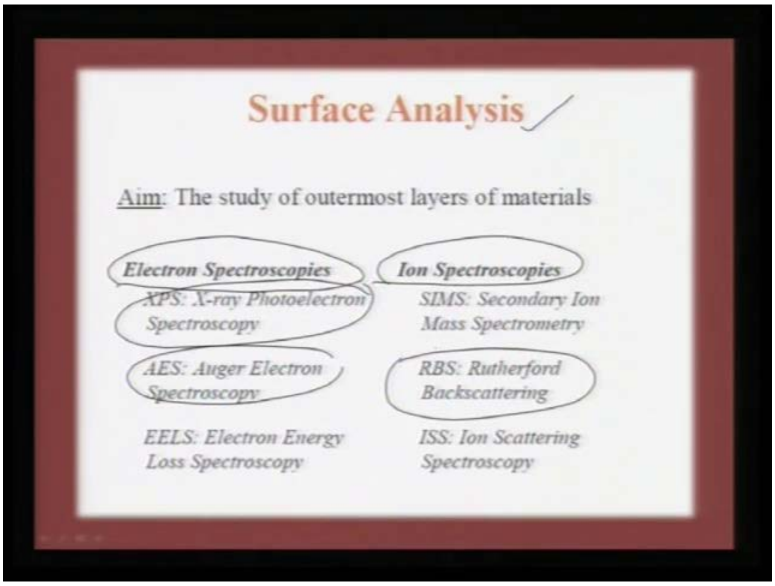

Surface Analysis

Aim: The study of outermost layers of materials

Electron Spectroscopies	*Ion Spectroscopies*
XPS: X-ray Photoelectron Spectroscopy	*SIMS: Secondary Ion Mass Spectrometry*
AES: Auger Electron Spectroscopy	*RBS: Rutherford Backscattering*
EELS: Electron Energy Loss Spectroscopy	*ISS: Ion Scattering Spectroscopy*

In the last lecture I showed this same view graph, where I characterized two important techniques one is based on electron spectroscopies and one based on ion spectroscopies. Specially I talk to you about auger electron and discussed to you, in detail about x-ray photoelectron spectroscopy, gave you some idea about RBS whish is specially used to look at epitaxial layers and how the thin films are growing as single crystals.

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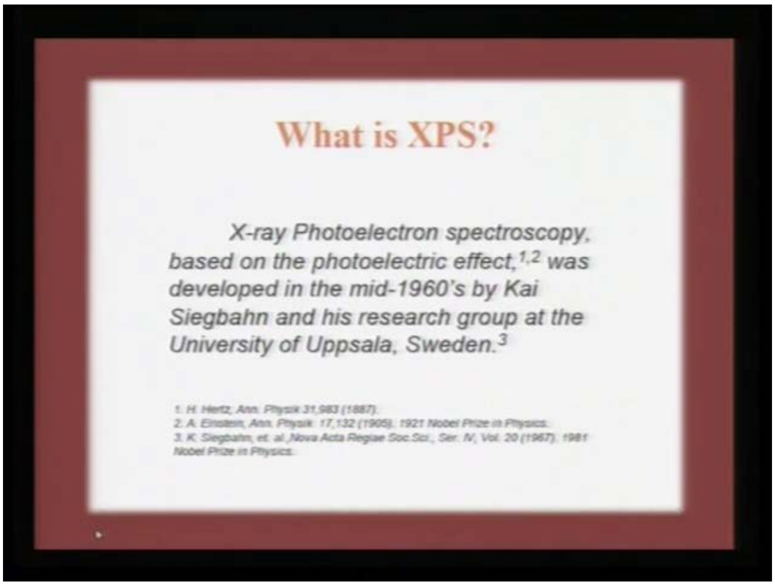

What is XPS?

X-ray Photoelectron spectroscopy, based on the photoelectric effect,[1,2] was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.[3]

1. H. Hertz, Ann. Physik 31,983 (1887).
2. A. Einstein, Ann. Physik 17,132 (1905). 1921 Nobel Prize in Physics.
3. K. Siegbahn, et. al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

Also I told what this x-ray photo electron spectroscopy is basically this is a reflecting photoelectric effect, and this simple photoelectric effect can be transformed or exploited to analyze and quantify several chemical reactions.

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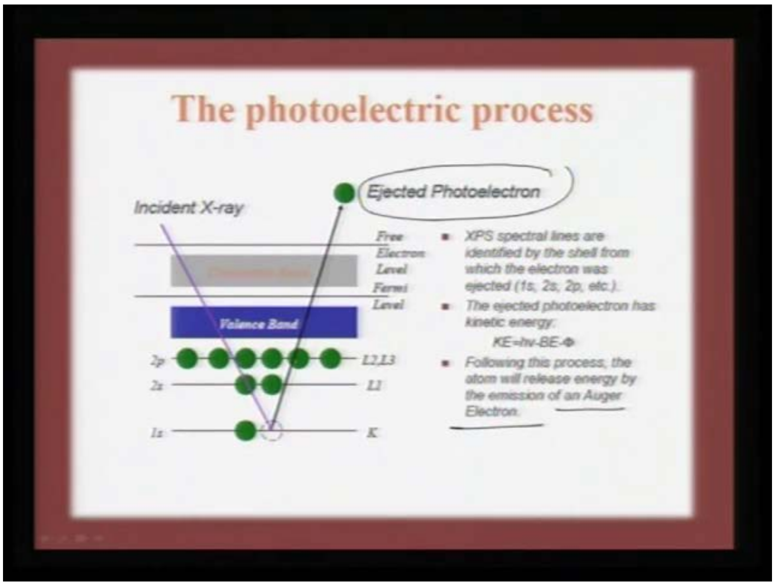

The photoelectric process

- XPS spectral lines are identified by the shell from which the electron was 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.

And there we looked at what this photoelectric process is the ejected photoelectron is what we are trying to map. And in the process you also have the auger electron that is coming out from here.

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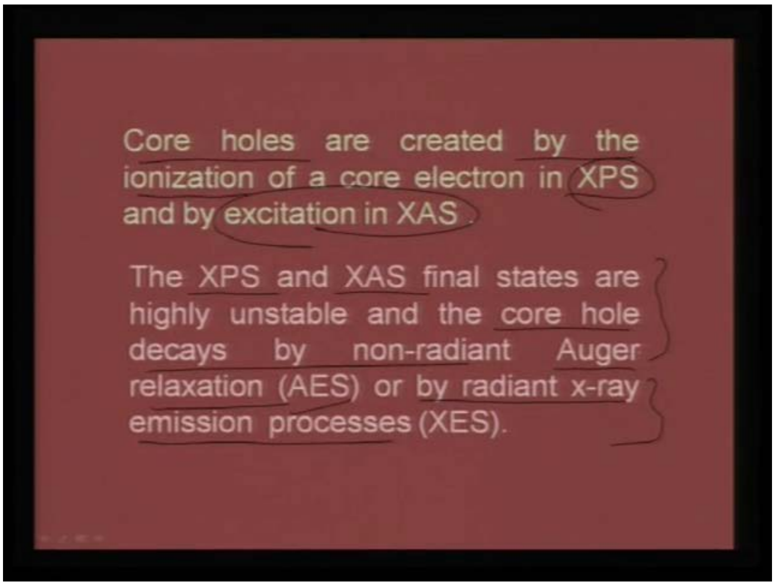

Core holes are created by the ionization of a core electron in XPS and by excitation in XAS.

The XPS and XAS final states are highly unstable and the core hole decays by non-radiant Auger relaxation (AES) or by radiant x-ray emission processes (XES).

Now, to draw a parallel between XAS and XPS I just want to make some comments, one is core holes are created anyway when there when a core electron is actually knocked out. And therefore, by ionization it can happen and that forms the basis for x-ray photoelectron spectroscopy, core holes are created by ionization by the incident x-rays and therefore, those are called as x-ray photoelectron spectroscopy. And core holes are formed by excitation of electron, which forms the bases for the x-ray absorption spectroscopy.

So, in both cases XPS and XAS we can say that the final states are highly unstable and the core hole decays by non radiant process, one is either a auger relaxation which ends up in a auger electron spectroscopy or by radiant x-ray emission process, which is called as x-ray emission spectroscopy. So, this x-ray emission spectroscopy is actually a secondary phenomena that goes along with XAS whereas, a AES is a secondary phenomena that happens because of XPS. So, in some sense both have a parallel.

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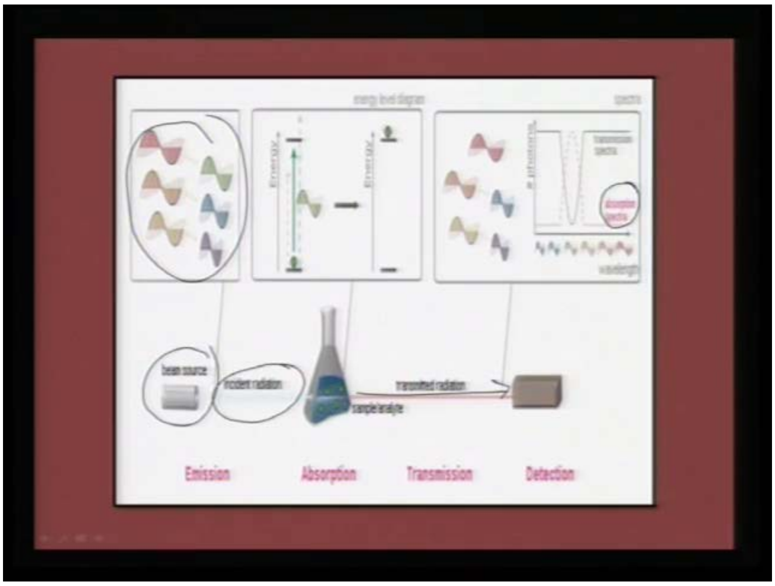

So, when we talk about XAS we also take into consideration x-ray emission that is coming out. To make things look simpler how do we get this absorption spectra, we can say that there is a beam of different wavelength, you can use any sort of a wavelength and this beam source is actually incident on the radiation. And now, the electron is actually absorbs energy and it can go to any of the bound states or to any of the states near to the continuum, that is the vacuum level or it can go into the vacuum level. And depending on that, then we can try to populate those regions selectively. And then the transmitted radiation can be mapped and this is what comes out as a absorption spectra, which we can try to analyze.

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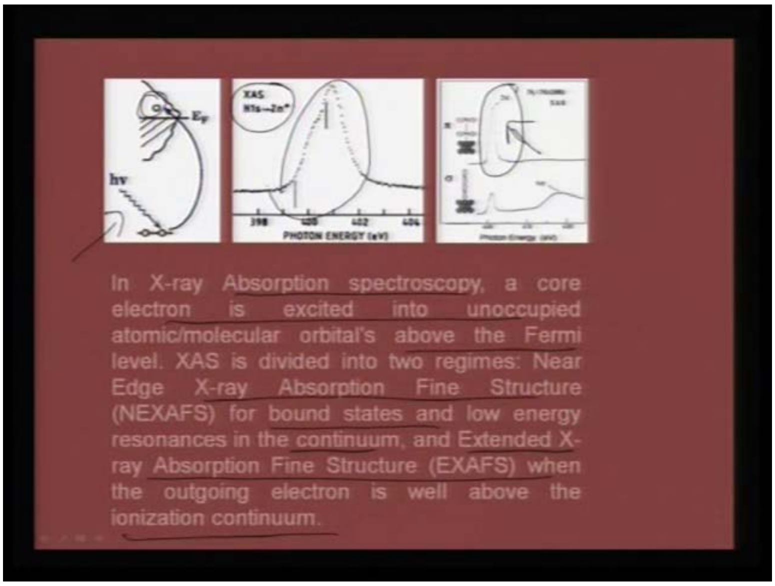

In X-ray Absorption spectroscopy, a core electron is excited into unoccupied atomic/molecular orbital's above the Fermi level. XAS is divided into two regimes: Near Edge X-ray Absorption Fine Structure (NEXAFS) for bound states and low energy resonances in the continuum, and Extended X-ray Absorption Fine Structure (EXAFS) when the outgoing electron is well above the ionization continuum.

Now, there are two things that we need to have in mind, one thing is when in x-ray absorption spectroscopy. If we have a core electron which is excited into unoccupied atomic or molecular orbital's, above the Fermi level, then XAS can be divided into two regimes. One we can call this as x-ray absorption fine structure or we can call this as extended x-ray absorption fine structure, when the outgoing electron is well above the ionization continuum.

But, if it is somewhere in the bound states for example, we talk about a 2 p going to 3 d level or 2 p to 4 d level, then we talk about bound states and low energy resonances in the continuum. So, either of this can happen as you see from this view graph, electron is knocked out and it is actually going above the Fermi level, but it is not actually going into the continuum. So, this is one of the bound states and depending on that the you will get a typical characteristic feature of x-ray, which will tell what sort of excitations are possible. In this case you can see nitrogen is absorbed on nickel 1,0, 0 and when it is glued to the surface, when it is absorbed to the surface then you get a clear reflection for a 2 pi interaction. And this is a typical XAS peak that you would get, for nitrogen one is to 2 pi transition, 2 pi star transition, we will come to this issue in example.

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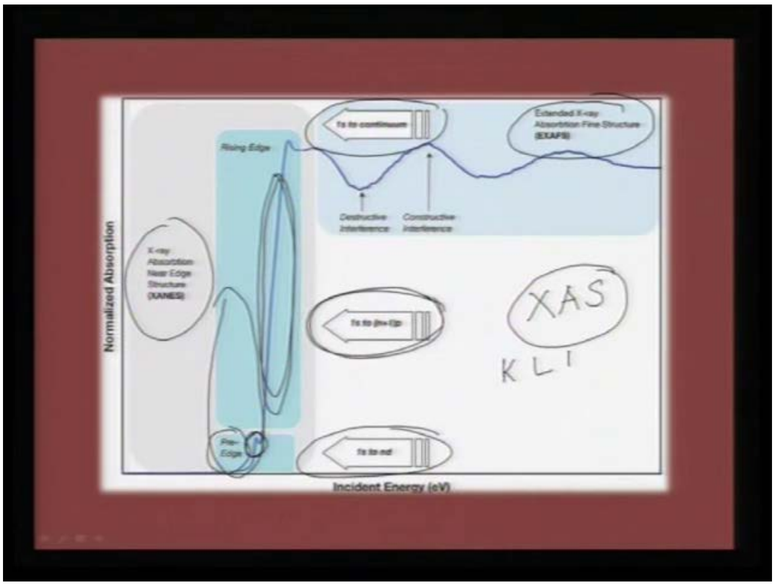

So, just to map what are all the different studies that we can do in XAS, we can actually talk about a pre edge which can be characterized here. As x-ray absorption near edge structures, x-ray NES and this is what is the region, where you can actually map the information that your getting. In fact, you would get several features around this edge. So, this is what you call it as x-ray absorption near edge structure and this is the region where you actually play around for x-ray absorption spectroscopy, I will tell you what sort of peaks that you can get out of this. And this is the region where you have the transitions happening between 1 s to n plus 1 p level or it could be p 2 n plus 1 d level.

So, this region actually takes care of such bound states and this is the region where you can talk about the pre edge. And if you are talking about 1 s electron knocked out of the continuum of or the knocked out electron is well within the continuum, then you talk about the extended x-ray absorption fine structure. So, several of this processes happen all these are mapped under the same phenomena of x-ray absorption spectroscopy.

So, we will specially look it is not possible in one single lecture to cover the whole spectrum of manifestation of this spectroscopy. So, I would like to take some interest to talk about different things that can happen, in this edge that is why, it is called as edge spectroscopy and this edge is actually attached to the sort of excitations that can happen, it can be called as K h or L or M we will see that in the next slide.

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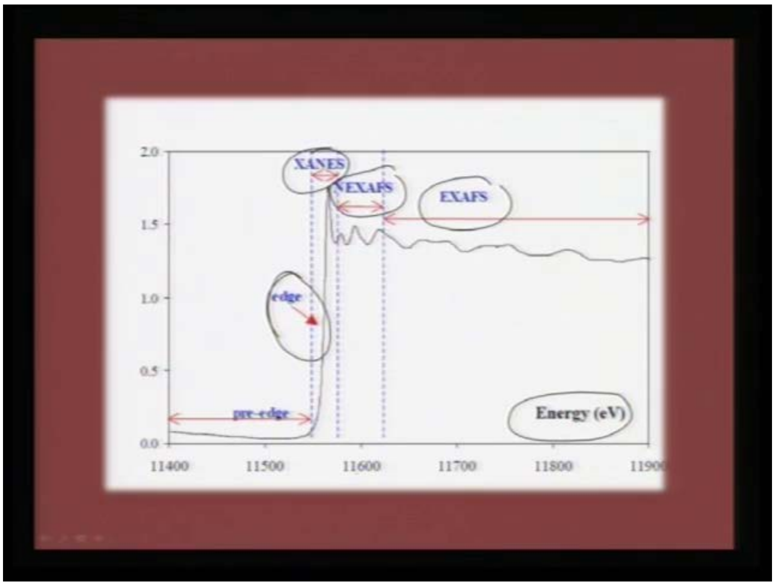

As I told in the previous one, we are talking about different forms of spectroscopy here. And this is the XAS edge spectroscopy that we are precisely talking about and the relative scale of energy that involves each of this spectroscopy is also given therefore, we can single out and say that I am exactly talking about EXAFS or I am talking about XANES or I am talking about XAS based on the energy range that we are using for these spectroscopies.

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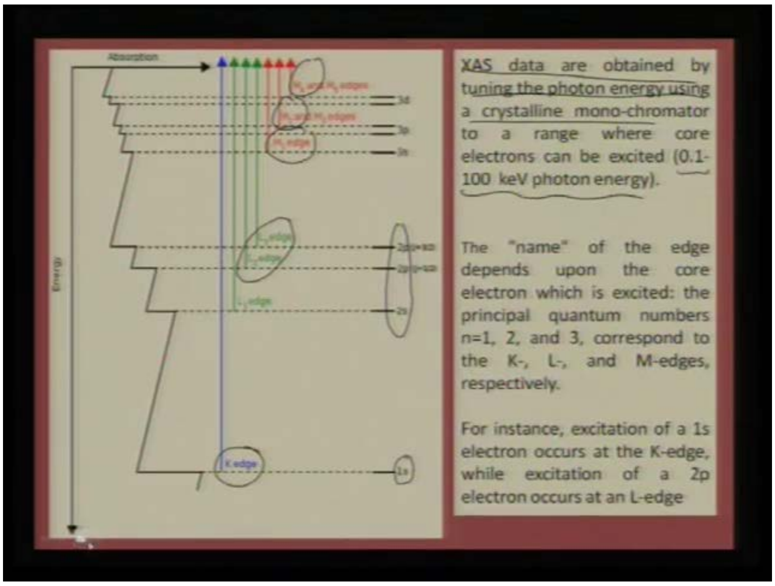

XAS data are obtained by tuning the photon energy using a crystalline mono-chromator to a range where core electrons can be excited (0.1-100 keV photon energy).

The "name" of the edge depends upon the core electron which is excited: the principal quantum numbers n=1, 2, and 3, correspond to the K-, L-, and M-edges, respectively.

For instance, excitation of a 1s electron occurs at the K-edge, while excitation of a 2p electron occurs at an L-edge

Now, when we talk about edge we are talking about different transitions that can happen absorptions that can happen. If k edge is happening then the electron from one s is actually excited and therefore, we call this as a k h, if it is L then you can involve both 2 s and 2 p, but we differentiate that between L 1, L 2 and L 3. L 1 is typical for 2 s electrons getting to the continuum or it could be 2 p or 2 p 3 by 2.

So, both these are characterized by L 2 and L 3, when we actually talk about bigger metal ions this L 2 and L 3 give a very rich information about the oxidation states. Similarly, we can go for M 1, M 2 and M 3, so on each one is designated by the orbital's that are associated with it. So, XAS data are obtained by tuning the photon energy using a crystalline mono chromator, to a range where core electrons can be excited. And the range is typical of the order of 0.1 to 100 k e V photon energy, depending on the range then we can selectively try to knockout the particular core electron. So, if we talk about k then we are talking about a very high energy radiation, if we talking a about 2 p levels that is L h medium range and then still smaller ranges for 3 d, 3 s and 3 p.

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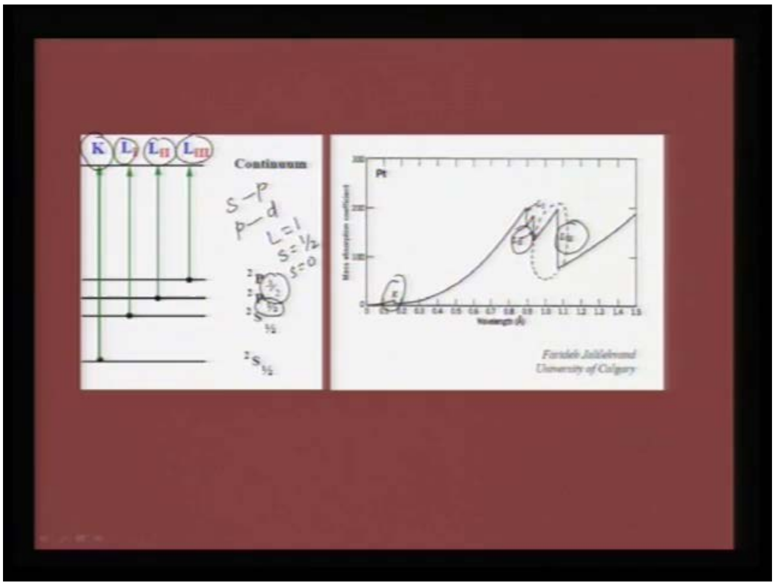

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So, this how we designate this K h L 1, L 2 and L 3, L 2 and L 3 we try to categorize based on the L s coupling. So, if your transition is from p to d or s to p then your L is equal to 1 and this, one can couple with either s is equal to half or s is equal to 0 and depending on that you will actually get this half or 3 by 2 which is nothing but your L s coupling. So, based on this you can get L 2 and L 3 always we can remember, as a notation L 3 we always talk about 3 by 2 it is easy to remember that way L 2 is half.

So, L 2, L 3 edges are nothing but two states from the same transition resulting out of the spin orbit coupling. Typically if you look at x-ray map XAS mapping, you can see sharp edge for k and this is for L 1, this is for L 2 and this is for L 3 and as you would see here L 3 always comes at higher energy compared to L 2. So, in a typical spectra of XAS your higher energy spectra will always be associated with L 3 and the low energy peak will be associated with L 2.

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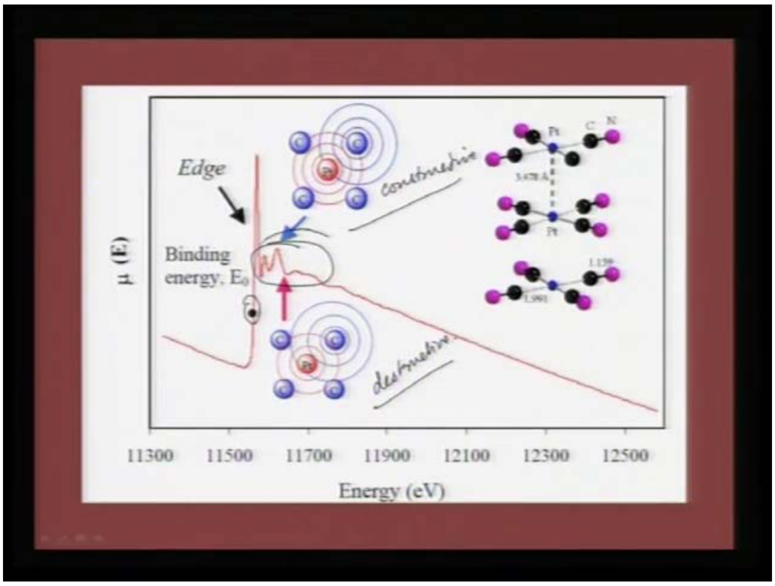

And there are other things that happen apart from the edge, where you have for example, this platinum tetrazino complex. Where you see additional features that are coming and these are called the near edge fine structure due to XAS and this peak comes from a constructive interference and this peak comes from distractive interference. So, these fine structures can give us idea about the local coordination and other information’s about bonding, and their nearest neighbour occupancy and so on. So, this is also a very useful tool that is being probed.

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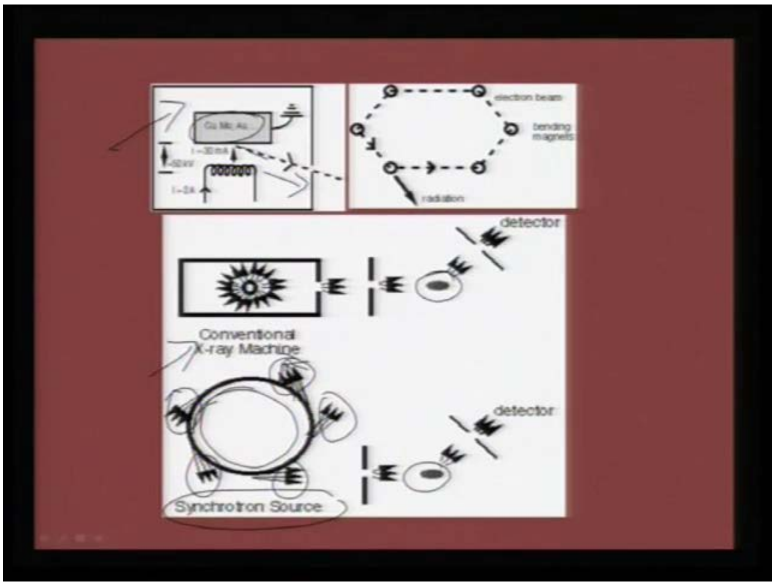

Now, where is XAS becoming more crucial and more sophisticated. As I mentioned to you, the way we produce x-rays are very typical, we use a filament to get electrons which will knock at a particular target, which is copper molybdenum or anything any particular metal. And when it strikes a characteristic x-ray comes out of it, which we categorize as k alpha or k beta radiation, but in synchrotron radiation or in XAS we actually get a high energy x-ray.

And not the conventional one that we generate in our usual lab practices, what we do here is get the same x-ray and this x-ray is actually confined to a ring. And in this ring we try to boost the speed of this electron, such a way it is a accelerated electron which will x-ray beam, which will actually come out. And that will collide with your material to have a very selective excitations made.

So, what we are trying to do is generate the same x-ray as that of the lab experiments, but we are trying to accelerate in a confined space. So, this is your conventional x-ray machine, x-ray comes interacts with your material and then it goes to the detector, in synchrotron source we actually try to boost the speed of the electron. And then the x-ray beam is actually brought out with a greater force.

So, one of this can selectively go and hit, so when it is actually spinning at different points you can collect the x-ray beam. Therefore, this is called synchrotron because in one space you can have many stations where you can try to get it, with the different centrifugal inclination at different tangents you can try to get the source output and as a result, we can study from one synchrotron source many experiments parallelly. So, this is that way a sophisticated instrumentation.

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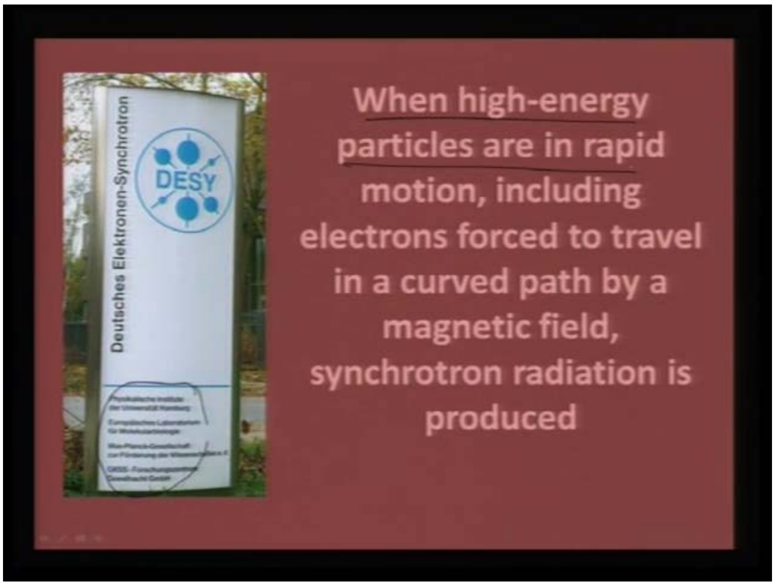

When high-energy particles are in rapid motion, including electrons forced to travel in a curved path by a magnetic field, synchrotron radiation is produced

And just to show you, one of the major facilities is in Germany it is called DESY and there is another it is called besy in Berlin, and DESY in is in Hamburg. As you would see here it is more of a consortium it is not a single mans property, most of the research institutes foundations including government, they pitch in to sustain such a major facility. Therefore, this is not a simple stuff. Definition of a synchrotron we can take it from here, when high energy particles are in rapid motion including electrons, they are forced to travel in a curved path by a magnetic field, which we call it as booster. And then synchrotron radiation is thus produced.

We will look at bird’s eye view of one synchrotron facility which is there; this is your linear accelerator I will also show a animation in the next slide. This linear accelerator actually pumps in x-ray, which is actually getting boosted here with a magnetic coil and then on gaining momentum, this will actually go into the outer sphere. And then from here at different points you can actually collect this fast moving x-rays, these are your substations where you can bring any of your instrument.

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If you are only interested in analyzing a particular sample, you can try to do that or if you want a deposition chamber also to be transported you are free to come and house your equipment here, study for a particular time and then you can take it back. So, therefore, this is more of a central facility confined in a very large apace and many laboratories can be housed together, and the output is actually shared by everyone at the same time. So, therefore, it is a very sophisticated structure and the dimension of this synchrotron facility is quite huge, we will look at one of the slide to understand this.

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We will see a short animation on what this facility will look like. And this is the inner side of the advance light source, where you can see the inner core actually is generating x-ray from a linear accelerator, which is boosted up by the booster rings. And the booster rings are those which are having magnetic field.

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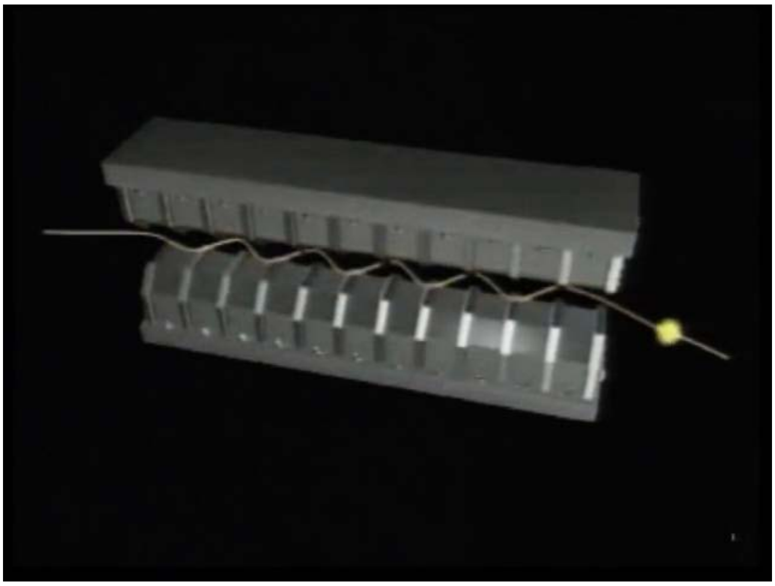

And once it comes out to the periphery then it can actually go through, several substations where this accelerated x-rays can be used and this is how the booster actually works.

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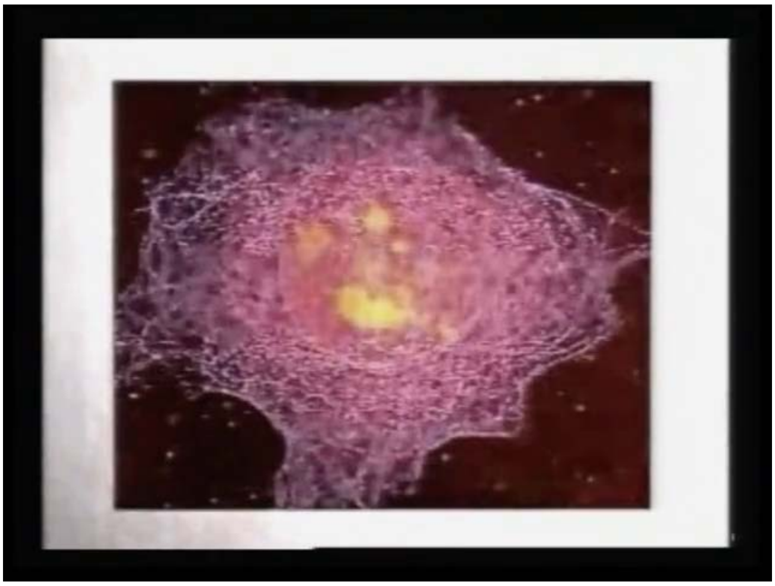

And once it comes out, then it can be monochromatized and it can interact with the material giving many information’s that is needed, not just on the spectroscopy. In fact, even imaging of structures can be used using this map.

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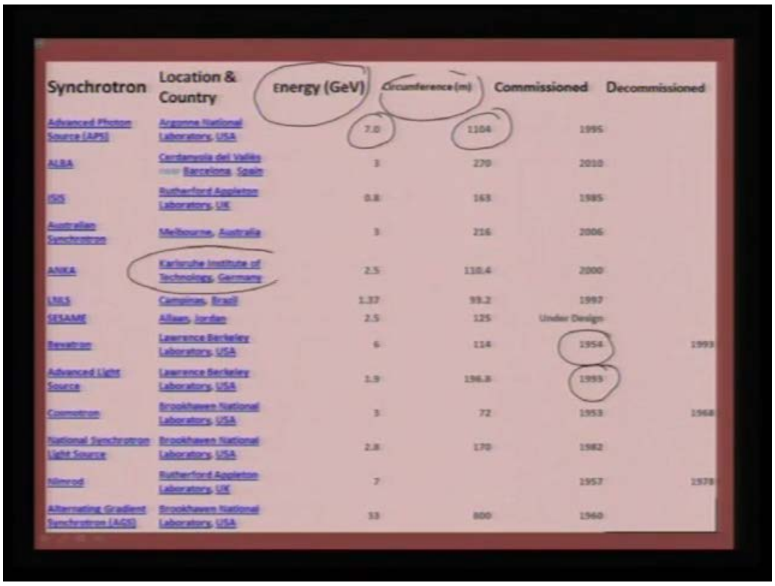

Synchrotron	Location & Country	Energy (GeV)	Circumference (m)	Commissioned	Decommissioned
Advanced Photon Source (APS)	Argonne National Laboratory, USA	7.0	1104	1995	
ALBA	Cerdanyola del Vallès near Barcelona, Spain	3	270	2010	
ISIS	Rutherford Appleton Laboratory, UK	0.8	163	1985	
Australian Synchrotron	Melbourne, Australia	3	216	2006	
ANKA	Karlsruhe Institute of Technology, Germany	2.5	110.4	2000	
LNLS	Campinas, Brazil	1.37	93.2	1997	
SESAME	Allaan, Jordan	2.5	125	Under Design	
Bevatron	Lawrence Berkeley Laboratory, USA	6	114	1954	1993
Advanced Light Source	Lawrence Berkeley Laboratory, USA	1.9	196.8	1993	
Cosmotron	Brookhaven National Laboratory, USA	3	72	1953	1968
National Synchrotron Light Source	Brookhaven National Laboratory, USA	2.8	170	1982	
Nimrod	Rutherford Appleton Laboratory, UK	7		1957	1978
Alternating Gradient Synchrotron (AGS)	Brookhaven National Laboratory, USA	33	800	1960	

Having seen the sophistication that is involved in this, I should also mention to you that this is a very selective facility that is available across the world. And here is a list of all the synchrotron radiation facilities that is available, it is also called as advanced light source. And as you would see here many countries are really competing in this field, what is important to notice is the circumference of the synchrotron radiation source that we can look for in terms of meters.

And then, the energy that is generated in this list you would see that the major players are actually in Europe, and in US and most of the facilities are housed in US therefore, this is a very, very costly equipment that has to be sustained. And one of the oldest as you would see here, is from Lawrence Berkley laboratory commissioned and it was also decommissioned, in 1993 subsequently a new advanced light source has come, into picture. And then another one has been commissioned, when the previous one was decommissioned that is in 1993. You can actually look at the sophistications involved the amount of Giga electron volt that you can generate, these are some of the largest facilities in the world. As of now, with a very, very massive infrastructure, one is in Argonne national lab and equally important are those in Germany.

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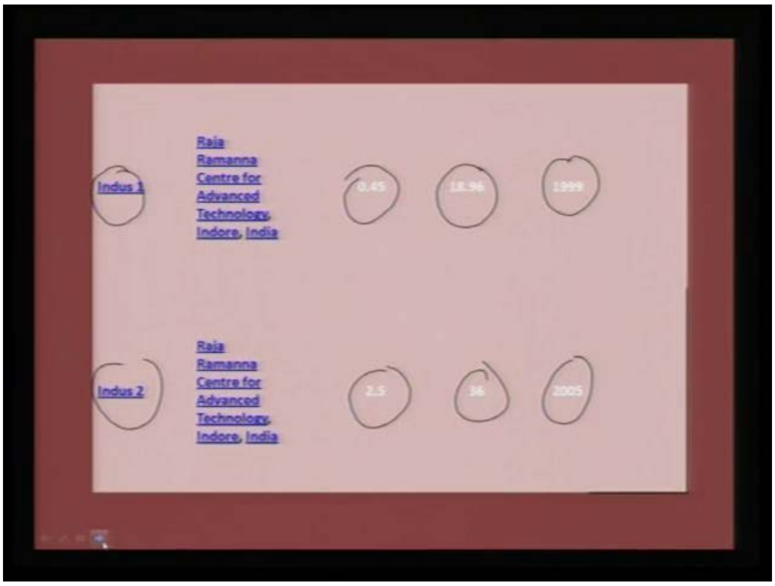

Indus 1	Raja Ramanna Centre for Advanced Technology, Indore, India	0.45	18.96	1999
Indus 2	Raja Ramanna Centre for Advanced Technology, Indore, India	2.5	36	2005

But, we are also in the game in a smaller way for example, if you look at Indian situation we have two synchrotron light source, both are housed in Indore and this is called Indus 1 and Indus 2. But, you would see that the circumference or the dia of your sources very, very small compared to what we saw in the earlier case, they have a circumference of 1000 meters. But, we have fairly very small unit and the capability also is very less therefore, we can only study organic molecules, using this facility it is not possible to study heavier atoms.

So, this is limited nevertheless we are also in the map. As far as synchrotron radiations are concerned, I am sure in the days to come there will be lot more progress and we will improvise on this facility as a nation. So, this is just to give you some idea about how these are localized, and there is there are also programs in our own country where we tie up with this advanced light source, specially our country encourages lot of projects which can be written to Trieste in Italy, where there is a synchrotron facility.

So, it is possible for those who are looking for this spectroscopy to make a proposal and go and do a time bound research. But, what we should also understand is that if you are really looking for in situ experiments, then we need to take the whole equipment and attach it to the beam line to study this. Most of the reactions that are done is all in situ it is not ex situ. So, therefore, it is a very sophisticated way of looking at it.

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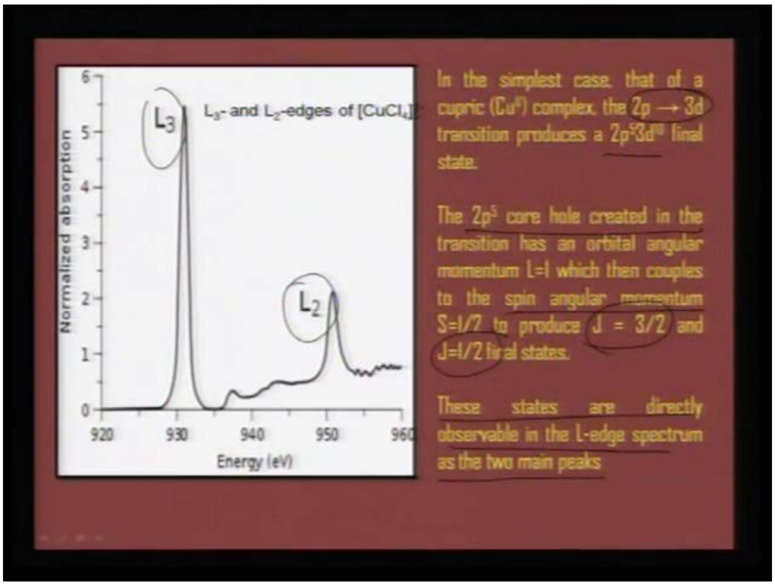

In the simplest case, that of a cupric (Cu^{II}) complex, the $2p \rightarrow 3d$ transition produces a $2p^5 3d^{10}$ final state.

The $2p^5$ core hole created in the transition has an orbital angular momentum L=1 which then couples to the spin angular momentum S=1/2 to produce J = 3/2 and J=1/2 final states.

These states are directly observable in the L-edge spectrum as the two main peaks

Now, let us look at the spectral features of this study and then, understand little bit about what we can learn. In the simplest case that of a cupric that is copper two complex, the 2 p to 3 d transition actually produces a 2 p 5, 3 d 10 final state. So, when an electron is actually removed from 2 p 5 then what really happens to that the 2 p 5 core, actually which is created in the transition, this has a orbital angular momentum and which couples with the spin angular momentum. Therefore, it produces two states J is equal to 3 by 2 and J is equal to 2 half state.

And this actually comes out as a XAS peak, which we call it as L 2 and L 3 edge. So, the intensities also are almost of the same order, these states are directly absorbable in the L h spectrum as the two main peaks. So, whenever we talk about L h spectra using XAS, we are talking about L 3 and L 2 that is actually coming from a transition of p to d or s to p orbital.

So, as we move across the periodic table specially from copper you go down go on the left side, across the period. Then you will see we create additional holes in the metal 3 d orbital’s, let us take the case of iron which is a low spin and in low spin it is actually iron 3 is t 2 g 5 e g 0. And therefore, this is your ground state and in t 2 g 5 e g 0, resulting in transitions to the t 2 g and e g d sigma sets.

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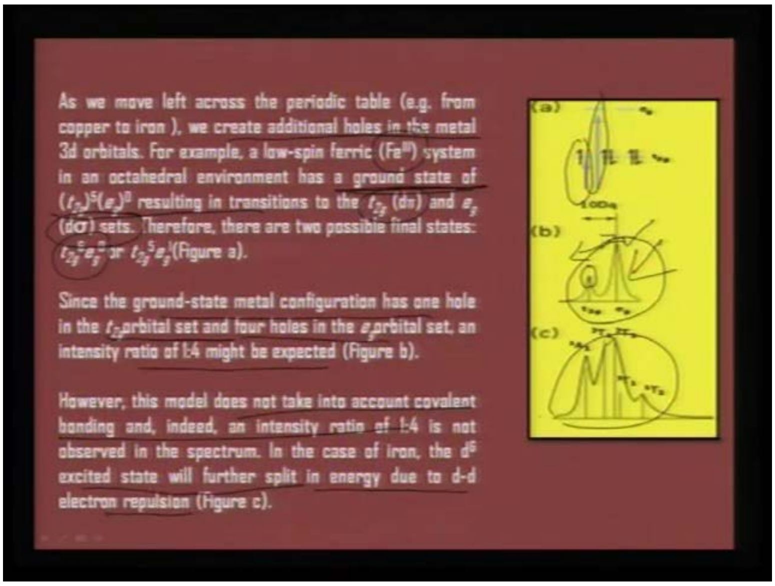

As we move left across the periodic table (e.g. from copper to iron), we create additional holes in the metal 3d orbitals. For example, a low-spin ferric (Fe^{III}) system in an octahedral environment has a ground state of $(t_{2g})^5(e_g)^0$ resulting in transitions to the t_{2g} (dπ) and e_g (dσ) sets. Therefore, there are two possible final states: $t_{2g}^6e_g^0$ or $t_{2g}^5e_g^1$(Figure a).

Since the ground-state metal configuration has one hole in the t_{2g} orbital set and four holes in the e_g orbital set, an intensity ratio of 1:4 might be expected (Figure b).

However, this model does not take into account covalent bonding and, indeed, an intensity ratio of 1:4 is not observed in the spectrum. In the case of iron, the d^6 excited state will further split in energy due to d-d electron repulsion (Figure c).

Therefore, there are two possible final states that can happen when you are actually promoting a 2 p electron, through two either of this 3 d orbital’s. You can end up with a t 2 g 6 that is what is denoted here or we can end up with a t 2 g 5 e g 1 and depending on these two, then you can actually get a peak like this. And this peak actually corresponds to the electron promoted to this final state, and this peak corresponds to electron that is promoted to this state.

So, since the ground state metal configuration has one hole in the t 2 g orbital set and four holes in the e g orbital set. And intensity ratio of 1 is to 4 is actually expected, as you would see here between t 2 g and e g depending on the number of holes, the intensity of the peak also would vary in the ratio 1 is to 4. But, it is not always true what will happen is this does not d 6 exited state will further split in energy due to d, d electron repulsion as a result, you would see a much more complicated or a split pattern of these two peaks. So, these two peaks need to be analyzed rather more carefully because there are other things that would compound with these structures.

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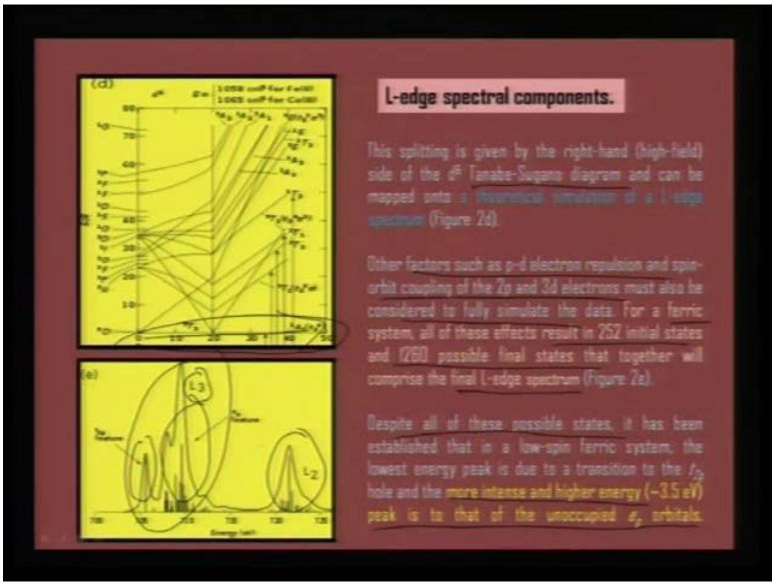

L-edge spectral components.

This splitting is given by the right-hand (high-field) side of the d^5 Tanabe-Sugano diagram and can be mapped onto a theoretical simulation of a L-edge spectrum (Figure 2d).

Other factors such as p-d electron repulsion and spin-orbit coupling of the 2p and 3d electrons must also be considered to fully simulate the data. For a ferric system, all of these effects result in 252 initial states and 1260 possible final states that together will comprise the final L-edge spectrum (Figure 2e).

Despite all of these possible states, it has been established that in a low-spin ferric system, the lowest energy peak is due to a transition to the t_{2g} hole and the more intense and higher energy (~3.5 eV) peak is to that of the unoccupied e_g orbitals.

So, if you single out just the L h spectral component and try to look at it, specially for complexes with the metal centre. Then your tanabe sugano diagram will help you simulate theoretically how many L h edge spectrum can originate, as you would see here you go from lower energy to higher energies region. The spectral features actually becomes more complicated therefore, more and more transitions are expected, when you go to higher regions.

And that is what you see here other factors like p d electron repulsion, spin orbit coupling all this has to be considered, when you try to simulate all the possible L edge spectral components that are there. So, for ferric system if you consider there theoretically there are 252 initial states, and 1260 possible final states are possible together with the final L edge spectrum.

But, what you would find here despite all this possible state it has been established that, the low spin ferric system the lowest energy peak is due to the transition to the t 2 g hole and a more intense higher energy peak is that to the unoccupied e g orbital’s. So, although there are several states possible, selectively these two states predominate over the other contributions, which can actually be mapped. And you can see that from the L 3 edge although, there are split patterns then you will be able to resolve which one is due to t 2 g and which one is due to e g. So, there are two things that we need to understand within L 3 there will be two peak, which will correspond to excitation to t 2 g or e g and then you also have the L 2.

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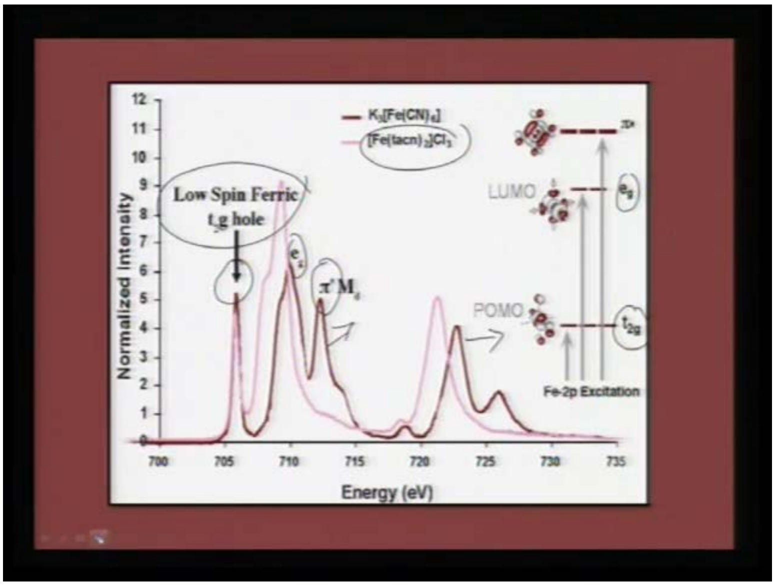

So, both these come into picture when we look at the XAS for a complex like this, which is a hexazinone iron three complex you would see for a low spin. This first peak corresponds to transition to t 2 g, and this second peak actually corresponds to e g and then the third peak corresponds to the M level that is your pi star. So, this is for L 3 and this is for L 2 and similarly for other transition metals you can see, this is a inner sphere complex and this is a outer sphere complex, and in both cases you would see the spectral features are actually different.

I will take one example from our own work on perovskite manganites and try to see, how we have resolved some of the fundamental interactions that are happening within the unit cell, using XAS as a tool. As you know perovskite manganites show interesting properties both in terms of magnetism and electrical conductivity.

And this actually comes from a phenomena called double exchange, where you have from M n 3 the e g electron actually goes to M n 4 plus e g shell, which is unoccupied. As a result when this is actually, transferring to the M n 4 plus core and if it is ferromagnetic ally aligned to the localized t 2 g electrons, then this will actually become a M n 3 plus because the electron has come here. And in the process this M n 3 will actually become M n 4, as a result there will be a shift of this electron back and forth, which is called as double exchange.

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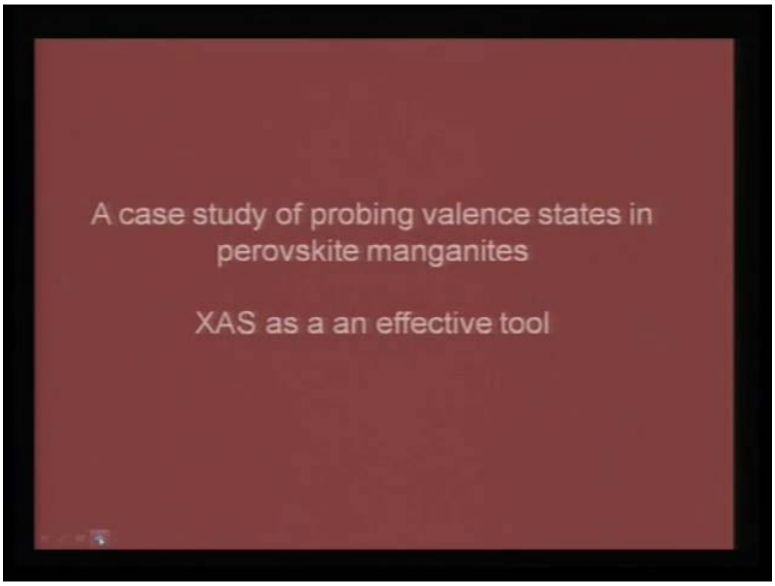

A case study of probing valence states in perovskite manganites

XAS as a an effective tool

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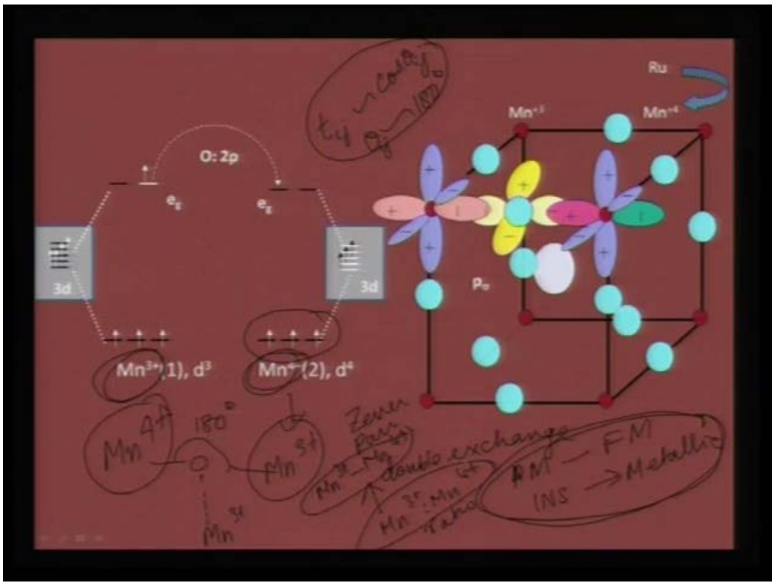

And because of this double exchange phenomena that is happening mainly because of the presence of M n 3 and M n 4 then there is a interesting change from paramagnetic to ferromagnetic state and from a insulator to a metallic state. So, two things happen when we try to initiate this electron transfer process, and this transfer of electron is given as transfer integral that is t i j which is proportional to cos theta i j.

So, this ((Refer Time: 33:55)) theta i j is nothing but the angle that is made between these two iron cores. So, if this is going to be 180 then the transfer integral is going to be at it is maximum, if this is actually going to be like this for example, then this is will get locked up at 90 degree. So, this transfer integral has to be theta has to be approximately theta i j 180 degree for a collinear ferromagnetism to operate.

Now, in this situation you need both the case of M n 3 and M n 4 which is called as zener pair M n 3 plus and M n 4 plus which is very crucial. So, I just want to emphasize that this zener pair M n 3, M n 4 plus ratio is critical for this spectacular manifestation of magnetic and electrical conducting properties to occur, at the same transition temperature.

Now, as I told you M n 3, M n 4 is more sensitive therefore, if I try to alter this M n 3, M n 4 ratio M n 4 plus ratio, then this double exchange or this strange occurrence of paramagnetic to ferromagnetic transition will be disturbed or it will be killed. As a result we this ratio has to be maintained at all cost, what we have tried to do is to put ruthenium into this site, either manganese 3 plus or 4 plus z. And try to see whether this interaction can still be maintained, and how XAS can be used to ascertain the interaction between manganese and ruthenium core centres.

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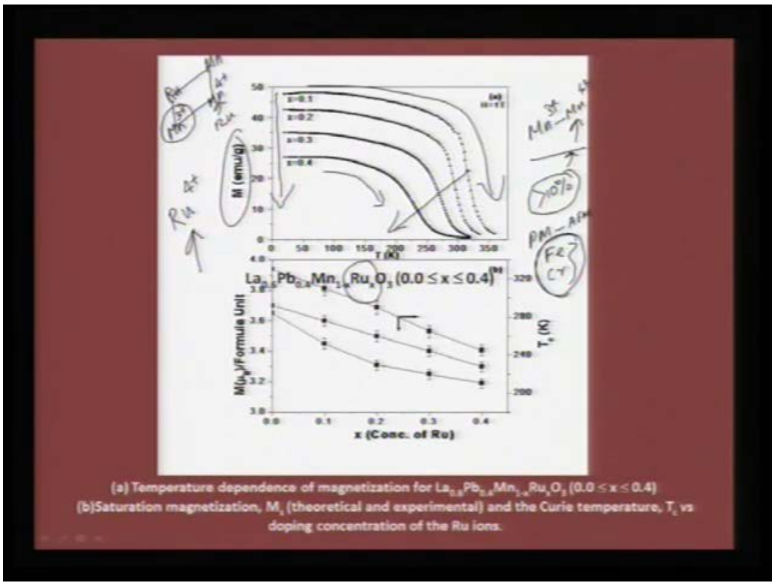

(a) Temperature dependence of magnetization for $La_{0.6}Pb_{0.4}Mn_{1-x}Ru_xO_3$ $(0.0 \leq x \leq 0.4)$
(b)Saturation magnetization, M_s (theoretical and experimental) and the Curie temperature, T_c vs doping concentration of the Ru ions.

In the next slide we will see, how a ruthenium when it is substituted into manganese sites what will happen to the ferromagnetic interaction, from this cartoon in the top you would see the plot of magnetization as a function of temperature. And this is a typical ferromagnetic transition that is happening, and during this transition if you keep on adding ruthenium as I told you M n 3 plus M n 4 plus ordering, is very important. And if little amount of M n 4 plus is also reducedM then immediately it will spoil the double exchange phenomena.

And you can clearly see that, the more ruthenium that is doped the lesser the ferromagnetic transition. And the ferromagnetic transition is decreasing to lower temperature, from room temperature, but what is interesting is even up to 40 percent of ruthenium that you dope into the manganese site. You can still observe a very strong co linear ferromagnetism, and this suggests that something else should be happening for this double exchange phenomena to occur or to sustain.

Otherwise even 10 percent of any 3 d metal, if we try to dope in manganese site will actually kill this whole magnetic interaction from a paramagnetic to a anti ferromagnetic or to a insulating phase. So, this is the maximum that has been considered as the limiting composition for doping into manganese site, either by iron chromium or any other metal ions. So, what is special about this ruthenium, why when ruthenium four is substituted this long range ferromagnetism is still sustained, why I am particularly emphasizing this here is when you consider a unit lattice of manganese, manganese, manganese.

And ruthenium for example, so ruthenium manganese 3 plus is there, manganese 4 plus is there. If you are increasing the proportion to 40, we are saying at every alternate position next to manganese, we are almost bringing an another ruthenium. So, in a Basel plane a b Basel plane where we have manganese ruthenium, manganese ruthenium then we are almost evolving at a new perovskite phase and this is not know or reported, so far. So, in this case what is that which is happening special to ruthenium doping compared to all other transition metals is the question, and how we can use XAS to prove this point.

As I told you from the previous graph, this long range ferromagnetism is also exemplified in the plot of resistance versus temperature. As you can see here, even with 30 and 40 percent ruthenium doping, 40 percent ruthenium doping you can still this see this metal insulated transition on, and in these three cases metallic behaviour is still see. So, this is quite unusual for a ruthenium doping to show such a long range ferromagnetism.

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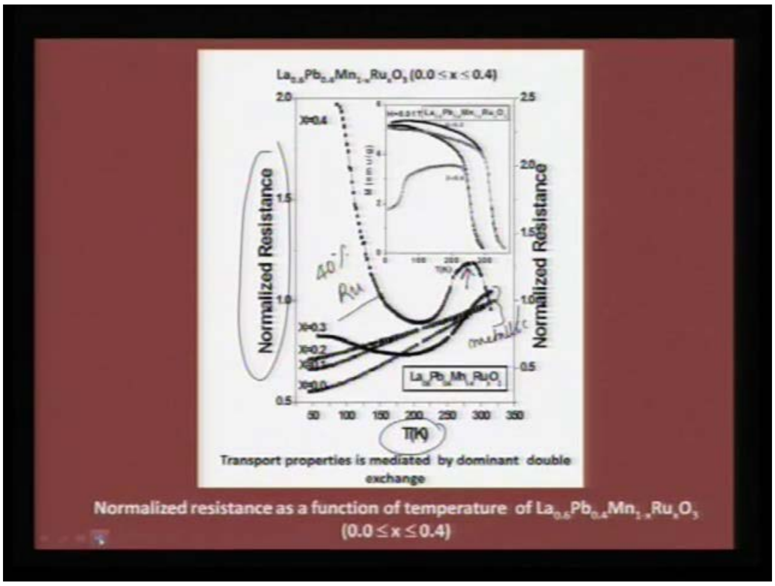

$La_{0.6}Pb_{0.4}Mn_{1-x}Ru_xO_3$ $(0.0 \le x \le 0.4)$

Transport properties is mediated by dominant double exchange

Normalized resistance as a function of temperature of $La_{0.6}Pb_{0.4}Mn_{1-x}Ru_xO_3$ $(0.0 \le x \le 0.4)$

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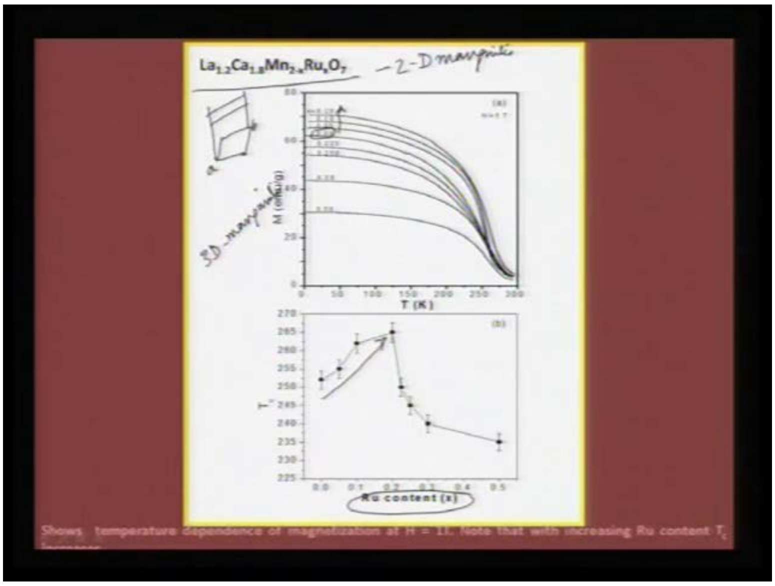

$La_{1.2}Ca_{1.8}Mn_{2-x}Ru_xO_7$ – 2-D manganite

Shows temperature dependence of magnetization at H = 1T. Note that with increasing Ru content T_c

And not only to this 3D perovskites or 3D manganites, if we take any two dimensional layered manganese like this, in two dimensional layered manganese like a L a 1.2 c a 1.8 m n 2 minus x r u x you actually have this collinear ferromagnetism which is confined only in the a b axis. And along the c axis it is not possible, along the c axis it is not magnetically ordered.

So, this is called as two dimensional manganites where, magnetism is confined only in two dimensions, but even in this case as you would see, if you put ruthenium instead of killing the ferromagnetism, it is only improving on the ferromagnetic transition. In other words with more and more of ruthenium concentration, your able to push the t c even to 20 Kelvin which is a very unusual state. So, something very unusual is happening when ruthenium is doped into manganese.

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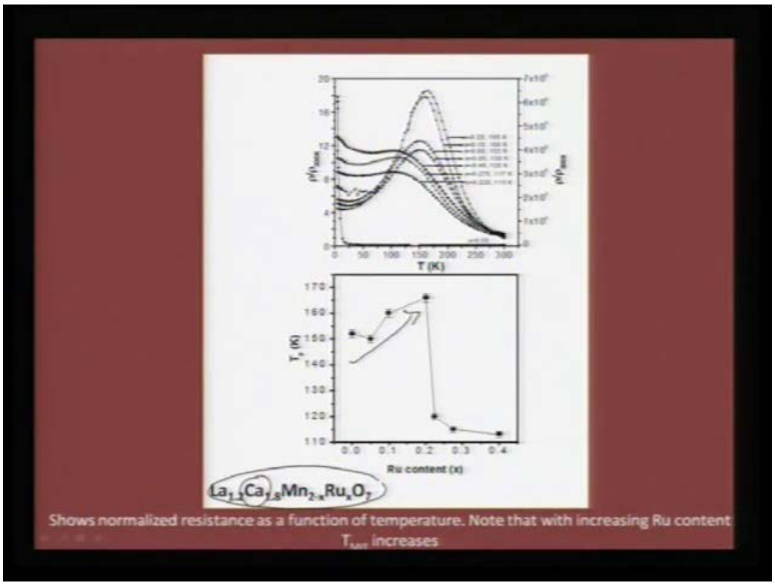

Shows normalized resistance as a function of temperature. Note that with increasing Ru content T_{MIT} increases

And you can see that, the same case happens when you change from strontium to calcium again increase in magnetization.

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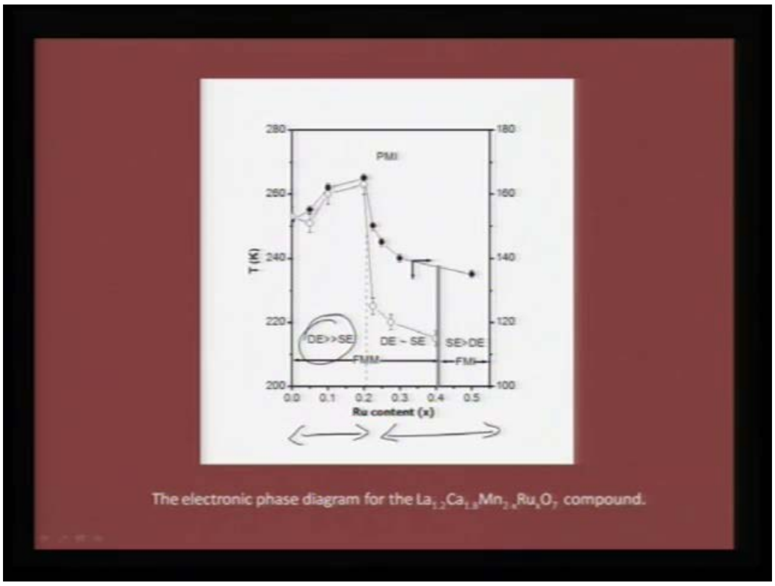

The electronic phase diagram for the $La_{1.2}Ca_{1.8}Mn_{2-x}Ru_xO_7$ compound.

And therefore, there is something that we can draw; there is a clear double exchange which is dominating over super exchange, in the up to 20 percent of ruthenium doping. Beyond which there seems to be some competing magnetic interactions which I will discuss in some other module about the different magnetic phase.

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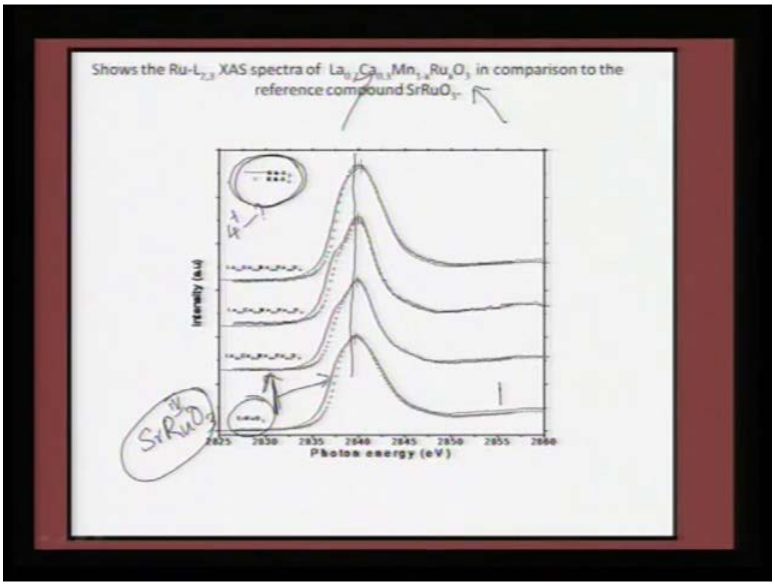

Shows the Ru-$L_{2,3}$ XAS spectra of $La_{0.7}Ca_{0.3}Mn_{1-x}Ru_xO_3$ in comparison to the reference compound $SrRuO_3$.

I will quickly go through another example of a simple manganite L a 0.7, calcium 0.3, manganese 1.x, ruthenium x. In this case even, if you keep on changing ruthenium you can look at the L 2, L 3 edge and see, how the nature of this x-ray absorption peak changes. For example, you we can actually try to compare the L 2, L 3 edge with respect to strontium ruthinate S r R u O 3 because S r R u O 3 in this case the valency of ruthenium is proven. So, if you make a comparison with that and you can clearly see that in the case of the ruthenium L 2, L 3 edge, we can clearly see that there is a shift for above ruthenium 0.2 in these compositions. So, therefore, the ruthenium valency seems to be varying somewhere from 4 plus to some other valency, which is actually contributing to stabilizing the ferromagnetic interaction.

And as you see here, the solid lines represent L 3 and the open circles represent L 2 and L 2 is actually shifted, L 2 is supposed to come here in the lower energies L 2 is supposed to come somewhere here, but it is purposely pushed here. So, that there is a comparison between L 2 and L 3 edges are made, so what we see from this curve is that there is some issue that is significantly happening with the ruthenium oxidation state.

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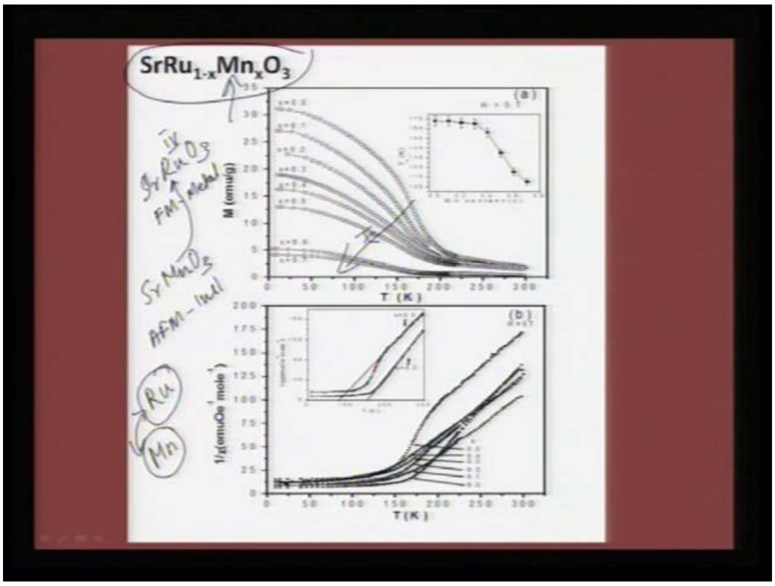

SrRu$_{1-x}$Mn$_x$O$_3$

Now, let us take another example of S r R u 0 3 as I told you in S r R u o 3 which is the parent compound, ruthenium is in 4 plus. Therefore, instead of doping ruthenium into manganite, we can now do a reverse doping where we put manganese into a know ruthenium oxide. So, in that case also you would see this is a ferromagnetic metal whereas, S r M n O 3 is a anti ferromagnetic insulator.

Now, if you keep on doping manganese into ruthenium, you would see that there is a very strong ferromagnetic signal there, even up to 70 percent we can see a ferromagnetic transition that is happening there is a sustained t c this is very, very unusual. So, there is something happening not only in ruthenium, there is something happening in manganese also. So, what is that which is stabilizing ferromagnetism between ruthenium and manganese centres this is what we can probe.

And I am just listing out some of the parameters from the magnetic study t c as you can see. Because, it is a broad transition we can try to derivatize the curve and take the t c even up to 50 percent of manganese doping, we still see a very clear curie temperature that is ferromagnetic ordering and although the t c is dropping nevertheless it is not becoming nonmagnetic.

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Some properties of the $SrRu_{1-x}Mn_xO_3$ compounds

Composition	θ (K)	C (emu K mol^{-1} Oe^{-1})	p_{eff} (Exp.)	p_{eff}*(Theo.)
SrRuO3	160	1.01	2.83	2.84
$SrRu_{0.9}Mn_{0.1}O_3$	153	1.31	3.23	2.95
$SrRu_{0.8}Mn_{0.2}O_3$	124	1.38	3.32	3.07
$SrRu_{0.7}Mn_{0.3}O_3$	115	1.40	3.35	3.18
$SrRu_{0.6}Mn_{0.4}O_3$	105	1.57	3.54	3.29
$SrRu_{0.5}Mn_{0.5}O_3$	95	1.91	3.89	3.39

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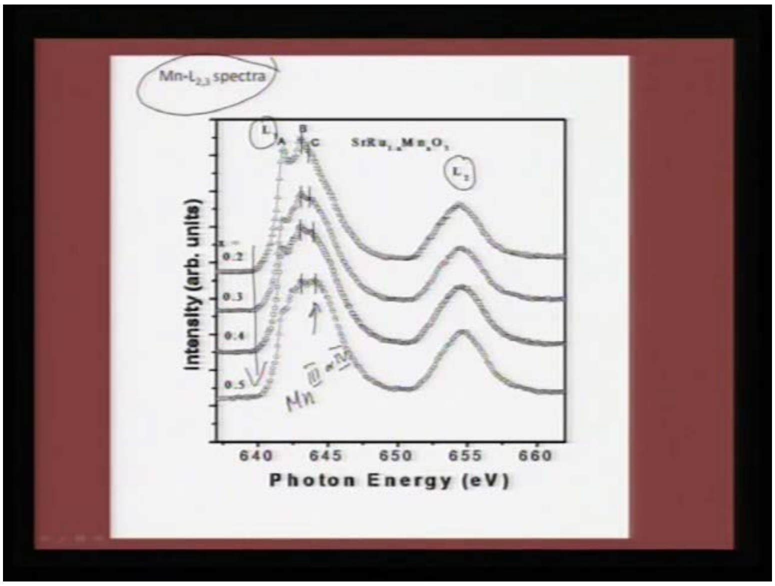

Now, to probe this let us take the case of manganese L 2, 3 spectra. And if you look at the L 2 h and the L 3 h, L 3 h seems to be going through a very different feature compared to L 2. And therefore, if you carefully probe this as you increase the concentration of manganese, in strontium ruthinate this particular c peak is actually growing in strength than B. So, we can say that as we increase the concentration of manganese then something is happening to the oxidation state of manganese, it may be either 3 or it should be 4. And that is why this particular intensity has grown, very significantly compared to position B.

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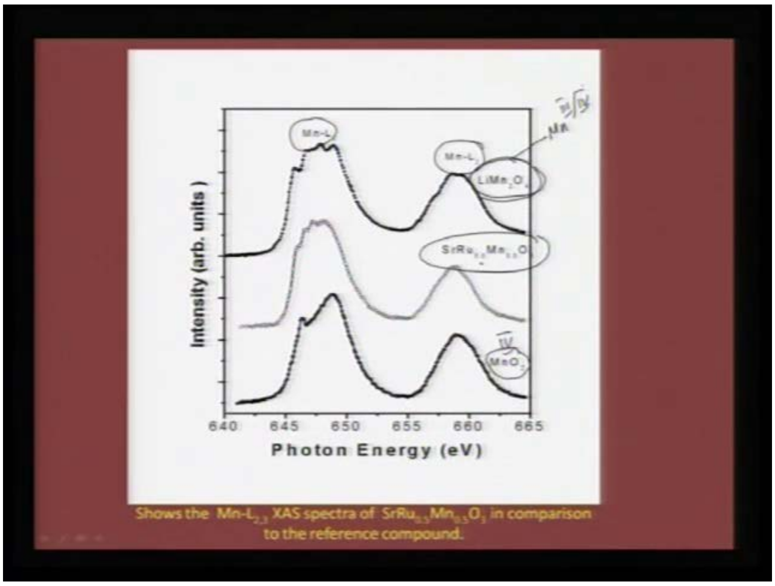

Shows the Mn-$L_{2,3}$ XAS spectra of $SrRu_{0.5}Mn_{0.5}O_3$ in comparison to the reference compound.

And now, let us take the same L 2, 3 edge for manganese core and try to compare this equip atomic composition that is 50, 50 of ruthenium and manganese. And make comparison between M n o 2 and L i M n 2 o 4 you can clearly see that this 50, 50 composition is resembling more of L i M n 2 o 4 compared to M n o 2. Because, in M n o 2 you actually have M n only in 3 plus state whereas, L i M n 2 o 4 is a solid state battery material, it is a electrolyte sorry it is a electrode. And in this case manganese is present both in 3 and 4 state. So, what we can say at this stage is, when manganese is doped into ruthenium or ruthinates, manganese is undergoing a mixed valence state. Similar to what we see saw in ruthenium substituted manganites.

Now, let us go 1 more step and try to map the ruthenium L 2, 3 spectra carefully, for all this substitutions, as a function of x. As you see here this x is equal to 0 is S r R u O 3 and once you go up to 0.5, you can clearly see that there is a shift in the edge for both L 2 and L 3 and also this L 3 peak intensity is growing in intensity. So, that clearly says that there is a shift in the ruthenium valence. So, instead of 4 plus ruthenium there seems to be a shift to higher valence state because the shift is more towards higher energy. Therefore, it should be ruthenium 4 to either ruthenium 5 or ruthenium 6, this much we can analyse from there.

So, let us take a comparison now we will compare it with S r R u O 3 which is 4 plus state, and here is another well known S r 4 R u 2 O 9, which actually shows ruthenium in

5 plus state. Now, if you compare the S r R u M n signal, it is neither in S r R u O 3 state which is 4 plus nor in S r 4 R u 2 O 9 state which is 5 plus. So, we can say clearly that the position of the 50, 50 composition clearly suggest that ruthenium is in both 4 plus and 5 plus state.

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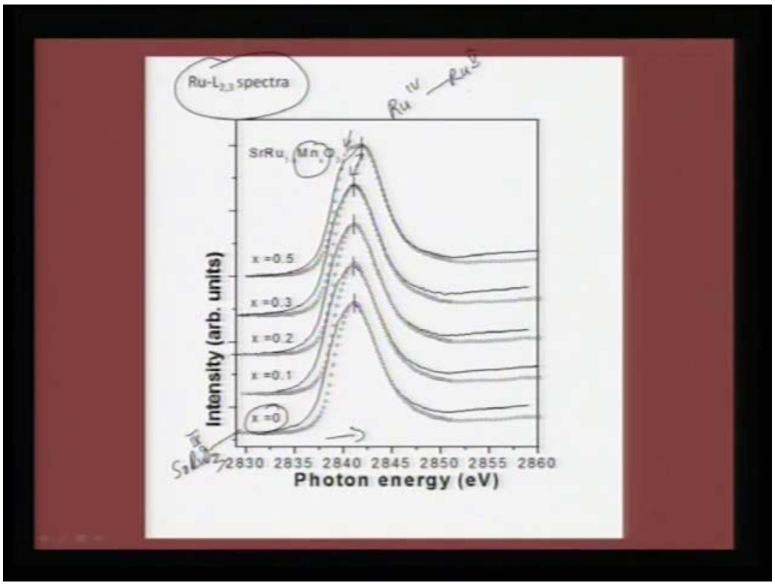

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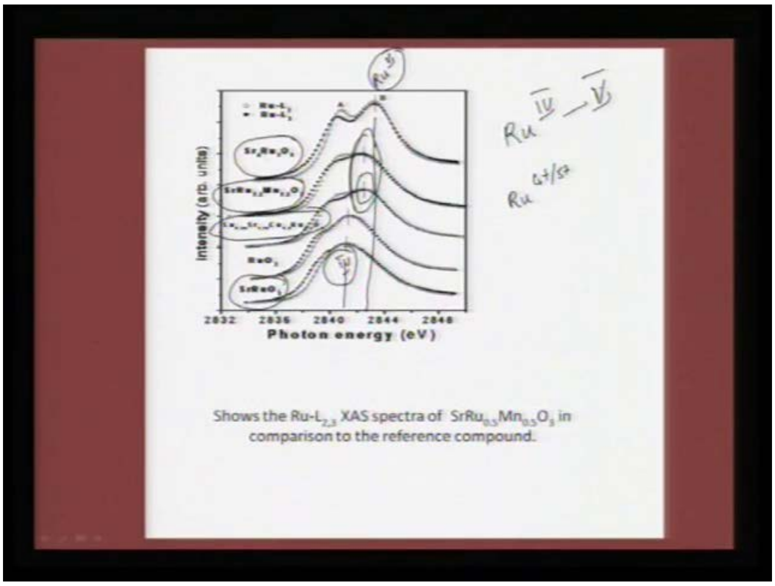

Shows the Ru-$L_{2,3}$ XAS spectra of $SrRu_{0.5}Mn_{0.5}O_3$ in comparison to the reference compound.

So, because of that we seem to be seeing a unusual ferromagnetic interaction. Now, this can actually be compared to another well known, well characterized system which is L a s r copper ruthinate structure, which is a recently found ferromagnetic compound. And this particular, one has ruthenium in both 4 plus 5 plus ratio and as a result, we can say that it is ruthenium which is undergoing a transformation to 5 plus state.

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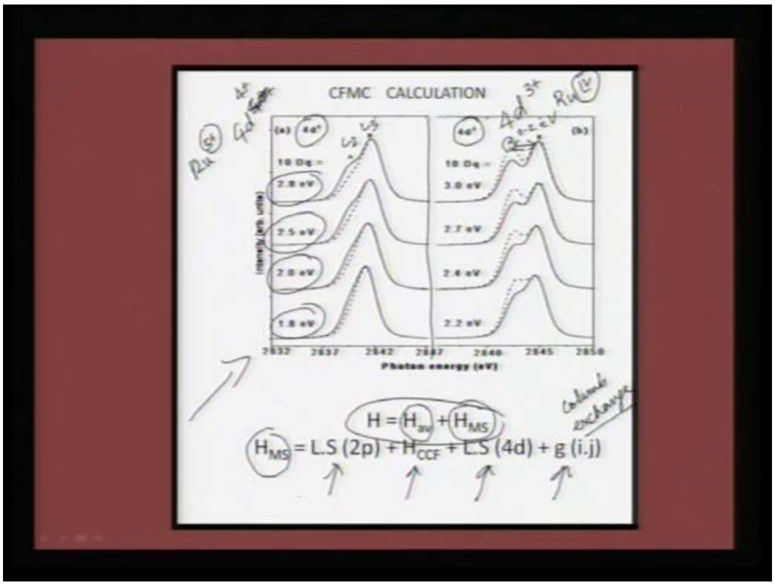

CFMC CALCULATION

$$H = H_{av} + H_{MS}$$

$$H_{MS} = L.S\,(2p) + H_{CCF} + L.S\,(4d) + g\,(i.j)$$

Now, to exclude the possibility of the crystal field contributions that can come, other than or due to manganese doping. We can actually try to do a theoretical calculation also, where we can try to map the L 2, L 3 edge of both 4 d 4 and 4 d 3 states. In this case we can try to change the Slater angle, which is nothing but your 10 D q value and see how the L 2 and L 3 edges behave. And this is the case for 4 d 4 this is the case for 4 d 3 plus 4 d 3 plus incidentally is your ruthenium 4 and 4 d 3 plus.

And in this case this is 4 d 4 plus which is your ruthenium 5 plus, as you would see very clearly not much change is happening because only in this case you see the intensity of this a peak growing. But, nevertheless you do not see any new features coming because this is corresponding only to 0.2 electron volt. So, 0.2 electron volt cannot substantiate for a promotion of 4 plus 2 or 5 plus state.

So, all we can say is the contribution is actually coming not from crystal field, but it is coming purely from the oxidation state. And for this calculation we have actually used a Hamiltonian, this Hamiltonian actually talks about the H average which is coming from the crystal field, and then this is the one which is the Hamiltonian due to multiple splitting. And this Hamiltonian M S is coming both from the L S coupling of your 2 p electron, L S coupling of your 4 d electron.

And then your cubic crystal field contribution and also this is from the exchange integral, and the coulomb integral of your electrons that is from 2 p to 4 d. So, this contribution is actually coming from your coulomb and exchange integral and this exchange integral g i j is what we call it as Slater integral. So, all we can say from this calculation is that the crystal field is not contributing to this splitting, but this is truly coming from c the oxidation state.

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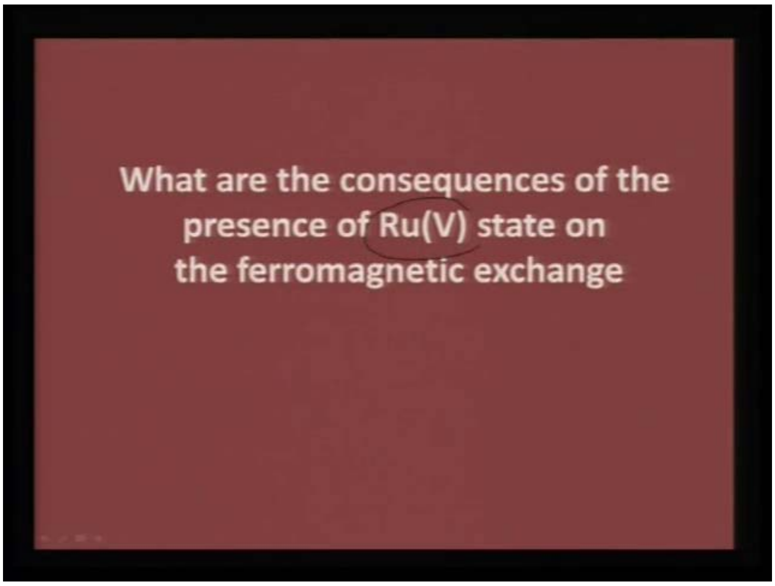

What are the consequences of the presence of Ru(V) state on the ferromagnetic exchange

Having said that, what we can say what are the consequence of the presence of ruthenium 5 plus in this state and how does it influence on the ferromagnetic state. So, this is a sum of contour just to understand having understood that there is a mixed valence state in manganese, and having understood that there is a mixed valency in ruthenium, how can we make a case for this. As you would see from a typical perovskite of manganite, the a axis and the b axis can be represented like this. And in this we told that this e g electron can go to this site, if it is ferromagnetic ally ordered when this angle is 180 degree.

Now, when we try to substitute ruthenium into this place what is happening, ruthenium 4 plus gets oxidized to ruthenium 5 plus, and in the bargain part of your manganese 4 plus is actually getting reduced to manganese 3 plus. As a result now, if you carefully look at the t 2 g e g level of ruthenium 5 plus and t 2 g e g level of your manganese 4 plus, the parent parentage of the t 2 g e g orbital is the same.

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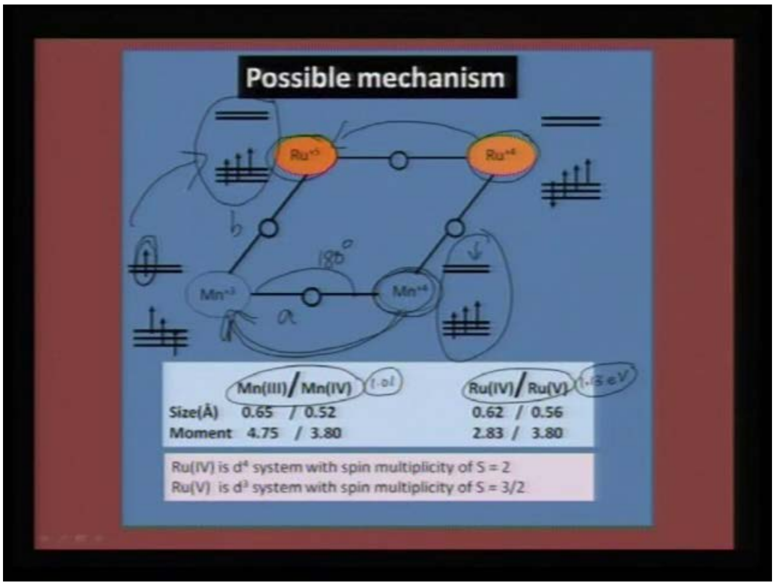

Possible mechanism

	Mn(III)/Mn(IV) 1.01	Ru(IV)/Ru(V) 1.13 eV
Size(Å)	0.65 / 0.52	0.62 / 0.56
Moment	4.75 / 3.80	2.83 / 3.80

Ru(IV) is d^4 system with spin multiplicity of S = 2
Ru(V) is d^3 system with spin multiplicity of S = 3/2

In other words we are almost providing two pathways for this itinerant e g electron to hop. One it can go from here to manganese 4 plus or it can go from here to ruthenium 5 plus because as far as the t 2 g e g occupation it remains the same for both. As a result even if you are going to substitute ruthenium to the order of 50 percent, you still can see a ferromagnetic ordering because of the isoelectronic configuration, not only that the coupled manganese 3, 4 has a size, which is comparable to that of manganese 4, 5 and also both have a comparable redox potential.

In this case redox potential for this is 1. o 1 and in this case it is 1.13 e v therefore, because of the matching redox potential. Whenever you try to put ruthenium 4 plus into manganese immediately it promotes to ruthenium 5 plus. So, even though ruthenium 4 plus is getting reduced to manganese 3 plus, you are almost creating another site for this electron hopping to occur, as a result a ferromagnetism can be substantiated. So, this is one case that we have I have tried to explain to you where excess can without any doubt, can resolve this issue because it gives you precise information about the local structure, the oxidation state as a result we can propose a mechanism, which is very unique of this particular compound.

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So, with this I would like to finish and there is a small animation that we can try to look at and how the instrumentation is housed and what are all the facilities. That we can see, here is where the yellow line signifies that the high energy x-rays are diverted to many places. And we can also typically see, how this can be used in different substations.

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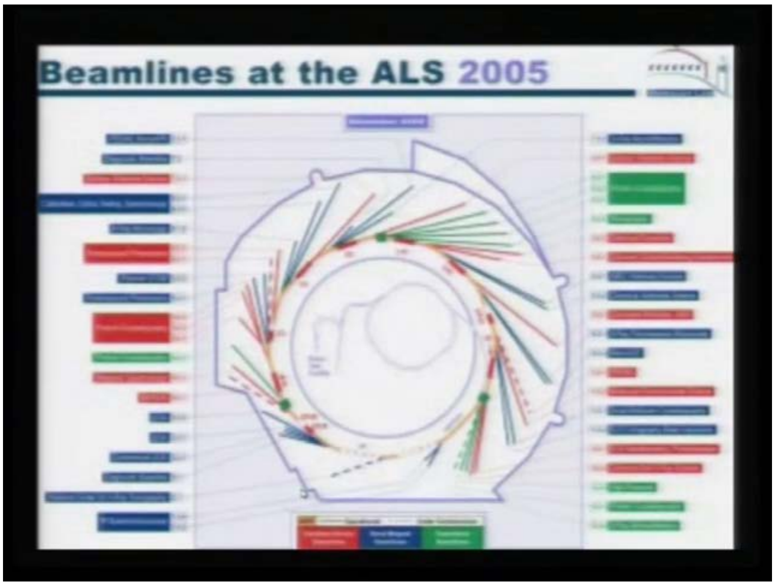
Beamlines at the ALS 2005

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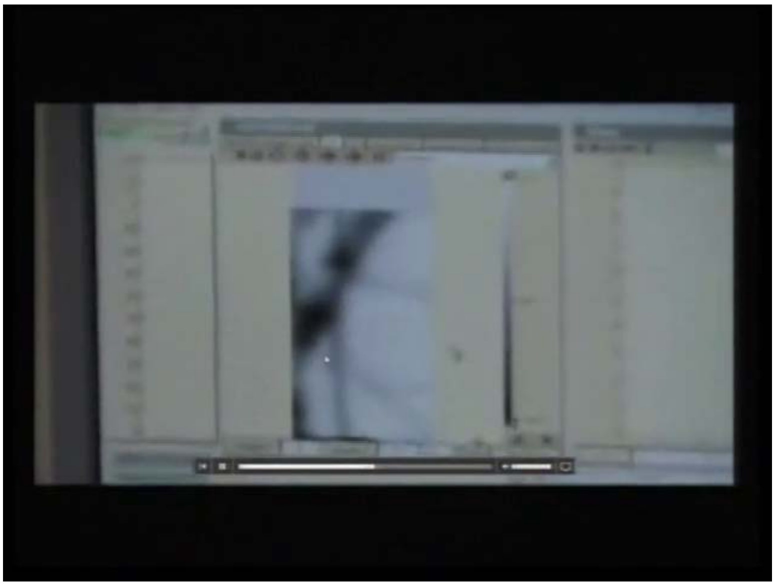

And these are the many beam lines that we see in this ((Refer Time: 55:45)) live source. A typical substation actually will have a lab as, the lab that we see here. And not only we can look at the spectroscopy as you would see, in this particular lab which is using ALS source, we actually have a scanning tunnelling microscopy which is being conducted. And this is specially on a isolated carbon nanotube and here is a person working on carbon nanotubes, and the images are being seen here.