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Course Title
Advanced Characterization Techniques

Lecture-18

by…
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This is the last lecture on the advance spectroscopic technique.

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Which we have been discussing so the last technique which I started discussing on EELS that is on electron energy loss spectroscopy and I have discussed with you the basics of EELS is technique relies on the aspect that electron when falling on the samples of any types undergoes something known as scattering obviously electrons are used for electron diffraction in the

electron microscopes and electron diffraction is mostly because of the inelastic scatter both energy in the momentum are consumed.

But in case of inelastic scattering there is always some energy loss of the incident electron and the electron which as pass through which is basically pass through the sample. These energy losses can be always due to certain kind of electron transitions happening in the material or it can be actually termed as atom electron excitation which are taking place. So therefore if we analysis this electrons which are basically undergone inelastic scattering we can get information regarding electron structure brand structure electronic diode and quantitically be also we can measured sudden amount of element present in the material.

So fast and foremost thing which I have done is that I looked at different kinds of energy loss and electron can undergo and so that there are different types of energy loss as possible I will go back to this slide.

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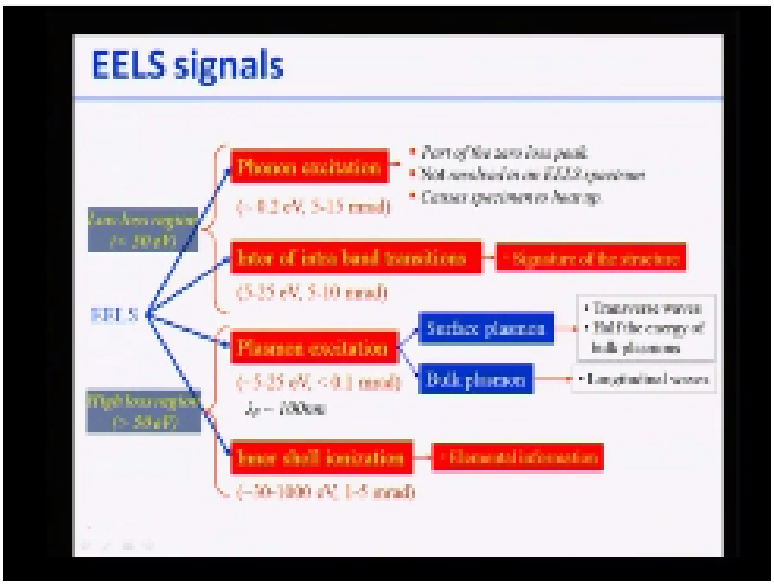

Where I have shown you the first thing which happens is energy loss spectroscopic is revision of the region spaced on the energy. So in case of low loss regions which is less than over 50 electron poles we always transitions which is very small actually close to EV and less than one EV. They have not of any significant for the measurements because being feature used for measurement for electron spectroscopic or not so much is that.

We can talk about this energy split of our point five so that not resolved at all. Second important thing is which all is happens the low loss region is called integrand or intraband transitions between the electrons. As you know the electron most of the orbital in the atoms. So therefore when an electron coming from high energy source like an electron microscope is applies in all energy to eject certain electron from one cell.

So that thing become that place become vacant and this can lead to intraband transition and this kind of things can give us a signature of the structure of the material, because electronic energies are basically propositional to the type of atoms or type of element it is and they actually happens in the energy range of 5 to 25 electron poles and these are very important and we are going to we have already discussed about it and we have discussed more and then you have something known as high energy loss where energy loss is more than 50 electron poles.

And things which happened there are two things one is called plasma are basically collective oxidation of the electron for the medals and the electron enlarge. They are very strong and there can be both plasmas because this are all collective oxidation. So therefore, there were been in nature. A last thing which can happened is basically inner shell ionization that means you have different sales in the atoms KMNLOP you know that inner shell which is k, l, m or k, l, m basically they contains very tiny molecular task.

Electrons and the energy of electrons are very high. This can eject an inner shell electron and this can lead to an ionization of the element and that can be used detect and elemental fact because energy levels of this electron in the k,l, m, n shells are very well defined for different elements. So this is actually not shell the e signals. And this is what I have discussed with you and that is what actually obtain in particular signal I will show you the EELS spectra.

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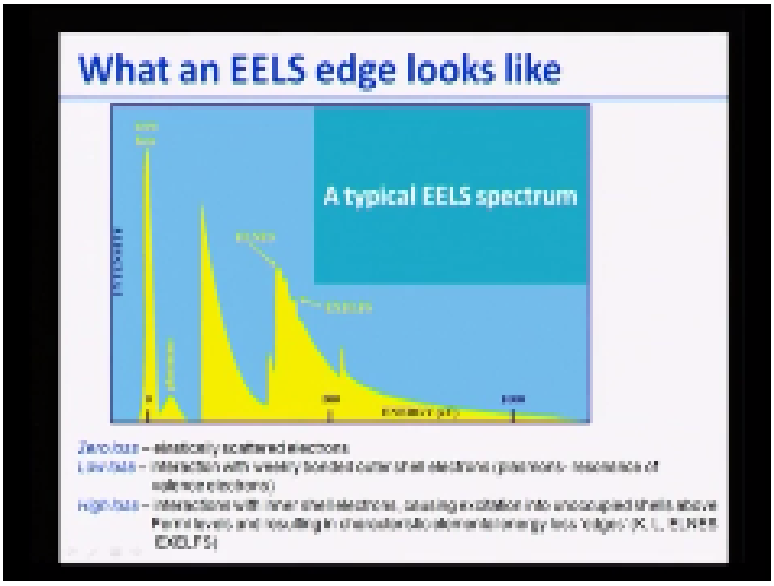

So that zero loss in a EELS spectra corresponds to elastic catering that means the electron which as past through and any kind of electron microscopes will tell you that large number of electron pass through the sample therefore this particular peek in EELS spectra were very high intensity. In fact this is the highest intensity. This is followed by Plasmon's. Plasmon's comes in a energy range very close to the zero loss peek and then there are characteristic peeks like elemental peeks followed by other things like we know as e, l, n, e, s and e, x, e, l, f, s.

There all energy loss near structures or extended energy loss near final structures which will discuss now. So these gives you lot of things about the electron structure in the material before that let me just go into fan structure which we started with and where I will tell you how the bad can be up you know that

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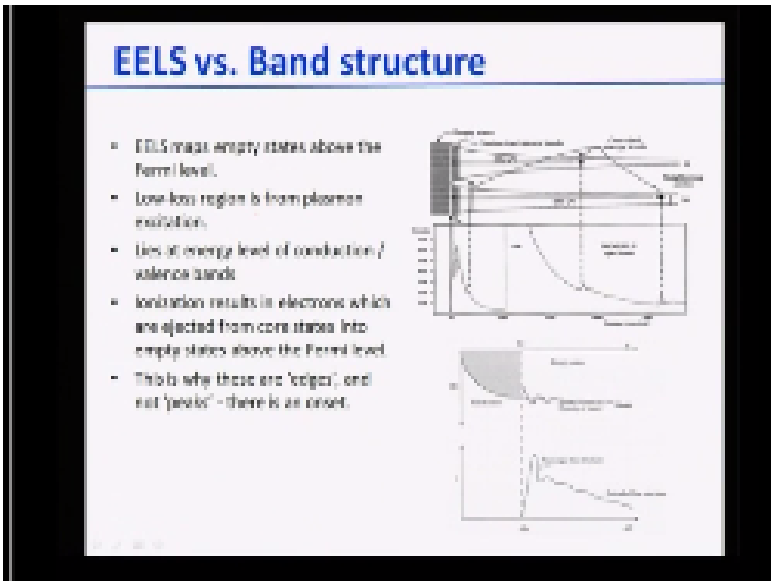

Maps can be used to get a band structure in a material it is positive actually this is what is shown in slides also it is basically the electrons which are ejected on the electrons where the k element which is discussed so what are electron which are scattered all in the available states, which are available to the them and thus energy imparted by the incidence electrons to get them basically to this transitions when reflect the density of the states is as simple as that.

So analyses the results in electrons which are ejected core steps into the empty states above the fin levels and when that happens we can get information's of the band structure this is why these are the silicon areas not fixed because they are not looking at the axis explains is suppose this is what the first picture so in the empty state and below level you have the condition and the corresponds bands as you can see here well now let us assume that k or m that is and energy levels coming out or electrons which are injected form are can basically have energies sufficient have to travel into this.

In fact n it may have energy state cross this any level and entering empty states so this is highly possible so showing you the case of in spectrum but you can see even in the MC energy move into the very close to the energy levels and this is the end condition and this is because corresponds to that states which you are unfiled at the beginning because in spectrum the band structure of the material can be obtained this is the plot between NE versus as you can see here and this is the level which are full state which are the empty states and then we have basically density of states to show like this so if I do if I have more than potential energies okay then you

can reject the electrons on the ions of electrons on the empty states you can get something like this kind of extended structure information in the spectrum.

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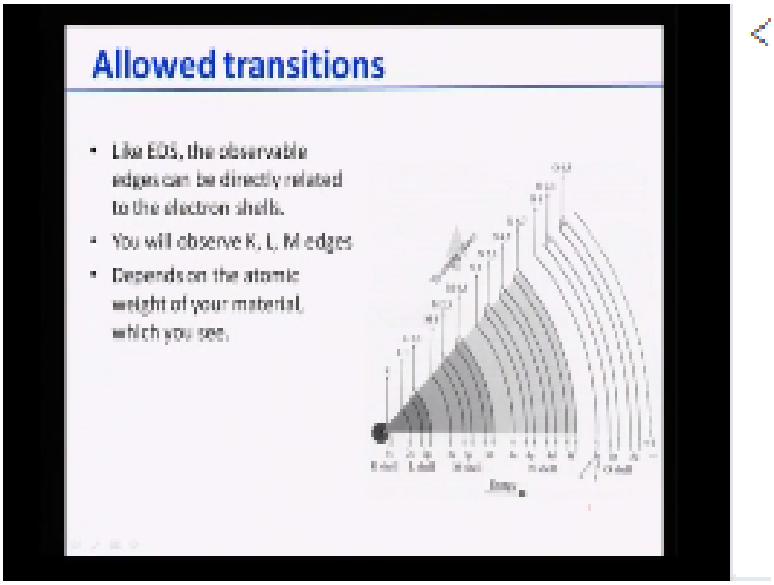

Well there is a you know totally depend upon some kinds of conditions you are having diluted to the that means you can always get but depended to the material also we see that but here even intra banded conditions within cells.

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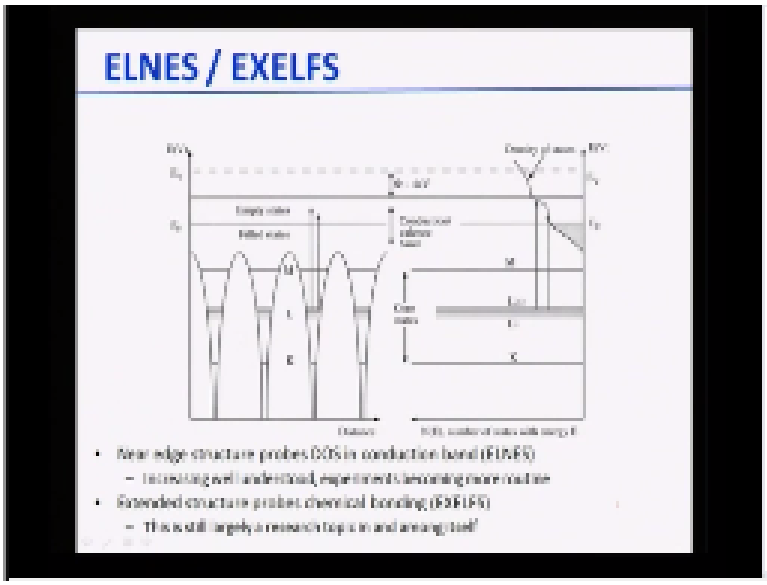

Obviously we can also do the information about the energy loss structures which are there in the last slides so let us now look at the energy band ev versus slide on the left side and then you see this is the familiar level and these are actually different atoms 1,2,3,4 and 5 So actually what happens you can have an instant electron with sufficiently high energy. It can eject one of the electron m , l, k in the shells and they can then moving to this MT states and if they have even higher energy, they can even move into the balance bands also. Now if I go back to the extend structure it is more clear.

So these e, k, l, m of the core states and they have l bands and that you have connection bands and then EV is there. So these kinds of terminations from L232 even MT states can give us information regarding these part of the energy levels. And this is actually called electron loss energy, electron loss near structures or extended electron loss final structure. So first one is gives you Dos step connection bands.

These are actually very well known and well understood now and they are used extensive play. Second one if not surely used it actually can give us information regarding chemical bonding , but it is still a lot of vision needs to be done to understand this electron transitions for electron extended energy loss fine k structure. This is just like excepts incase of x-rays. Let me give you some more things about els. How it can be use the finger printing. In fact this is what is actually people do now a day to know exactly the electronics states particular atom.

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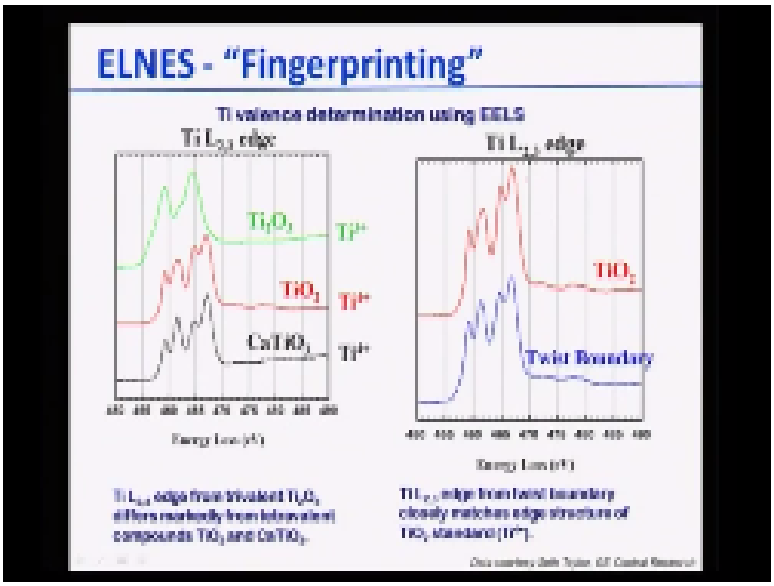

First let us talk about titanium. Titanium defend compounds calcium triturate, titanium dioxide in TI203. So in both calcium titanium TI02 the titanium actually has a flash four states and in case of TI203 it has pastry states. If I look at the EELS spectra of titanium in all these three compounds, I could see that depending on this electron state. There is this thing different in terms of this EELS spectrum.

In case of calcium titanium dioxide you can see four splits, but in case of TI2O3 this only 2. Not only that there is shift of energy losses to the lower values for the TI2O3. So that means Ti L2 -3 edge obtain from TI2O3 differs murkily from the tetravalent compound like TI2O3 or calcium triturate, not only that in fact one can look at difference of TI2O3 that enough state of titanium in TI2O3 form a green and form a 2 boundary. This can be done in electro microscopic and you can see my boundary with twist divert till time.

You can see the nature the spectrum actually the names same for both for the titanium oxide. Oxide is presented in the crane inside the crane or at the small ring but there is a distinct difference energy level are concerned they are not same. So therefore the EELS 238 for twist boundary all the closely matches with the structure TI2O3 standards, but the fine structures at different.

That cannot be discussed within this lecture, because one use to know what is still boundary structure and what will think can be there, boundary structure. So therefore it can be done. This

particular things are taken from they are very important information. Well, so after giving you balance structure let us just compared EDS with EELS. There are many compresses in EDS and EELS. I will give you chart also end of this lecture. Here is actually much more in qualitatively much more superior than EDS much more superior than EDS that is what it will be taught by different books.

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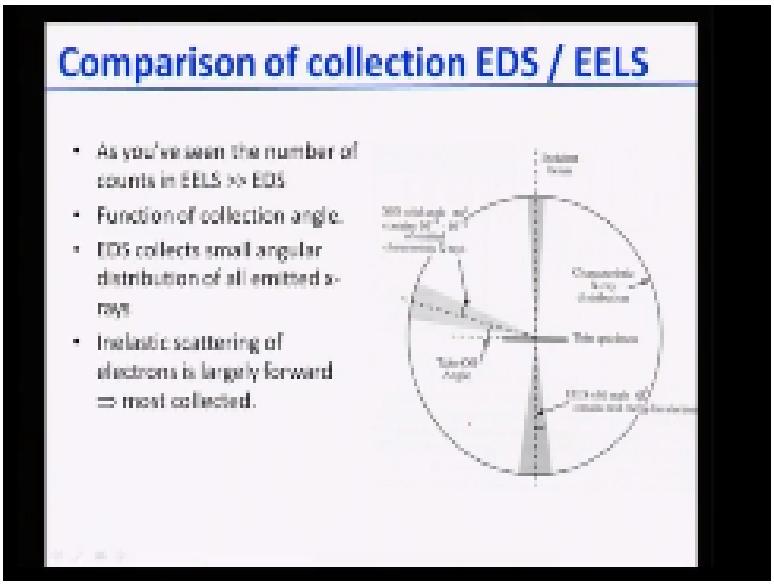

As you have seen number of very, very large as compared to EDS first of all and both of them function actually like a collection angle EDS collects small angle distribution of the all emitted x-rays, but EELS actually inelastic catering of electron of elastically forward castrated to therefore they are collected and that is why if the signals are more, so therefore they will be higher quality of data. Now it is can be soon here also. You have a electron are falling on the incident beam.

When you have atoms in a surrounded by several atoms some of this black atom is surrounded by six atoms other atoms types and this is what actually we would like to know how this atoms are distributed around the black atom. So in a plural scattering the electron which comes like that. It can come from the actually get scatter from the black atom then goes and scatter from all of the six atoms and then come out that will carry the information regarding all the surrounding atoms.

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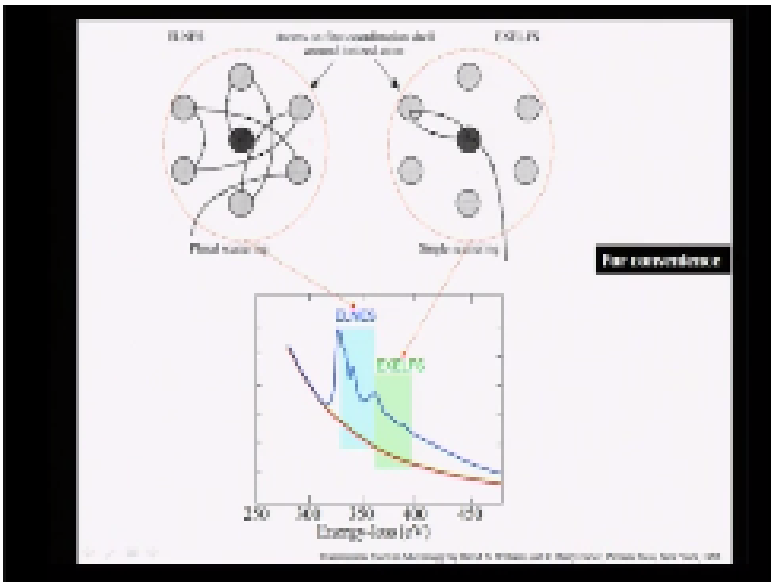

And that is what the actually there in electron laws near structures, but on the other hand in case of extended in the electron energy fine scale structures you have all a single scattering. So one electron as the scatter from the black atom goes to the one of the surrounding atoms and then comes back. So this is just for understanding or convenience I am talking about this is all available in this book which is effort to you.

So this kind of scattering actually are reflected in the x that is why in x, c, e, l, f, s, only very small meaning of the present, but in case of e, l any as you have large minima or maxima So these signals are not so strong but this signals are quite strong as fine can be used to determine then states of manufacture. But warning time information which are there in the x, c, e, l, f, s is not so clear. It is still under investigations or this has to be done.

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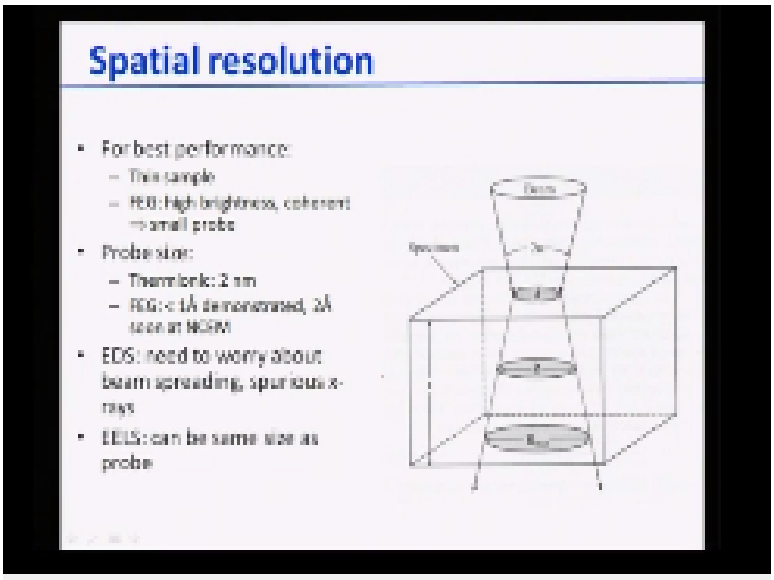

Well after give you lot of things about the different kind of information which EELS can generate. We need to talk about what is the kind of the solution we can get, or what is the kind of species we can get now a days, costly microscope come up with very nice beam, trope, stable beam, but still for the best performance you need to have very thin specimen, because the more thickest specimen the lesser and that can mask the information which are coming out from the electrons which EELS catering to the sample.

We also need to have electron gun of FEG diabetes filamation gun gives you very high brightness of the beam and coherent. Because energy spread of the electron on the filamation gun is very small. So therefore and also because high brightness. So you can also have a small probe and normally the FEG has a probe size is less than now a day's possible about two Armstrong. So we can actually obtained resolutions of that level. This is what has been shown suppose the beam which is focused on the sample of diameter T and then once this possible sample, you can see spread increases.

So therefore resolution actually not only depend on this size, that also this size so that is why we need to your find probe. So this size is to find out that is what I am saying and incase of thermionic commission emission like for 11s the probe size what are some larger, so therefore you cannot get kind of information which you would like to get for the microscope when you analyzing the samples. Second important which you also like to know when you are doing.

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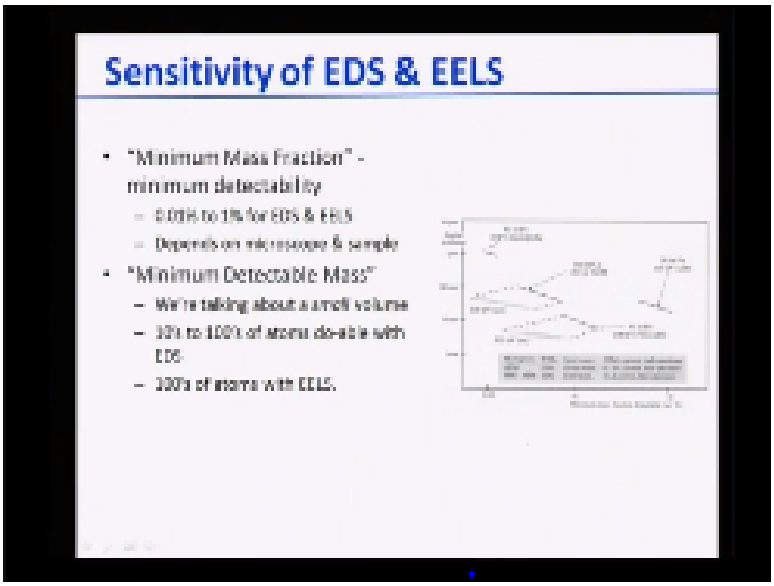

Such a kind of investigation in the sensitivity of the hills as suppose to EDS and sensitivity means if I have a element suppose 0.01% can I detect. All well set and done EDS cannot detect an elements or other resolution of EDS actually the sensitivity EDS is very poor in the element percentage is as well as 0.01%. So the minimum detect will mass in case of EDS is 10s to 100s of atoms but ethic is very large. It is to be 100s of atoms.

So that is why the EELS actually better and so it depends on microscope sample. This is what has been shown here minimum mass detectable with percentage possible special resolution. You can see here this is the very large probe size, but you have a detectable EDS very small. Let me you can detect 0.01% of the mass, but here you can detect only 1%.

So in case of magnetism copper actually about 120kw analytical electron microscope This is what is the case, but in case of FEG that basically you can have very small probe size and you can also have minimum mass fraction as slow as less than 0.1 so that is why we use always FEGs. FEG means filiations gun electron microscopes.

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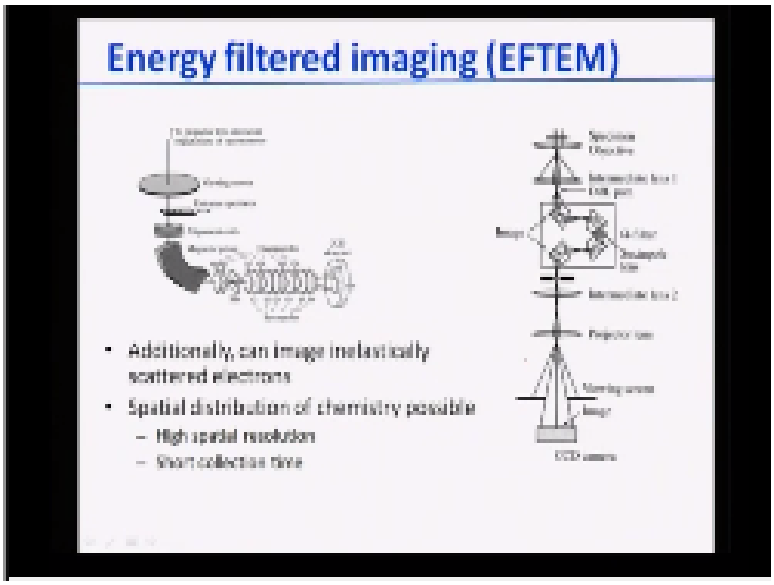

The last thing which I am going to talk about is energy filter imaging what is known as EFTM. As you know the electron which is coming out from the sample which inelastic scatter the contains all the chemical informations I showed you that high element presents what is called amount able element present, we can also do that the electronics state. So why cannot use this electron maps actual image. So that knows filter imaging.

Obviously if one needs to map properly you need to filter the electrons which inelastic scatter depending on the transcripts levels. So I will tell you how it is possible as a slides shown so what is done here this is symmetry map and in spectrums and there are basically. This is what sample is sitting here, this is and the energy inelastic electron passes to the then some alignment then it passes to six quarter poles and six poles follow finally we get a So we can actually map this electron alignment, that is what I am trying to say and that can be done as I said by energy filter.

So what can be done actually at the change of my configuration in a microscope associate this is the specimen this is objective lens and there are all intermittent lens and then one this things are coming out from the intermittent lens it passes through this kind of set of which is known as lens gamma filter is pertinent by compression user and they can split actually the inter scatter electron and different analogy levels.

They can filter actually and then it can passes to set of all lenses and then you can get image. So that means you have mean to attach this part inside the electron microscope to obtain is kind of

energy filter imaging. That is what I am to say. So that means extra cast basically you have to add these filters within the columns to get as a filter imaging.

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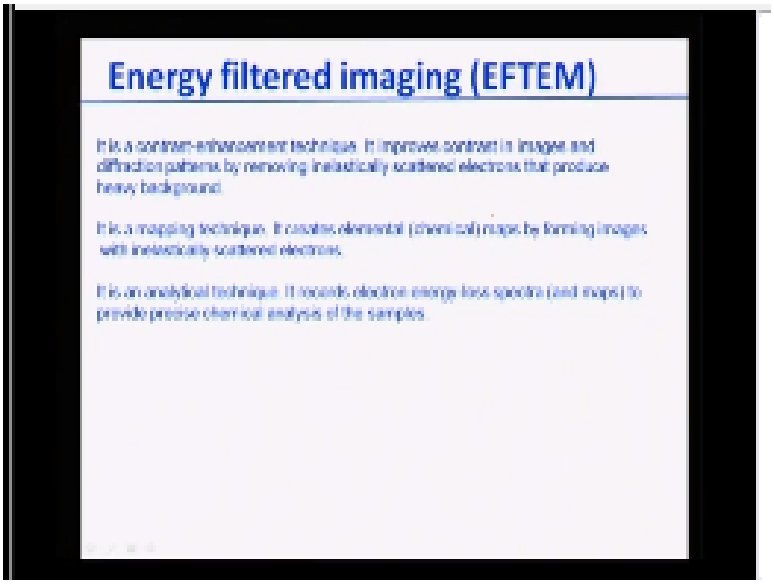

Let us see how this is basically done. It is nothing but a contrast enhancement technique as I said. It improves the contrast images also diffraction patterns by removing the in elastically scattered electrons that produce heavy background. That is the first thing. It is also a mapping technique. So first thing you can do is that you can remove the inelastic scattering unit you can block them all of them. You can only have image produce by inelastic scattering electrons. So that way the quality of the image or contrast of image will be improved.

There is the first thing one can do. Second thing one can do is used to mapping EDS can used some mapping technique. So this is also can be used to create elemental maps by falling images

with inelastic scattering electron particular energy levels. Also this is analogical technique, it can records electron energy low spectra or even maps to provide precise chemical analysis of the samples. So this actually and official and EFTM can do.

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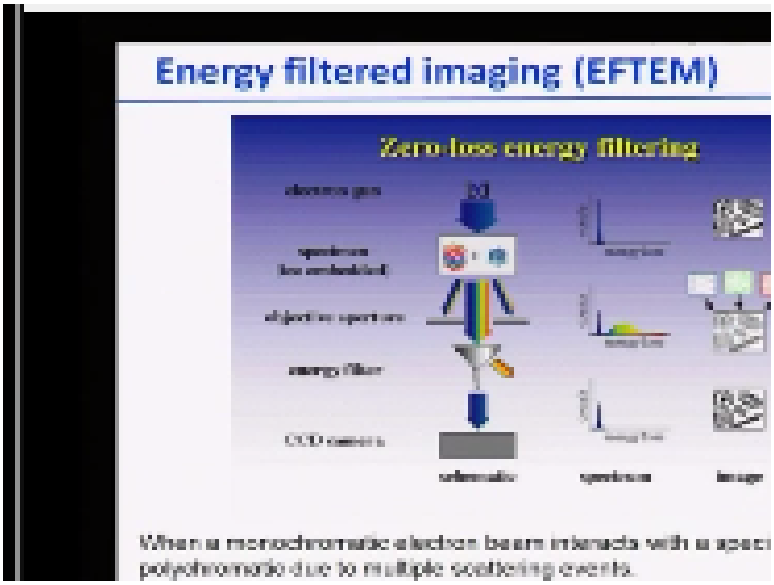

So first thing I will show probably the first example, and this is I think to no need to show you, this is actually exactly what stand I will show only to you. So let me skip and in energy electromagnetic prism is needed to separate the resultant wavelengths.

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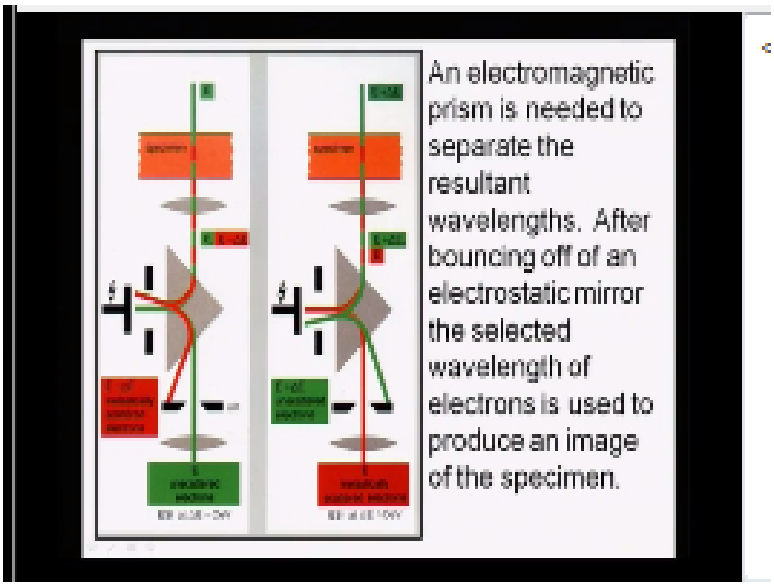

That is what is done here. You see this is the energy loss. This is what is called scattered inelastic scatter. So therefore you can separate them and therefore you can put the filter. If I just put if I allow only this inelastic scatter and then I can basically get nice image is contrast analyzing if I only this wants in elastic scattering electrons that I can get much other information. That is what I am trying to say.

So can use a presume electron electromagnetic prism extra which is nothing but omega filter and to separate them out in fact one can actually take this inelastic scatter electron and then separate them. I will depending on energy levels. That is also possible.

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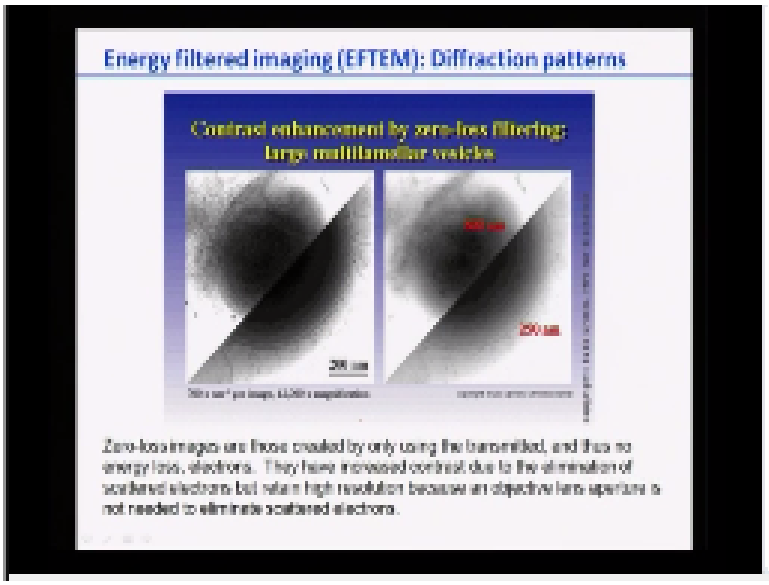

So let us give me some examples this is taken from biochemist and as you see here this is basically zero loss contrast analysis by zero loss filtering and you see once this is original image. This is after the filtering, so you can see there is huge change from the contrast. I do not know whether it can be seen on the screen. But I release for the image I can see this lot of other features of managed and you can see when the diffraction but on quality has improved. So you can always claim that using EFTM we can analysis create that images and diffractions part on it.

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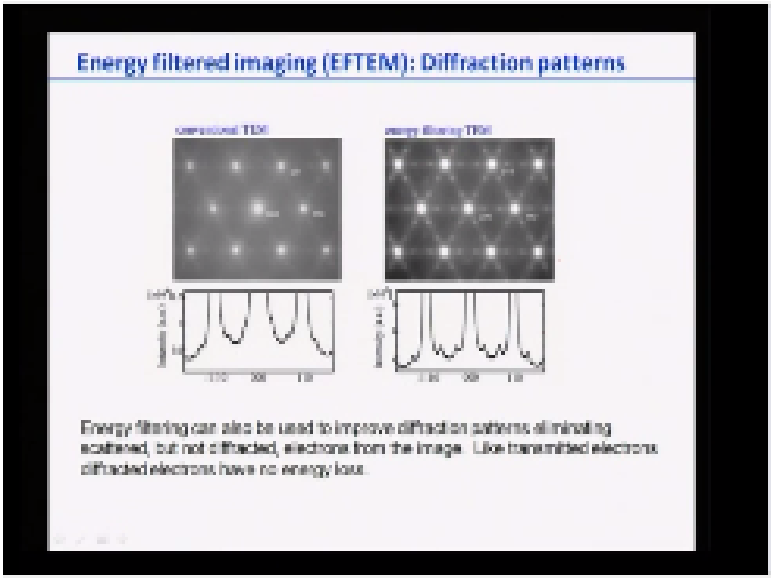

To give some more information how energy EFTM can be used whether diffraction patterns. This is the conversional TM. We can see this passing through this and once you map the intensity you can see this kind of broad things and also followed by this small pins, but once use EFTM we can enable this small pins what is see here.

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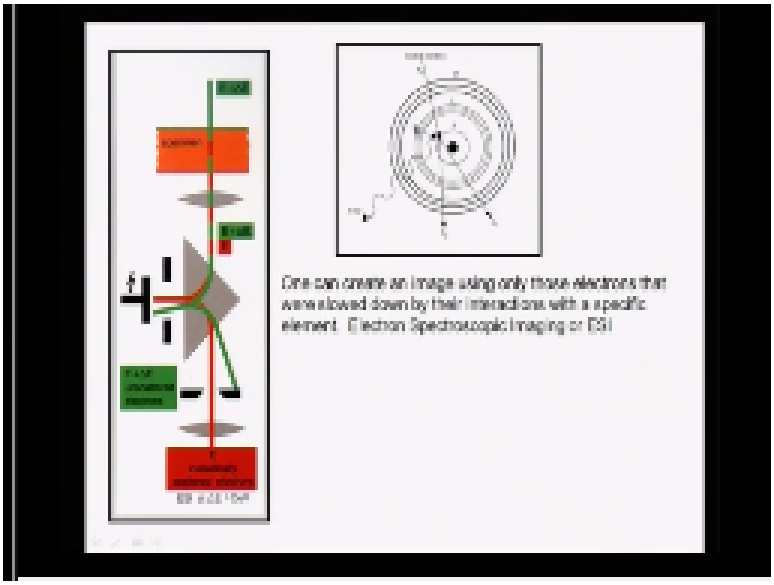

Is very clearly change on electron diffraction pattern this bright as parts of the surrounded by six week which is not visible there. So that is why we can actually you can improve the contrast of the electron diffraction patterns which is not possible use of that. So here we have removed all the inelastic scatter electron by using the prism. Well one can actually create an image using that electron that is slow down by the interaction the specific elements and they all inelastic scattering spectrum that is what I showed here.

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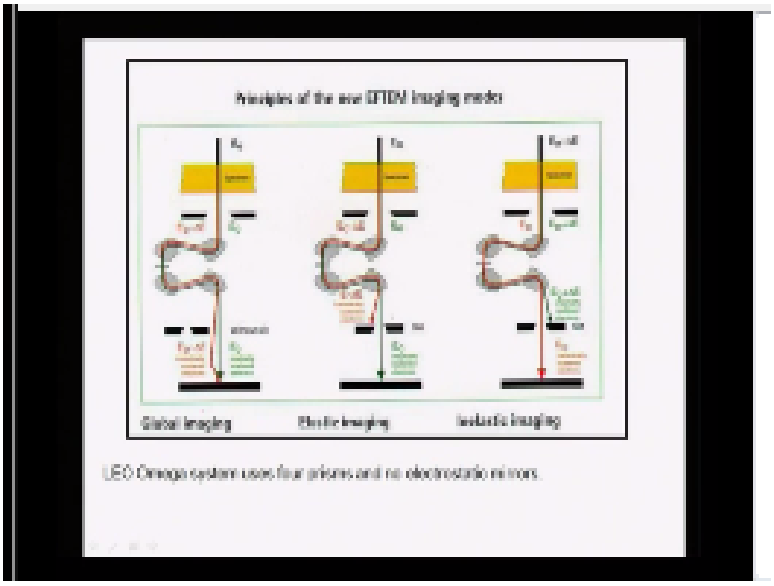

So basically it is saying inelastic scattering electron which are produced image and this is accomplish by using increasing the extending voltage of TM one can go actually after 1000AV, what is done here is simple like this. This is the global imaging sector this is what is the quarter pole gamma filter, omega filter.

So you have specimen electro magic comes energy loss and then is passes through that and then you can basically have elastic scatter electron which basically without slit. So if you use a slit you can separate them out nicely. This is what is actually done in a omega filter.

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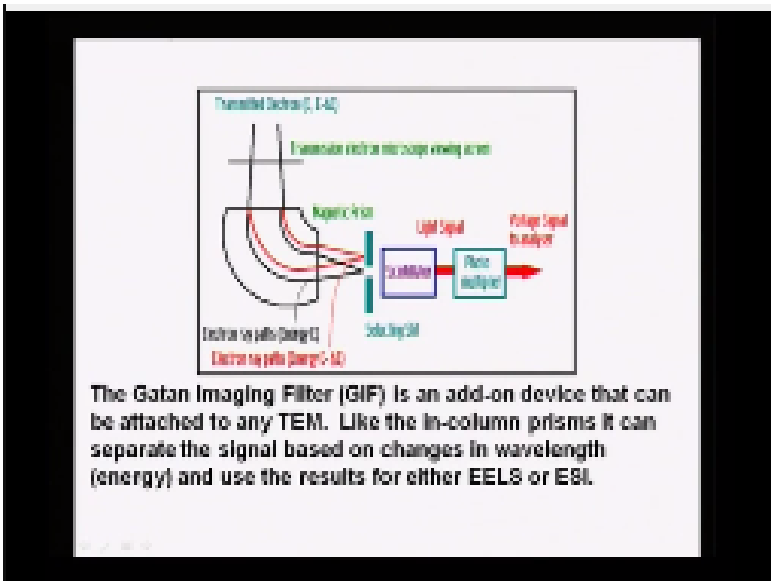

And one can use different kind of filter there is no need of showing that it is gating imaging filters. We have also filters even making different filters.

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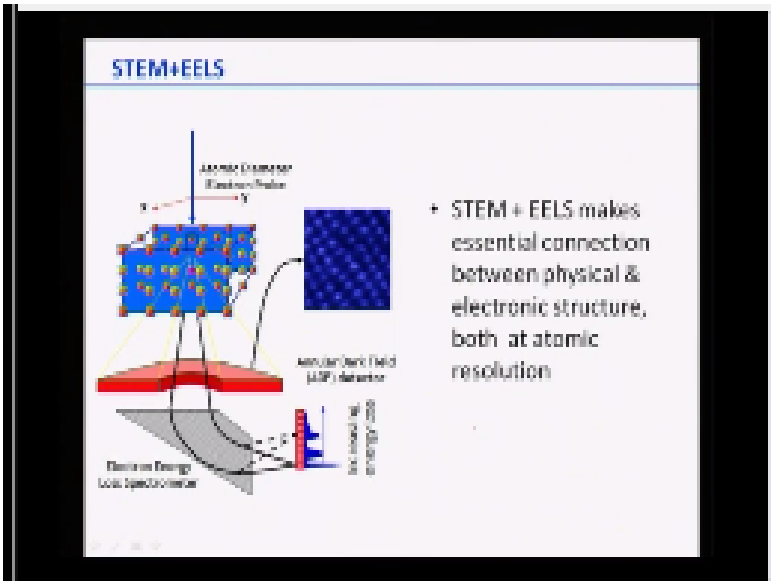

Last things which I am going to show you is called STEM EELS. STEM EELS in a sense that it can be used to determined that particularly atom present in the high lesion are microscopic actually what is done is let me tell you that suppose this is the atom gas mannum certain compound elements or let us a compound that because of different colors atoms. So you have a electron falling on to that and then each atom has different scattering power. That depends on the atomic electronic configurations.

So depending on this scattering power electron they will get scatter different angles. Now if we applied an analog detector like this is a central hole, this like this central hole and this is the detector. So if analog detector I can collect the electron I means scat electron coming a different angles from the incident beam. This like that which is scatter sample. The sample is here. And once I correct that and I know the different atoms different scatting power. So therefore I can actually image the atoms in a microscope. At the same time if I take EELS each of this atoms I can detect what atom is presents.

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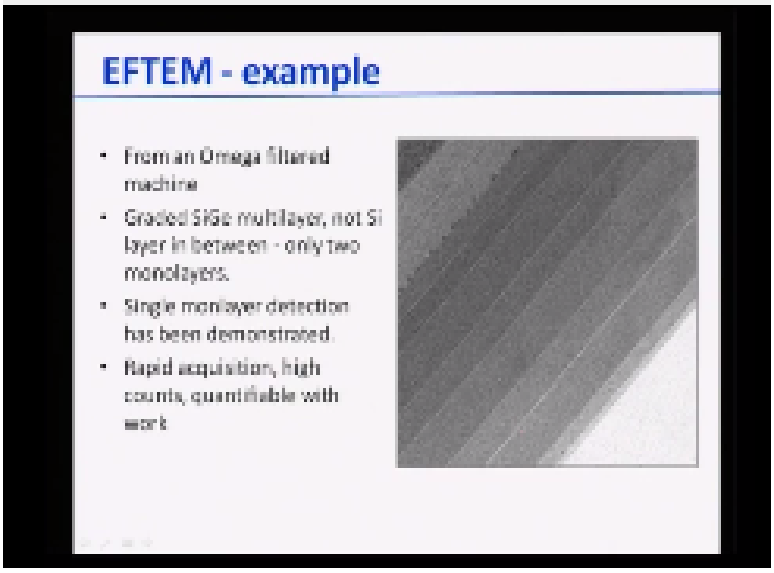

If I use so lf a energy that means if I all allow the energy loss to do so lf are atoms in the EELS spectra and then image that so I can see that all these are getting brighten up. You can see here. You can see there. So you can see there, so that means indeed sulfur items are presented boundaries. So that means our postulation that Pieria can be proved by this way. This is not published in the repeated journals.

So one can actually look at details part, It is possible to take a certain kind of issue and then to the energy filter imaging and show that these are actually true. Well, what I am going to ask you actually do much better thing. This is again taken from our minute work or our own examples. These are actually in a particle created when you have aluminum , nickel, cobalt So they create this kind of crystals and you can see these are actually nickel cobalt FCC and you know nickel cobalt has almost in atom nearby.

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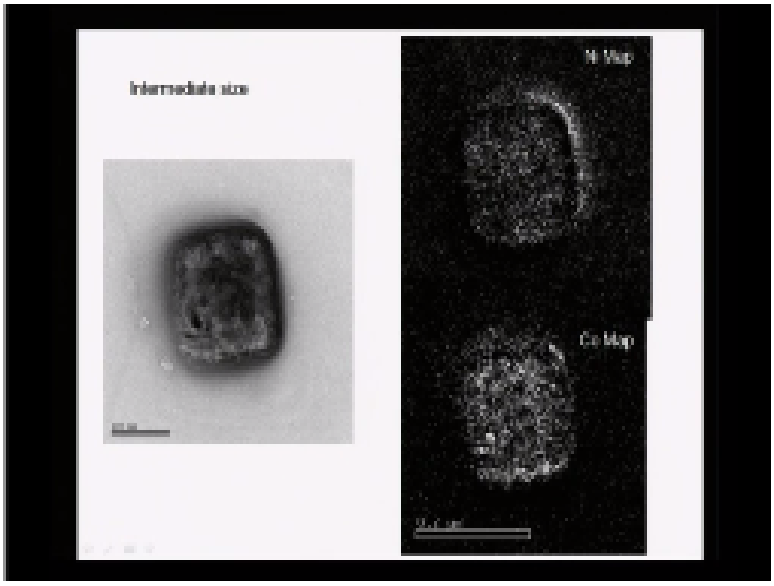

So it is very difficult to say that nickel or cobalt present in this particles while EDS analysis. So only we can show is by using EFTM mapping. So you can see this is a big size particles even more than 100 nanometers quite close to 250 nanometers. You can map nickel and cobalt in this and if you look at carefully the nickel is much less in this particles then cobalt.

Cobalt map shows much better is in the nickel map and if I do it to a functional size, suppose you can go into intermediate size, you can see still nickel quantity is less than the cobalt in those particles, if you do the nickel and cobalt. It is impossible in EDS actually, you cannot do that, because they are atom nickel and cobalt atom numbers are nearby. If you got a very small particles you can see look at this one nickel and cobalt distribution almost to uniform. You may ask me what the need of doing this.

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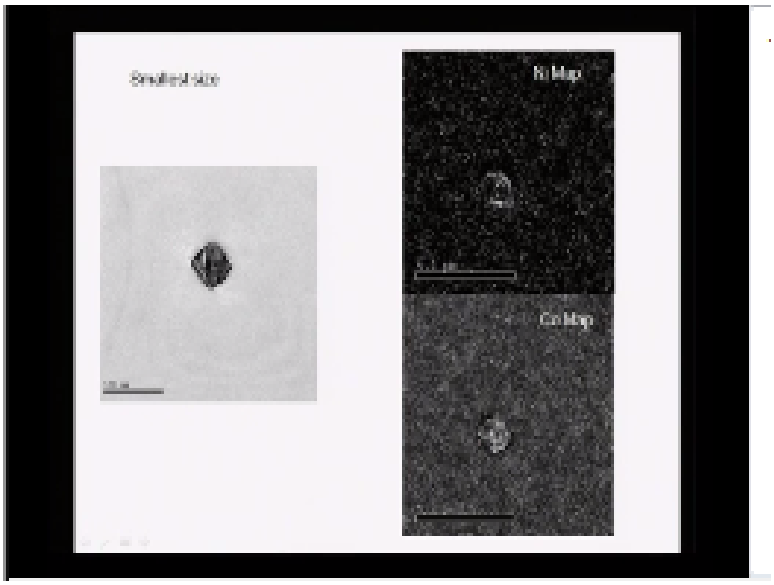

Well, as you know these small particles which is nickel and cobalt antibiotic they used those particles are depend on the distribution and also the atomic the electron structure. So by using this one can actually obtain all kind of information and then use it understand a acrobatic wave of this. This is what is our aim also to do that but I am showing a part of the work.

So by this way if you can actually go down to very small particles which is actually approximately about nickel and cobalt This is not so good, but still you can see cobalt is almost same as the nickel. So by this way we can actually do all kinds of analysis. So as I say that some time in the lecture that I will tell you detail comparison of the EELS and EDS.

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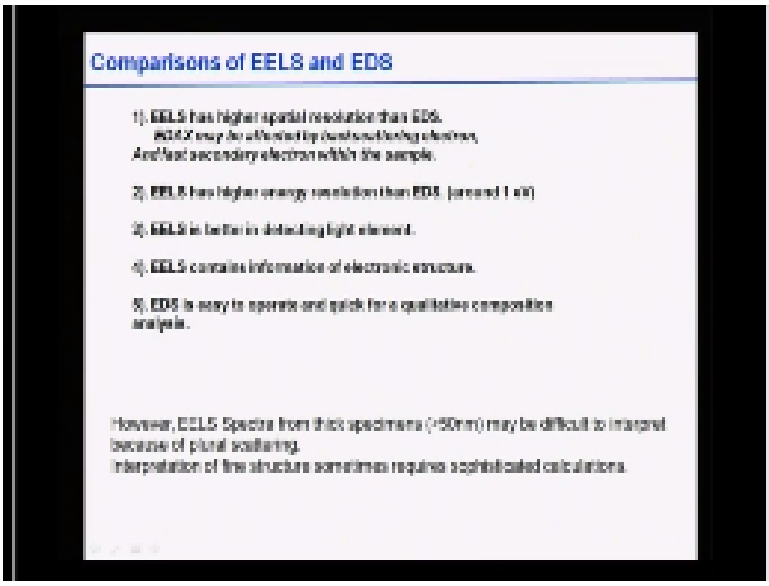

Well EELS has specialization as EDS. EDS may be affected by EELS has a high energy revolution than EDS around one electron pole EELS is better integrating elements than EDS. EDS can be used to detect elements which are EELS contain information of electronic structure we does not content, EDS is easy to that is why everybody use this and quick for qualitative analysis intermittent, because of the scattering which has shown you.

Interpreting of fine structure sometime requires software lot of sophisticated calculations which I could not show you because the time constant. So with this I conclude this lecture, next lecture I am going to start with the surface catenation techniques mostly XPS and move on.

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