Nanostructure and Nanomaterials: Characterization and Properties

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Lecture - 41
EELS
Electron Energy Loss Spectroscopy

In this lecture, we learn about electron energy loss spectroscopy. So, the overall thing what we can see is electrons energy loss and spectroscopy.

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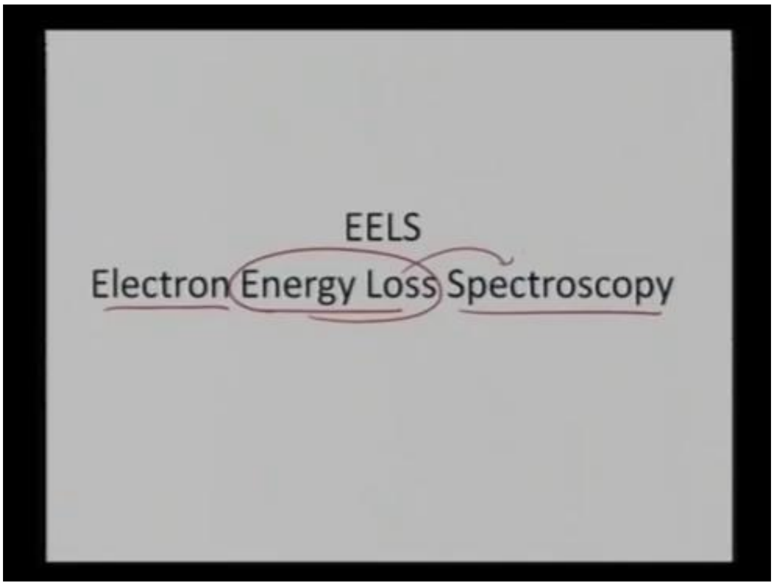

EELS

Electron Energy Loss Spectroscopy

So, in this particular case we incident a particular electron been of known energies of known kinetic energy and we let it interact with the material. Depending on how much energy is being lost from that we obtain a particular spectrum to comment on the maybe of the chemical nature or the electronic stake state of the directive state particular material.

So, in these particular characterising techniques EELS we call it electron energy loss spectroscopy. We allow a particular known set of electron energies known kinetic energy of electron we are literally attracted to the material. We see how what is the overall loss energy loss is occurring because of certain vibration modes or some elastic scattering to attend a particular spectrum.

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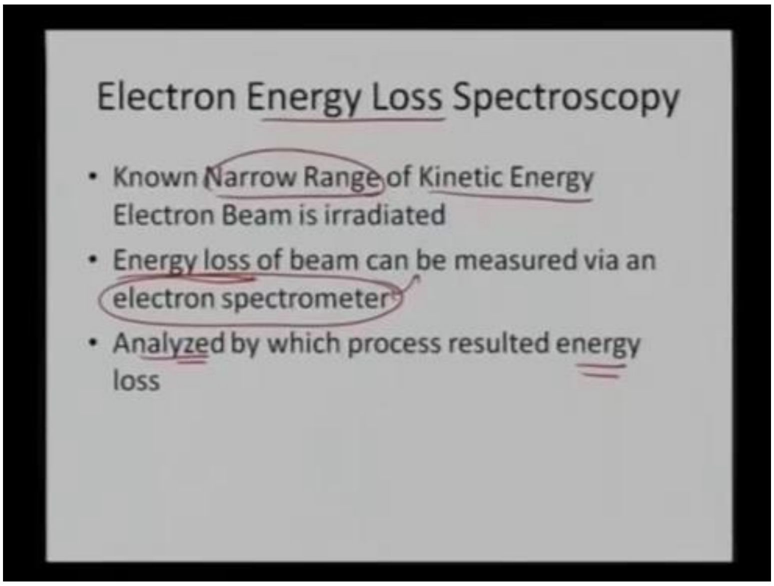

Electron Energy Loss Spectroscopy

- Known Narrow Range of Kinetic Energy Electron Beam is irradiated
- Energy loss of beam can be measured via an electron spectrometer
- Analyzed by which process resulted energy loss

Since the overall term is energy loss it means that the electrons are interacting in elastically, so there are certain losses. So, it is not an elastic interaction, but more or less like a inelastic interaction with the material result, certain scattering. In this particular case, we allow a known narrow range of kinetic energies, so in this particular case we take particular known spectrum. So, we use a we can utilise such a cylindrical mirror analyser, so we can allow only a certain range or narrow range of kinetic energies to pass through the channel.

Then, once we have that known narrow range of kinetic range of electrons, we can let it interact, we can bombard those electrons on a samples office. Then, we can measure the energy loss of a beam via this electron spectra metre, so once we attain this is a incident energy of the electron. Later on, after it has interacted with the material we can attain a overall electron spectrum from the interaction of electron with the sample.

Then, we can analyse that which all processes have resulted this particular energy loss, so the known energy of electrons bombard on a sample then we measure the output energy. So, the difference in the energy or the loss of energy is now being analysed from the processes, which are responsible for that particular loss. So, then those particular process can let us they can let us know what all interactions are recurring and what is the characteristics of a particular atom or the dilative nature of the material which are causing this particular losses.

From those information we can comment on many of the structures, it can be compositional it can be dialectic it can be ionisation. So, we can comment on those particular aspects of a particular material by using electron energy loss spectroscopy.

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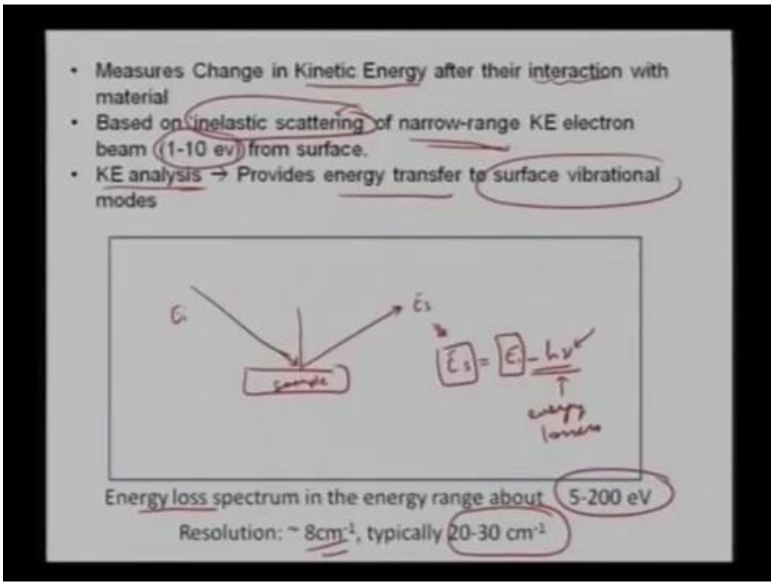

- Measures Change in Kinetic Energy after their interaction with material
- Based on inelastic scattering of narrow-range KE electron beam (1-10 ev) from surface.
- KE analysis → Provides energy transfer to surface vibrational modes

Energy loss spectrum in the energy range about 5-200 eV

Resolution: ~ 8cm^{-1}, typically 20-30 cm^{-1}

So, in this particular case we are measuring the kinetic energy after they have interacted with a material and it is definitely based on the inelastic scattering because we are worried about the loss, the electron energy loss which is occurring after the interaction. That interaction of measuring via supplying and on the narrow range of kinetic energy of electron and that energy range is between 1 to 10 electron volt. Then, again we are analysing those kinetic energy and that will provide us the energy transfer which is happening because of certain surface vibrational modes.

So, depending on that we can attain different kind of scattering with the material, so in this particular case what we can that is we have a sample we apply certain sort of energies to interact with the sample. Again, these interactions can be specular or off specular and then once we get this particular spectrum particular scattering in certain cases. So, we have incident energy and this scattered electron, so what we can get finally, is scattered electron is equal to e i minus certain losses, which have occurred h mu.

So, we have the overall energy of the electron which is coming after interacting with the sample, so we have sample here with this the incident so incident energy minus certain energy which is now been absorbed by the material. Those are nothing but the energy loses so that is what we are interested in this particular term how much energy is being loss. So, we can define them that how much energy is now loss because of the inelastic scattering and that energy is responsible for the surface vibrational modes and that can give us much more information about the overall loss spectrum.

So, in this particular case, we have energy loss spectrum which is running between 0 to 5 to 200 electron volts and typically the resolution is approximately 20 to 30 inverse of centimetre. In certain special cases, the resolution can be as better as 8 centimetre inverse, so that is what we can get from the EEL spectrum.

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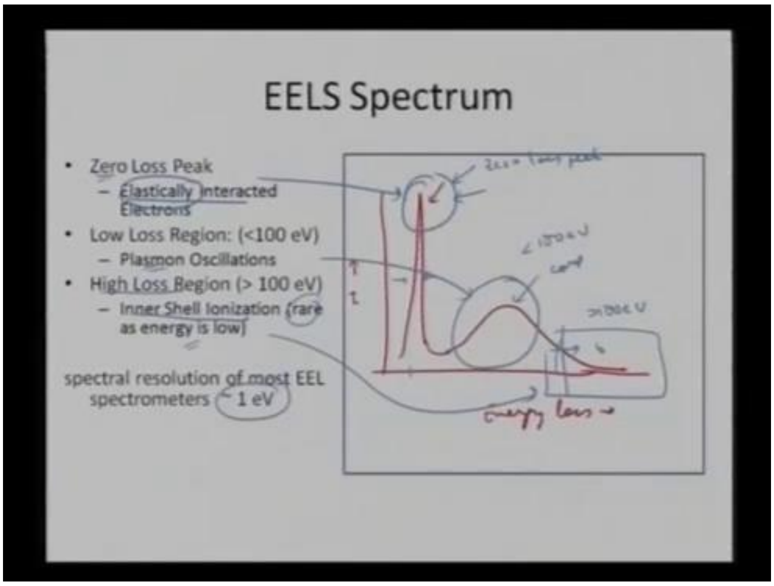

EELS Spectrum

- Zero Loss Peak
  - Elastically interacted Electrons
- Low Loss Region: (<100 eV)
  - Plasmon Oscillations
- High Loss Region (> 100 eV)
  - Inner Shell Ionization (rare as energy is low)

spectral resolution of most EEL spectrometers ~1 eV

Again, the EEL spectrum we see a typical spectrum which appears more like this the initial a we have a 0 loss p. Then, it is followed by a certain valley and we have the first p and then we have high loss region so in this case we can see energy loss along this side, this is the intensity of the frequency. So, first what we see is nothing but the 0 loss p, so if we can come to the 0 loss p, so this is a 0 loss p and in this case we are achieving the interaction of electron which are elastically scattered. So, there is no loss there is no loss of energy s in this case the overall electron energies same as that of incident electron.

So, in this case this is called as a 0 loss peak because electrons are coming back coming back after their elastic scattering after their elastic interaction with the material can they result the 0 loss p. So, this is the of this particular 0 loss p will tell us about the resolution of this particular ell spectrum and then later on we have low loss region which is consisting, comprising of this particular region. This case we have energy loss less than 100 electron volts and this is basically dominate by the plasma on oscillations. So, once we have some plasma on plasma on oscillations or those of interactions which are occurring because of the polarisation of electrons in a particular in a particular area.

So, those particular interactions they are very rapid and those can be captured easily via ell spectrum whereas, 0 loss p comprises mostly the interactions. So, those basically tend to ate up the material and those energy losses are very fine less than 0.2, 0.3 electron volts. So, those can be detected by the EEL spectrum, but this plasma on oscillations they can they appear in the low less region and from that we can detect much more of the dialectic nature of composition of a particular material. So, the first p the 0 loss p provides like the resolution of the EEL spectrum the low loss region provides one of the composition or the dialectic nature of a particular material.

In the high loss region we have greater, than we can call it greater than 100 electron volts or greater than 50 electron volts. We can get a spectrum which tells much about the bonding or the ionisation structure of a particular material, so in this case we can see initial ionisations which is rare because energy is low. We can see those spectrum very easily in the high loss region around this side, so we see high loss region we see a low loss region and we see a 0 loss p in the EEL spectrum. Generally, the resolution spectrum resolution is generally approximately one electron volt this particular spectrum.

We cannot really measure which energy losses when they are lesser than 1 electron volt such as losses they comprise between 0.2, 0.3 electron volts, so that can be related detected by the EEL spectrum.

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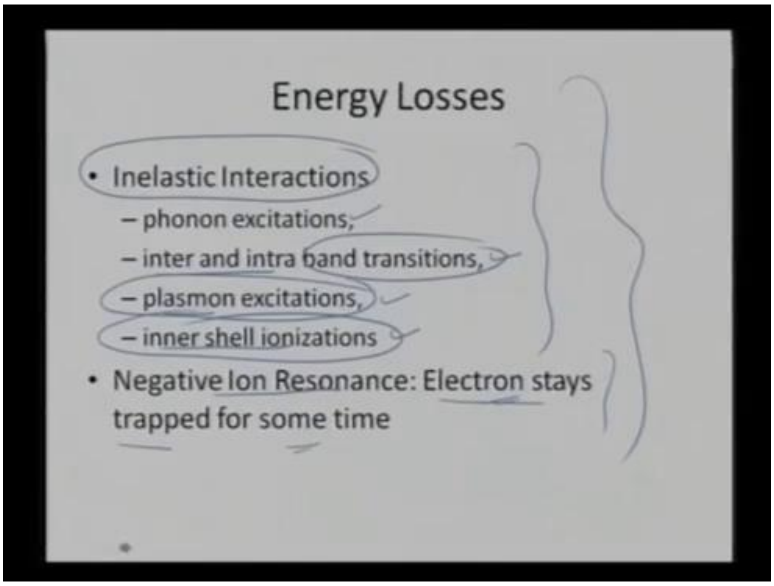

Energy Losses

- Inelastic Interactions
  - phonon excitations,
  - inter and intra band transitions,
  - plasmon excitations,
  - inner shell ionizations
- Negative Ion Resonance: Electron stays trapped for some time

There were a variety of manners in which a energy can be loss and those all have to be in elastic interaction because some emery is bring absorbed by the material. So, we can have excitations we can have inter interval transitions we can also have plasma on oscillation excitation we can also have initialisations and at the same time we can also have some negative ion resonance. So, excitation means that we are allowing some lattice vibrational and those tend to heat up the material and the energy losses are very low.

In this particular cases, we can also have inter and intra vent transitions, so in that particular case we can have an electron jumping from one shell to another shell or higher shell to another shell, then even between two different items. So, that is nothing but the inter and intra vent transitions and within a particular shell there can be some transition between the two p 1 2 p 2 3. So, that part can also happen with an inter intra vent transition we can also have some plasma on excitations that means the localisation or the polarisation of the electrons in a particular entity.

Then, that can also lead to the absorption of energy we can also have some initialisation we can allow electron to get ionise an atom to get ionise by release of an electron at the same time we can also see certain negative. In that particular case we can have certain different transitions which can allow electron to stay much for much longer time in a certain molecular orbital.

So, electron will sit state trap for certain time, so it might appear that energy is being observed for a certain duration of time. So, these are certain energy loses which can occur and those can be an incorporated in the EEL spectrum, but the on these are the losses which are basically contributed into energy loss spectrum. It does not mean that all the losses can be easily visualise such as losses they can be really resolved in the EEL spectrum.

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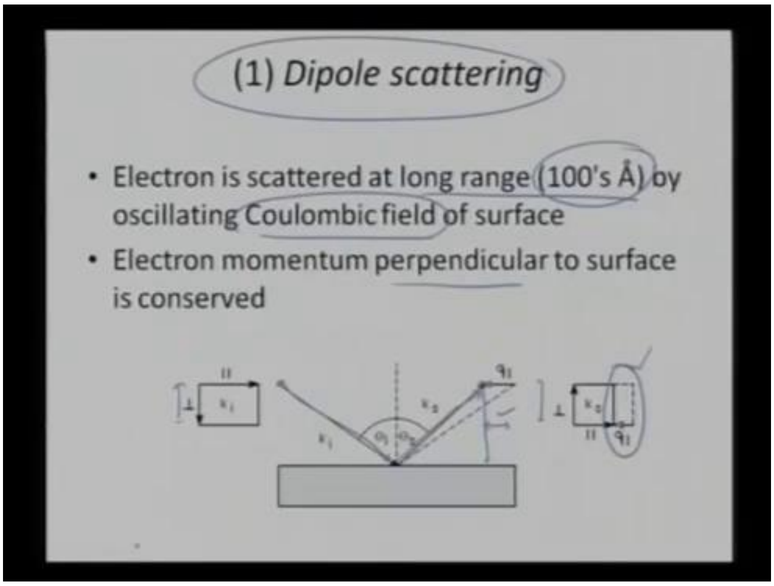

(1) *Dipole scattering*

- Electron is scattered at long range (100's Å) by oscillating Coulombic field of surface
- Electron momentum perpendicular to surface is conserved

Again, there can be variety of scattering which can occur in this case in the dipole scattering, we have a scattering to a long range hundreds of Angstorm via columbic strong columbic field. So, if electron is coming interacting with the surface and it goes of via certain loose lose in the momentum in the vertical, in the horizontal direction. So, in this particular case the perpendicular momentum is now conserved, so we can see that the perpendicular motion is now conserved.

So, we have the similar perpendicular plane, but the horizontal part is basically being lost, so horizontal momentum is basically being lost, so that part we see how a here or so much energy is being observed by the electron in the horizontal direction. So, in this particular case in the dipole scattering we can achieve scattering in case of a because of columbic field. In this particular case, we have the retention of the k, momentum in the perpendicular direction, but there is loss of momentum in the horizontal direction, it is happening because of the columbic field of the surface.

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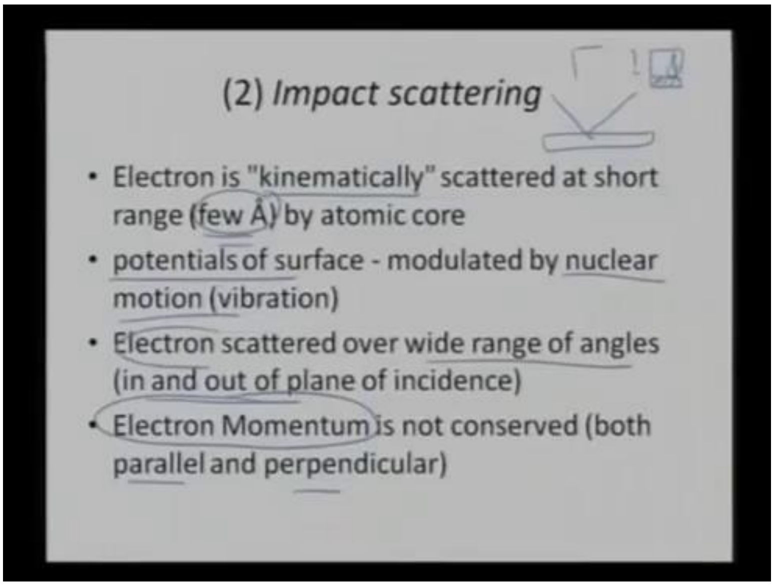

(2) *Impact scattering*

- Electron is "kinematically" scattered at short range (few Å) by atomic core
- potentials of surface - modulated by nuclear motion (vibration)
- Electron scattered over wide range of angles (in and out of plane of incidence)
- Electron Momentum is not conserved (both parallel and perpendicular)

It can all attain certain out of plane scattering can also occur and in this particular case we have kinematic scattering. That is only for a shorter range in couple of samples, but in this particular case when an electron is basically interacting with the material, it is losing both perpendicular as well as the horizontal momentum. So, in this particular case we whatever the distances we had momentums, we had in the horizontal and vertical direction those are basically being lost in both the cases. So, we have some extra loss in this part as well as some extra loss in the vertical direction, so we have loss in vertical direction as well as some loss in the horizontal direction.

That occurs because of certain strong nuclear motions or vibrations and that results some potentials on the surface and because of that electron gets scattered over wide range of angles. So, angles are much wider, but they are at short ranges few, so they go in and out of the plane of incidence and we are not able to retain the electron momentum in both the direction, which are both parallel in the perpendicular direction.

So, we had dipole scattering and that we were able to retain the momentum in the perpendicular direction, but because of impact scattering those occurring because of the nuclear motions or vibrations. In the particular case, we achieve very wide range of angles, but for a shorter distances and in the particular case we destroy both the perpendicular and the perpendicular in the parallel motion or the momentum of the electron.

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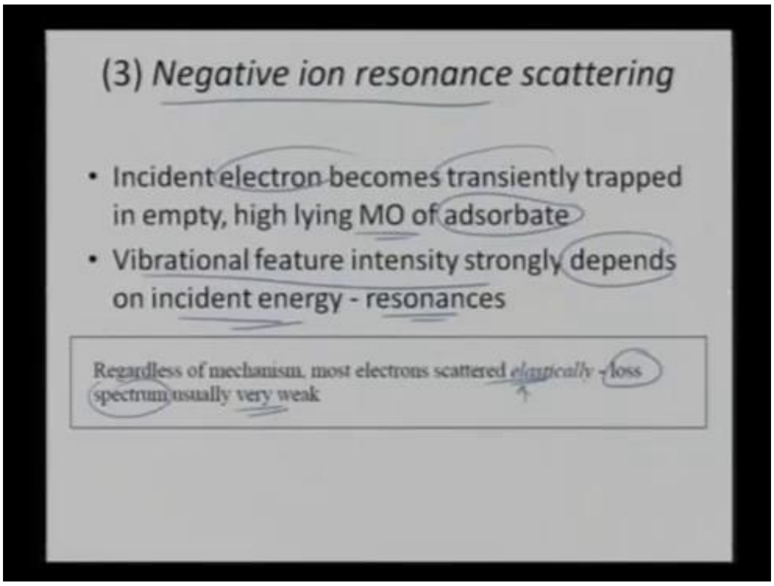

(3) *Negative ion resonance scattering*

- Incident electron becomes transiently trapped in empty, high lying MO of adsorbate
- Vibrational feature intensity strongly depends on incident energy - resonances

Regardless of mechanism, most electrons scattered *elastically* - loss spectrum usually very weak

Again, we can also has so negative and in that particular case we can reduce some impurities and those basically induce some molecular orbits also that can come because of the edge of it. So, we have incidental electron, it interacts with the sample, but since then there are some, which are present on the surface of a particular sample, they generate some extra molecular orbitals.

As a result of that, the electron can stay trapped out there, electron can stay transiently trapped on those particular empty high line molecular orbitals and because of that some energy is being basically utilised out there. That vibrational feature intensity strongly depends on the incident energy or which causes the resonance, so that is also happening, we have dipole scattering. We had impact scattering and we can also have negative resonance scattering and that particular case were able to have the electron being transiently trapped in certain molecular orbitals for certain duration of time.

Though these are some lost features most of the interaction is occurring elastically, so we get the strongest peak is coming out because of the elastic interaction and that basically takes care of the 0 loss peak. So, basically our overall spectrum of the loss spectrum or the overall loss spectrum is generally very weak because major of the phenomena, they are occurring elastically. So, that is a reason our spectrum which is coming out as a loss spectrum it is generally very weak. So, eventually our detection system has to be strong enough to be able to detect that weak spectrum and comment on the overall nature or the structure of the composition of the sample, so that is what the overall field of EEL spectroscopy is.

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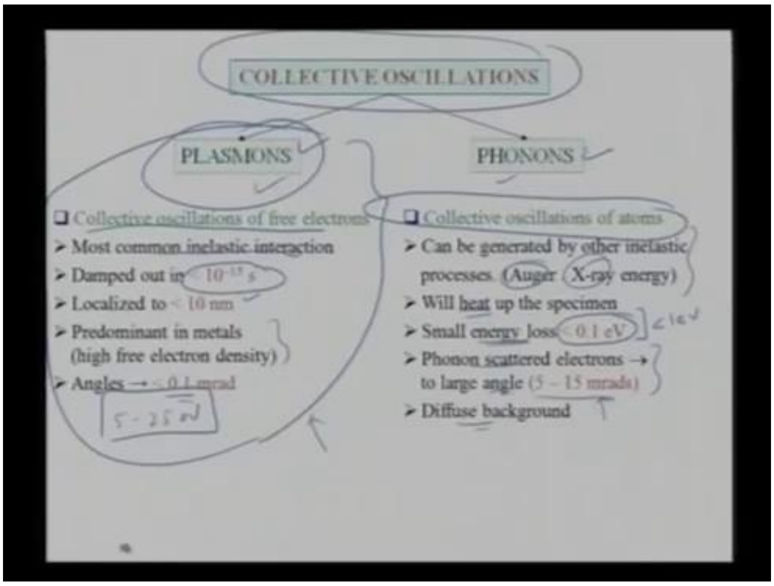

COLLECTIVE OSCILLATIONS

PLASMONS

❑ Collective oscillations of free electrons
- Most common inelastic interaction
- Damped out in < 10^{-15} s
- Localized to < 10 nm
- Predominant in metals (high free electron density)
- Angles → < 0.1 mrad

5 - 25 eV

PHONONS

❑ Collective oscillations of atoms
- Can be generated by other inelastic processes. (Auger, X-ray energy)
- Will heat up the specimen
- Small energy loss < 0.1 eV

< 1 eV

- Phonon scattered electrons → to large angle (5 – 15 mrads)
- Diffuse background

Depending on what kind of an information we have, so we can see that we can have collective oscillations, they can come out either from plasmons or they can come out of phonons, so plasmons are nothing but the collective oscillations of free electrons. So, in this particular case we have polarisation of electrons and electrons are generally very free entities. So, they tend to we dispersed like in a metal matrix, so we have it is basically predominated metals when we have high density of electrons which are floating without any bound to a particular atom.

So, they are flowing freely on a metal surface and they cause basically the common most common inelastic interactions, but the problem with them is they die out very quickly in 10 to the power minus 15 seconds. They are also localise to less than in a metre and they basically are scattered to less than 0.1and there energy is approximately 5 to 25 electron volt. So, once they have energy much greater than 1 electron volt, these particular signals can be easily captured by the EEL spectrum. So, we can see that the plasmon loss is they rise because of the localise polarisation of the electrons because they arise from the collective oscillations of electrons and a very pre dominate in the metals.

So, because they have very high electron density and because their energy loss are in the order of 5 to 25 electron volt, they can be easily captured by the EEL spectrum. On the other hand, we can also have some phonon oscillations those are the collective as oscillations of atoms or they also arise because of the lattice vibrations and because of that tend to generate heat. They tend to ate up the specimen t and they can also be generated by certain other inelastic processes such as energy or the x ray energy and those can also cause the lattice vibrations or the oscillations of the atoms. The problem with them is they generally tend to have very low energy loss which is of the order of less than 0.1 electron volt.

Since that it is less than the resolution limit of EELS which is approximately one electron volt we are not able to detect all these losses in the EEL spectrum and the one more thing is that the phonon cancan get scattered to a very large angles to the order of 1 to 15. They can generally give a very high order defuse background in the case of phonon, so the collector oscillations they are limited to plasmons and phonons and plasmons. They are collective oscillations of electrons, whereas phonons tend to with the collective oscillations of atoms and depending on what kind of energy losses they have.

We can get a certain spectrum which can basically grab the particular picture or the density of electrons can be easily captured by the plasmon peak or the low loss energy low loss regime of the EEL spectrum.

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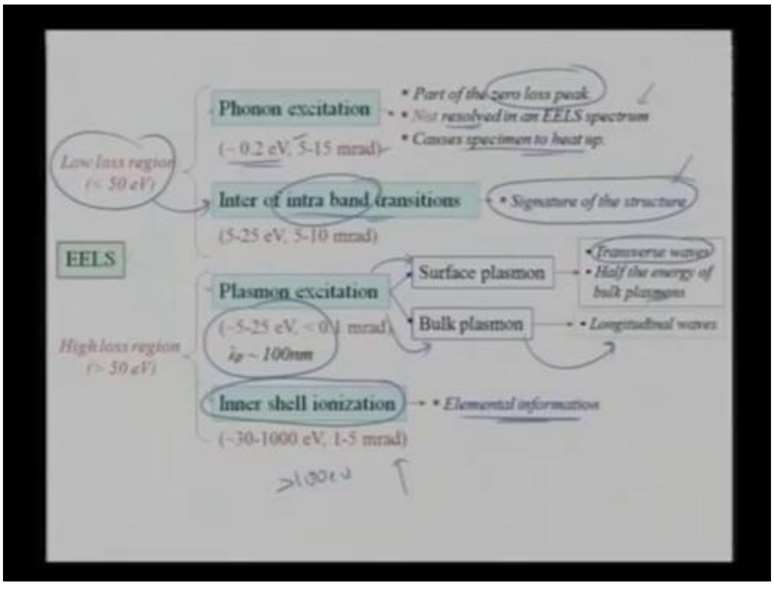

EELS

Low loss region (< 50 eV)

Phonon excitation (~ 0.2 eV, 5-15 mrad)
- Part of the zero loss peak
- Not resolved in an EELS spectrum
- Causes specimen to heat up

Inter of intra band transitions (5-25 eV, 5-10 mrad)
- Signature of the structure

High loss region (> 50 eV)

Plasmon excitation (~5-25 eV, < 0.1 mrad) $\lambda_p \sim 100nm$

Surface plasmon
- Transverse waves
- Half the energy of bulk plasmons

Bulk plasmon
- Longitudinal waves

Inner shell ionization (~30-1000 eV, 1-5 mrad)
- Elemental information

>100 eV

So, overall e can see that that our phonon excitations they are limited to 0.2 electron volt and they give out us a very diffuse background and they basically come out in the 0 loss peak. Since the overall energy loss is very low, they can’t get resolved and because of that, it can create certain problem in the resolution of the particular EEL spectrum, at the same time they tend to heat up the specimen t. So, anyway those particular things appear in the 0 loss peak and they tend to heat up the specimen t, then later on we can also have some intravent transitions and that can provide us a signature.

So, in the low loss region we can get some signals, which are basically between the 5 to 25 electron volt and those transitions can be easily captured, which can provide us a structure of a particular material and plasmon excitations. They can be limited either as a surface plasmons or as a bulk plasmons and the energy again comes in the low loss region and we can in the surface plasmons. We have basically the transfers waves which can provide, they are basically half the energy of the bulk plasmons and the bulk plasmon.

We generally have interaction with the interaction as the longitudinal way and this particular spectrum can be easily attain in the low loss region and later on once we have much higher loss. So, that is basically been created by the initialisation and that generally is greater than 100 electron volt and from that we can always attain a elemental information because we know what are the transitions or the ionisations which are responsible for causing this much loss of the energy.

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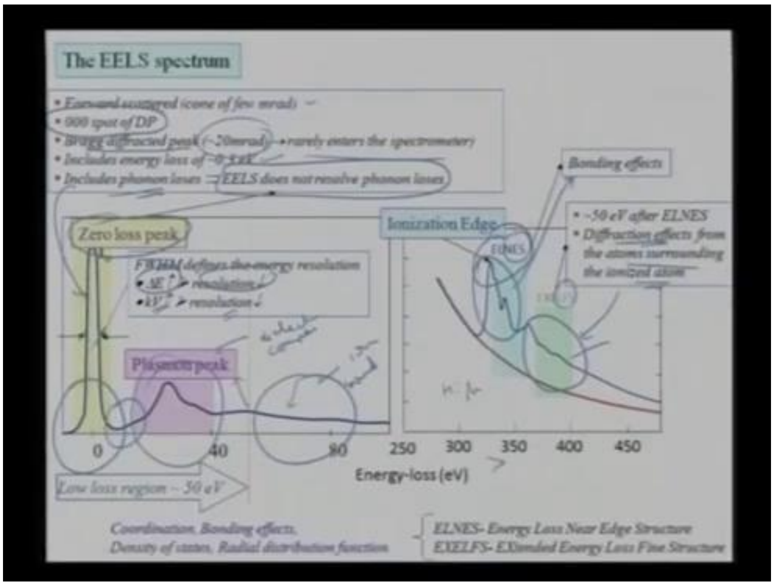

The EELS spectrum

- Forward scattered (cone of few mrad)
- 000 spot of DP
- Bragg diffracted peak (~20mrad) → rarely enters the spectrometer)
- Includes energy loss of ~0.5 eV
- Includes phonon losses ⇒ EELS does not resolve phonon losses

Zero loss peak

FWHM defines the energy resolution
- ΔE ↑ → resolution ↓
- kV ↑ → resolution ↓

Plasmon peak

Low loss region ~ 50 eV

Coordination, Bonding effects,
Density of states, Radial distribution function

Ionization Edge

Bonding effects

- ~50 eV after ELNES
- Diffraction effects from the atoms surrounding the ionized atom

ELNES- Energy Loss Near Edge Structure
EXELFS- EXtended Energy Loss Fine Structure

So, overall we can see that we have a zone distributed in three regimes, we have 0 loss peak 0 loss peak, basically it defines the overall energy resolution, higher the basically energy loss, the poor is a resolution because the broader. The particular peak is the poor the resolution will be and higher the k v, the poor will be the resolution and again this thing is arising. This thing is arising because of the format scattering which is to the order of a few and as we saw that the overall broadening is because of the phonons which basically give us give out a diffused pattern.

Again, this corresponds to more like the 0 spot of the affected pattern and again the blurred peak which are to the order of 25, they really enter the spectrometer. So, we have this much particular resolution which is now been the containing factor and this also includes energy loss of 0.3 electron volts which comes out from the phonon interaction.

So, though it is include into phonon losses, it is not able to resolve those phonon losses, so we can see that 0 loss peak. It is responsible for the overall defending, the overall resolution or the energy resolution of the spectrometer. Later, we have plasmon peak and then we have a high energy loss at peak, so again this is again the kind of a value before the plasmon peak and the information, what you can get from the plasmon peak is basically the overall dielectric nature of a material. So, we can get the overall dielectric nature of particular material and also we can find the composition, whereas the high loss regime can provide us much more information on the overall ionisation structure or the bonding.

Those ionisation are occurring in this particular high loss regime and then again we have energy loss which is near the edge structure this is the edge and we have energy loss near the edge structure. This regime is the extended energy loss structure, so we have either fine structure or nearest structure and again is it is in the high loss region and from this we can get much more of the bonding effects how is how is the overall bonding which is happening.

We can also attain overall the affection of effect which can occur from the atoms surrounding the ionised atom, so we can get much more information as either energy loss structure or as energy loss near the structure. So, we have a regime which we which is nothing but the 0 loss p and then we have slow loss p which is limited to 5200 electron volt and then we have high energy loss regime which is basically that. Either, it can be fine structure or the near edge structure and from that we can get much more bonding of the ionisation effects.

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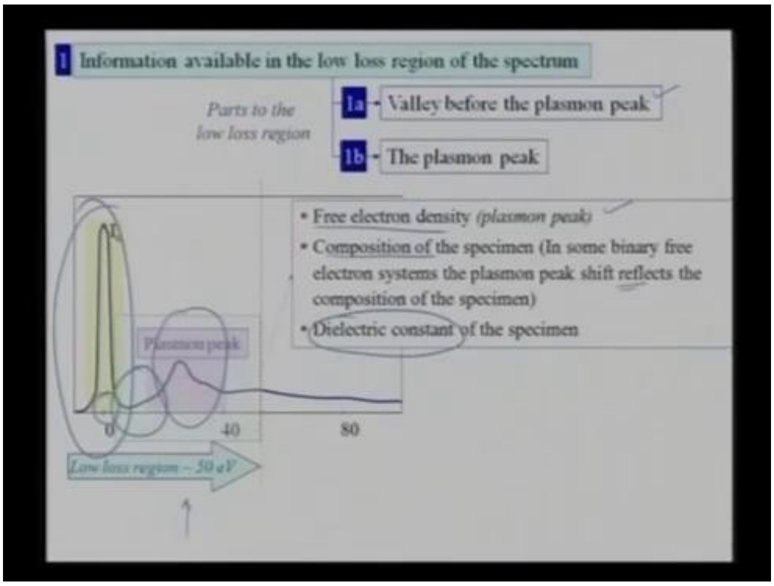

1 Information available in the low loss region of the spectrum

Parts to the low loss region

1a - Valley before the plasmon peak

1b - The plasmon peak

- Free electron density *(plasmon peak)*
- Composition of the specimen (In some binary free electron systems the plasmon peak shift reflects the composition of the specimen)
- Dielectric constant of the specimen

So, again there are different parts of the spectrum, so again coming to the initial part, we already saw that this is nothing but the 0 loss p. So, we have incident beam energy it interacting with the material and it is getting elastically interacted and that energy is being captured back as a 0 loss peak because the incident electron they have not lost any energy while interacting with the specimen t. So, the result of the 0 loss peak and later on they have plasmon peak in this case we are observing plasmon losses those are because of the polarization of the electrons and because of that, it is losing certain energy via certain oscillations.

We can we have one regime of value before the plasmon p and then again the peak the plasmon p. So, in this case we tend to see this particular p because of the free electron density and that can tell us more about the dialectic constraint of the particular specimen t as well as the composition of specimen t. So, that part we can attain from the plasmon peak of the low loss regime that we can comment because that distribution of electrons. The polarisation of electrons will tell about the dilated nature of the material how easily the electrons can flow and how easily they can reduce the energy loss. So, that part can be easily obtained and again we can also form that we can also attain the overall composition of the specimen t from the free electron density.

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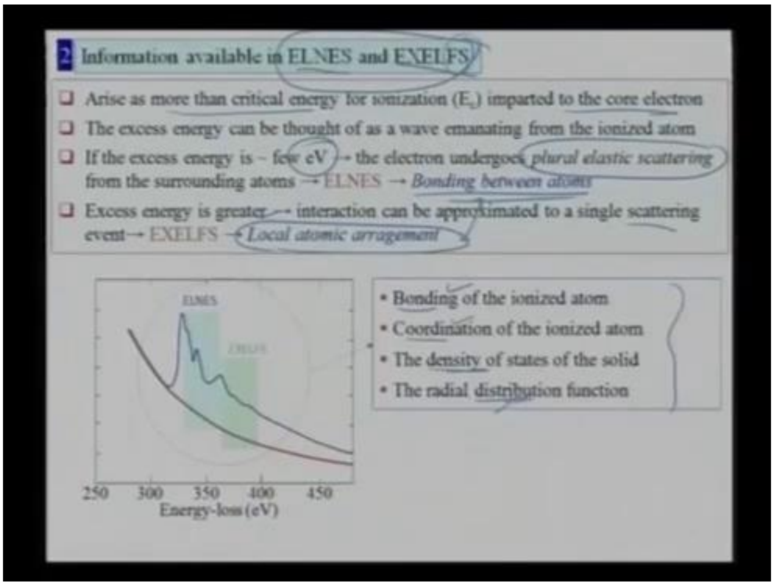

2 Information available in ELNES and EXELFS

- ❑ Arise as more than critical energy for ionization (E_c) imparted to the core electron
- ❑ The excess energy can be thought of as a wave emanating from the ionized atom
- ❑ If the excess energy is ~ few eV → the electron undergoes *plural elastic scattering* from the surrounding atoms → ELNES → *Bonding between atoms*
- ❑ Excess energy is greater → interaction can be approximated to a single scattering event → EXELFS → *Local atomic arragement*

- Bonding of the ionized atom
- Coordination of the ionized atom
- The density of states of the solid
- The radial distribution function

Second, from the high energy loss regime, we have near edge structure and the fine structure which is the accidental region and it can arise as more than the critical energy for the ionisation is imparted to type core electron. So, from that we can attain what is the overall ionisation which is happening out there and this is the excess energy which is approximately few electron volts. We can also achieve attain some plural elastic scattering and that can give us the bonding structure between the two items and if the excess energy is greater and that can be correlated to the single scattering event.

That can provide us a local atomic arrangement, so we can achieve the bonding between the atoms or what is happening in terms of the arrangement of the local atoms. So, we can get overall structure either the bonding of ionisation item how the ionised item is coordinate the other items from the overall arrangement. That can also provide us the density of straits of solid as well as the radius distribution function for all these entities, so that part we can attain from the extended regimes of the which is near edge and the extra extended fine structure. So, that part that information we can get from the high energy loss spectrum either from the energy loss near edge structure which is ELNES or from the extended energy loss EXELFS. So, we can attain that much information from out here, so later on we can also see that the overall information what we can get from here is if we get an intensity.

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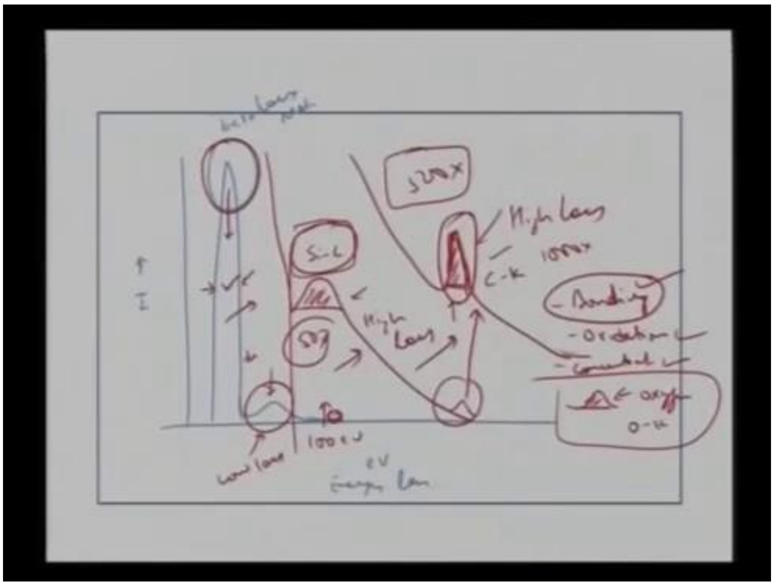

So, we are getting certain intensity out here and then in this case we have energy loss which is e V, so we have energy, so we are having this, which is coming out exactly at at 0. Then, we have a very fine plasmon losses and that is it and then we have high loss period, so if you can we strait basically extending it or increasing magnifying it. So, this is nothing but 0 peak 0 loss peak and then we can go back and see this particular regime, so this is nothing but the plasmon peak of a strait magnifying, then we can we can see that.

We are seeing certain peaks, so at certain higher peaks we can see that there is some information which can be available certain information which can be available and these regimes occur basically at around 100 electron volts. So, this is the low loss region and we can start seeing something at much at the high loss regime high loss again this is high loss. So, we can start magnifying it, so in this particular case we are seeing 0 loss peak those are nothing but arising from the elastic scattering and that can tell us more about the resolution part of this particular EEL spectrum.

Then, once we once we are going and seeing the plasmon, we can tell much more about the dialectic nature of the composition and as we see here we can have some certain spectrums, so in this case it can be silicon L shell. So, we can get certain information about the bonding that what kind of energy irresponsible in creating this particular ionisation it can also be arising from some other materials say k of carbon S. This particular part tells us two things first of all what overall bonding is because this is nothing but ionisation energy. So, that is telling directly about the bonding and then it can also tell us about the oscillation strait whether how much energy is base basically being provided here.

So, from that we can also get the oscillation strait and we can also know what the overall concentration because depending on the height of this particular peak. We can know how much carbons are really interacting to give out this particular intensity or giving out this particular regime and we can also see that there can be certain secondary secondary basically peaks out here. So, we can further magnify it, so we can see the extension of this one, so if this can be 50 x, this can be 500 x and this can again be 1000 x. so, later on we can all again see some more peaks which can belong to this. So, from one spectrum we can keep magnifying it, so the blue one what we saw earlier is the initial spectrum.

Then, we magnify it by 50 times and then we see certain spectrum that tells much more information about whether there is some silicon in it. It will tell us the bonding or the oscillation strait we magnify it further to say 5 to 500 x and then what we get we can see some presence of some carbon. That will tell us about the overall concentration carbon we can magnify it further in what to see is some presence of some oxygen. So, we can get couple of information from here the bonding the state and the concentration even the electronic structure of this particular entities. Those are what we can get very easily from the EEL spectrum, so that is what we can see in this particular case.

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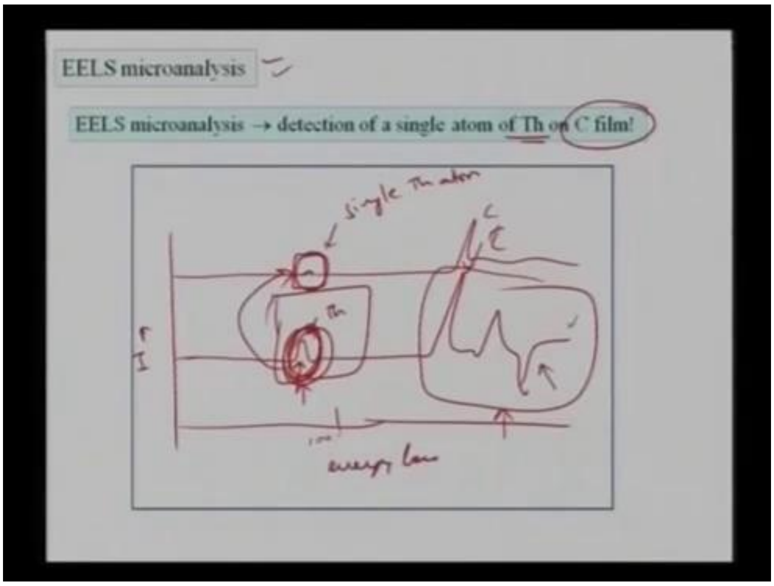

EELS microanalysis

EELS microanalysis → detection of a single atom of Th on C film!

Further, we can also do some EELS microanalysis and in this particular case, we can’t even detect a single atom of theorem even on a carbon film. So, if we see we can get a particular spectrum, we can get a particular spectrum and in the high in the in the low loss regime we can see some presence of some theorem if I had a particular film. So, I can get some signals which are basically for carbon this peak is coming from a theorem with the cluster of theorem, but if I only have one single atom of theorem, this is the energy loss the intensity. I can also compare it with a say if I had certain peaks of carbon and then if I will allow only one theorem atom to basically get deposit get absorbed on the surface to see some bump out here and with the similar kind of a carbon peak.

So, I can even did back even when I have a single theorem atom which is now absorbed on the carbon surface I still will be able to detect that particular part. So, that tells how sensitive that EEL spectrum that I can detect even a single theorem atom, so I can detect that because the theorem atom if it forms a cluster I can still see the similar peak at the at the similar energy loss Regime. That might be at either at lower energy or maybe less than 100 electron volt, so that part I can see from the EELS micro analysis and I can detect even a single atom of theorem on a carbon film. So, that is the overall sensitivity of the EEL spectrum, so in this particular case I have carbon, I had a carbon film.

So, I do peaks which are arising, because of carbon and those are generally in the height of regime, so they can tell me about the overall excitation nature or the bonding nature of the electron and in the ionisation strait. So, I can get much more information of what are the transition which are occurring in the carbon alone, so depending on what kind of carbon it is I can the pie interactions or the sigma interactions which are occurring for the electrons and for the theorem. It is now absorbed on the carbon surface, so I am getting a much bulk or the peak on the carbon film and that is because of the cluster of theorem atoms, but when I have single theorem atoms sitting on the surface of carbon as I can still detect that, so that is the overall sensitivity of the EEL spectrum.

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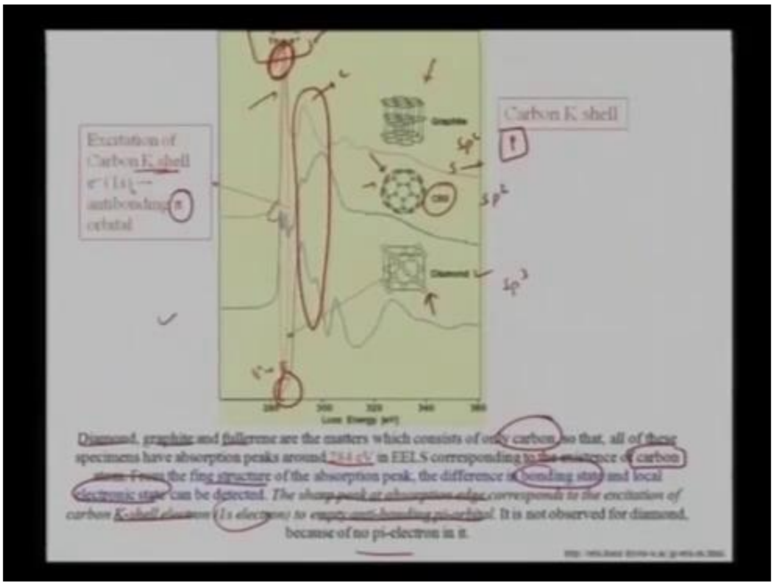

Excitation of Carbon K shell e^- (1s) → antibonding π orbital

Carbon K shell

Diamond, graphite and fullerene are the matters which consists of only carbon, so that, all of these specimens have absorption peaks around 284 eV in EELS corresponding to the existence of carbon atom. From the fine structure of the absorption peak, the difference in bonding state and local electronic state can be detected. *The sharp peak at absorption edge corresponds to the excitation of carbon K-shell electron (1s electron) to empty anti-bonding pi-orbital.* It is not observed for diamond, because of no pi-electron in it.

So, again in certain cases, we have diamond graphite and fullering and again they only have carbon in it nothing else. So, when considering three systems diamond graphite and fullering and they all consist because basically carbon, but they have absorption peak of around 284 electron volt in the EELS in the EEL spectrum which correspond to the existence of carbon atom. So, we see two 84, we have certain regime carbon which is present, so we do see that the carbon is present out there and from the fine structure of the absorption peak the difference in the bonding state in the local electronic state can be detected.

So, you can find the bonding and the local electronics strait from the fine structure of the EEL spectrum and again if you go further we can see for the graphite we have this particular bonding which is 1 s as or the pi bonding 1 s to pi bonding. We have certain energy absorption, so we are able to see this particular peak in the graphite and the similar p we can also see in the c 60, but that peak is totally absent in the diamond structure. So, we can see that because the diamond we s p 3, so we don’t have a transition which is which can really see 1 s to going to the empty pi bond. So, we can see that carbon electron from 1 s it is not able to bond to EEL a pi bonding orbital in case of diamond.

So, that can be very nicely being that is very nicely being observed out here it is sharp peak at the absorption h which corresponds to the excitation of the carbon electron. The 1 s electron to the empty orbital that is present only in the graphite as well as in the c 60 because they both have s p 2 type. So, they still have 1orbital, which is empty, so there can be a transition from the s shell or the 1 s shell to the p bond and that particular energy regime is following in the regime out here. From this, we can say that diamond we have and there is no empty pie electron basically which can come out here, so there is no 1 s electron which can jump to the empty pi electron.

That is the reason we have this particular energy level vacant out there, so that is a kind of information. We can get that from a difference between the graphite c 60 and a diamond where everything is now composed of carbon only and that thing is now being captured from the EEL spectrum.

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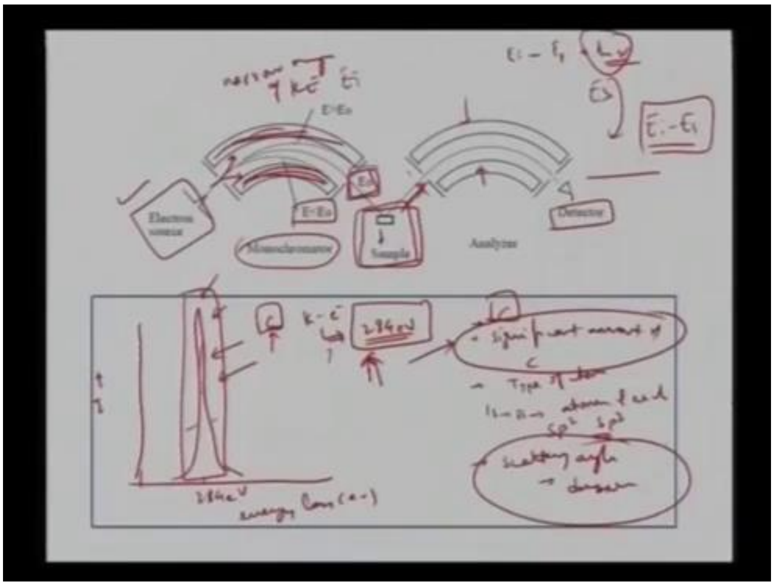

So, in the EEL spectrum we can see that if you have if you have large number of particular electrons at say 284 electron volt, what we saw? So, we have overall spectrum and then from 280, we are seeing very large number of spectrum, this thing is that 284 electron volt. So, from this we directly know that that we have energy loss happening much more at the 284 and it means that there entity some ionisation which is happening at this particular level only because some particular atom is present. That is leading to this particular energy loss, so this happens to be electron energy loss, which equals to the ionisation of carbon from k shell.

So, if we k shell electron present in the carbon atom and that equals to the energy of that particular electron equals to 284 eV. So, directly means that if you have loss which is happening at 2854 electron volt, so we have energy loss out here in eV and we have intensity out here. So, once we have once we see a high intensity exactly 284 electron volt we can directly correlate it to the ionisation of carbon from the k shell. So, that directly tells us that we have some atom present out here and that leading to the ionisation of this particular atom and incident beam is somehow interactive of this particular atom and it is ionising the carbon.

So, that is the first information what we can get from here that is equal to the energy which is required to remove and electron from the k shell of the carbon. So, this tells we have presence of carbon and the intensity of this also tells us what is approximate composition or the approximate content of this particular carbon because the more the carbon the higher the intensity of this peak at 184 electron volt. So, we can also say that there is a significant amount of carbon which is present the material and from that from the interaction that we saw if we have certain bonding or a bonding present, so from s shell to the p of from the pi shell if you can see, we see that particular p.

It means that type of a bonding can be present, if not then it means it is not there, so we can also find what is the type of atom its overall, its overall amount and number of atoms of each type. So, in this case we have certain, which is happening, so we can know whether which have s p 2 or s p 3, which is present in a particular case and also we can find the scattering angles. So, depending on that, we can also find the overall scattering angles and that can provide us much more of dispersion relations for a particular atom. So, from this overall information from the EEL spectrum first of all we can identify where the particular peak is getting where we are getting the exact p and that will tell us how much energy loss is occurring.

From that, we can correlate it to the ionisation of a particular entity say carbon in this case they will tell us the amount of carbon type of bonding which is happening the overall scattering angle from the dispersion for a for a particular entity. So, all this information we can get easily from a EEL spectrum and how do we get that is we initially we have electron source. First of all, you have providing a narrow range of kinetic energy, so we have narrow range of kinetic energy and that thing is being achieved from a cylindrical mirror analyser or we have certain two cylinders out there and we apply certain bias to it.

So, we have energy less than a naught it gets basically gets interrupt out there if I have e greater than e naught then it gets interrupt out here, so what we can get out is a narrow range of energy which has limited e naught. That particular energy of known e naught value will now interact with the sample and once it interacts with the sample after the interaction how much energy is being lost by the electron that thing is again sent back to the analyser. We can again do the same operation and we can select what all energies are coming out.

So, by putting the biased at a basis to the particular analyser, we can somehow detect the overall spectrum from a detector. So, we can get overall spectrum of what is overall energy loss which is happening because once you know the incident energy minus the energy which is being observed. Later on, that is nothing but equal to the energy loss which is occurring for the foe a particular electron, so that is what we are getting from the overall spectrum that we are sending.

Second energy we have electron source we are sending it through a mono chromator to get a particular set of non narrow range of kinetic energy for electron. Those are interacting with the sample and upon interaction with the sample it is now sent to an analyser. So, those will separate out the energies once we are able to separate out the energies we know the incident energy we know the final energy as the subtraction of that e i minus e s.

This will tell us how much energy loss is now occurring and that energy loss is now being an overall structure of a particular material or even form for an even. We can also find out the overall dialectic nature or the ionisation strait or the bonding strait for a particular material and that thing we are getting from this EELS spectrum.

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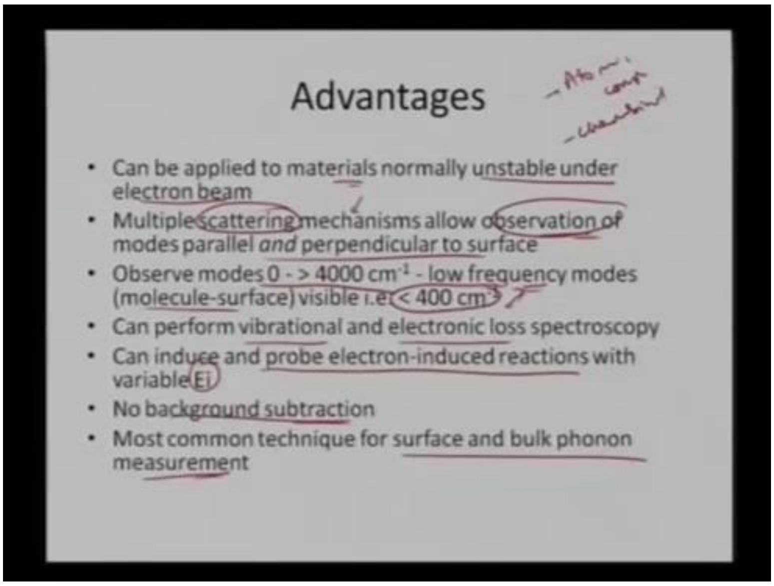

Advantages

- Can be applied to materials normally unstable under electron beam
- Multiple scattering mechanisms allow observation of modes parallel *and* perpendicular to surface
- Observe modes 0 - > 4000 cm^{-1} - low frequency modes (molecule-surface) visible i.e. < 400 cm^{-1}
- Can perform vibrational and electronic loss spectroscopy
- Can induce and probe electron-induced reactions with variable Ei
- No background subtraction
- Most common technique for surface and bulk phonon measurement

Again, the advantages of the EEL spectator, it basically can be applied materials which are normally unstable under electron beam, because in this particular case our energies are very low. So, because our energies are very low we can also apply it to the materials which are basically unstable under the electron beam and again in this particular case we can have multiple scattering occurring because we have a dipole scattering. We can also have a specular scattering we have impact scattering dipole scattering and we can also have and ion resonance. So, all those mechanisms have behave very differently in this in one case, we can retain the momentum in the perpendicular strait in as second case.

The momentum was not at all conserved both parallel as well as perpendicular and all those at basically scattering mechanisms are allowed and that will allow us to observe the overall energy loss. So, we can observe all the modes which are parallel and perpendicular to the surface, so that can reveal much more information at the same time we can observe modes between 0 to 4000 inverse of centimetre. Also, we can attain spectrums which are which have a lower energy or the lower frequency modes we can also attain the spectrum for that and that basically we can also observe the molecular surface. So, that part gives us the information much more about the what is happening at the surface level or the low energy level low energy losses also we can attain.

We can perform vibrational electronic loss spectroscopy, we can also induce an prove current induce interactions with the variable incident energy. This case we don’t need any background subtraction because we know what the incident beam is and what is the beam, which is coming out. So, we don’t need to any background subtraction and it is very common technique for the surface and bulk phonon measurements because that will create the initial broadening of the 0 loss peak. So, that part we can tell very nicely what is the overall surface and bulk phonon interaction which is happening with the material.

In this particular case we can find the atomic composition, so we can also attain what is atomic composition which is out there what is the overall chemical bonding which is happening in the mutual h because from the intensity of a particular intensity. If a particular EELS peak, we can find what is the overall how much is the overall presence of a particular entity, which is causing this particulate increase in the peak intensity. So, that can tell us about the overall composition and it can tell us about the overall bonding nature because depending on where the particular peak is appearing.

So, like in the case of carbon from 1 s to pi shell we saw that peak was operating in 284 electron volt, which is not present we can tell much about the bonding nature of a bonding nature of carbon itself. So, we know whether its s p 2 or s p 3 and again it can tell us about the electron profile. So, that part can also be obtained from the ionisation part, we can also get much more of surface properties because we saw even when a single theorem atom is present on a carbon surface. It can be basically detected, so this particular instrument is highly sensitive, so we can much more information even from the EEL spectrum.

Again, we can find the elements specific distribution function as we know as we have seen earlier from the distribution to the distribution of the secular scattering we can find the correlation between the radiant profile. So, that can also provide us much more information about how the specific instance is now being distributed. So, that part we can also obtain in this particular EEL spectrum, so overall advantage is that it is basically we can find atomic composition, we can also find the chemical bonding, we can also find the variants and conduction profiles, we can get surface properties.

We can also get some elements specific properties and it can also give us the modes which are lower frequency modeless than four hundred centimetre inverse and we can perform many vibration electronic loss spectroscopy. We can also find some phonon measurements, we can also do some phonon measurements and also we have no need to do any background corrections for in this particular spectrum. So, these are certain advantages of the EELS spectrum, what we can get, we can get very fine detailed information.

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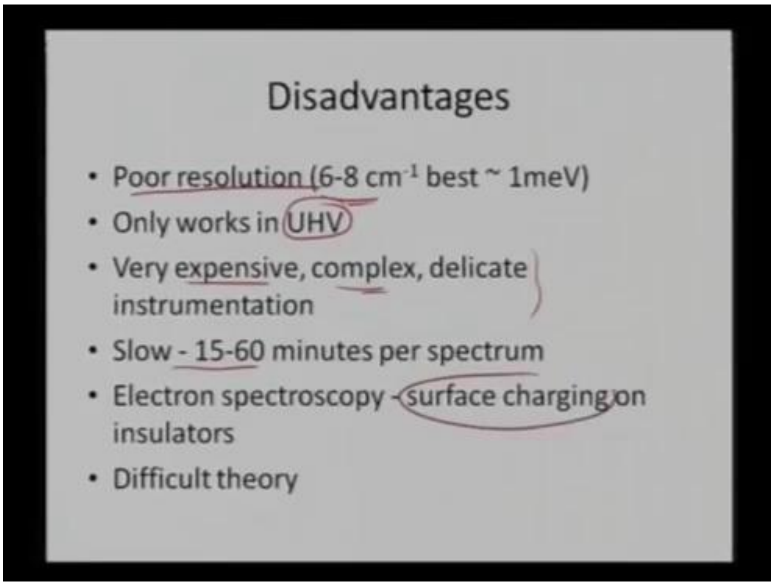

Disadvantages

- Poor resolution (6-8 cm^{-1} best ~ 1meV)
- Only works in UHV
- Very expensive, complex, delicate instrumentation
- Slow - 15-60 minutes per spectrum
- Electron spectroscopy - surface charging on insulators
- Difficult theory

There are couple of challenges out here that it is a poor resolution the best it can achieve as approximately 6 to 8 centimetre. Since we are very low energy electron which are utilised in this particular case we can work only in the ultra high vacuum or to the order ten to power minus 10 to 12. So, that is overall regime, we need to work in because the electrons need to travel very large distances. So, they can be a detector, so we need to perform all these operations under ultra high vacuum, so that is the most problem with it and that makes it very expensive. It is very complex because we need to generate a first of all a monochromatic beam and then let it pass through analyser and then again get it detected.

So, again it is very complex and it requires a delicate instrumentation because we also need to detect what is the beam energy and what is the energy we are getting after it interactive with the sample. At the same time, electron should be maintained well within the ultra high vacuum so that makes it very delicate, it requires very instrumentation and also we detect that some spectral information in terms of their dispersion or the diffused spectrum what we get?

So, that tells more about the phonon interactions and that makes the instrumentation much delicate and thus attending the spectrum is little slower 15 to 60 minutes per spectrum. Again, it can also result some surface charging because we are dealing with the flow of electrons on the sample surface some plasmon oscillations. So, it can also lead to surface charging so generally conducting samples are much more preferred in this particular case. So, again it also has a difficult theory because what all ionisation are occurring how the loses are occurring they require exact identification of how those how those processes are leading to the loss and energy.

That makes the theory little difficult to grasp, so the overall advantage include that it worked in vacuum, it requires very sophisticated instrumentation it is very complex and its very expensive and it is a little slower 15 to 60 minutes. It is a poor resolution in comparison to the reflection spectroscopy, so that makes it much more poorer resolution, but in spite that it is still very appealing.

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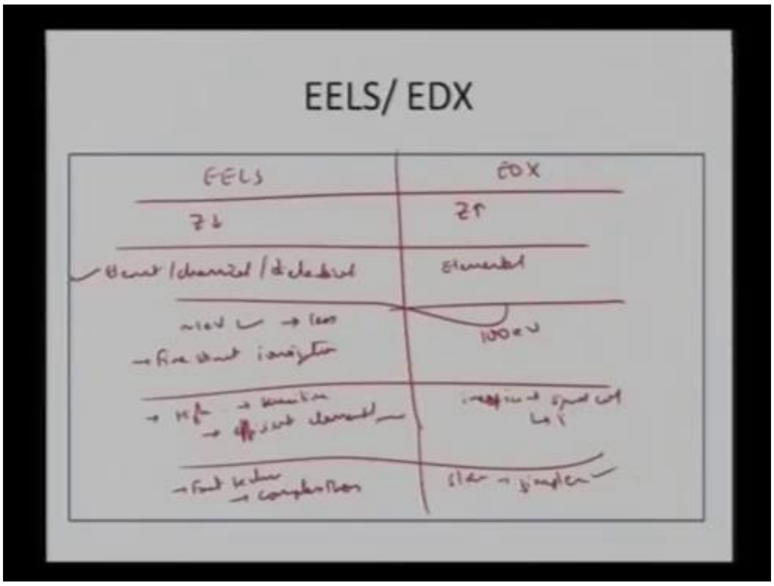
EELS/ EDX

EELS	EDX
Z↓	Z↑
Bond / chemical / dielectric	Elemental
~10 eV → loss → fine structure ionisation	100 eV
→ HR → resolution → different elements	insignificant spectral [illegible]
→ Fast [illegible] → complications	slow → simpler

In comparison to the EDX, the EELS we have, we can just basically have a correlation between the EELS and the EDX. That means like an EDX, we have sensitivity for higher atomic number elements whereas, for the EELS we have high detection efficiency for the low atomic number elements.

So, that is one part out here and in EDX, we can get only elemental information, but in this case EELS we can get elemental we can get chemical as well as we can get the dielectric information. So, in that part we can get the composition, we can also get the ionisation strait and those all information we can get easily from the EELS. In the EDX we have energy resolution limited to 100 electron volts, whereas in this particular case approximately 1 electron volt. So, in this particular case energy resolution is much higher as compared to EDX and we can also get generally tends to give less number of peak over lapse it can also provide us very fine structure for the ionisation edge ionisation edge.

So, this part also we can get from the EELS and in case of EDX, we have an inefficient similar collection and that makes it very time consuming that elemental mapping generate which is very time consuming in this particular case. In EELS, we have very high efficiently very high or efficient signal collection because it is highly sensitive and it can detect EDX a single theorem atom which is which is sitting on a carbon film and that makes it very, very efficient in terms of mapping. So, it can provide efficient elemental mapping on the particular surface at the same times since it is very efficient, it becomes very fast technique its fast technique nut.

It requires very complex theory though EDX is little slow, it was much more simpler and we can write a spectrum very quick, but again this is a slow process, slow technique, but it can have very simpler processing is required in the EDX. So, that is the overall thing about EELS that we can have, known electron energy and we are letting it interact with the material and from the detection of the loss which is occurred upon interaction of electron with the material and from that energy. We can distinguish the overall spectrum either at 0 loss low loss and the high loss in the 0 loss, we have mostly the elastic scattering or that tells us most about the phonon loses which are occurring in the material.

Then, later on we have the plasmon losses and then plasmon losses basically are the main thing which we can have more about the overall composition of a information compositional order dialectic nature of the materials. In the high loss regime, we can see the nearest structure or the fine structure which is near the extended which is called the extended energy loss fine structure.

So, we can get some information out from there which tells us more about the ionisation strait or what is the ionisation of a particular material and also about the bonding which is predominant in that particular location. All these information we can get from the high loss regime in the EEL spectrum and as we see it is a very sensitive technique and it can detect a very fine edge of it which are there on the surface of a particular entity or a particular surface. This can serve as a very fine tool in terms of resolution in terms of resolving any element, which are there on the sample surface, so basically with that I will end my lecture here.

Thank you.