Indian Institute of Technology
Kanpur

NP-TEL
National Programme
on
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-31

by…
Prof. N.P Gurao&
Prof. Krishanu Biswas
Dept. Materials Science &Engineering

Hello everyone.

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Advanced Characterization Techniques

Nilesh Prakash Gurao
Assistant Professor
Materials Science and Engineering
Indian Institute of Technology Kanpur

In today's class for advanced characterization techniques.

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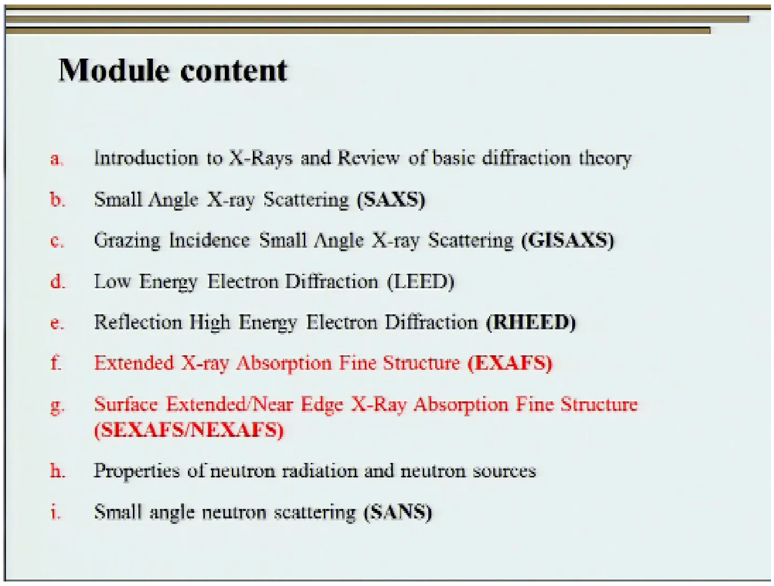

Module content

a. Introduction to X-Rays and Review of basic diffraction theory
b. Small Angle X-ray Scattering **(SAXS)**
c. Grazing Incidence Small Angle X-ray Scattering **(GISAXS)**
d. Low Energy Electron Diffraction (LEED)
e. Reflection High Energy Electron Diffraction **(RHEED)**
f. Extended X-ray Absorption Fine Structure **(EXAFS)**
g. Surface Extended/Near Edge X-Ray Absorption Fine Structure **(SEXAFS/NEXAFS)**
h. Properties of neutron radiation and neutron sources
i. Small angle neutron scattering **(SANS)**

We are going to try and learn something about extended x-ray absorption fine structure as well as surface extended x-ray absorption fine structure, and near edge x-ray absorption fine structures. In the last couple of classes, we have been talking about diffraction as well as scattering of x-rays as well as electrons. But in today's class, we are going to focus on how we can use x-rays for getting spectroscopic information and therefore chemical information from the material or substance under consideration.

So, as you can see over here, there are two different techniques, namely the extended x-ray absorption fine structures. The same technique with different geometry known as surface extended x-ray absorption fine structure and near edge x-ray absorption fine structure, which are put together as x-ray absorption spectroscopy. So, in today's class, we will just get acquainted with this technique.

I would like to mention that both the techniques, namely the extended x-ray absorption fine structures as well as the near edge x-ray absorption fine structure is based on similar principle. Otherwise they differ in the regime of operation in terms of energy more about it later.

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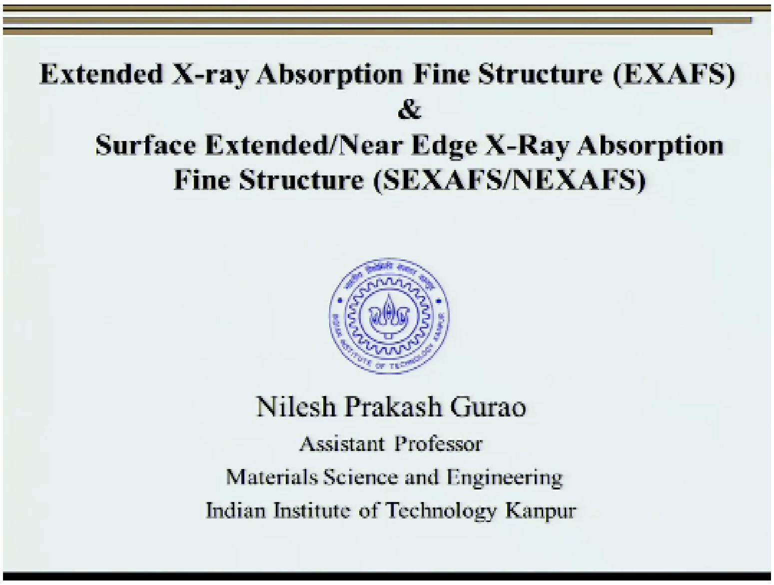

Extended X-ray Absorption Fine Structure (EXAFS)
&
Surface Extended/Near Edge X-Ray Absorption Fine Structure (SEXAFS/NEXAFS)

Nilesh Prakash Gurao
Assistant Professor
Materials Science and Engineering
Indian Institute of Technology Kanpur

So, let us go back and see what exactly we have understood earlier in the course of our earlier lectures.

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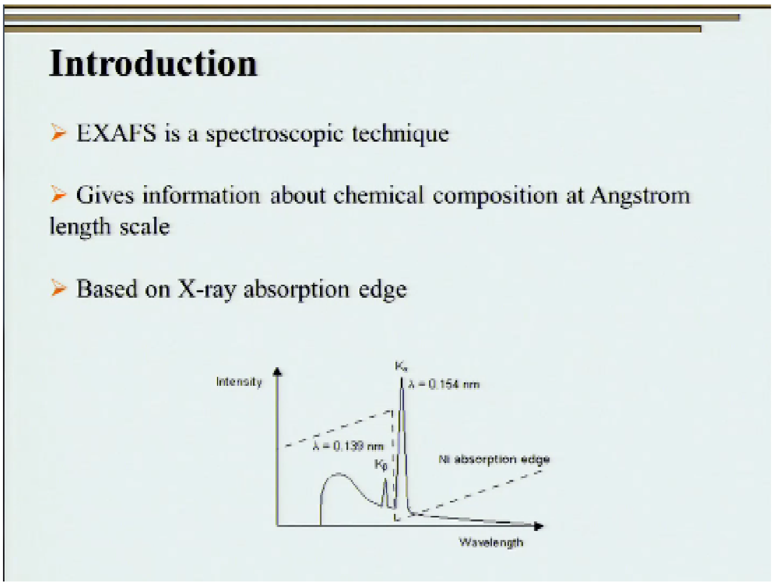

Introduction

- EXAFS is a spectroscopic technique
- Gives information about chemical composition at Angstrom length scale
- Based on X-ray absorption edge

So all of us know, something that I emphasized that extended x-ray absorption fine structures is essentially was spectroscopic technique and it gives us information about the chemical composition. However, unlike techniques like EDS, that is energy dispersive spectroscopy EX, EXAFS gives us information at the angstrom level about the chemical content or the chemical environment of a particular atom under consideration.

It is based on the same x-ray absorption edge, which we have touched upon in our second class, while you are understanding the instrumentation involved in x-ray diffraction. So, just to recollect it again, here you can see a normal spectrum as a function of wavelength for say something like copper target.

Here in you see how with that the absorption for a nickel filters, and here you see that the absorption essentially increases with the increasing wavelength. However, at a particular wave length there is a sudden drop in the intensity and this occurs because of absorption. So, our today's technique, EXAFS essentially focuses on this kind of phenomenon. This absorption edge that we are seeing in the figure discussed over here.

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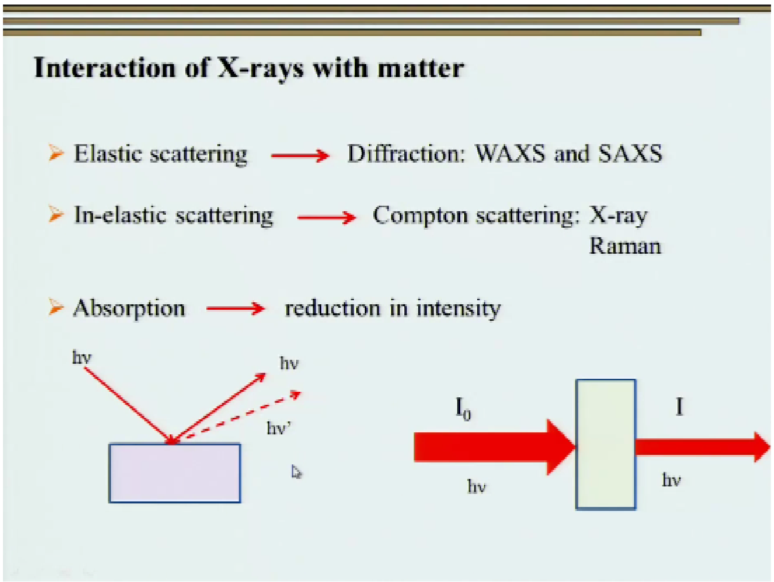

Interaction of X-rays with matter

- Elastic scattering ⟶ Diffraction: WAXS and SAXS
- In-elastic scattering ⟶ Compton scattering: X-ray Raman
- Absorption ⟶ reduction in intensity

So, we know that how does x-ray interact with matter. We have talked about elastic interaction, which leads to diffraction. Now the diffraction can be either wide angle x-ray scattering, which we carry out on a routine basis in laboratories or it can be according to small angle x-ray scattering, which we have touched upon in the third and the fourth lecture.

At the same time, in elastic scattering that leads to Compton scattering, which is studied using the x-ray Raman Effect, was also touched upon in the earlier lecture by my colleague. However, what we are going to talk today about essentially is x-ray absorption. So herein you can see that there is a decrease in intensity of the x-ray as it passes through a material.

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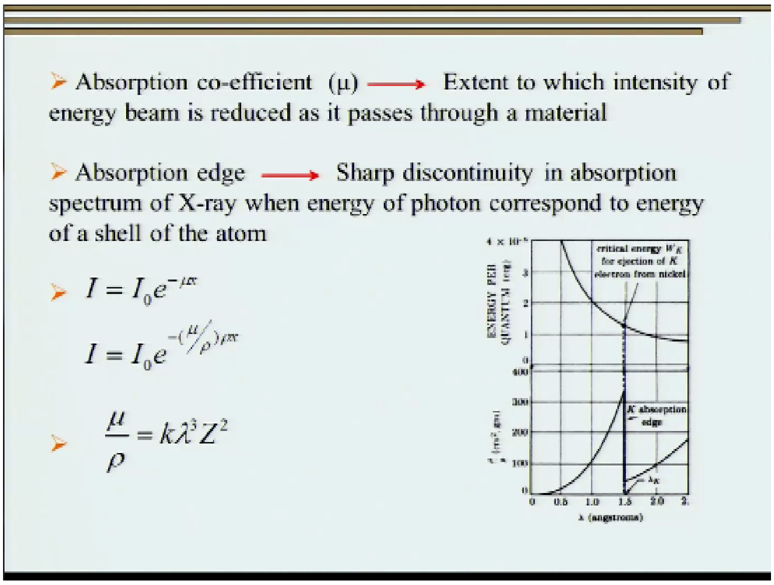

- Absorption co-efficient (μ) ⟶ Extent to which intensity of energy beam is reduced as it passes through a material
- Absorption edge ⟶ Sharp discontinuity in absorption spectrum of X-ray when energy of photon correspond to energy of a shell of the atom
- $I = I_0 e^{-\mu x}$

  $I = I_0 e^{-(\mu/\rho)\rho x}$
- $\dfrac{\mu}{\rho} = k\lambda^3 Z^2$

So, the extinct to which this decrease in intensity occurs depends on the absorption coefficient μ which essentially decides the extent to which intensity of energy beam is reduced as it passes through a material. The absorption edge that we had seen earlier is essentially a sharp discontinuity in absorption spectrum of x-ray when energy of photon corresponds to energy of a shell of the atom.

Now, we are going to talk about it in the next slide, but let me just put it mathematically that how absorption can be quantified. So, if the incident beam is of the intensity I_0 passes through a material with thickness of edge, the amount of attenuation that occurs is actually $e^{-\mu/x}$ where μ is the absorption coefficient. And therefore, the intensity after passing through the material gets modulated as $I=I_0\ e^{-\mu/x}$.

If we incorporate the density of material you can get $I=I0\ e^{-(\mu/\rho)\rho x}$. This is particularly important when they are considering instead of various material and we can take the weighted average of the absorption coefficient as well as the density. Generally, it has been found out that the relationship between μ and ρ is not only wave length dependent but also atomic number dependent.

Now, on the right hand side we can again see the similar curve, what we had seen earlier there. Where we have a critical energy WK for ejection of K electrons from nickel, and this corresponds to a steep drop in the intensity and leads to absorption of the copper x-rays, what we had seen in the earlier case.

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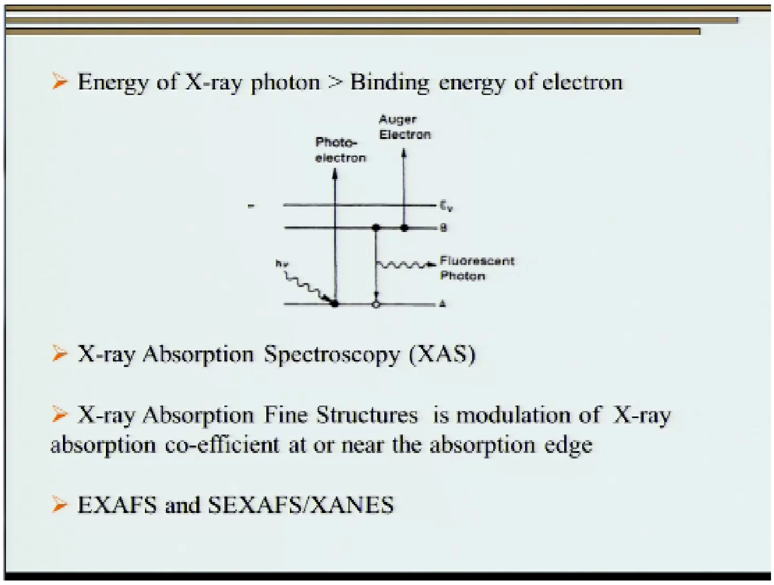

- Energy of X-ray photon > Binding energy of electron

- X-ray Absorption Spectroscopy (XAS)
- X-ray Absorption Fine Structures is modulation of X-ray absorption co-efficient at or near the absorption edge
- EXAFS and SEXAFS/XANES

Having said that what are the kinds of interactions that can occur when a particular photon of a particular wavelength is incident on a material. So if x-ray photon of energy, hµ is incident and has sufficient energy it can knock off an inertia electron. In order to that the energy of the x-ray photon has to be greater than the binding energy of the electron. Once this electron is knocked off from the inertial it can go and become a part of the continuum.

There are other possible scenarios that can also occur. Having said that, if the electron from the inertial is knocked off and goes to the continuum, we can get a transition from outer shell to the inner shell and this transition is accompanied with a release of another photon, which has a wavelength that is different from the incident photon. This phenomenon is known as florescence.

And we can also use the fluorescent photon to uniquely characterize the material under or rather the element under consideration. Another possibility is that in case this inertial electron is knocked off, we can also have a release of another anti-electron from the outer shells in order to accommodate this phenomenon. So all this including the fluorescent photon as well as the RJ electron, or the photo electron will essentially characterize the element under consideration.

If we can uniquely identify and correlate either the photoelectron, the RJ electron, or the fluorescent photon with a particular element we can get chemical information about the same. Now this philosophy is used in a variety of spectroscopic technique and X-ray absorption spectroscopy which comprises of extended X-ray absorption fine structures as well as near edge X-ray absorption fine structure which is also known as Xanes is no exception.

These techniques comprise of modulation of X-ray absorption coefficients at or near the absorption edge. So here again let us go back and have a look. So this is where we have an absorption edge and here you can see the wavelength. So how and therefore the frequencies also and you can see that what all modulation occurs near the absorption edge is what is used as a fingerprint for the presence of a particular element in these techniques.

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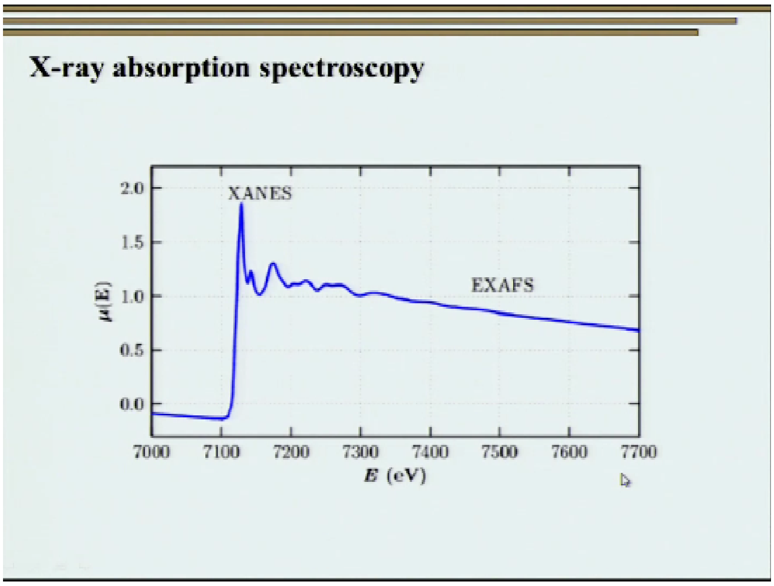

X-ray absorption spectroscopy

So let us look how exactly the pattern looks like. So if you recollect, this is how the absorption edge looks like. So in this case since it is energy, you see we are going this way. Here is the absorption edge, and again it goes on increasing with decrease in energy. However, you notice if the modulations which can be seen in this pattern. Here again I would like to point that the technique Xanes X-ray absorption near edge structures are found very close to this particular absorption edge.

While extended X-ray absorption fine structures, as the name suggests is far away. Therefore, extended right, so all of them these modulations which are far off are essentially known as extended absorption fine edge structures. Now to emphasize that whenever we talk about absorption edges, it has to be specific. So if you want to study a particular element you have to focus a particular edge.

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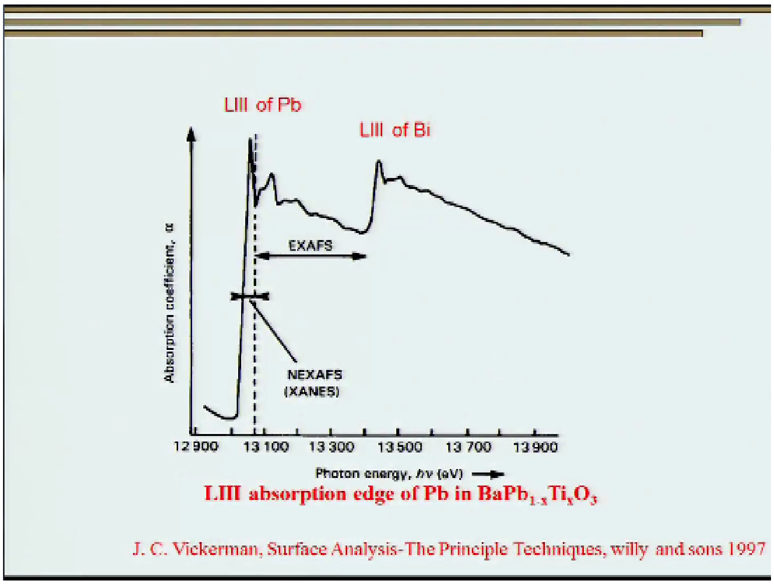

LIII absorption edge of Pb in $BaPb_{1-x}Ti_xO_3$

J. C. Vickerman, Surface Analysis-The Principle Techniques, willy and sons 1997

Now this point is made clear in the spectrum shown over here. So here again we see that indeed we are having two absorption edges. The L3 edge of lead, and the L3 absorption edge of bismuth, so in the present scenario, we are focussing on the L3 absorption of lead the region, which is very near to this edge essentially comprises of xanes spectra while the region far away comprises of extended x-ray absorption fine structure.

So this transition or this differentiation between EXAFS and xanes is a bit arbitrary. Though there are ways of kind of fontifying it, as a thumb of rule generally it is considered that at a wavelength or energy of the order of 100eV from the absorption edge, xanes is valid while beyond say 50-100 electron volts extended x-ray absorption fine structure are valid.

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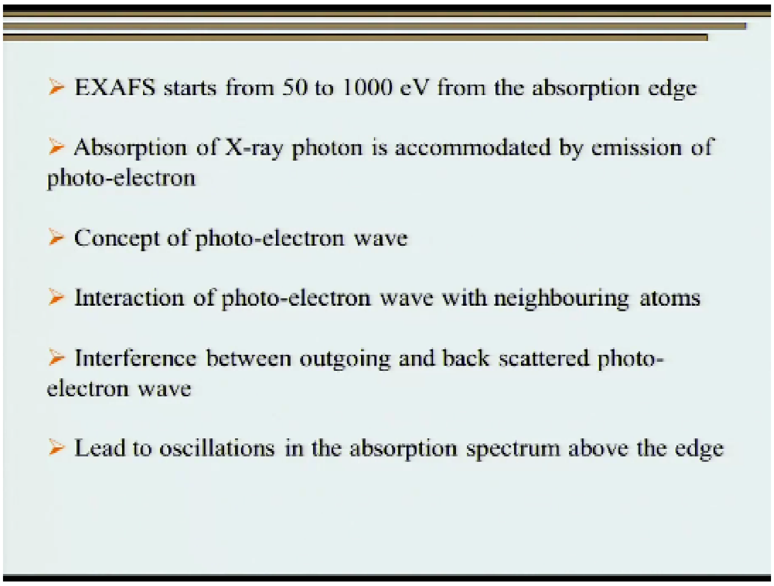

- EXAFS starts from 50 to 1000 eV from the absorption edge
- Absorption of X-ray photon is accommodated by emission of photo-electron
- Concept of photo-electron wave
- Interaction of photo-electron wave with neighbouring atoms
- Interference between outgoing and back scattered photo-electron wave
- Lead to oscillations in the absorption spectrum above the edge

So as I had mentioned EXAFS starts from 50-1000 eV from the absorption edge. I hope you appreciate that at with increasing the energy, we see that the oscillations that we are getting essentially die out having said that absorption of x-ray photon is actually accommodated by emission of photoelectron. Now this photoelectron unlike in the normal case tends to behave like a wave like this is the basis of wave particle duality where in you see that our subatomic particles can also behave as wave.

Having said that the waveform because of the photoelectron actually interacts with the neighbouring atoms, and therefore they get scattered from there. Not only that, there is an interference between outgoing as well as back scattered photoelectron wave and this leads to interference. Now this is something that we had talked about time and again like we have the X-rays which are going they meet in phase, there is constructive interference if they meet out of phase there is destructive interference.

So something very similar to it is happening. However this is happening very locally and at the atomic level and these modulations are essentially seen in the xanes or for that matter EXAF spectra and this essentially contributes to all the oscillations that we have seen over here. So all these oscillations that come will have a better figure later in the class.

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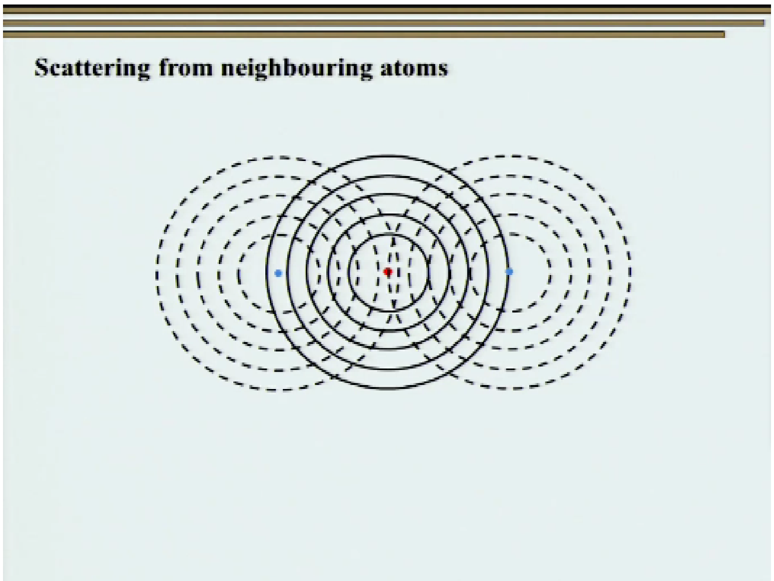

Scattering from neighbouring atoms

But the situation is very similar to what has been shown in the figure. So here we see we have our essentially atom which is actually emitting electron waves. So you see the electron waves are going. The moment they interact with another atom, what actually happens is they are back reflected, they are back scattered. And once these propagating and these back reflected, they interfere and depending on that we get if there is constructive interference, high intensity.

And if there is destructive interference, we get low intensity and these leads to essentially the oscillations that we saw in the EXAF spectrum.

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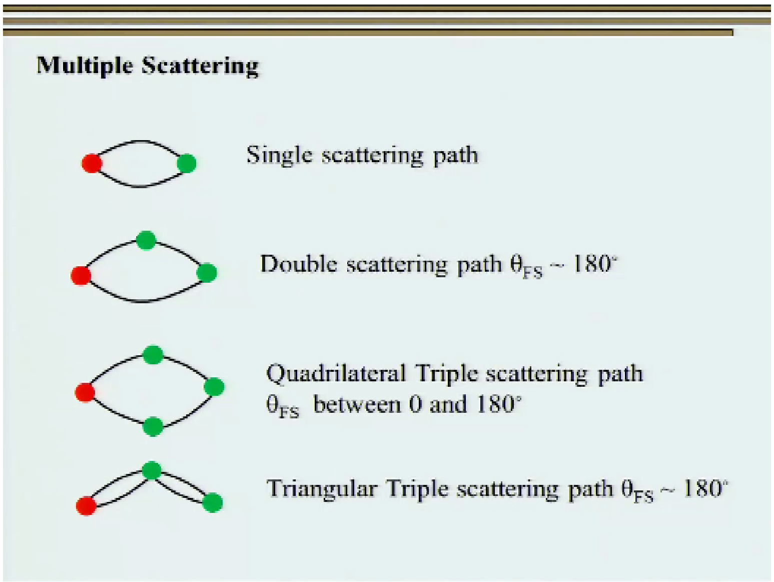

Multiple Scattering

Single scattering path

Double scattering path $\theta_{FS} \sim 180^\circ$

Quadrilateral Triple scattering path
θ_{FS} between 0 and 180°

Triangular Triple scattering path $\theta_{FS} \sim 180^\circ$

So what kind of interaction that can take place, what I showed in the earlier figure is a very simplistic assumption, and here each and every atom is essentially just reflecting the waves in nice spherical form. However, this may not be true. There are various kinds of interaction that may occur. So here we have some possible scattering or multiple scattering events have been figured out over here.

So here in the first case we see a single scattering path. So the electron wave is scattering from the red atom to say the green atom and it is getting reflected from the green back to the red. While in this case we have a double scattering path which is shown over here and we get mostly for forward scattering angle of close to 180 degrees. Similarly, there is also quadrilateral triple scattering path and also triangular triple scattering path.

I am not going to go in details, but I hope you appreciate that depending on the kind of interaction we are having, all the mode of oscillation of the pattern is going to vary. Now having said that we can always find out what kind of interaction is going to occur between the two neighbouring atoms and what do we expect to get as an output. More about it later but remember that for a given atom, the kind of interaction that takes place depends on its neighbourhood.

Now this is the very genesis of the X-ray absorption spectroscopy technique, wherein we can get literally information about the atomic neighbourhood of a particular atom or particular element under consideration, because remember in this case we are focusing only at the absorption edge of one particular element like we can see over here. So you focus on particular element and you see the modulations for that particular element.

So we see okay if I have lead somewhere, what is the neighbourhood of lead. So this is how it works out.

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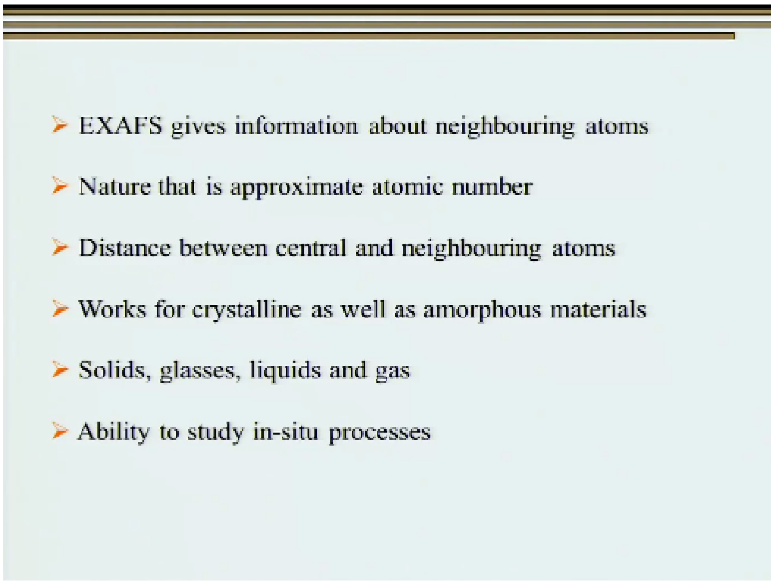

- EXAFS gives information about neighbouring atoms
- Nature that is approximate atomic number
- Distance between central and neighbouring atoms
- Works for crystalline as well as amorphous materials
- Solids, glasses, liquids and gas
- Ability to study in-situ processes

Now moving ahead as I had mentioned, EXAFS gives information about the neighbouring atoms. Not only that, it tells us what is the approximate atomic number, because remember at the end of the day, the scattering tendency of the atoms is essentially dependent on their structure factor and which you are quite aware varies as a function of the atomic number.

Having said that another important point that is very relevant is the distance between the two atoms.

If you remember whenever we talk about interference, what really matters is we are essentially going from the real space to reciprocal space. So the same kind of thing happens over here and depending on the distance, we are going to see whether we get constructive or destructive interference. So all these information we do get using EXAFS. However it is highly modulated.

Having said that, one of the biggest advantage that we have with EXAFS is that it works very well for crystalline as well as amorphous materials. While our X-rays, particularly when we talk about diffraction, gives us very little information about amorphous material. At the same time, EXAFS can also be used for studying solids, glasses, liquids and even gas. Having said that, one of the biggest advantage of an EXAFS is in studying in-situ processes that occur in different class of materials.

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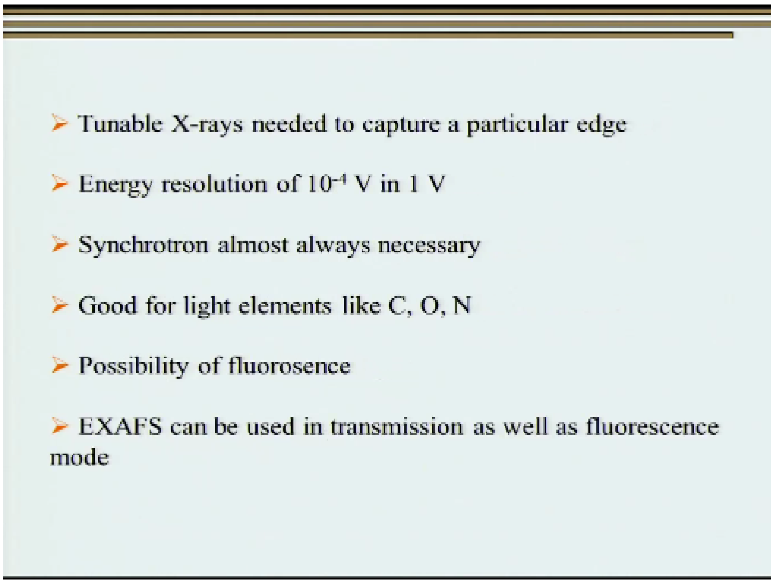

- Tunable X-rays needed to capture a particular edge
- Energy resolution of 10^{-4} V in 1 V
- Synchrotron almost always necessary
- Good for light elements like C, O, N
- Possibility of fluorosence
- EXAFS can be used in transmission as well as fluorescence mode

However, EXAFS is not really as common as other spectroscopy technique EDS and the main reason for that is we need tunable X-rays to capture a particular edge. I hope you appreciate that. Whenever I showed the earlier images, you were going at a particular value of the absorption edge, and this means we need a source for X-ray which can gives us energy over a particular range.

And this not only that, we also need a energy resolution which is very, very good of the order of 10^{-4} V in 1 volt. And therefore, most likely and in most cases, we have to use a synchrotron source for carrying out EXAFS study. Having said that, the main driving force for carrying out EXAFS is to study light elements like carbon, oxygen and nitrogen. Now these elements cannot be very well studied using conventional spectroscopic technique.

Having said that, we talked about different kind of interactions that occur namely the electron, free electron that is given out once a photon energy is absorbed. We also talked that there can be a fluorescent X-ray that can come off and there can also be a object electron. So these signals can be used in EXAFS in one way or the other to get some information about the localized chemical composition. Having said that, EXAFS is generally used in transmission as well as fluorescent mode to get the relevant information.

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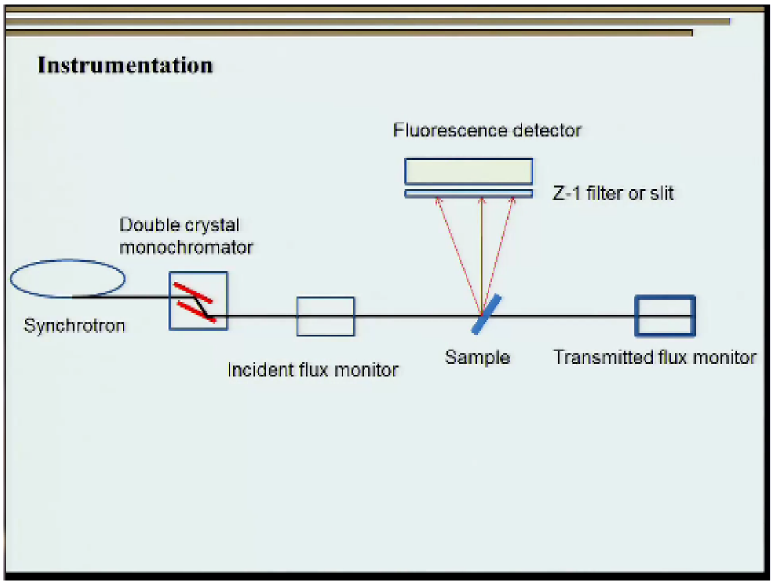

Instrumentation

Fluorescence detector

Z-1 filter or slit

Double crystal monochromator

Synchrotron

Incident flux monitor

Sample

Transmitted flux monitor

A general instrument that wherein we can carry out EXAFS is shown over here and you can see that we have a beam coming out from synchrotron. However, we need a double crystal mono-chromator to get a particular range of energy, and we need an incident flux monitor to see what is the intensity of the incident X-rays. Then it has to interact with our sample. If it is working in transmission mode you can see that the synchrotron beam passes right through the sample.

And we have a transmitted flux monitor which monitors the intensity after the X-rays have passed through the sample. At the same time we also have a fluorescence detector to see what all kind of fluorescent photons or fluorescent X-ray that we are getting. So having said that, I hope you appreciate that we can get information about the chemical environment in a particular material either using the fluorescent signal or the transmission signal.

The point that is to be noted here is that, in the transmitted signal the frequency of the incident and the transmitted wave remains the same while in fluorescence there is a change in the intensity of the not only there is change in the incident photon.

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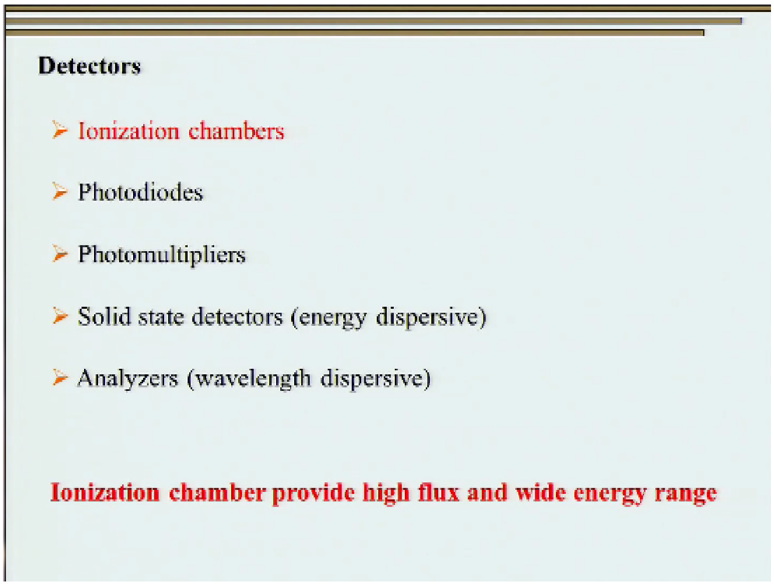

Detectors

- Ionization chambers
- Photodiodes
- Photomultipliers
- Solid state detectors (energy dispersive)
- Analyzers (wavelength dispersive)

Ionization chamber provide high flux and wide energy range

Having said that, for detecting the intensity of the X-rays, we essentially use ionization chambers. Other detectors like photo diodes, photo multipliers as well as solid state energy dispersive detectors as well as wavelength dispersive detectors which we had touched upon earlier in this module. As well as I am sure it must have been covered in the earlier part of this course by colleague.

But most likely what we use in case of extended X-ray absorption fine structures are ionization chambers as they provide high flux and wide energy range. Now that we have gone, so you see how simple we have a very simple EXAFS technique. The instrumentation part has got nothing exotic. However, one of the most important criteria is the availability of synchrotron.

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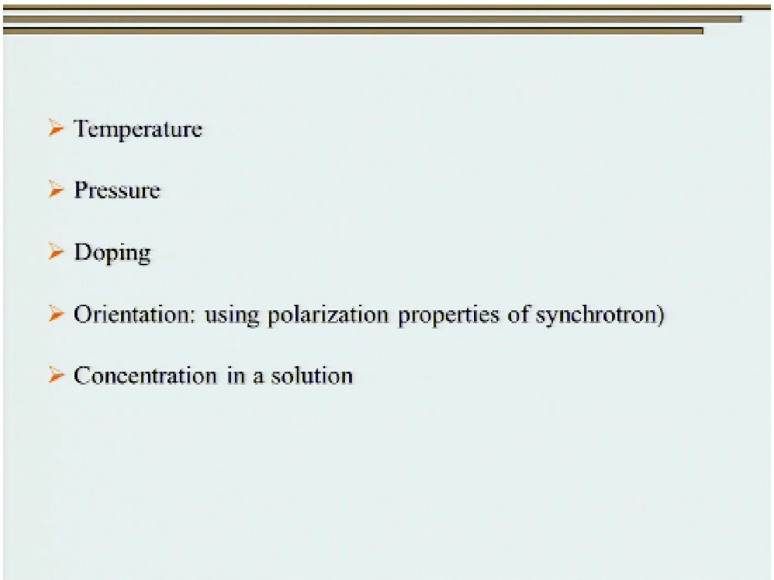

- Temperature
- Pressure
- Doping
- Orientation: using polarization properties of synchrotron)
- Concentration in a solution

Having said that you see with such a simple instrumentation, there is a strong capability to carry out in-situ experiments. So we can vary temperature, pressure, doping, as well as orientation and concentration in the solution and study how the chemical composition of the material under consideration is changing as a function of external stimuli. Another important thing that I have not mentioned yet is that, there is ability for us to get the synchrotron and use a polarized property of EXAF.

And if you have polarized wave of a synchrotron or X-rays we can see get sufficient information about the orientation. Orientation I mean like the kind of bonds that we are having between A and B. So by EXAFS that you can know that A is surrounded by B but if you use polarized X-rays we can not only know that A is surrounded by B or C but also at what angle it is aligned with respect to A. This is particularly important for deciding the chemical bonding between the two species.

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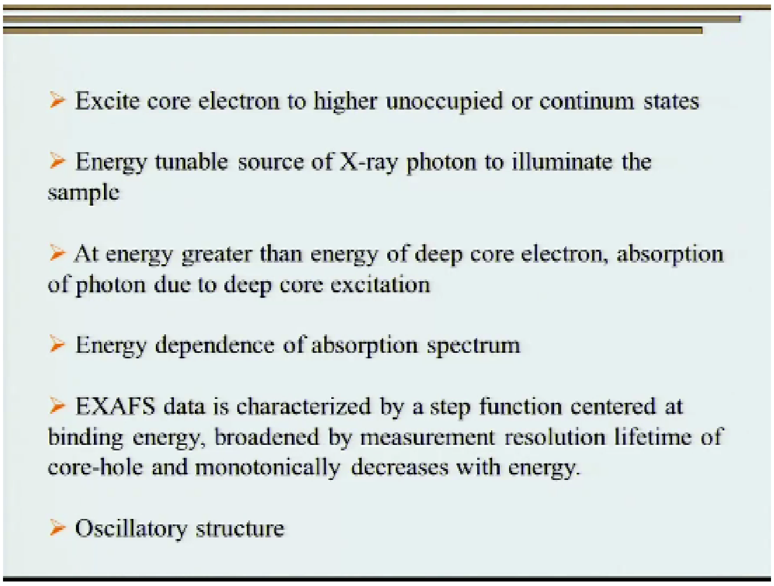

- Excite core electron to higher unoccupied or continuum states
- Energy tunable source of X-ray photon to illuminate the sample
- At energy greater than energy of deep core electron, absorption of photon due to deep core excitation
- Energy dependence of absorption spectrum
- EXAFS data is characterized by a step function centered at binding energy, broadened by measurement resolution lifetime of core-hole and monotonically decreases with energy.
- Oscillatory structure

So as we had already discussed, EXAFS what we do? We excite the core electron to higher unoccupied or a continuum state. Now for this we need a energy tunable source of X-ray photon to illuminate the sample. For instant, if I am having a compound say ABCD, and I want to study what is the neighbourhood of CA and A or B. Then I should be in a position to tune my energy to the absorption edge of ABC or D.

Having said that, another important point is that what all patterns we are getting, it is not just absorption edge as the name suggests, this is extended X-ray absorption fine structure. So we should have the ability to provide photons with energy of few 100s of electron volt below the absorption edge and up to few 1000s of electron volt beyond the absorption edge. So there is a strong energy dependence of the absorption spectrum.

And we should be in a position to control the energy. And therefore, we have to use a synchrotron which gives us a energy resolution of 10^4 volt in about 10 volt. So as we can see, the EXAFS data is characterized by a step function centered at binding energy, broadened by measurement resolution lifetime of core-hole and monotonically decreases with energy. Remember what all we are getting is happening at the absorption edge.

So let us go back and just look at the absorption edge. So if you go to the absorption edge, this is where you knock off an electron from the inner shell and then there are these interaction between the electron wave and this interaction leads to the oscillations that we are getting. So in order to get that, there is a lot of super impositions of the signals, because there is not just one scattering event, there is easily a situation wherein you can get multiple scattering. And therefore this makes analysis of the data slightly complicated.

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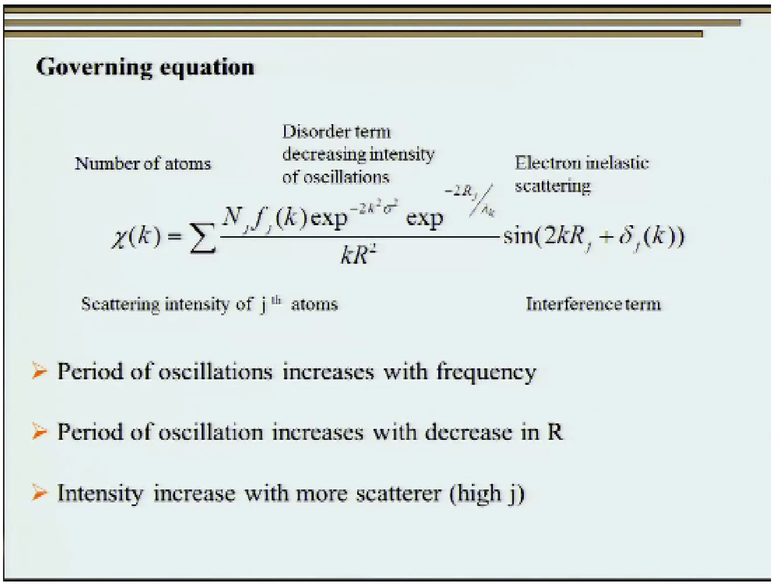

Governing equation

Number of atoms

Disorder term decreasing intensity of oscillations

Electron inelastic scattering

$$\chi(k) = \sum \frac{N_j f_j(k) \exp^{-2k^2\sigma^2} \exp^{-2R_j/\lambda_k}}{kR^2} \sin(2kR_j + \delta_j(k))$$

Scattering intensity of j th atoms

Interference term

- Period of oscillations increases with frequency
- Period of oscillation increases with decrease in R
- Intensity increase with more scatterer (high j)

However, a very simple governing equation is given over here. So here you see the χ(k) is essentially ∑ N_j which is nothing but the number of atoms which are surrounding a particular atom or element under consideration. The F_j(k)exp$^{-2k2/\sigma2}$ is essentially the disorder term which has actually decreases in intensity with the number of oscillations, and there is a electron inelastic scattering term.

So here you see we have a scattering term which essentially comes from elastic scattering and here we have the inelastic scattering term which actually determines the interference. So we have to see how much interference is occurring. So this electron inelastic scattering term is this one, the second exponential. The first exponential over here is actually the elastic scattering like which dampens.

And this interference turn essentially decides what kind of an oscillation pattern that we are going to get. As you can see from this equation, the period of oscillations increases with the increase in frequency. Having said that also there is an increase in the period of oscillation with increasing R, where R is the distance between the atoms under considerations. And also the intensity χE actually increases as we have more and more J or more and more atoms. Assuming that all of them are scattering in fees. So let us go and see how exactly EXAFS data looks like.

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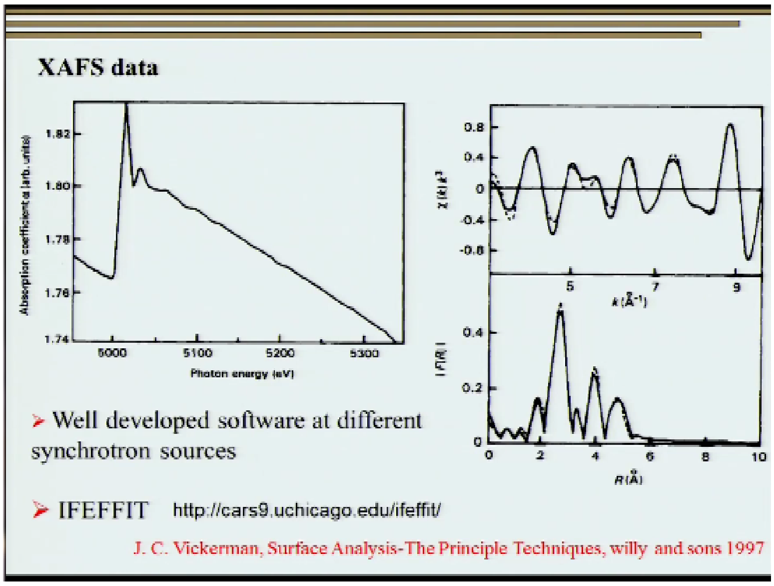

XAFS data

- Well developed software at different synchrotron sources
- IFEFFIT http://cars9.uchicago.edu/ifeffit/

J. C. Vickerman, Surface Analysis-The Principle Techniques, willy and sons 1997

So you see here this is again our energy versus absorption coefficient and you see the same thing we do see instead of getting a sharp drop, you do see a few modulations over here. This does not show a lot of information. However, once we convert it to χK, K cubed versus K we see that there are lot of oscillations. I will tell you the reason why we are multiplying with K cubed.

And I hope you appreciate that essentially it is done to actually see the oscillations at higher value of energy. As we move away from the absorption peak, we see that there is a lot of damping effect. So in order to see the oscillations if we plot, $\chi(k)$ versus K cubed, we do see all the oscillations. Now another important thing is this K is essentially in the reciprocal space.

So that is why you see over here we have the angstrom inverse right. Now this information can be taken back and plotted in the real space, and we do get this as a function of R which is nothing but the actual distance between the atoms under considerations. And this shows the intensity right. So this is what we are going to try and match when exactly we take the data.

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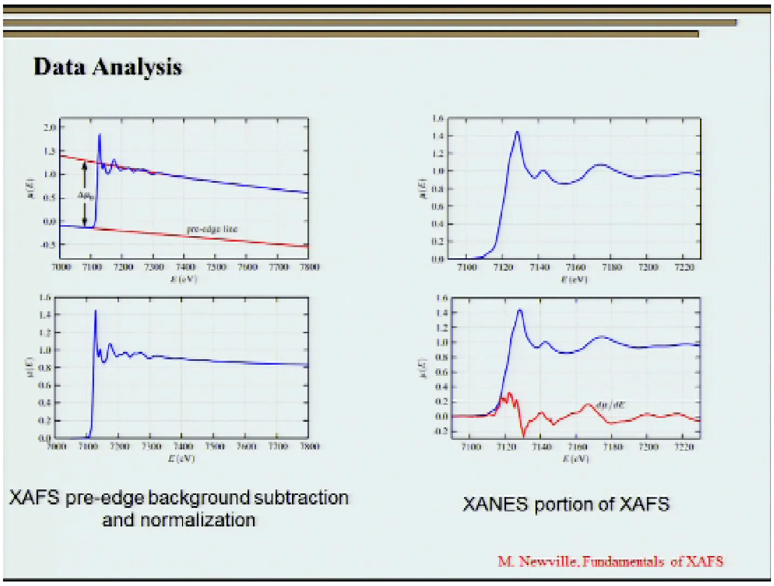

Data Analysis

XAFS pre-edge background subtraction and normalization

XANES portion of XAFS

M. Newville, Fundamentals of XAFS

So now I am going to show you something about how exactly we do EXAFS data analysis. Having said that, I should mention that we use well developed software at difference in proton sources and one such software is IFEFFIT which is used at University of Chicago. Now these are available for free and what you can do is, you can take and try to analyze what all data we are getting from different synchrotron sources.

So you see over here this is what we have, this is what the kind of data that we get fine which is nothing but mew of E versus the energy. So this μ(e) comprises of both the things. For your xanes data which is very close to the absorption edge which is shown over here and which we can separate and the data which is far off from the absorption edge. But even before we do that once we get a signal, the first and the foremost thing that we do is to subtract the background and this is what has been shown over here.

So we subtract the pre edge background and then we normalize it. We can also separate the xanes or a region which is very close. So you see we have gone almost up to 100 eV and said that up to 100 eV I have xanes and beyond that I have X-ray absorption fine edge structures. We continue with that and after doing all our pre edge subtraction we carry out post edge subtraction and here you see the kind of oscillations that we are getting. Quite a few bit of oscillations.

Now what we do is we take the same part after subtracting the background and our χ(k) versus the K, and you see this is the actual data that we get after doing the entire background correction. As we had seen earlier, in order to see or kind of modulate and see the oscillations, we can plot χ(k) versus k^2xk^2 versus K. And here you see how we get the modulated oscillations and they are easily visible. Now all these modulations correspond to a particular interference occurring between two atoms.

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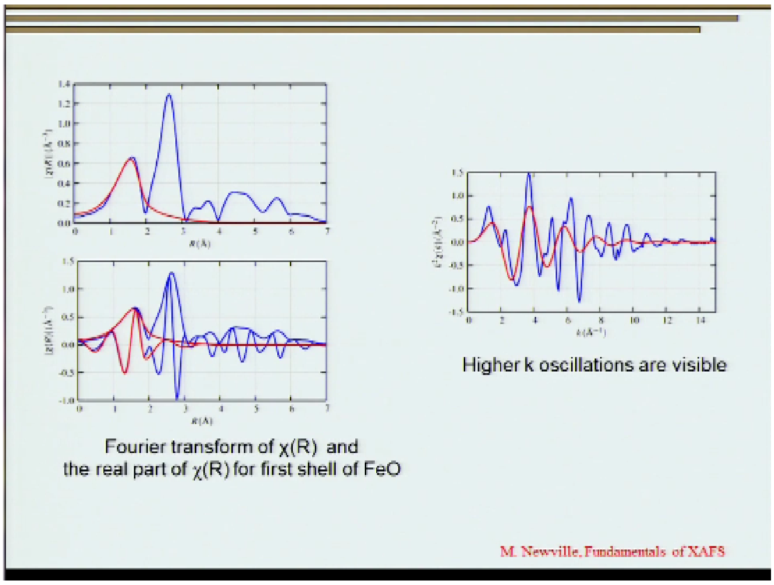

Fourier transform of χ(R) and
the real part of χ(R) for first shell of FeO

Higher k oscillations are visible

M. Newville, Fundamentals of XAFS

So, now if you see this is how it looks like, we had plotted χ(k) versus K. Now the same information can be taken back and plotted in real space, so now you see we have χ(R) versus R, and this R is in angstrom and here we see, we are seeing some characteristic peaks. Having said that, if you remember, this χ(R) that we are having as well as R itself, the Fourier transform of χ(R), it has a real part and an imaginary part.

So, we have tried to match the real part and we do indeed see the red one shows that okay there is a good match. Having said that, please note that you know the intensities are dying off at higher values of R, and once we plot, you know, K2 versus χ(K) versus K, you see that you know all the oscillations are visible and we can see then there is a good match, though it is not visible over here.

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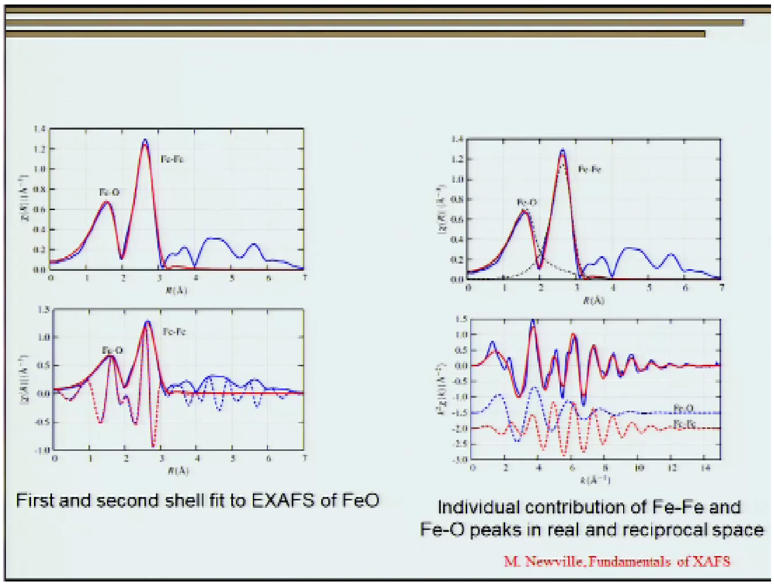

First and second shell fit to EXAFS of FeO

Individual contribution of Fe-Fe and Fe-O peaks in real and reciprocal space

M. Newville, Fundamentals of XAFS

Having said that once we get our χ(R) versus R, we can go back in the literature and actually find out which P corresponds to what. So this is just like JCPDS or ICDD, where we have a data base. So here, we can see that this peak which we get between 1 and 1.5 angstrom essentially corresponds to FEO, while between 2-3 actually corresponds to FEF and FE.

So by doing like this, we can see that we get fitting all different kind of peaks and get individual contribution from individual for that matter, here iron, iron and iron oxide piece, not only in the real but also in the reciprocal space. I hope with this analysis, it is very clear that we can identify not only what all atoms are present in the neighbourhood but also at what distance they are present. And therefore, this technique uses information about the chemical surrounding at the angstrom level.

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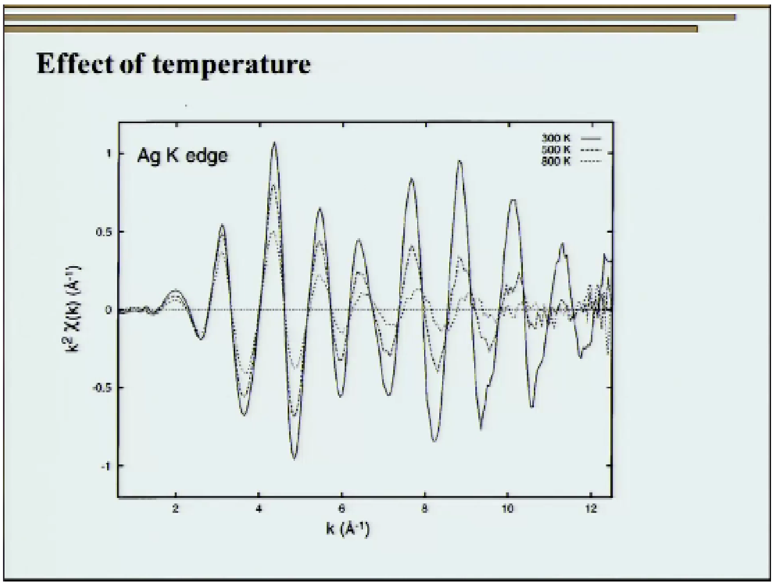

Effect of temperature

Here again, I have just mentioned to you that we can carry out various tests in-situ, like heating as well as applying pressure, so just to show you what kind of effect we have if we apply temperature we see when there is a continuous decrease with increase in temperature, so these are some practical limitations that we have, but remember the kind of oscillations, all these oscillations actually corresponds to the interference between the waves that are being scattered from the surrounding atoms.

And you see that as we increase the temperature, there is a decrease in the oscillations okay. Another important parameter, this χ(K), I hope you remember like if we start, if we go back to the first curve we see in this case, we have μ(E), which is nothing but your distribution and here I have swiftly shifted and I did not mention what exactly is χ(E).

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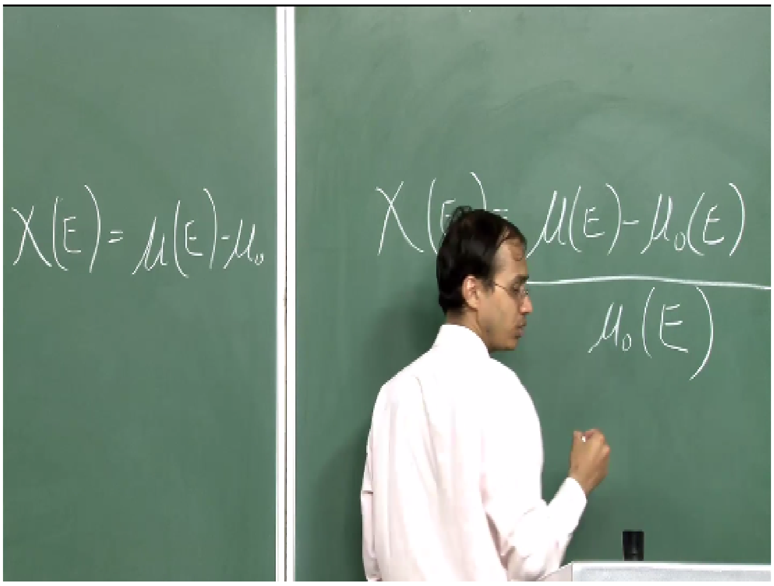

But let me just write that χ(E)= μ(E) – μ0(E) this is nothing but the differential term okay μ0 okay.

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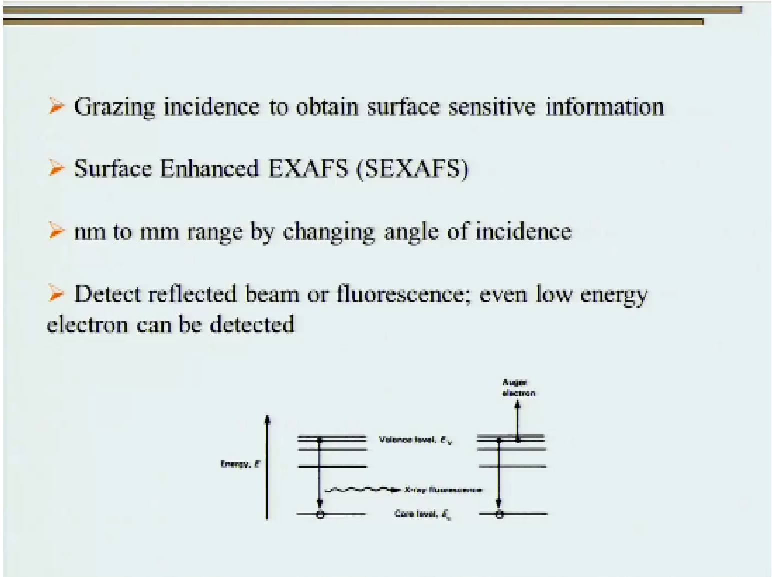

- Grazing incidence to obtain surface sensitive information
- Surface Enhanced EXAFS (SEXAFS)
- nm to mm range by changing angle of incidence
- Detect reflected beam or fluorescence; even low energy electron can be detected

So this is what we have done over here. So having said that what all we have talked about up until now is the basic, right, the basic physics for doing extended x-ray absorption fine structures. And I hope that you appreciate that we are talking about very thin samples, most I mentioned that you know, you have sample large enough so that the x-rays are able to pass through it.

However, there are instances when we are looking at surface phenomena and that is where grazing incidents is very important. And if we carry out the same x-ray absorption fine structures in grazing incidents more, it is known as surface enhanced EXAFS or SEXAFS. Now the biggest advantage that we have is that we can irradiate a region extending from nanometre to millimetre range just by changing the angle of incidence.

Having said that we can also use the same concept of detecting either the reflecting beam, or the fluorescence, or even low energy electron namely the aujee electrons to get some information about the chemical environment of a particular element under consideration.

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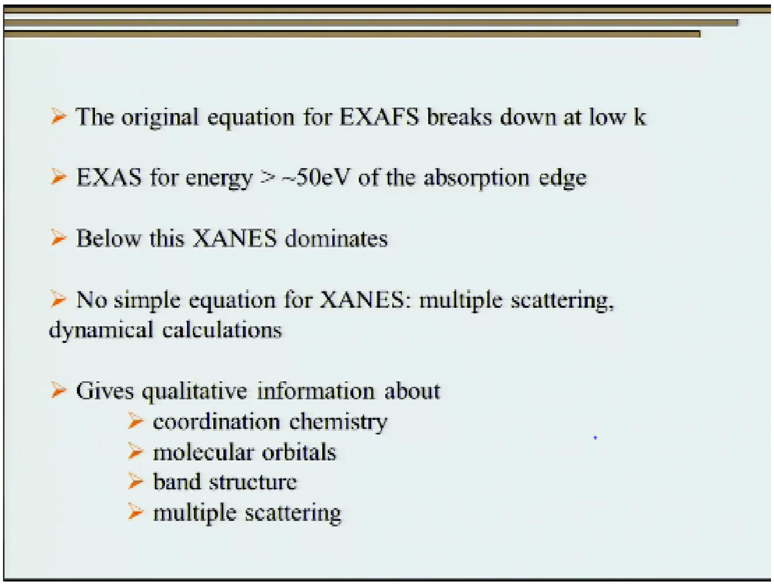

- The original equation for EXAFS breaks down at low k
- EXAS for energy > ~50eV of the absorption edge
- Below this XANES dominates
- No simple equation for XANES: multiple scattering, dynamical calculations
- Gives qualitative information about
    - coordination chemistry
    - molecular orbitals
    - band structure
    - multiple scattering

As I had already mentioned, that the original equation of EXAFS breaks down at lower K, where we have this near edge x-ray absorption fine structures. In this energy range, actually what happens is there are multiple scattering events and the dynamical calculations have to be incorporated. Now, these are two involved and as such xanes rather xanes or near edge x-ray absorption fine structures is actually used only as a finger print technique.

By which I mean that if you see a particular peaks in the xane spectra we can say that okay this particular element is present. However, the quantitative analysis of this technique has not developed till date. However, the xanes use a lot of qualitative information about the coordination chemistry, molecular orbitals, band structure as well as various multiple scattering event that can occur in a material.

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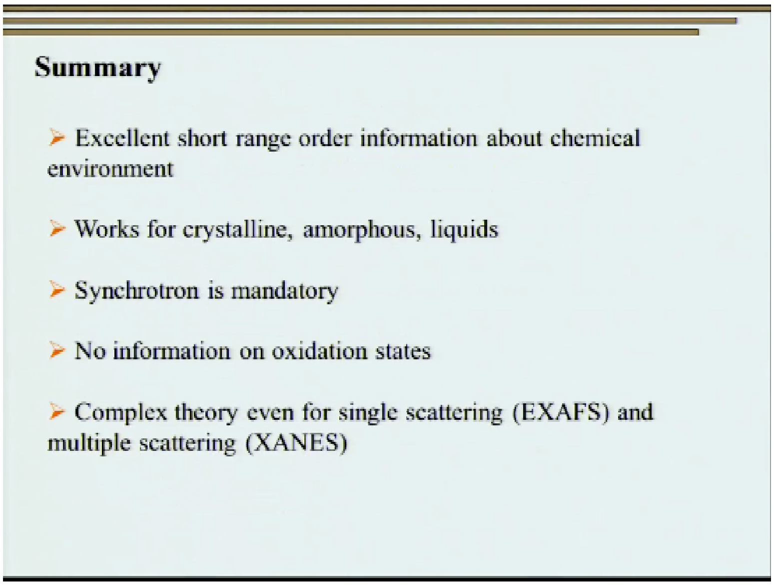

Summary

- Excellent short range order information about chemical environment
- Works for crystalline, amorphous, liquids
- Synchrotron is mandatory
- No information on oxidation states
- Complex theory even for single scattering (EXAFS) and multiple scattering (XANES)

Having said that, I hope you appreciate that we can get excellent short range order information about chemical environment using x-ray absorption spectroscopy. We can also use this technique to study crystalline amorphous as materials as well as liquids. However, synchrotron radiation is almost always necessarily for carrying out x-ray absorption spectroscopy.

Another important disadvantage that we have is though we know the chemical composition or the chemical surrounding, we have absolutely no idea about the oxidation states. And the theory that is involved for understanding EXAFS as well as xanes is pretty complicated and this complicate the use of this technique in getting information with high fidelity.

(Refer Slide Time: 35:52)


Thank you

Thank you.

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Camera
Ram Chandra
Dilip Tripathi
Padam Shukla
Manoj Shrivastava
Sanjay Mishra

Editing
Ashish Singh
Badal Pradhan
Tapobrata Das
Shubham Rawat
Shikha Gupta
Pradeep Kumar
K.K Mishra
Jai Singh
Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar

Ashutosh Kumar

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Sharwan
Hari Ram

Production Crew
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

Office
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

Production Manager
Bharat Lal

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