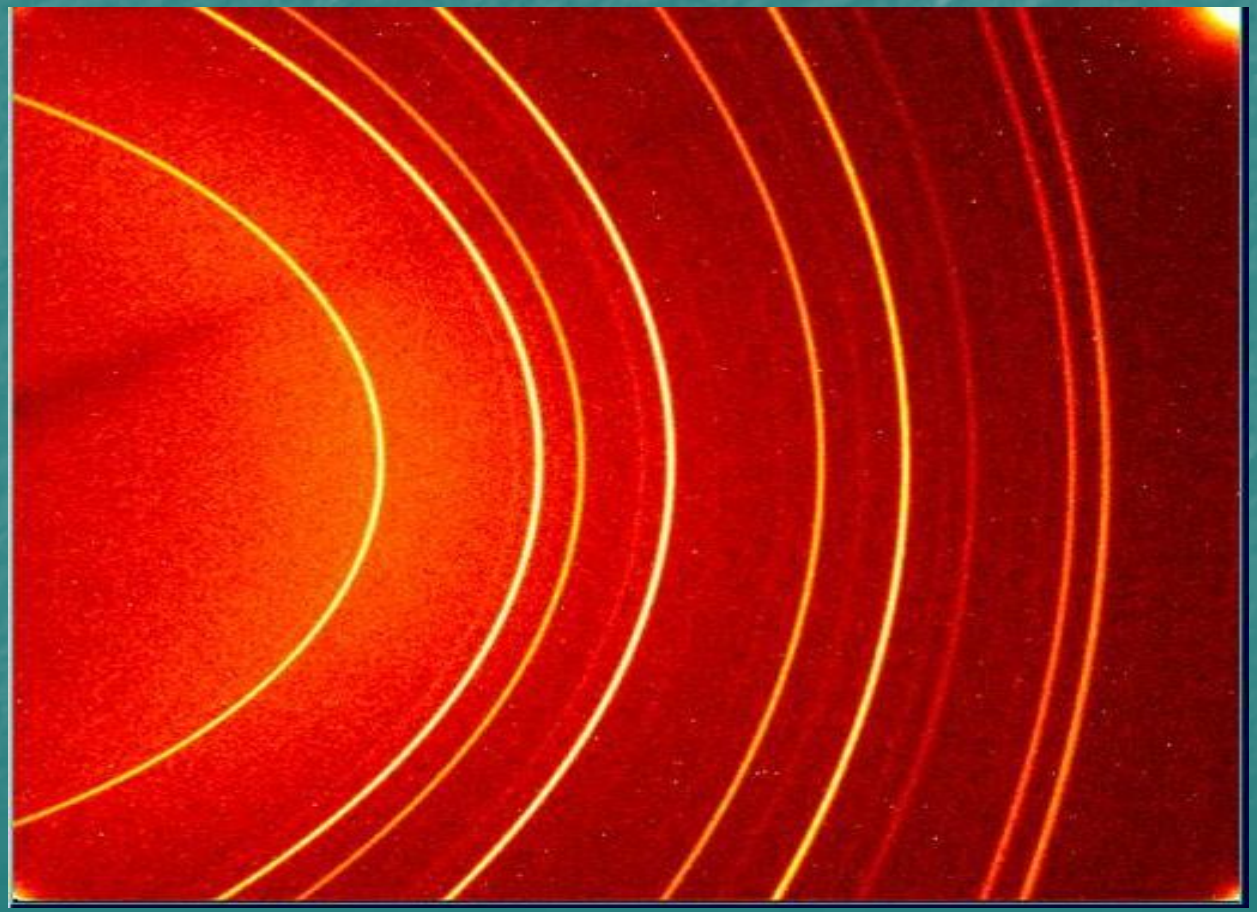
EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS): Theory & Application



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Some important definitions

X-ray & X-ray spectroscopy

EXAFS and its data analysis

Manufacturing Requirements

Example: EXAFS / XANES & Thin film

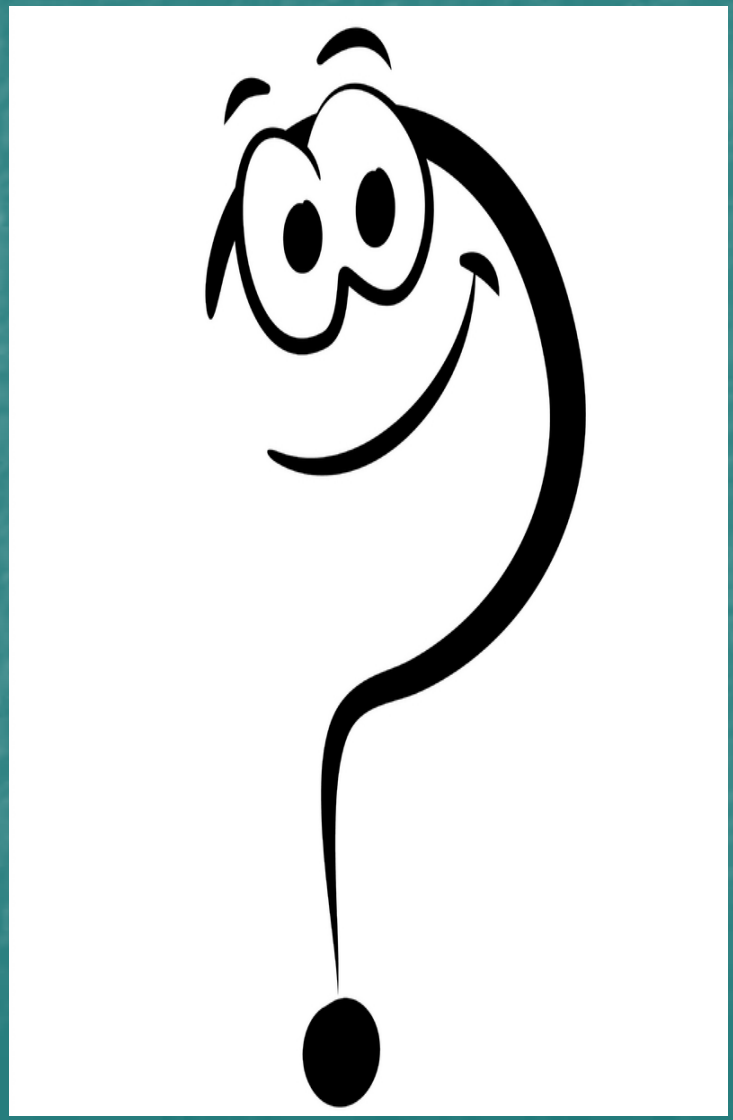
Summary

Some Important Terms & Definitions

1. X-ray absorption spectroscopy

2.Extended X-ray Absorption spectroscopy (EXAFS) and its application

3. X-ray Absorption Near edge Spectroscopy (XANES)



Some Important Terms & Definitions

- **Absorption coefficient (μ)**

  It describes the extent to which the intensity of an energy beam is reduced as it passes through a specific material

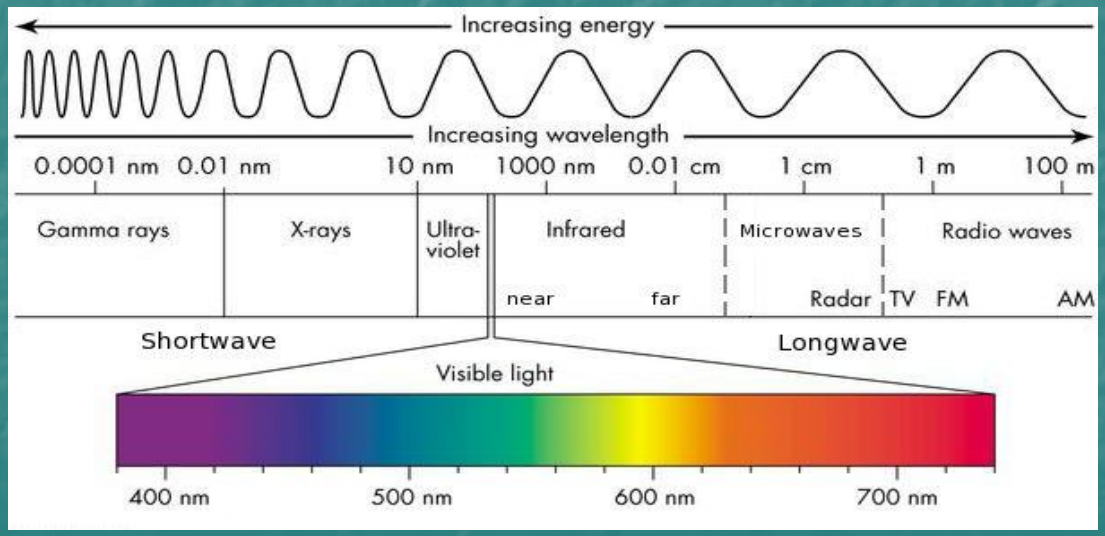
- **Absorption edge**

  It is a sharp discontinuity in the absorption spectrum of X-rays by an element that occurs when the energy of the photon corresponds to the energy of a shell of the atom.

Recall: X-ray

X-rays like any other electromagnetic radiation, can be treated either a particle or a wave. This characterization of a light is defined by Einstein relation:

$$E = h\upsilon = hc/\lambda \qquad (1)$$



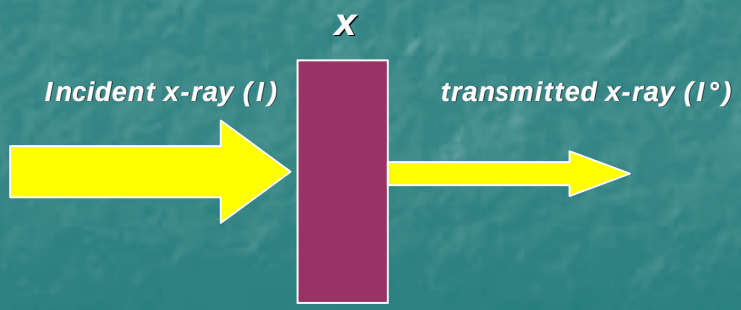
X-ray Absorption Fine Structure

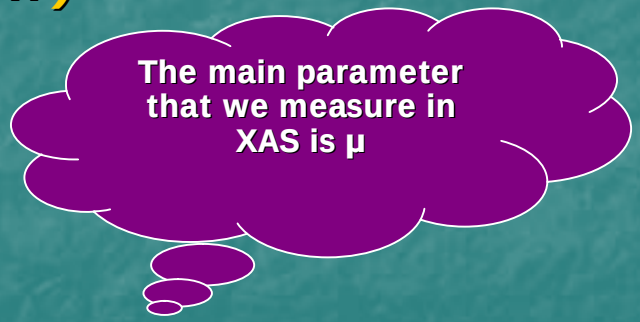
In the interaction of X-rays with matter, there are three main processes:

1) absorption
2) inelastic scattering : non-conservative energy for the incident particle
3) elastic- scattering : conservative energy for the incident particle

The absorption can be characterised by the following equation:

$$I = I_{\circ} \exp(-\mu x)$$

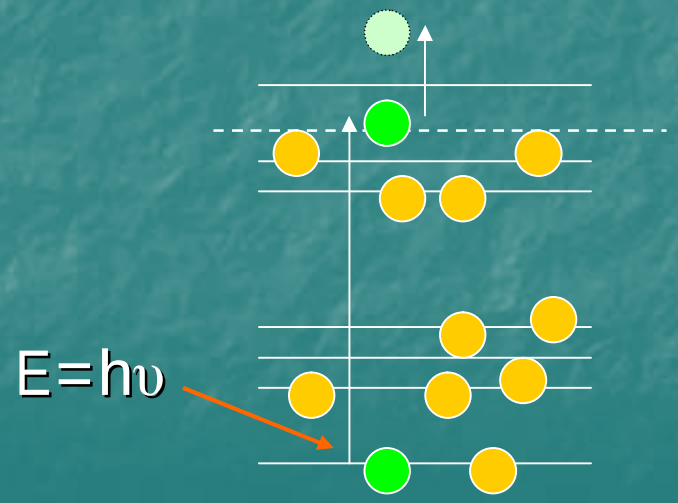




What happens when the x-rays are absorbed by the sample?

What is absorption ?

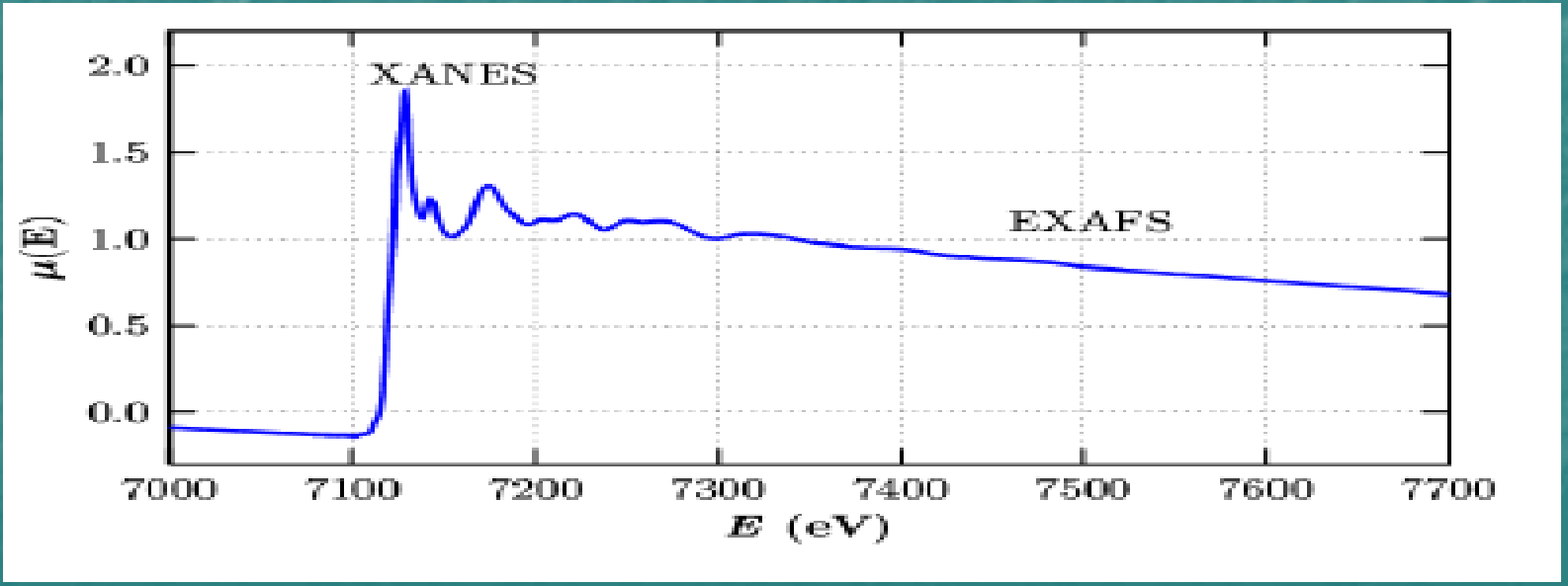
The photon is absorbed when its energy consume for excitation of an electron, So the energy should be greater that bonding energy of an electron.



WHAT IS XAS?

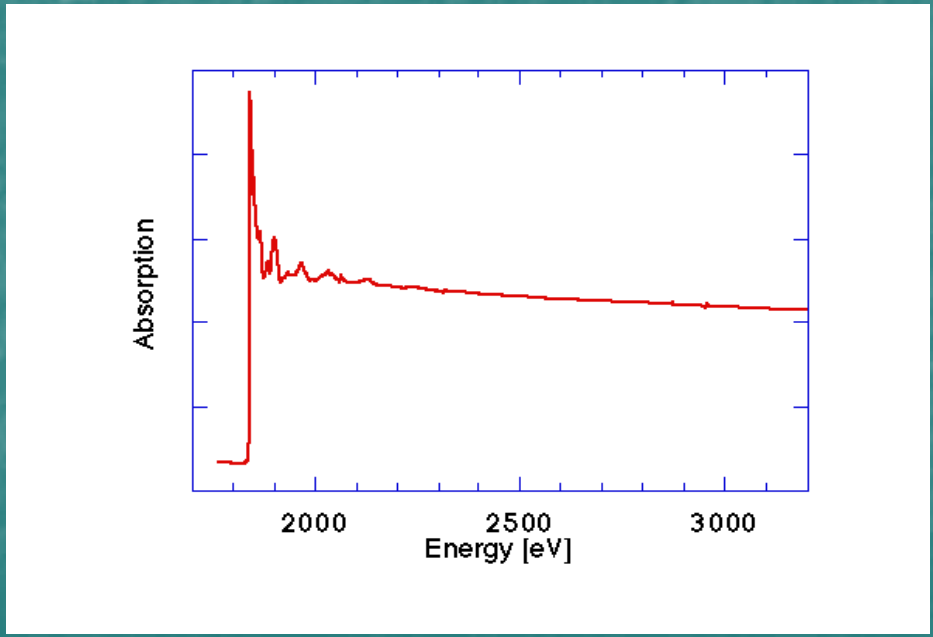
X-ray Absorption Fine-Structure (XAFS) is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge. XAFS is also referred to as X-ray Absorption Spectroscopy (XAS) and is broken into 2 regimes:

XANES X-rayEXAFS Extended X-ray Absorption Fine-Structure which contain related, but slightly different information about an element's local coordination and chemical state.

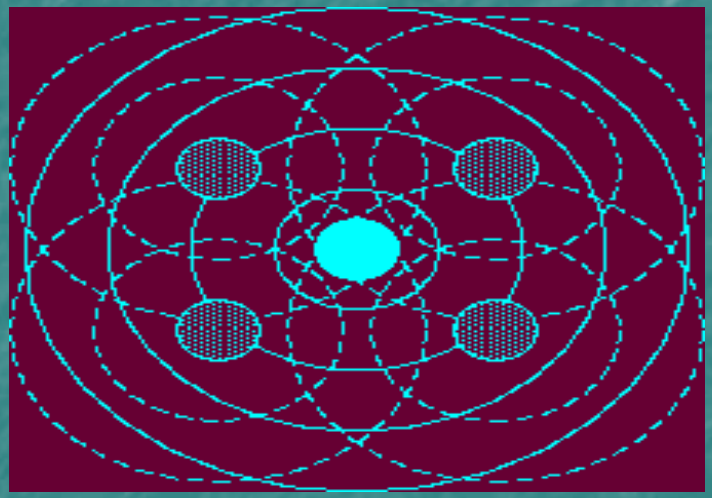


What is EXAFS???

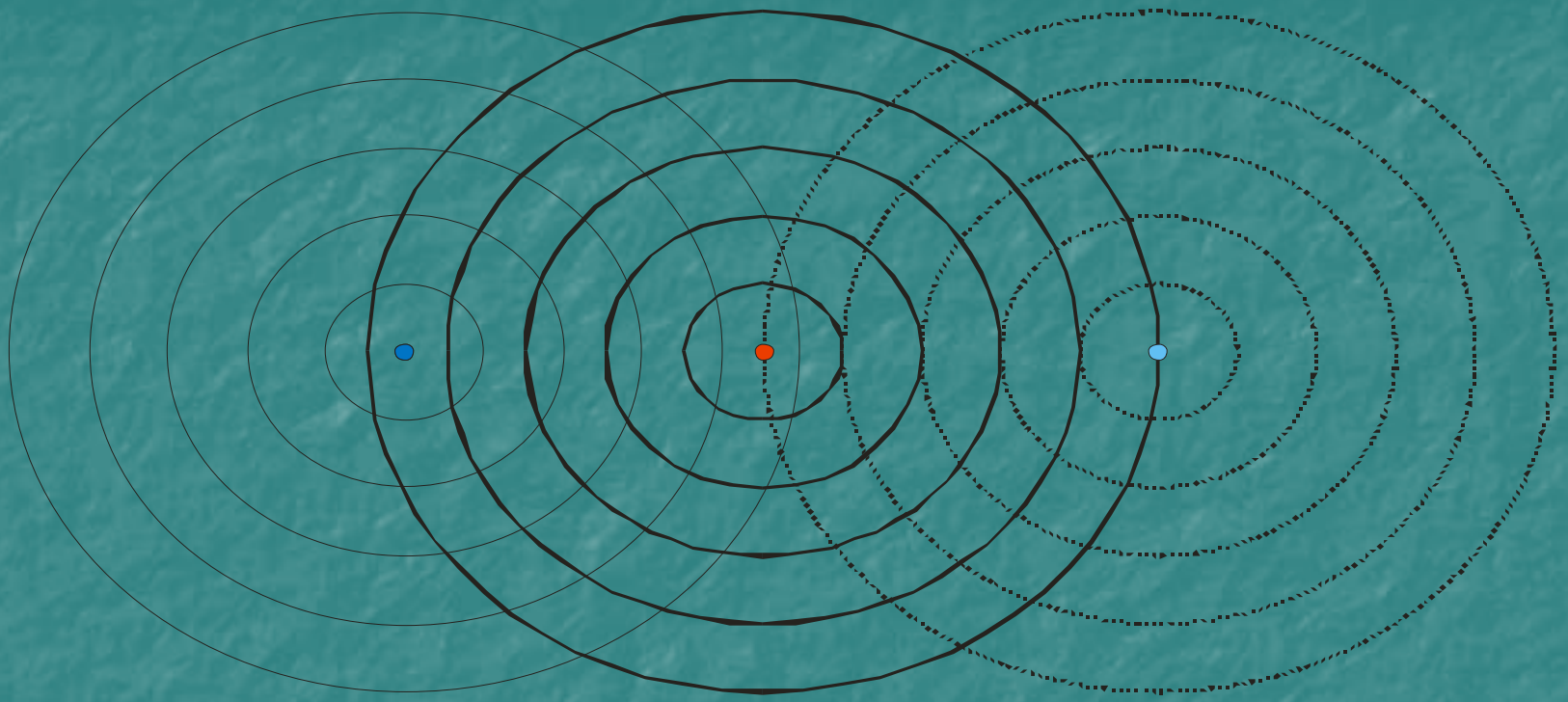
- EXAFS is a region of XAS spectrum which is started approximately from 50 e V up to 1000 e V above the absorption edge.

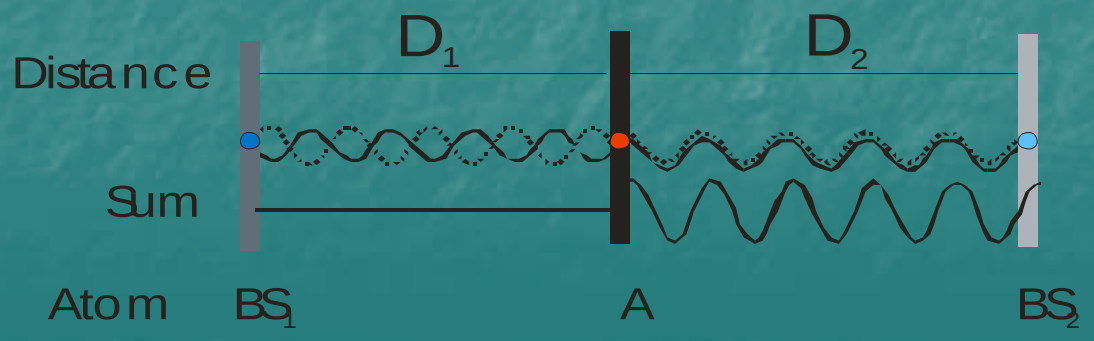


In condensed matter or (multi-atomic gas molecules) the ejected photo-electron wave will be scattered by neighbouring atoms.



It is the interference between the outgoing electron and the back-scattered ones which leads to oscillations visible in the absorption spectrum above the edge. These can extend to up to 1000 eV past the edge. These oscillations are the EXAFS.





Interference shown for two distances D_1 and D_2 with $D_1 < D_2$

Courtesy E. Welter

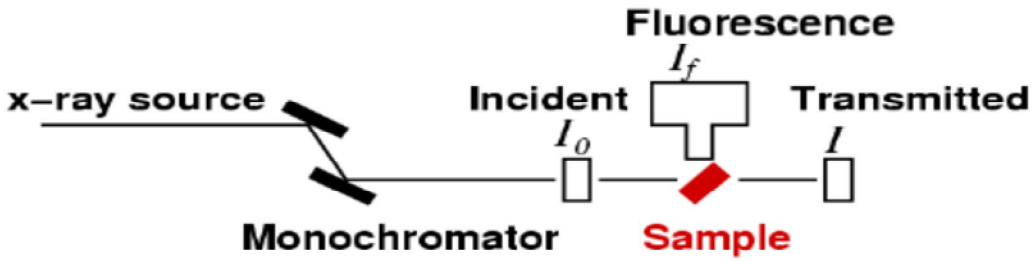
WHY EXAFS???

- **The number of neighboring atoms.**
- **The nature of neighboring atoms (their approximate atomic number)**
- **Distances between central and neighboring atoms.**
- **It is not just limited to crystals.**

Dealing with data

- Steps in traditional EXAFS data analysis:
- 1) correction for instrumental effects
- 2) normalization to unit edge step
- 3) interpolation to k-space
- 4) background subtraction
- 5) Fourier transform

X-ray Absorption Measurements



XAS measures the energy dependence of the x-ray absorption coefficient $\mu(\mathrm{E})$ at and above the absorption edge of a selected element. $\mu(\mathrm{E})$ can be measured two ways:

Transmission: The absorption is measured directly by measuring what is transmitted through the sample:

$$\mathrm{I} = \mathrm{I_0 e^{-\mu(E)t}}$$

$$\mu(\mathrm{E})\mathrm{t} = \ln(\mathrm{I/I_0})$$

Fluorescence: The re-filling the deep core hole, is detected. Typically the fluorescent x-ray is measured.

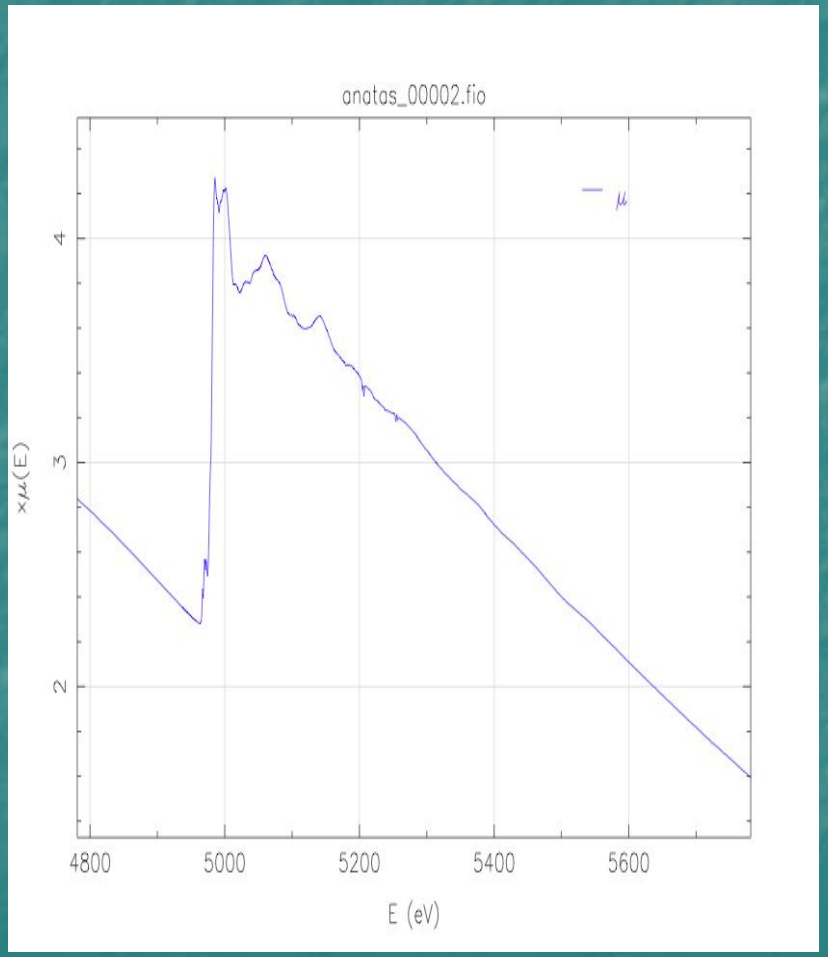
$$\mu(E) \sim I_f/I_0$$

Dealing with data

Raw data

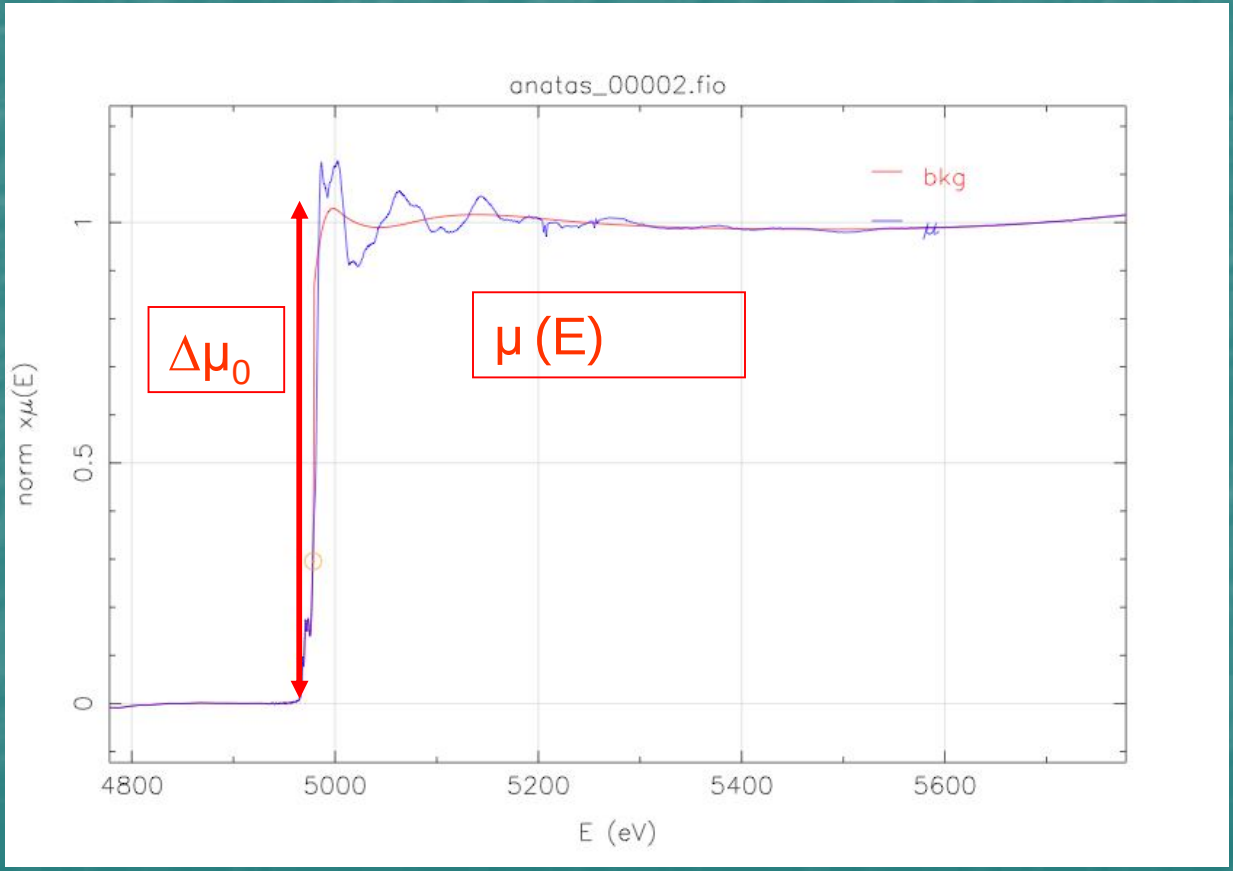
1)Convert experimental variables in to experimental spectrum

$\mu(E)X=\ln(I^o/I)$



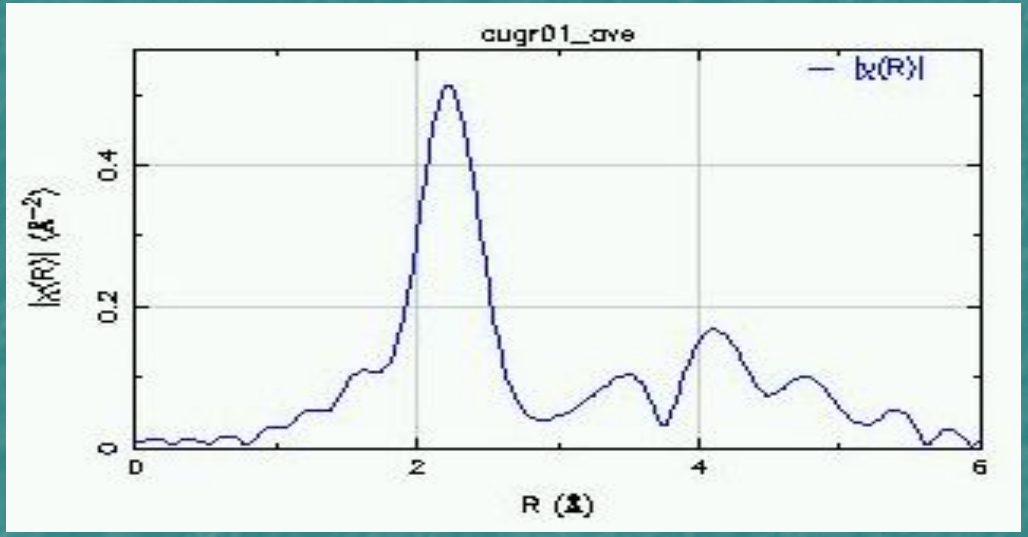
normalization

Normalised XAFS spectrum of pressed powder tablet



Fourier Transform of $\chi(k)$

- **Similar to an atomic radial distribution function**
  - Distance
  - Number
  - Type
  - Structural disorder



  - It is easier to analyze
  - XAFS in terms of photo electron wave(k)

The EXAFS Equation

To model the **EXAFS**, we use the ***EXAFS Equation***:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

where $f(k)$ and $\delta_j(k)$ are *scattering* properties of the neighboring atom.

Knowing these, we can determine:

R	distance to neighboring atom.
N	coordination number of neighboring atom.
σ^2	mean-square disorder of neighbor distance.

The scattering amplitude $f(k)$ and phase-shift $\delta_j(k)$ depend on atomic number ***Z*** of the scattering atom.

Manufacturing Requirements

Set up:

1.X-ray source(High intensity beam is needed)

2.A monochromatic crystal

3. Incident beam detector

4.Sample

5.transmission detector

6.Flourescence

From the x-ray source, the beam of x-rays are directed towards a sample, monochromatic crystal, which redirects the beam toward the sample. The beam intensity must be measured prior to entering the sample, so an incident detector is in-line before the sample. After the sample, another detector is used to determine the transmission intensity. Generally there is also a fluorescence detector to the side of the sample, for fluorescence studies.

EXAFS /XANES & THIN FILM

Surface structure and thermal vibrations of Ni and Cu thin films studied by extended x-ray absorption fine structure:

***Investigation of dynamical properties of the surface metal-metal bonds

Steps:

1. HOPG (Highly Ordered Pyrolytic Graphite) substrate was cleaved with tape in ultrahigh vacuum chamber

2. Annealing at 1200K to remove all contaminations on surface

3.Cooling down, Ni OR Cu was deposited (deposition rate was measured by quartz crystal monitor)

4. XAFS spectrum was measured at hard x-ray double crystal monochromator stations

XANES & THIN FILM

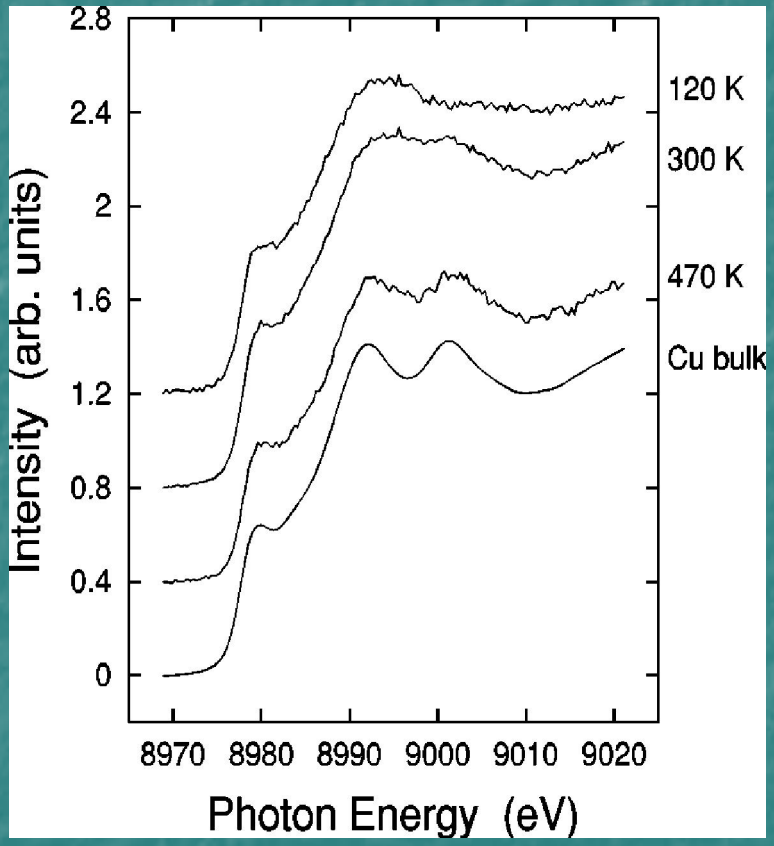
Some information can obtained from XANES spectrum:

Compare to Cu foil spectrum, absence of

2 peaks in 120 k shows that this film doesn't

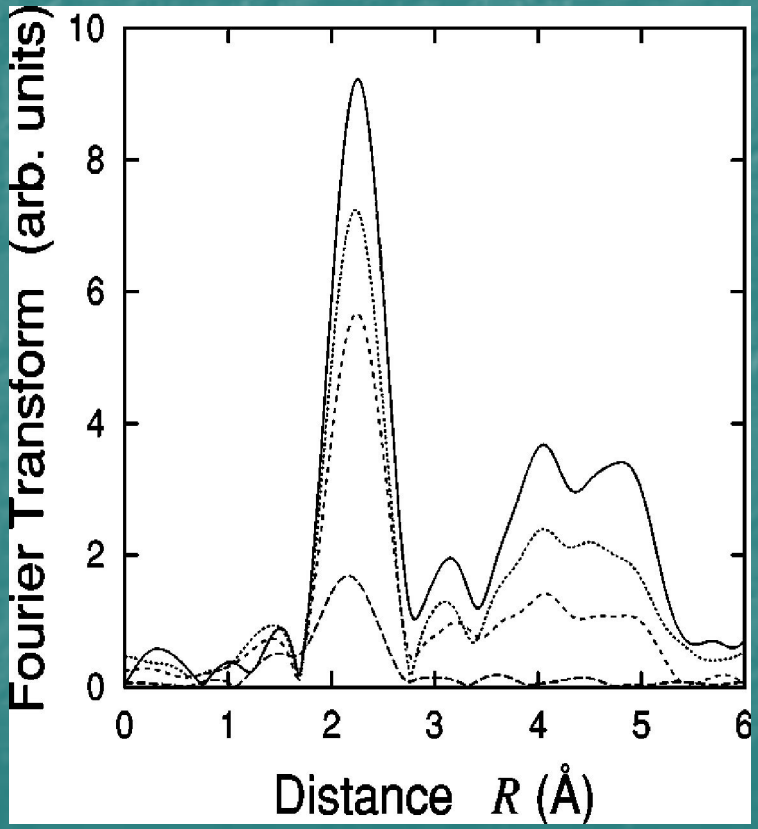
have a good crystallization.

After annealing in other temperature you can see the characteristic peaks appear.



"change of Cu k-edge XANES spectrum"

EXAFS & THIN FILM



The Fourier transform for the Cu thin film:

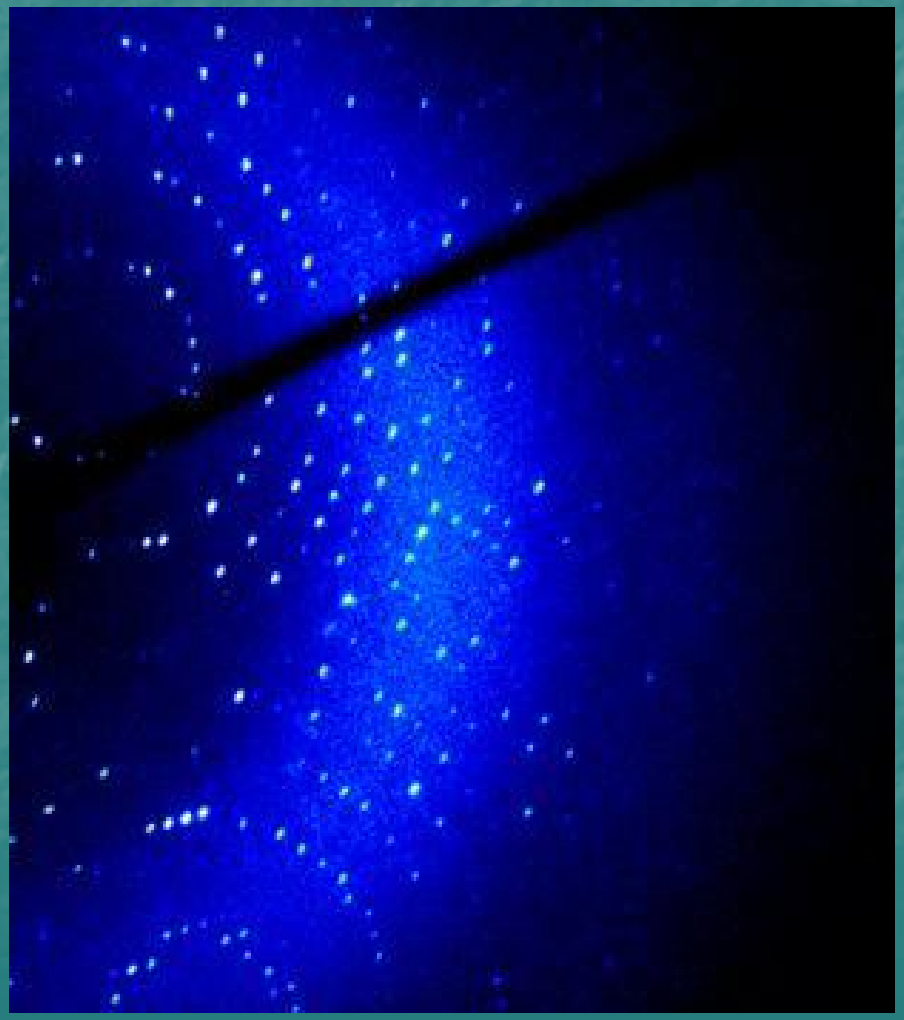
- The dominant peaks at 2 A° are ascribed to the (NN) metal-metal coordination.
- Drastic change at 120K spectrum.

Smaller EXAFS amplitude shows smaller coordination number and larger disorder of the film.

- The absence of higher shells means the film doesn't crystallized completely.

Summary

Theoretical standards allow the EXAFS experimentalist to quantitatively analyze problems of significant complexity. With theoretical standards higher shells, multiple scattering contributions, mixed shells, polarization and many other effects can be treated rigorously. Using the theory is easy and accessible. Many current analysis programs make excellent use of existing theory.



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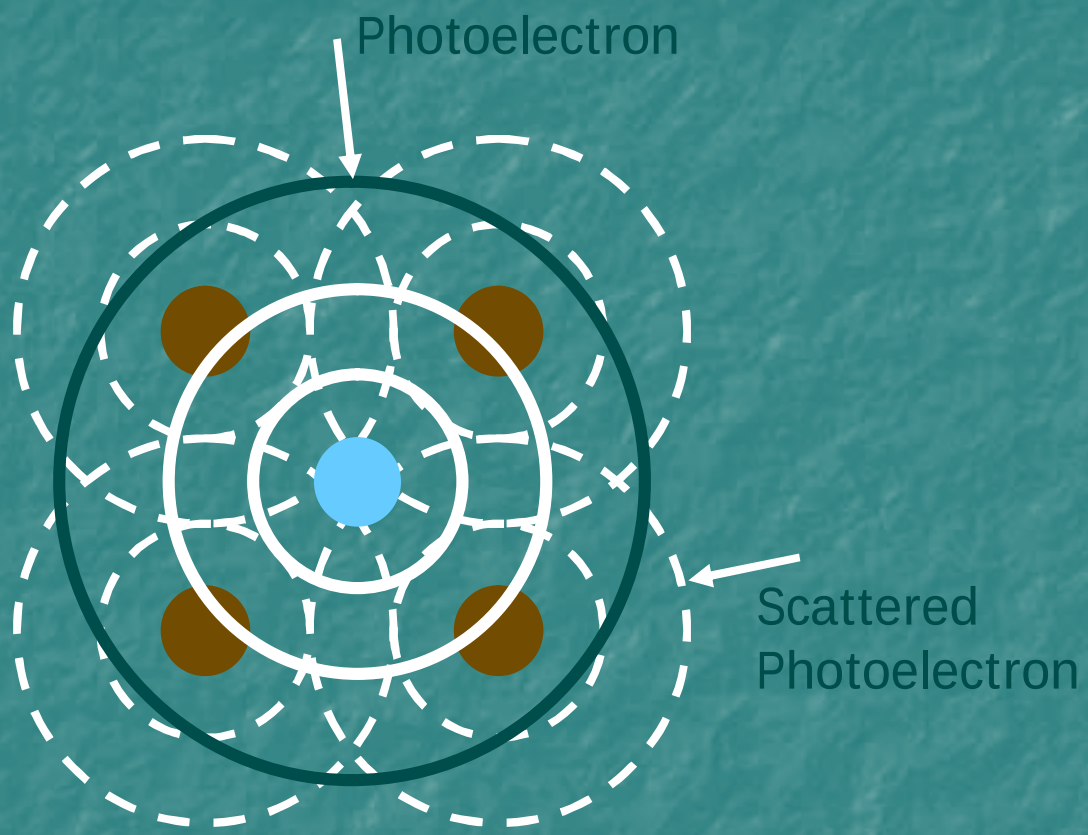
- 2/http://images.google.ca/imgres?imgurl=http://www.lightsource.ca/education/images/science/xas.gif&imgrefurl=http://www.lightsource.ca/education/science.php&usg=__uYjrE7b-VdLaReUjsnOaAC6C_EA=&h=270&w=351&sz=8&hl=en&start=2&um=1&tbnid=j5u0jTZMaYpl0M:&tbnh=92&tbnw=120&prev=/images%3Fq%3Dxas%26um%3D1%26hl%3Den%26sa%3DX
- 3/Basic principles and data analysis(Boon K.Teo)

THANK YOU!


Photoelectron
Scattered
Photoelectron

What happens when the x-rays are absorbed by the sample?

When an x-ray photon is absorbed by an atom, it enters an excited state for an extremely short period of time.

When the atom de-excites it will emit an electron from near the core of the atom. This will only happen if the energy of the x-ray is higher than the energy level that is binding that electron to the core of the atom.

That electron wave leaving the originating atom comes in contact with other atoms that are near it ,causing them to become excited and the process repeats itself.

This electron ‘interference’ can be detected and measured and yields information about the location and distance between atoms within a molecule.

"EXAFS Equation"

Scattering intensity of the jth atom

"disorder" term (decreases intensity of oscillations)

Electron scattering (λ=inelastic mean free path)

Number of atoms

$$\chi(k) = \sum_{\text{shells}} \frac{N_j f_j(k) \exp^{-2k^2\sigma^2} \exp^{-2R_j/\lambda(k)}}{kR_j^{\,2}} \sin\left(2kR_j + \delta_j(k)\right)$$

Interference factor