The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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IAEA
International Atomic Energy Agency

2332-18

School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

XAS: principles

G. Aquilanti
Sincrotrone Trieste

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Trieste – Italy, 19-30 March 2012

Wednesday, 21 March 2012

14:00 – 15:30	G. Aquilanti / *Sincrotrone Trieste* XAS: principles
15:30 – 16:00	---BREAK---
16:00 – 18:30	G. Aquilanti / *Sincrotrone Trieste* XAS data analysis: (lecture with exercises)

Thursday, 22 March 2012

09:00 – 10:00	S. Pascarelli / *ESRF (France)* Advances in energy dispersive X-ray absorption spectroscopy
10:00 – 10:30	---BREAK---
10:30 – 11:30	S. Pascarelli / *ESRF (France)* Time resolved and high pressure science

XAS, XANES, EXAFS, and XMCD

- X-ray Absorption
- X-ray Absorption Fine Structure
- Simple Theoretical Description
- XANES
- Major historical EXAFS breakthrough
- Applications at XAFS at Elettra
- EXAFS data analysis
- Introduction to XMCD

today

Energy Dispersive XAS

- X-ray Absorption Spectrometers
- EDXAS
  - Basic principles, historical evolution
  - Examples of applications at ESRF
  - Future opportunities for studies of matter at extremes
- Probing laser induced extreme states of matter

tomorrow

XAS, EXAFS and XANES

Giuliana Aquilanti

Elettra Laboratory

Material from
- S. Pascarelli: EXAFS lecture at the HERCULES school 2010
- http://xafs.org/Tutorials, in particular from Matt Neuville's Tutorial
- P. Fornasini: "An introduction to X-ray absorption spectroscopy"

Outline

1. X-ray Absorption
2. X-ray Absorption Fine Structure
3. Simple theoretical description
4. XANES
5. Major historical EXAFS breakthrough
6. Applications at XAFS at ELETTRA

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Main X-ray-Matter interactions

- **Photoelectric absorption**

  one photon is absorbed and the atom is ionized or excited

- **Scattering**

  one photon is deflected form the original trajectory by collision with an electron

  - coherent (Thomson scattering)

    the photon wavelength is unmodified by the scattering process
    (scattering from bound electrons)
  - incoherent (Compton scattering)

    the photon wavelength is modified

  For an aggregate of atoms:
  - elastic scattering: the photon energy is conserved
  - inelastic scattering the photon energy is not conserved

- **Pair creation**

  the photon annihilates, giving rise to a pair e+ e− (for energies > 1 MeV)

Main X-ray experimental techniques

- **Spectroscopy**

  electronic structure of matter
    - absorption
    - emission
    - photoelectron spectroscopy

      (electrons emitted after X-ray absorption are collected and analized)

- **Scattering**
  - elastic

    Microscopic geometrical structure of condensed systems ((non)crystalline, liquids)

    Diffraction: elastic scattering from crystalline solids
  - inelastic

    Collective excitations

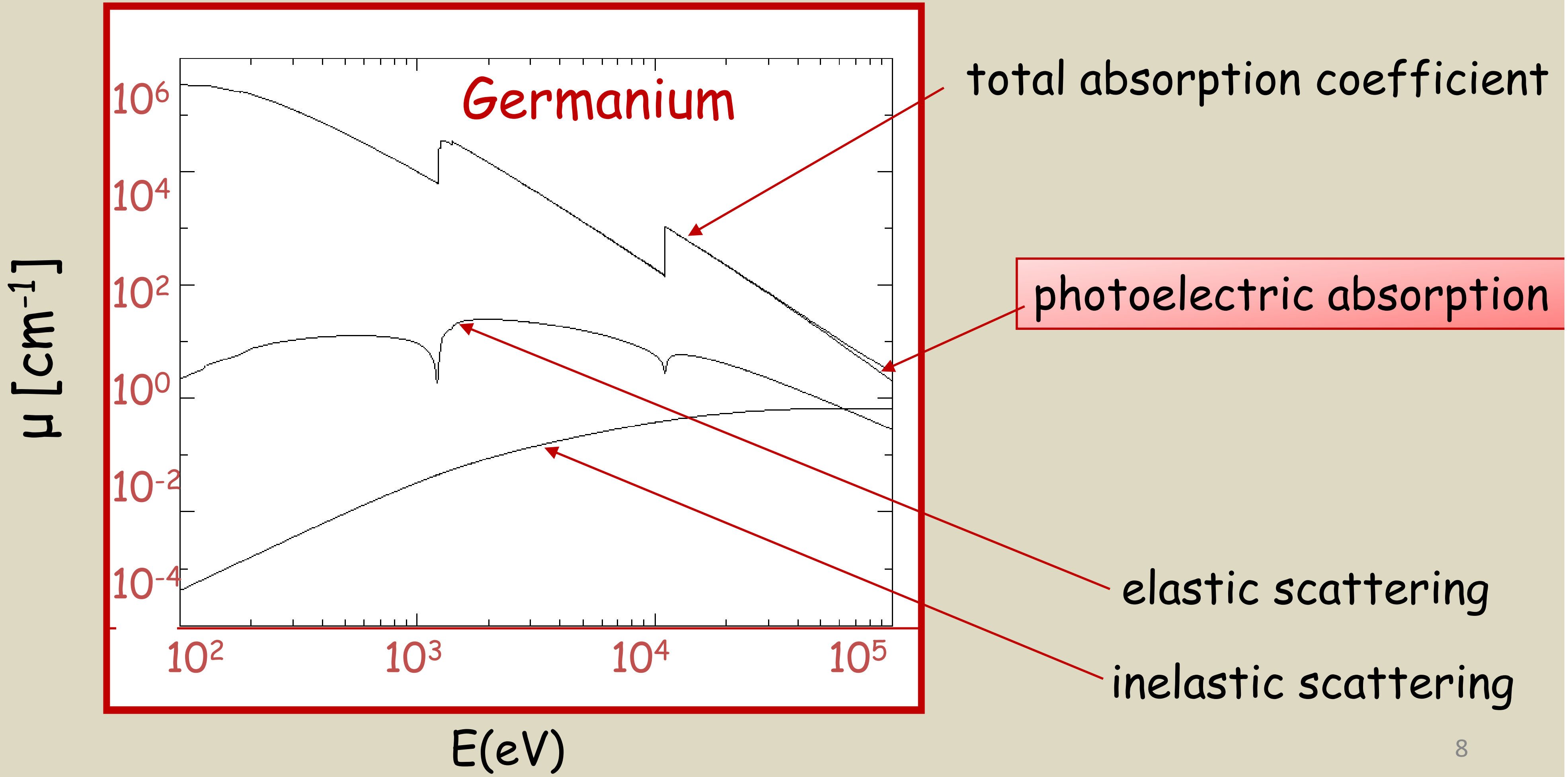
- **Imaging**

  macroscopic pictures of a sample, based on the different absorption of X-rays by different parts of the sample

  (medical radiography and X-ray microscopy)

Cross section quantifies the strength of the X-ray – matter interaction

For photon energies between 1 and 30 keV
the photoelectric absorption is the leading interaction with matter



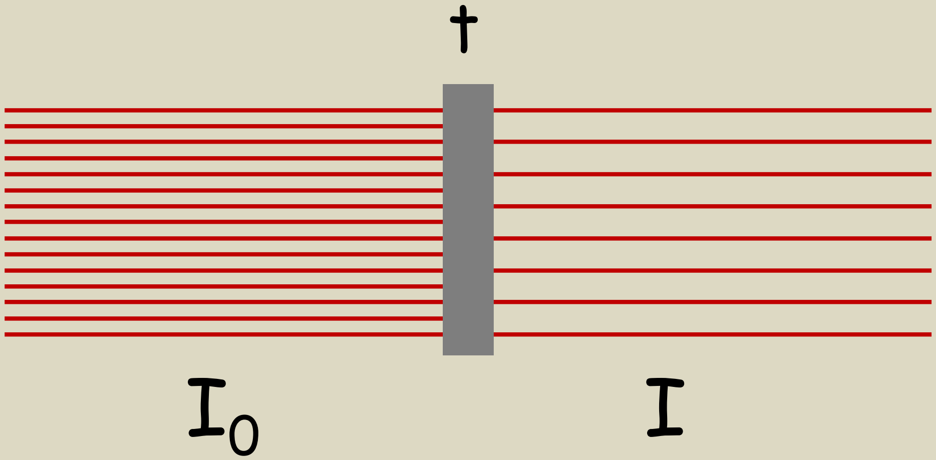
total absorption coefficient

photoelectric absorption

elastic scattering

inelastic scattering

The absorption coefficient μ



$$I = I_0 \exp(-\mu t)$$

↓

linear absorption coefficient

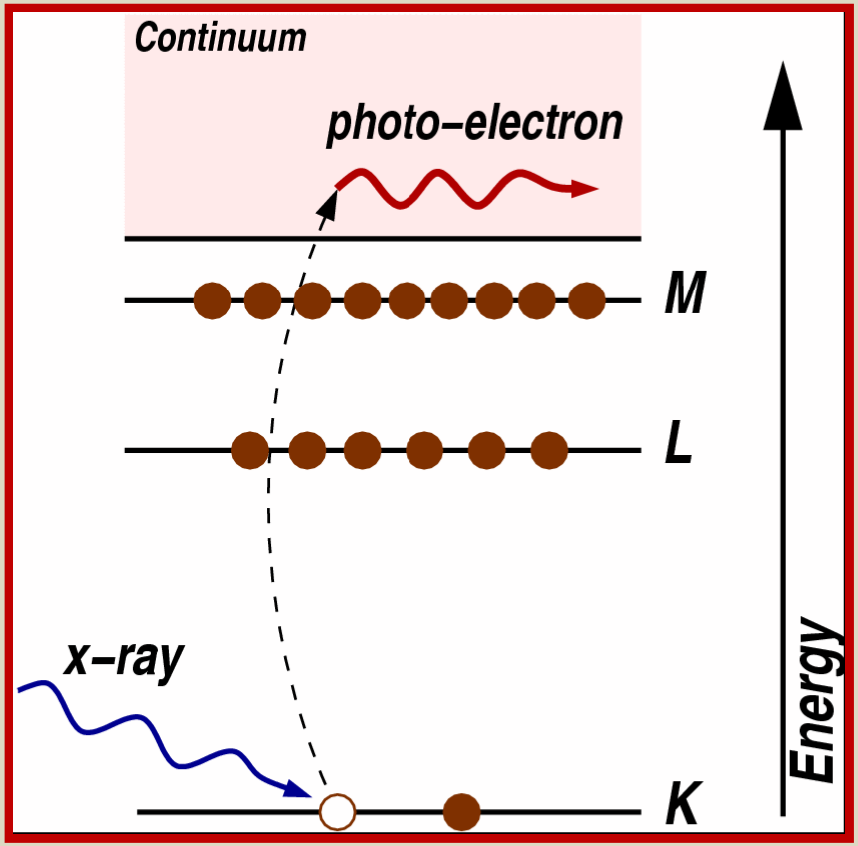
$$a = \mu t = \ln (I_0/I)$$

Photoelectric absorption

An X-ray is absorbed by an atom when the energy of the X-ray is transferred to a core-level electron (*K*, *L*, or *M* shell) which is ejected from the atom.

The atom is left in an *excited state* with an empty electronic level (a *core hole*).

Any excess energy from the X-ray is given to the ejected *photoelectron*.

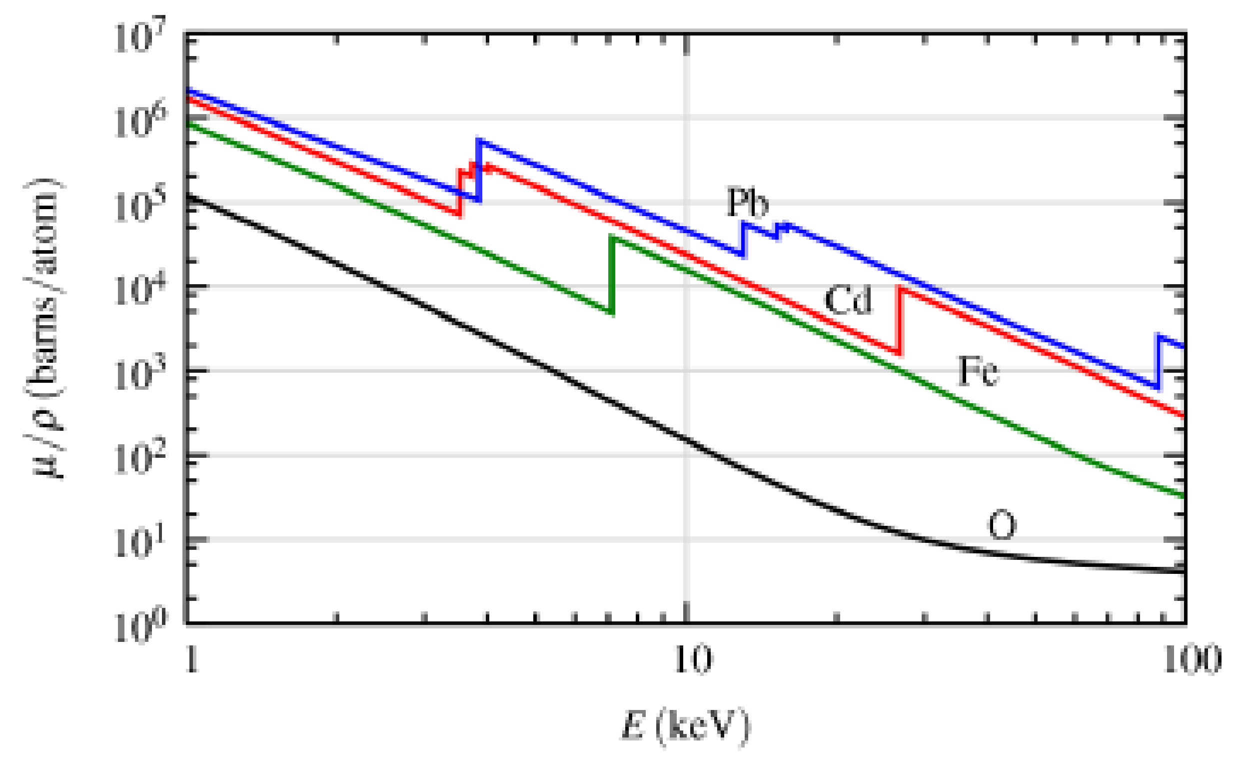


μ vs E and μ vs Z

μ depends strongly on:

- X-ray energy E
- atomic number Z,
- density ρ
- atomic mass A

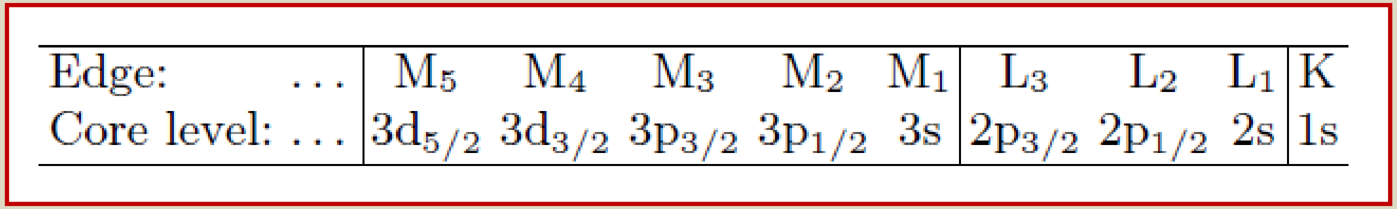
$$\mu \approx \frac{\rho Z^4}{A E^3}$$



In addition, μ has sharp *absorption edges* corresponding to the characteristic core-level energy of the atom which originate when the photon energy becomes high enough to extract an electron from a deeper level

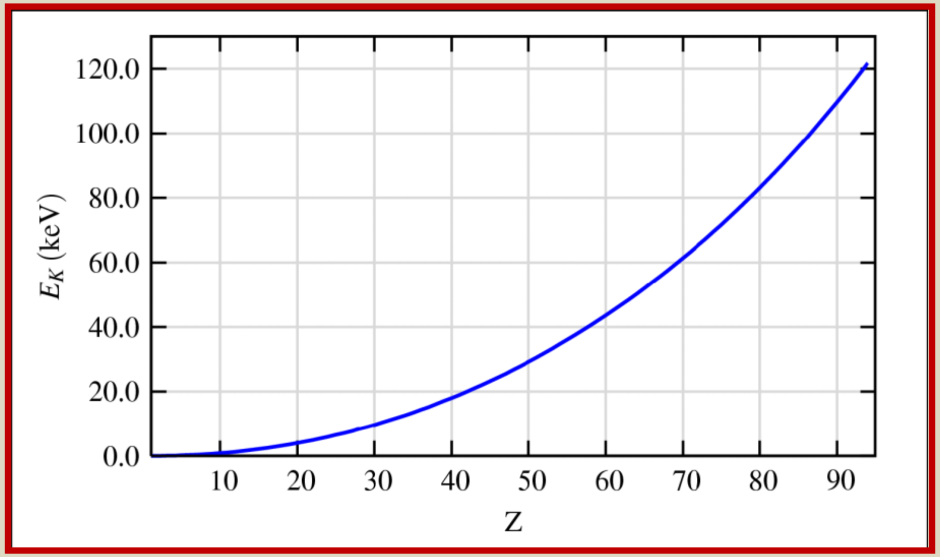
$$\mu \approx \frac{\rho Z^4}{AE^3}$$

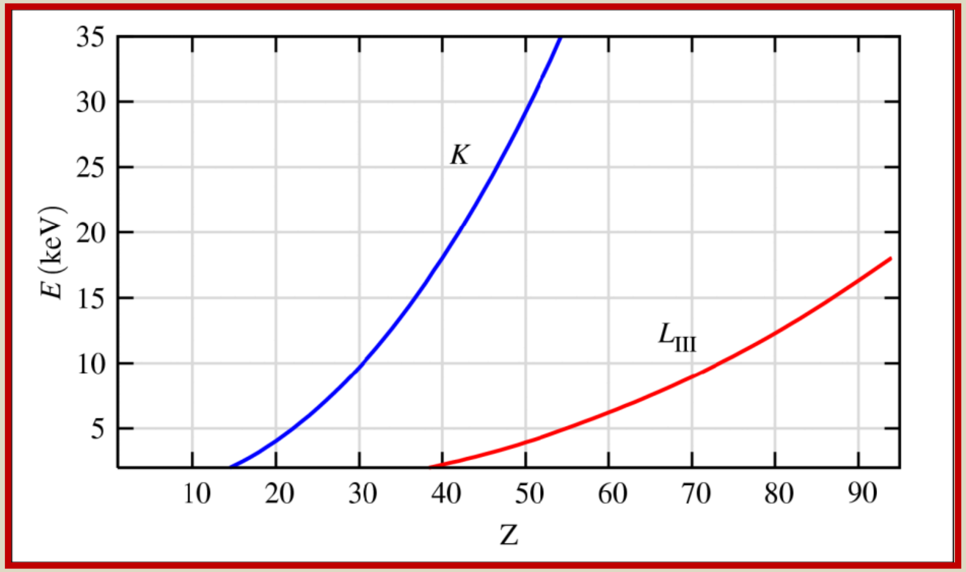
Absorption edge energies



Edge:	…	M_5	M_4	M_3	M_2	M_1	L_3	L_2	L_1	K
Core level:	…	$3d_{5/2}$	$3d_{3/2}$	$3p_{3/2}$	$3p_{1/2}$	3s	$2p_{3/2}$	$2p_{1/2}$	2s	1s

The energies of the *K* absorption edges go roughly as $E_K \sim Z^2$





All elements with Z > 16 have either a *K*-, or *L*- edge between 2 and 35 keV, which can be accessed at many synchrotron sources

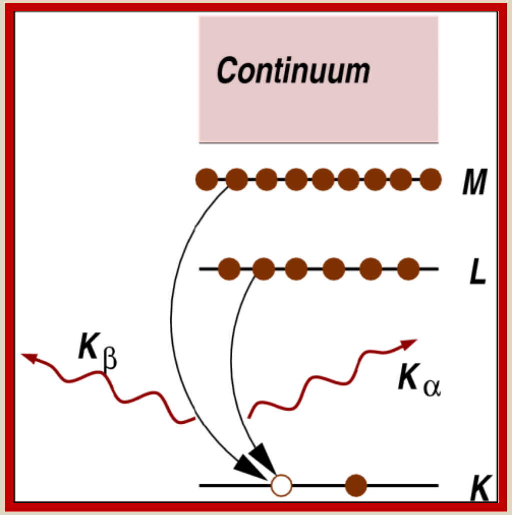
De-excitation processes

Absorption → Excited state → Decay to the ground state

Core hole + photoelectron

X-ray Fluorescence

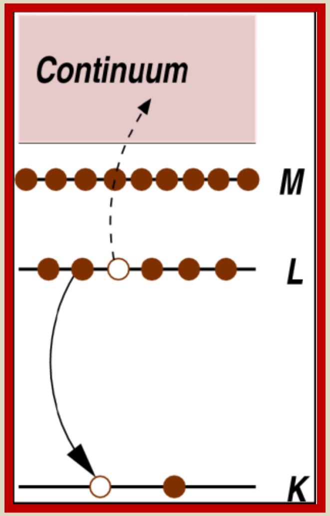
An x-ray with energy = the difference of the core-levels is emitted



K_α : $L \rightarrow K$, K_β : $M \rightarrow K$.

Auger Effect

An electron is promoted to the continuum from another core-level



X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom.

Core hole lifetime ($\tau_h \sim 10^{-15} - 10^{-16}$ s)

Total de-excitation probability per unit time

The deeper the core hole and the larger the atomic number Z

⬇

The larger the number of upper levels from which
an electron can drop to fill the hole

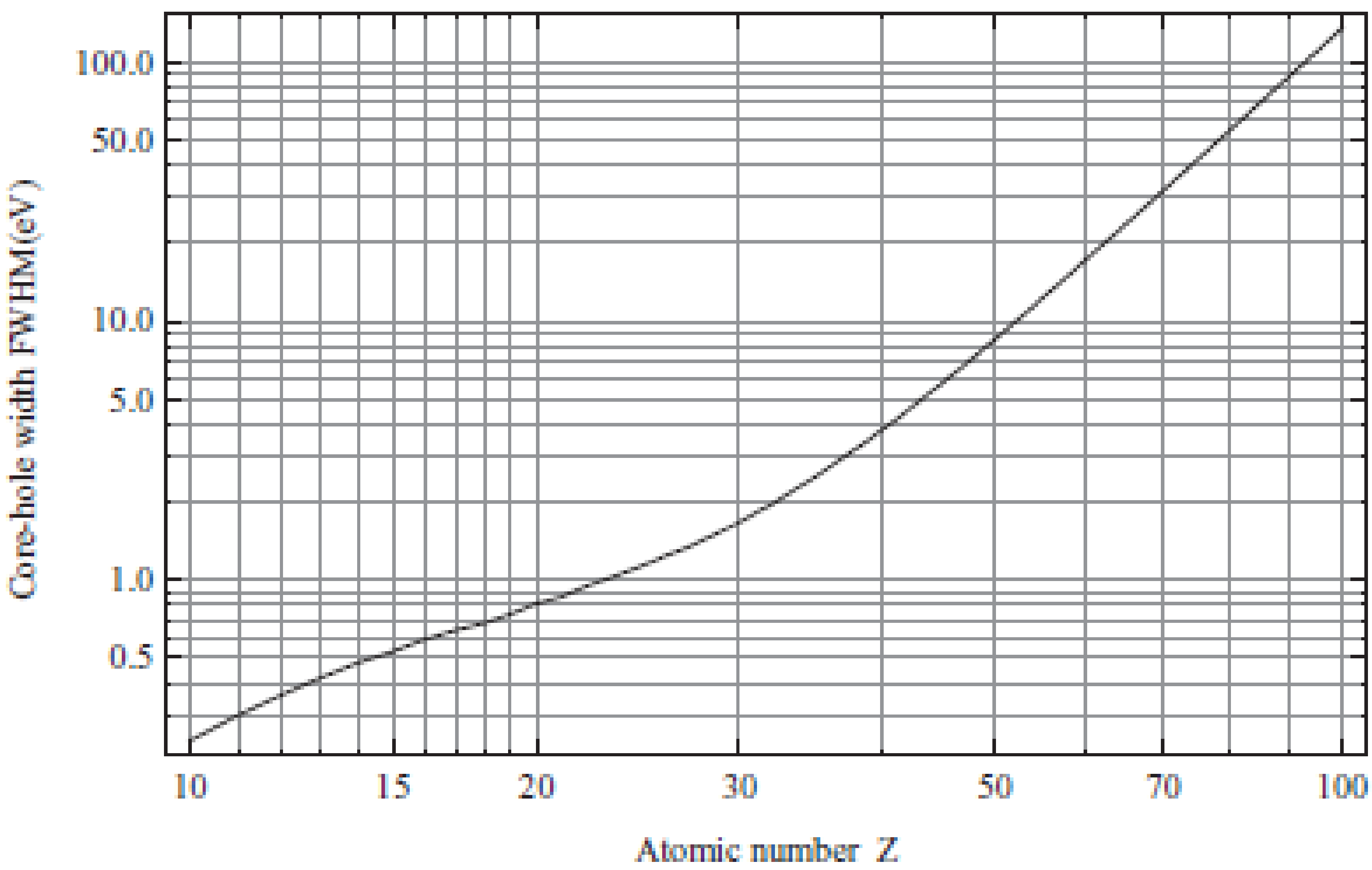
⬇

The shorter the core hole lifetime

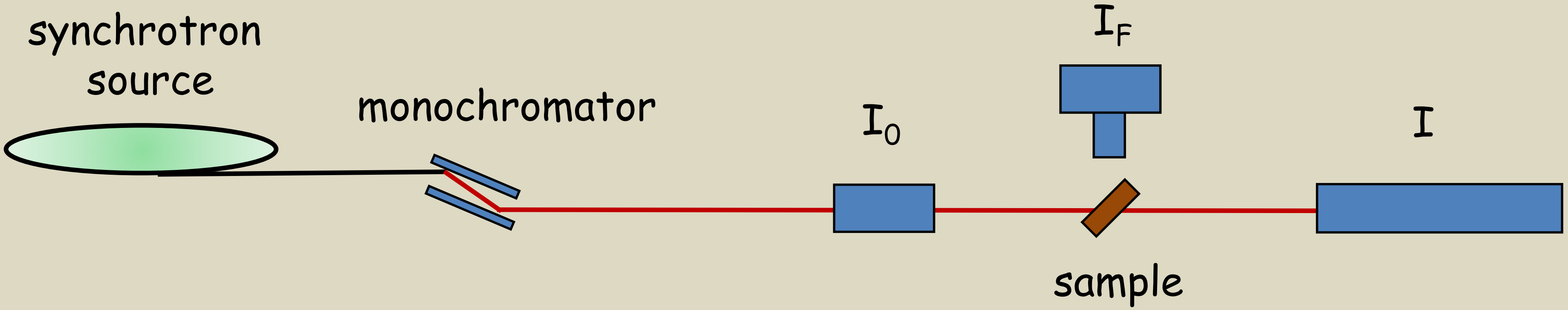
τ_h is un upper limit to the time allowed to the photoelectron for probing the local structure surrounding the absorbing atom

From the time-energy uncertainty relation: $\Gamma_h \simeq \hbar/\tau_h$ the core hole lifetime is associated to the energy width of the excited state Γ_h *(core hole broadening)* which contributes to the resolution of the X-ray absorption experimental spectra

K-edge core hole broadening as a function of Z



XAS measurements in real life



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

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

$$\mu(E)\, t = -\ln(I/I_0)$$

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

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

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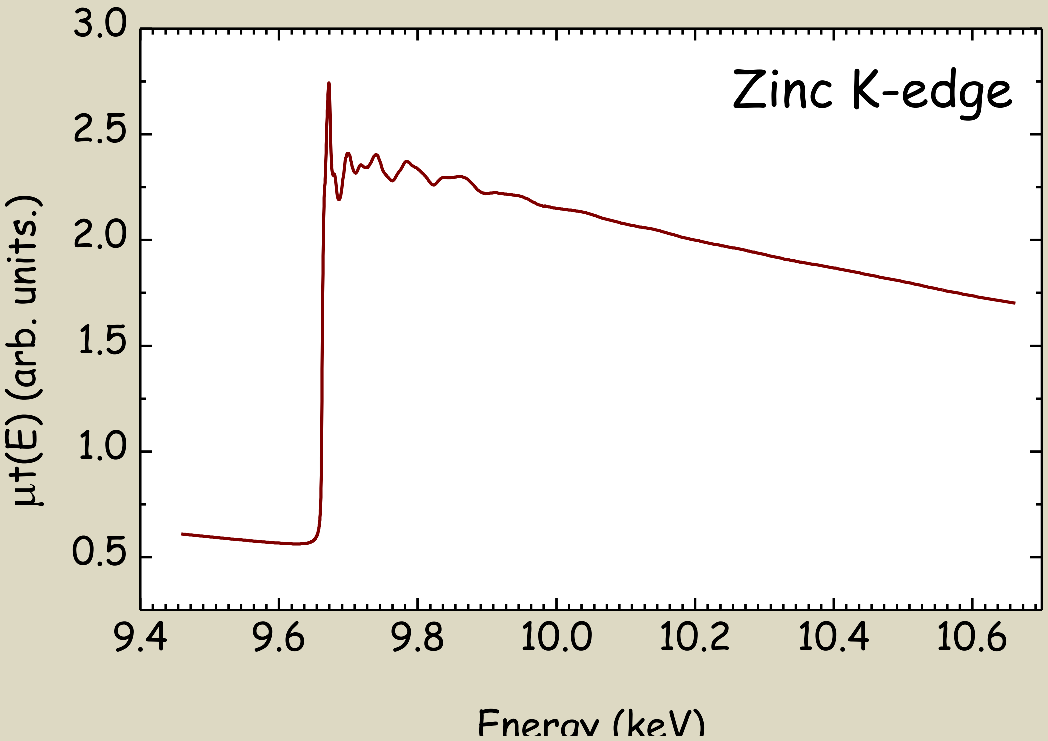
X-ray
Absorption
Fine
Structure



What? Oscillatory behaviour of the of the X-ray absorption as a function of photon energy beyond an absorption edge

When? Non isolated atoms

Why? Proximity of neighboring atoms strongly modulates the absorption coefficient

A little history...

1895	Discovery of X-rays (Röngten) (high penetration depth)
1912	First X-ray diffraction experiments (Laue, Bragg)
1913	Bohr's atom electron energy levels
1920	First experimental observation of fine structure
1931	First attempt to explain XAFS in condensed matter (Krönig)
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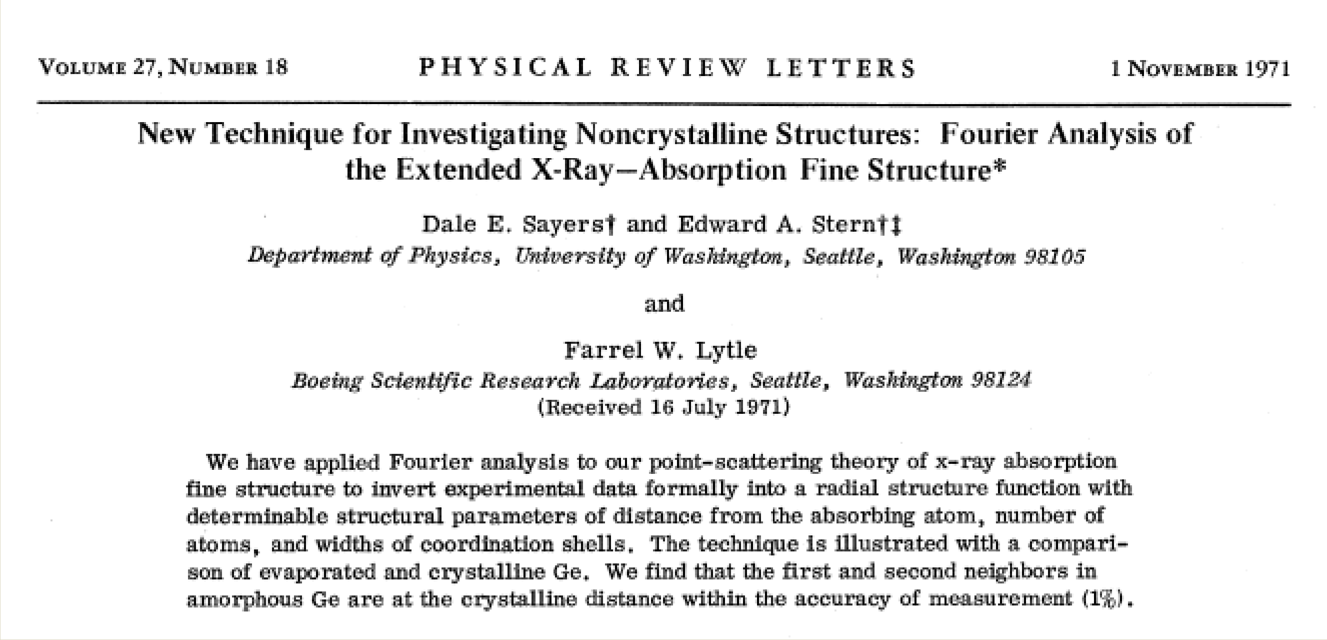
.	
1970	Availability of synchrotron radiation sources for XAFS
1971	XAFS becomes a quantitative tool for structure determination



Volume 27, Number 18 PHYSICAL REVIEW LETTERS 1 November 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray–Absorption Fine Structure*

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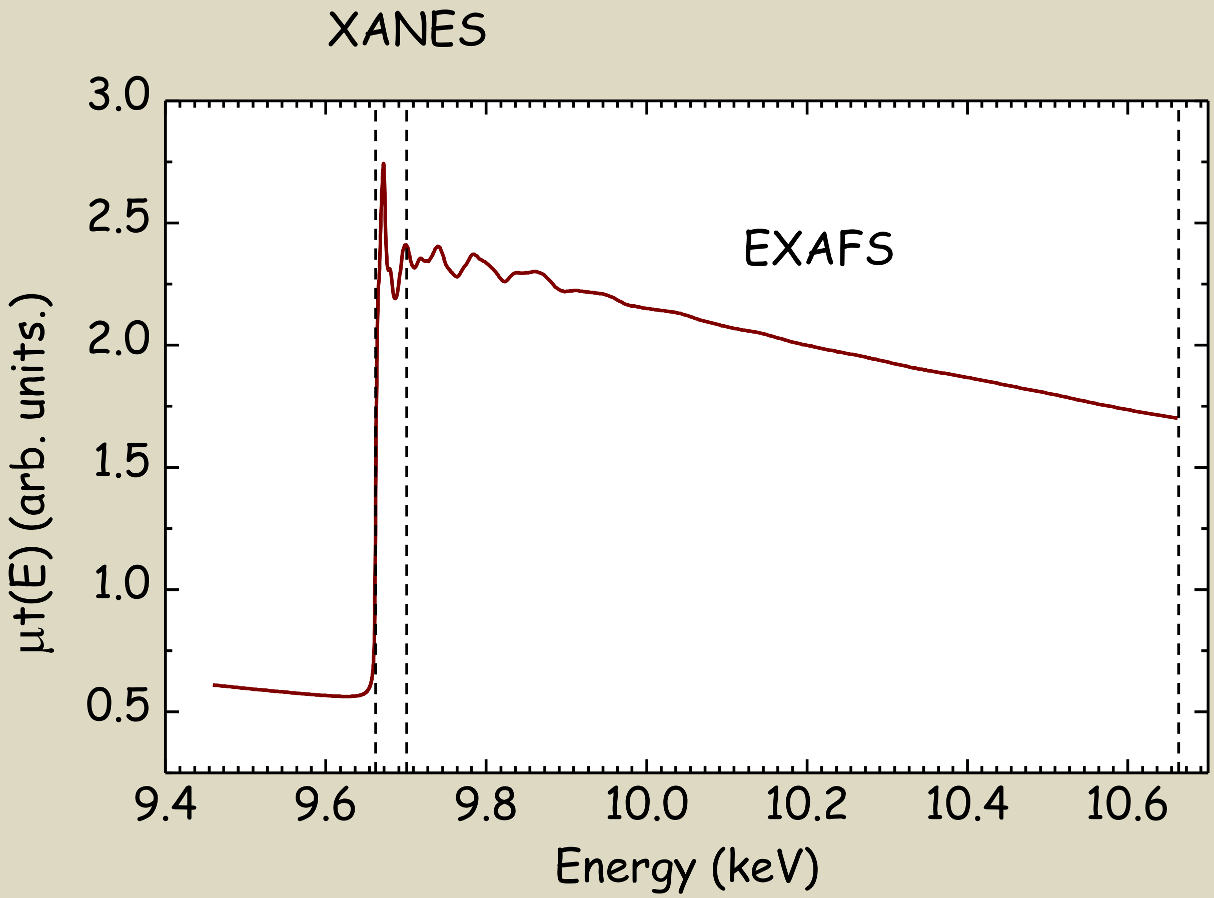
(Received 16 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).

XANES and EXAFS



X-ray
Absorption
Near
Edge
Structure

up to ~ 60 eV
above the edge

Extended
X-ray
Absorption
Fine
Structure

from ~ 60 eV
to 1200 eV
above the edge

XANES and EXAFS

XANES ← same physical origin → EXAFS

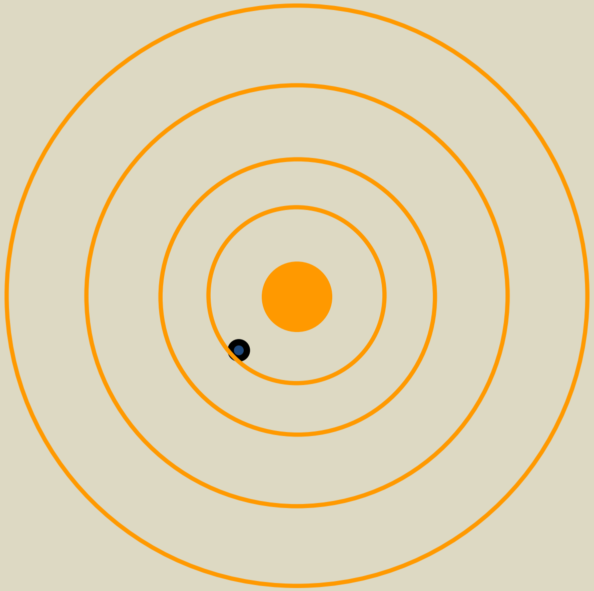
transitions to
unfilled bound states,
nearly bound states,
continuum

- Oxidation state
- Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
- Orbital occupancy

transitions to
the continuum

- Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)

EXAFS qualitatively - isolated atom



- X-ray photon with enough energy ejects one core (photo)electron (photoelectric effect)

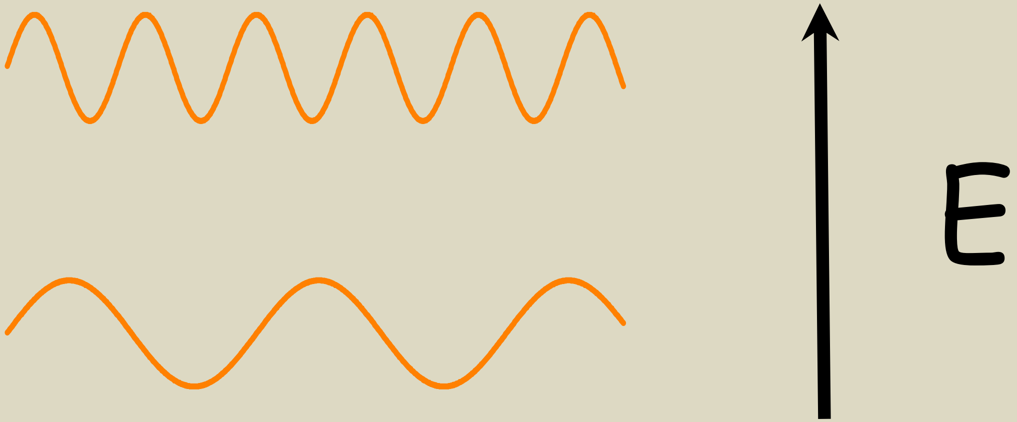
$$E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$ Kinetic energy of the p.e.

$$k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$$ wavevector of the p.e.

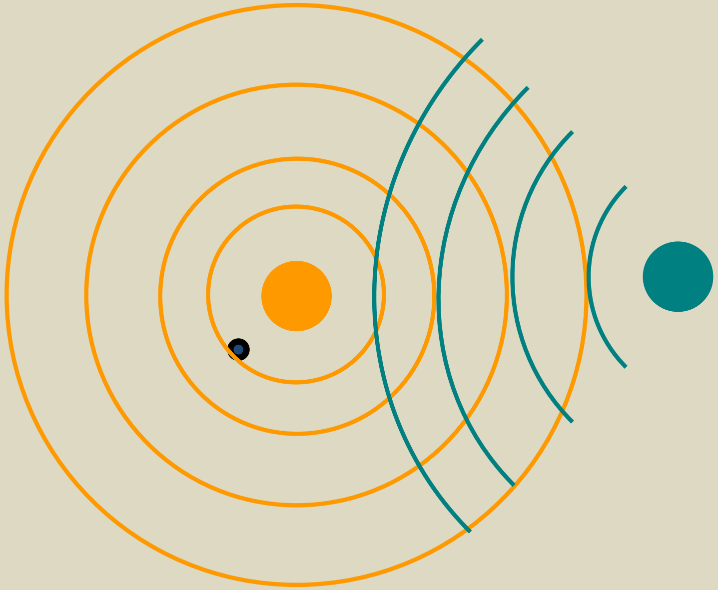
$$\lambda = 2\pi/k$$ wavelength of the p.e.

- The photoelectron can be described by a wave function approximated by a spherical wave

$\lambda \sim 1/(E-E_0)^{1/2}$

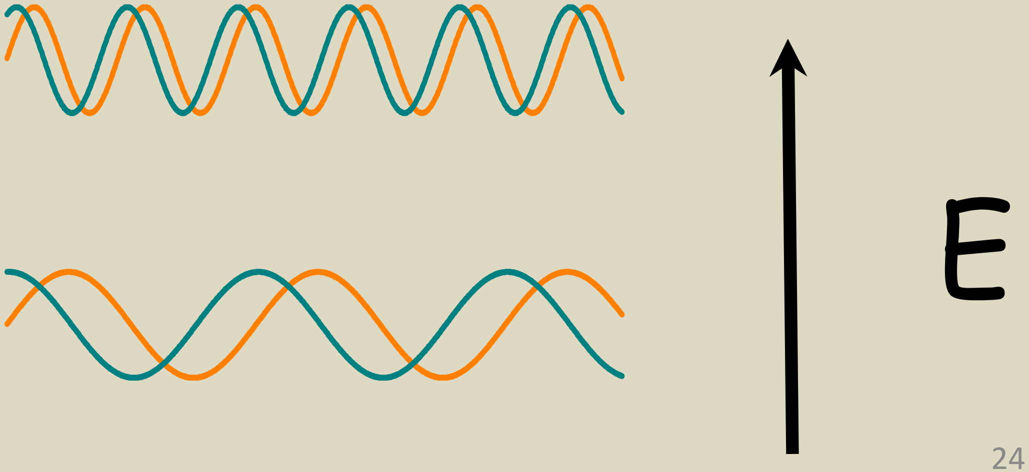


EXAFS qualitatively – condensed matter



- The photoelectron can scatter from a neighbouring atom giving rise to an incoming spherical wave coming back to the absorbing atom
- The outgoing and ingoing waves may interfere.

$\lambda \sim 1/(E-E_0)^{1/2}$



Origin of the fine structure (oscillations)

The interference between the outgoing and the scattering part of the photoelectron at the absorbing atom changes the probability for an absorption of X-rays i.e. alters the absorption coefficient μ(E) that is no longer smooth as in isolated atoms, but oscillates.
In the extreme of destructive interference, when the outgoing and the backscattered waves are completely out of phase, they will cancel each other, which means that no free unoccupied state exists in which the core-electron could be excited to.
Thus absorption is unlikely to occur and the EXAFS oscillations will have a minimum.

The phase relationship between outgoing and incoming waves depends on photoelectron wavelength (and so on the energy of X-rays) and interatomic distance R.

The amplitude is determined by the number and type of neighbours since they determine how strongly the photoelectron will be scattered

Frequency of the oscillations → Distance of neighbours

Amplitude of the oscillations → Number and type of neighbours

The EXAFS signal χ(k)

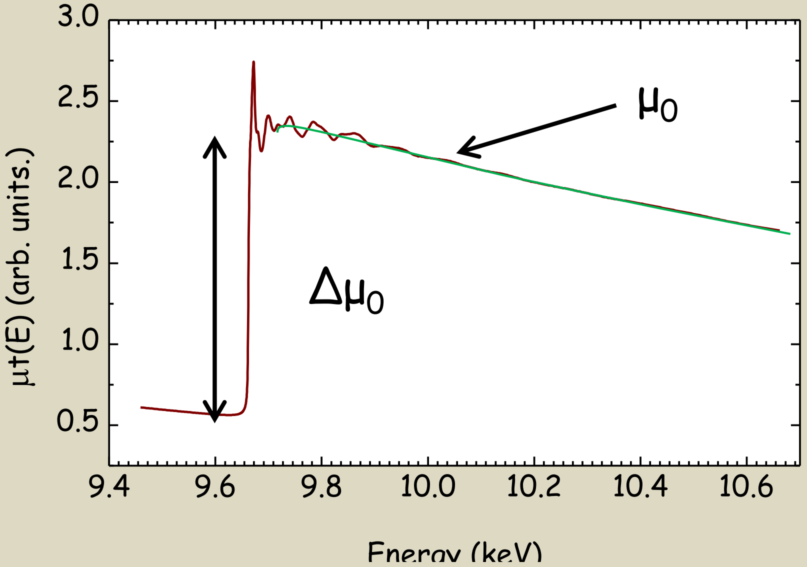
The EXAFS signal is generally espressed as a function of the wavevector of the photoelectron

$$k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$$

The oscillatory part of the spectrum contains the structural information

We define the EXAFS function as

$$\boxed{\chi(k) = \frac{\mu - \mu_0}{\Delta\mu_0}}$$



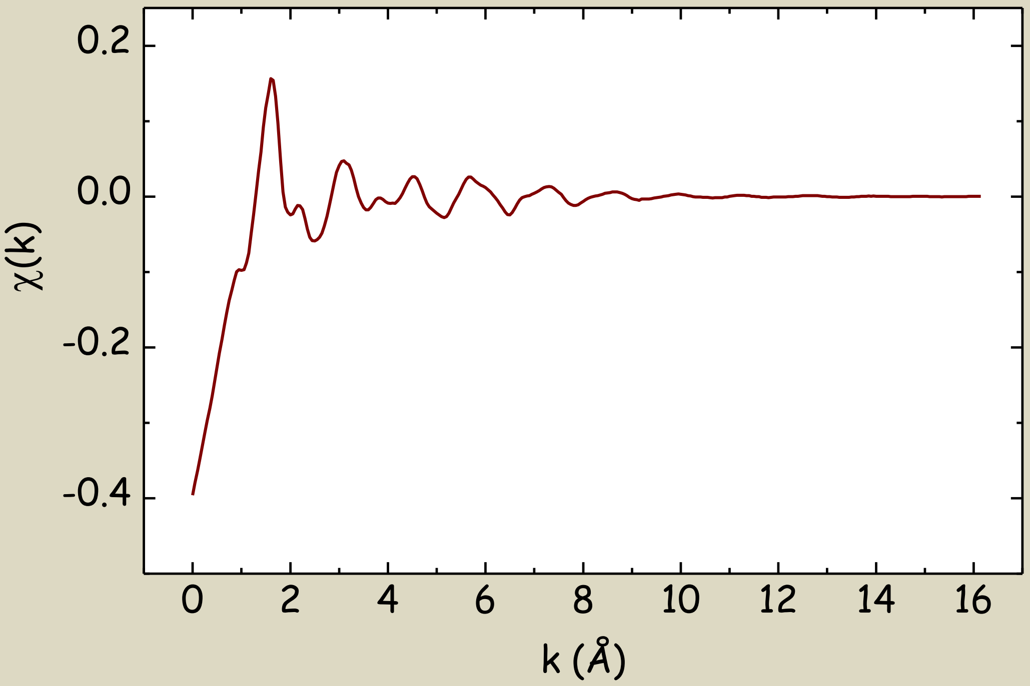
$\mu_0(E)$ Smooth function representing the bare atomic background

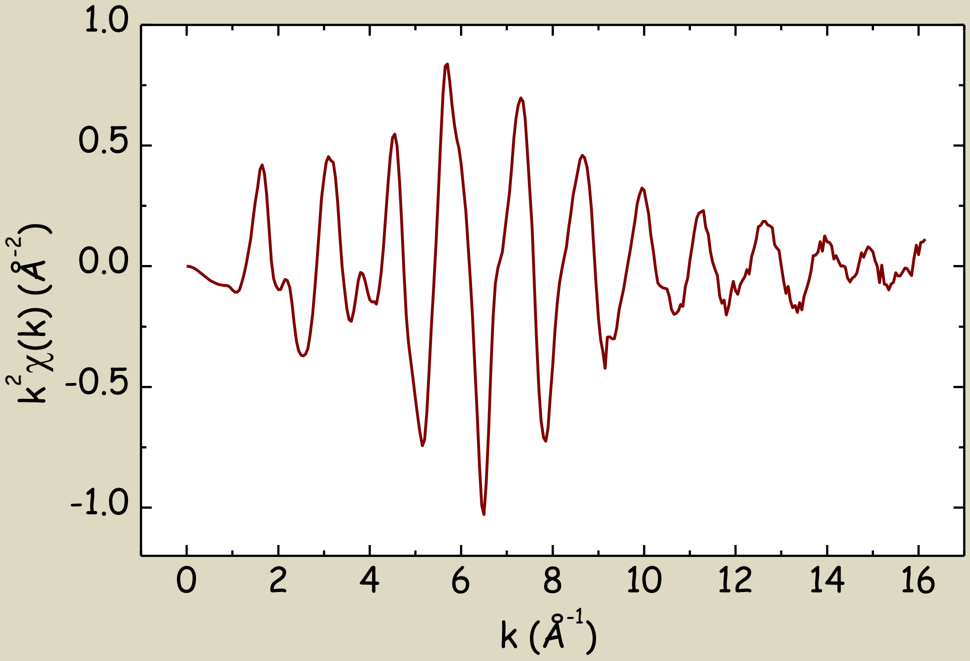
$\Delta\mu_0$ Edge step at the absorption edge normalized to one absorption event

EXAFS : χ(k)

XAFS originates from an *interference effect,*
and depends on the wave-nature of the photoelectron.

χ(k) is often shown weighted by k^2 or k^3 to amplify the oscillations at high-k



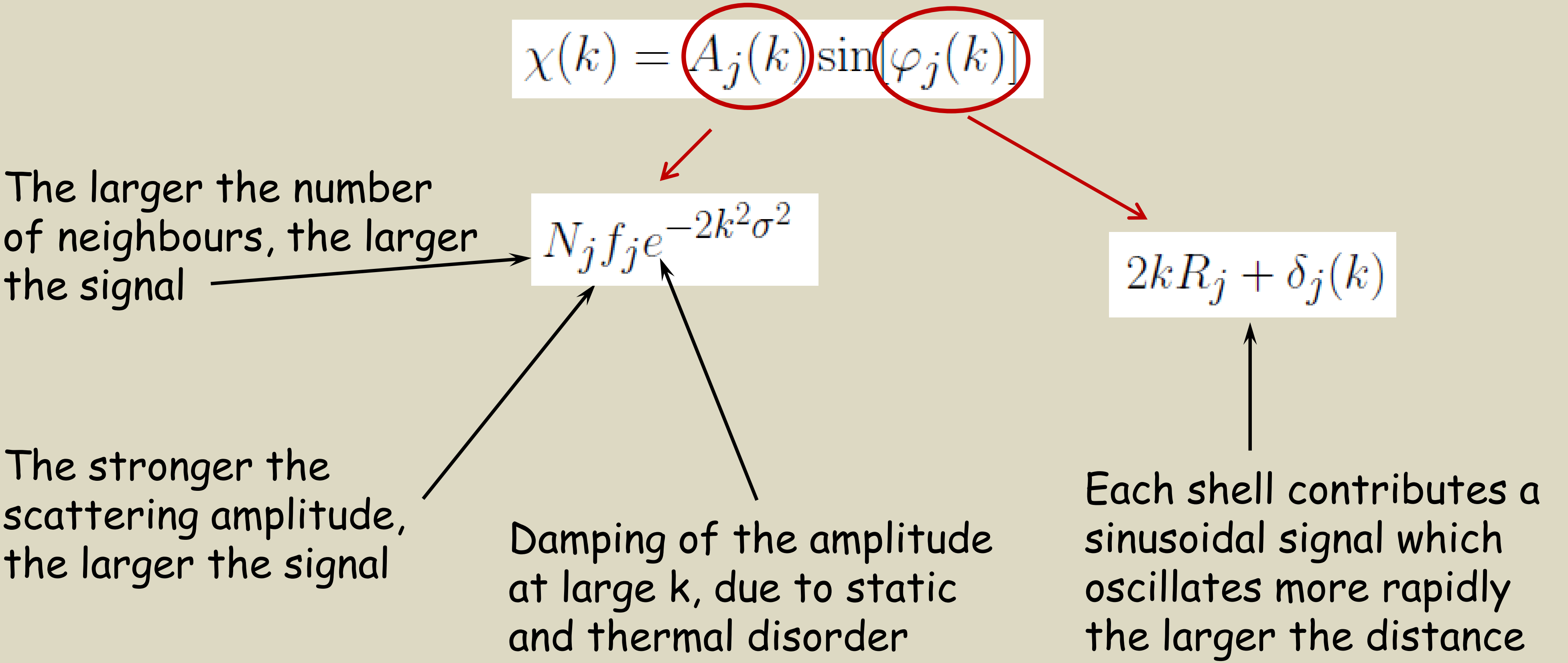


$\chi(k)$: sum of damped waves

$\boldsymbol{\chi}(k)$ is the sum of contributions $\boldsymbol{\chi}_j(k)$ from backscattered wavelets:

$$\chi(k) = \sum_j = \chi_j(k)$$

Each $\boldsymbol{\chi}_j(k)$ can be approximated by a *damped* sine wave of the type:



$$\chi(k) = A_j(k) \sin[\varphi_j(k)]$$

$$N_j f_j e^{-2k^2\sigma^2}$$

$$2kR_j + \delta_j(k)$$

The larger the number of neighbours, the larger the signal

The stronger the scattering amplitude, the larger the signal

Damping of the amplitude at large k, due to static and thermal disorder

Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance

EXAFS formula

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} \, e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

$f(k)$ scattering amplitude

$\delta_j(k)$ phase-shift

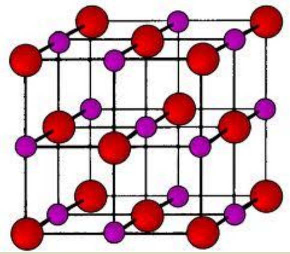
$\Big\}$ scattering properties of the atoms neighbouring the photoabsorber (depend on the atomic number)

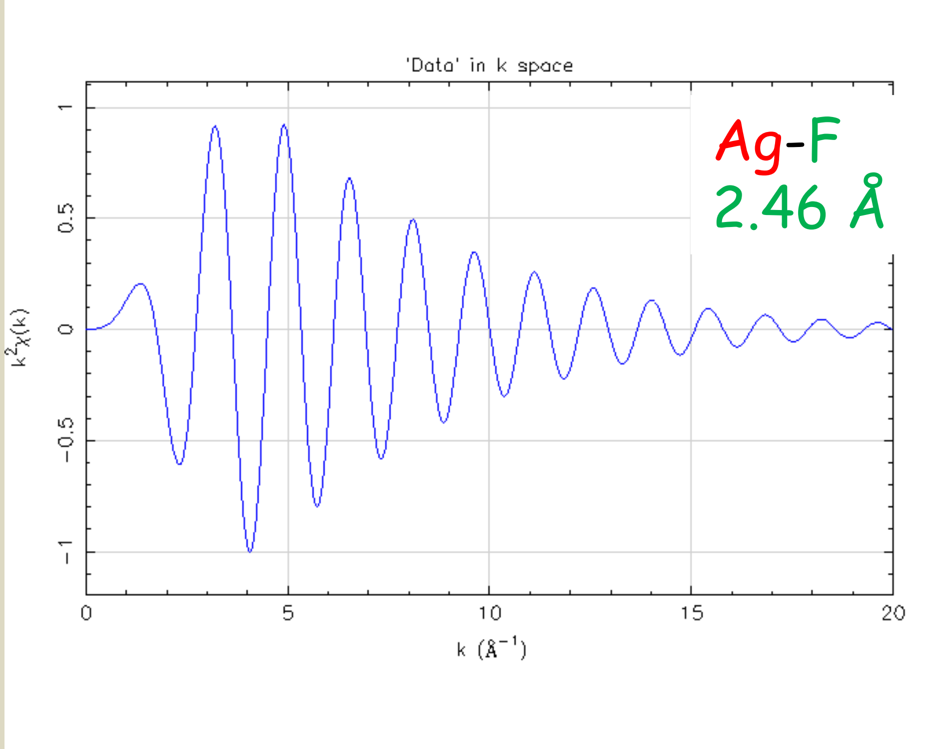
R	Distance to the neighbouring atom
N	Coordination number of the neighbouring atom
σ^2	Disorder in the neighbour distance

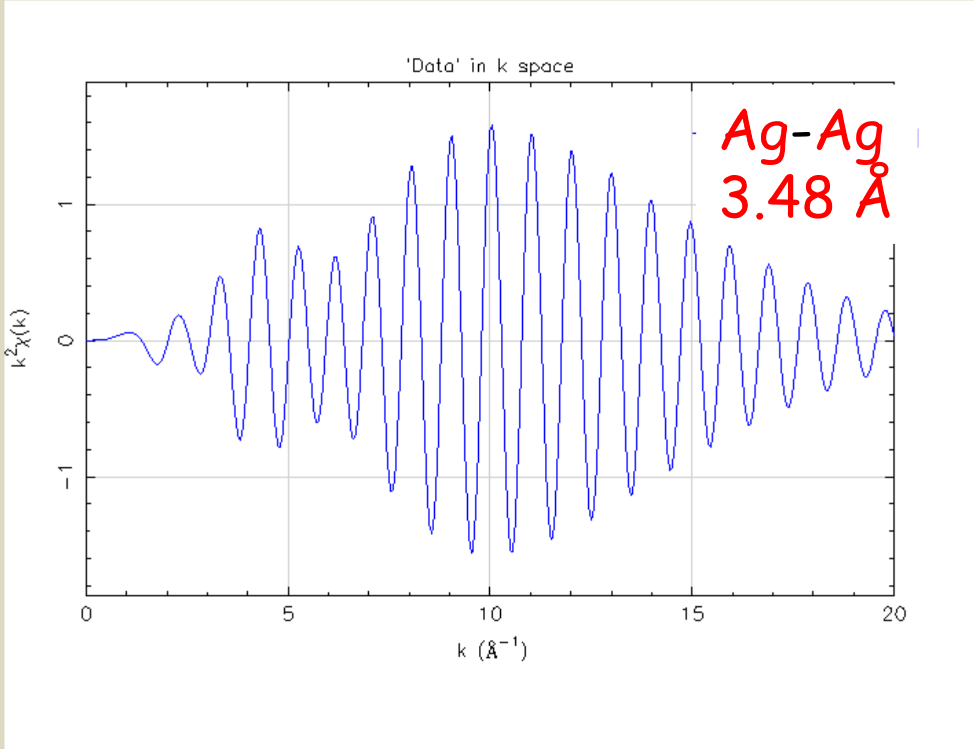
Amplitudes

The shape of the envelope of each wave is indicative of the nature of backscatterer atom

AgF (rocksalt structure)



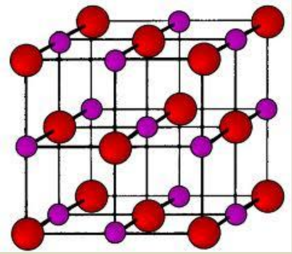


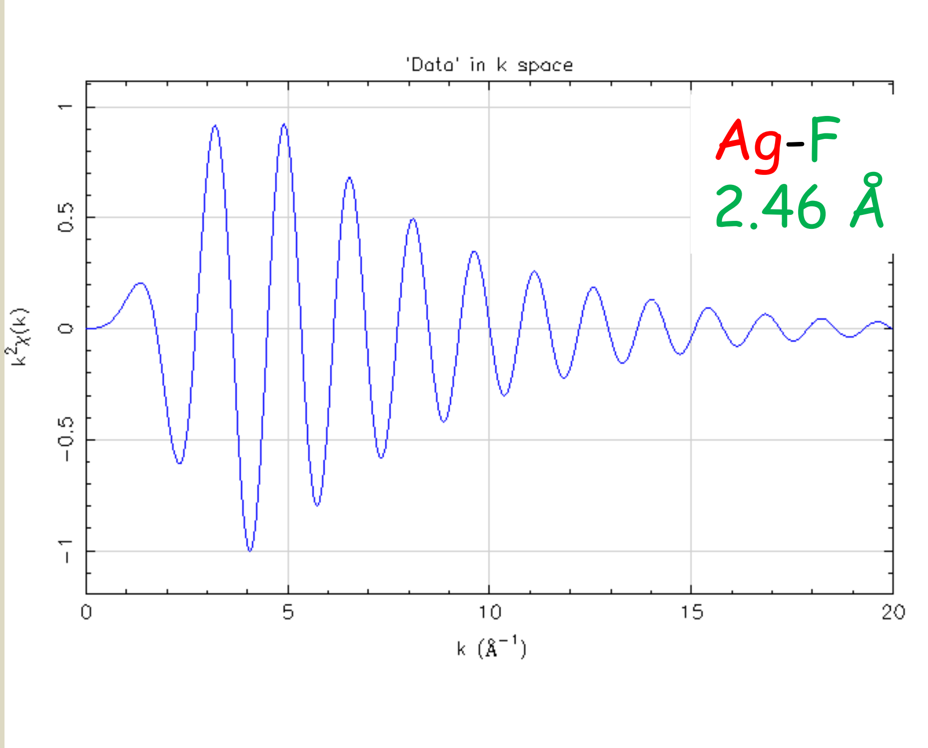


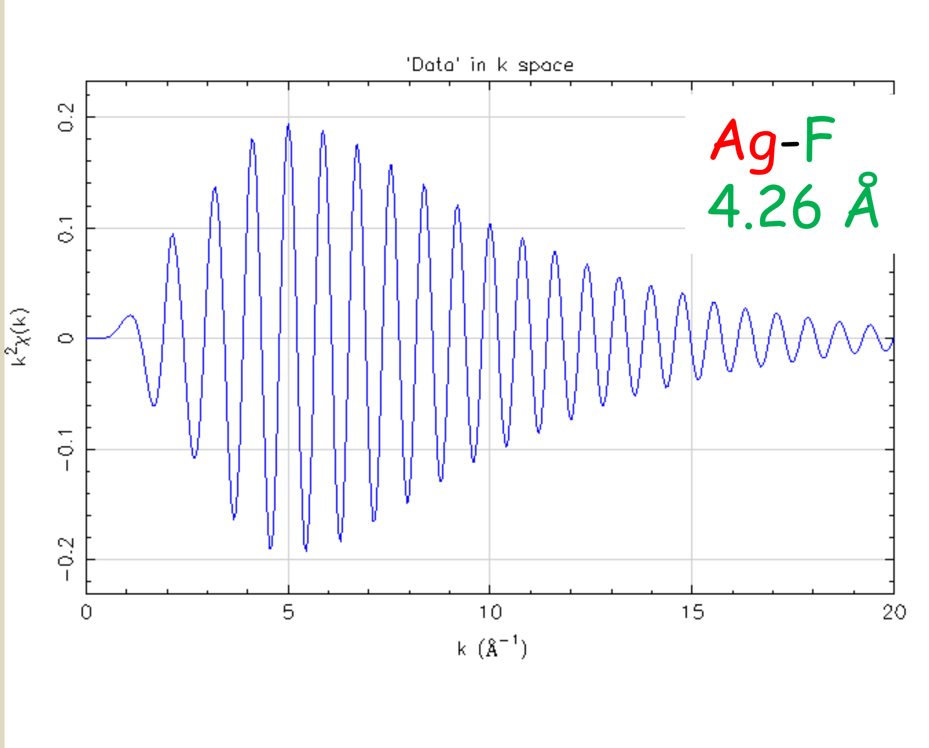
Frequencies

The frequency of the single wave, for the same atomic pair, is indicative of the distance of the backscatterer atom (the lower the frequency the closer the neighbour)

AgF (rocksalt structure)







Multiple scattering

Multiple scattering events may occur. The photoelectron scatter from more than one atom before returning to the central atom

SS ⇨ $g_2(r)$

$f = 2\,R_1$

MS ⇨ $g_2(r)$

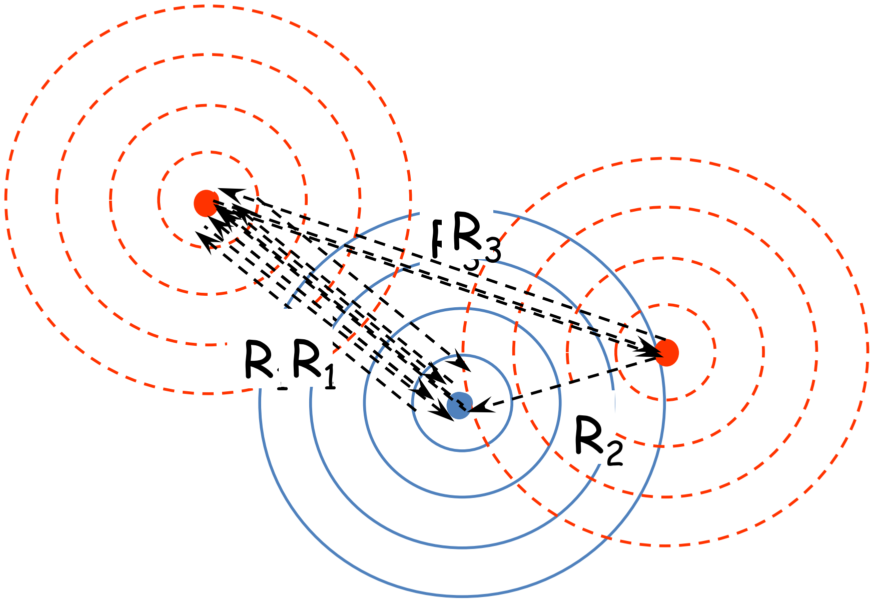
$f = 4\,R_1$

MS ⇨ $g_3(r)$

$f = R_1 + R_2 + R_3$

MS ⇨ $g_3(r)$

$f = 2R_1 + 2R_3$

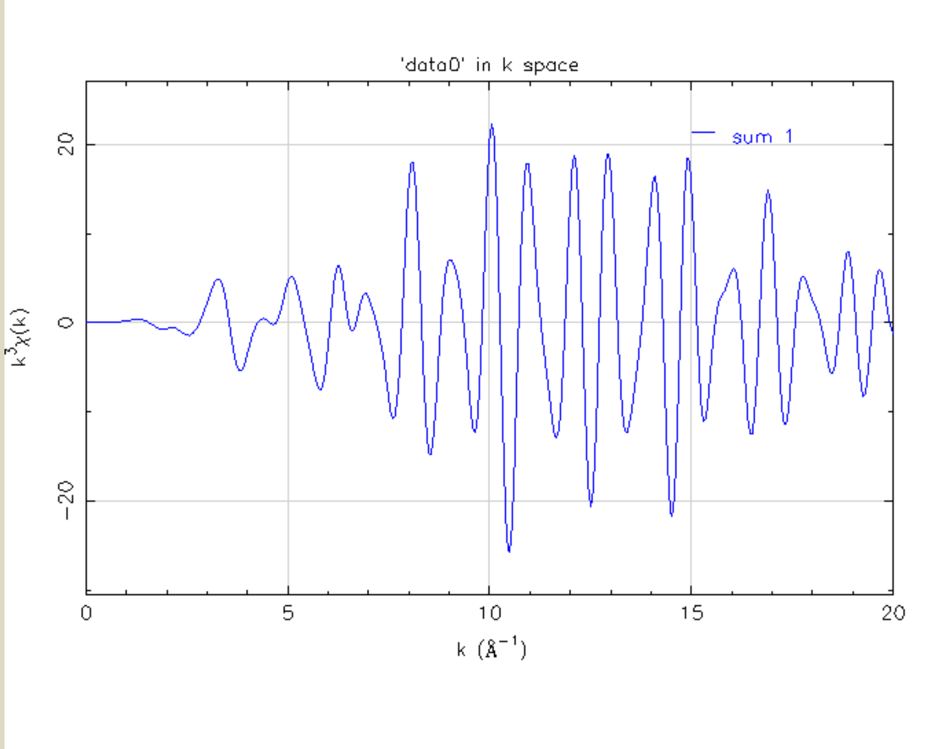


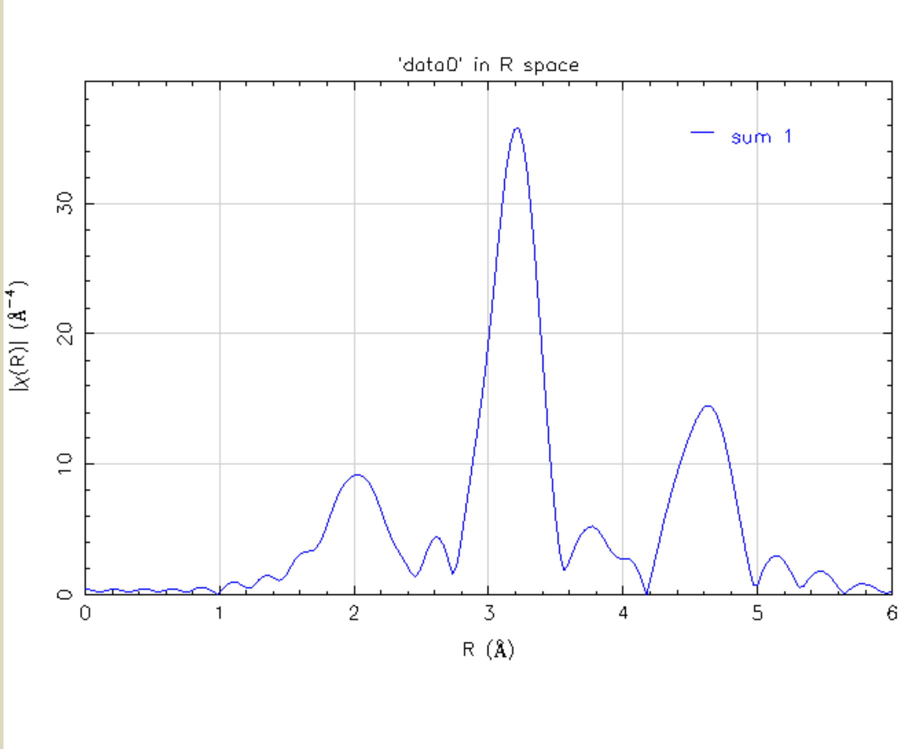
Through multiple scattering EXAFS can give information on the n-body distribution functions $g_n(r)$

Qualitative picture of local coordination in R space

The frequencies contained in the EXAFS signal depend on the distance between the absorbing atom and the neighbouring atoms (i.e. the length of the scattering path).

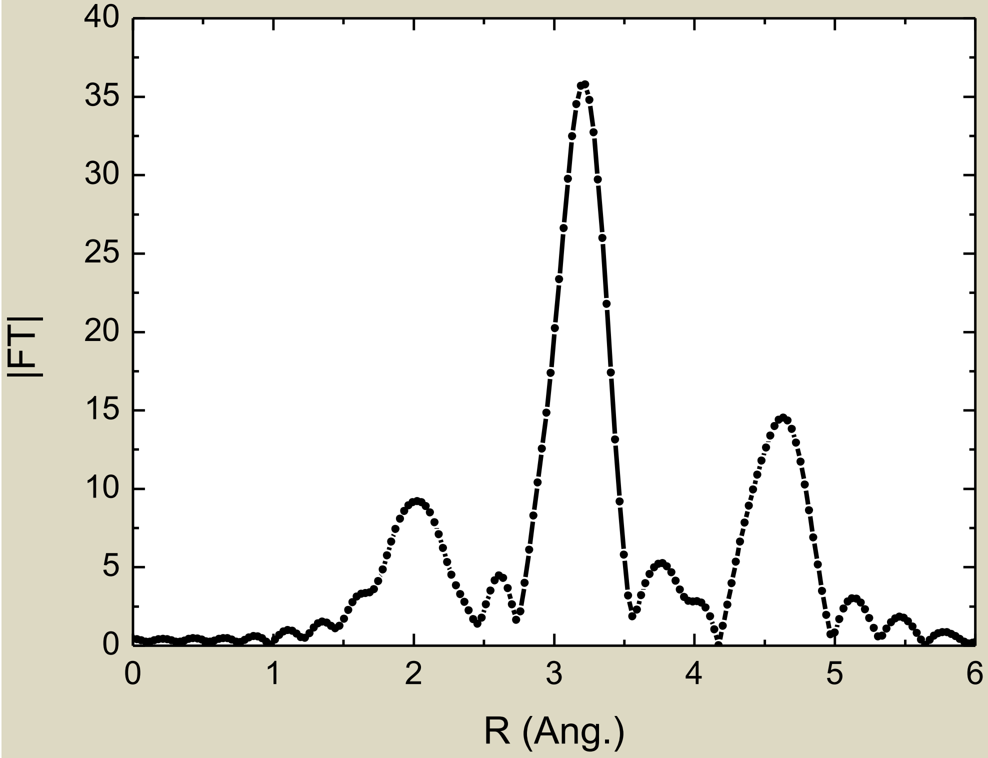
A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.

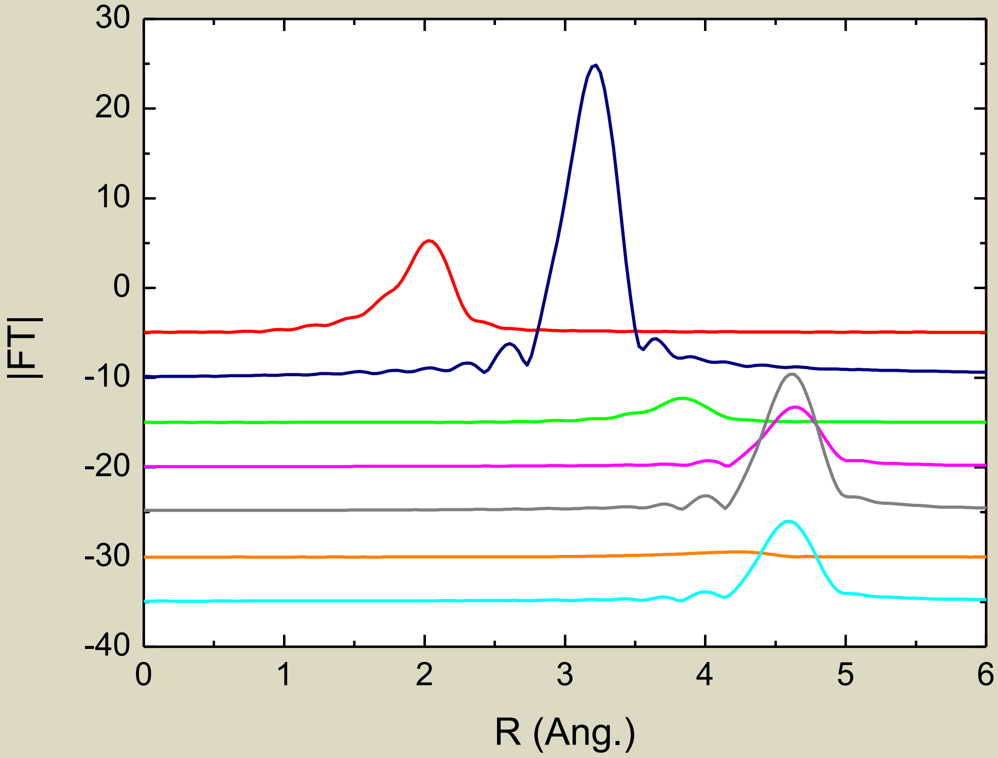




Quantitative structural determination

Structural determinations depend on the feasibility of resolving the data into individual waves corresponding to the different types of neighbours (SS) and bonding configurations (MS) around the absorbing atom





XAFS vs. Diffraction Methods

- Diffraction Methods (X-rays, Neutrons)
- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
- Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D RDF containing interatomic distances due to all atomic pairs in the sample

- XAFS
- 1D radial distribution function (centered at the absorber)
- Element selectivity
- Higher sensitivity to local distortions (i.e. within the unit cell)
- Charge state sensitivity (XANES)
- Structural information on the environment of each type of atom:
  - distance, number, kind, static and thermal disorder
  - 3-body correlations
- Investigation of matter in the solid (crystalline or amorphous), liquid, solution or gaseous state with same degree of accuracy.

EXAFS: typical applications

Element selectivity

Local structure sensitivity

- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure

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XAFS : quantum mechanical phenomenon

↓

Quantum mechanical treatment based on the time dependent perturbation theory

Semiclassical description:

- classic electromagnetic field
- quantistic atom

Absorption process

It is a transition between two quantum states induced by an external time-dependent perturbation: electromagnetic wave

|i> : initial state of energy E_i

- core electron (*e.g.* 1s electron wave function)
- very localized
- NOT altered by the presence of the neighboring atoms

|f> : final state of energy $E_f = E_i + \hbar\omega$

- core hole + photoelectron
- multibody process
- altered by neighbouring atoms (photoelectron is a superposition of ougoing and ingoing waves)

$\hat{H}_{int}$: external time-dependent perturbation

Transition probability: Fermi's golden rule

The absorption coefficient μ(ω) depends on:

- the sample atomic density n
- the probabilities of transition per unit time (transition rate) from |i> to |f>

$$\mu(\omega) = (2\hbar/\varepsilon_0 \omega A_0^2)\, n \sum_f W_{if}$$

According to the time-dependent perturbation theory the transition rate, to first order in the perturbation, is given by the Fermi's golden rule

$$\boxed{W_{if} = \frac{2\pi}{\hbar} \left|\langle f|\hat{H}_{int}|i\rangle\right|^2 \rho(E_f)}$$

where: $\langle f\,|$ is the initial state, $\langle i\,|$ is the final state, $\hat{H}_{int}$ is the interaction Hamiltonian between the e.m. field and the electrons, and $\rho(E_f)$ is the density of the final states compatible with the energy conservation

$$E_f = E_i + \hbar\omega$$

In the limit of low intensity field (single photon interaction):

$$\hat{H}_{int} = -\frac{e}{m}\sum_j \mathbf{A}(\mathbf{r}_j)\cdot\mathbf{p}_j$$

This describes the action of the potential vector on the momentum operator

where: $\mathbf{A}(\mathbf{r}_j)$ is the potential vector and $\mathbf{p}_j$ is the momentum operator of the j-th electron.

Considering the photon a classical wave $\mathbf{A}(\mathbf{r}_j) = \overset{\substack{\text{X-ray polarization vector}\\ \downarrow}}{\hat{\epsilon}}\, A_0\, e^{i\mathbf{k}\cdot\mathbf{r}}$ and using the commutation law between the position operator and the Hamiltonian

$$p = m/i\hbar\,[r, \mathbf{H}]$$

$$\boxed{W_{if} = \left(\frac{\pi\hbar e^2}{m^2}\right)\left|\langle f|\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}\,\hat{\epsilon}\cdot\mathbf{r}|i\rangle\right|^2\rho(E_f)}$$

Dipole approximation

$$W_{if} = \left(\frac{\pi \hbar e^2}{m^2}\right) |\langle f| \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \hat{\epsilon} \cdot \mathbf{r}|i\rangle|^2 \rho(E_f)$$

Expanding in series this term

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} - \frac{\mathbf{k}\cdot\mathbf{r}}{2!}\ldots$$

If $|\mathbf{k}\cdot\mathbf{r}|^2 \ll 1$, then $\boxed{e^{i\mathbf{k}\cdot\mathbf{r}} \simeq 1}$

This condition is fullfilled because of the strong localization of the initial state (core electron)

The quadrupolar term $i\mathbf{k}\cdot\mathbf{r}$ is ~ Z/2*137 times smaller than the dipolar term

For heavy elements (Pb, Au, Pt) is not negligible, although it is actually neglected

One electron approximation

- The absorption process involves in principle all the electrons within the atom.

- |f> influenced by the environment of the absorber atom.

$$\mu(\omega) = \mu_{el}(\omega) + \mu_{anel}(\omega)$$

- large part of μ due to "elastic" transitions:
  - only 1 electron out of N modifies its state: leaves its deep core level
  - all other N-1 "passive" electrons relax their orbitals to adapt to the new potential created by presence of core hole

- remaining part of μ due to "inelastic" transitions:
  - primary excitation of core electron provokes successive excitations of other external electrons.

By writing $\langle f| = \langle \Psi_f^{N-1}\psi_f|$

and $|i\rangle = |\Psi_i^{N-1}\psi_i\rangle$

Ψ^{N-1}

Slater det. for passive electrons

$$\boxed{\mu_{el}(\omega) \propto \left|\langle \Psi_f^{N-1}\psi_f|\hat{\epsilon}\cdot\mathbf{r}|\Psi_i^{N-1}\psi_i\rangle\right|^2 \rho(\epsilon_f)}$$

The interaction Hamiltonian operates only on the active electron

Sudden approximation

If the photoelectron energy is high enough (E > 10 eV above the edge):

- time to exit the atom << relaxation time of passive electrons
- its interaction with the passive electrons of the absorber can be neglected

The atomic wavefunction can be factorized

$$\mu_{el}(\omega) \propto \left|\langle \psi_f | \hat{\epsilon} \cdot \mathbf{r} | \psi_i \rangle\right|^2 S_0^2 \, \rho(\epsilon_f)$$

$$S_0^2 = \left|\langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle\right|^2$$

Superposition integral of the passive electrons wavefunctions

(S_0^2 ~ 0.7 - 0.9)

Allows to reduce interpretation of EXAFS to the calculation of the final state of ONLY the photoelectron

Initial and final states

Wavefunction of the **initial state**:

$$|i>= Y_{l_0,m_0}(\hat{\mathbf{r}})R^0_{l_0}(r)$$

Where: l_0 angular momentum of the electron

$Y_{l0,m0}$ spherical harmonic functions

(solution of the angular part of the Schrödinger equation)

For the **final state** a potential must take into account that the electron moves in the condensed matter

Muffin Tin Potential

Spherical regions centered on each atom in which the potential has a spherical symmetry. Wavefunctions described by a radial + angular part

Interstitial region with a constant potential. Wavefunctions described by plane waves

Dipole approximation: consequences

- Given the angular part of the wavefunctions of the photoelectron
- Given that the dipole term $\hat{\epsilon} \cdot \mathbf{r}$ can be expressed in term of spherical harmonics

The matrix element can be separated in angular and radial coordinates

The dipolar selection rules determine the
transition from the initial to the final state

$$\boxed{\begin{aligned} \Delta\ell &= \pm 1 \\ \Delta s &= 0 \\ \Delta j &= \pm 1, 0 \\ \Delta m &= 0 \end{aligned}}$$

EDGE	INITIAL STATE	FINAL STATE
K, L_1	s (ℓ=0)	p (ℓ=1)
L_2, L_3	p (ℓ=1)	s (ℓ=0), d (ℓ=2)

More details in Sakura Pascarelli's lecture (tomorrow morning)

EXAFS: physical description

Absorption coefficient for an isolated atom

$$\mu_0(\omega) \propto \left|\langle f_0|\hat{H}_{int}|i\rangle\right|^2$$

Absorption coefficient in condensed matter

$$\mu(\omega) \propto \left|\langle f_0 + \delta f|\hat{H}_{int}|i\rangle\right|^2$$

- The initial states are the same for both cases because, being tightly bound are not altered by the surrounding.
- The final state is influenced by the surrounding ($\langle f| = \langle f_0 + \delta f|$) as the photoelectron is able to see it.

Development of $\mu_0(\omega) \propto |\langle f_0 + \delta f|\hat{H}_{int}|i\rangle|^2$

$$
\begin{aligned}
\mu_0(\omega) &\propto |\langle f_0 + \delta f|\hat{H}_{int}|i\rangle|^2 \\
&= \langle f_0 + \delta f|\hat{H}_{int}|i\rangle \langle f_0 + \delta f|\hat{H}_{int}|i\rangle^* \\
&= \left(\langle f_0|\hat{H}_{int}|i\rangle + \langle \delta f|\hat{H}_{int}|i\rangle\right)\left(\langle f_0|\hat{H}_{int}|i\rangle^* + \langle \delta f|\hat{H}_{int}|i\rangle^*\right) \\
&= |\langle f_0|\hat{H}_{int}|i\rangle|^2 + \langle \delta f|\hat{H}_{int}|i\rangle\langle f_0|\hat{H}_{int}|i\rangle^* + \langle f_0|\hat{H}_{int}|i\rangle\langle \delta f|\hat{H}_{int}|i\rangle^*
\end{aligned}
$$

Since:

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

then:

$$\boxed{\chi(k) = \frac{\langle \delta f|\hat{H}_{int}|i\rangle\langle f_0|\hat{H}_{int}|i\rangle^* + C.C.}{|\langle f_0|\hat{H}_{int}|i\rangle|^2}}$$

$$\chi(k) = \frac{\langle \delta f|\hat{H}_{int}|i\rangle \langle f_0|\hat{H}_{int}|i\rangle^* + C.C.}{|\langle f_0|\hat{H}_{int}|i\rangle|^2}$$

Or, alternatively, as a superposition integrals of wavefuntions

$$\chi(k) = \frac{2\mathrm{Re}\int d\boldsymbol{r}\ \left[\psi_i(\boldsymbol{r})\ \hat{\eta}\cdot\boldsymbol{r}\ \underbrace{\psi_f^{0*}(\boldsymbol{r})}_{\text{Outgoing wavefunction}}\right]\ \left[\psi_i^*(\boldsymbol{r})\ \hat{\eta}\cdot\boldsymbol{r}\ \underbrace{\delta\psi_f(\boldsymbol{r})}_{\text{Scattered wavelets}}\right]}{\int d\boldsymbol{r}\ \left|\psi_i^*(\boldsymbol{r})\ \hat{\eta}\cdot\boldsymbol{r}\ \psi_f^0(\boldsymbol{r})\right|^2}$$

The integral gives rise to the interference, that therefore is the origin of EXAFS

Dominant contribution to integral comes from spatial region close to absorber atom nucleus, where the core orbital wavefunction $\Psi_i \neq 0$.

The region where $\Psi_i \neq 0$ represents simultaneously
the source and the detector for the photoelectron
that probes the local structure around the absorber atom

EXAFS formula

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

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)}\, e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

$$\left.\begin{array}{ll} f(k) & \text{scattering amplitude} \\ \delta_j(k) & \text{phase-shift} \end{array}\right\} \text{scattering properties of the atoms neighboring the photoabsorber (depend on the atomic number)}$$

R Distance to the neighbouring atom

N Coordination number of the neighbouring atom

σ^2 Disorder in the neighbour distance

Derivation of the EXAFS formula: sinusoidal functions

The scattering of the outgoing wave from the neighbouring atoms affects the amplitude of the incoming wave which results in the oscillatory behaviour of the absorption coefficient with energy

- EXAFS is defined with respect to the photoelectron wavevector

$$k = \sqrt{[2m(E_{h\nu} - E_0)/\hbar^2]}$$

- The outgoing photoelectron can be described as a spherical wave whose amplitude is proportional to:

$$\psi(k,r) = \frac{\exp(ikr)}{kr}$$

- The incoming wave scattered by the neighbours (emanating from R) is again a spherical wave whose intensity F(k) depends on the type of backscatterers.
  At the photoabsorber (R=0):

$$\chi(k) \propto 2kF(k)\frac{\exp(2ikR)}{k^2R^2} + C.C.$$

$$= \frac{F(k)}{kR^2}\sin(2kR)$$

Derivation of the EXAFS formula: Phase shifts

- Since the electron is not moving in a constant potential a phase shift $\delta(k)$ has to be added. $\delta(k)$ takes into account of the phase shifts of the absorbing (a) and neighbouring (b) atoms.

$$\delta(k) = 2\delta_a(k) + \delta_b(k) - \ell\pi$$

➡

$$\chi(k) \propto \frac{F(k)}{kR^2} \sin(2kR + \delta(k))$$

- This has to be summed over the scattering contributions of all neighbours

- Atoms at the same radial distance and of the same element contribute to the same components of the EXAFS signal.

This group of atoms is called a coordination shell.

The coordination number of each shell is N_j and the sum runs over all shells j

$$\chi(k) \propto \sum_j \frac{N_j F_j(k)}{kR_j^2} \sin(2kR_j + \delta_j(k))$$

Derivation of the EXAFS formula: Debye Waller (disorder)

- The distance between the absorber and the backscatterers in one shell might not be identical due to structural disorder and moreover the atoms vibrate due to thermal excitations.

- Thus the contributions from atoms in one shell will not be exactly in phase.

- If the disorder is small and has a Gaussian distribution around the average distance R, the dephasing can be taken into account for by

$$\exp(-2k^2\sigma_j^2)$$

$$\sigma_j^2 = \langle [\mathbf{r}_j \cdot (\mathbf{u}_j - \mathbf{u}_0)]^2 \rangle$$

EXAFS Debye-Waller

Mean square average displacement u_j-u_0 of the backscatterer j and the absorber

* EXAFS takes place on a time scale much shorter than that of atomic motion, so the measurement serves as an instantaneous snapshot of the atomic configuration

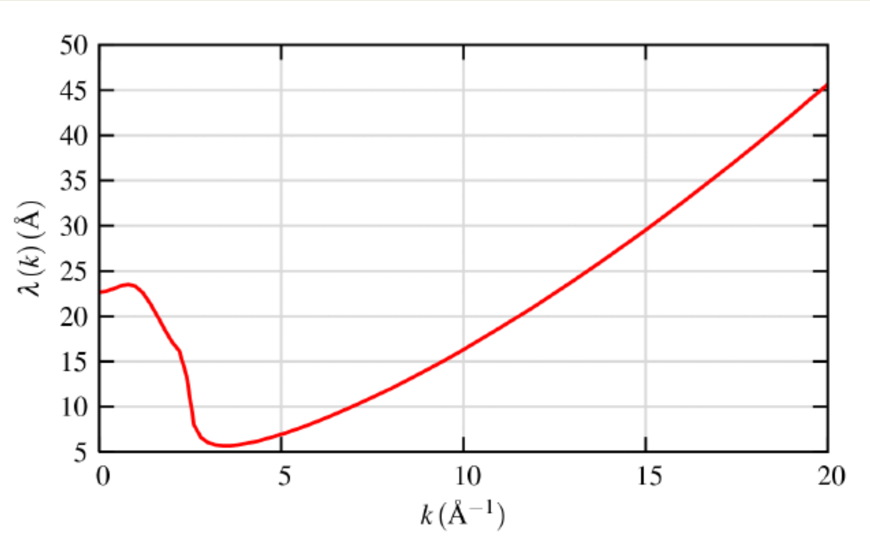
Derivation of the EXAFS formula:
Mean free path

Since the photoelectron also scatter inelastically, it may not be able to get back to the absorbing atom*.

Within the lifetime of the photoelectron, the outgoing and the backscattered waves are coherent, and thus can interfere.
Beyond the lifetime of the photoelectron the coherence is lost producing a damping of the oscillations due to backscattering from atoms at higher distances.

The damping factor is $\exp(-2R_j/\lambda(k))$

Where $\lambda(k)$ is the mean free path



The mean-free-path depends on k.
For the EXAFS k-range, $\lambda(k) < 25$ Å

The $\lambda(k)$ and R^{-2} terms make EXAFS a *local atomic probe*

*Electrons that have suffered inelastic losses will not have the proper wave vector to contribute to the interference process.

Derivation of the EXAFS formula: Amplitude reduction factor S_0^2

Another important Amplitude Reduction Term is due to the relaxation of all the other electrons in the absorbing atom to the hole in the core level

$$S_0^2 = \left| \langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle \right|^2$$

Typically S_0^2 is taken as a constant:

$$0.7 < S_0^2 < 1.0$$

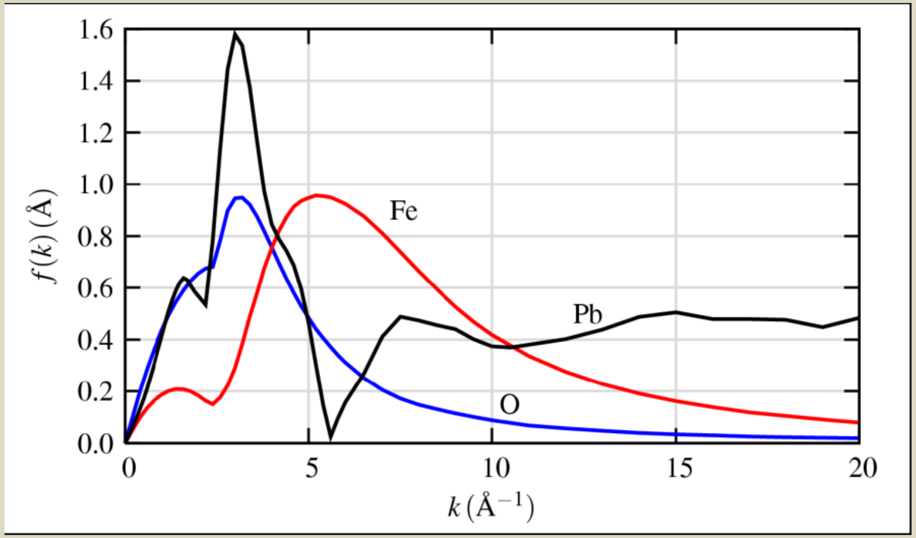
which is found for a given central atom, and simply multiplies the XAFS $\chi(k)$

Note that S_0^2 is completely correlated with N

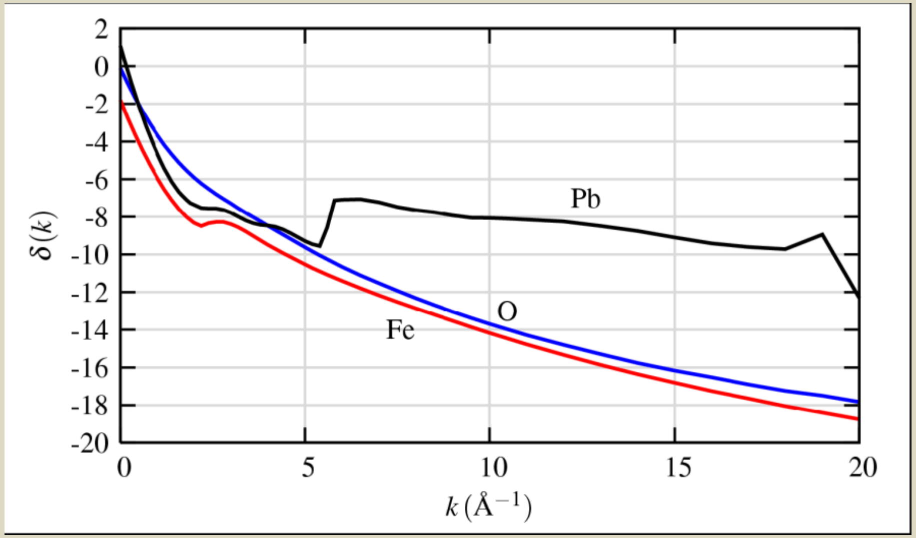
This, and other experimental issues, make EXAFS amplitudes (and therefore N) less accurate than EXAFS phases (and therefore R)

Scattering amplitude and phase shift: F(k) and δ(k)

The scattering amplitude F(k) and phase-shift δ(k) depend on atomic number.



The scattering amplitude F(k) peaks at different k values and extends to higher-k for heavier elements. For very heavy elements, there is structure in F(k).



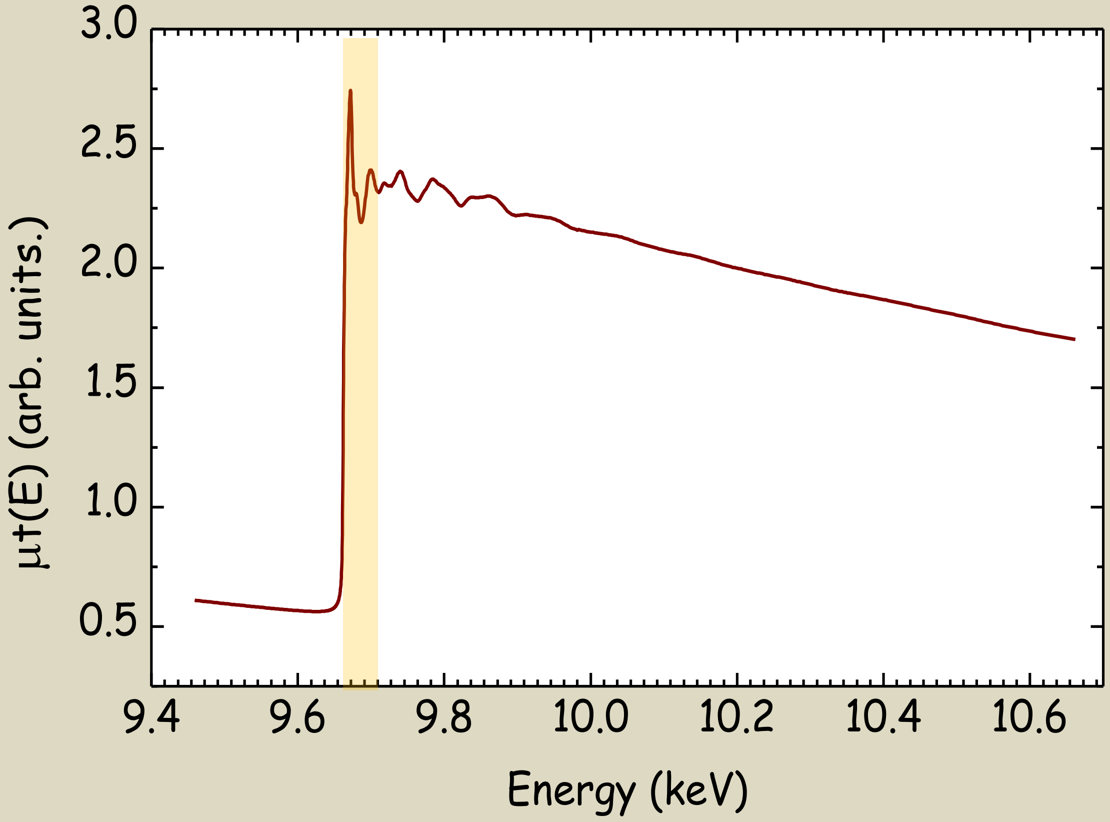
The phase shift δ(k) shows sharp changes for very heavy elements.

These scattering functions can be accurately calculated (programs FEFF, GNXAS, etc.), and used in the EXAFS modeling.

Z can usually be determined to within 5 or so. Fe and O can be distinguished, but Fe and Mn cannot be.

Outline

1. X-ray Absorption
2. X-ray Absorption Fine Structure
3. Simple theoretical description
4. **XANES**
5. Major historical EXAFS breakthrough
6. Applications at XAFS at Elettra

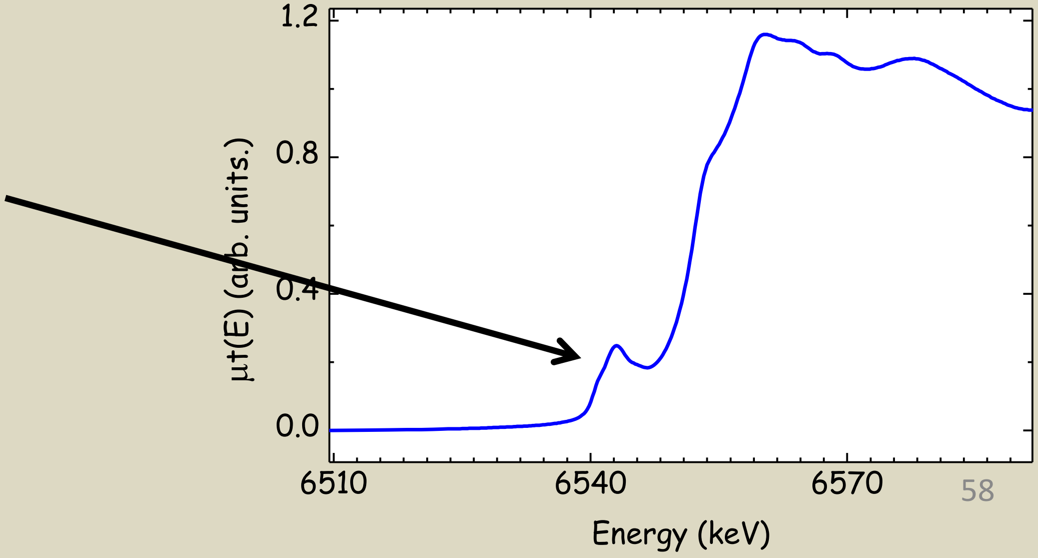


Recall:

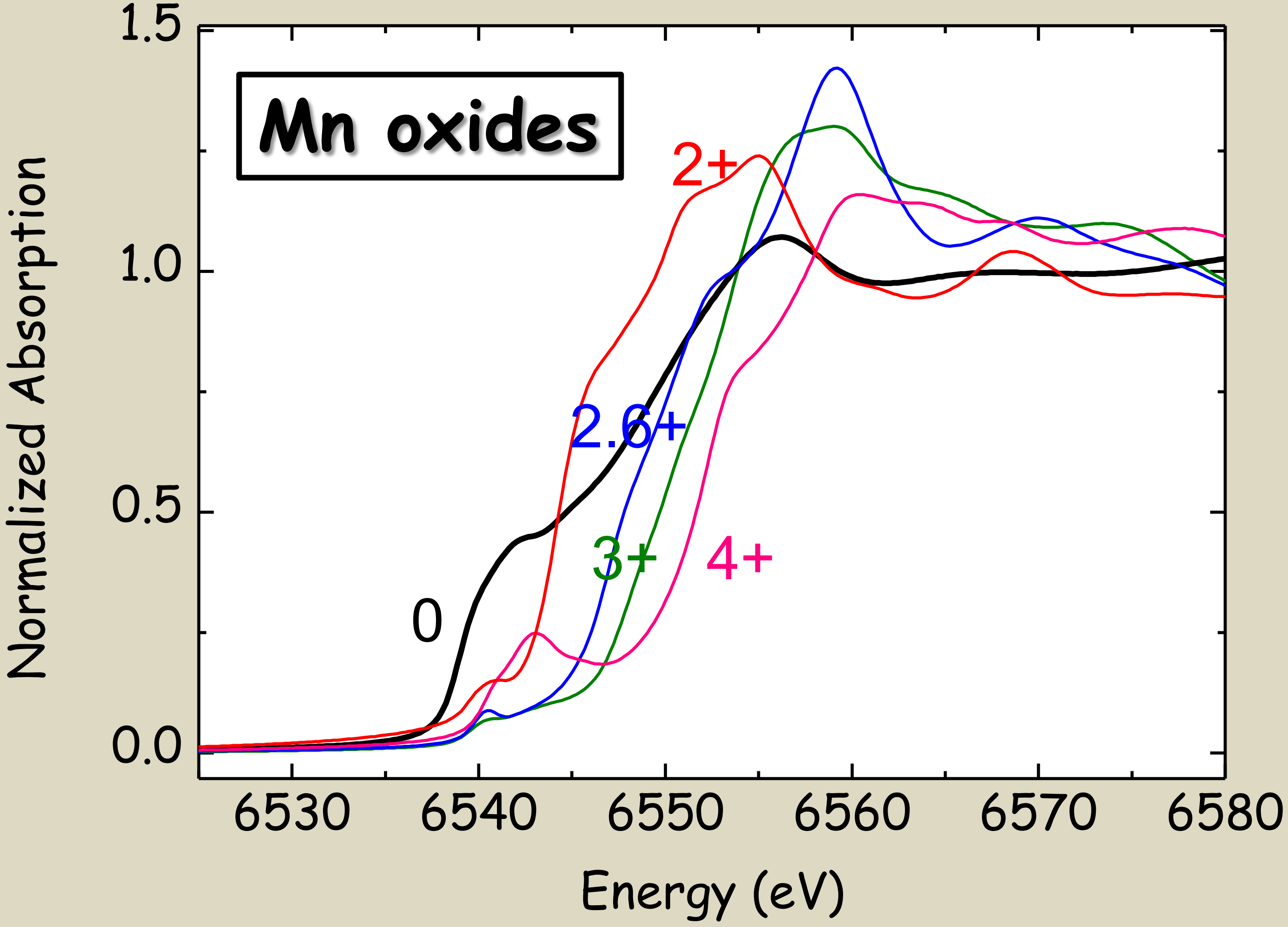
XANES is the region of the absorption spectrum within ~ 60 eV of the absorption edge

X-ray
Absorption
Near
Edge
Structure

XANES includes also the "pre-edge features" if any

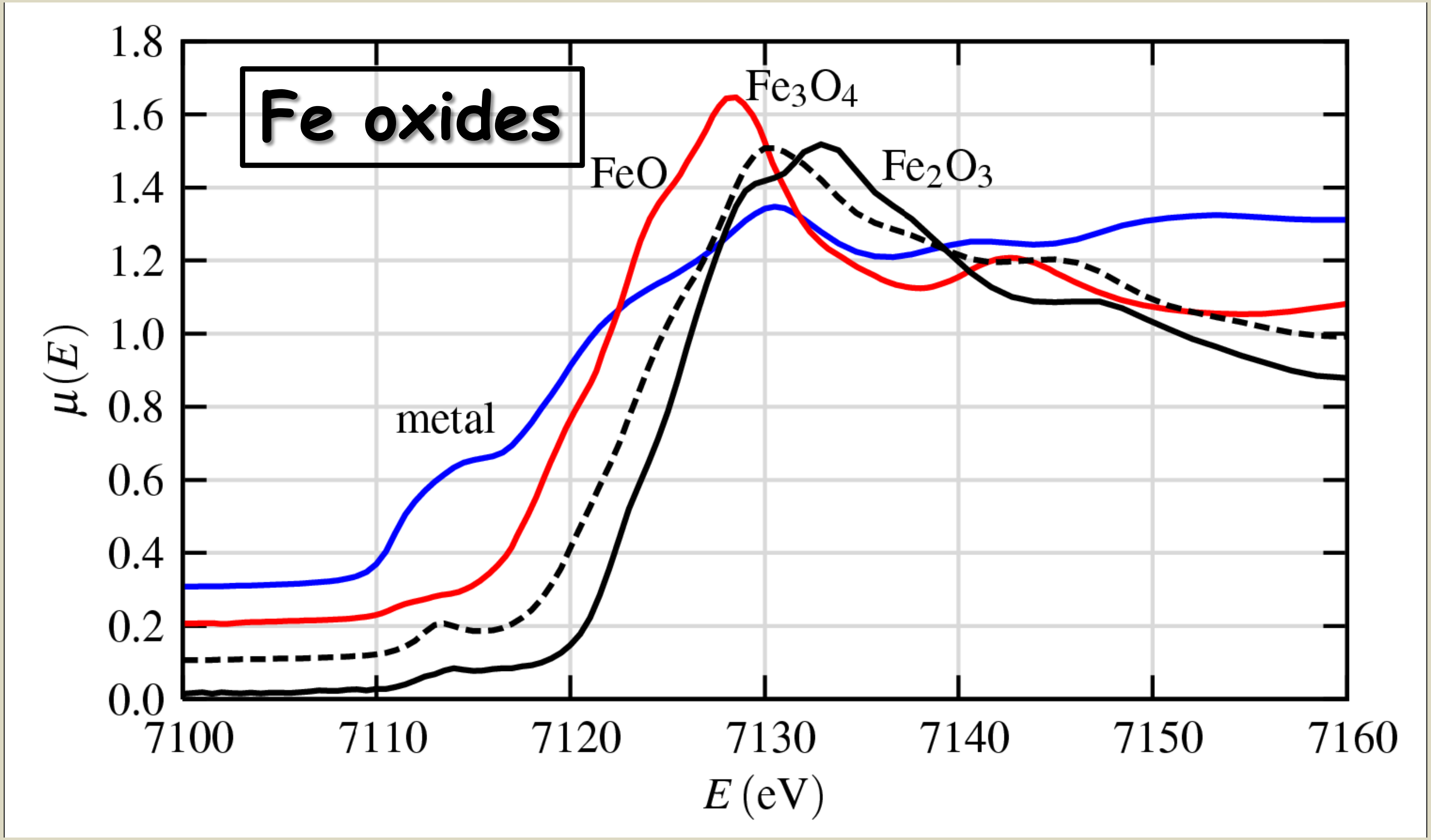


Edge position: oxidation state



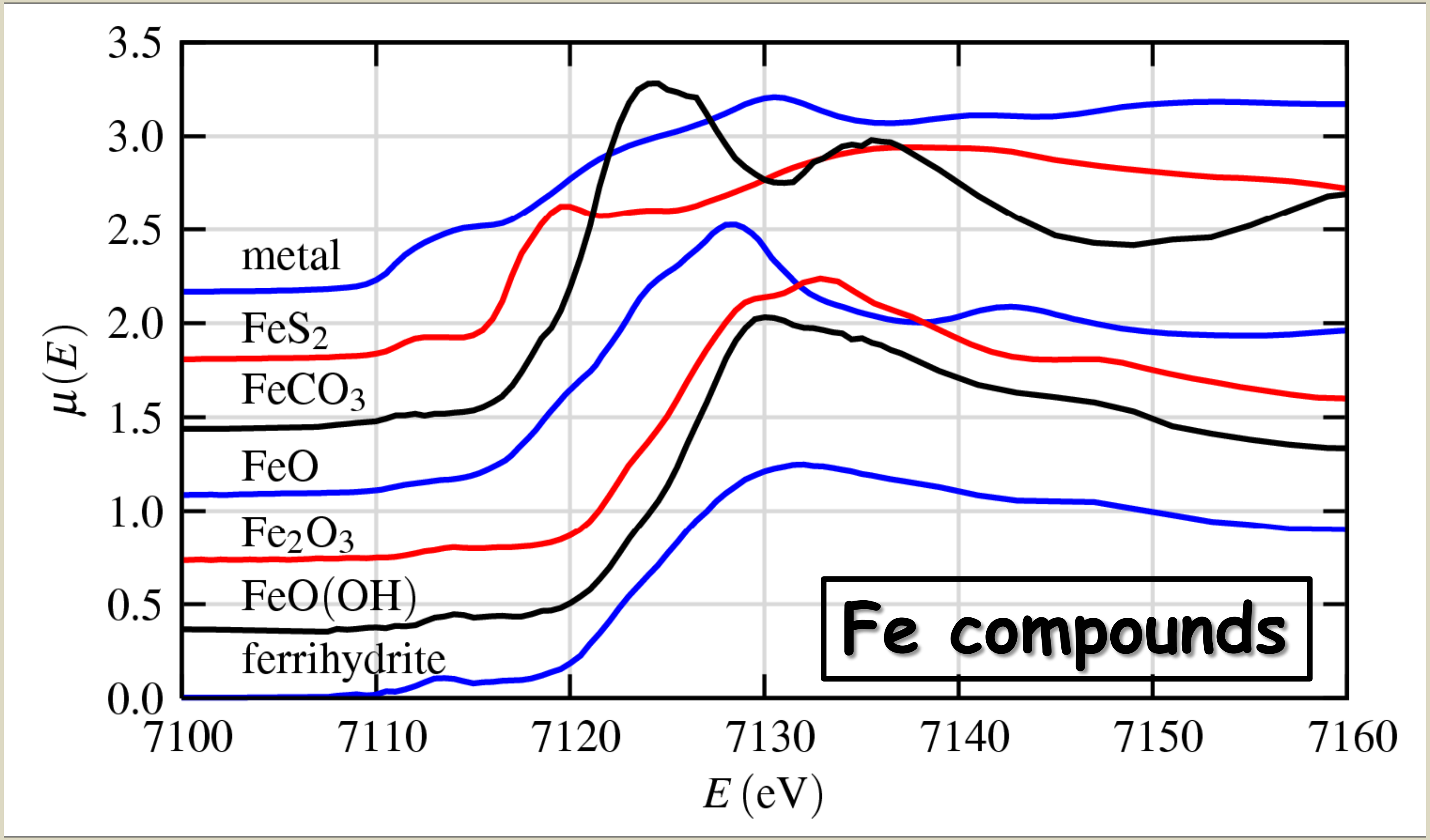
Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

Edge position: oxidation state



The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

Edge position: oxidation state



XANES can be used simply as a fingerprint of phases and oxidation state.

XANES analysis can be as simple as making linear combinations of “known” spectra to get compositional fraction of these components

XANES transitions

- Dipole selection rules apply:

$$\begin{aligned}\Delta\ell &= \pm 1\\ \Delta s &= 0\\ \Delta j &= \pm 1, 0\\ \Delta m &= 0\end{aligned}$$

EDGE	INITIAL STATE	FINAL STATE
K, L_1	s (ℓ=0)	p (ℓ=1)
L_2, L_3	p (ℓ=1)	s (ℓ=0), d (ℓ=2)

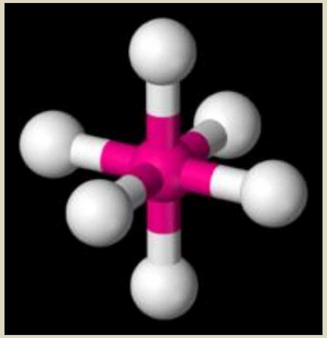
- The final state is usually not atomic-like and may have mixing (hybridization) with other orbitals.

This is often the interesting part of the XANES!

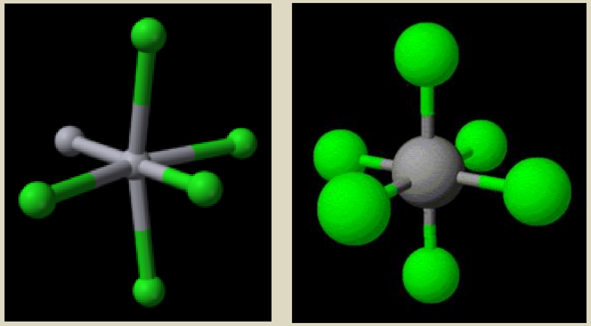
Transition metals K pre-edge peaks

Transition from 1s to 4p states

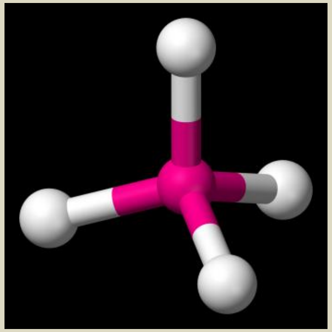
Pure octahedron
Centro-symmetry: no p-d mixing allowed
only (weak) quadrupolar transitions
No, or very low intensity prepeak



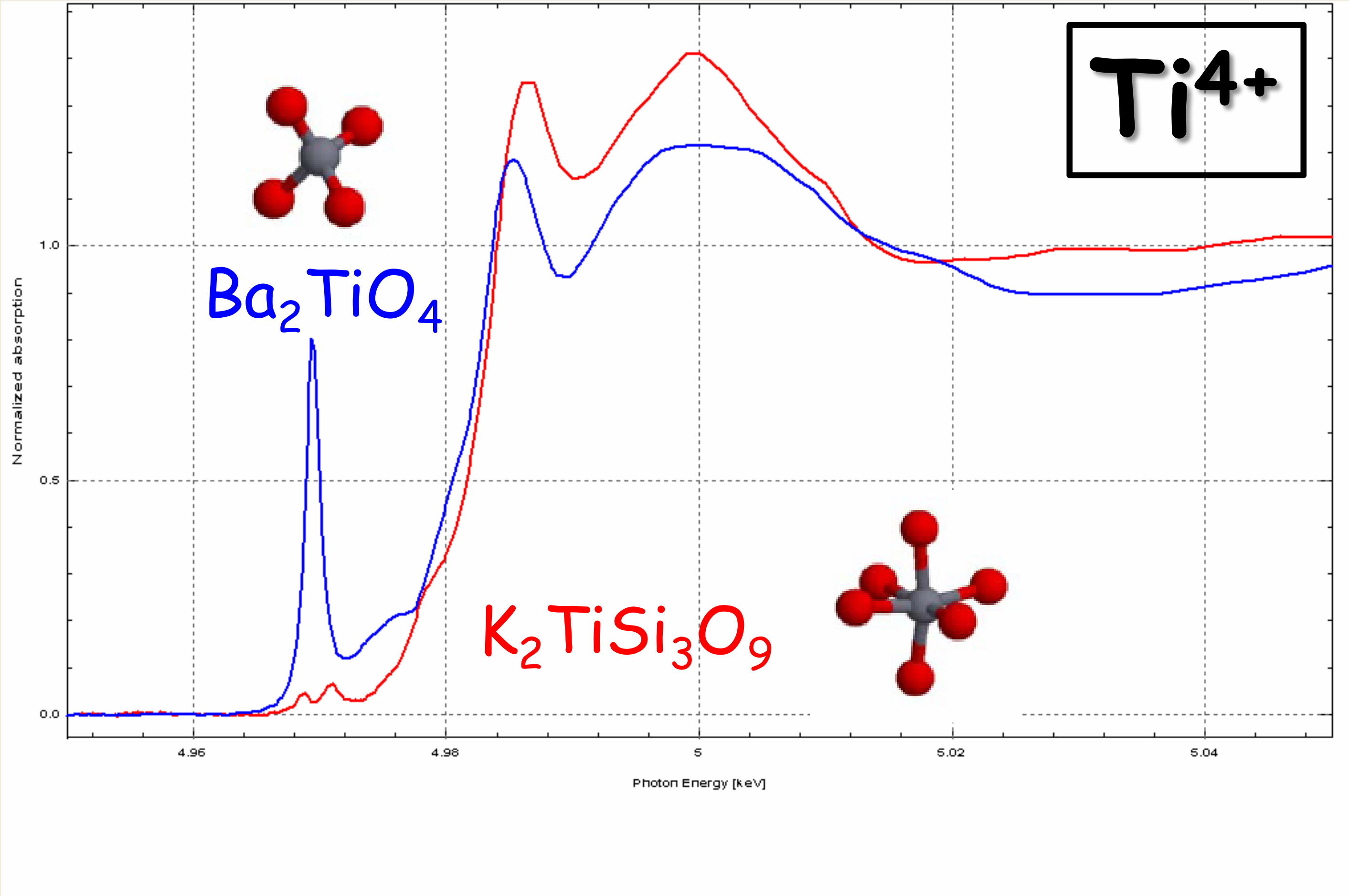
Distorted octahedron
Centro-symmetry broken: p-d mixing allowed
dipole transition in the edge
moderate intensity prepeak



Tetrahedron
No Centro-symmetry : p-d mixing allowed
dipole transition in the edge
high intensity prepeak

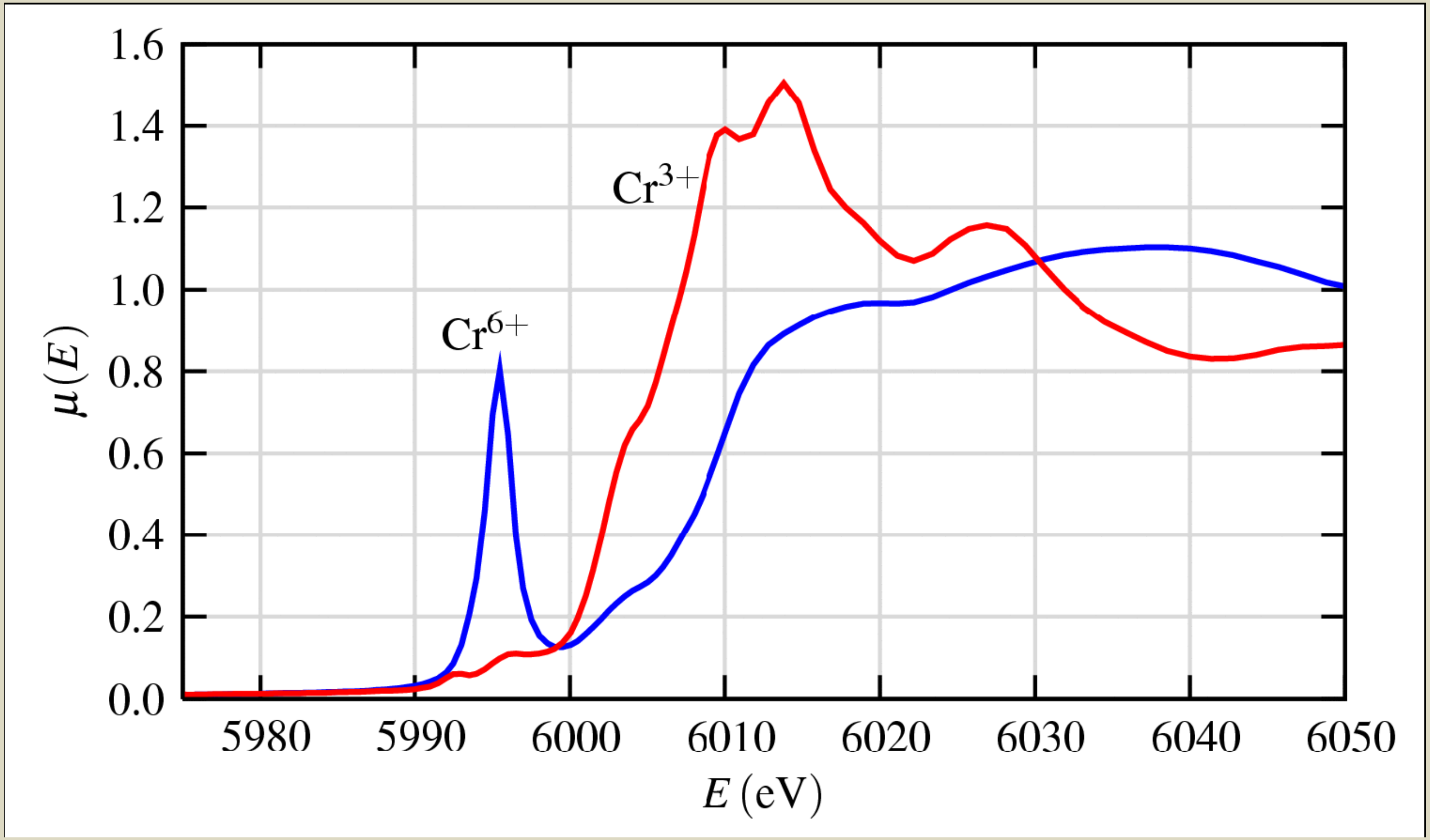


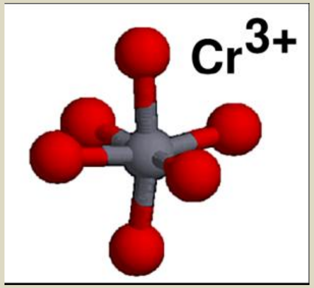
Pre-peak: local coordination environment

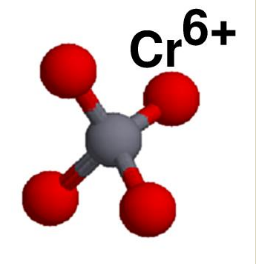


Ti K-edge XANES shows dramatic dependence on the local coordination chemistry

Pre-peak: local coordination environment



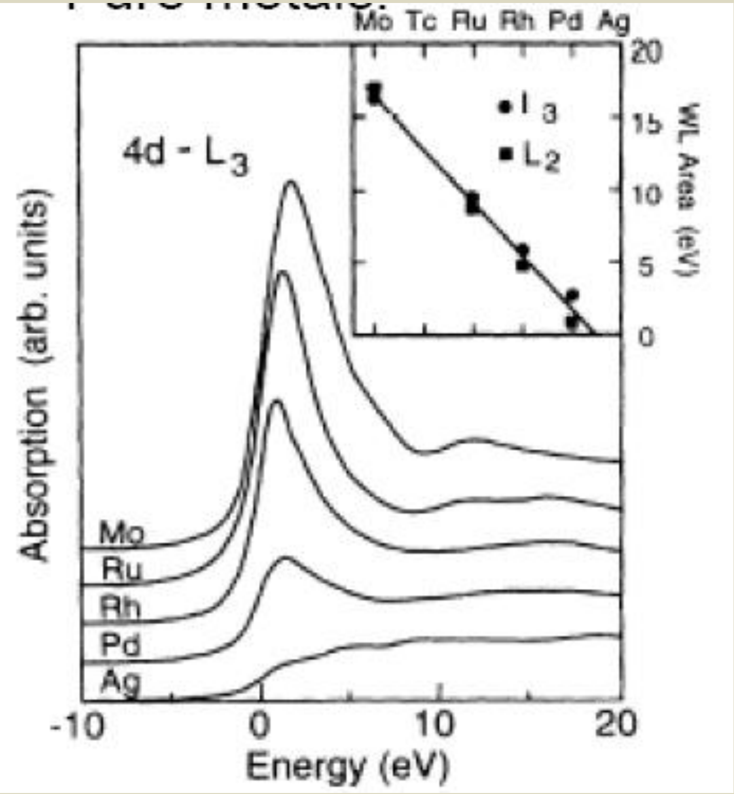




The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

White line intensity of L_3-edge XANES of 4d metals

Transition from $2p_{3/2}$ to 4d states

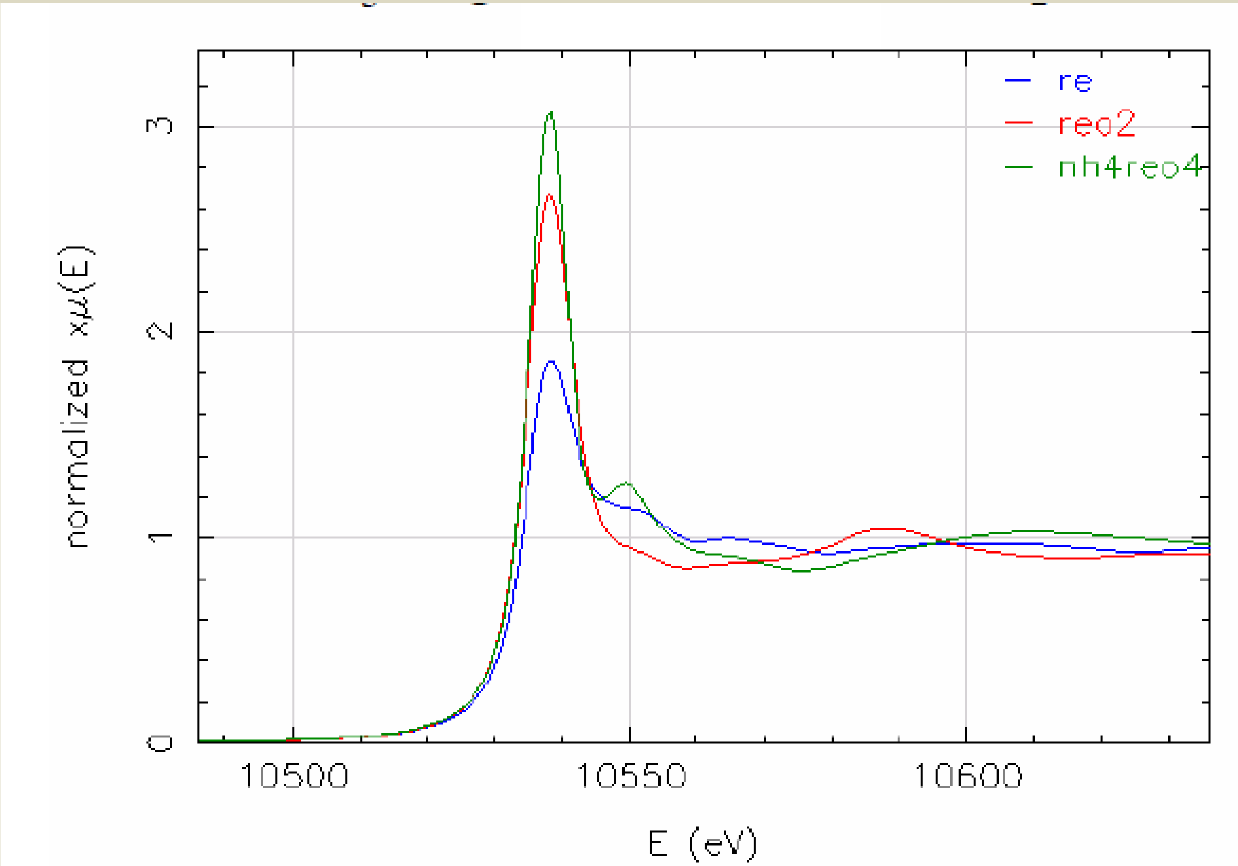


Linear correlation between white line area and number of 4d-holes for Mo to Ag

Increasing d states occupancy

White line intensity: oxidation state

Re L_3 edge: transition from $2p_{3/2}$ to 5d states



Re metal (Re^0) - $5d^5$

ReO_2 (Re^{4+}) - $5d^1$

NH_4ReO_4 (Re^{7+}) $5d^0$

XANES interpretation

The EXAFS equation breaks down at low-k, and the mean-free-path goes up.
This complicates XANES interpretation:

A simple equation for XANES does not exist!

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states
multiple-scattering	multiple bounces of the photoelectron

XANES calculations are becoming reasonably accurate and simple. These can help explain what *bonding orbitals* and/or *structural characteristics* give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are also possible

XANES: Conclusions

XANES is a much larger signal than EXAFS

XANES can be done at lower concentrations, and less-than-perfect sample conditions

XANES is easier to crudely interpret than EXAFS

For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient

XANES is harder to fully interpret than EXAFS

The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

This situation is improving, so stay tuned to the progress in XANES calculations …

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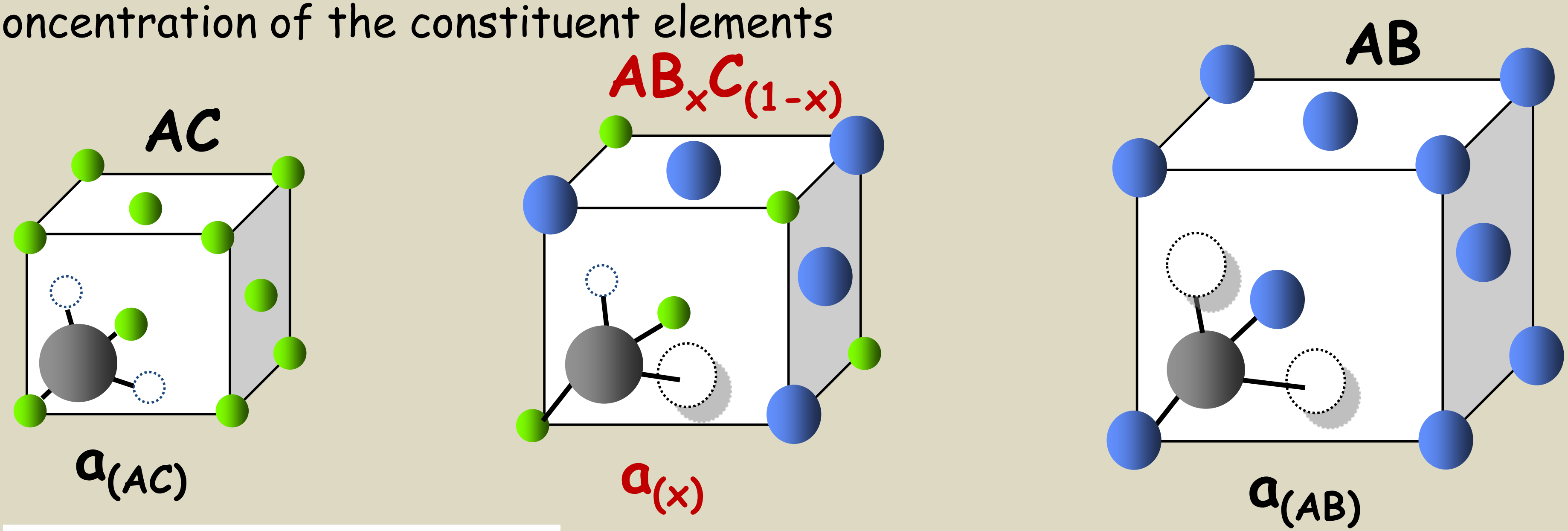
Atomic scale structure in solid solutions

Vegard's law

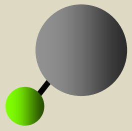
linear relation between the crystal lattice parameters of an alloy and the concentration of the constituent elements



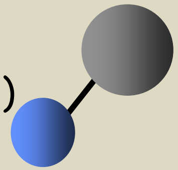
$$a_{(x)} = x a_{(AB)} + (1-x) a_{(AC)}$$

If

$$R^0_{(AC)} = (\surd 3/4) a_{(AC)}$$



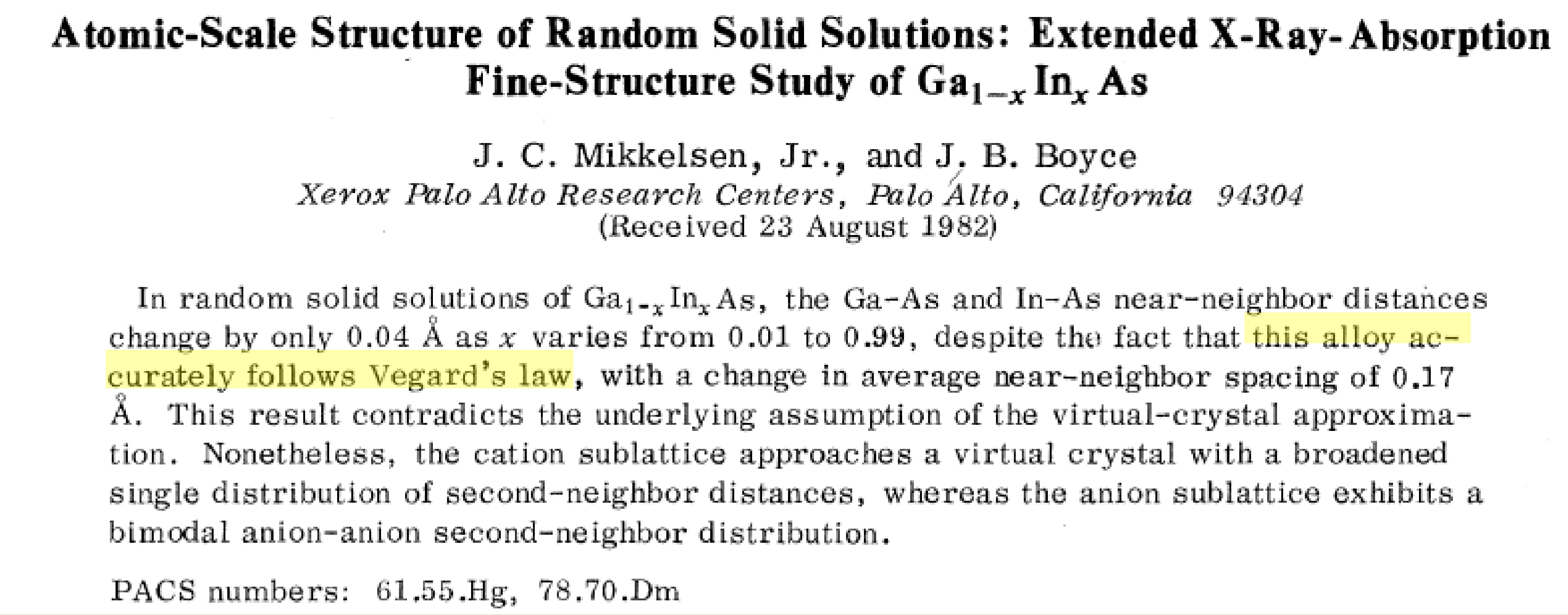
$$R^0_{(AB)} = (\surd 3/4) a_{(AB)}$$



then

$$R_{(AC)x} = R_{(AB)x} = (\surd 3/4) a_{(x)}$$

Virtual Crystal Approximation (VCA)



Atomic-Scale Structure of Random Solid Solutions: Extended X-Ray-Absorption Fine-Structure Study of $Ga_{1-x}In_xAs$

J. C. Mikkelsen, Jr., and J. B. Boyce
Xerox Palo Alto Research Centers, Palo Alto, California 94304

(Received 23 August 1982)

In random solid solutions of $Ga_{1-x}In_xAs$, the Ga-As and In-As near-neighbor distances change by only 0.04 Å as x varies from 0.01 to 0.99, despite the fact that this alloy accurately follows Vegard's law, with a change in average near-neighbor spacing of 0.17 Å. This result contradicts the underlying assumption of the virtual-crystal approximation. Nonetheless, the cation sublattice approaches a virtual crystal with a broadened single distribution of second-neighbor distances, whereas the anion sublattice exhibits a bimodal anion-anion second-neighbor distribution.

PACS numbers: 61.55.Hg, 78.70.Dm

$Ga_{1-x}In_xAs$ follows Vegard's law

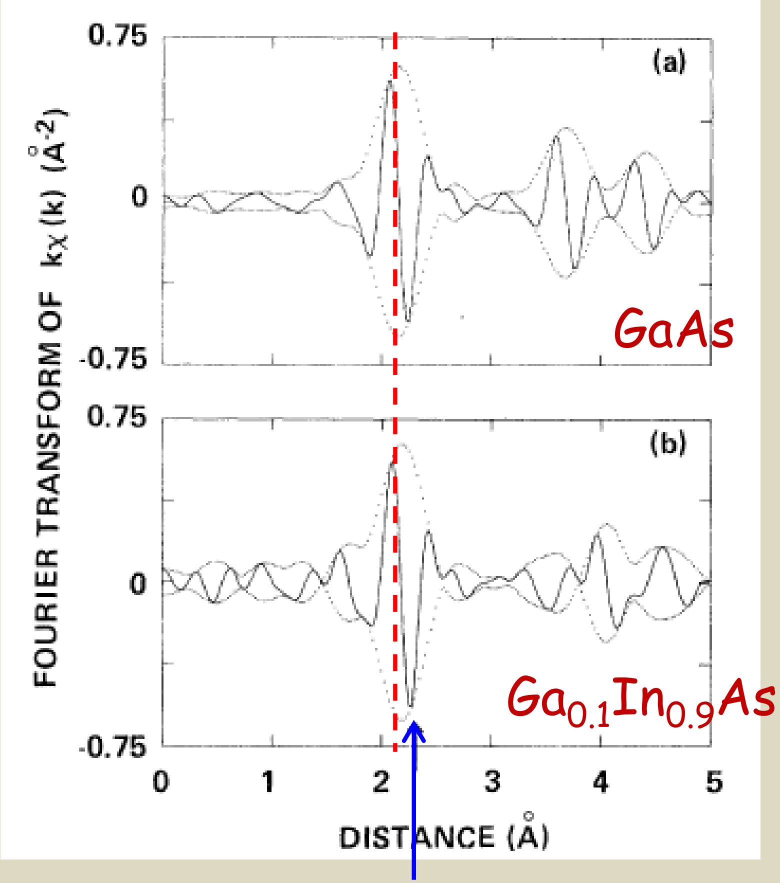
According to the VCA:

- $d_{Ga\text{-}As}=d_{In\text{-}As}$
- $\Delta d = 0.17$ for x varying from 0.01 to 0.99

This study has shown that:

1. For a given composition

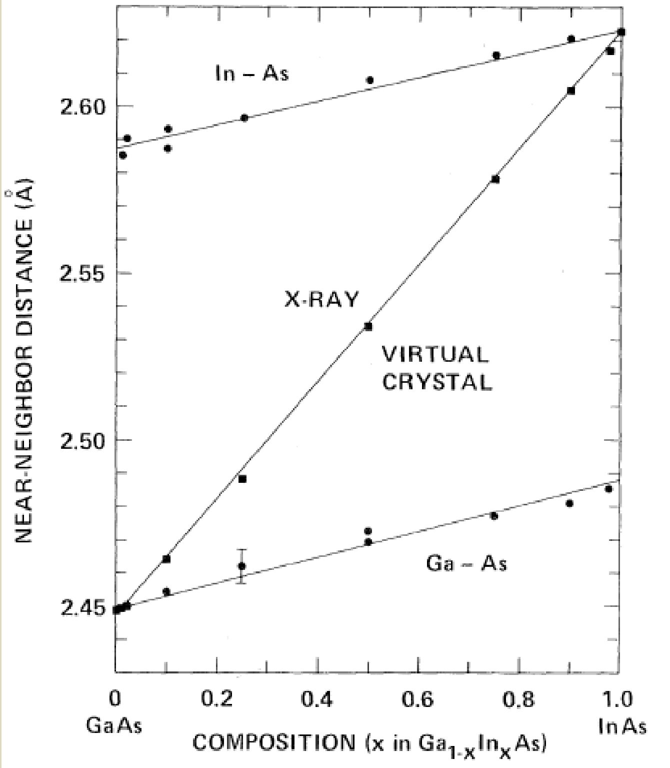
- $d_{In\text{-}As}$ in the solid solution is closer to $d_{In\text{-}As}$ in InAs than to the value of the VCA
- $d_{Ga\text{-}As}$ in the solid solution is closer to $d_{Ga\text{-}As}$ in GaAs than to the value of the VCA



Value foreseen by the VCA

2. With varying composition

- $\Delta d_{In\text{-}As}$ and $\Delta d_{Ga\text{-}As}$ change only 0.04 instead of 0.17 foreseen by VCA



Determination of nanoparticles' size

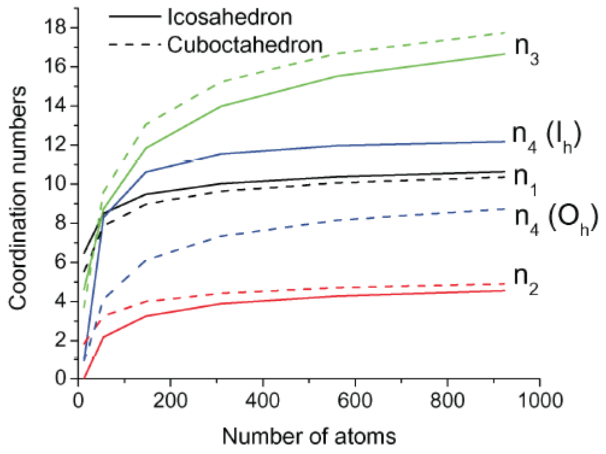
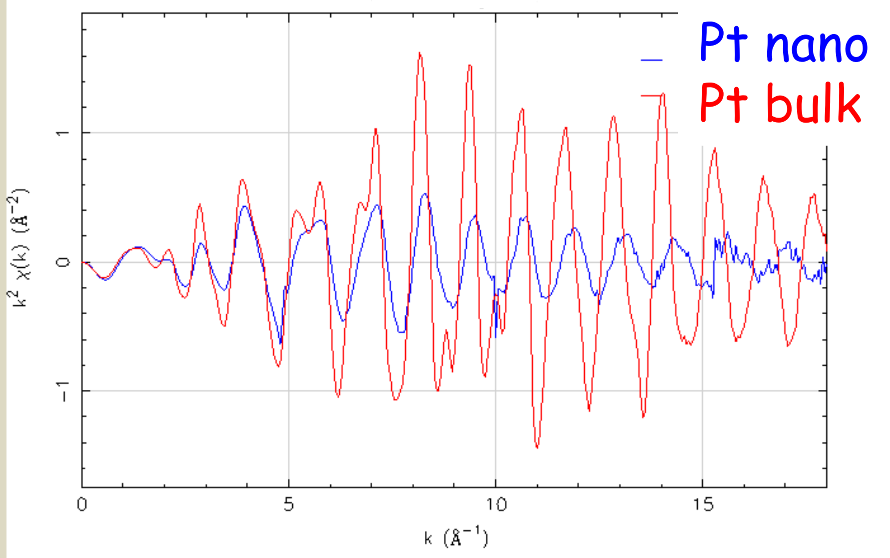


FIGURE 3. Coordination numbers n_1 through n_4 for icosahedron and cuboctahedron clusters.

Glasner and Frenkel, AIP Conf. Proc. **882** 746

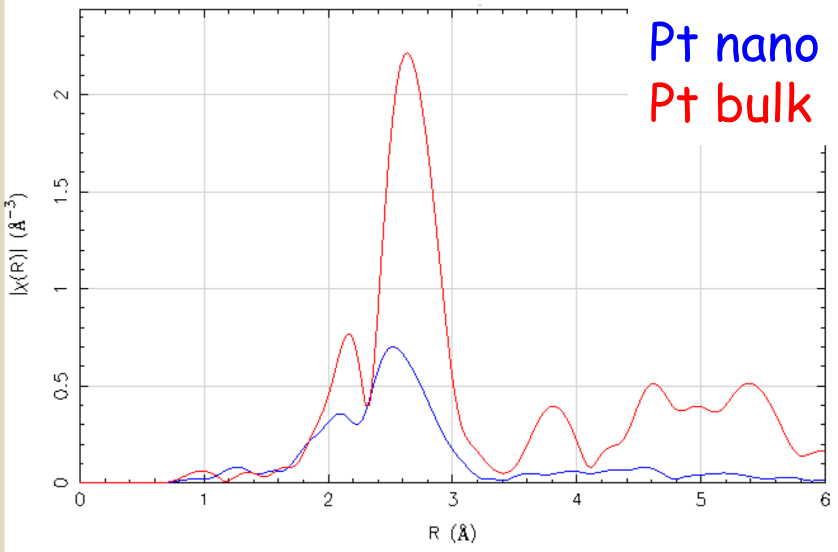
Coordination number on the nearest neighbours in NPs is a non linear function of the particle diameter (for diameters < 3-5 nm).

This property is widely used in EXAFS for determine the size of the NPs



Pt bulk: CN 12, Pt-Pt 2.77 Å

Pt nano: CN 7, Pt-Pt 2.71 Å



Outline

1. X-ray Absorption
2. X-ray Absorption Fine Structure
3. Simple theoretical description
4. XANES
5. Major historical EXAFS breakthrough
6. Applications at XAFS at Elettra

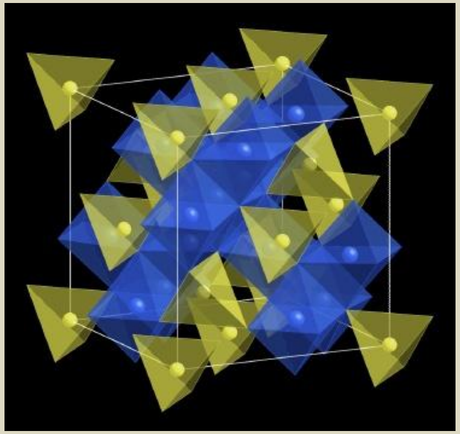
Site occupancy in spinel nanoferrites

Aquilanti et al., *Cation distribution in Zn Doped Cobalt Nanoferrites Determined by X-ray Absorption Spectroscopy* J. Supercond. Nov Magn **24** (2011) 659.

Spinel nanoferrites

- Remarkable magnetic, optical and electrical properties

- Applications: - magnetic storage systems
  - site-specific drug delivery
  - ……



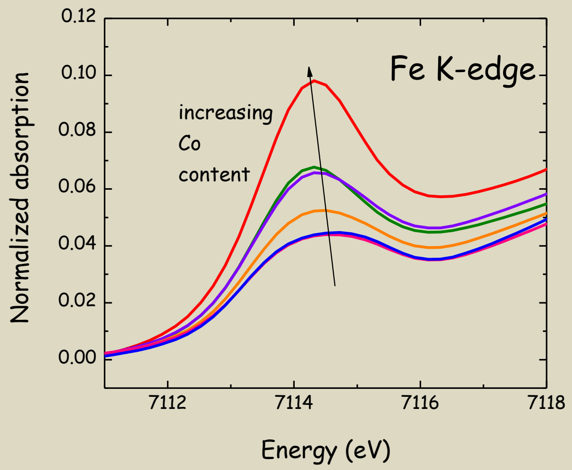
$$[M_{1-i}Fe_i]^A[M_iFe_{(2-i)}]^BO_4$$

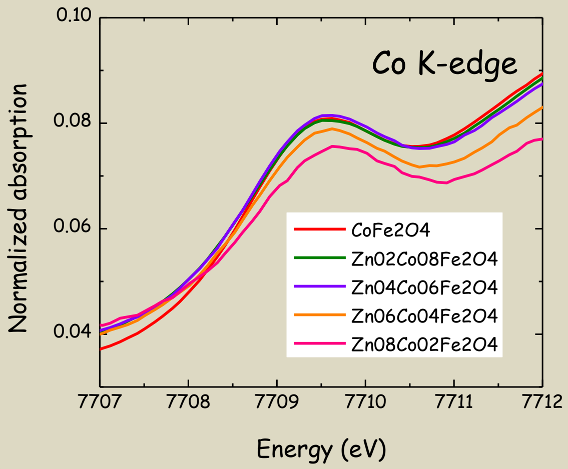
A Tetrahedral site
B Octahedral site

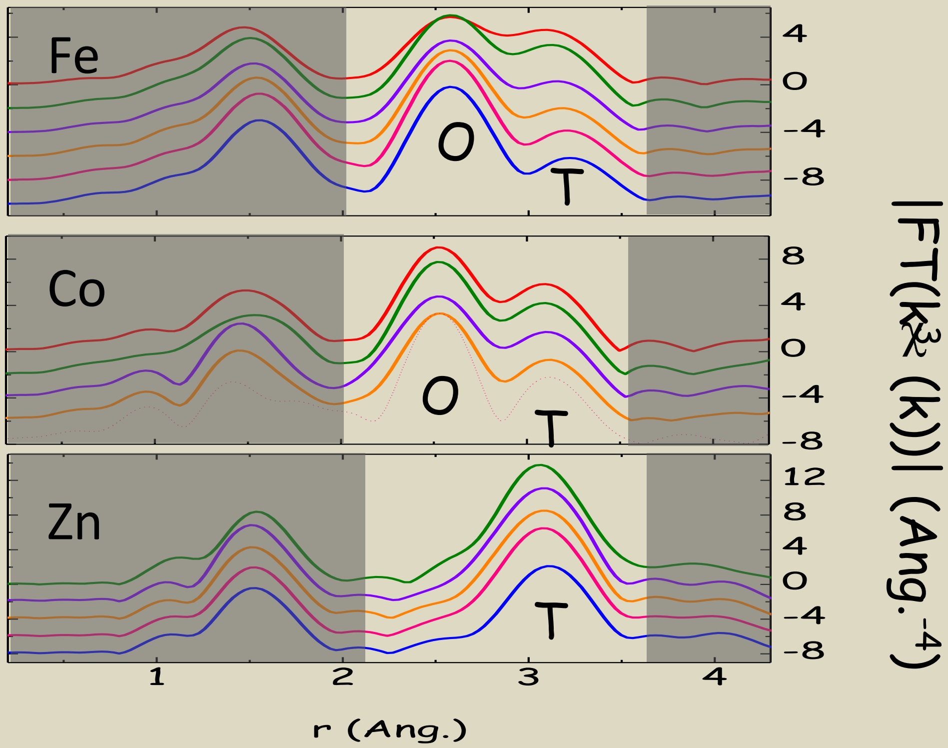
To determine the cation occupancy within the spinel structure from which depend the exceptional properties of these systems

$Zn_xCo_{1-x}Fe_2O_4$

at Zn K-edge (E= 9659 eV)
Co K-edge (E=7709 eV)
Fe K-edge (E=7112 eV)





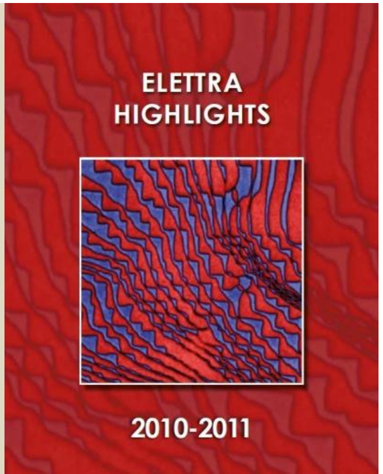


- Simultaneous fitting of the Zn, Fe and Co data
- Zn data: only tetrahedral model
- Co data: only octahedral model
- Fe data: tetrahedral + octahedral
  with fractions determined by the stoichiometry

Qualitative information on the inversion of the spinel can be obtained analyzing the FT

Quantitative information on the inversion parameter 'i' can be obtained recording and fitting multiedge data http://www.elettra.trieste.it/science/highlights/pdf/elettra_highlights_2011.pdf

Correlating sulfur reactivity of Pt_xPd_{1-x} nanoparticles with a bimetallic interaction effect



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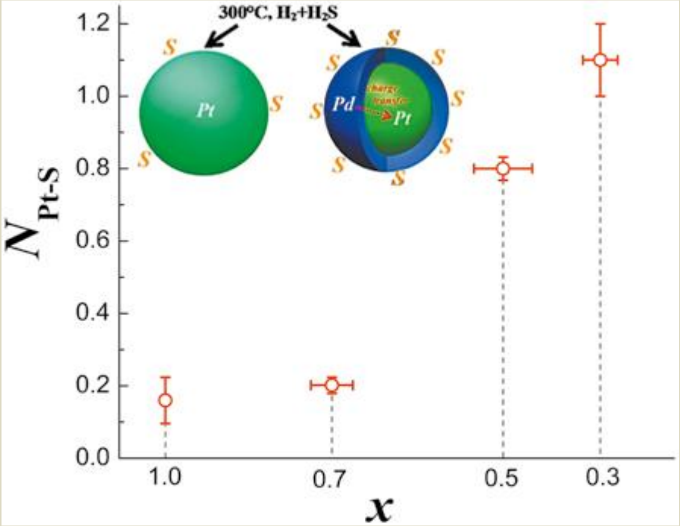
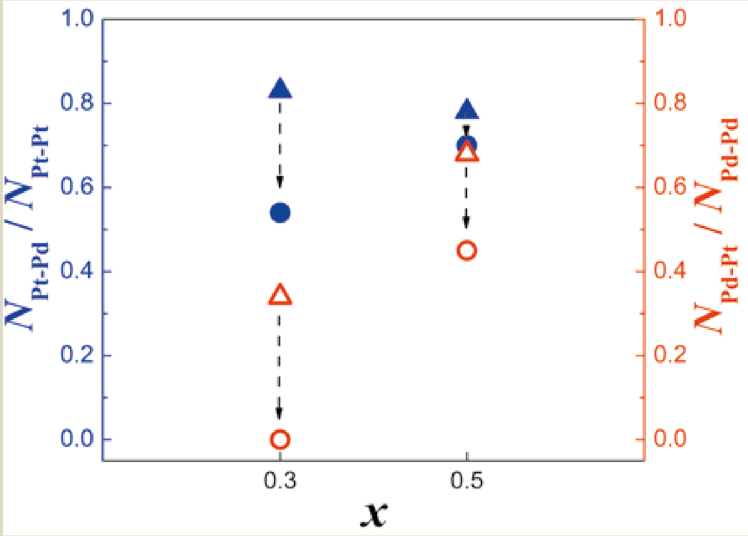
Sulfur poisoning in metallic catalysts

To change the electronic properties by using supports (Al_2O_3 or zeolites)

To alloy the active metal to another metal

"XAS has been used to monitor the local structural changes after reduction and sulphidation and to correlate the S reactivity with the bimetallic interaction"

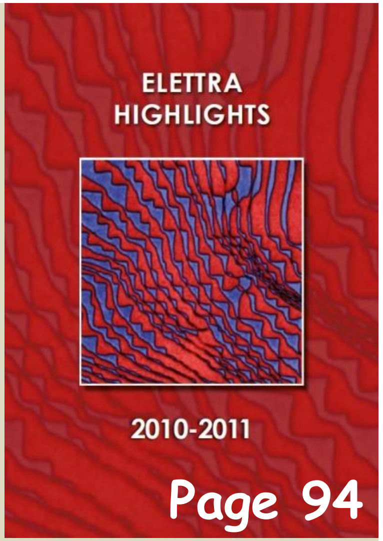




http://www.elettra.trieste.it/science/highlights/pdf/elettra_highlights_2011.pdf

Structural studies of copper complexes as potential bioinorganic target-specific drugs

"Relation between the structure and the cytotoxic activity of copper complexes containing scorpionate ligands "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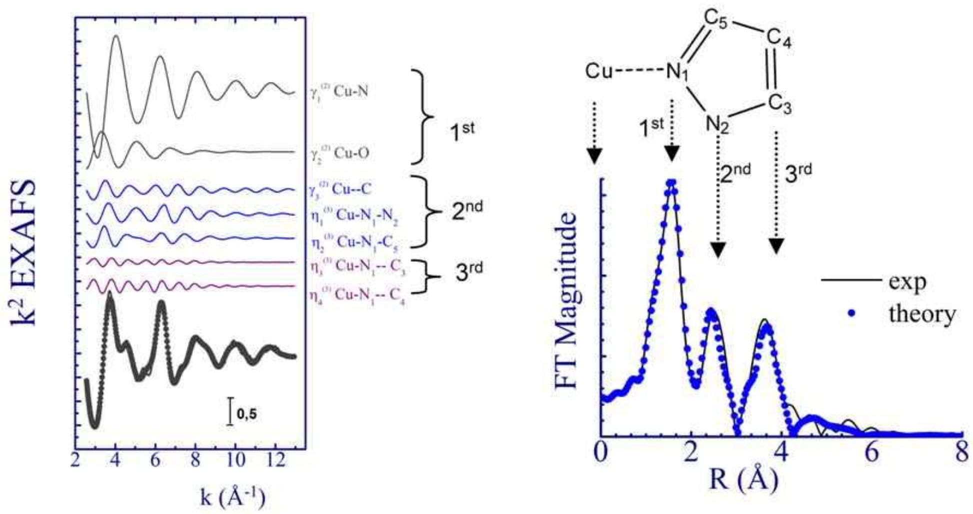
COVER ARTICLE
Pellei *et al.*
Nitroimidazole and glucosamine conjugated heteroscorpionate ligands and related copper(I) complexes

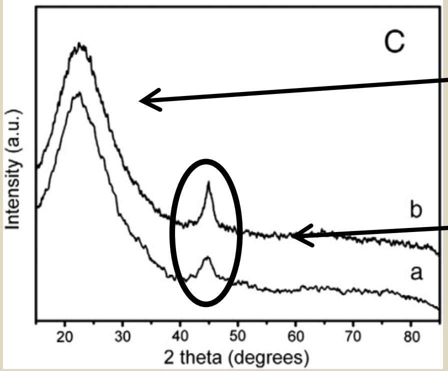
International Year of CHEMISTRY 2011

1477-9226(2011)40:38;1-N



Nanomaterials

Carta et al., *An X-ray absorption spectroscopy study of FeCo alloy nanoparticles embedded in ordered cubic mesoporous silica (SBA-16)* . J. of Non-Cryst. Sol. **357** (2011) 2611.

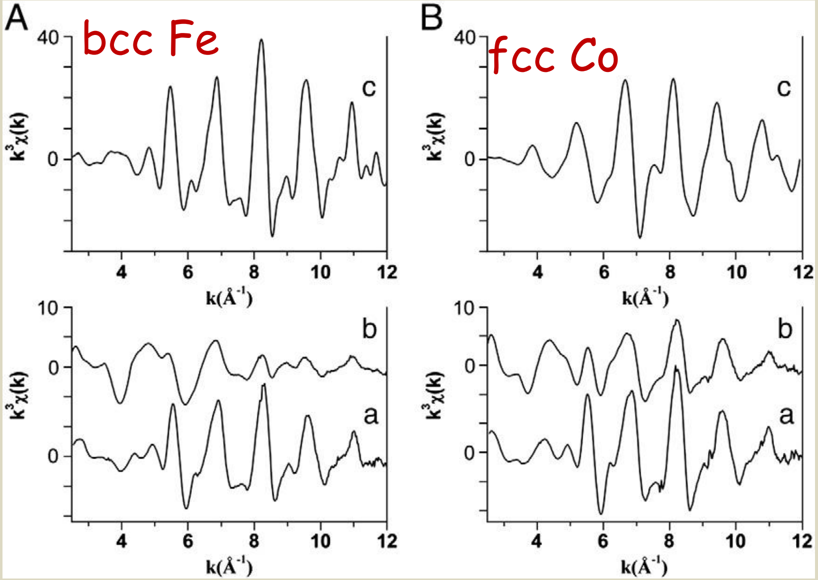


a-SiO_2

bcc Fe or bcc FeCo

Two prep methods:

a) co-precipitation
b) impregnation

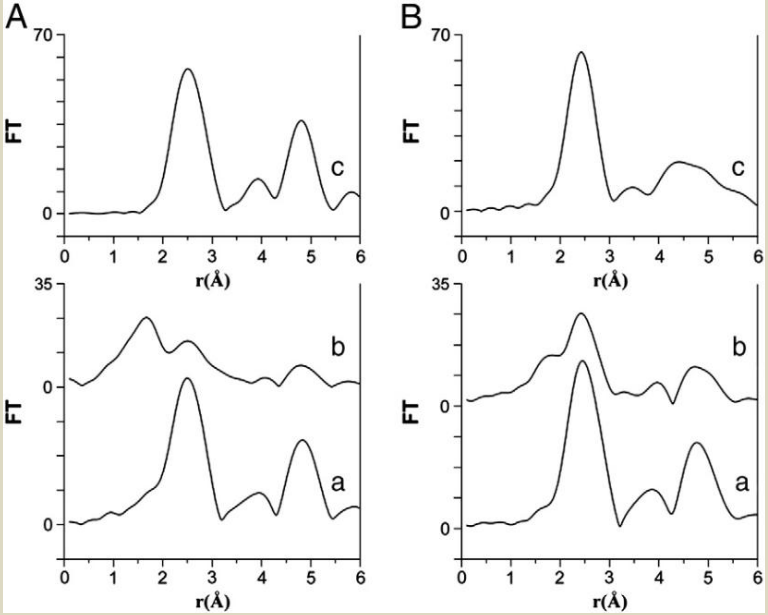


bcc Fe

fcc Co

Fe K-edge

Co K-edge

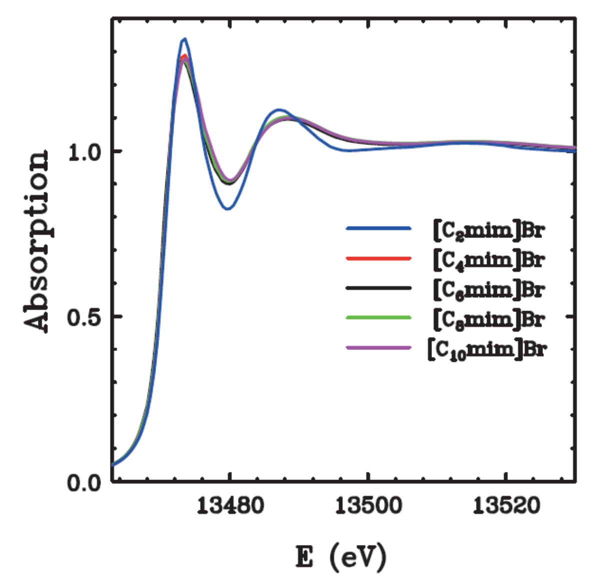


Green chemistry - Ionic liquids

D' Angelo et al., *X-Ray absorption spectroscopy investigation of 1-alkyl-3-methylimidazolium bromide salts* J. of Chem. Phys. **135** (2011) 074505.

- Low vapor pressure → nonvolatile, nonflammable
- organic cations + inorganic anions

The aim is to elucidate the structural changes that take place around the Br^- ion when the alkyl chain length is modified.



C_2mim, C_4mim solids
$C_n$mim (n>4) liquids

- The difference between the two solids depends on the number of hydrogen bonds
- Local structure independent from the alkyl chain length
- Crystalline order is preserved in the liquid

Literature

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More information: web links

International XAFS Society: http://ixs.iit.edu/

Tutorials and other Training Material: http://xafs.org/Tutorials

Software Resources EXAFS:

http://xafs.org/Software
http://leonardo.phys.washington.edu/feff
http://gnxas.unicam.it/