Introduction to X-ray Absorption Spectroscopy

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Part 1:

- What is XAFS?
- What does it tell us?
- The EXAFS equation

Part 2:

- Basic steps in the analysis
- Quick overview of typical analysis
- Example for Co doped ZnO films

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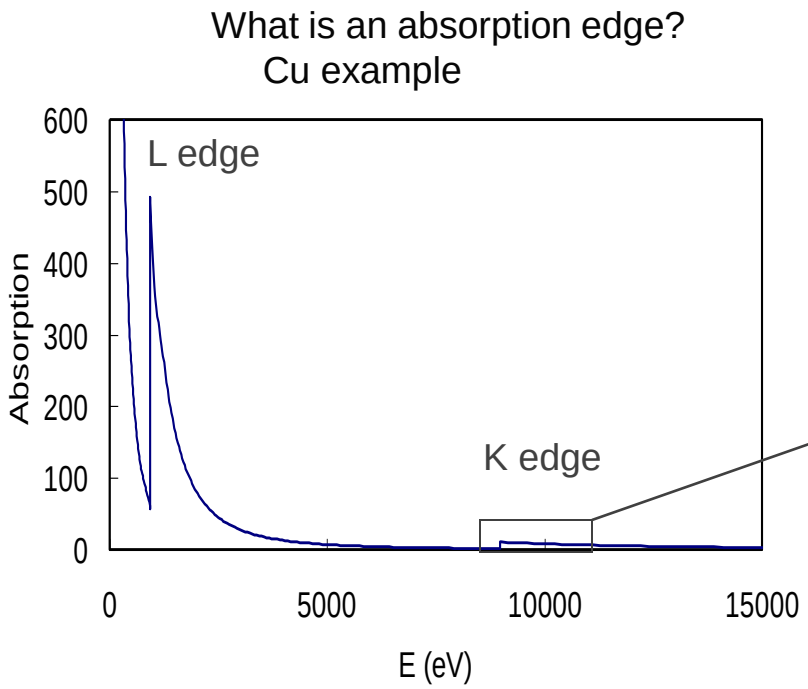
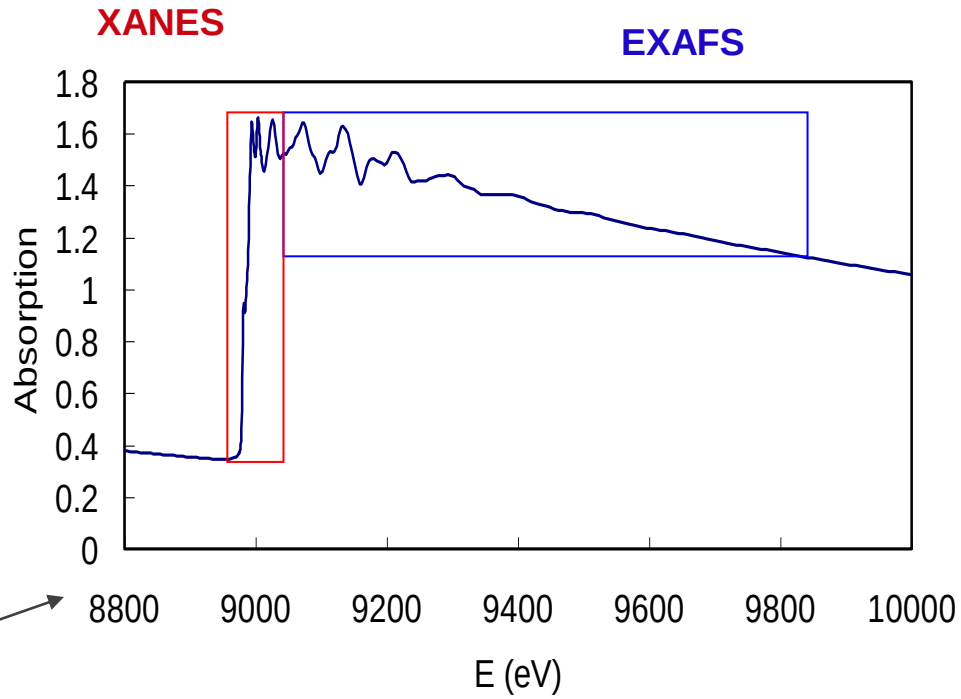
What is XAFS?

XAFS stands for X-ray Absorption Fine Structure and appears in the vicinity of absorption edges

EXAFS – Extended XAFS

XANES – X-ray Absorption Near Edge Structure





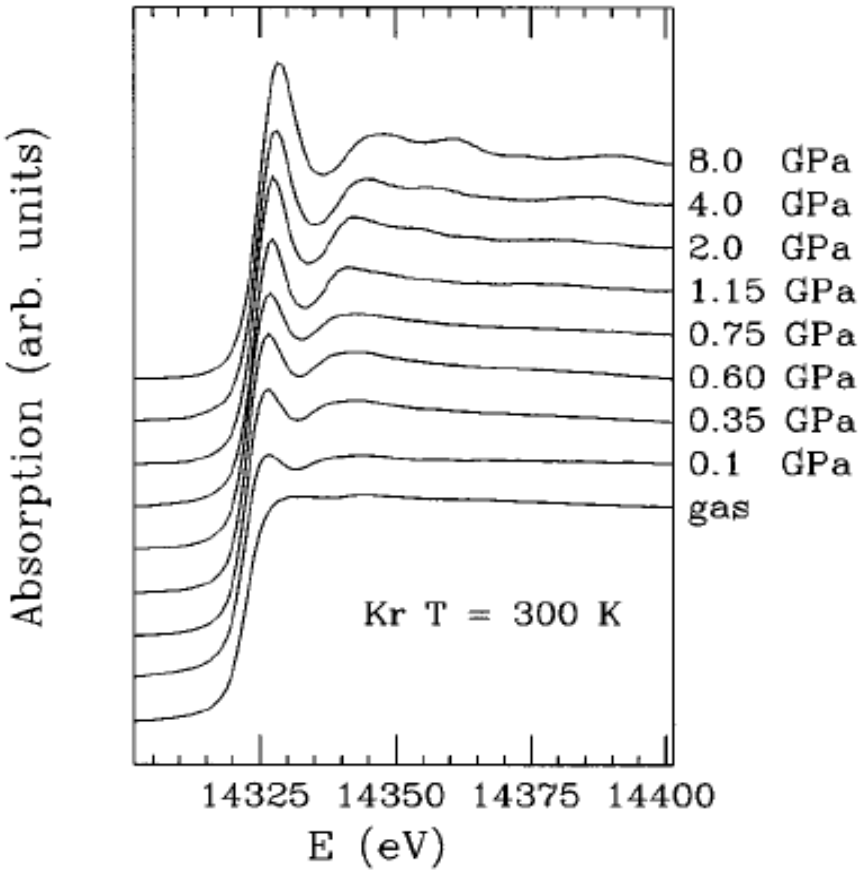
EXAFS sensitive to local atomic structure

Nearest neighbor information:

- Distance
- Atomic type
- Coordination number
- Vibrational amplitude

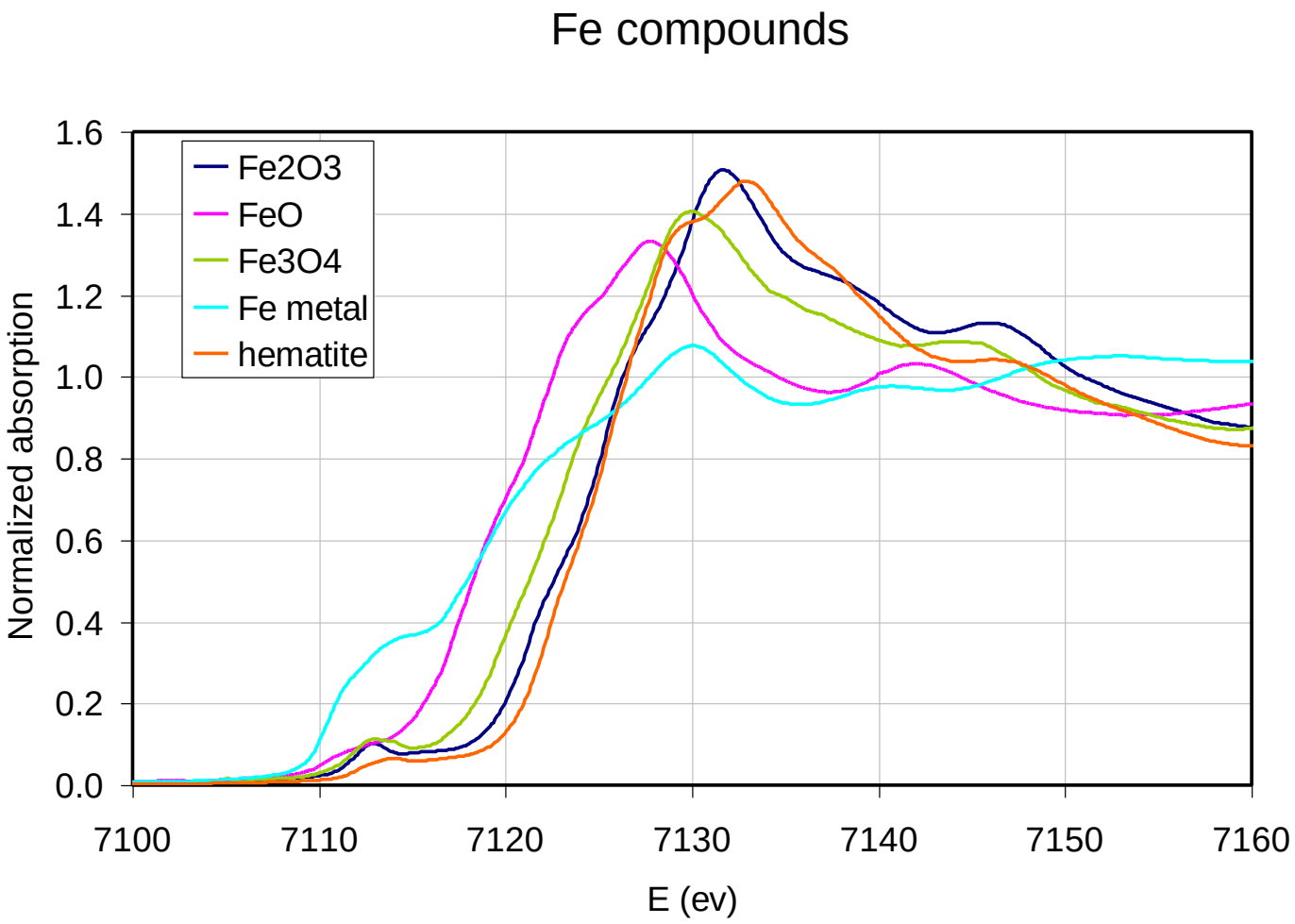
Typically useful for the first few coordination shells

Kr under pressure



DiCicco etal PRB 54, 9086

XANES sensitive to chemical state and valence



Why is x-ray absorption useful?

- Short range order probe - crystallinity not required
- Element specific (Fe – 7111 eV, Cu – 8980, etc.)
- Near edge sensitive to chemistry
  - Valence
  - Site symmetry
- Extended structure sensitive to atomic neighbors
  - Number and type of neighbors
  - Distance to neighbors
  - Disorder in neighbors
  - Orientation of bonds (using x-ray polarization)
- Can be applied to dilute systems

Calculation of Absorption

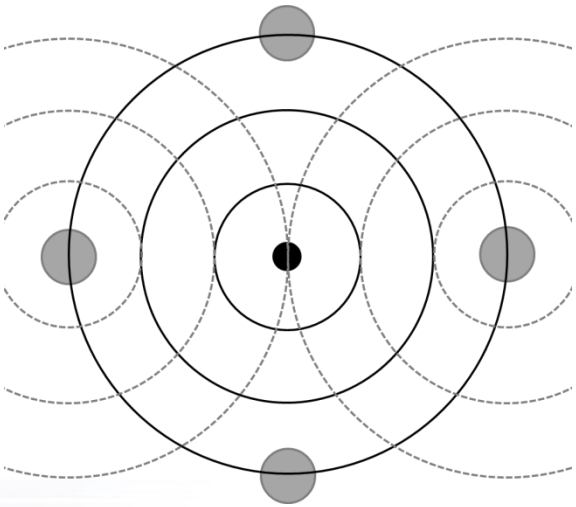
From Fermi's golden rule

$$\mu = \frac{4\pi\omega e^2}{c} N \left|\langle i|r|f\rangle\right|^2 \rho(E_f)$$

i – Initial state: 1s or 2p electron localized in the core of the atom

f – Final state: outgoing photoelectron wave + interactions with the neighboring atoms

$\rho(E_f)$ – Density of final states



The XAFS equation

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} = \sum_j \frac{N_j}{kR_j^2} A_j(k)\, p_j(\mathbf{e}) \sin\left[2kR_j + \psi_j(k)\right]$$

$$k = \frac{\sqrt{2m_e E}}{\hbar}$$ The electron wavevector, $E=E_{x\text{-}ray}-E_{edge}$

μ_0 - "atomic" absorption

R - distance to atoms of shell j

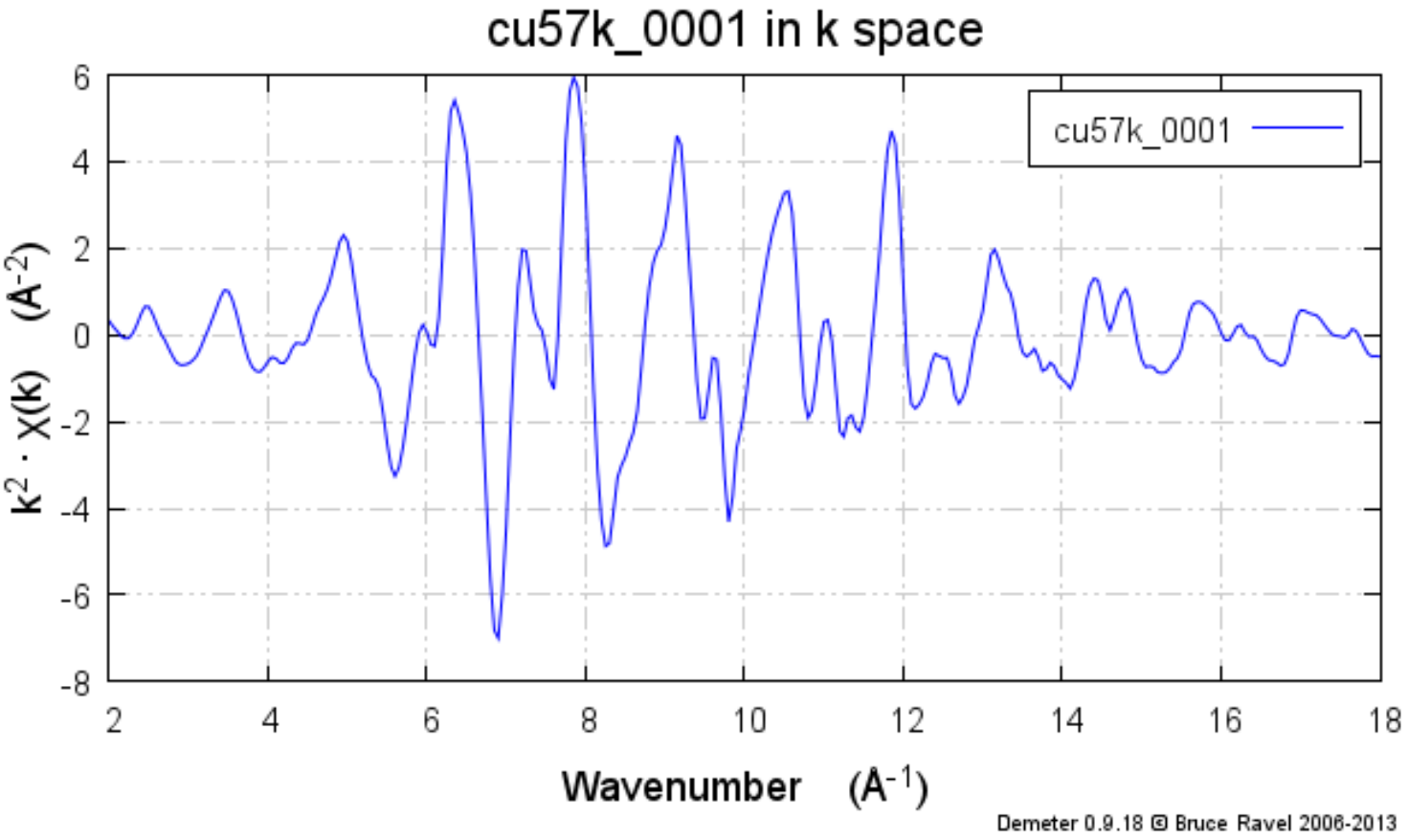
N - number of atoms in shell j

A - amplitude factor

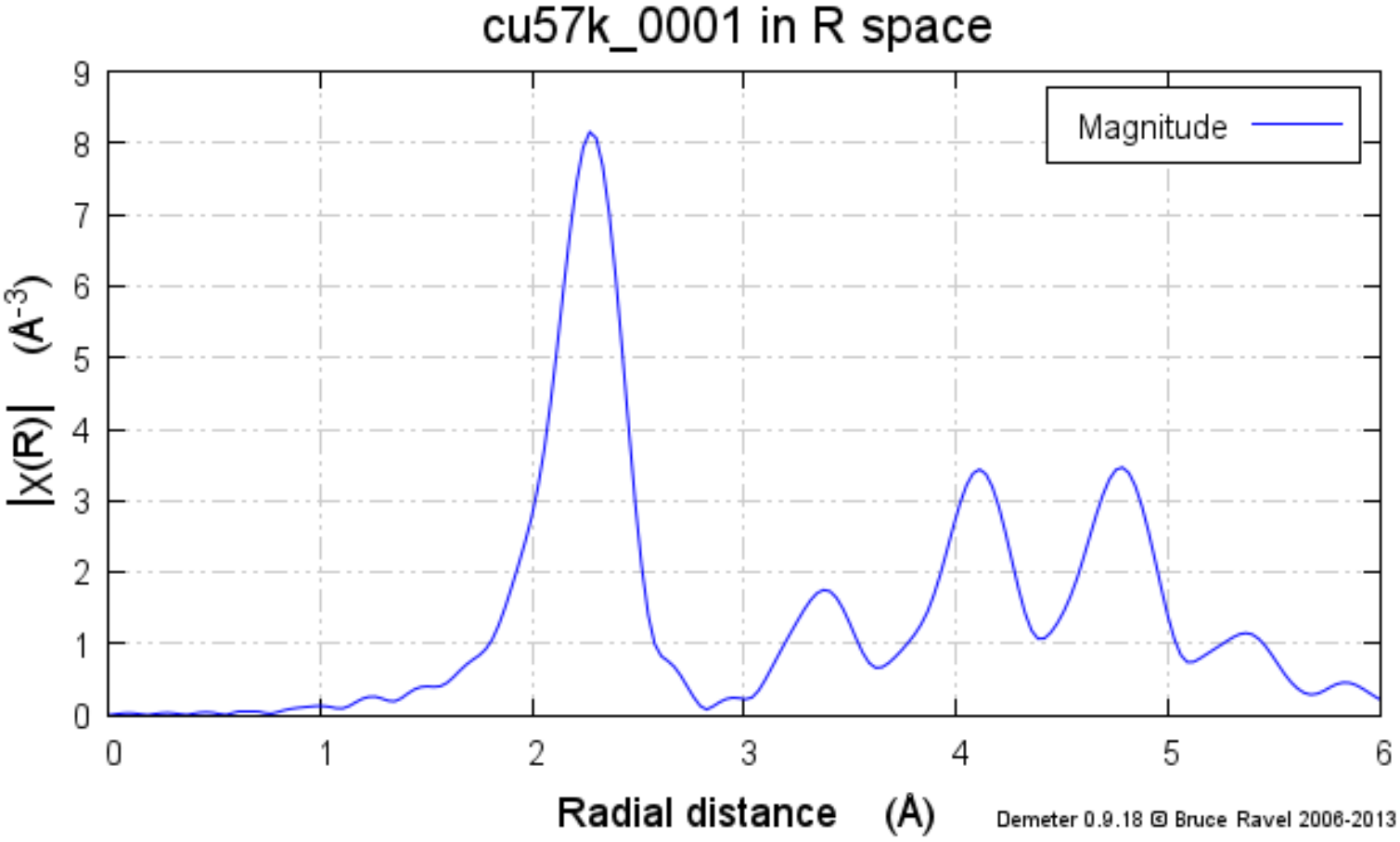
p - polarization factor

ψ - phase factor

Cu EXAFS


cu57k_0001 in k space
cu57k_0001
$k^2 \cdot \chi(k)$ (Å^{-2})
Wavenumber (Å^{-1})
6
4
2
0
-2
-4
-6
-8
2
4
6
8
10
12
14
16
18
Demeter 0.9.18 © Bruce Ravel 2006-2013

Fourier Transform can separate the shells



The amplitude factor

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} A_j(k)\, p_j(\mathbf{e}) \sin\left[2kR_j + \psi_j(k)\right]$$

$$A_j(k) = S_0^2 F_j(k) Q_j(k) e^{-2R_j/\lambda}$$

S_0^2 - amplitude reduction due to multi-electron excitation

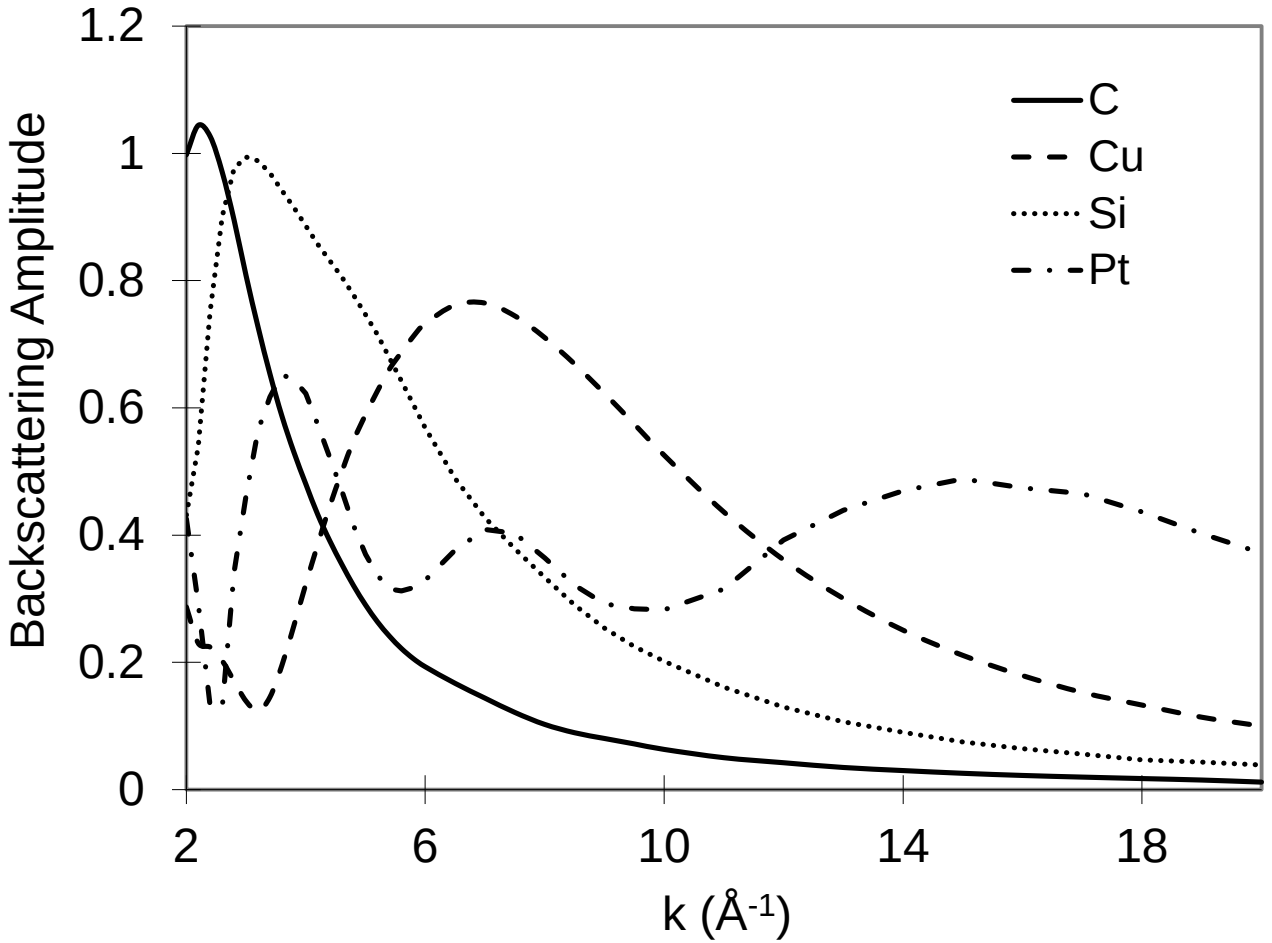
Typically 0.7 -0.9 (almost constant with *k*)

$F_j(k)$ - magnitude of the complex backscattering amplitude $f_j(k,\pi)$

$Q_j(k)$ - disorder term

λ - mean free path of photoelectron (includes contribution from core hole lifetime)

$f_j(k,\pi)$ calculated with theory such as FEFF


1.2
1
0.8
0.6
0.4
0.2
0
Backscattering Amplitude
2
6
10
14
18
k (Å-1)
C
Cu
Si
Pt

The Phase factor

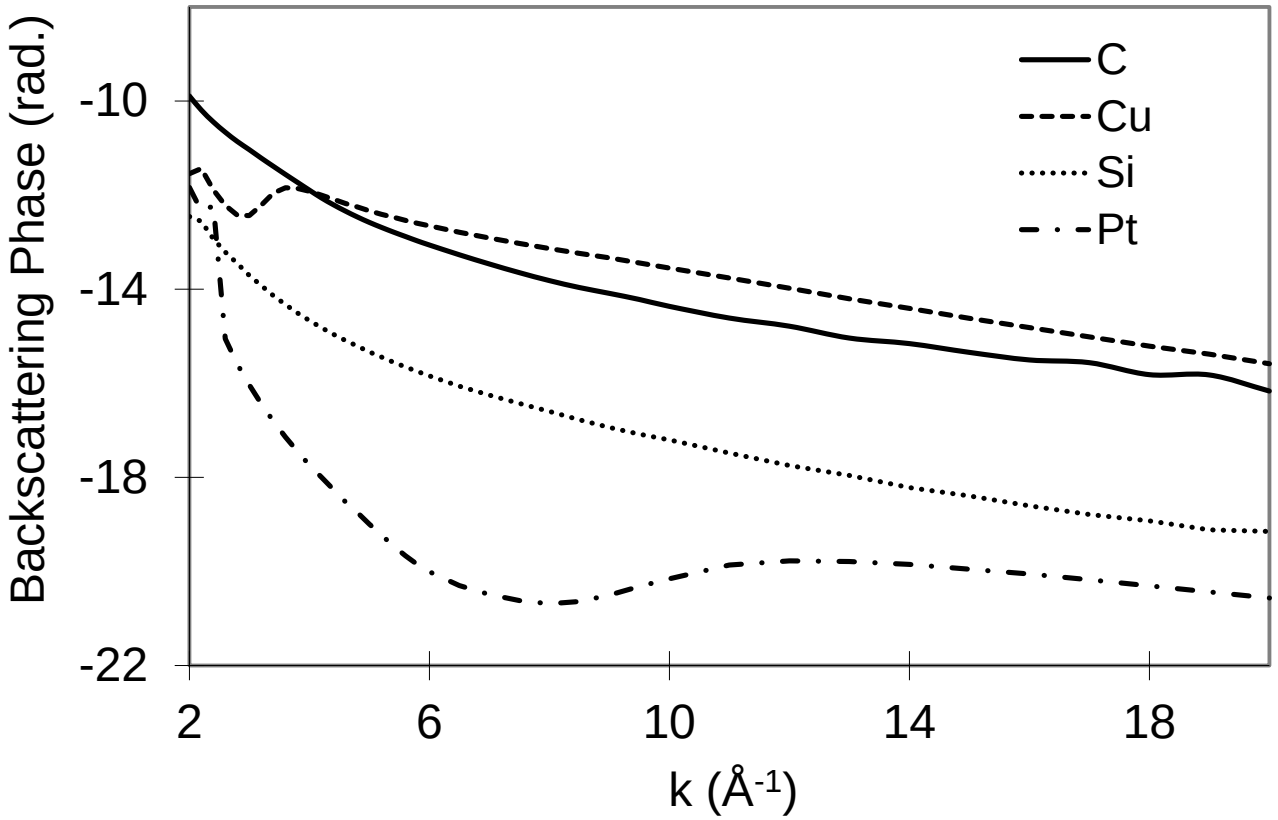
$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} A_j(k)\, p_j(\mathbf{e}) \sin\left[2kR_j + \psi_j(k)\right]$$

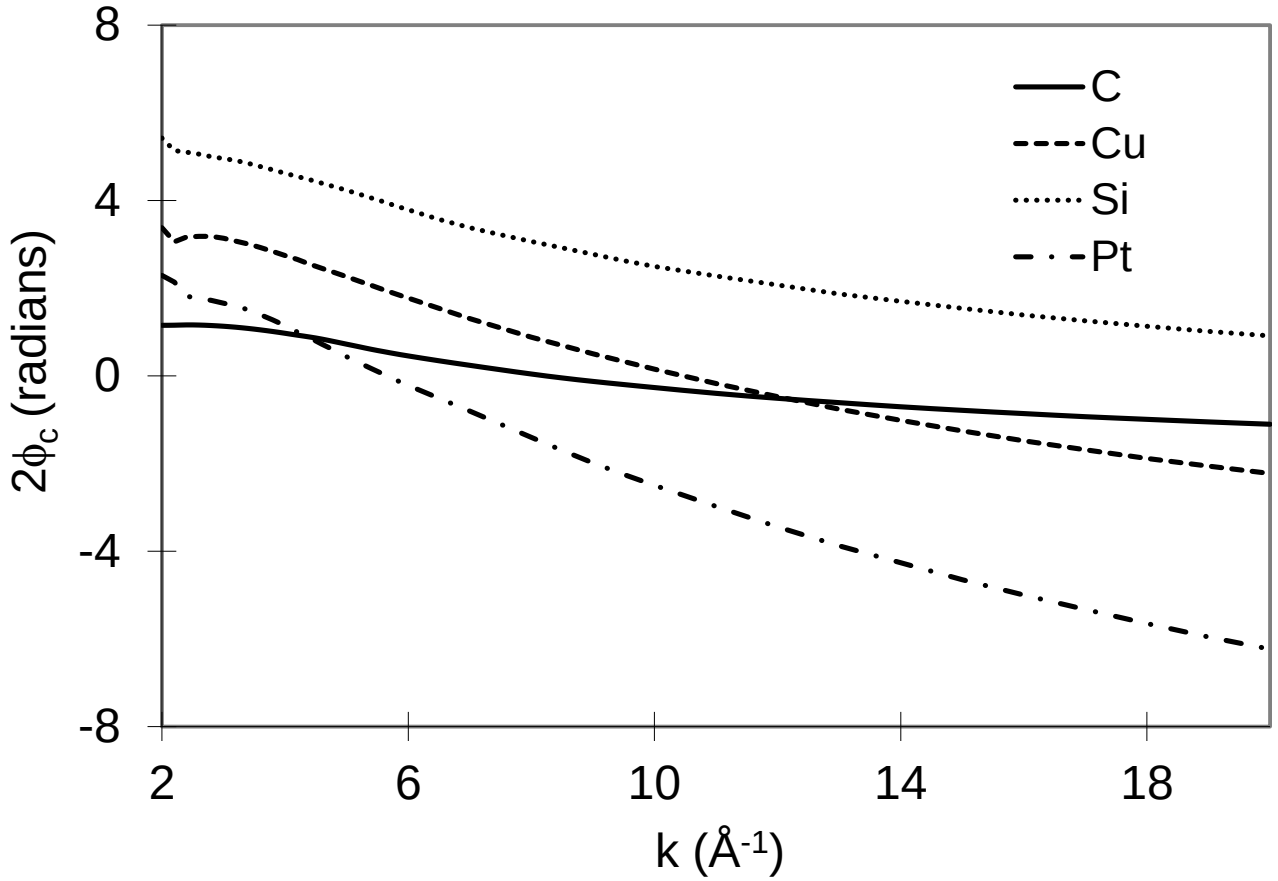
$$\psi_j(k) = 2\phi_c + \theta_j(k) + \varphi_j(k)$$

ϕ_c - p-wave (for K-edge) phase shift due to central atom potential

$\theta_j(k)$ - the phase of the backscattering factor $f_j(k,\pi)$

$\varphi_j(k)$ - phase factor related to the disorder of the j^{th} shell


Backscattering Phase (rad.)
-10
-14
-18
-22
2
6
10
14
18
k (Å-1)
C
Cu
Si
Pt


8
4
0
-4
-8
2
6
10
14
18
2ϕc (radians)
k (Å-1)
C
Cu
Si
Pt

Polarization Factor

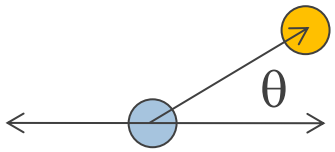
$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} A_j(k)\, p_j(\mathbf{e}) \sin\left[2kR_j + \psi_j(k)\right]$$

Synchrotron radiation generally linearly polarized

For the K-shell the photoelectron emitted with p-wave symmetry:

$p_j(\mathbf{e}) = 3\langle\cos^2\theta\rangle$

$$\left\langle \cos^2\theta \right\rangle = \frac{1}{N_j}\sum_i \cos^2\theta_i$$



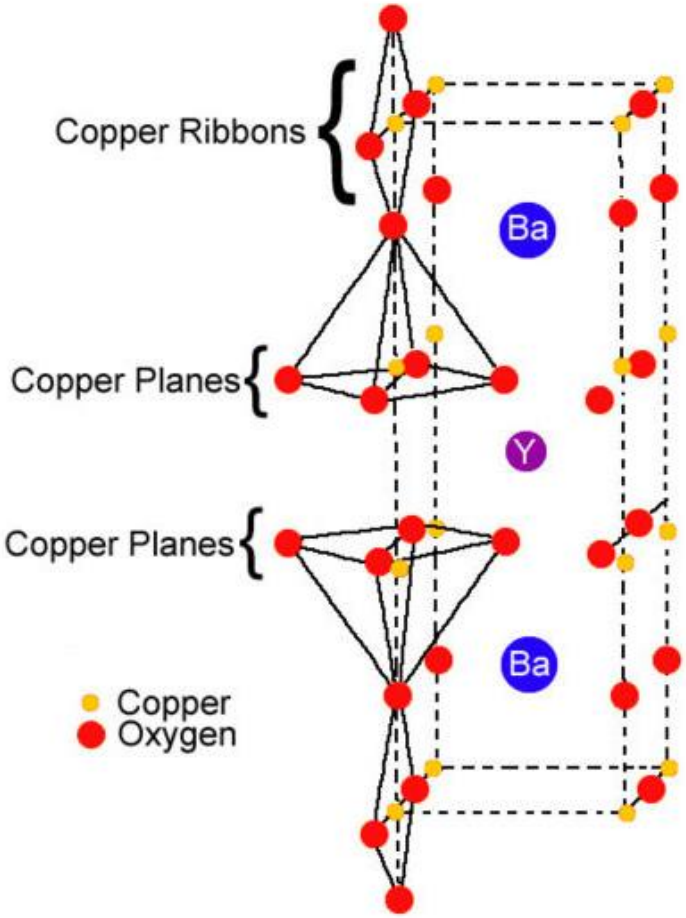
3-fold or higher symmetry $\langle\cos^2\theta\rangle = 1/3$, p=1

Uniaxial symmetry (i.e. surface):

$\chi(\Theta) = [2\chi_0\cos^2(\Theta) + \chi_{90}\sin^2(\Theta)]/3$

$YBa_2Cu_3O_7$ structure

Sample is oriented powder: c-axis of all grains are aligned, no alignment of a-b axes.



Two types of Cu sites:
- Planes – have bonds in a-b plane
- Ribbons – have bonds along c axis

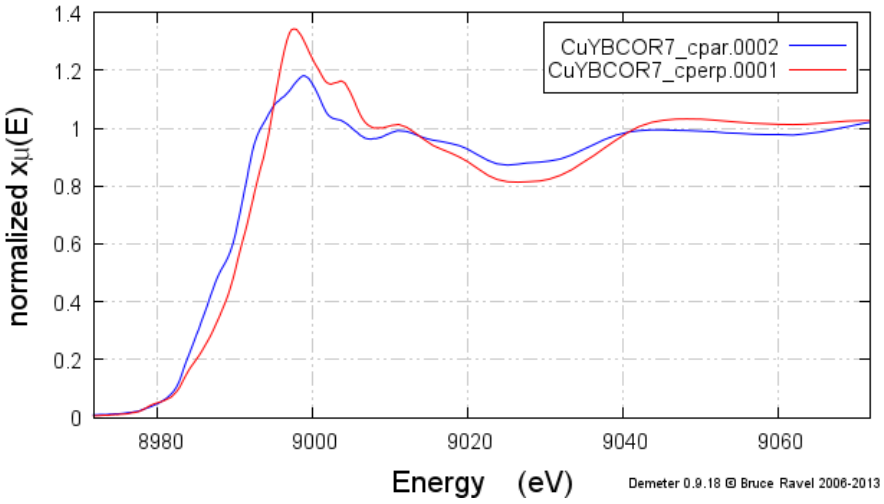
Consider the Cu-O near neighbor bonds:

Polarization in a-b plane both sites contribute, but dominated by Plane sites

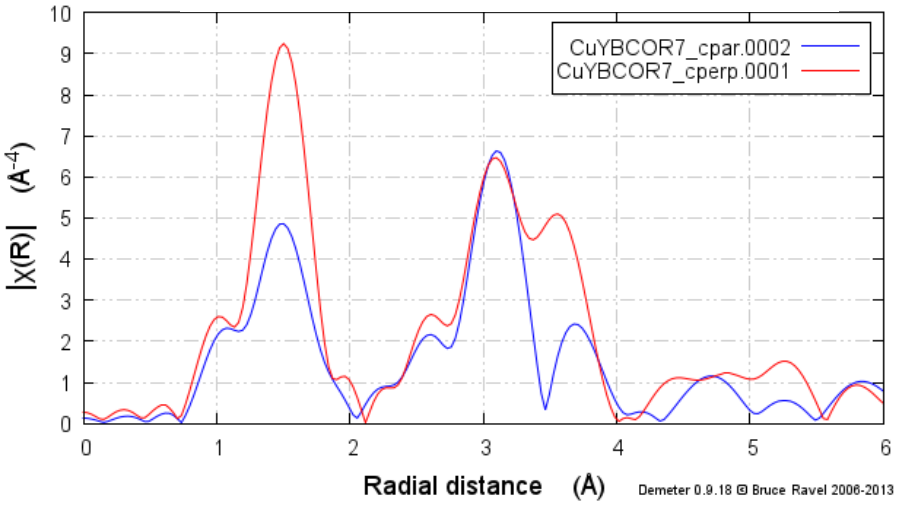
Polarization along c axis the signal is dominated by the Ribbon sites

Polarization dependence of $YBa_2Cu_3O_7$

XANES



EXAFS Fourier Transform



Disorder terms

$$\psi_j(k) = 2\phi_c + \theta_j(k) + \varphi_j(k)$$

$$A_j(k) = S_0^2 F_j(k)\, Q_j(k)\, e^{-2R_j/\lambda}$$

$$Q_j(k)\exp\left[i\varphi_j(k)\right] = \int dr P_j(r)\exp\left[i2k(r-R_j)\right]$$

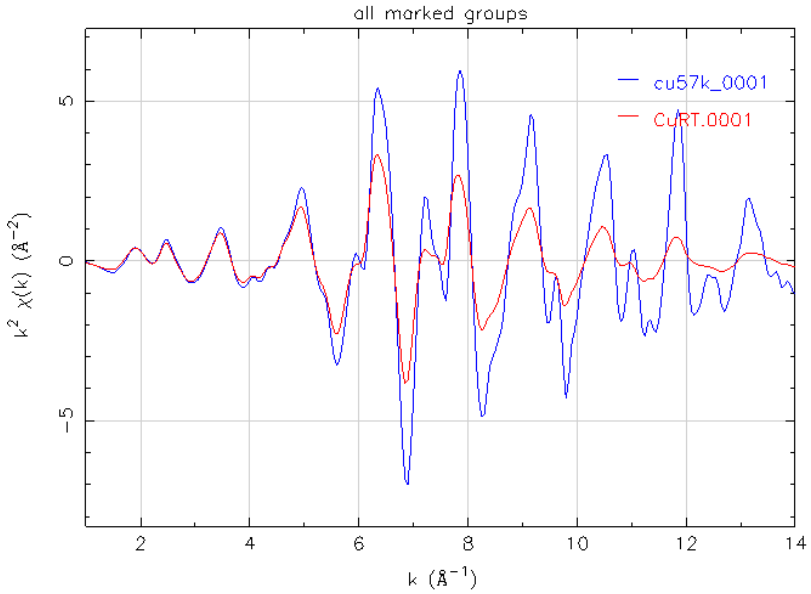
$P_j(r)$ - real space distribution of atoms in shell j

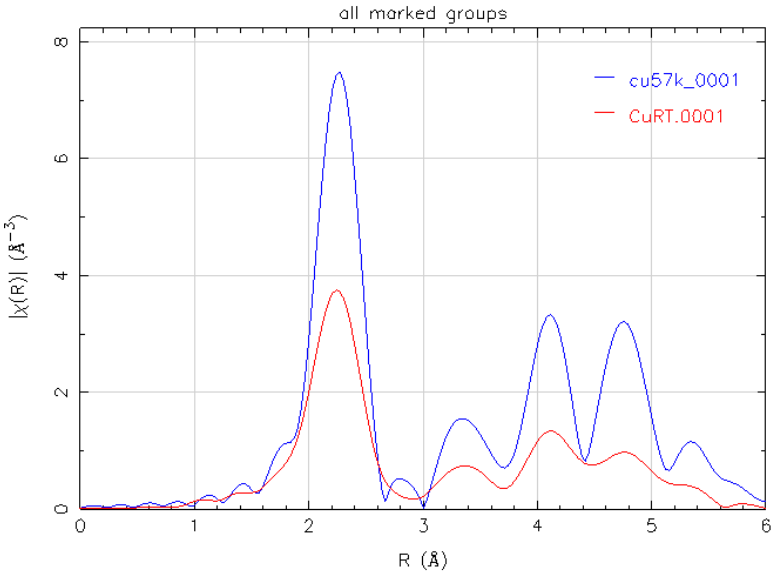
Simplest case is Guassian disorder (i.e. thermal motion)
To lowest order:
$Q_j(k)$ = exp(-2k$^2\sigma_j^2$) (Debye-Waller factor) $\varphi_j(k)$=0

σ_j^2 - mean squared vibrational amplitude of bond length
Different from the diffraction DW factor

Non-symmetric distributions can be handled with the cumulant method

Change in disorder with temperature





Choice of Absorption edge

- Low energies require high vacuum and x-ray penetration small
- At high energies lifetime broadening washes out the spectra
- Most convenient to work in range 4-30 keV

K edges:

Ca → Sn

L edges:

Sn → U

For lighter elements must work at low energies

L edges

L_1 - 2s initial state - Same symmetry as K edge

$L_{2,3}$ - 2p initial state - can have transitions to s or d final states

Three possible contributions to $\chi(k)$: χ_{ss}, χ_{sd}, χ_{dd}

$$\chi = \left(M_{21}^2 \chi_{dd} + M_{01}^2 \chi_{ss} + 2 M_{01} M_{21} \chi_{sd} \right) \Big/ \left(M_{21}^2 + M_{01}^2 / 2 \right)$$

Each contribution has its own polarization dependence

$$p_{22}^j = \frac{1}{2}\left(1 + 3\left\langle \cos^2\theta \right\rangle_j\right)$$

$$p_{00}^j = \frac{1}{2}$$

$$p_{02}^j = \frac{1}{2}\left(1 - 3\left\langle \cos^2\theta \right\rangle_j\right)$$

L edges (cont.)

Two important simplifications:

M_{01} typically about $0.2M_{21}$

→ can generally ignore M_{01}^2 term

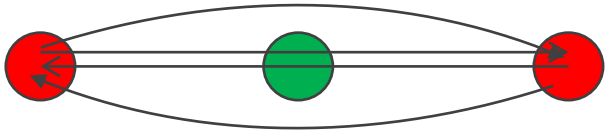
unoriented or symmetric samples: $p_{02} = 0$

For unoriented or symmetric samples L edges can be treated the same as the K edge

For oriented asymmetric samples (i.e. surface site) the crossterm must be included (40% of dd term)

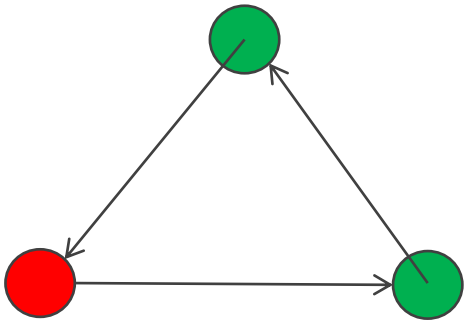
Multiple Scattering

Strong



Collinear (focusing)

Weaker

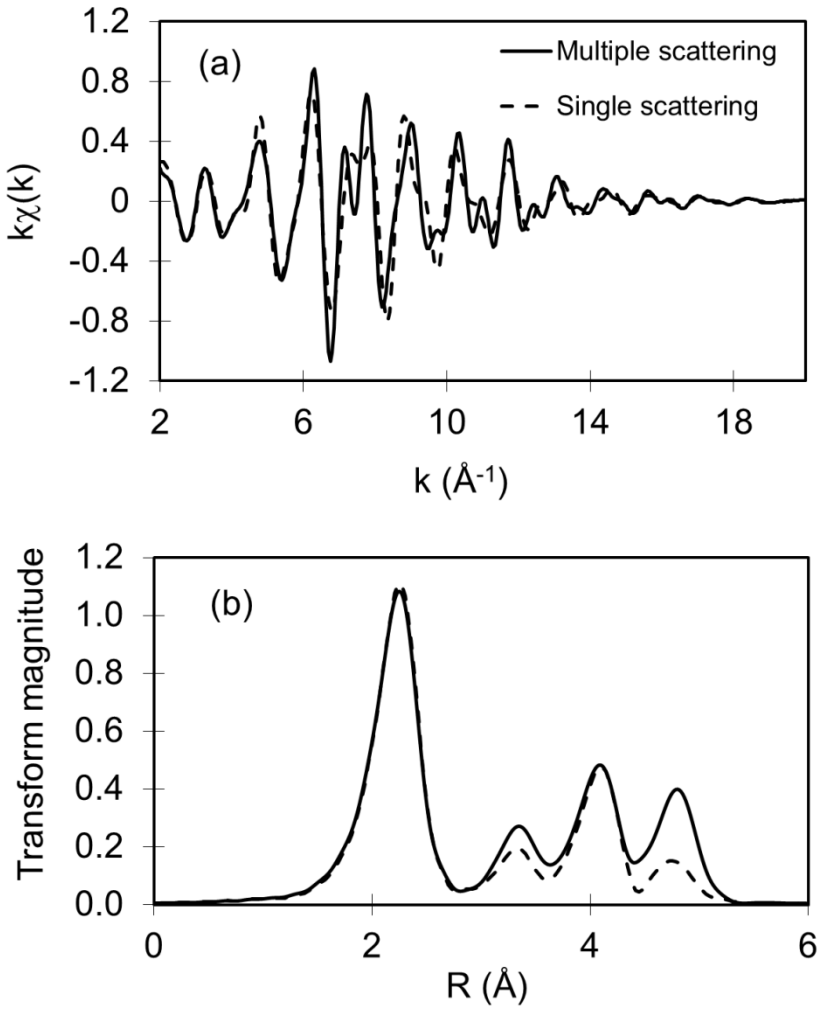


Triangular

- Not important for first shell
- Must be considered in analyzing all shells above first
- Dominates at large distances
- Typically limits analysis to first few shells

Multiple scattering in Cu

Calculated EXAFS for 1st four shells

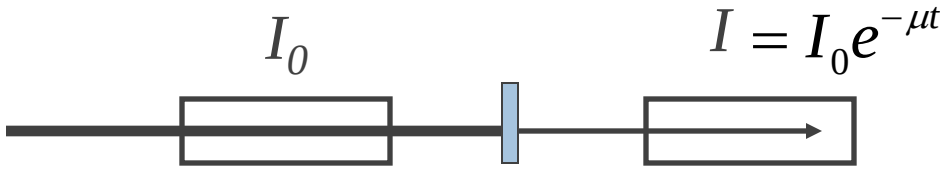


R	N	Rel. Amp	Type
2.556	12	100	Single
3.615	6	23	Single
3.834	48	10	Triangle
4.364	48	9	Triangle
4.428	24	55	Single
4.770	48	11	Triangle
4.770	96	22	Triangle
5.112	12	19	Single
5.112	24	44	Collinear
5.112	12	8	Collinear
5.112	12	33	Collinear

Measuring XAFS

Need to measure absorption

Direct method:

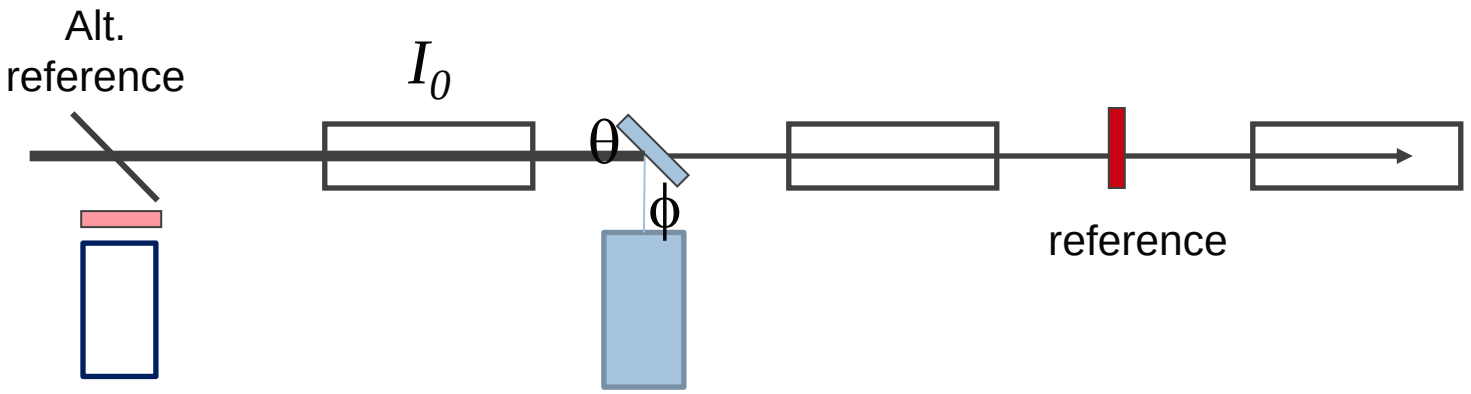


$$\mu t = -\ln(I / I_0) = \ln(I_0 / I)$$

Indirect methods (proportional to absorption)

- Fluorescence
- Electron Yield
- Reflectivity
- Optical emission

Fluorescence Detection



Need to consider absorption going in and out of the sample

$$\mu'(E) = \frac{I_f}{I_0} = \frac{\mu(E)\sin(\theta)}{\mu_t(E)/\sin\theta + u_t(E_f)/\sin\varphi}$$

μ_t - total absorption of sample ($\mu + \mu_{matrix}$)

Fluorescence detection - cont.

Typical case $\sin\theta = \sin\phi = 45$

Dilute sample: $\mu << \mu_{matrix}$ $$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu_{matrix}(E) + \mu_{matrix}(E_f)}$$ Denominator almost constant

Concentrated sample: $\mu = \mu_{matrix}$ $$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu(E) + \mu(E_f)}$$ For K edge: $\mu(E_f) \approx \mu(E)/8$

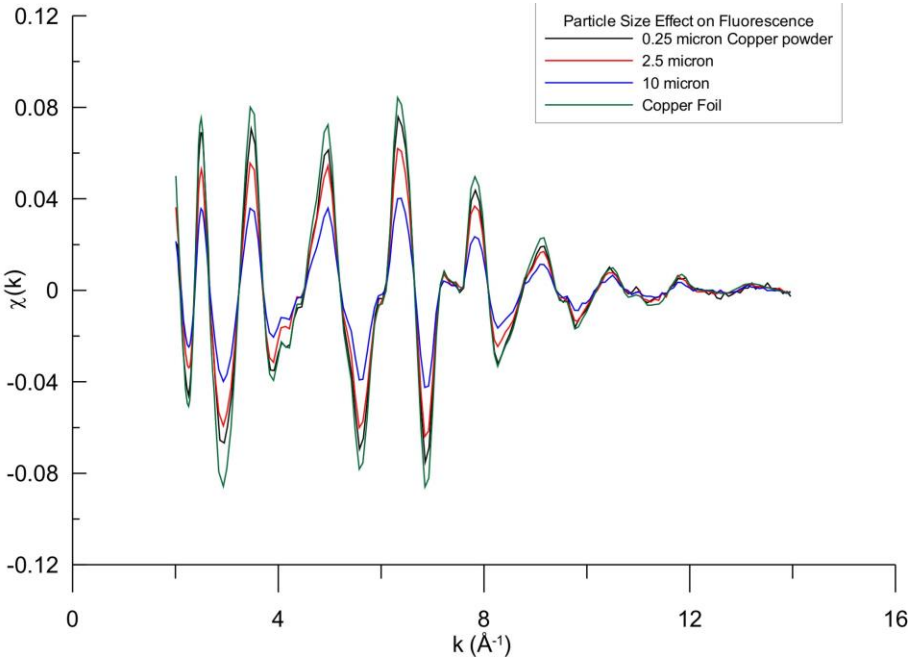
(self absorption)

Thin concentrated sample: absorption of x-rays entering and exiting sample are negligible $$\frac{I_f}{I_0} \approx \mu(E)$$

Glancing exit angle: $\sin\phi << 1$ $$\frac{I_f}{I_0} \propto \frac{\mu(E)}{\mu_{matrix}(E_f)}$$

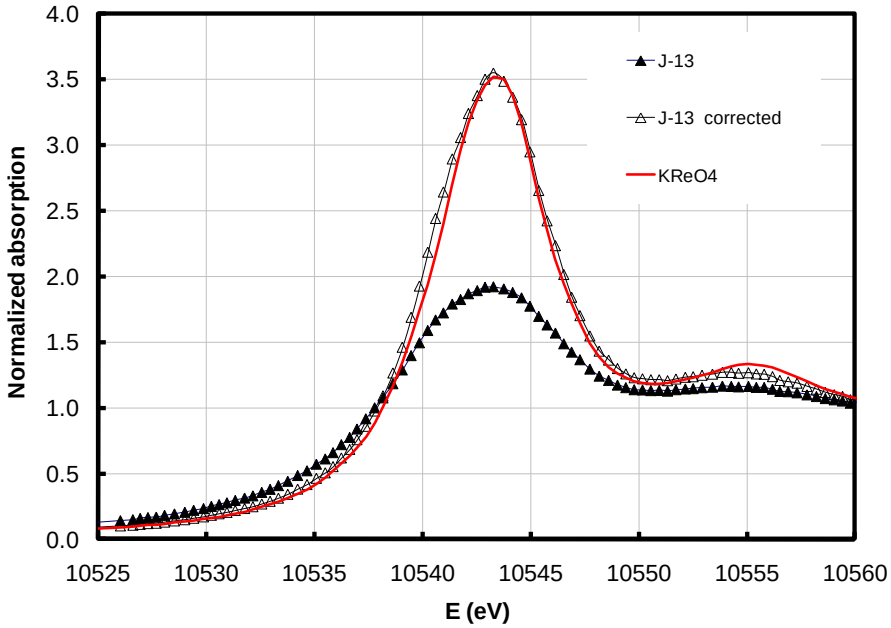
Self absorption

Cu metal



Data from R. Gordon

Re near edge



Fluorescence or transmission?

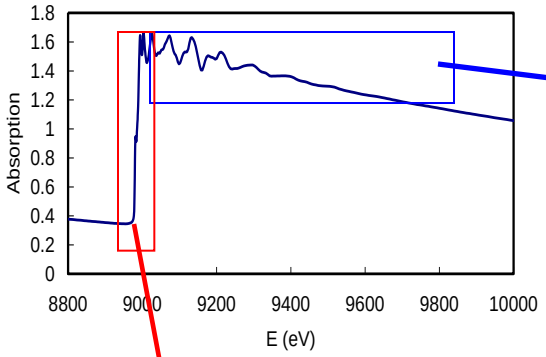
From statistics – $\Delta\mu x < 0.05 – 0.1$ fluorescence generally better

Many factors can influence this

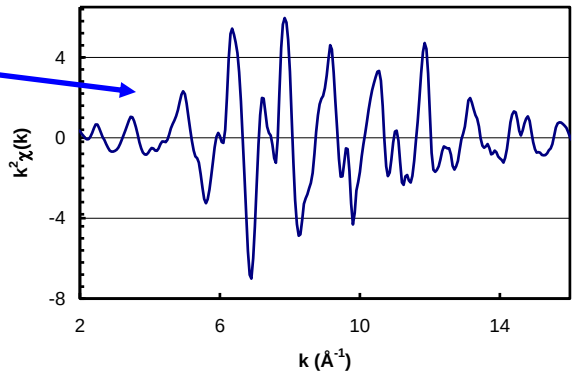
- monochromator glitches
- sample uniformity
- other fluorescence lines

Often can measure both simultaneously and choose the best one

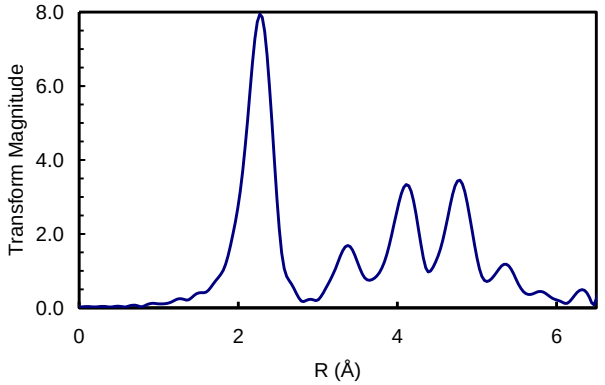
Part 2: Analyzing the EXAFS



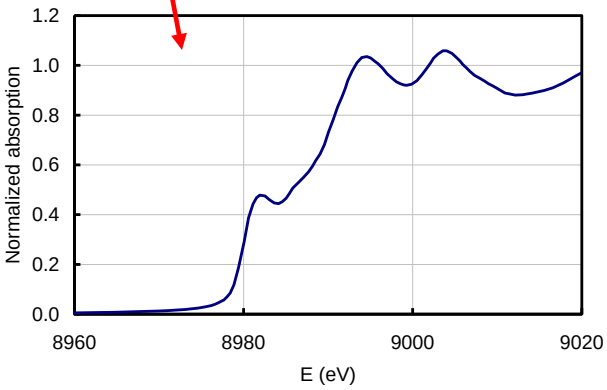
Background removal



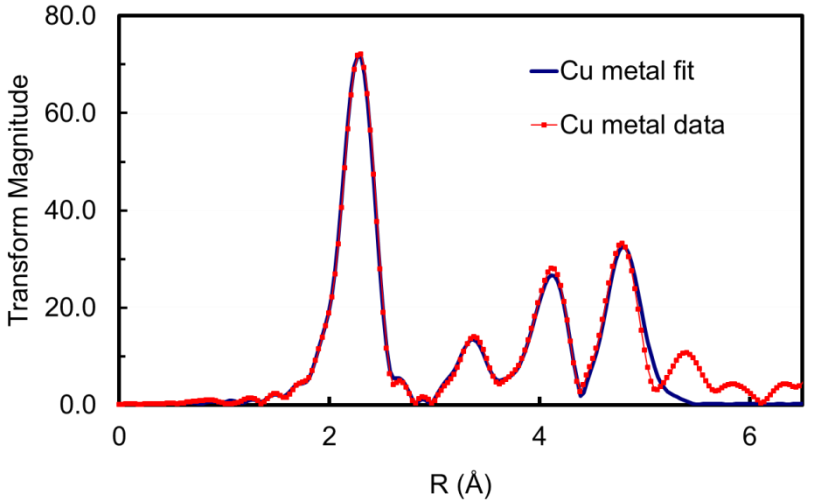
Fourier Transform



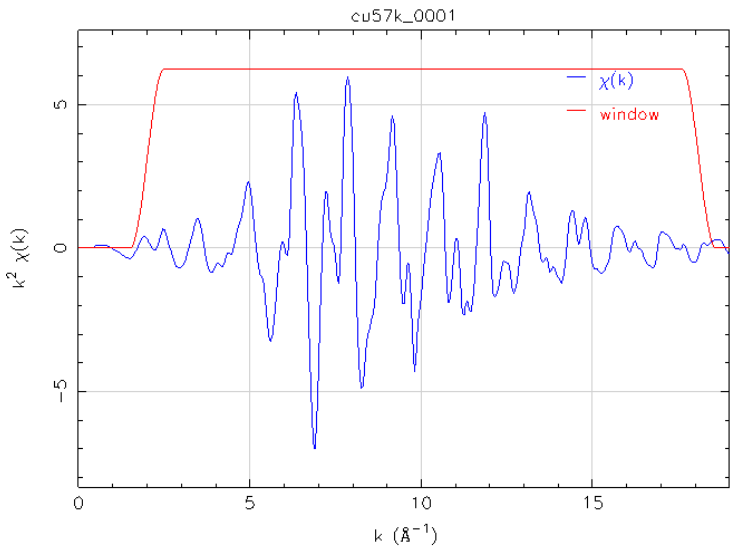
Normalization

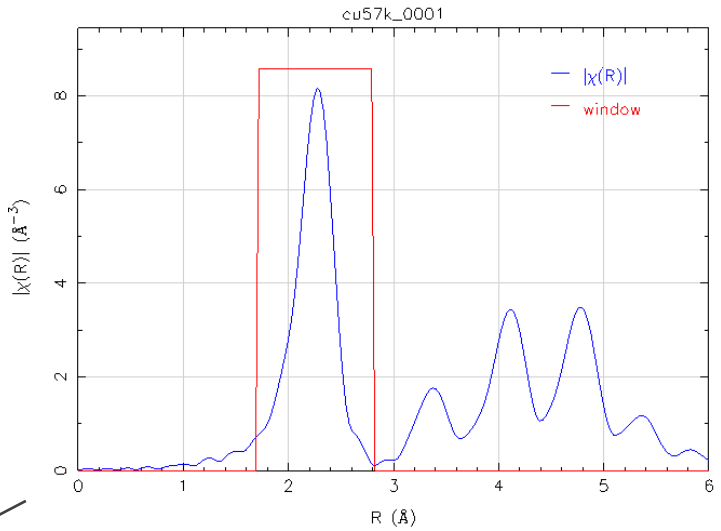


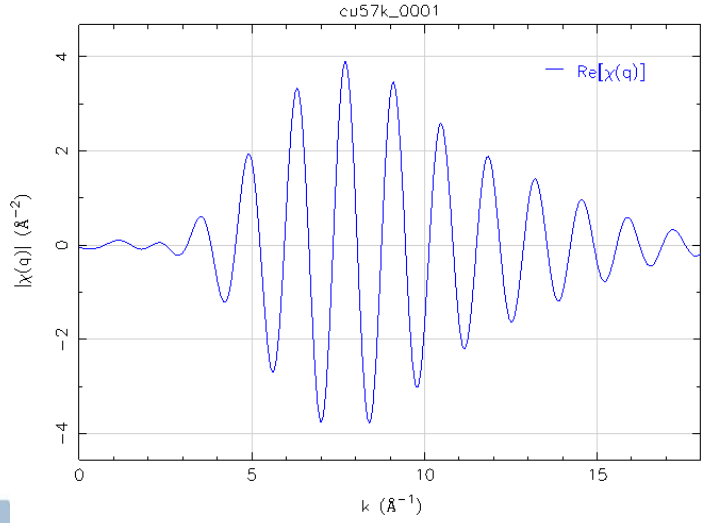
Fitting to extract structural parameters

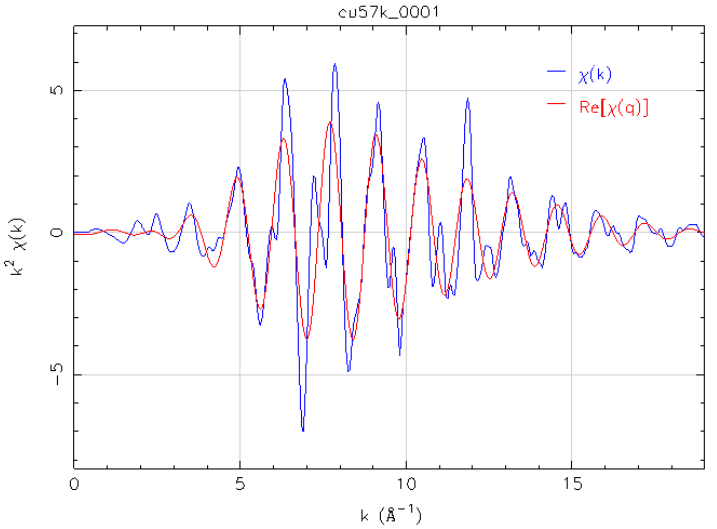


Fourier filtering









Independent Data Points

From information theory:

$N_I = 2\Delta k \Delta R/\pi + 1$

Δk - range of data used in k-space

ΔR - range of data used in R-space

Example:

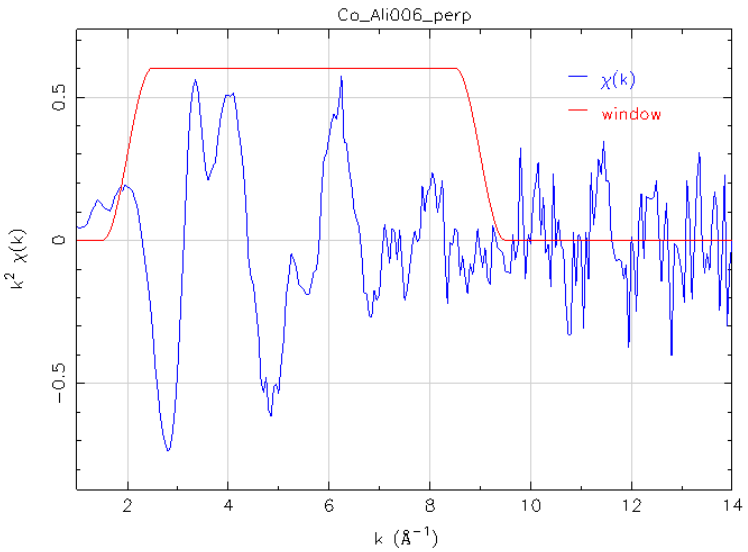
k range is 2 -18 $Å^{-1}$

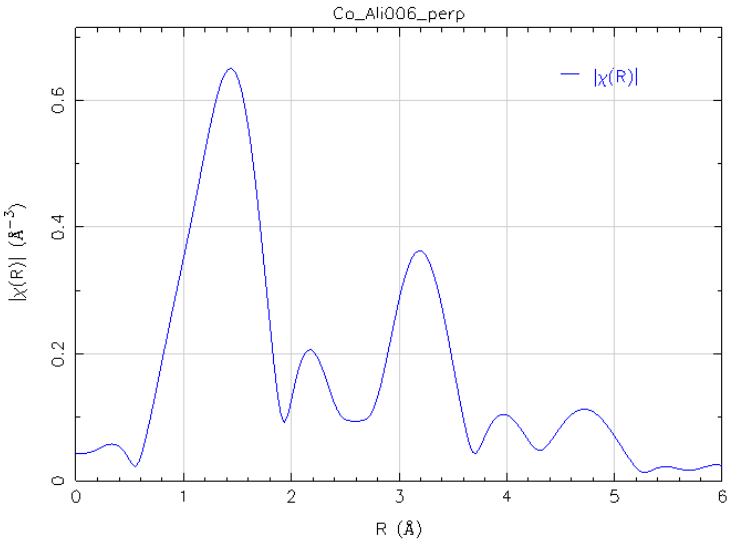
R space filtering or fitting window is 1.7 – 2.8 Å

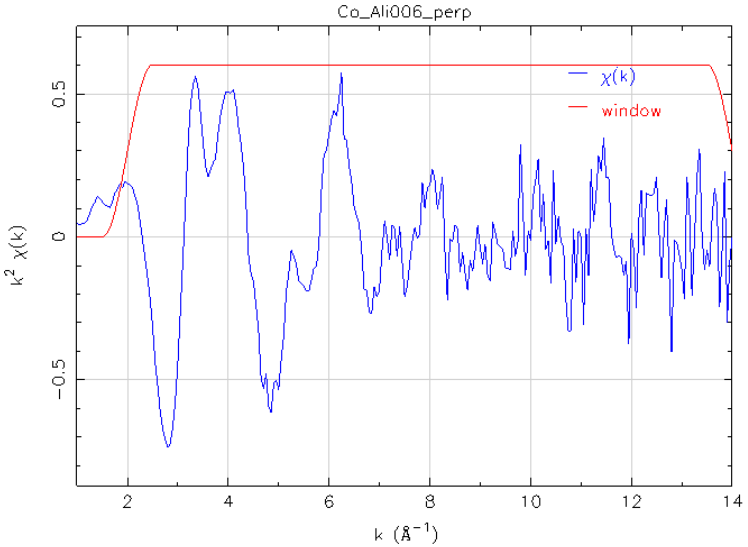
Then maximum number of independent fitting parameters is 11

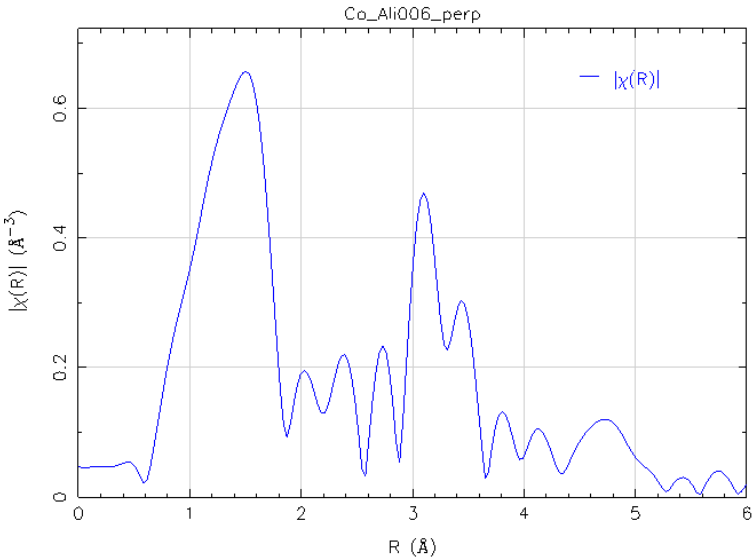
If data range short (kmax ~ 10) then number of possible fitting parameters will be constrained.

Example of noisy data









Typical fitting parameters

- ΔE_0 – match the experimental and theoretical edge positions
- Overall amplitude factor (S_0^2)
- Each shell needs disorder factor (σ^2)
- May also need ΔR

ΔE_0 and S_0^2 can generally be common to all shells

Therefore, typically need 4 parameters for simple first shell and 2-3 more for each additional shell.

Always good to constrain the fits with other knowledge about the sample.

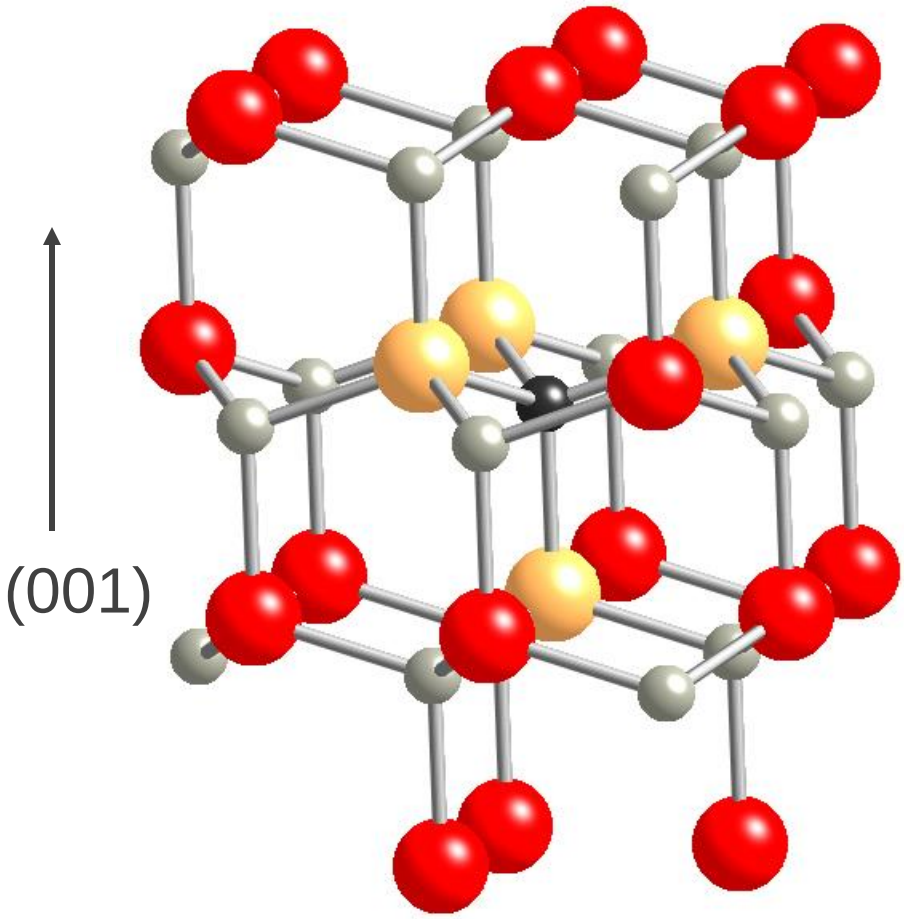
Co doped ZnO

- Candidate material for a dilute magnetic semiconductor
- Many reports of magnetism at room temperature
- Some cases have been shown to be due to secondary phases (metallic nanoparticles)
- Some cases of well characterized single phase materials without magnetism

EXAFS and XANES are sensitive to secondary phases

- Element specific - allows detection of dilute dopants
- XANES can see valence change if metallic Co present
- EXAFS can identify the secondary phase (dilute nanoparticles difficult to see with diffraction)
- Bulk probe of whole film

ZnO structure (wurtzite)



First shell tetrahedrally coordinated
- no orientation dependence

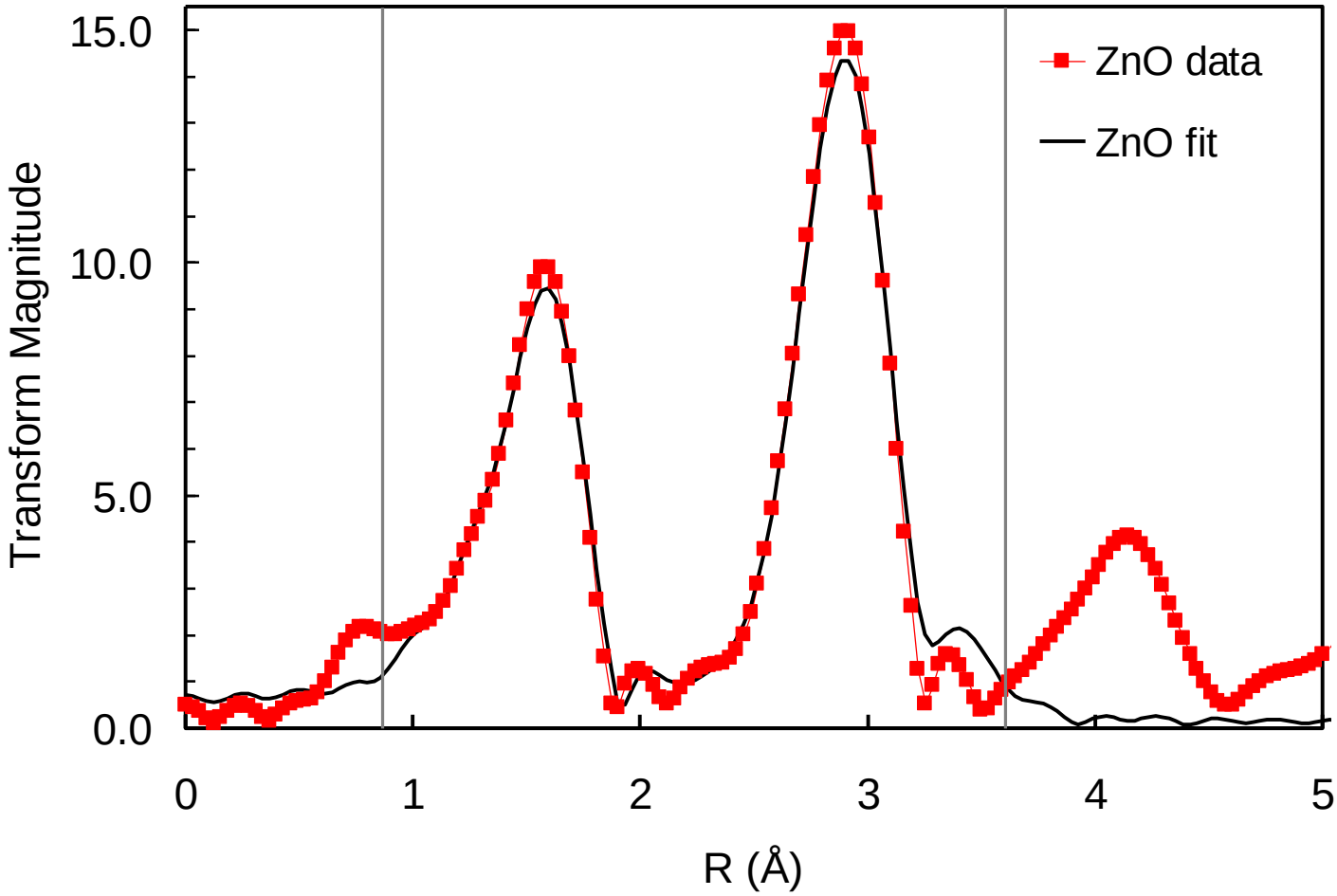
Higher shells have more orientation dependence

2 substrate orientations:

r-plane sapphire – film grows (110)

c-plane sapphire – film grows (001)

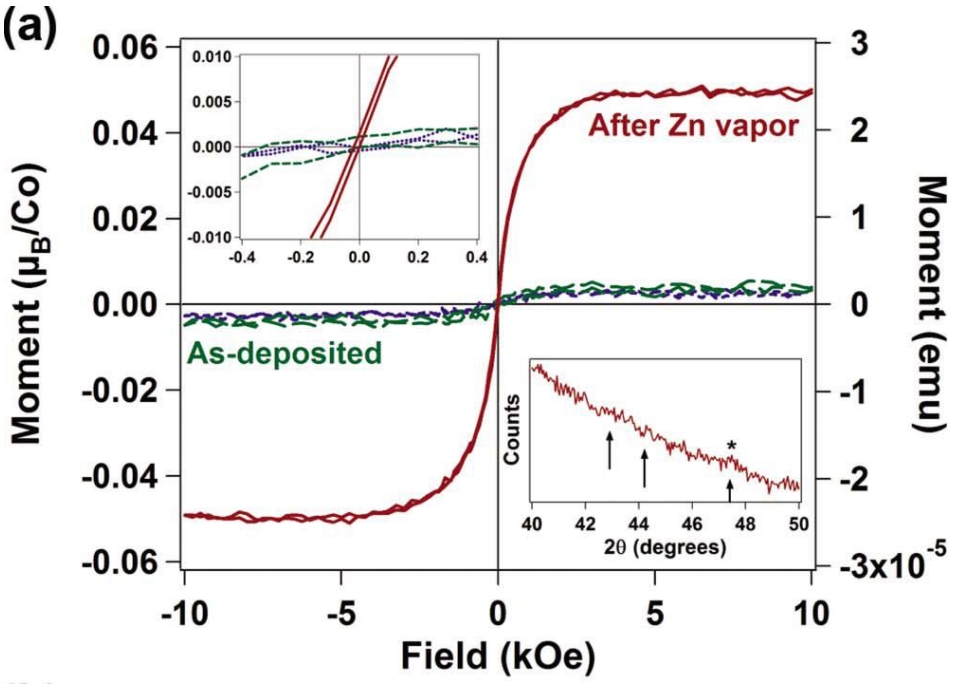
ZnO EXAFS



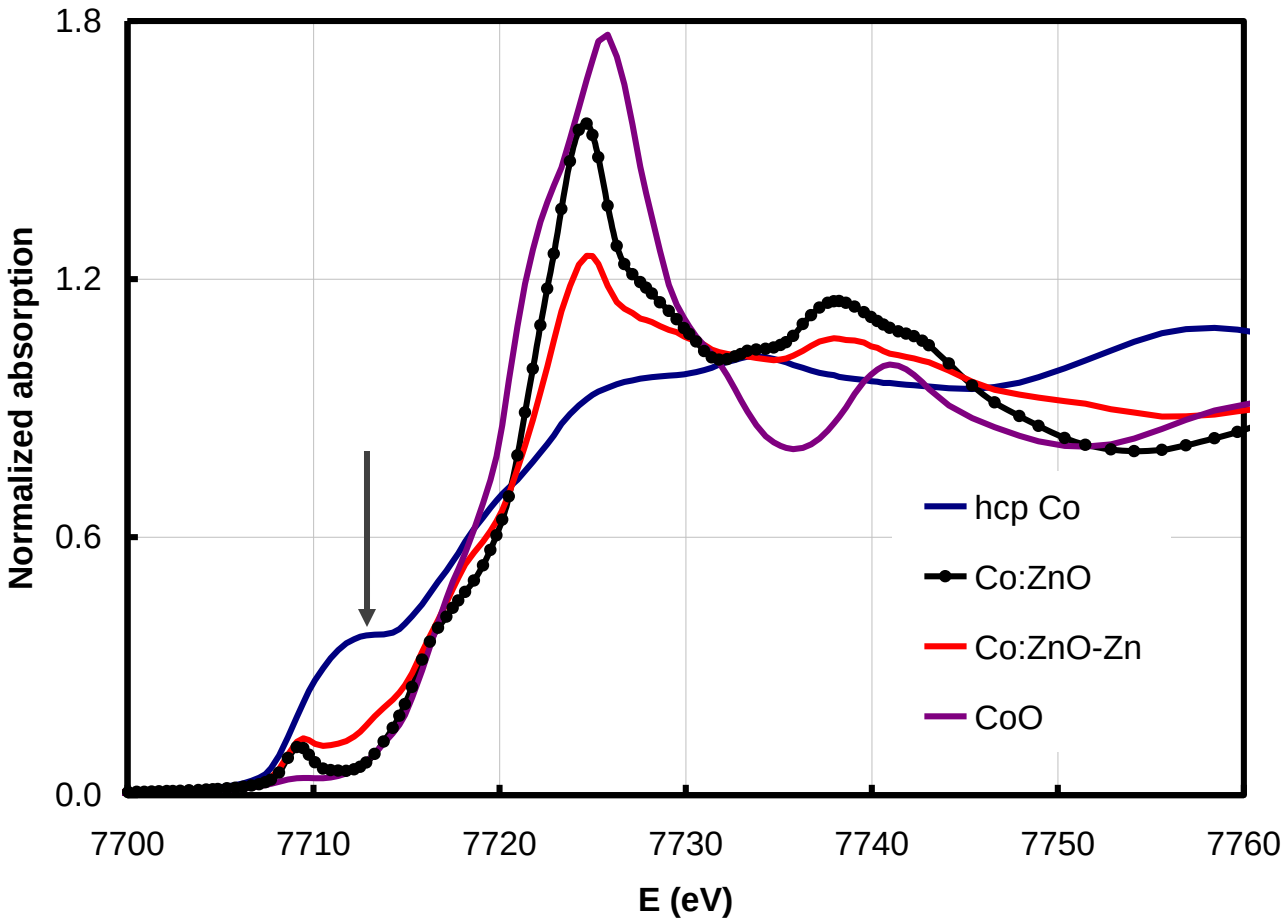
The Co doped ZnO samples

See Kaspar etal, PRB 77, 201303 and Heald etal PRB 79, 075202

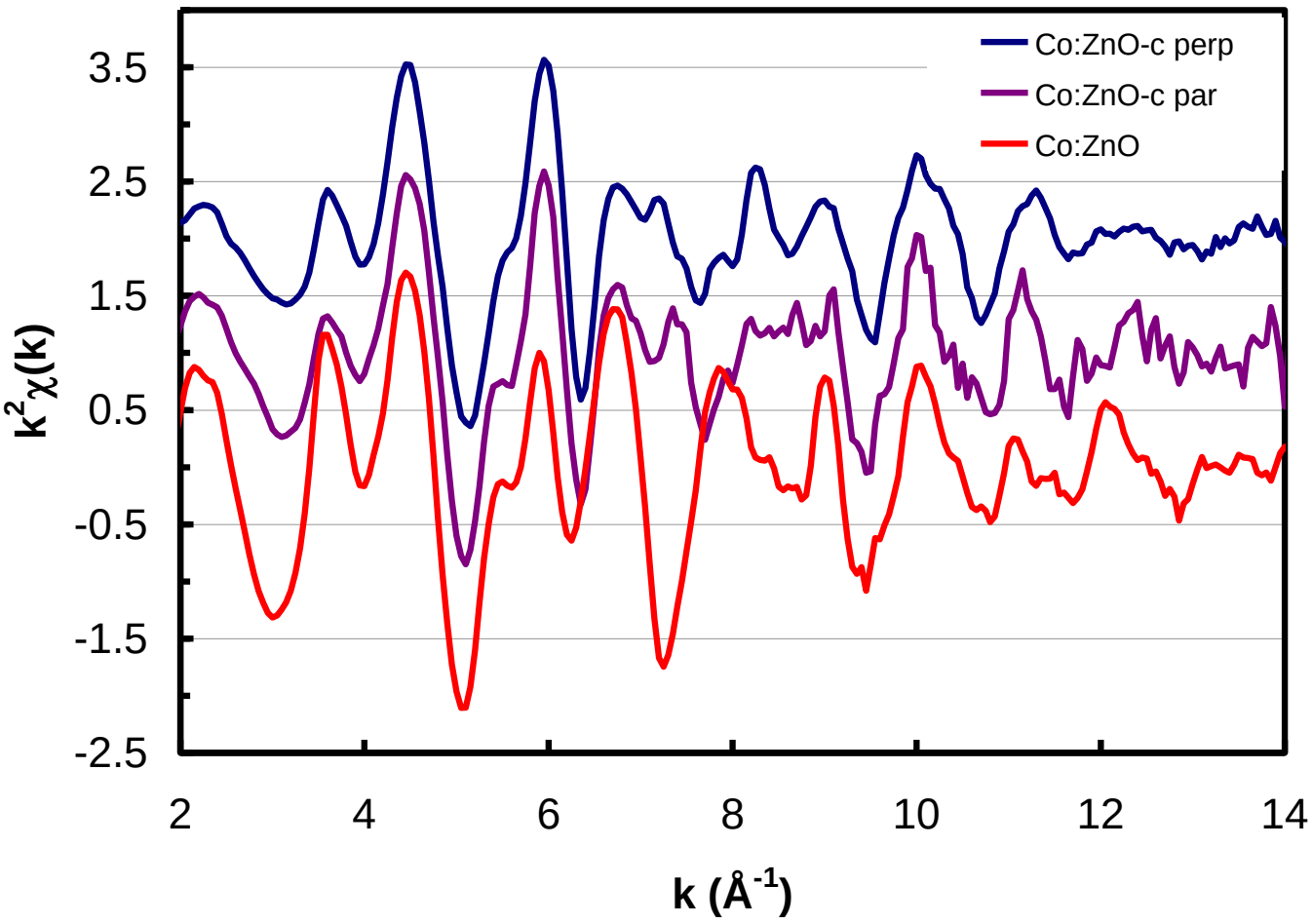
- PLD deposited samples on r- and c-plane sapphire
- 100 nm with about 16% Co
- Some samples annealed in Zn vapor to induce magnetism



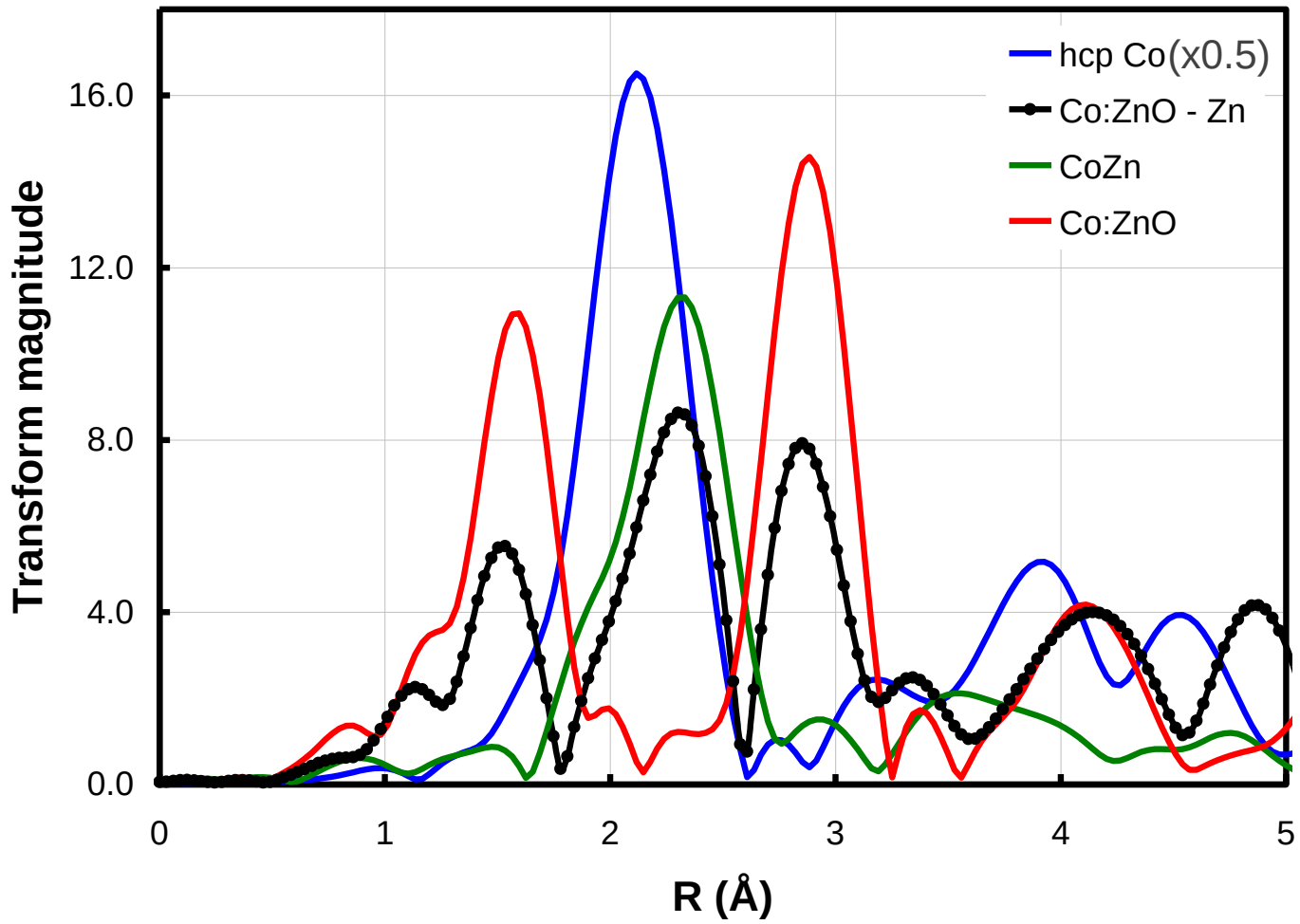
Detection of metallic Co – XANES



EXAFS for Co doped ZnO



Detection of metallic Co – EXAFS



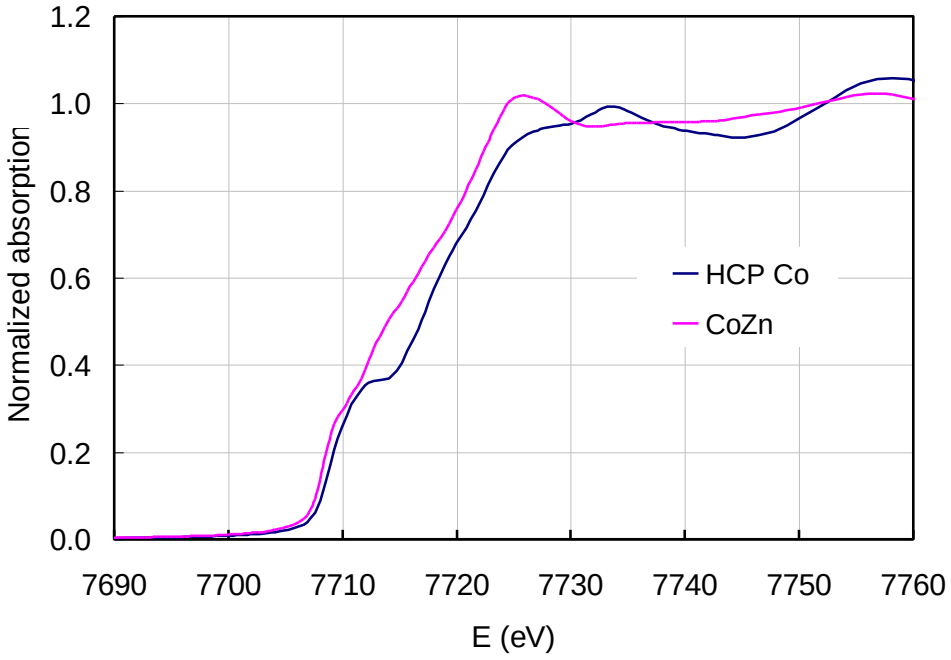
Possible magnetic forms of Co

- HCP Co
  - Identified previously by XRD and XAFS
  - Typically small nanoparticles
  - 1.72 μ_b/Co
- FCC Co
  - Stable at high temperatures
  - Can contain up to 40% Zn with accompanying lattice expansion
  - 1.72 μ_b/Co for the pure phase
- CoZn intermetallic
  - β-Mn structure
  - 1.35 μ_b/Co

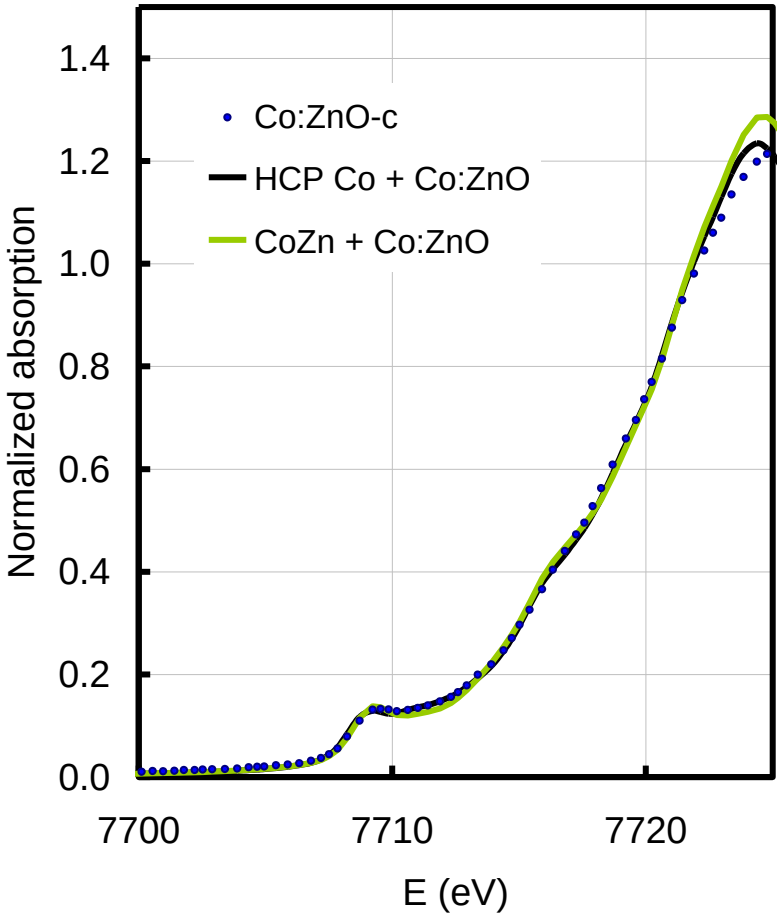
Fitting of near edge

Near edge inconclusive in distinguishing the metal component

Does provide an accurate estimate of the amount of metal

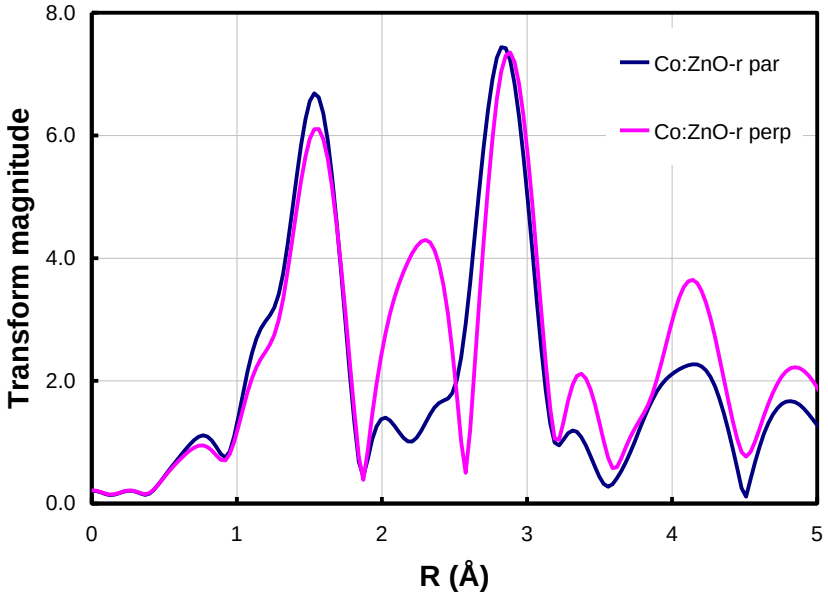


Near edge fits

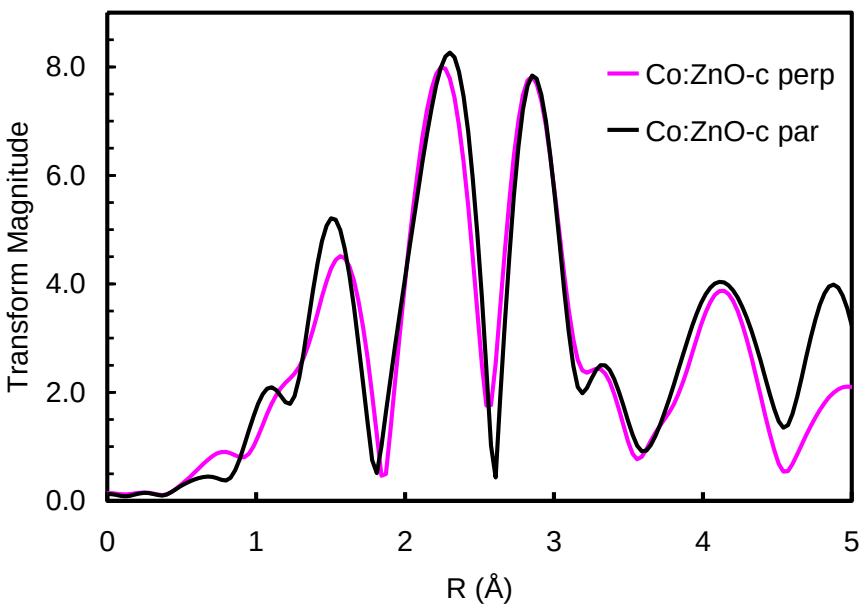


Co EXAFS polarization dependence

r-plane substrate



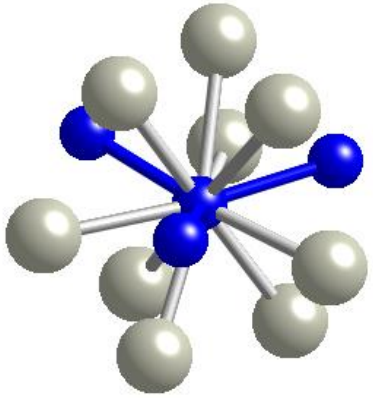
c-plane substrate



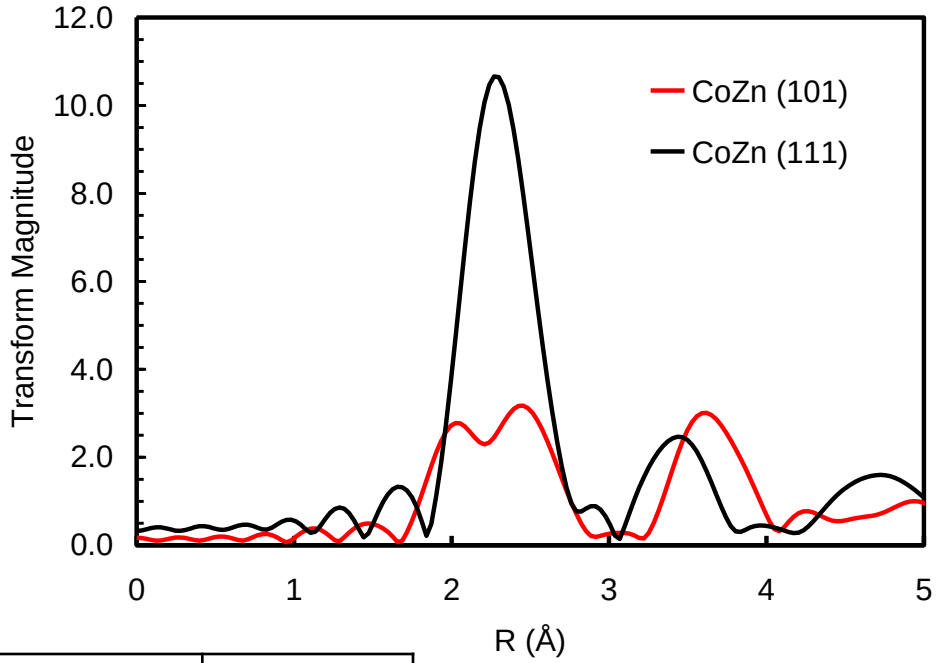
Origin of polarization dependence - CoZn

Co near neighbors

Co – blue, Zn – gray



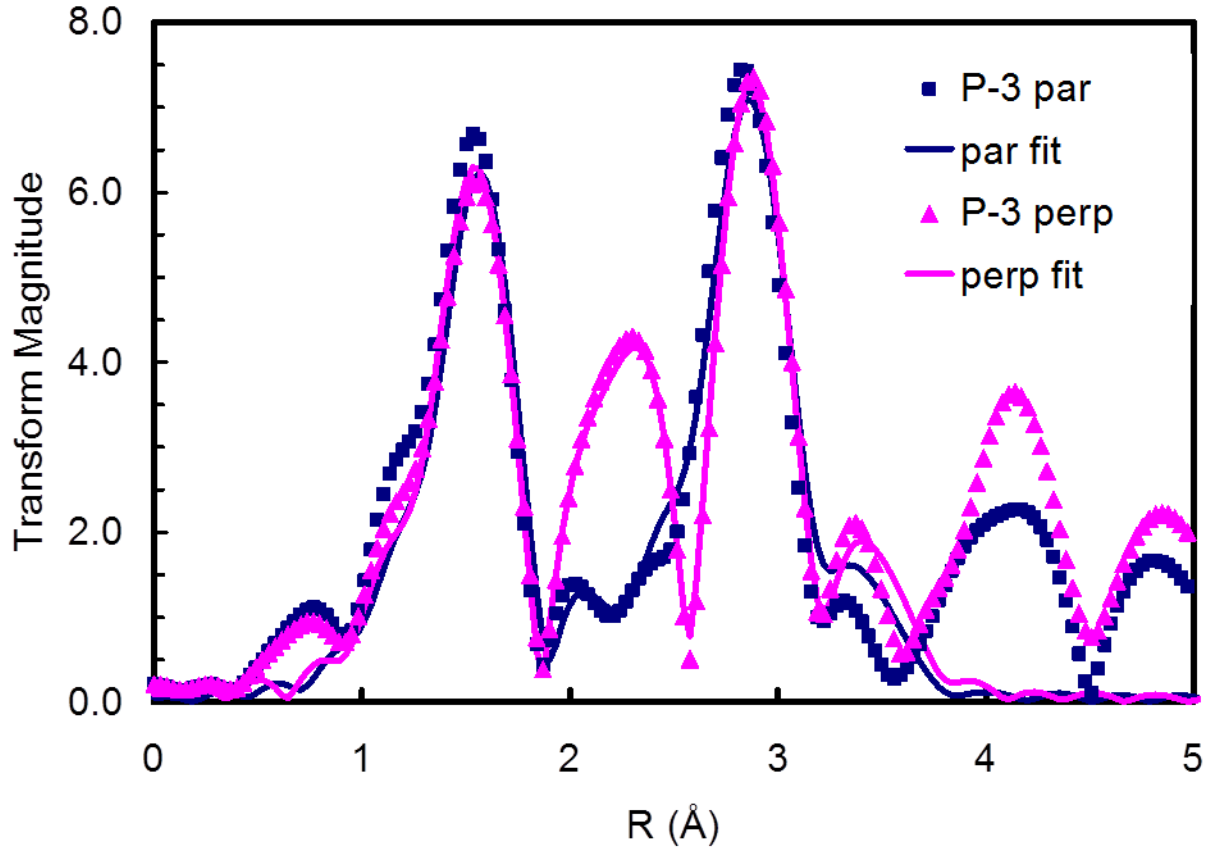
Theory



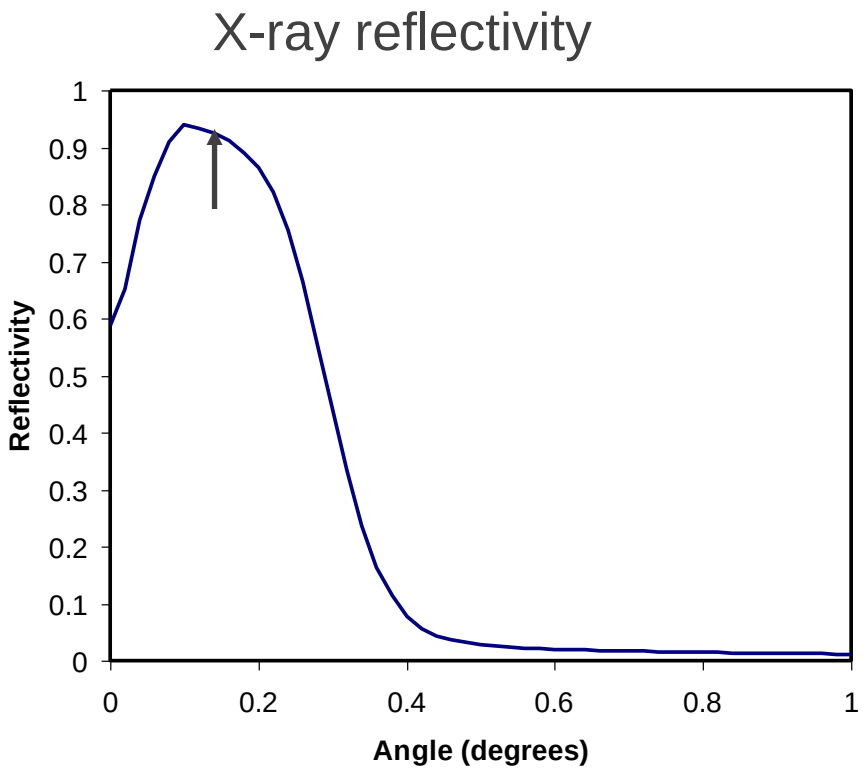
Neighbor	N	Distance	Measured
Co	3	2.36 Å	2.34
Zn	3	2.57	2.54
Zn	3	2.63	2.60
Zn	3	2.67	2.64

Fitting using CoZn model

Simultaneous fit to the two polarization directions with oriented CoZn second phase



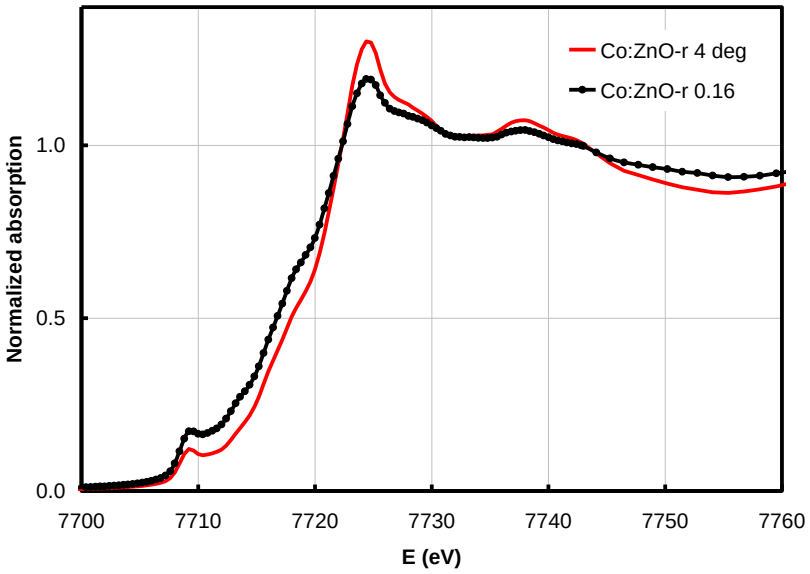
Glancing angle XAFS – surface sensitivity

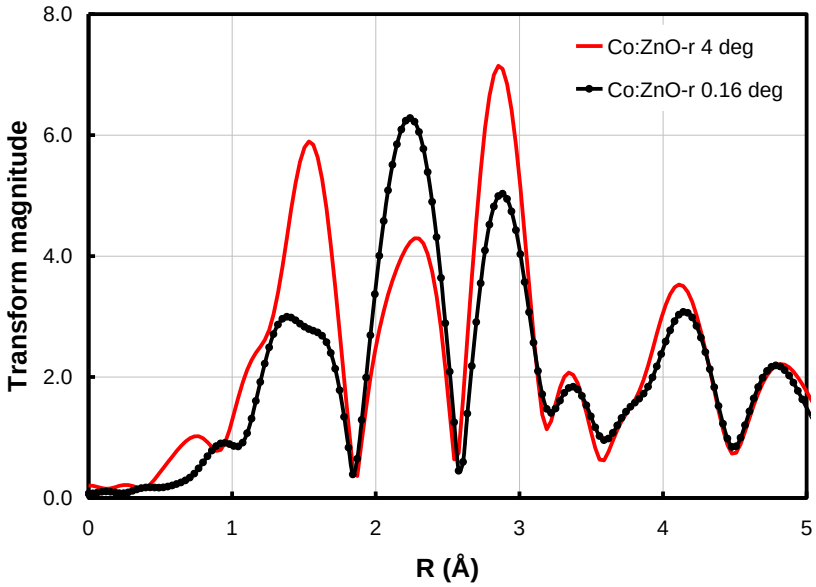


Small angles total external reflection
→x-ray penetration a few nm

Compare measurements at:
0.16 deg (surface)
4 deg (bulk)

Angle dependent results





Metallic component enhanced near the surface

X-ray Absorption Spectroscopy is a powerful tool that complements scattering methods

- Element specific
- Provides both structural (EXAFS) and chemical (XANES) information
- Fluorescence detection allows extremely dilute (ppm) components to be studied
- Does not need long range order – wide range of applications
  - Operando studies of catalysts, fuel cells, and batteries
  - Detailed study of the active site in metalloproteins
  - Hazardous elements in the environment
  - Magnetism using polarized x-rays
  - High pressure studies
  - Thin film growth and characterization
  - Many others…