Disordered Materials: Glass physics

- 2.7. Introduction, liquids, glasses
- 4.7. Scattering off disordered matter:
  static, elastic and dynamics structure factors
- **9.7. Static structures:**
  X-ray scattering, EXAFS, (neutrons), data interpretation
- 11.7. Dynamic structures and the glass transition

HELMHOLTZ GEMEINSCHAFT

Hermann Franz

Methoden moderner Röntgenphysik II
July 2013

DESY

Structure by X-rays - temperature dependence II

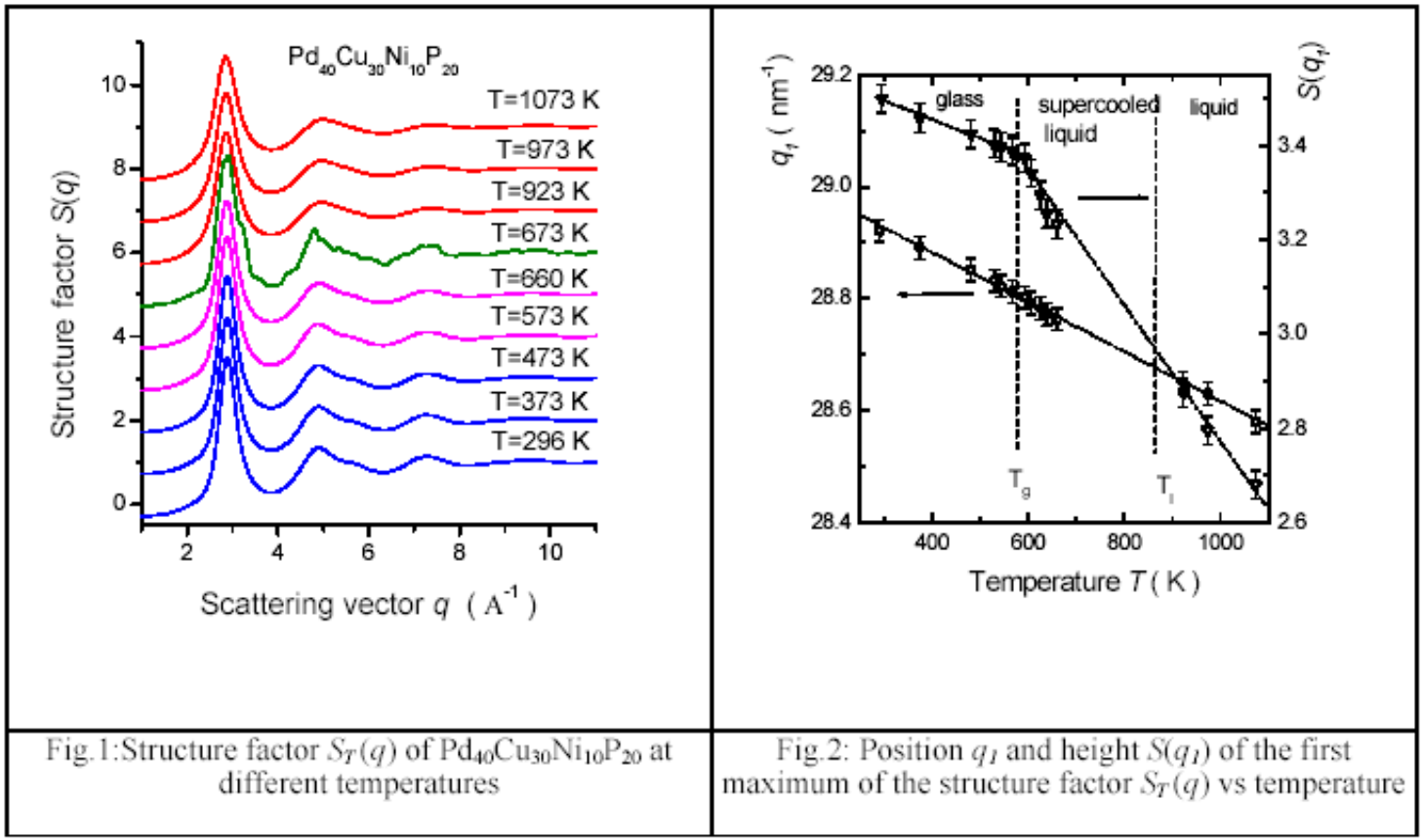


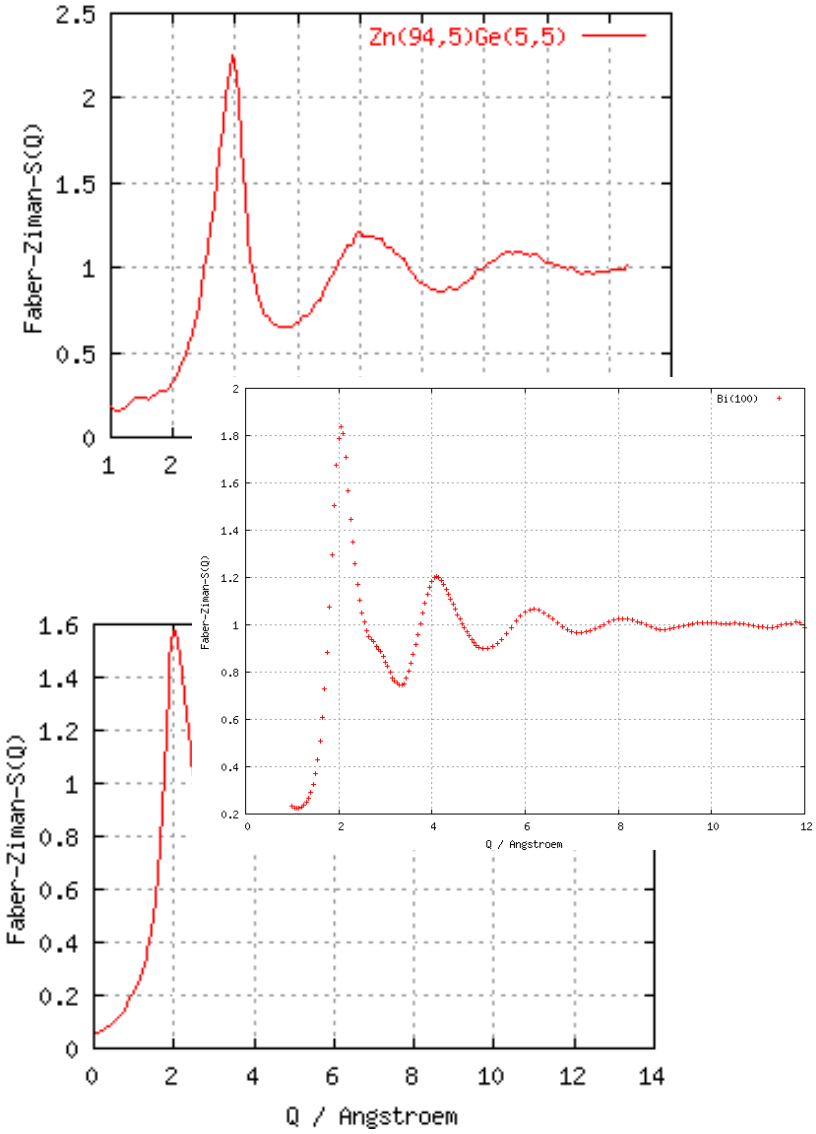
Fig.1:Structure factor $S_T(q)$ of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at different temperatures

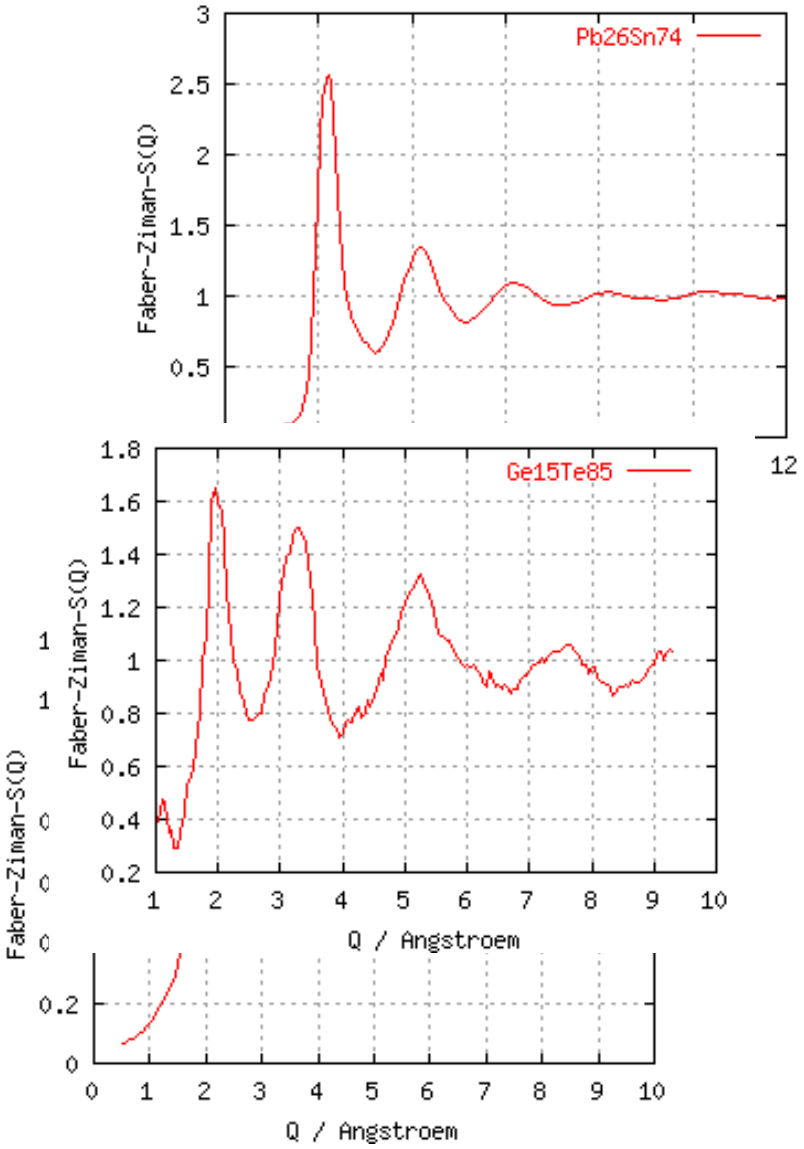
Fig.2: Position q_1 and height $S(q_1)$ of the first maximum of the structure factor $S_T(q)$ vs temperature

N. Mattern et al
APL 2003

Below T_g: harmonic change, described by Debye behavior
At T_g: Transition to lower Debye-temperature
+ structural changes

Structure by X-rays and neutrons

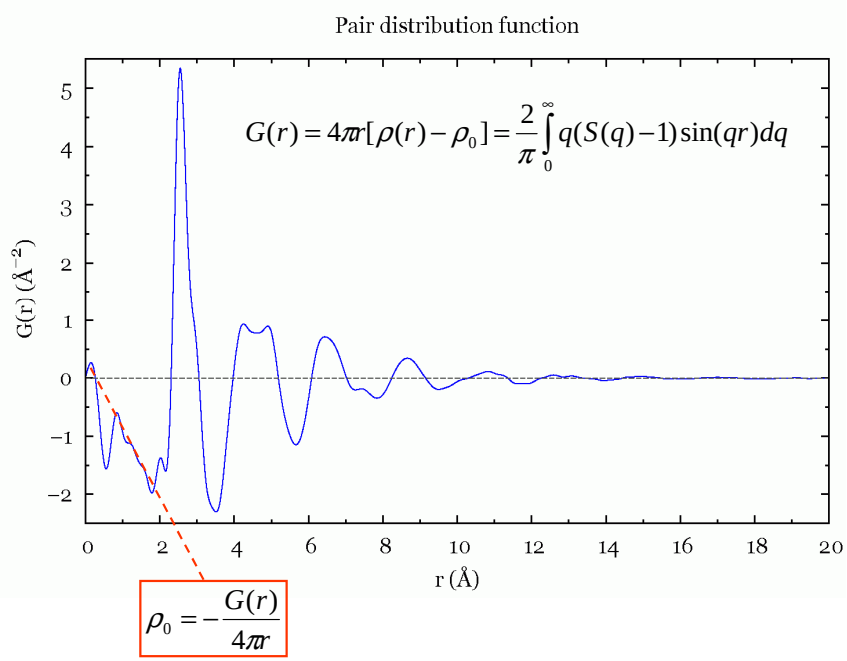


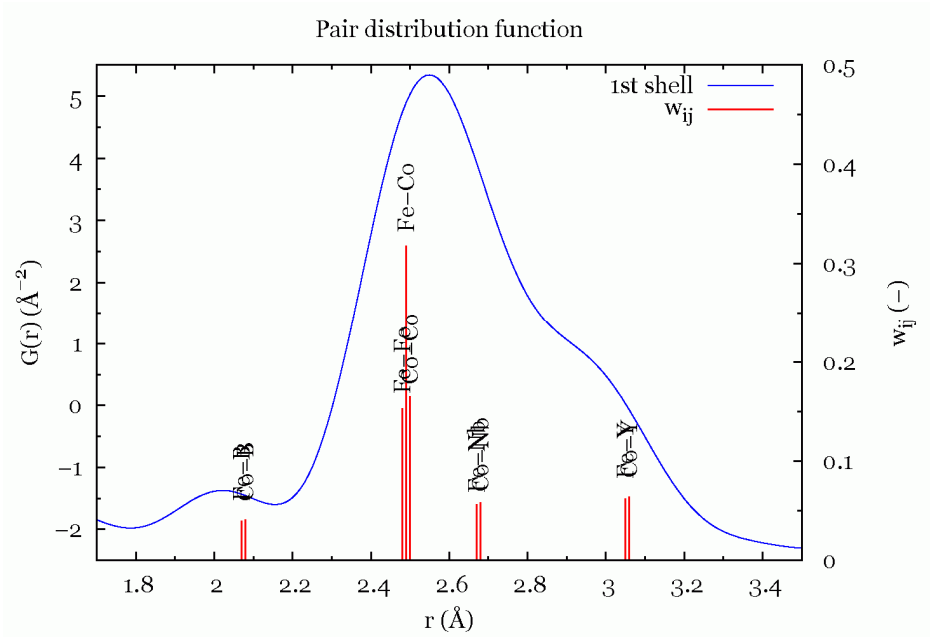


Homepage W. Hoyer, TU Chemnitz

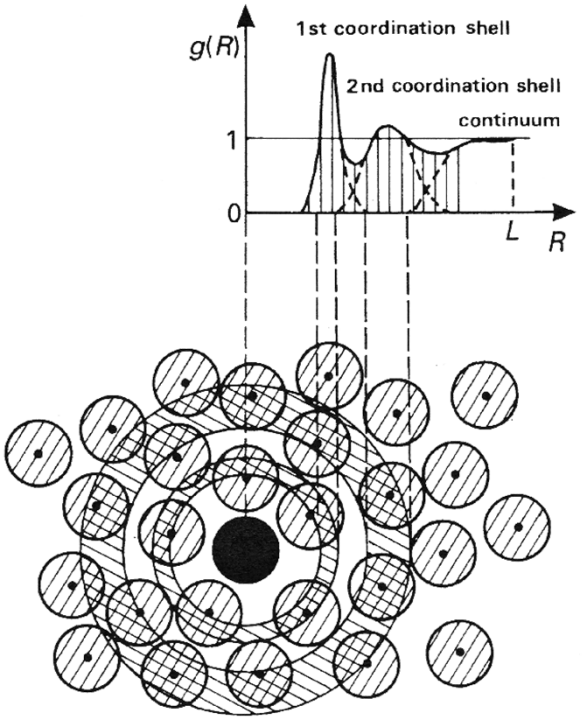
www.tu-chemnitz.de/physik/RND

Pair Distribution Function.





$$g(r) = \frac{\rho(r)}{\rho_0} = \frac{G(r)}{4\pi\rho_0 r} + 1$$

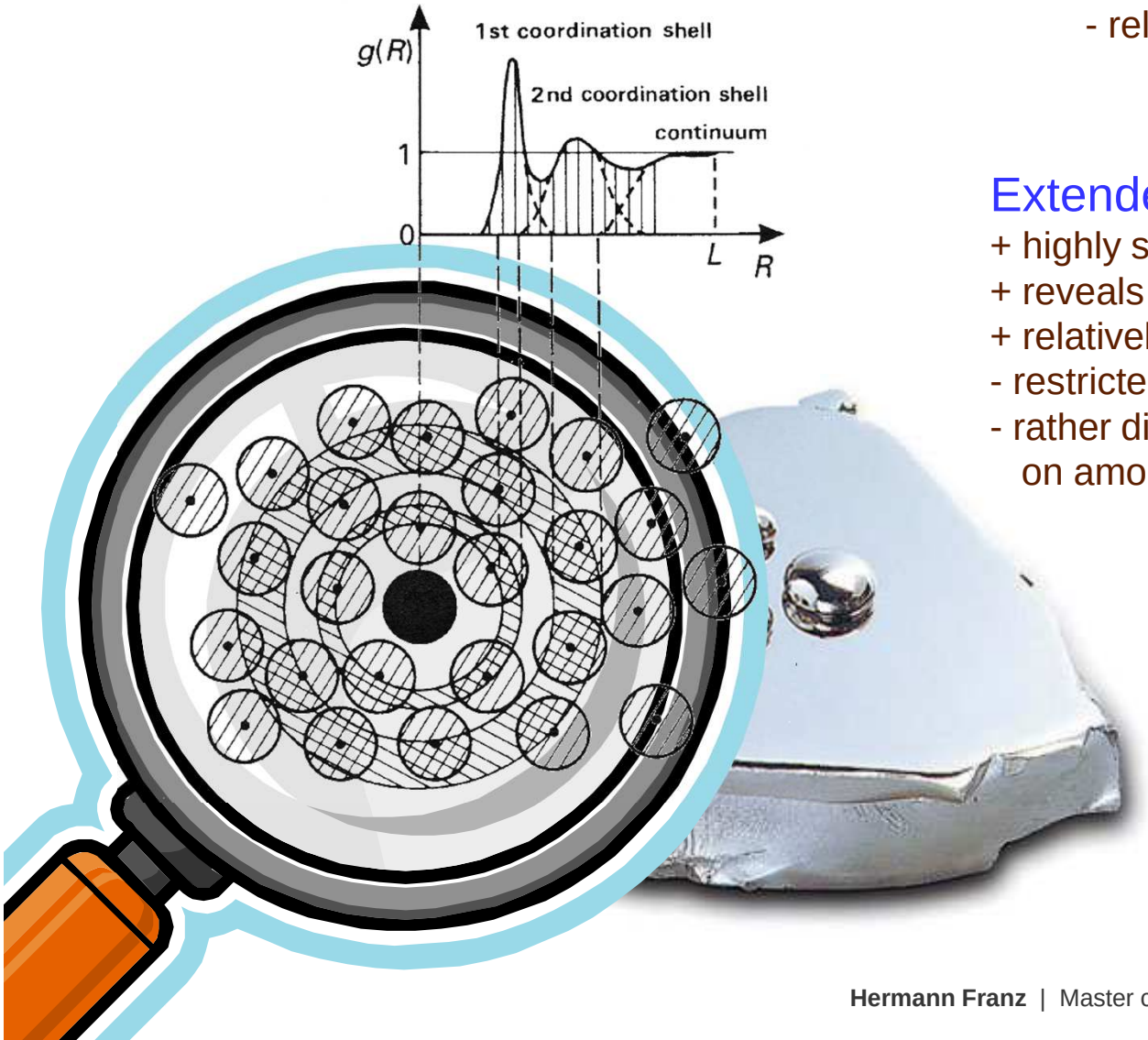


g(r) describes how the density of surrounding atoms varies as a function of the distance from a distinguished atom.

Structure determination of amorphous materials

X-ray diffraction using high energy photons

+ high penetration depths (mm-cm)
+ relatively fast, suitable for in-situ studies
- less sensitive to elements
- ASF depend on Q



Neutron diffraction

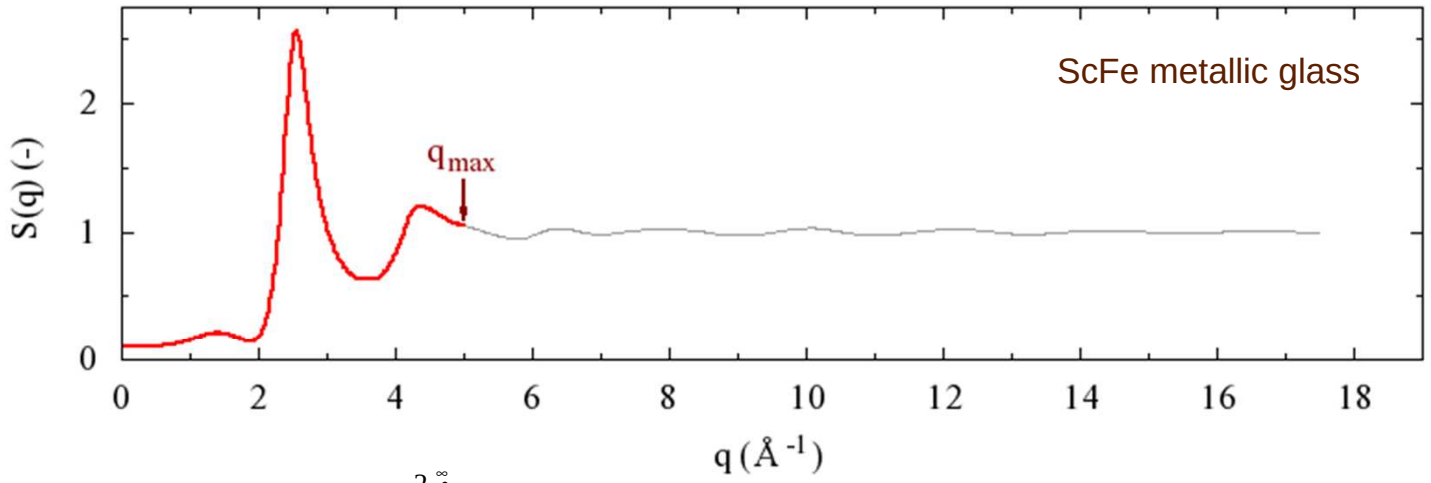
+ sensitive to different isotopes
+ ASF do not depend on Q
+ probes magnetic state of matter
- large sample volumes
- relatively slow, not suitable for in-situ studies

Extended X-ray Absorption Spectroscopy

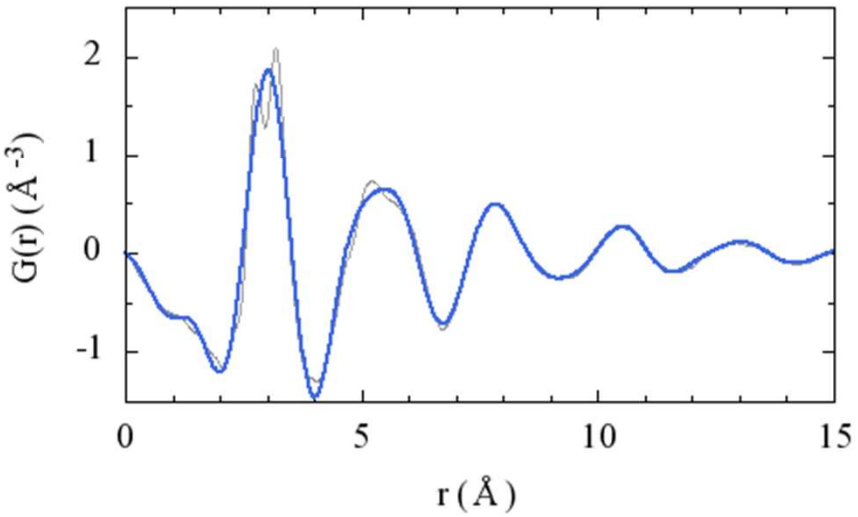
+ highly sensitive to elements
+ reveals local atomic configuration
+ relatively fast, suitable for in-situ studies
- restricted sample size, geometry
- rather difficult to quantitatively analyze data on amorphous samples

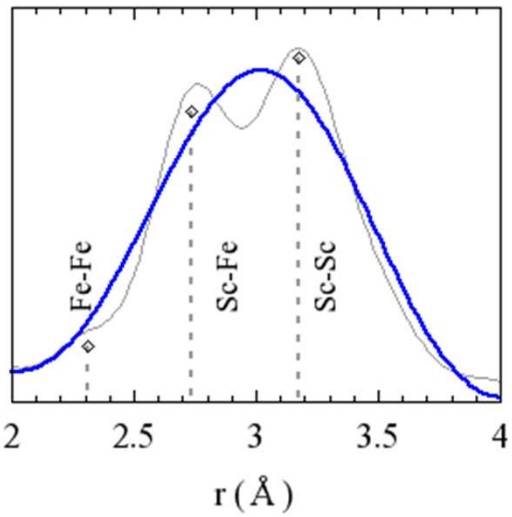
Resolution in real space.

- Collecting diffracted photons up to high q values significantly improves resolutions of pair distribution function

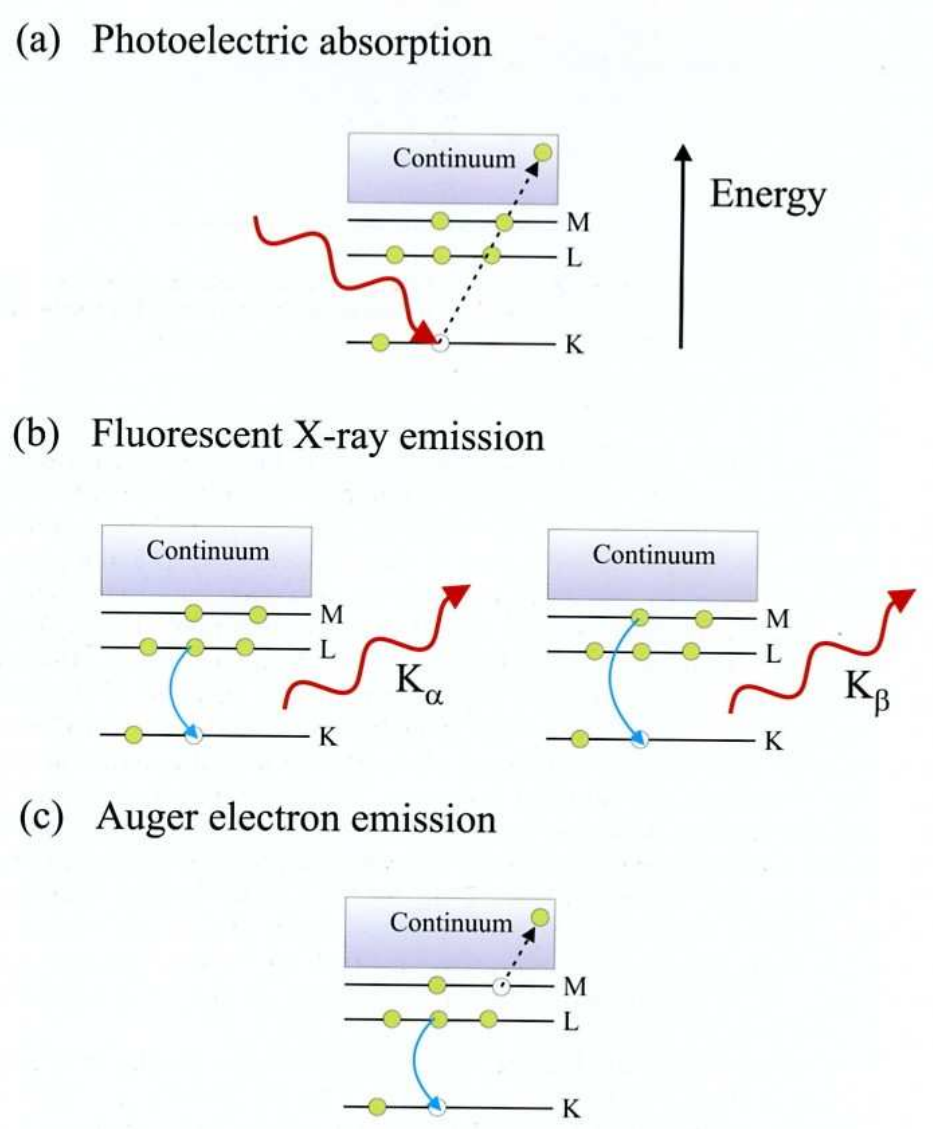


$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty q(S(q)-1)\sin(qr)dq$$

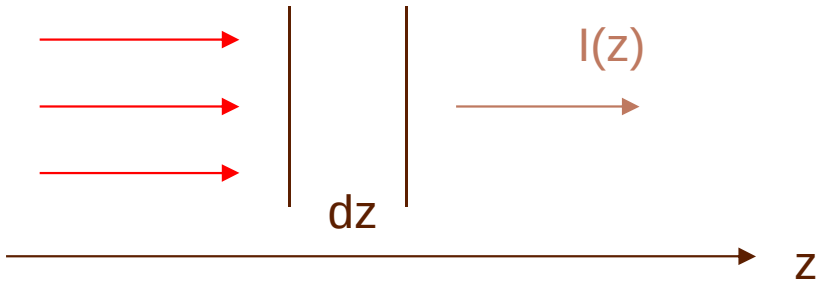




Photoelectric absorption



$-dI = I(z)\,\mu\,dz$



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

$\mu = \rho_a \sigma_a = (\rho_m N_A / A)\,\sigma_a$

ρ_a atomic number density

$\sigma_a = \sigma_a(E)$ absorption cross section

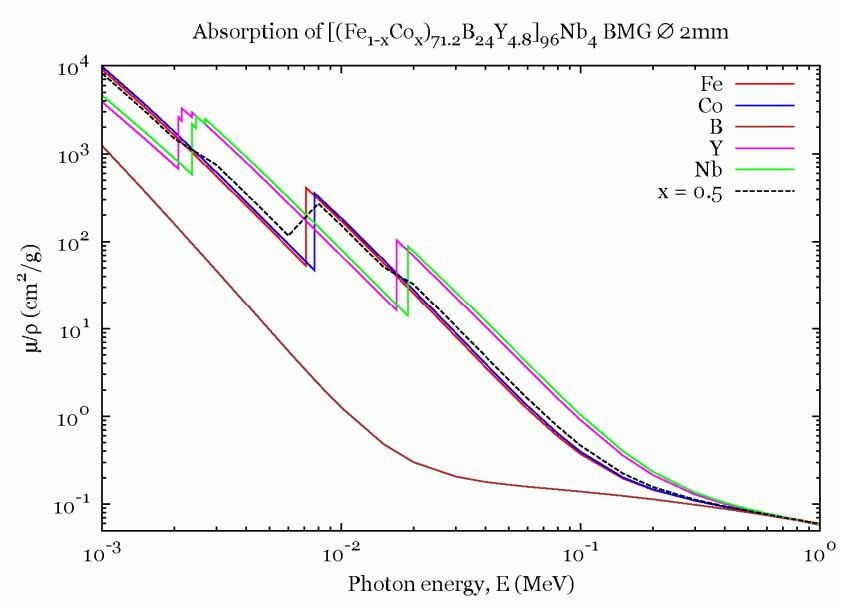
ρ_m mass density

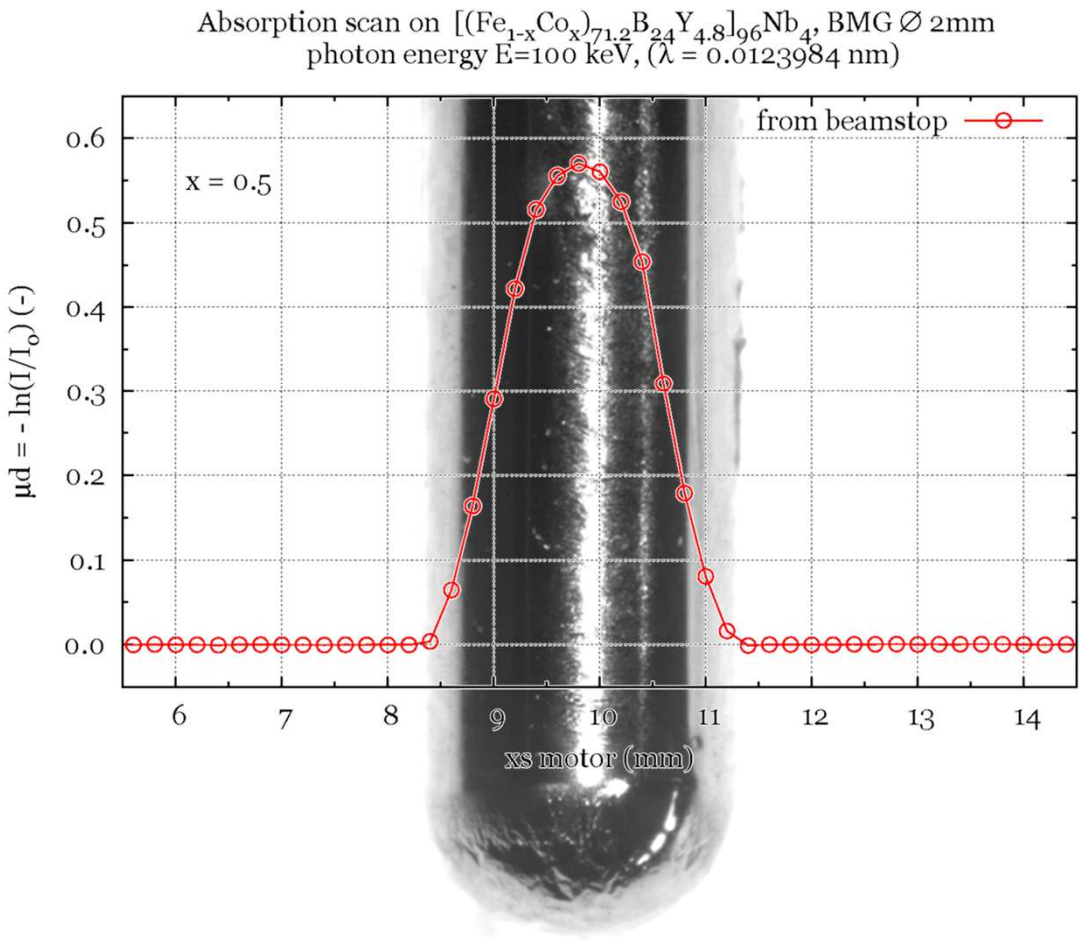
N_A Avogadro's number

A atomic mass number

Lecture 2: page 17

Absorption scan.





$$I = I_0 e^{-\mu d}$$

I_o represents incident intensity

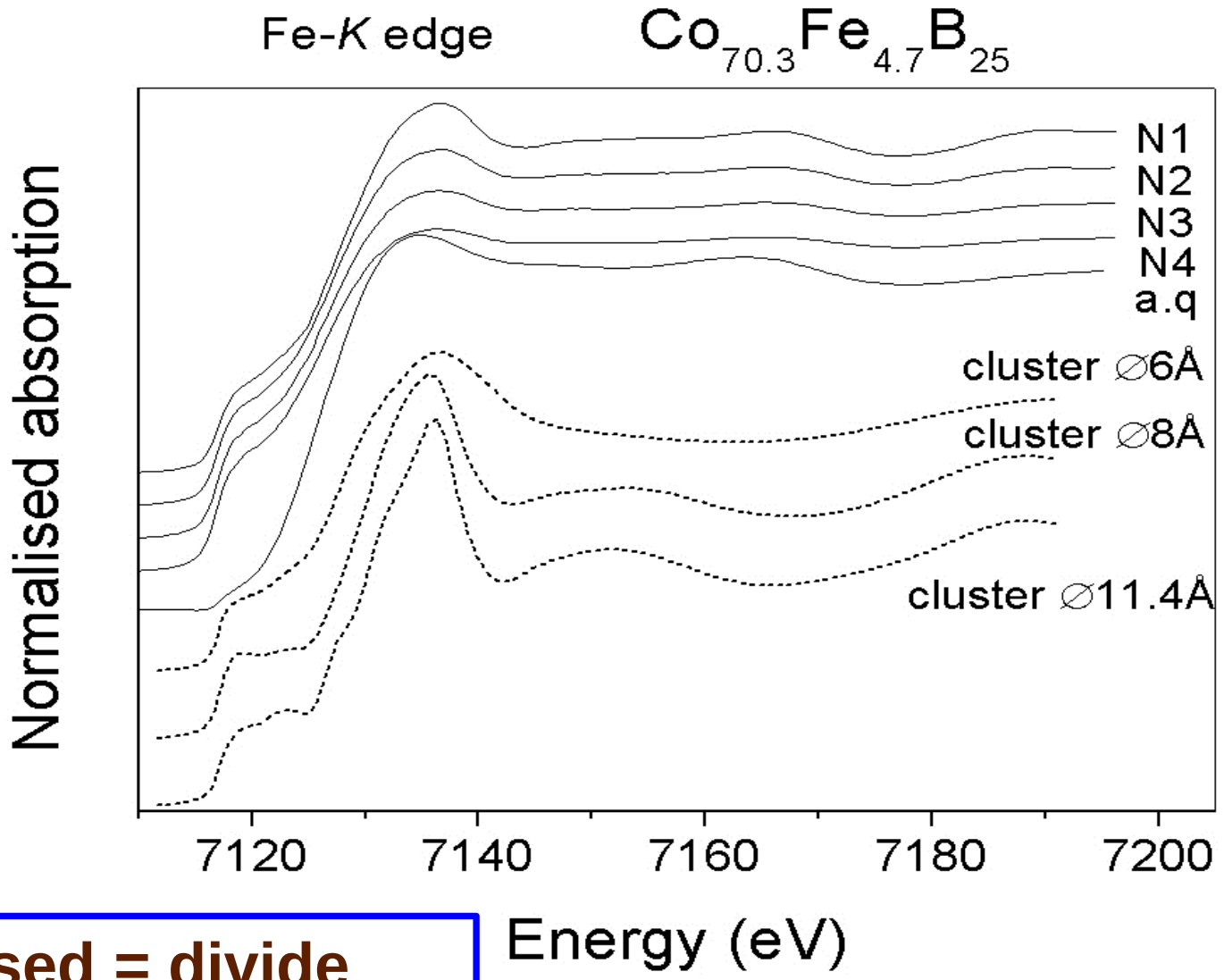
I is the transmitted intensity

μ is the absorption coefficient

d is the sample thickness

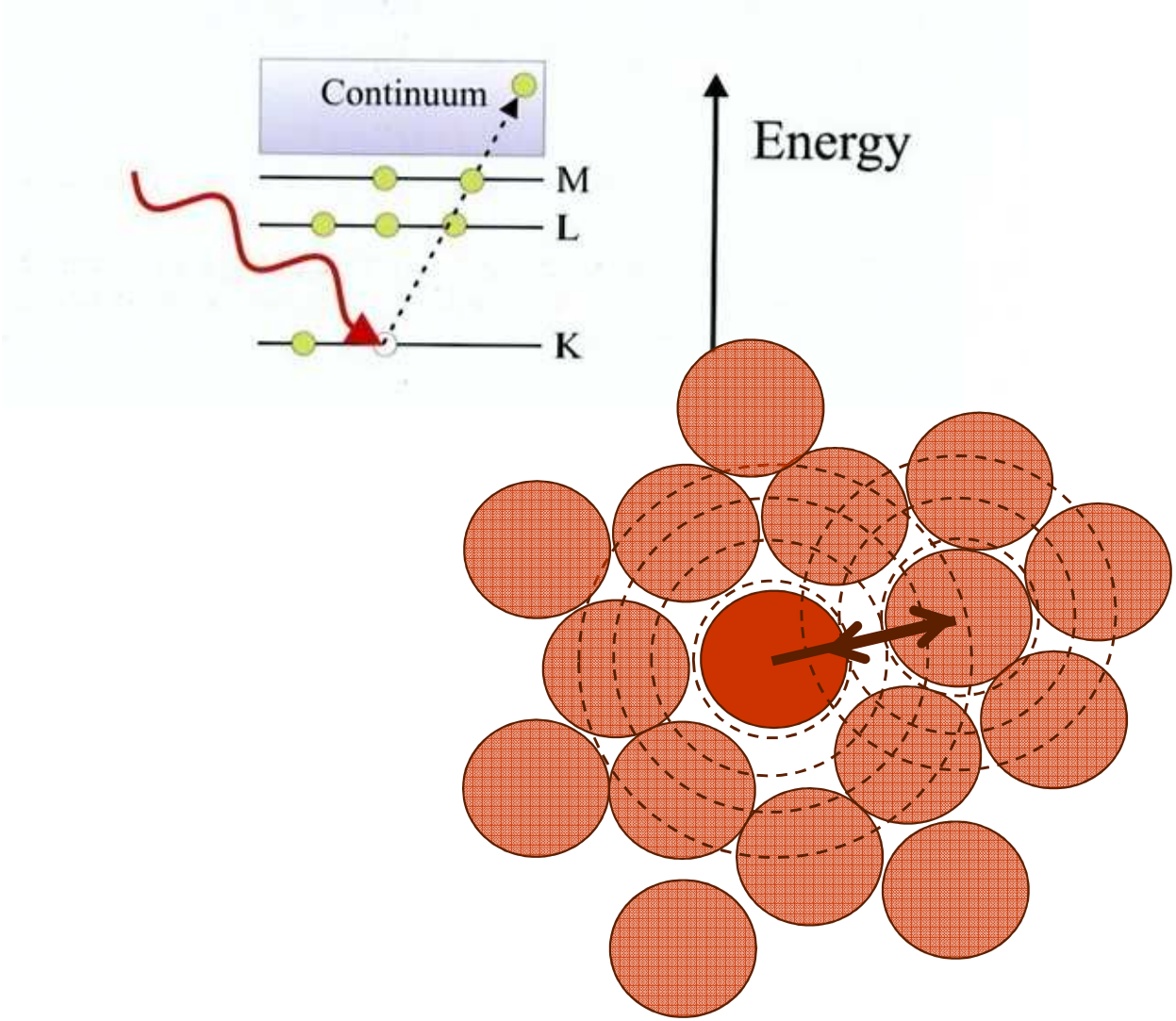
M. Stoica et al, *Journal of Applied Physics* 109 (2011) 054901

Absorption scan.



Normalised = divide out E^{-3} decay

EXAFS

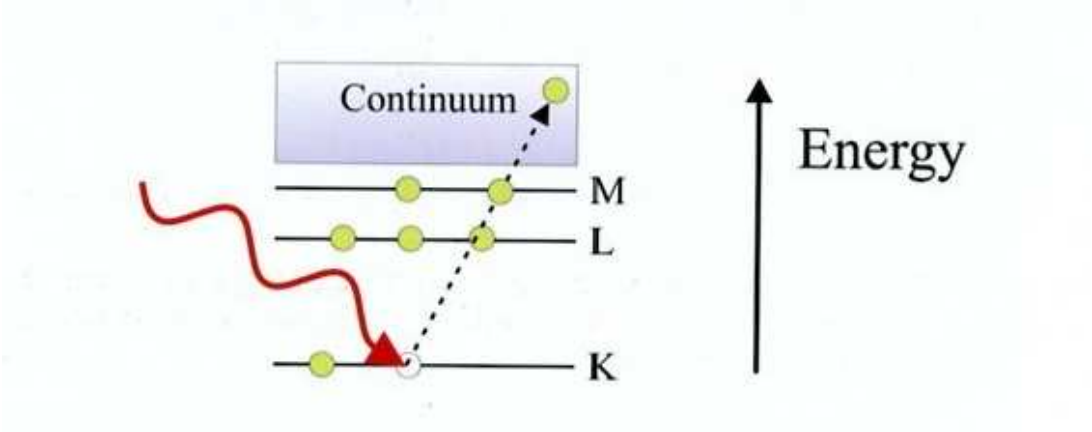


$$E_e = h\nu - E_K$$

$$k = \sqrt{\frac{2m}{\hbar^2}(h\nu - E_K)}$$

- **Outgoing and reflected wave interfere at the location of the ad-atom**
- **Requires sufficiently small bandwidth**

EXAFS



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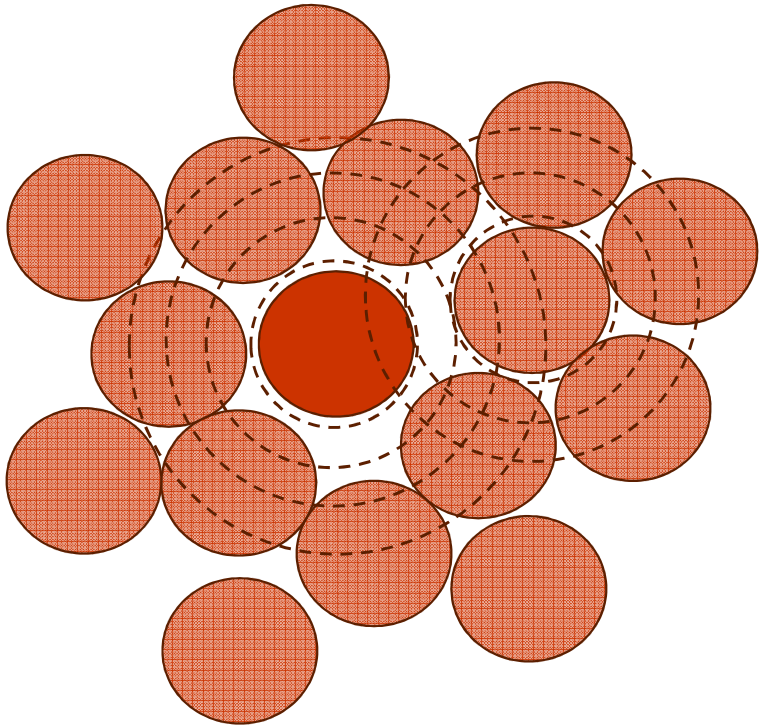
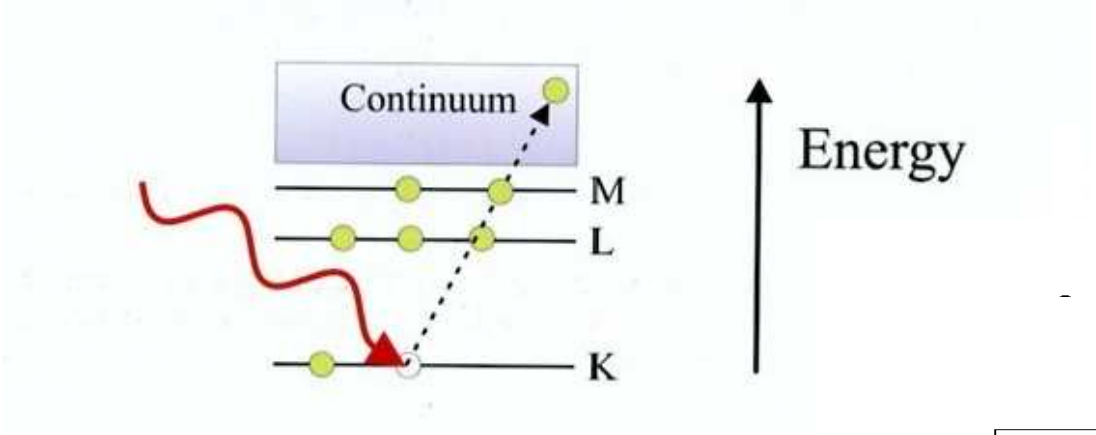


$$\chi(k) = \sum_i C_i(k)\sin[2kR_i + \varphi_i(k)]$$

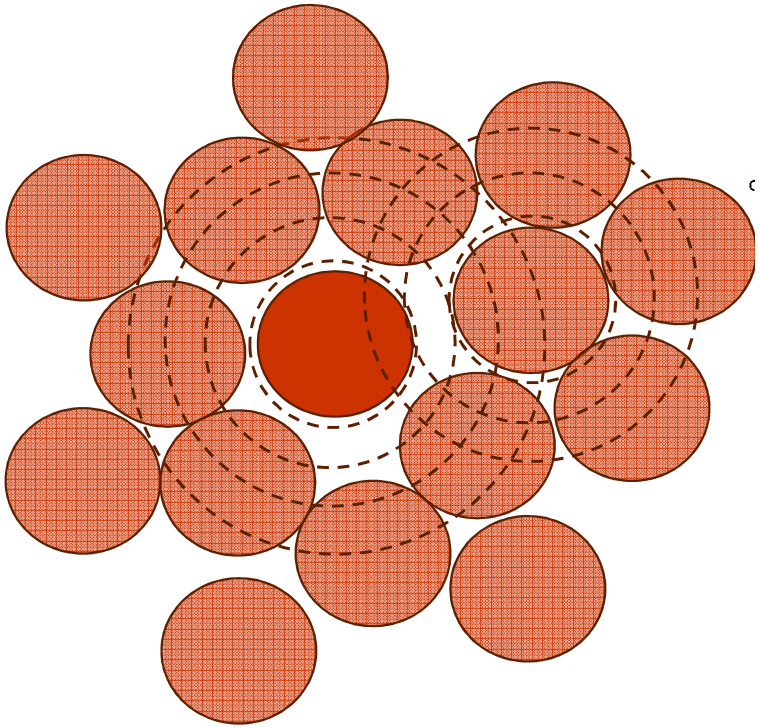
$$C_i(k) = \frac{N_i}{kR_i^2} S_0^2 F_i(k) \exp(-2\sigma_i^2 k^2)$$

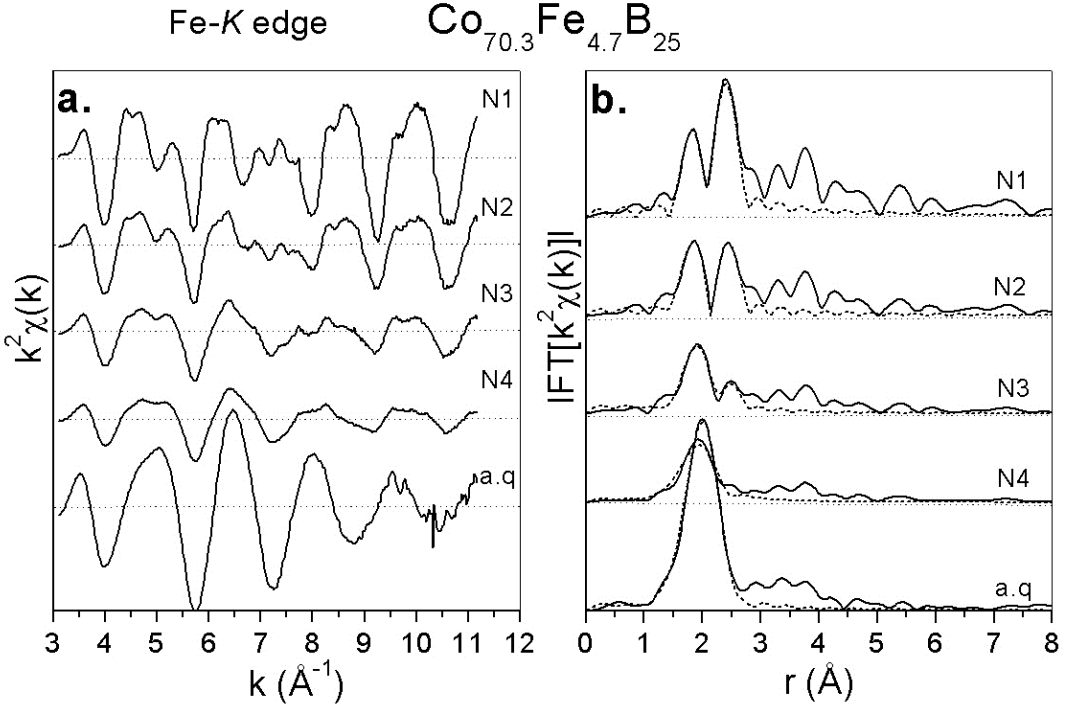
N_i = average number of scattering atoms (coordination number),
S_0 = many-body amplitude factor
$F_i(k)$ = backscattering amplitude characteristic of a particular type of back-scattering atom
σ = mean square relative displacement.

EXAFS example



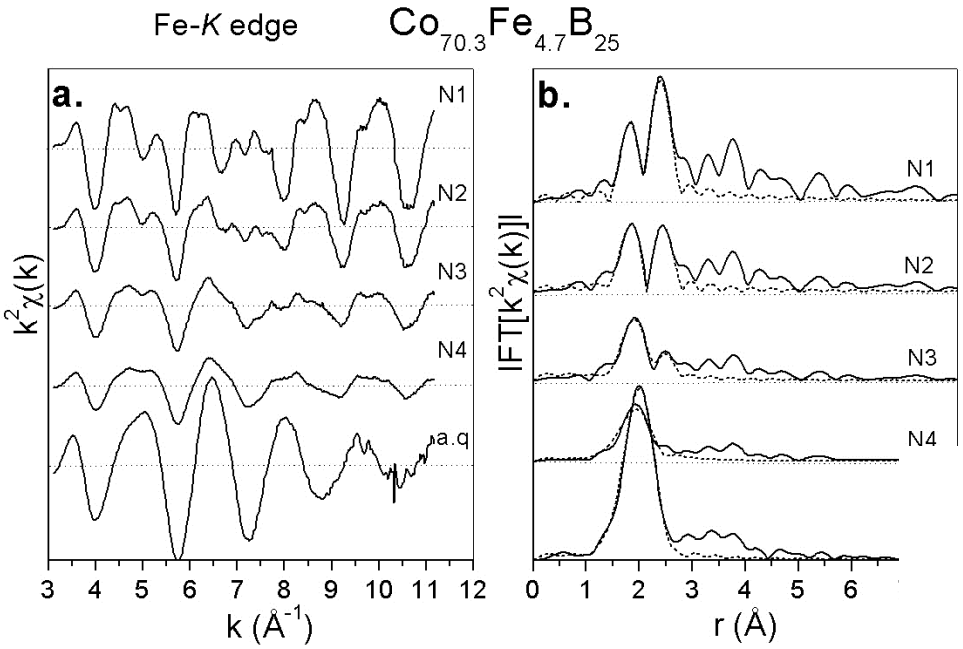
$$\chi(k) = \sum_i C_i(k) \sin\left[2kR_i + \varphi_i(k)\right]$$



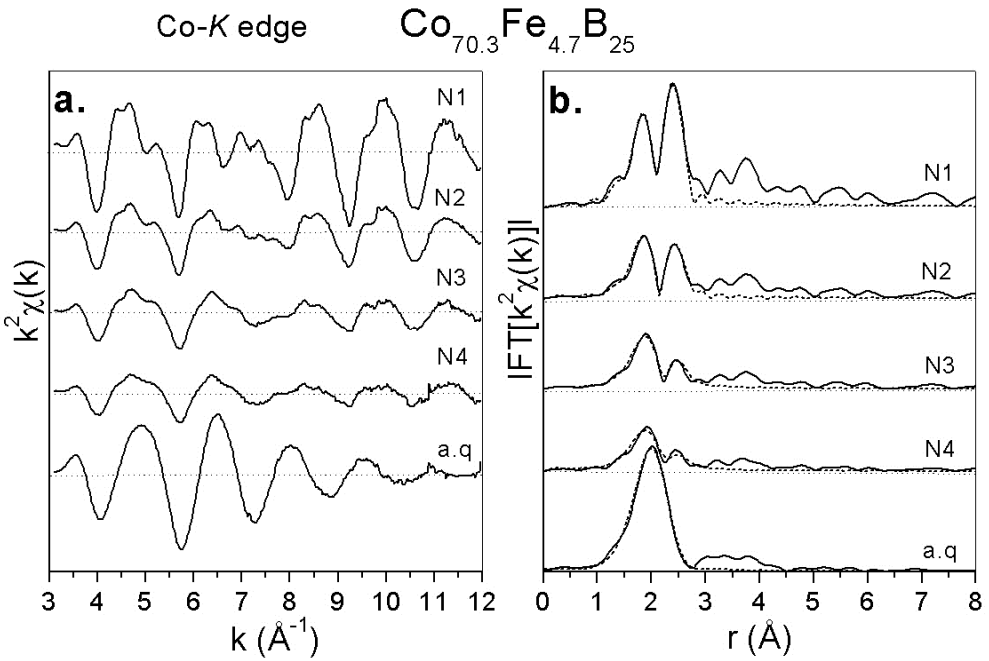


K. Saksl et al, (2007)

EXAFS example

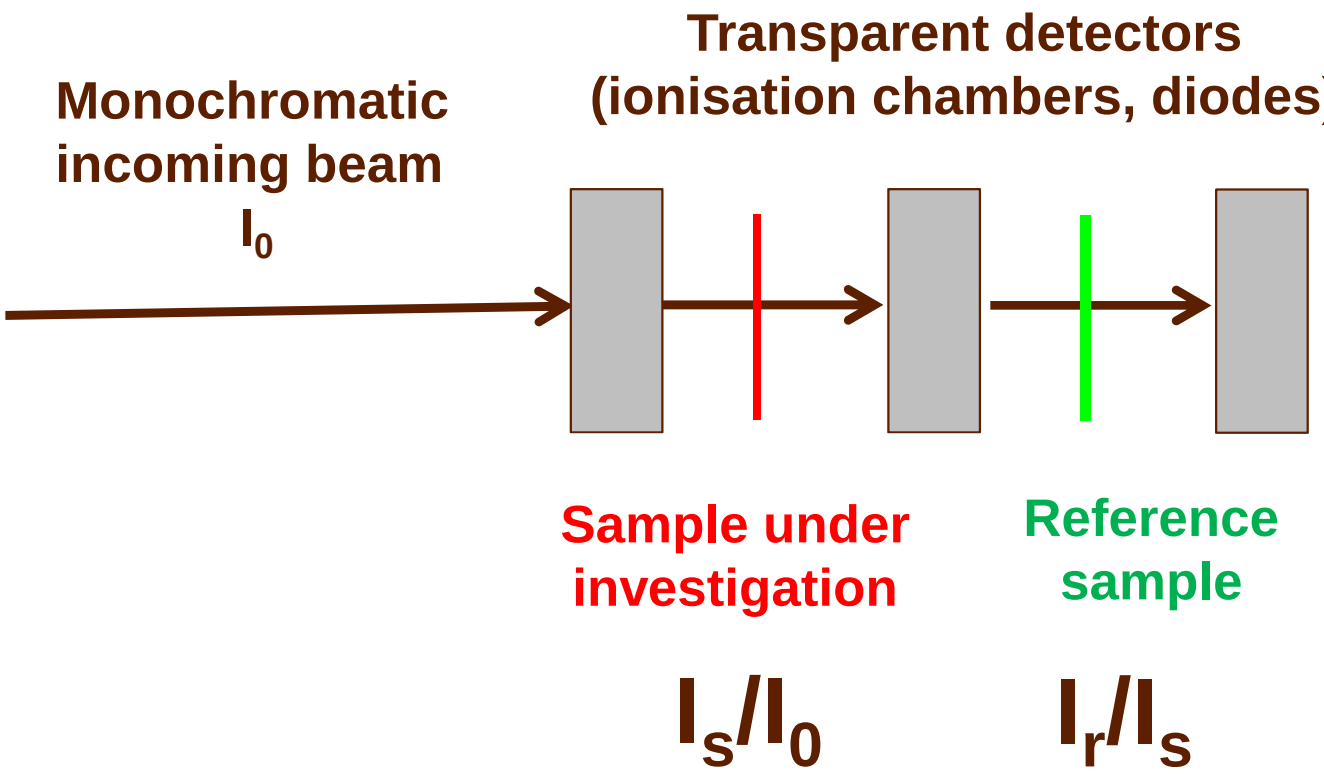


Element specific information!



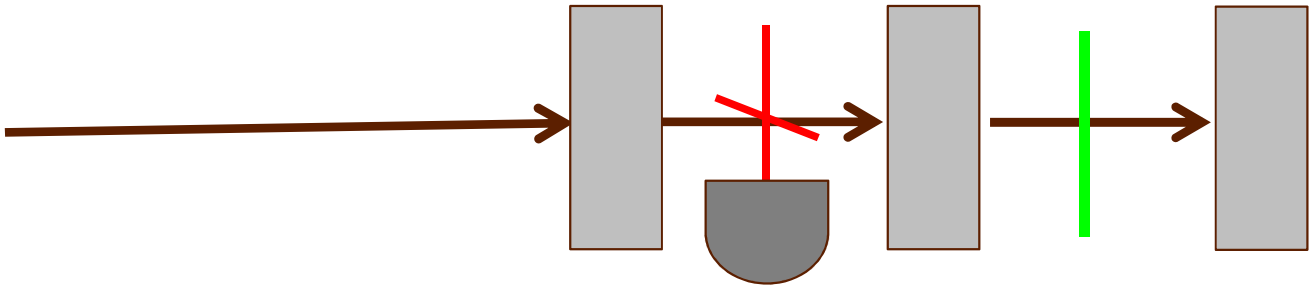
a.q. = as quenched
Nx = various particle sizes after milling

EXAFS set-up



- Reference samples allows to detect small energy shift of the absorption edge
- Chemical shift reflects the electron density around the ad-atom

EXAFS set-up



Problem: highly absorbing samples (low energy edges)

- **Electron yield**
- **Fluorescence detection**
- **Surface sensitivity combined with grazing incidence**

Reverse Monte Carlo modeling

Diffraction:

The partial $g_{ij}(r)$ functions are calculated from the atomic coordinates and transformed to reciprocal space:

$$S_{ij}(Q) = \frac{4\pi\rho c_j}{Q}\int r \sin Qr(g_{ij}(r)-1)dr$$

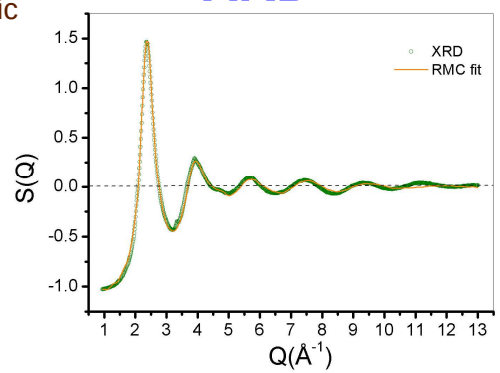
together with a weights (for ND $f(Q)=b$)

$$w_{ij} = \frac{(2-\delta_{ij})c_i c_j f_i(Q) f_j(Q)}{\sum_{ij} c_i c_j f_i(Q) f_j(Q)}$$

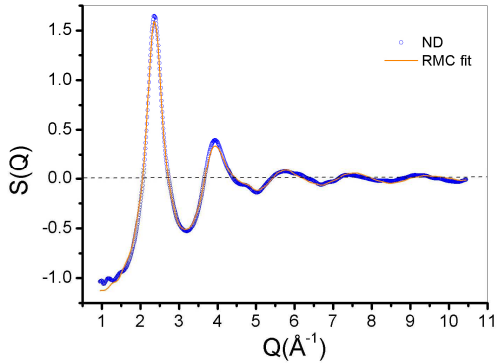
are combined in total structure factor

$$S^{RMC}(Q) = \sum_{ij} w_{ij}(Q) S_{ij}(Q)$$

XRD



ND



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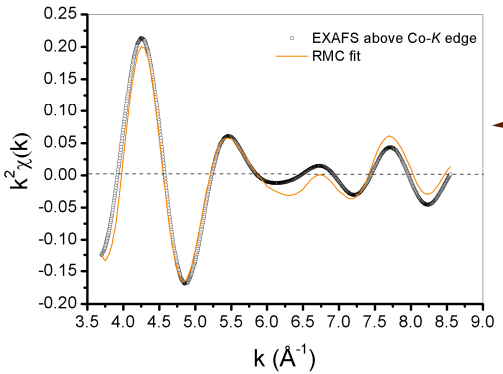


EXAFS:

The model of EXAFS signal $\chi_i(k)$, at the absorption edge of i-type atoms can be calculated from the g_{ij}:

$$\chi_i(k) = \sum_j 4\pi c_j \rho \int_0^\infty r^2 \gamma_{ij}(r,k) g_{ij}(r) dr$$

while γ_{ij} is the atomic pair backscattering signal

$$\gamma_{ij}(r,k) = A_{ij}(k,r)\sin(2kr + \Phi_{ij}(kr))$$

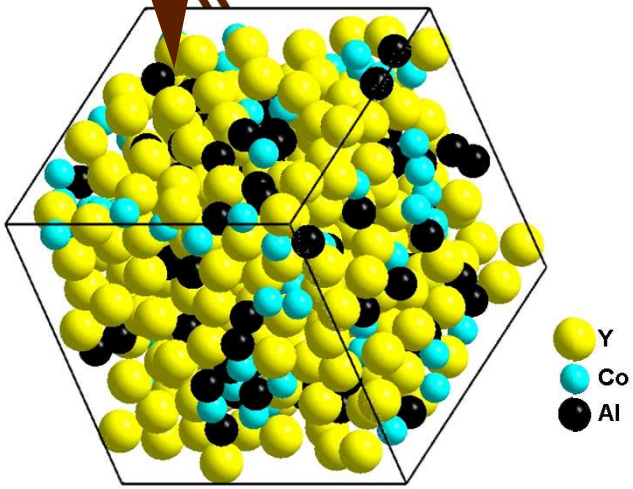
Courtesy of Dr. K. Saksl

Move:

One particle is moved randomly taking into account applied constraints.

Settling:

Everything is repeated until ψ^2 begins to oscillate around a constant value.



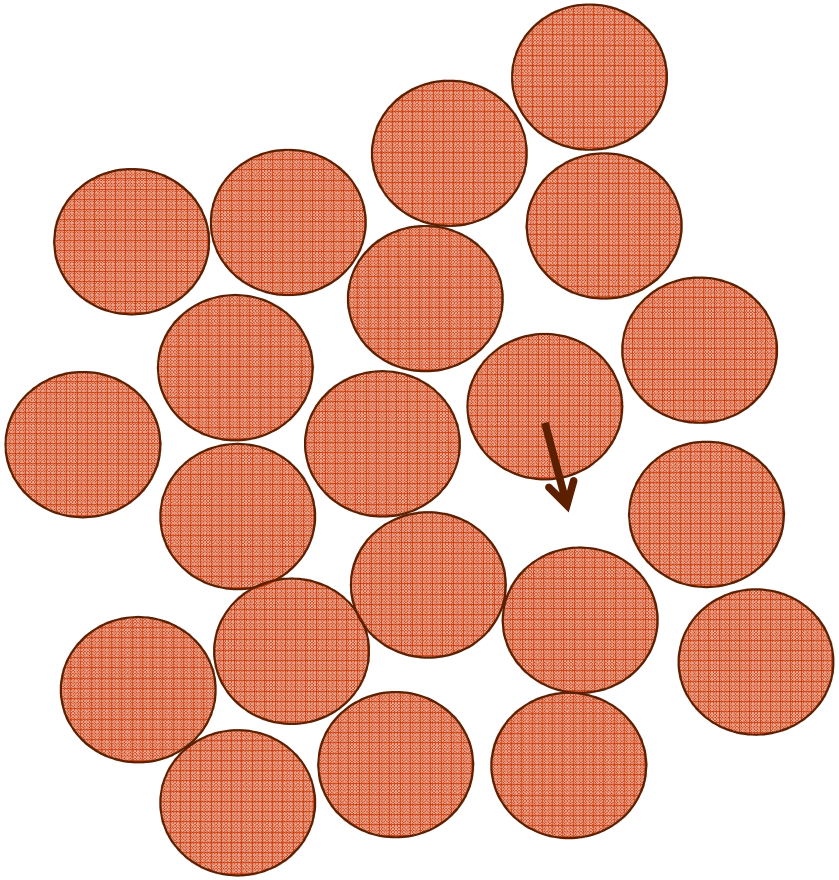
Acceptance of the move:

First the experiment-model difference is calculated

$$\psi^2 = \frac{1}{\delta}\sum_{i=1}^{m}\left[\zeta^{\exp} - \zeta^{RMC}\right]^2$$

If $\psi^2_{n+1} < \psi^2_n$ the move is always accepted.
If $\psi^2_{n+1} > \psi^2_n$ the move is accepted with the probability $\exp[-(\psi^2_{n+1} - \psi^2_n)/2]$

Monte Carlo move



- **Move each atom sequentially by a small stochastic displacement**
- **Boundary conditions:**
  - **Minimum NN distance**
  - **Chemical composition**
  - **Average density**

Reverse Monte Carlo modeling

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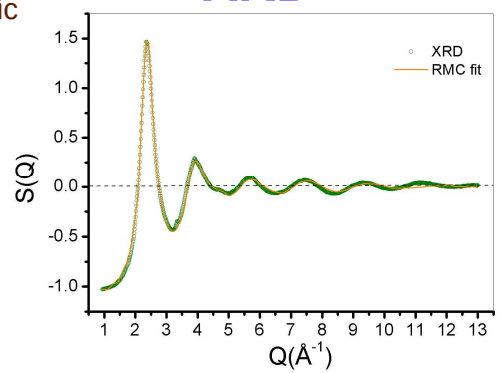
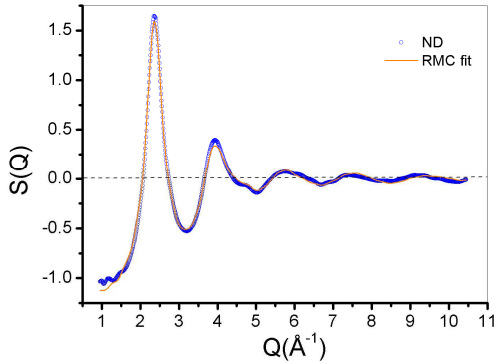


ND



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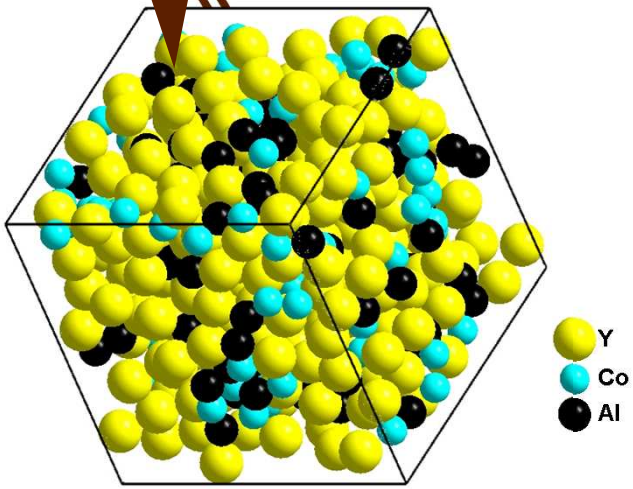

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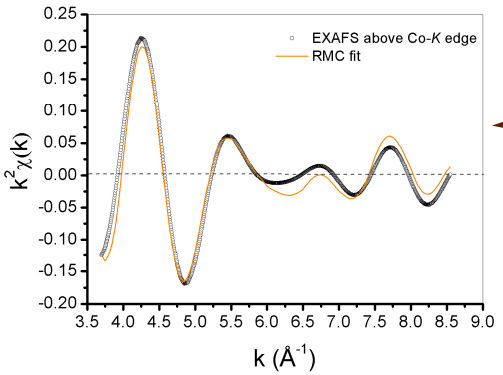

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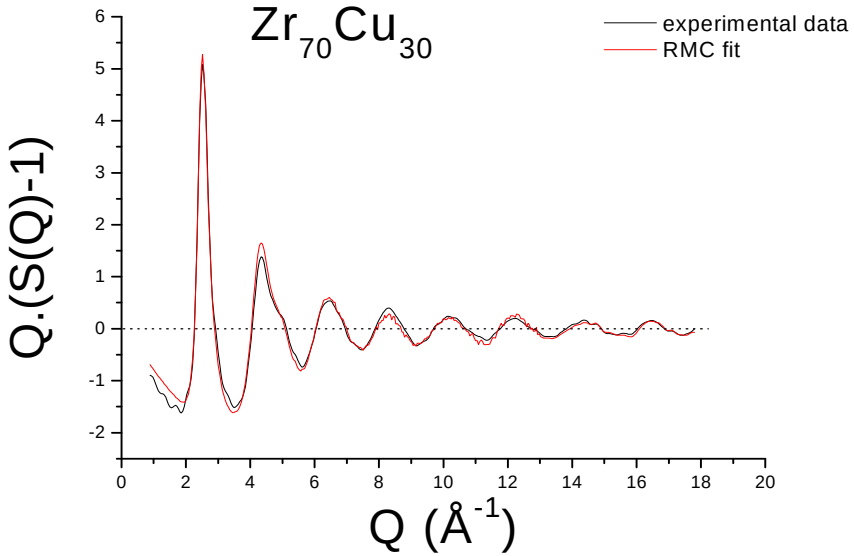
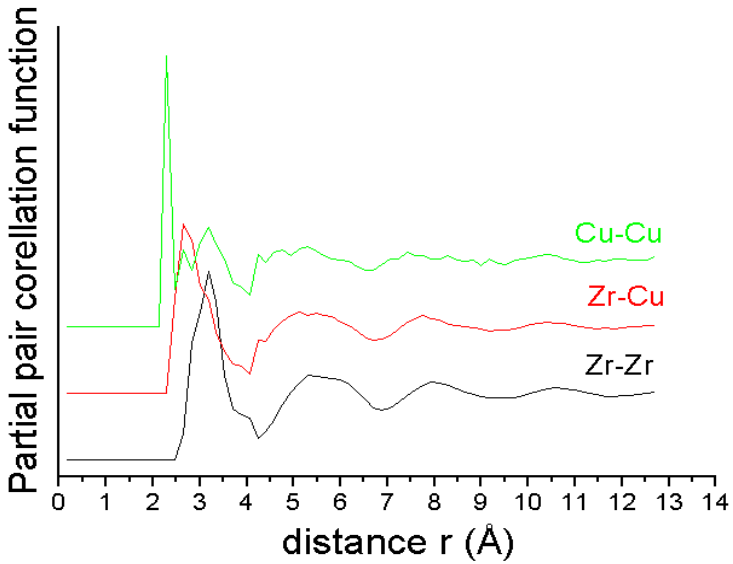
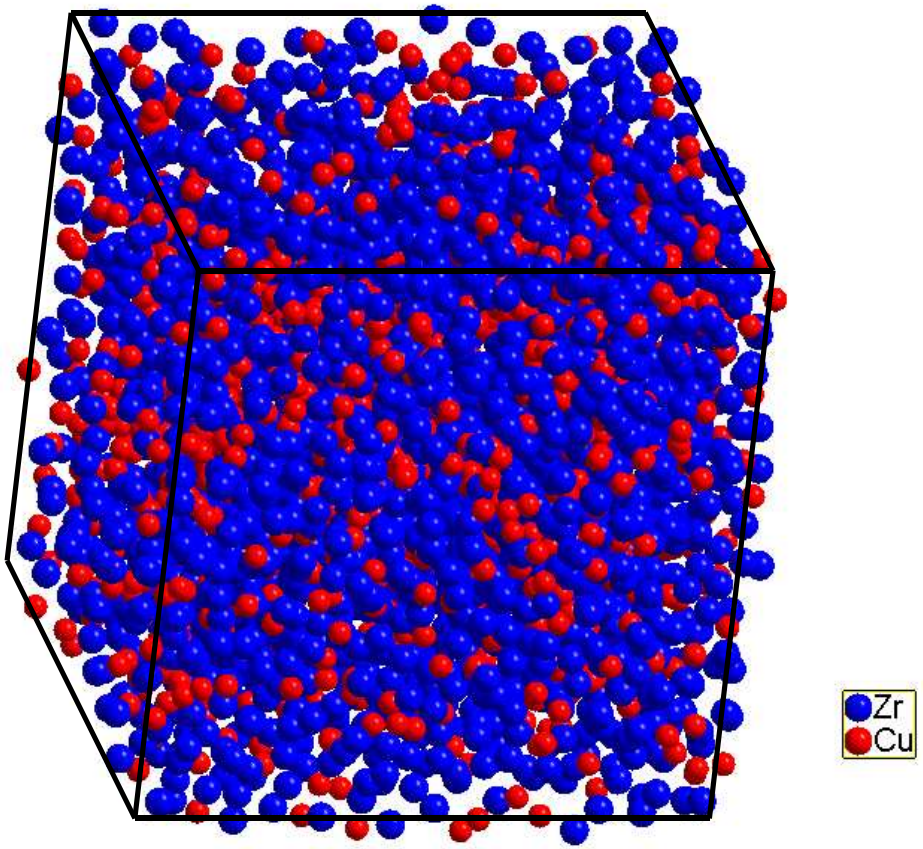
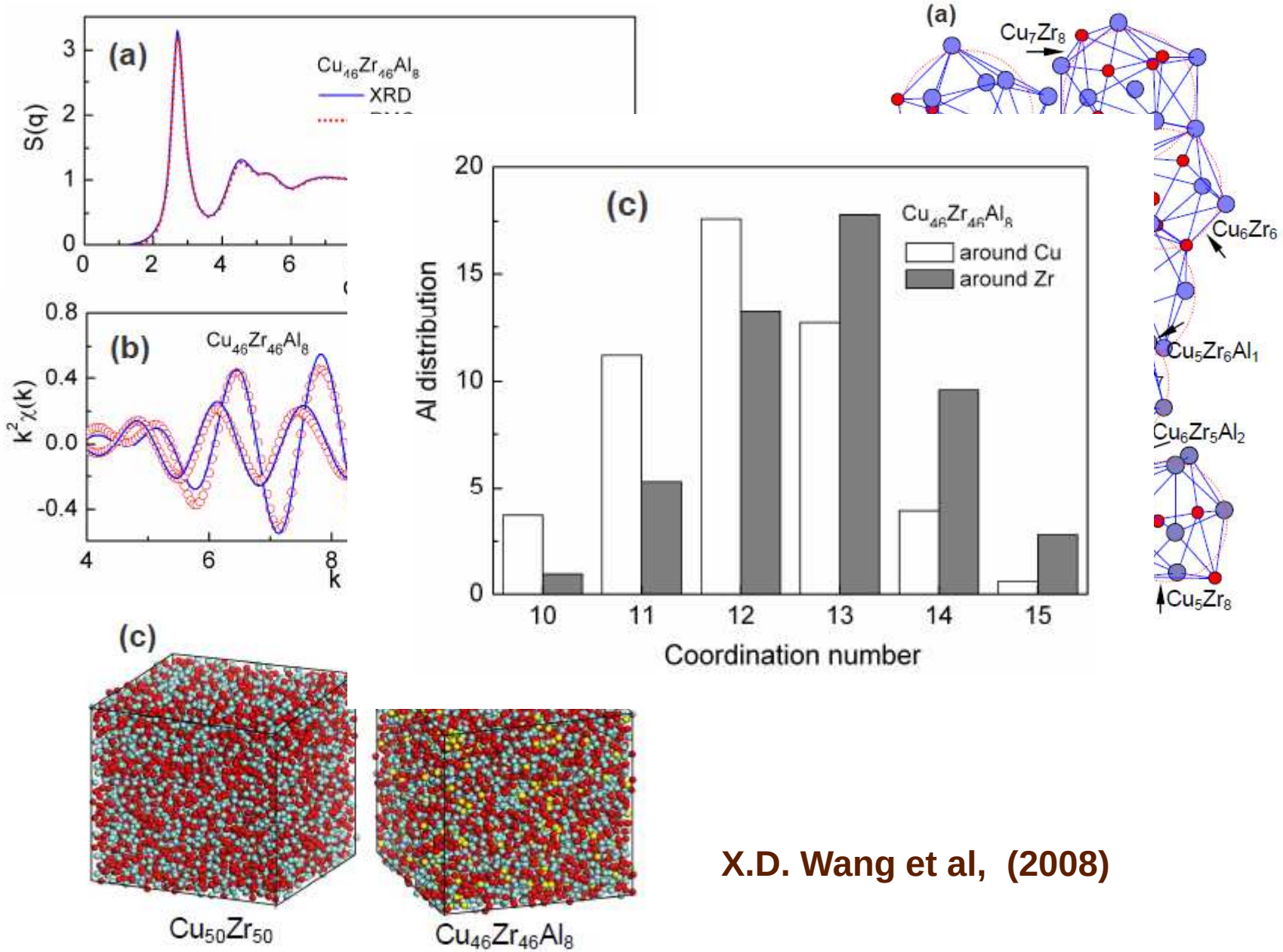
Reverse Monte Carlo result







Reverse Monte Carlo results



X.D. Wang et al, (2008)

Reverse Monte Carlo results

- **Usually this is a structure compatible with the experimental data**
- **For sufficiently independent input data this can be a unique solution**

Time dependent structures, inelastic scattering

Up to now:

$$F^{crystal}(Q) = \sum_{rj} f_j(Q)\exp(iQr_j) \sum_{Rn} \exp(iQR_n)$$

unit cell structure factor — lattice sum

$$I_s = r_o^2 \, F(Q) \, F^*(Q) \, P$$

But in general: $r_j = r_j(t)$

$$F(Q,t) = \sum f_j(Q) e^{iQr_j(t)}$$

Time dependent structures, inelastic scattering

$$F(Q,t) = \sum f_j(Q) e^{iQr_j(t)} e^{i\omega t}$$

Fully time dependent amplitude

In first approximation r(t) = r_0 + v*t

$$F(Q,t) = \sum f_j(Q) e^{iQ(r_0+vt)} e^{i\omega t}$$

$$F(Q,t) = \sum f_j(Q) e^{iQr_0} e^{i(\omega+Qv)t}$$

Doppler shift !

Dynamical structure factor:

$$S(q,\omega) = \frac{1}{N}\sum e^{-iq(R-R')}\int \frac{dt}{2\pi}\left\langle e^{iqu(R',0)}e^{-iqu(R,t)}\right\rangle$$

FT of the density-density correlation function

Time dependent structures, inelastic scattering

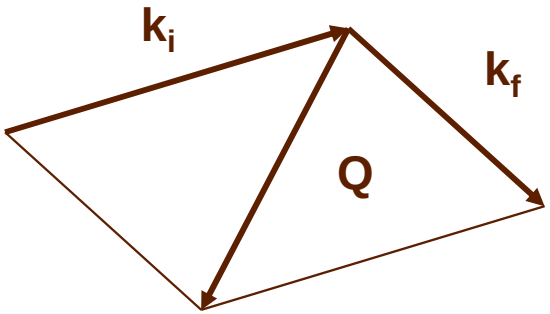
Static scattering cross-section:

$$\frac{d\sigma}{d\Omega} = \int d\omega S(q,\omega) = S(q,0)$$

Instantaneous position of all atoms (electrons)

Scattering from moving atoms

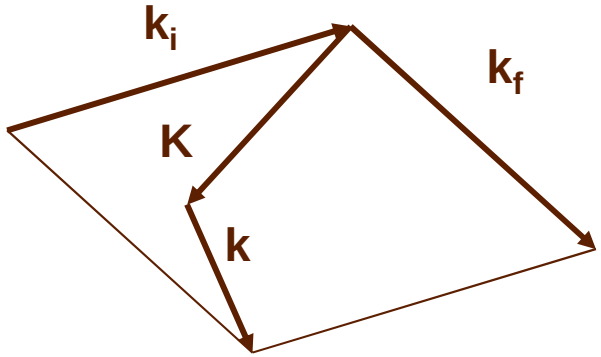
$$k_x = \frac{2\pi}{\lambda} = \frac{2\pi}{hc} E$$



Elastic (zero phonon) scattering

$E_i = E_f$

Q = K



Inelastic scattering

(one phonon)

$E_i = E_f \mp \omega(\mathbf{k})$

Q = K + k

Phonon creation or anihilation