Lecture 10
EXAFS Studies of Glass Structure

Bibliography (Posted on BB)

Elements of XAFS
Grant Bunker
http://gbxafs.iit.edu/training/xafsoverview.pdf

Fundamentals of XAFS
Matthew Newville
http://xafs.org/Tutorials?action=AttachFile&do=get&target=Newville_xas_fundamentals.pdf

Acronyms

XAS = X-ray Absorption Spectroscopy - the entire spectrum
XAFS = X-ray Absorption Fine Structure
XANES = X-ray Absorption Near-Edge Structure, the bit near the edge
NEXAFS = Near Edge X-ray Absorption Fine Structure
EXAFS = Extended X-ray Absorption Fine Structure- the extended, wiggly part
SEXAFS = Surface EXAFS

Thus XAS = XANES + EXAFS.

The terms *XANES* and *NEXAFS* are completely interchangeable.
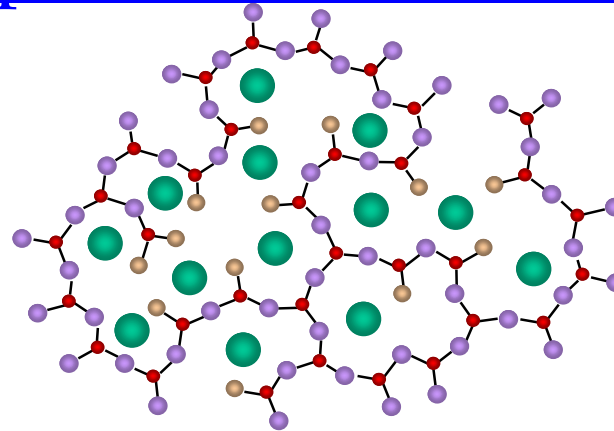The soft x-ray people (say, C through S) use *NEXAFS*, while others use *XANES*.

Electron analog of XAS – Electron energy loss spectroscopy (**EELS**)
Electron analog of EXAFS – Extended electron energy loss fins structure (**EXELFS**)
Electron analog of XANES – Electron energy loss near edge structure (**ELNES**)

Different Aspects of the Static Structure

Na   Si   B O   nB O

Physical structure

Physical arrangement of atoms with respect to each other (R_{M-O}, $\Delta\sigma_{M-O}^2$, CN, etc..)

- Short range order.
- Medium range structure.

Chemical structure

- Nature of bonding (covalency, ionicity, basicity, etc...) between different kinds of atoms.
- Charge distribution.

Vibrational structure

- Bond strength
- Local vibrations of the mobile atom.
- Vibrations of network structural units of small and medium size.
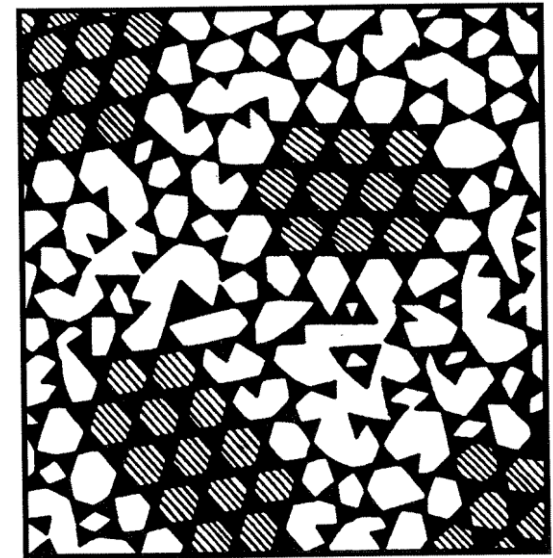
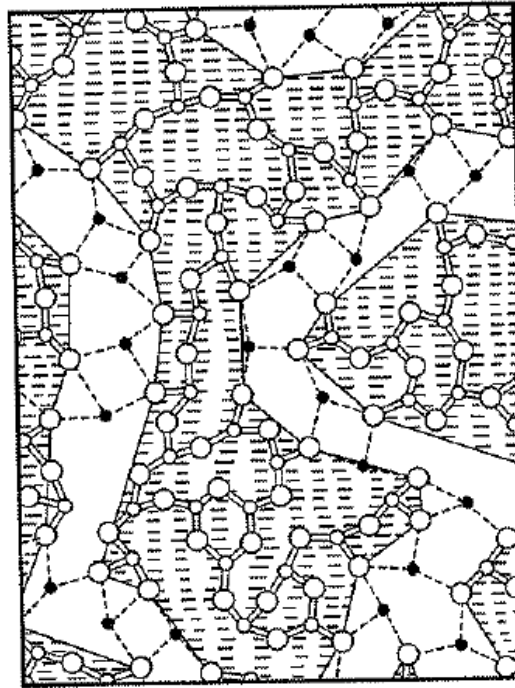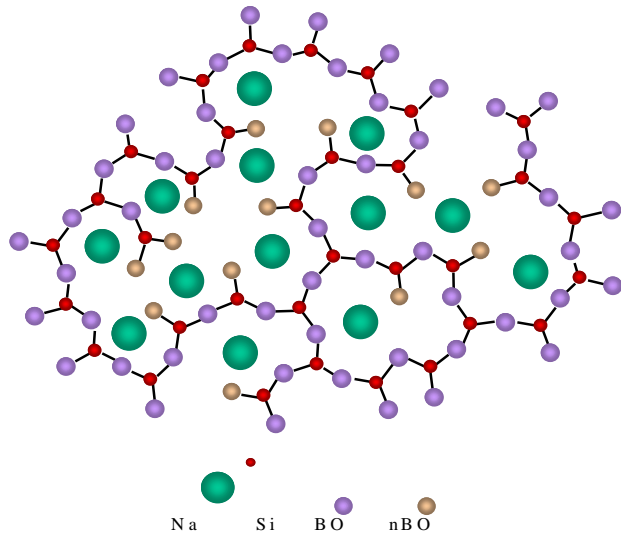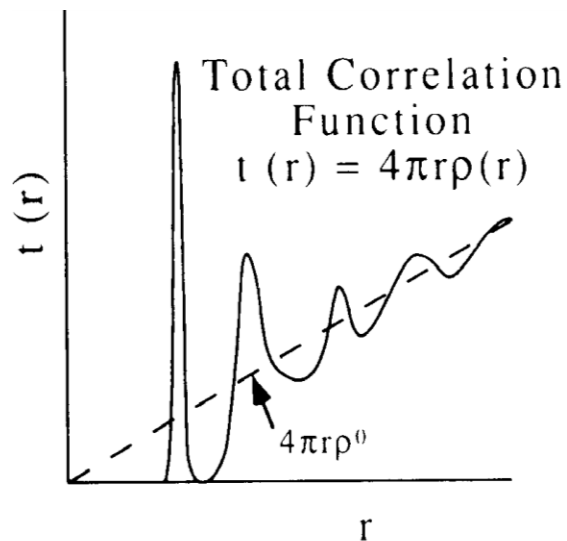# Important schematics of glass strcuture
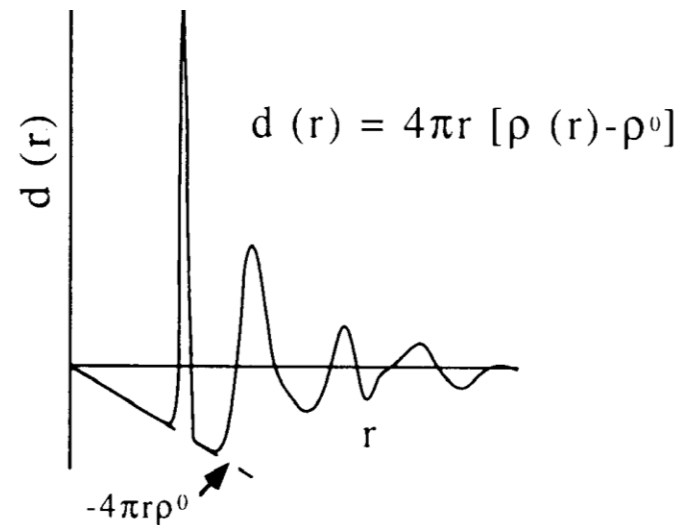

N a   S i   B O   n B O

Figure 3-4. Schematic diagram of Lebedev's crystallite theory. Regions of local order (crystallites) are separated by regions of disorder.

Reduced RDF

Total Correlation
Function
$t(r) = 4\pi r \rho(r)$

$d(r) = 4\pi r [\rho(r) - \rho^0]$

$4\pi r \rho^0$

$-4\pi r \rho^0$

(a)

(b)

2-3. (a) Total correlation function. (b) Differential correlation function.

Reduced RDF or total correlation function (Varshneya)
$t(r) = J(r)/r = 4\pi r \rho(r)$

Differential correlation function,
$d(r) = J(r)/r - 4\pi r \rho_o$
- called reduced RDF, G(r), by Elliott.

Radial distribution function (RDF):

$$J(r) = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_o g(r)$$

Area under the first peak in J(r) vs r plot gives the number of NN or the CN.
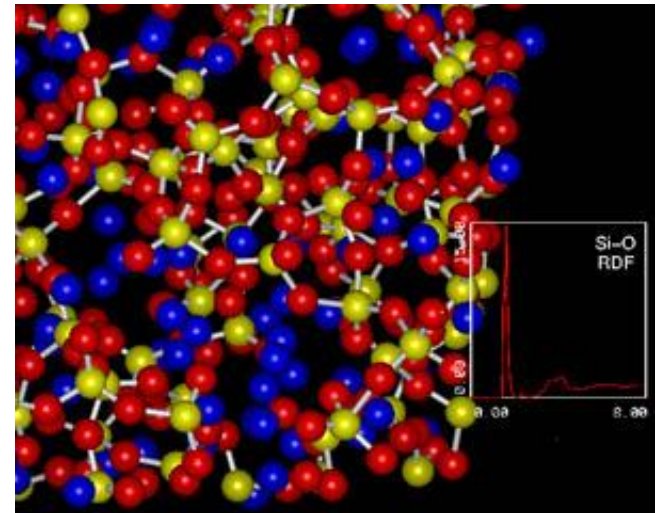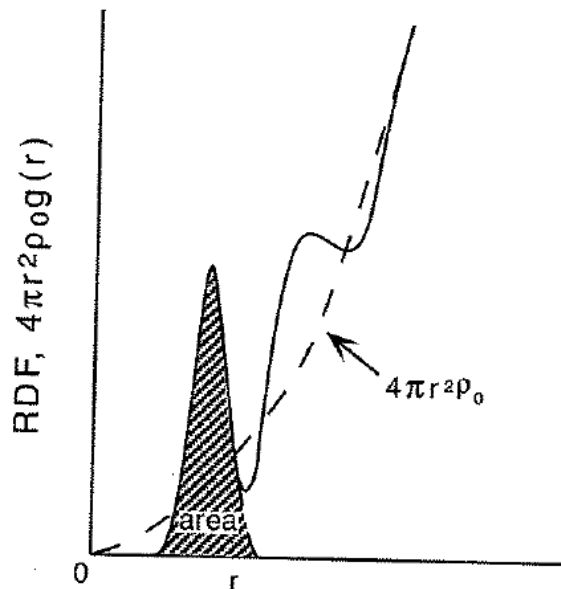

Figure 2-2b. Radial distribution function versus r. For uniform probability, the RDF is simply a parabola.

The X-ray, e or n scattering experiment: measure intensity, I (θ) i.e. I(K)

Elastic scattering of plane wave

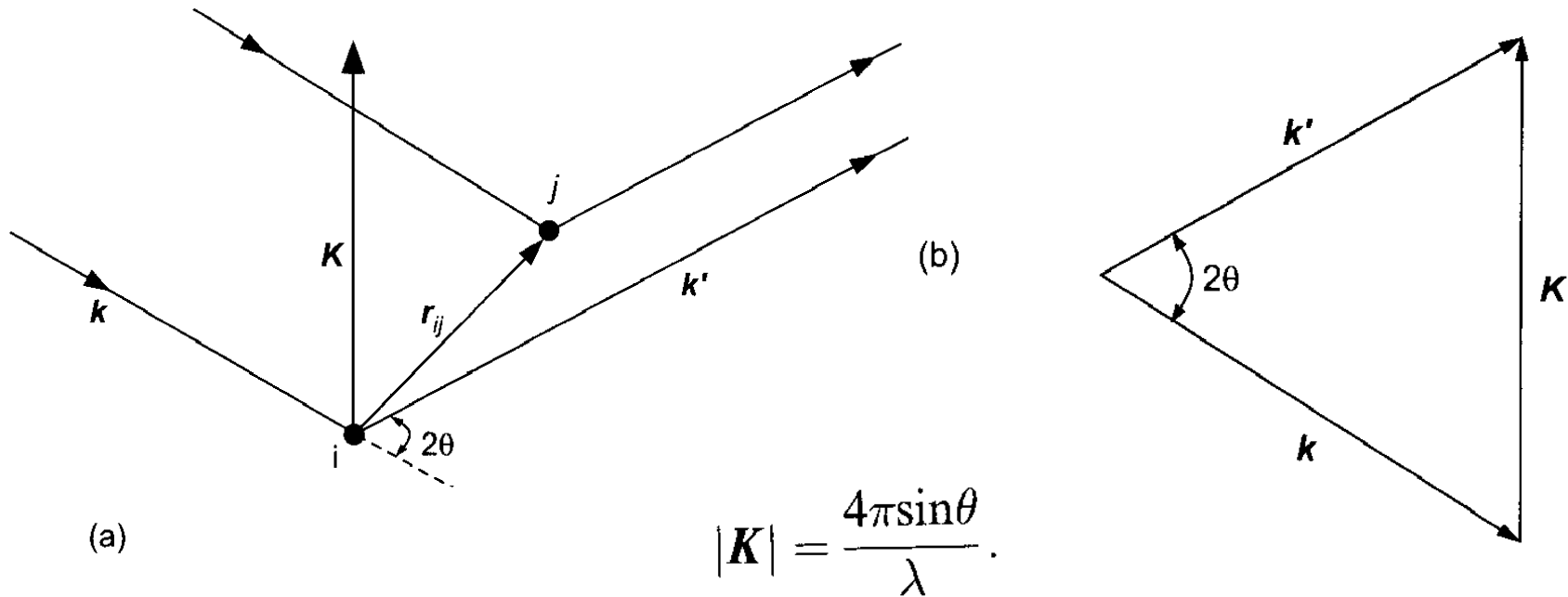$$|K| = \frac{4\pi \sin\theta}{\lambda}.$$

Fig.2.50 (*a*) Path difference for waves diffracted from two arbitrary scattering centres i, j, related by a vector r_{ij}: the incident beam has wavevector k and the diffracted beam has wavevector k'. The scattering vector K is also shown. (*b*) Definition of the scattering vector $K = k' - k$. K has the value $(4\pi/\lambda)\sin\theta$ for elastic scattering ($|k| = |k'| = 2\pi/\lambda$).

RDF J(r) or reduced RDF G(r) for a simple glass

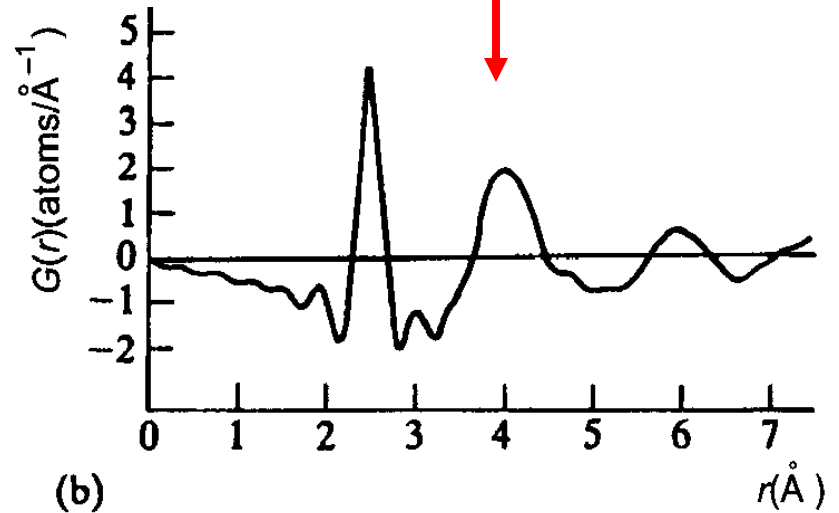Obtain G(r) from a suitable Fourier transform of I(K)

Data are for a-Ge.

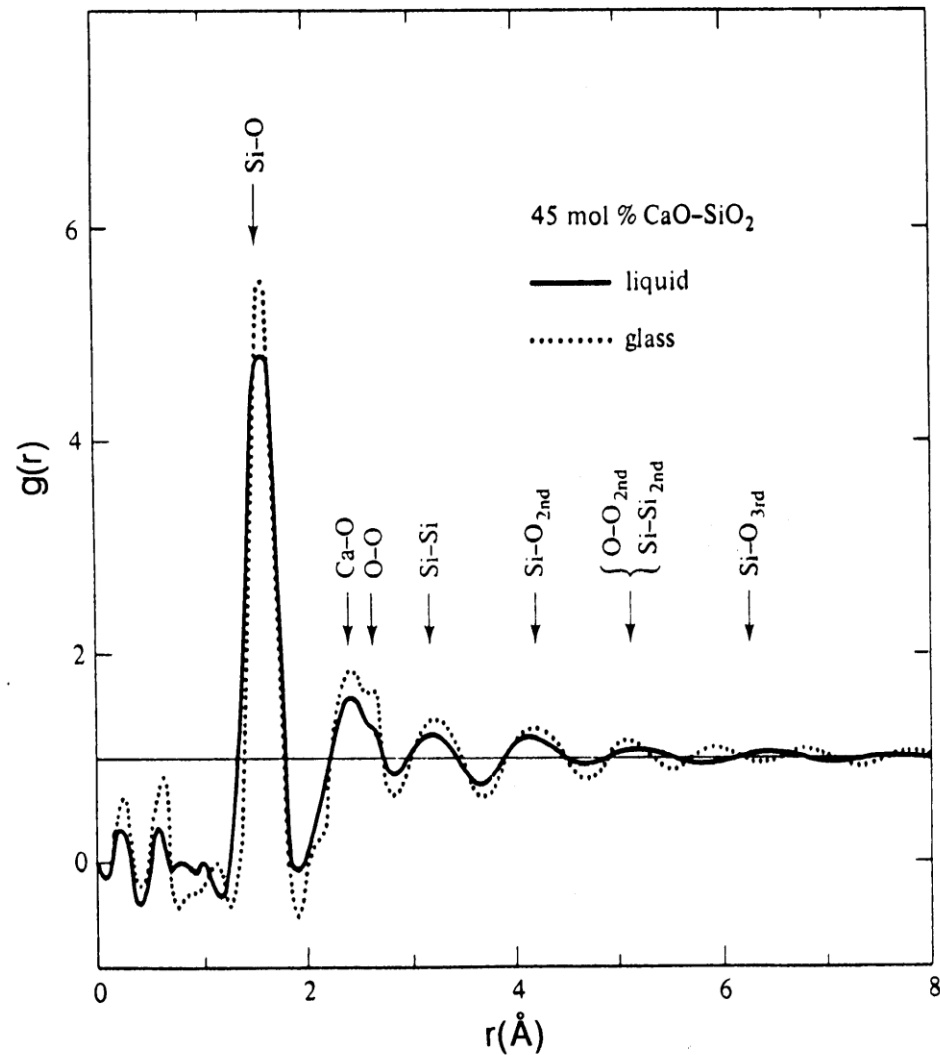Elliott: The Physics and Chemistry of Solids
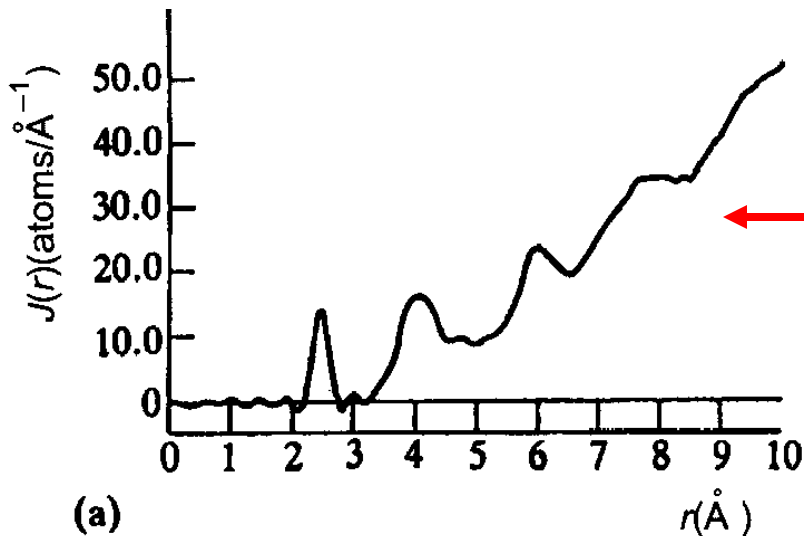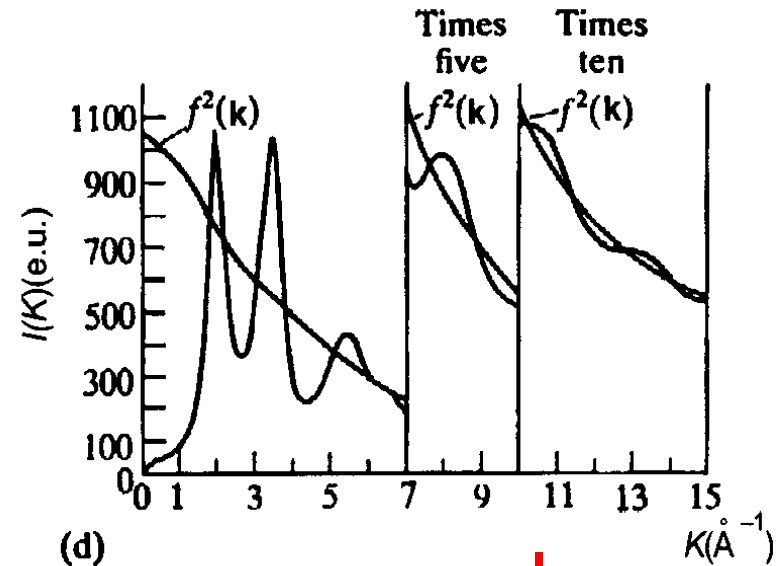
RDF of complex glasses

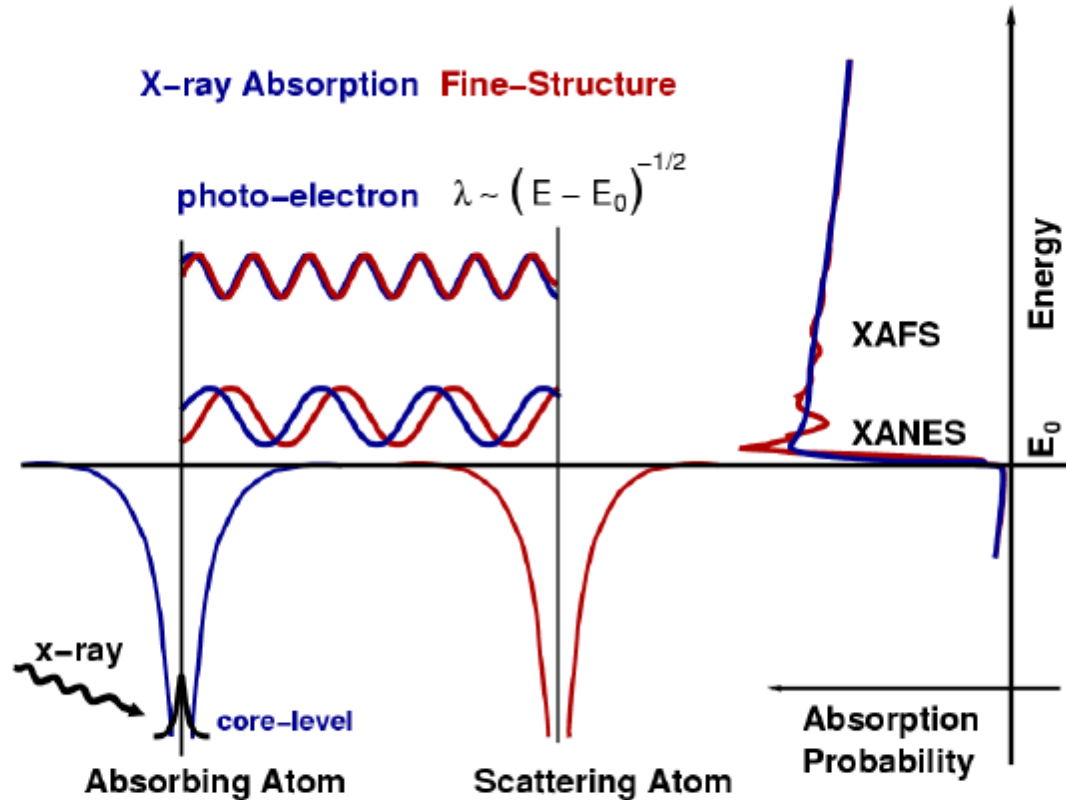**Figure 2-5.** Comparison of $g(r)$ between the glassy and the liquid states for $45CaO \cdot 55SiO_2$. (After Y. Waseda and J. M. Toguri, *MeT. Trans.* **8B**, 563 (1977).)

X-ray absorption spectrum

X-ray Absorption Fine-Structure

photo-electron $\lambda \sim \left(E - E_0\right)^{-1/2}$

XAFS

XANES

x-ray

core-level

Absorbing Atom   Scattering Atom

Absorption Probability

Energy

E_0

Smooth energy dependent absorption + characteristic sharp edges

Figure 3.2: XAFS occurs because the photo-electron can scatter from a neighboring atom. The scattered photo-electron can return to the absorbing atom, modulating the amplitude of the photo-electron wave-function at the absorbing atom. This in turn modulates the absorption coefficient $\mu(E)$, causing the EXAFS.
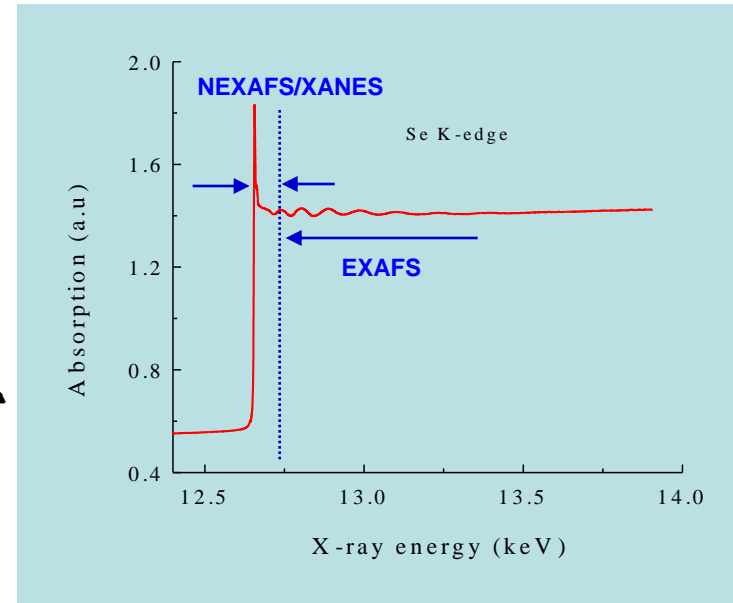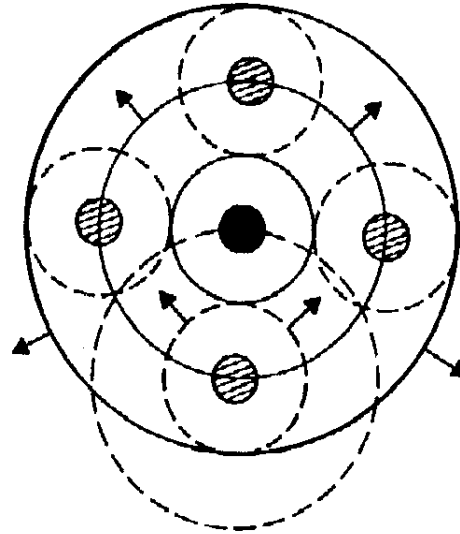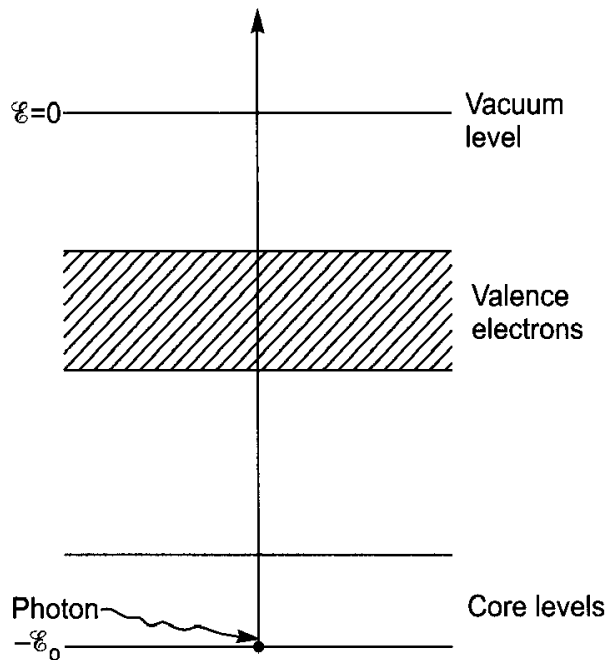
X-ray absorption process

Fig.2.64 Schematic illustration of the internal-diffraction process leading to X-ray absorption fine structure. An atom (filled circle) on absorbing an X-ray photon with energy greater than the electron binding energy, creates an outgoing photoelectron wave (solid circular line) that can backscatter (dashed circular lines) from neighbouring atoms (hatched circles). Interference takes place where outgoing and backscattered waves overlap, and this modulates the X-ray absorption coefficient.

The low energy (< ~ 50 eV) photoelectrons have significant probability of multiple scattering before returning to the emitting atom.

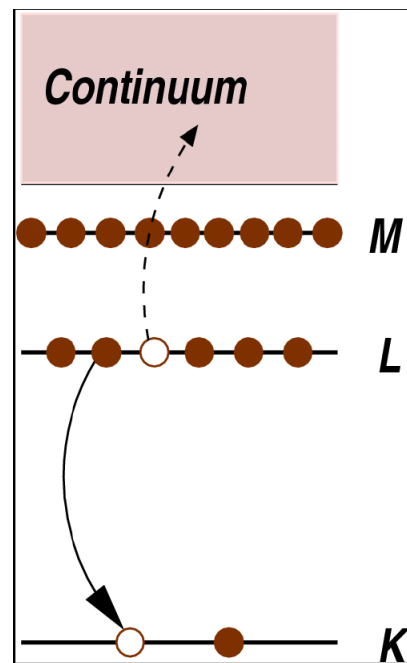# Subsequent to X-ray absorption

X-ray Fluorescence
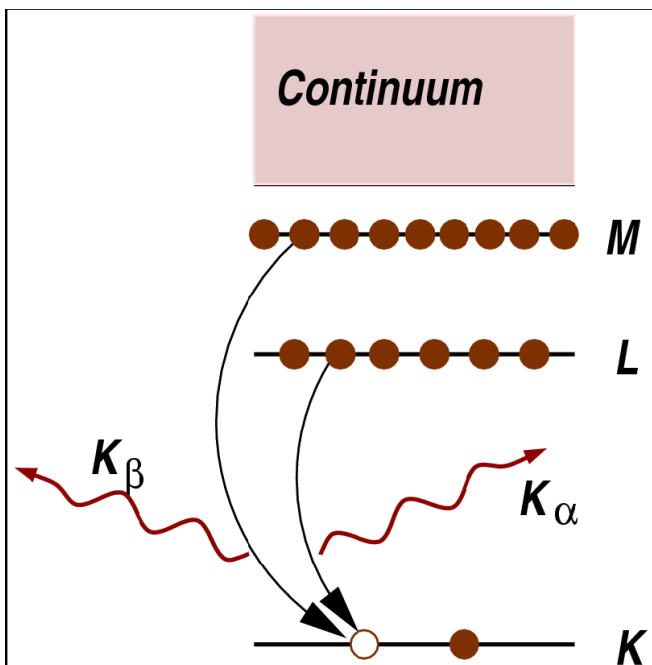
Auger e emission
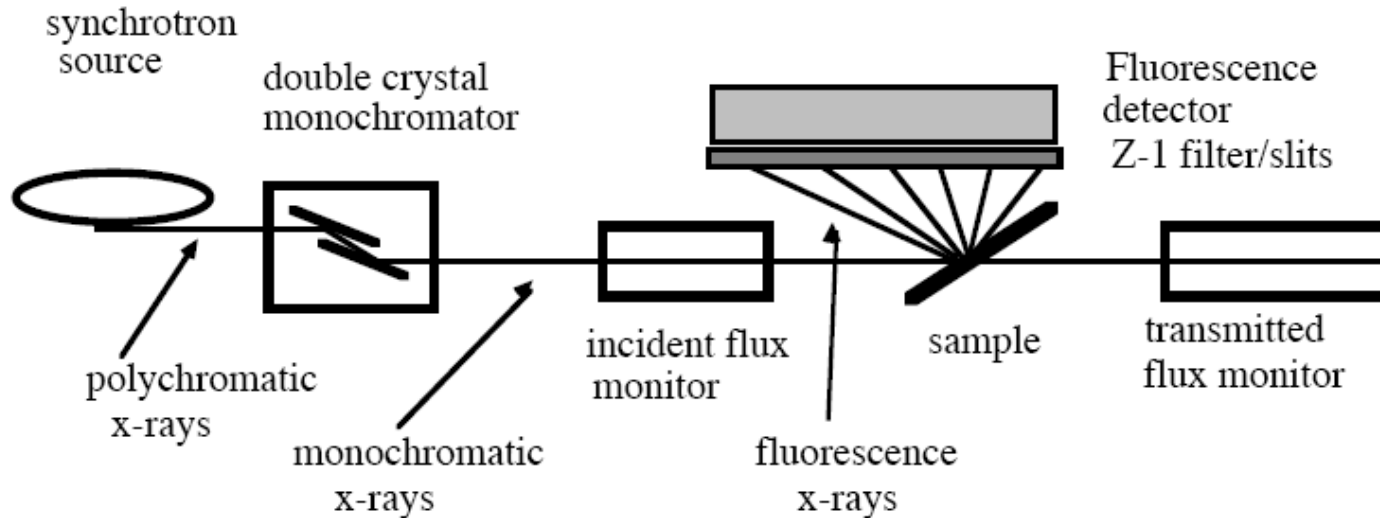
Experimental setup

Figure 1 – Schematic XAFS experiment

EXAFS: small signal on a large background
→
Need strong X-ray source i.e. a synchrotron

Measure transmitted intensity $I = I_0 \exp{-\mu(E)t}$; t is sample thickness

Obtain absorption coefficient, $\mu(E) = -(1/t) \ln(I/I_0)$

Alternatively, measure fluorescence signal $I_f = I_0 \mu(E)$.
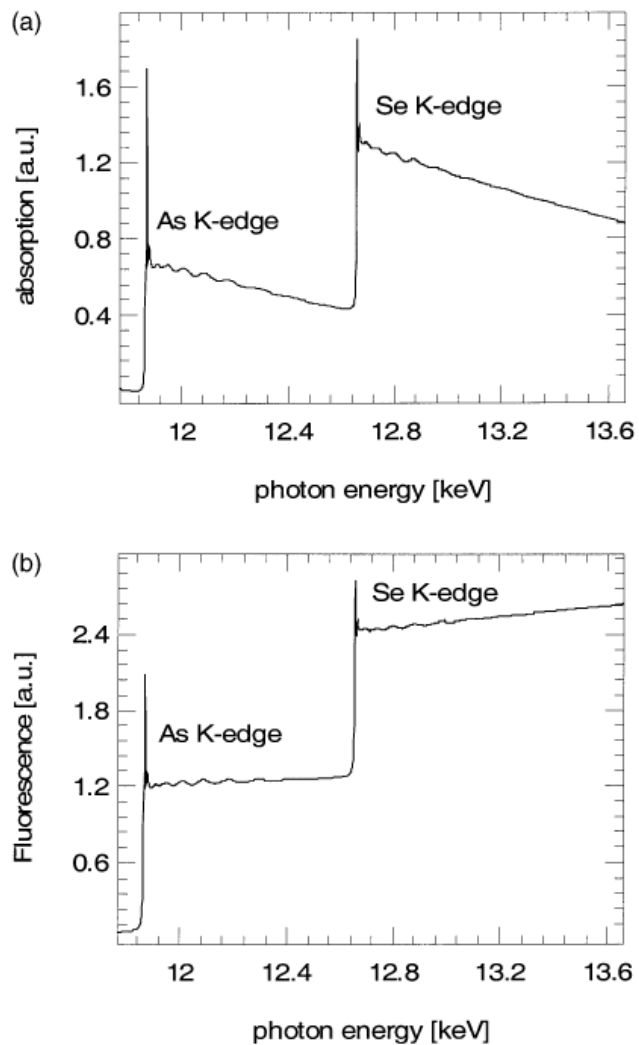
Fluorescence and transmission give same info

Fig. 2. As and Se K-edge transmission (a) and fluorescence (b) spectra for glassy As_2Se_3 at room temperature. These two spectra were taken during the same scan.

Experimental EXAFS definition:

$$\chi(\mathbf{E}) = \frac{\mu(\mathbf{E}) - \mu_0(\mathbf{E})}{\Delta\mu_0(\mathbf{E_0})}$$

Away from absorption edges, absorption coefficient μ depends strongly on x-ray energy E and atomic number Z, and on the density and Atomic mass A i.e. $\mu \sim Z^4/AE^3$
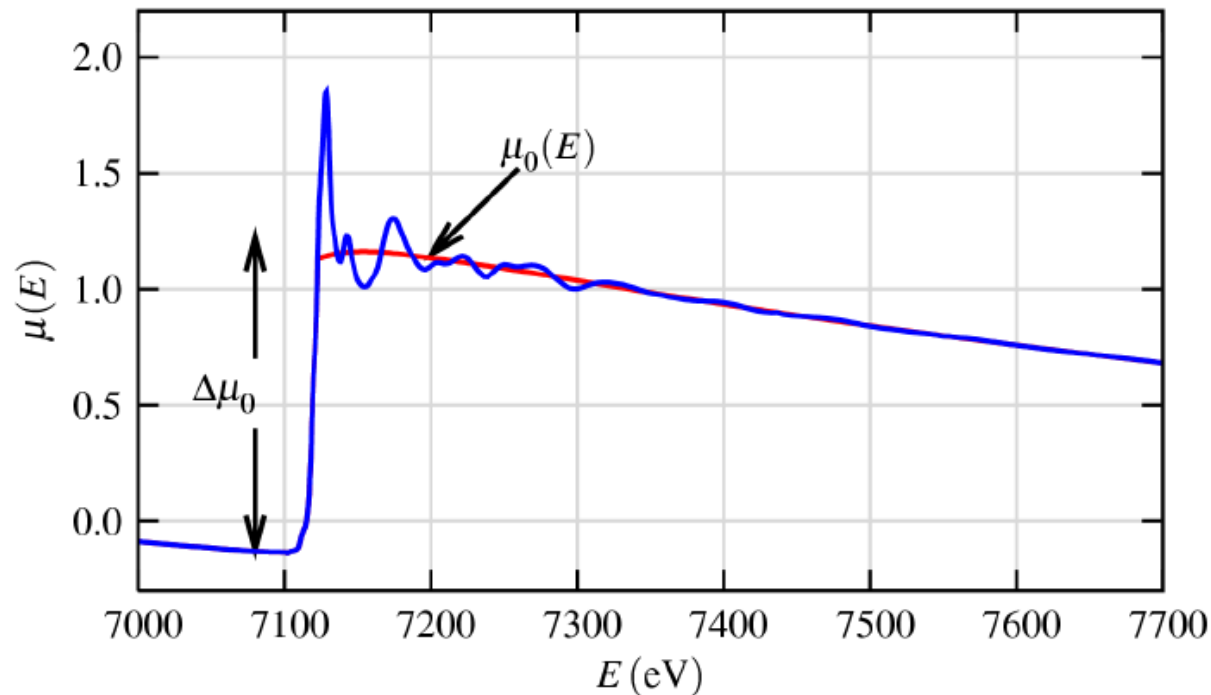
EXAFS of As-Se glass film
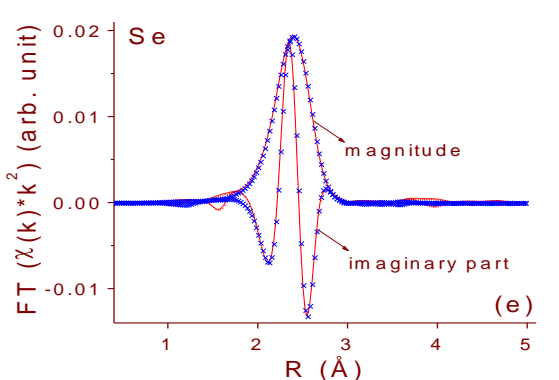
Chen et al. (2001)

Data Analysis: Standard EXAFS Equation
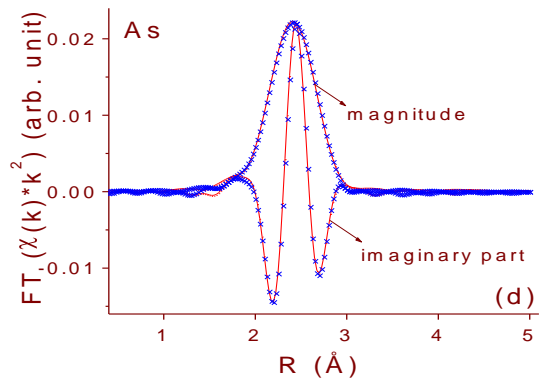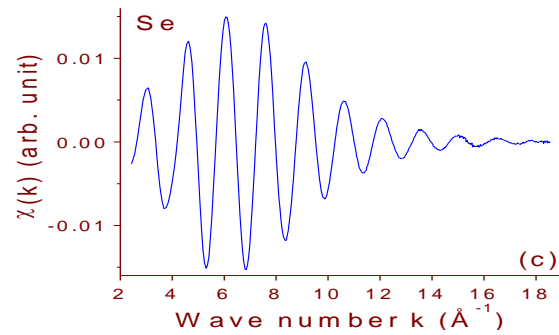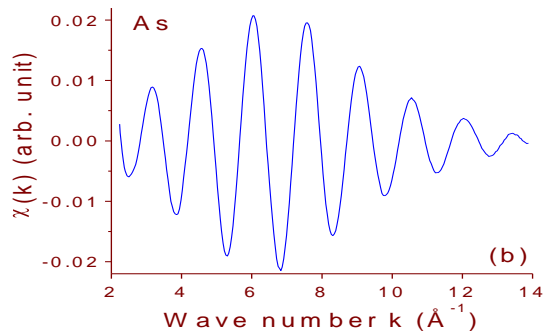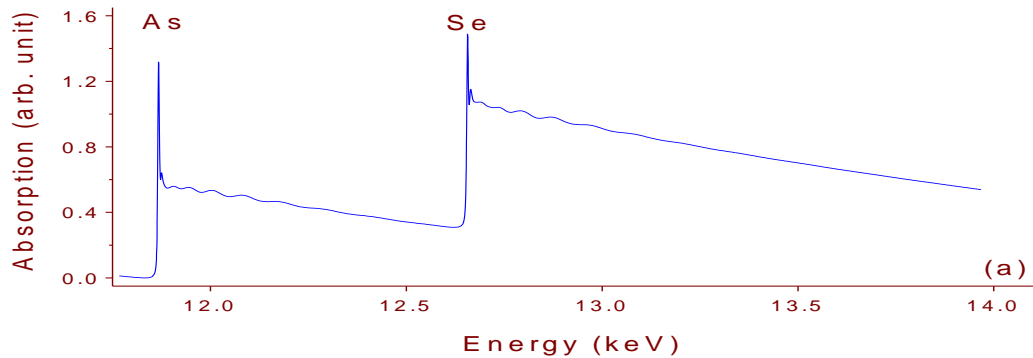
(Sayers, Stern, Lytle (1971))

$$\chi(k) = - \sum_i \frac{N_i}{R_i^2} \frac{|f_i(\pi)|}{k} \exp(-2R_i/\lambda_e) \exp(-2\sigma_i^2 k^2)$$

$$\times \sin[2kR_i + 2\delta(k) + \eta_i(k)], \quad k=2\pi/\lambda \quad = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$$

where sum is over all i shells of backscattering atoms, each containing N_i atoms at distance R_i. $f_i(\pi)$ backscattering amplitude, λ_e mean-free path of e in the glass, σ_i is r.m.s. displacement (so called Debye-Waller factor including static and thermal disorder). The sin term is the interference part including phase shift of photoelectron; $\delta(k)$ and $\eta_i(k)$ are additional phase shifts as the photoelectron encounters atomic potentials in emission and backscattering process.

w
h
e
If f(k), $\delta(k)$ and $\eta_i(k)$ are found from known structures, N_i, R_i and σ_i are obtained
from the fitting of data.
t
e

Note: N_i and σ_i are highly correlated in the data analysis, which introduces large uncertainty in their absolute value.

Photoinduced change in the structure of As-Se film
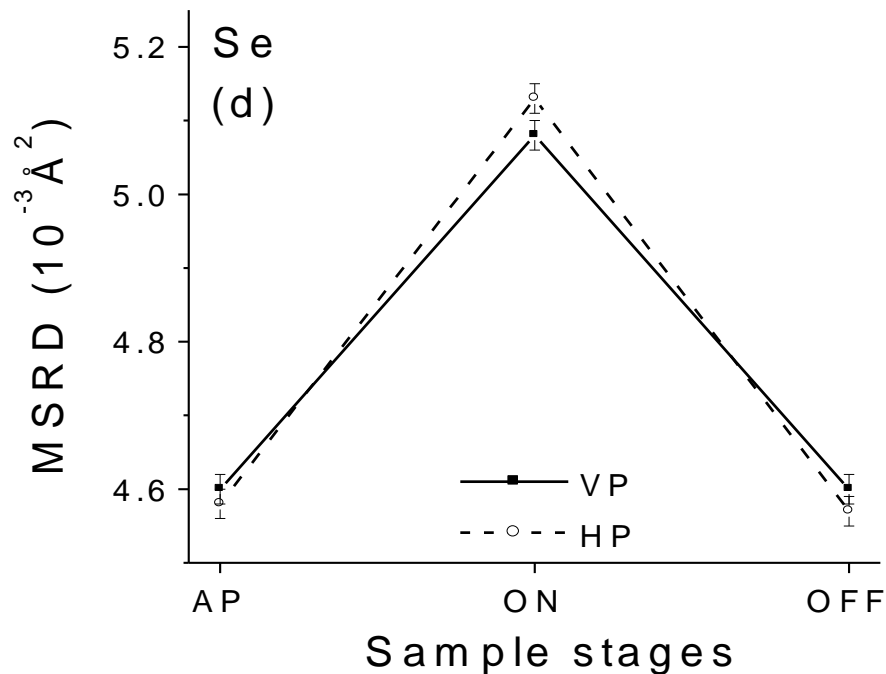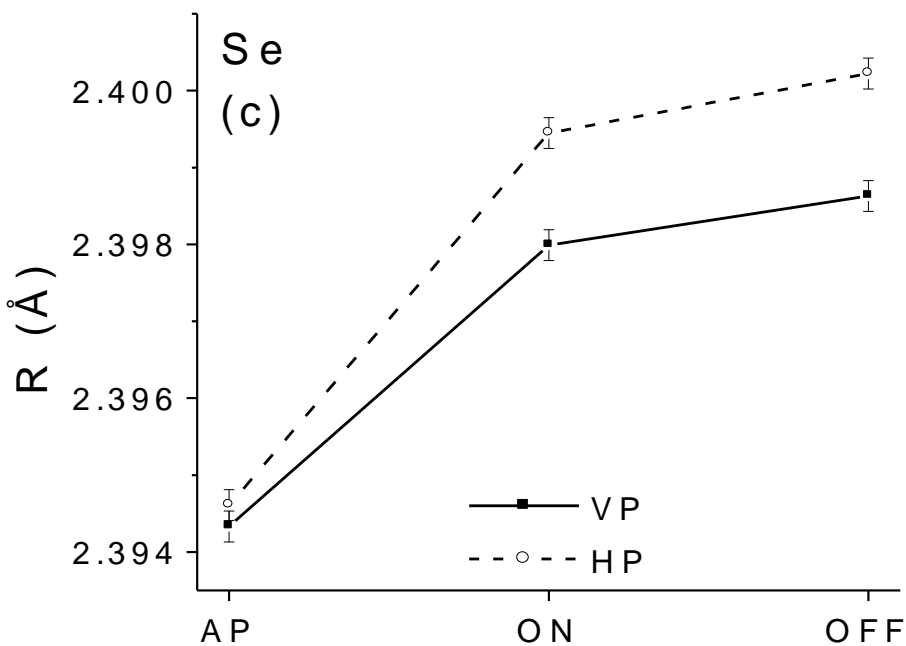
Note: EXAFS allows the determination of anisotropic aspects of structure.

Local structure: Si vs Na

Greaves et al. 1981, 1985

Fig. 4 *A*, Atomic distributions *F*(*r*) about silicon for: *a*, α-quartz; *b*, silica; *c*, sodium disilicate glass; *d*, soda-lime–silica glass. These were obtained by Fourier transforming the normalized EXAFS spectra given in Fig. 2. *B*, Atomic distributions *F*(*r*) about sodium for: *a*, sodium disilicate glass; *b*, soda-lime–silica glass. Following
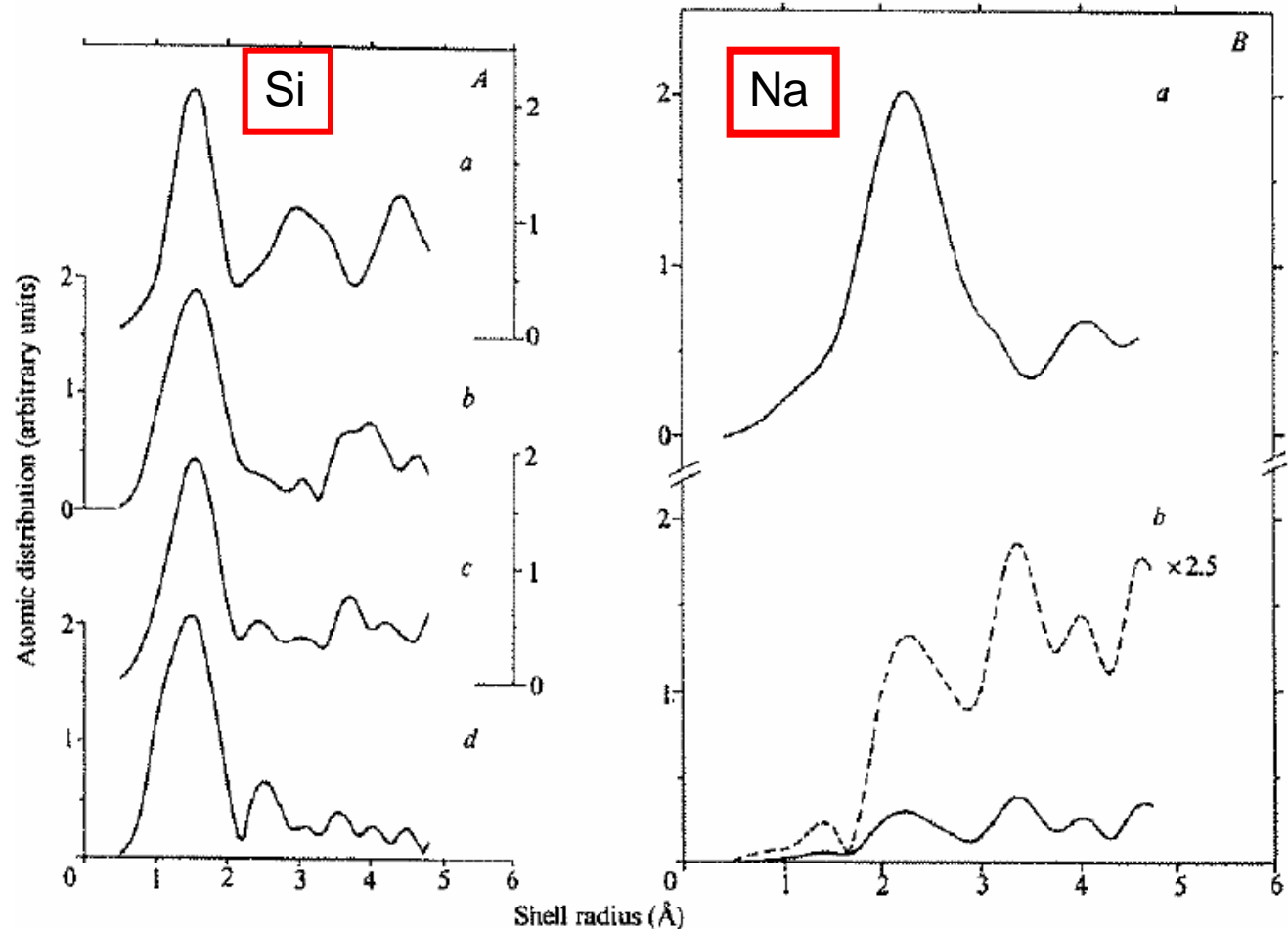
Structure of alkali silicates vs. germanates

1. The local structure around Si is nearly the same in various silicates and quartz crystal.
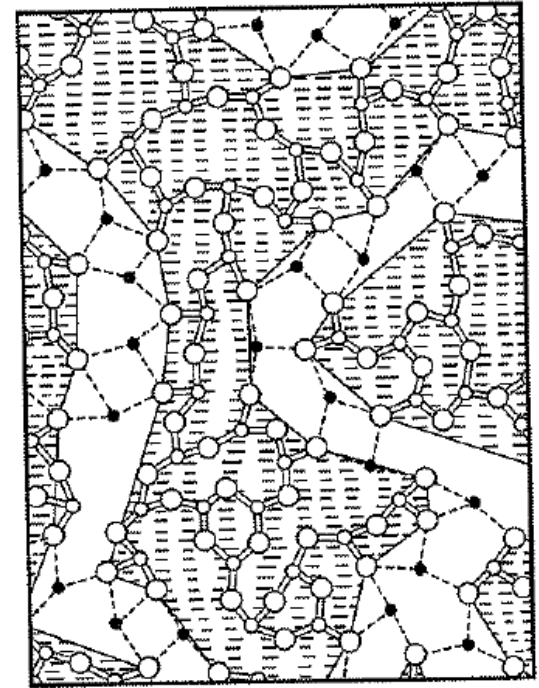2. The local environment around Na is quite different from that around Si, but similar to that found in corresponding crystals (which possess wide variety of Na coordination).
3. The MSRD for Na in glass is quite small, compared to that for Si i.e. Na has a highly ordered environment.

Greaves: The oxygen coordination around Si and Na must also be different i.e. BOs preferentially bond to Si and NBOs surround the alkali ions
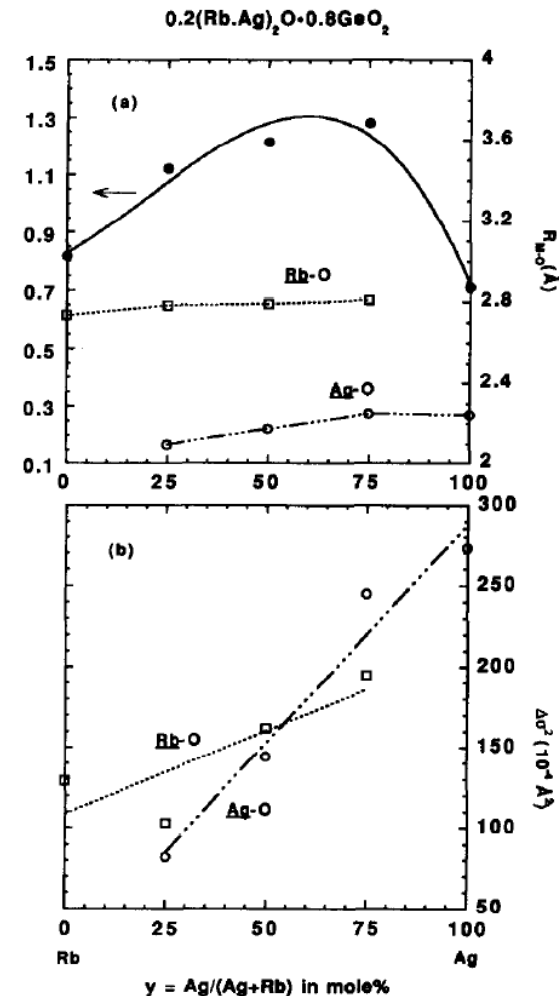=> Modified random network model of alkali silicates.

Na   Si   BO   nBO
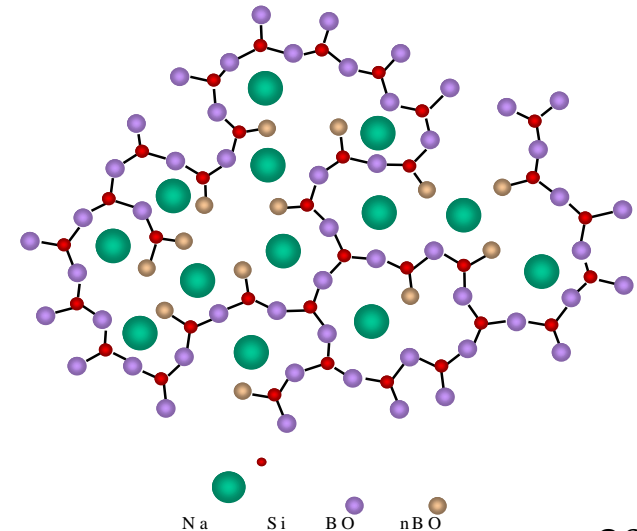
Local structure around Ge in Rb-germanate

Samples		R_{Ge-O} (Å)	CN_{Ge-O}	$\_\sigma^2_{Ge-O}$ ($\times 10^{-4}$Å^2)
1. $xRb_2O\bullet(1-x)GeO_2$				
%Ag$_2$O	**%Rb$_2$O**			
0	2	1.74(0)	4.8	7
0	5	1.74(1)	4.4	8
0	10	1.74(6)	4.8	23
0	15	1.76(1)	4.0	12
0	20	1.75(5)	4.2	16
2. $0.2[yAg\bullet(1-y)Rb]_2O\bullet0.8GeO_2$				
0	20	1.75(5)	4.2	16
5	15	1.75(2)	4.2	14
10	10	1.75(0)	4.0	19
15	5	1.74(4)	4.0	7
20	0	1.74(5)	4.0	6

Local structure around Rb in Rb-germanate

Samples		R_{Rb-O} (Å)	CN_{Rb-O}	σ^2_{Rb-O} ($\times 10^{-4}$Å^2)
1. $xRb_2O \bullet (1-x)GeO_2$				
%Ag$_2$O	%Rb$_2$O			
0	1	2.81(2)	5.6	220
0	2	2.82(6)	6.1	234
0	5	2.82(1)	5.5	185
0	10	2.82(4)	7.9	178
0	15	2.76(6)	5.6	119
0	20	2.73(5)	5.2	129
2. $0.2[yAg \bullet (1-y)Rb]_2O \bullet 0.8GeO_2$				
0	20	2.73(5)	5.2	129
5	15	2.78(3)	4.4	103
10	10	2.78(9)	6.5	162
15	5	2.80(9)	6.2	195
20	0			

0.2(Rb.Ag)$_2$O·0.8GeO$_2$

y = Ag/(Ag+Rb) in mole%

Huang et al. (1994): MSRD for alkali > that for Ge in germanate glasses. Also it is ~ an order of magnitude larger than in silicates => the MRN model may not be applicable to germanates.

Comparison of XRD, EXAFS and EXELFS

Figure 3. The FT[χ'(k)] using K-edge EXAFS and L-edge EXELFS are shown without phase shift corrections for (a) Ni and (b) Cu. In (a) the curves are displaced vertically for clarity
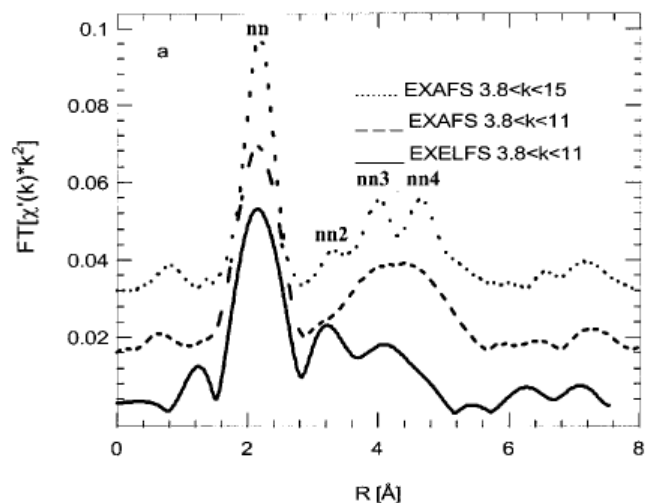
Table 1. Comparison between atomic neighbour distances and the coordination number of the first shell as determined by XRD, EXAFS and EXELFS for fcc Ni and Cu.

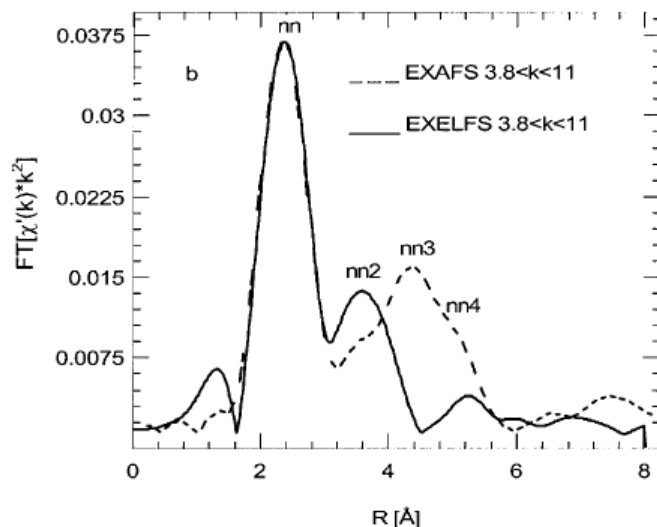|	Cu						Ni					
	nn (Å)	nn2 (Å)	nn3 (Å)	nn4 (Å)	N ($S_0^2 = 1$)	S_0^2 ($N = 12$)	nn (Å)	nn2 (Å)	nn3 (Å)	nn4 (Å)	N ($S_0^2 = 1$)	S_0^2 ($N = 12$)
XRD	2.56	3.62	4.43	5.02	—	—	2.49	3.52	4.32	4.98	—	—
EXAFS	2.54	3.76	4.48	5.02	10.98	0.91	2.47	3.57	4.28	4.93	10.67	0.89
EXELFS	2.52	3.77	—	—	10.10	0.84	2.48	3.66	—	—	9.66	0.80

Alamgir et al. Phil.Mag. Lett., 2001, VOL. 81, 213.

Homework for Section 6
Out: Feb 21. In: March 5, 2007.

1. Read the paper by Huang et al. JNCS 180 (1994) 40. Its pdf file is posted on BB within the Supplemental Reading folder.

2. In ~ ½ page (single space, 12 Times Roman font, 1" margin), describe what you think is the most significant message of this paper. Include justification in support of your answer.

3. In the remaining ~1/2 page, describe with reason either one deficiency of this work, or an extension of what you would propose to continue this work.

4. Submit the HW by March 5, 2007.