Applications of Quick EXAFS to Materials Science:
case studies of induced phenomena in disordered solids

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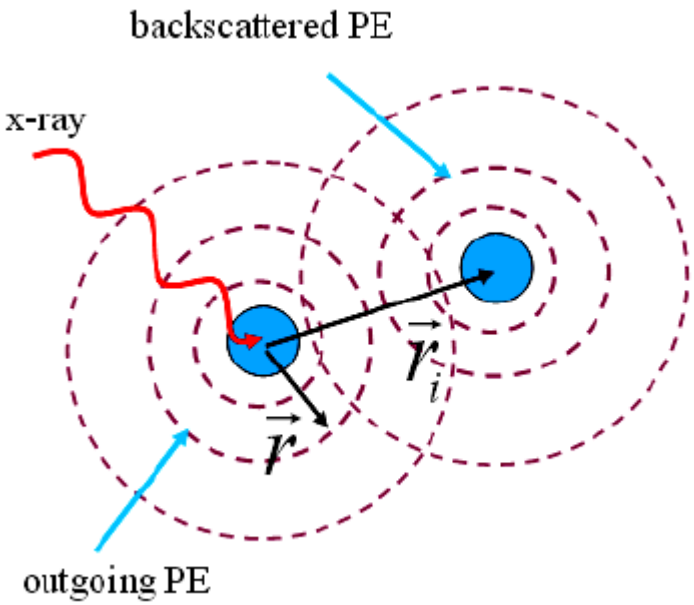
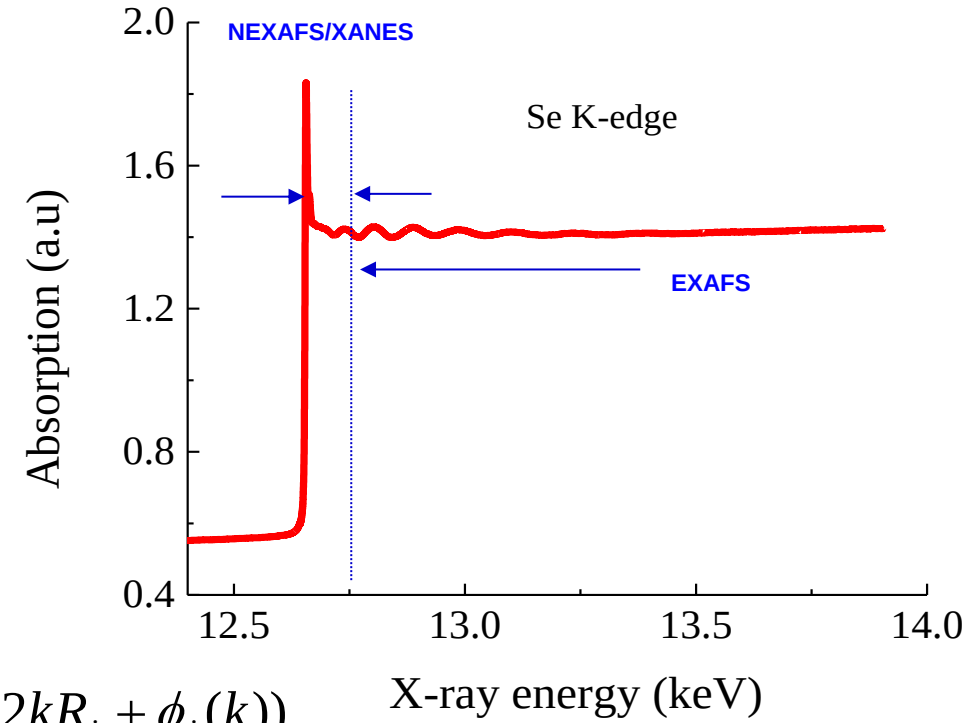
EXAFS





$$\mu_i(k) = \frac{\mu_1(k)}{\mu_0(k)} = \sum_j \frac{N_j F_j(k) S_0^2(k) \cdot \sin(2kR_j + \phi_j(k))}{kR_j^2 \cdot \exp\left(\frac{2R_j}{\Lambda} + 2k^2\sigma_j^2\right)}$$

$\mu_1(k)$ and $\mu_0(k)$ are terms contributed by single scattering and background, respectively (multiple scattering terms are negligible for the EXAFS region); $k \approx 0.512(E-E_0)^{1/2}$ Å^{-1} is the wavevector of the photoelectron, E_0 – threshold energy; S_{0j} – passive electron reduction factor; n_j – degeneracy of the path; $N_j = n_j S_{oj}^2(k)$ – number of neighbors in the *j*th shell at an average distance R_j; $F_j(k)$ is the effective amplitude of backscattered electron wave, $\phi_j(k)$ – effective phase shift between backscattered and outgoing electron wave; Λ is the mean free path of photoelectrons and $\sigma_0^2{}_j$ – the Debye-Waller factor related with disorder.

Sang-Wook Han, International Journal of Nanotechnology 3, 396 (2006)

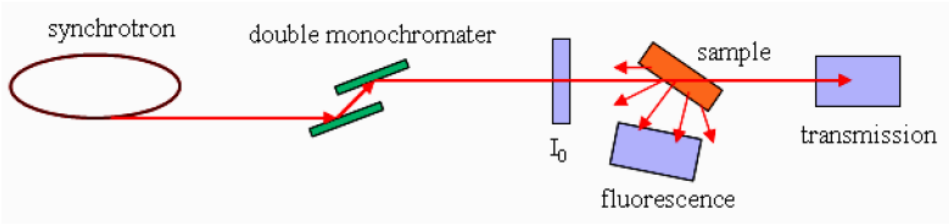
EXAFS

Typical acquisition time: ~20-60 min/scan

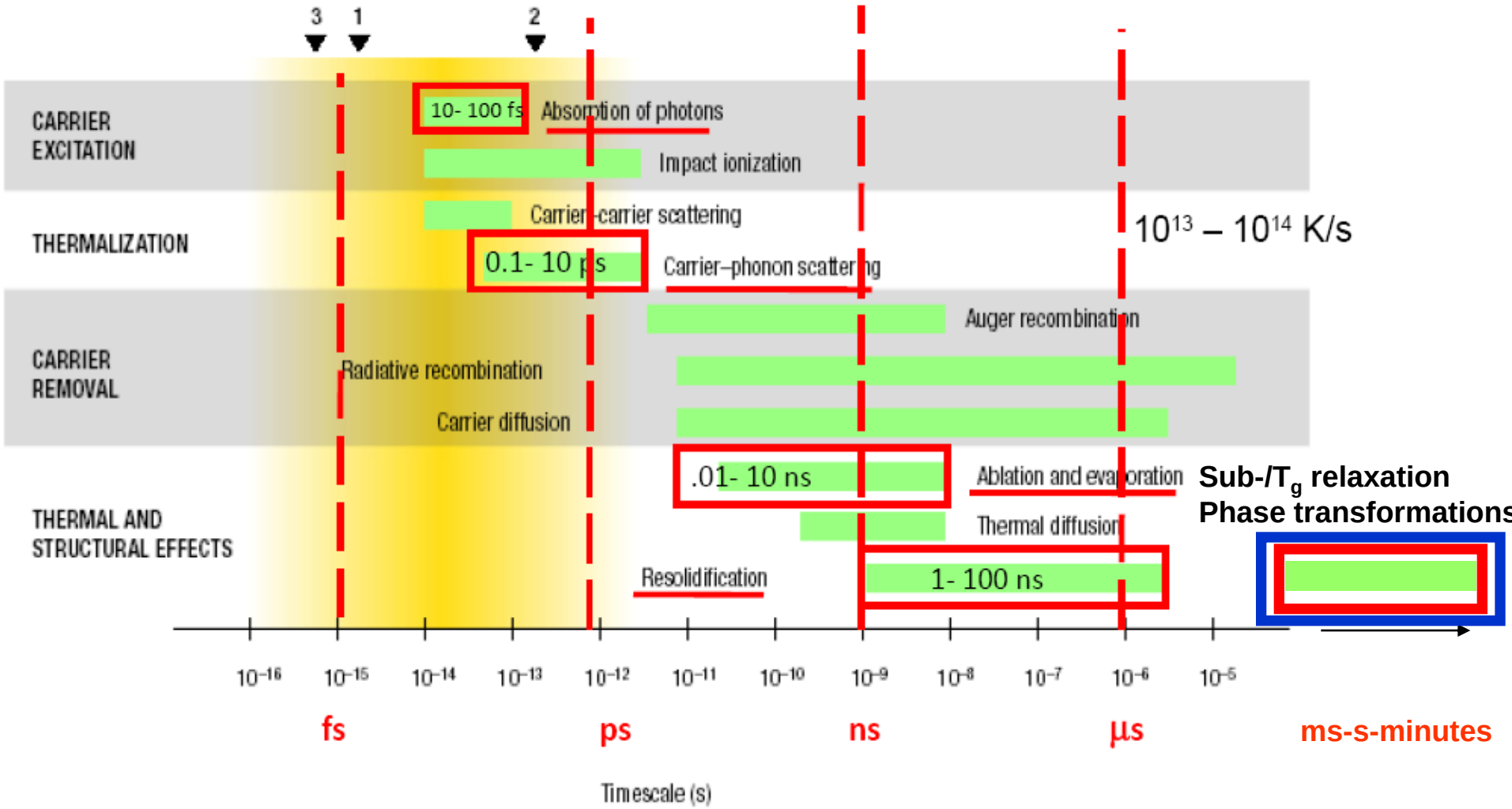
Suitable for

- **Local environment around specific sort of atoms (structure) – N_j, R_j, $\sigma_0^2{}_j$**
- **Difference between various phases/compositions/states**
- **Kinetics studies of suitably slow reactions**
- ***in situ* studies of stationary regimes**

Not suitable for *in-situ* studies of fast kinetics



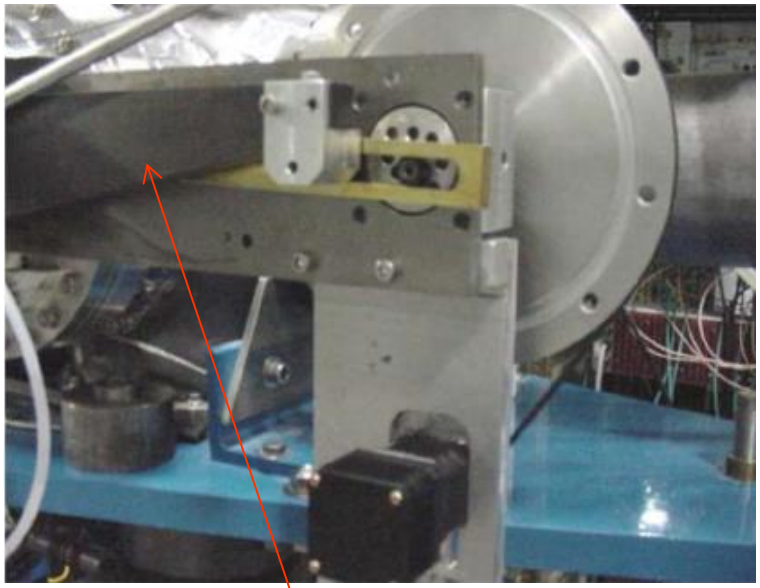
MODEL: Typical excitation and energy transfert time

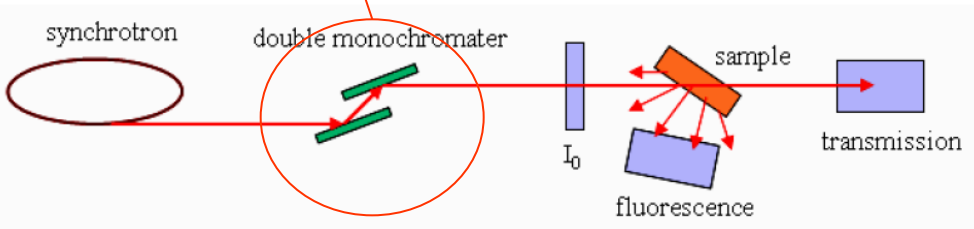


Sundaram et Mazur Nature-Materials 2002

QEXAFS

Figure 1. *A close up of the cam and the small brass lever arm. The rotating cam moves the small lever arm that is coupled to the monochromator tangent arm up and down around the pivot-point* (X18b)





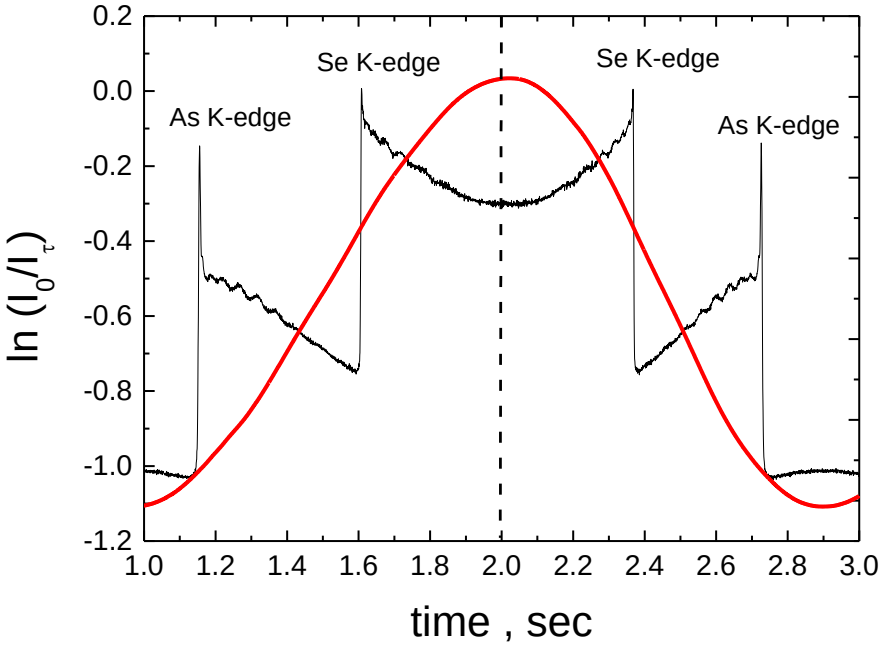


Figure 2. *Raw data obtained for vitreous As_2Se_3 with the setup shown in Fig. 1. Both As and Se K-edges are taken during interval in 1 second.*

Crop-Chop procedure (separate scans)

Athena-Artemis processing

A key instrumentation to achieve a quasi-continuous and smooth movement of the monochromator in QEXAFS setup is the employment of **micro-stepper to provide a large number of motor steps per Bragg degree** (such as 80 000 steps/deg).

S. Khalid, Rev. Sci. Instrum. 81, 015105, 2010.

QEXAFS

Limitations

Instrument related

- Beamline design
- Speed/reproducibility of stepwise monochromator movement
- Integration time required to obtain acceptable statistics
- Experimental setup
- Data acquisition system
- …

Samples related

- X-ray induced changes
- Composition (concentration of probed element)
- Time of reaction (should >> than time to collect 1 spectrum)
- …

QEXAFS limitations (examples)

Increase in X-ray flux (NSLS II)

↓

Better signal at short times

↓

More chances to produce X-ray induced changes

↓

Not the effect you want to measure

Increase in rotation rate

↓

Better time resolution

↓

More noisy signal

↓

Greater scattering in data

As a matter of fact, XAFS spectra may now be measured in 1-10 s time interval or less, depending on the type of monochromator used and energy interval scanned (as compared with minutes and hours using the point-by-point method).

S. Khalid, Rev. Sci. Instrum. 81, 015105, 2010.

QEXAFS

Applications to Materials Science

It's a relatively new technique, the first experiment being performed in 1988
[R. Frahm, Nuclear Instruments and Methods in Physics Research A270 (1988) 578-581].

Time resolution is in the seconds regime, which is suitable for:

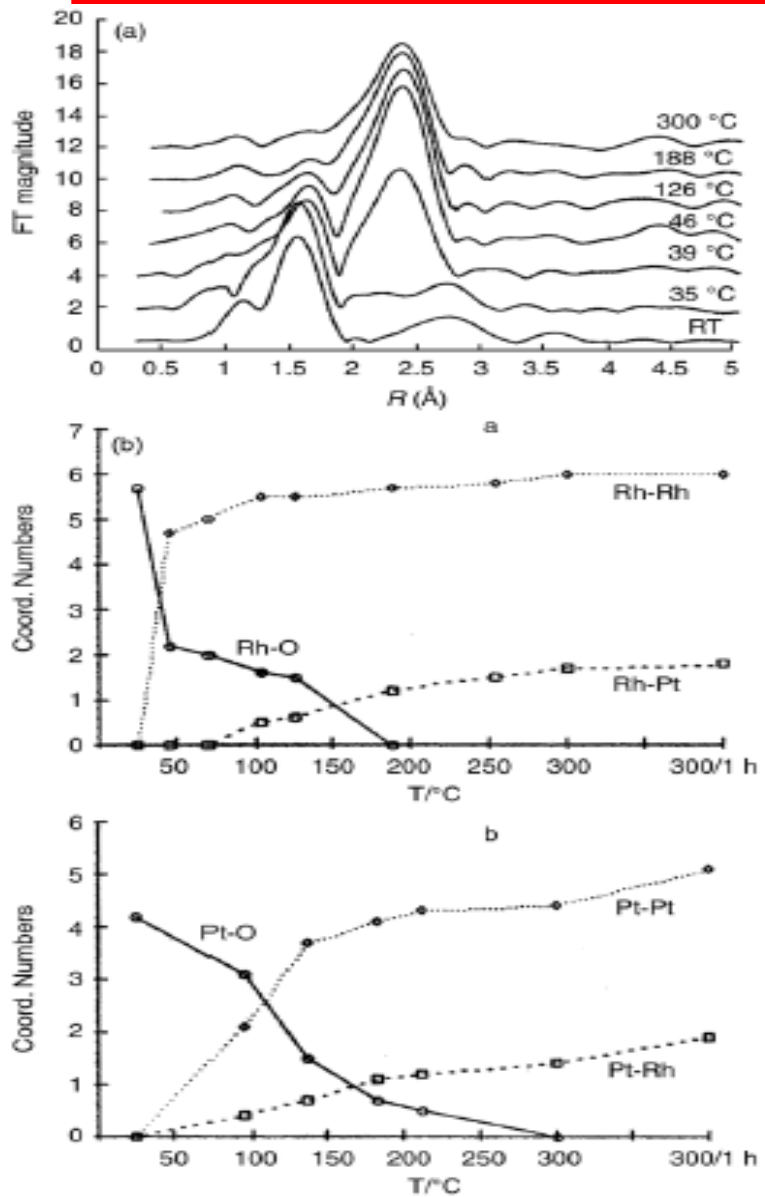
- **catalyst processing and other in situ reaction studies**
- **phase transformations**
- **thin-film deposition studies**
- **solid combustion**
- **reactions in solid/liquid phases**
- **various induced effects (photo, pressure, applied voltage, etc.)**

With the availability of third generation high brightness synchrotron radiation sources, QEXAFS may be used in conjunction with other techniques such as X-ray microprobe to perform microstructural characterization of multicomponent materials on a micron scale.

Sample may be bulk, dilute, powder, thin films, or surfaces.

QEXAFS: applications to Material Science

Catalysis



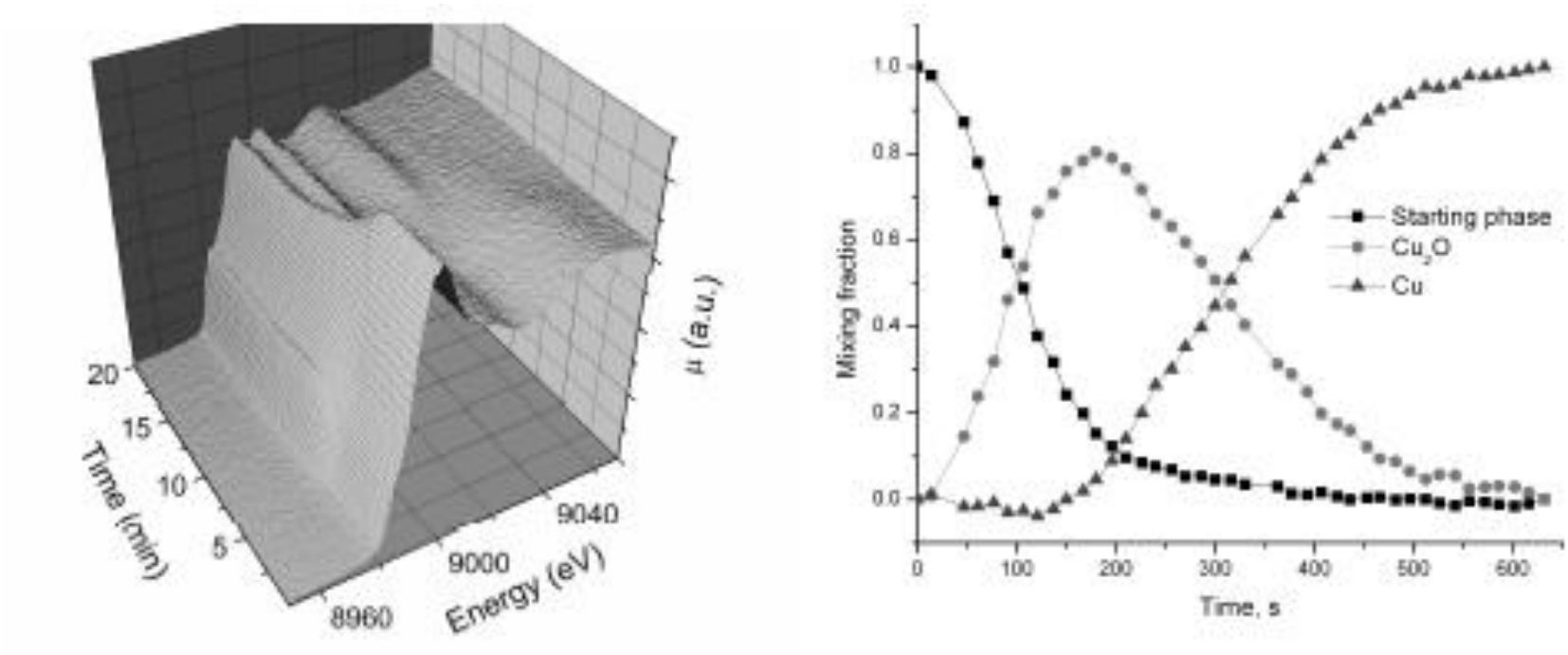
(a) Representative Fourier transforms derived from Rh K edge QEXAFS spectra (60 s acquisition time) obtained during the reduction of calcined 2.6wt% Pt–1.3wt% Rh–zeolite catalyst precursors.

(b) Evolution/diminution of elemental (Pt–Pt, Rh–Rh), metal–O and alloy (Pt–Rh) coordination during temperature programmed reduction derived from QEXAFS measurements made at the Rh K edge and Pt LIII edges.

F. Cimini and R. Prins, J. Phys. Chem. B, 1997, 101, 5277.

QEXAFS: applications to Material Science

Catalysis

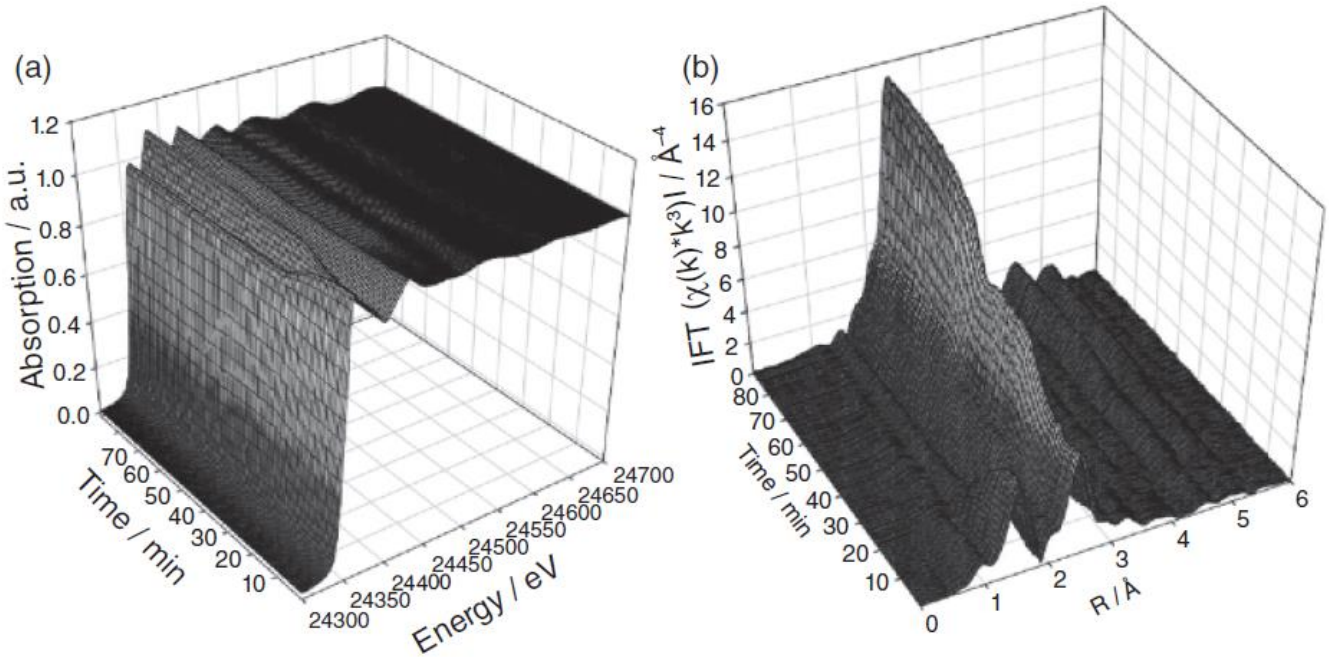


Time resolved Cu K-edge XANES spectra of Cu doped cerium oxide showing Cu phase transformation during reduction at 275°C under 5% H_2 in He (left panel). Results from principal component analysis analysis of CuO reduction at 275°C under 5% H_2 in He using three Cu phases (Cu starting phase, Cu_2O, and Cu(0)) (right panel).

A. Frenkel, NSLS-II BDP 2010.

QEXAFS: applications to Material Science

Catalysis



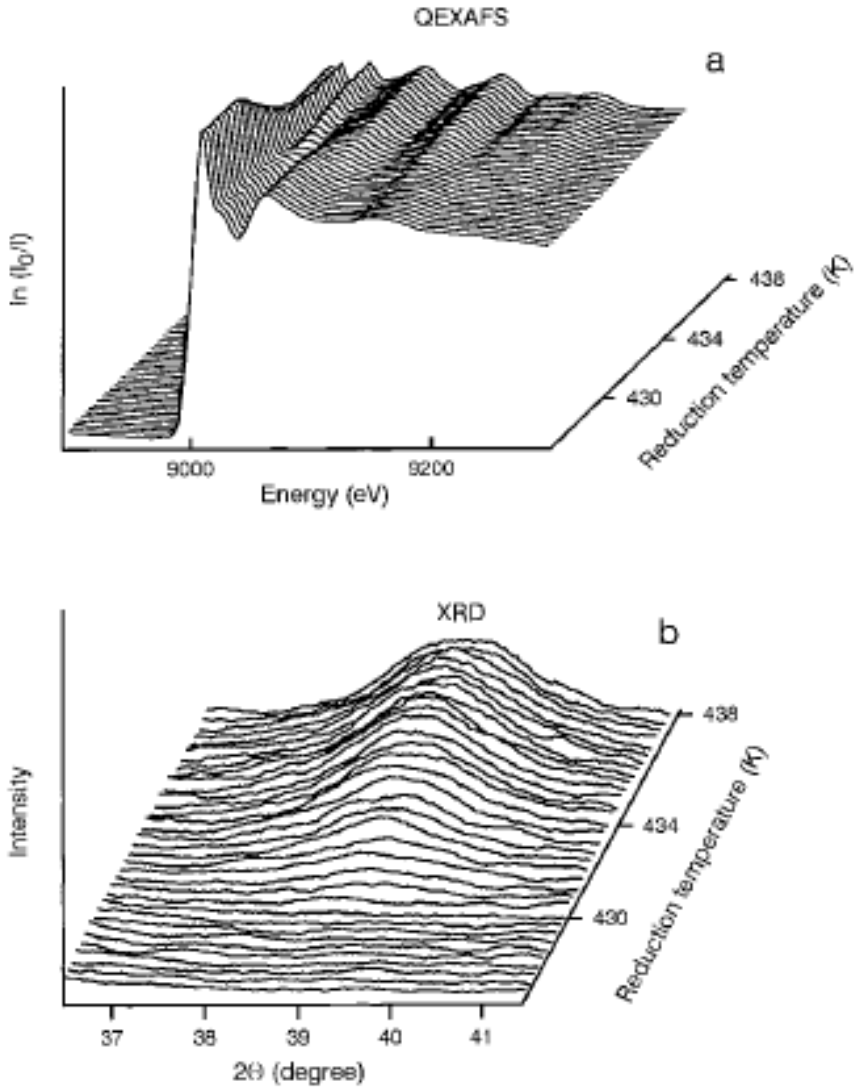
(a) Normalized XANES spectra of the 5 wt % Pd/Al_2O_3 catalyst as a function of time during heating.

(b) Fourier-transformed EXAFS spectra of the 5 wt % Pd/Al_2O_3 catalyst as a function of time.

S.Reimann et al, Journal of the American Chemical Society , 133 (2011) 3921–3930.

QEXAFS: applications to Material Science

Simultaneous measurements (catalysis)



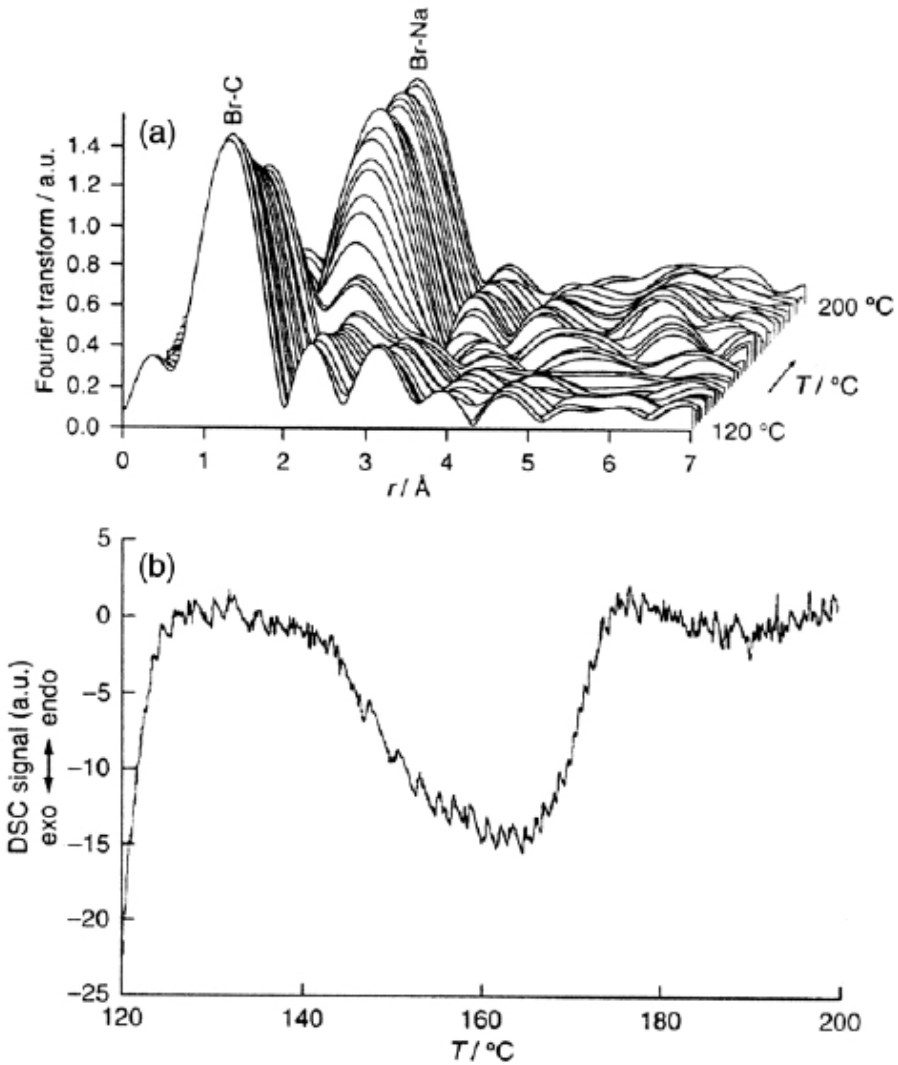
(a) Raw QEXAFS data near the Cu K-edge obtained *in situ* during reduction of a $Cu/ZnO/Al_2O_3$ catalyst. The recording time for each spectrum was 120 s.

(b) In situ XRD diffractograms of the Cu(1 1 1) line recorded simultaneously with the QEXAFS data in (a). The recording time for each diffractogram was 90 s

B.S. Clausen / Catalysis Today 39 (1998) 293-300.

QEXAFS: applications to Material Science

Simultaneous measurements (reactions in solid state)



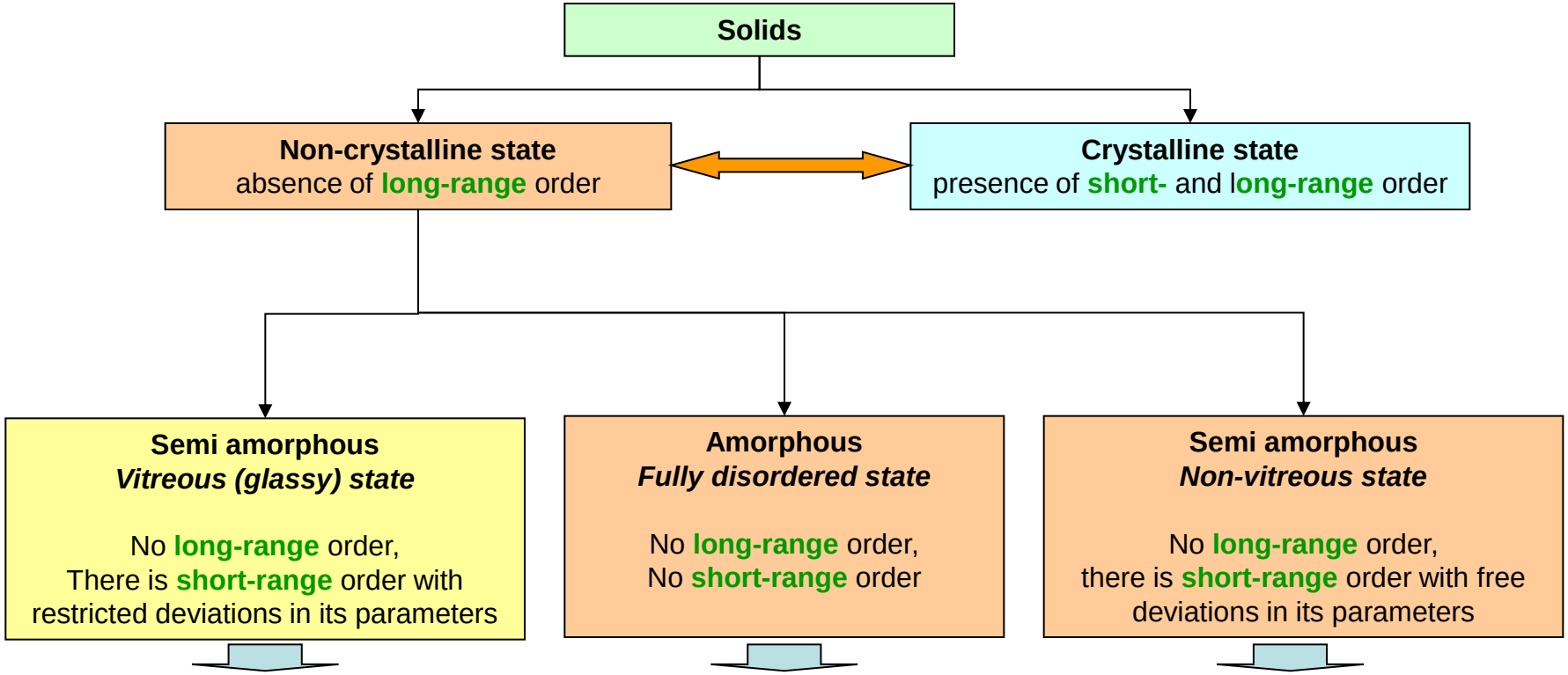
(a) Radial distribution functions derived from Br K edge QEXAFS during the solid state elimination of sodium bromoacetate in the temperature range 393–473 K (heating rate =1 K/min). Spectra recorded every 135 s.

(b) Baseline corrected DSC data collected simultaneously with the QEXAFS

M. Epple, et. al. *Chem. Commun.*, 1996, 1755.

QEXAFS: applications to Disordered solids

Classification of solids due to structural arrangement

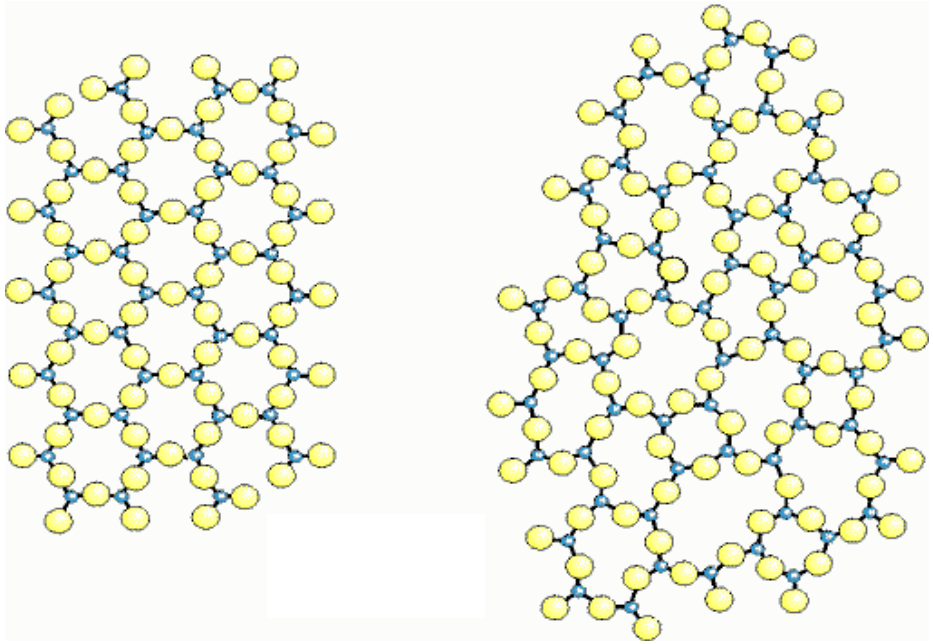


Structural Disorder is a general feature of non-crystalline materials

QEXAFS: applications to Disordered solids

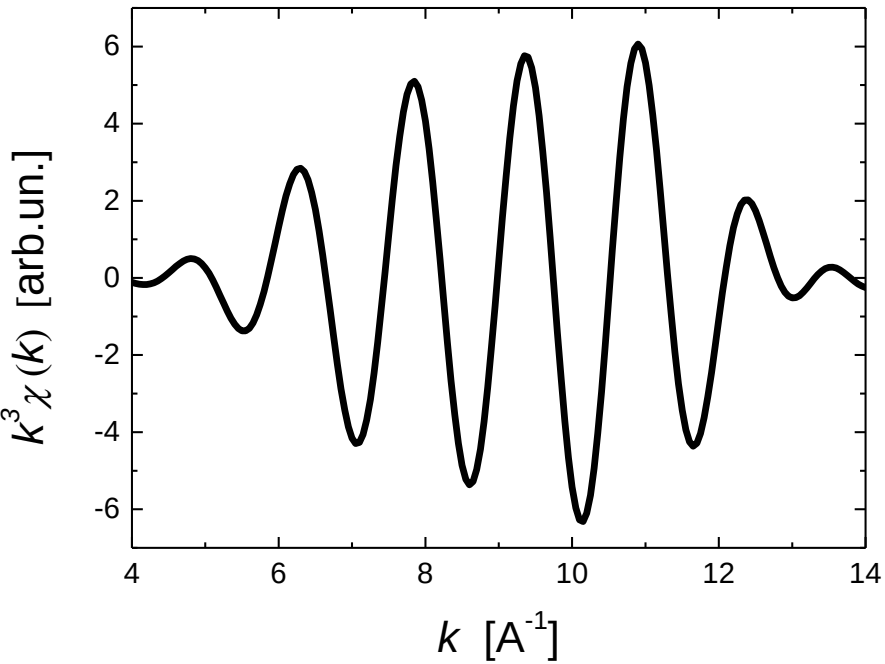
Network glasses

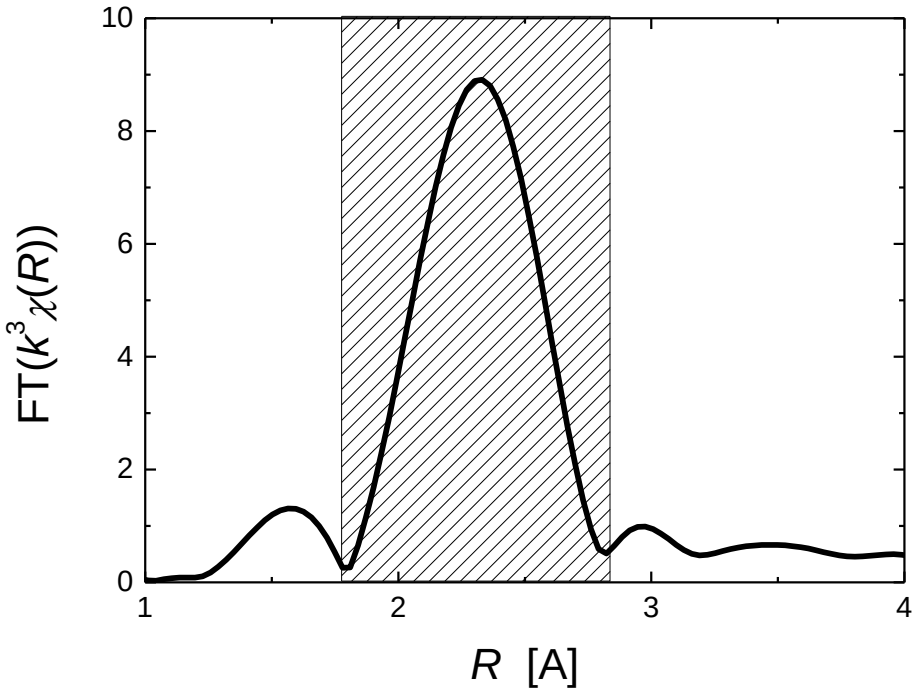
Crystalline **Glassy**



- Non-crystalline materials lack this long range order
- There is no prescription for which atoms/ions are located at which positions
- Atoms will align themselves chemically to:
  - Balance charge in the material
  - Minimize bond energies by filling appropriate bonding orbitals
- Hence, the structure is disordered at the long-range scale, but there is a possibility to have similar to crystalline phase structure at the nearest surrounding of the atoms – **short-range ordering**:
  - Coordination numbers are ~ same
  - Bond lengths are ~ same
  - Bond angles are ~ same

QEXAFS: applications to Disordered Solids

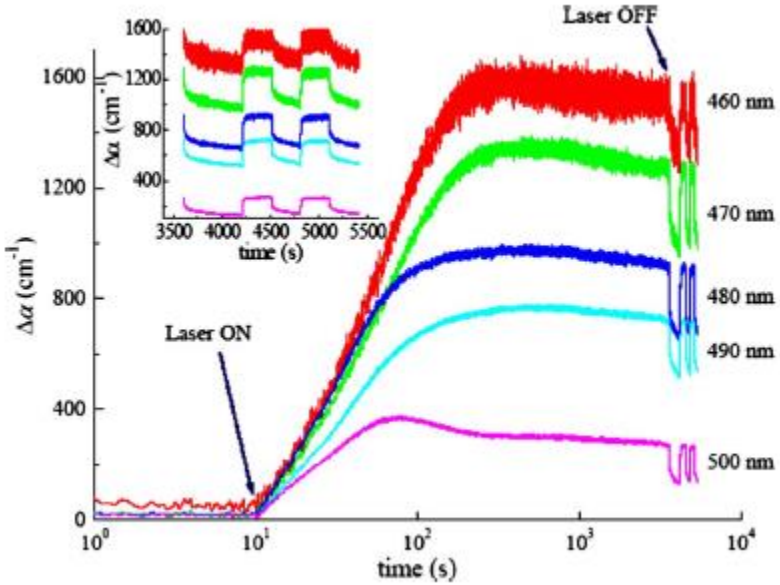




Because of disorder only **first coordination shell** can be unambiguously analyzed in network glasses with EXAFS/QEXAFS

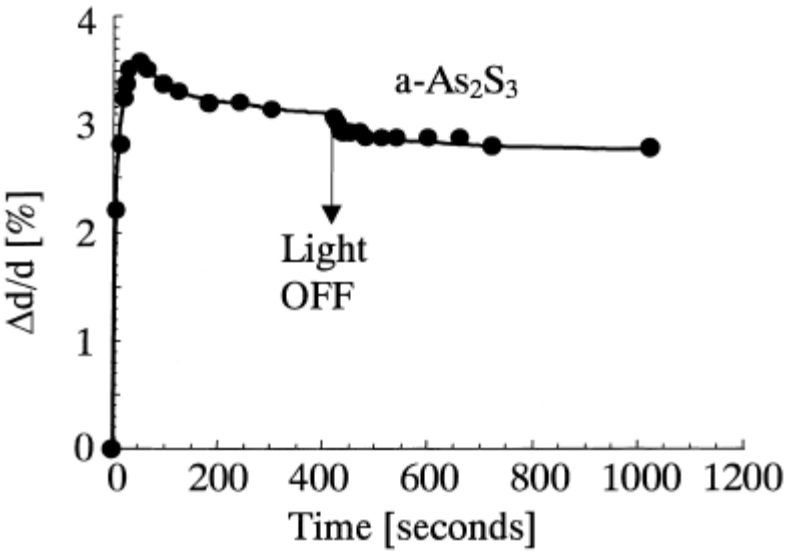
QEXAFS: applications to Disordered Solids

Photo-induced kinetics (examples)



Photoinduced changes in the absorption coefficient as a function of time with laser ON and OFF.

[A. Ganjoo et al, Phys. Rev. B 74, 024201 (2006)]



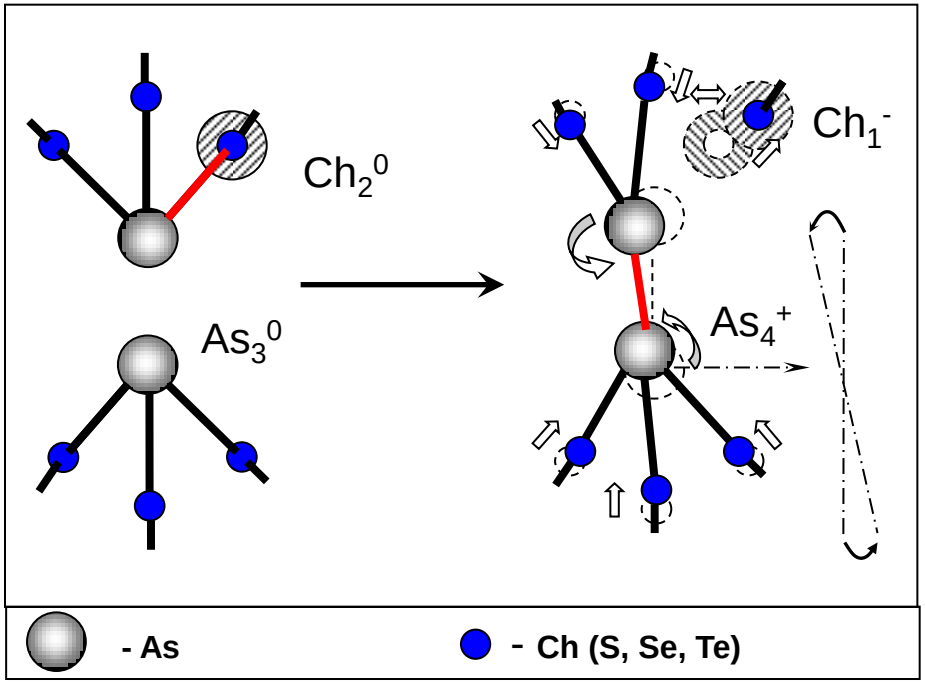
Relative changes in thickness, $\Delta d/d$, with time of photoexposure for obliquely deposited (80°) a-As_2S_3 films.

[A. Ganjoo et al, Journal of Non-Crystalline Solids 266±269 (2000) 919-923]

QEXAFS: applications to Disordered Solids

Photo-induced kinetics (examples)

Specific kind of structural defects in chalcogenide glasses – **coordination topological defects (CTDs)**



Sketch of CTD pair formation in As_2Ch_3 glass (the superscript means electric charge of the atom, and the subscript – its coordination number).

CTDs appear in a glass network

♣ by **pairs** (**under-coordinated negatively-charged and over-coordinated positively-charged diamagnetic defects**)

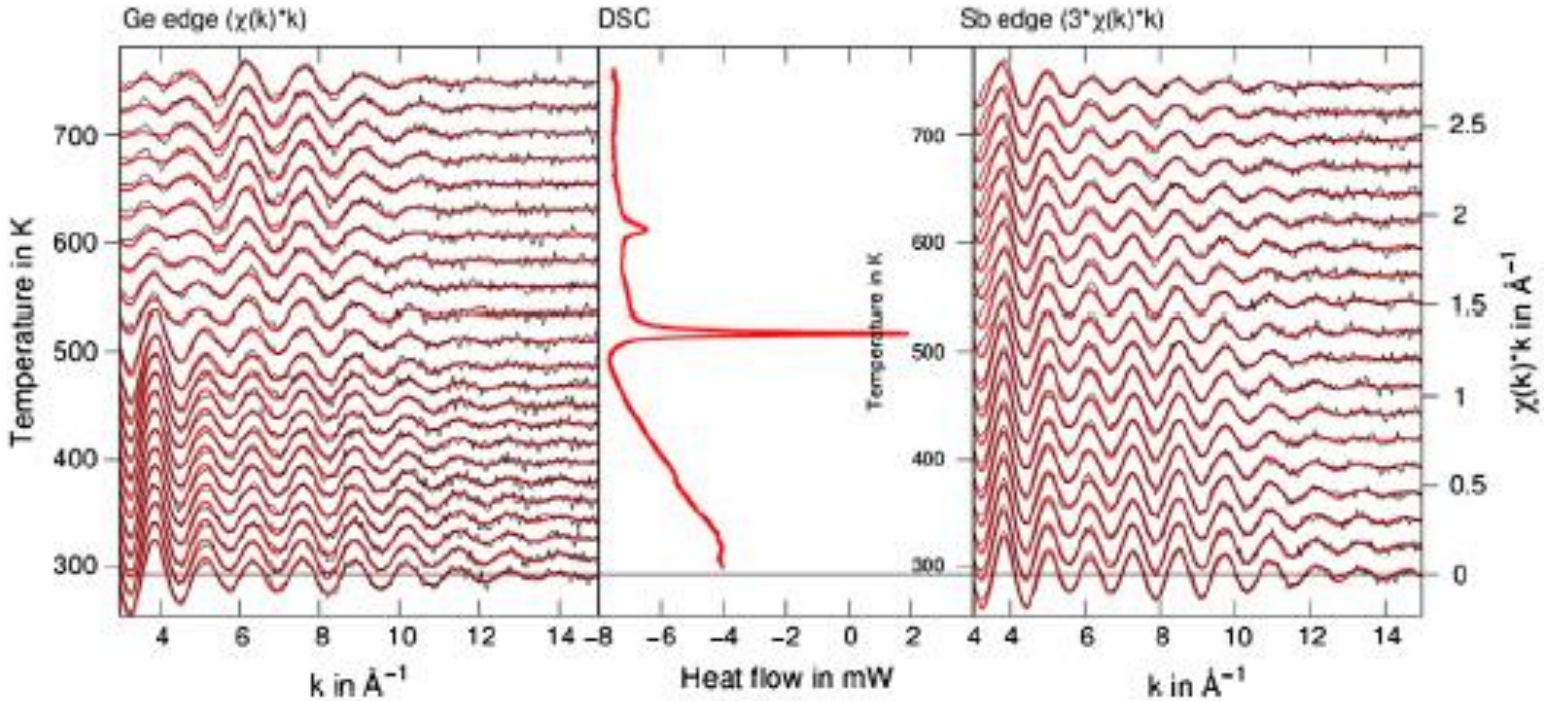
♣ as a result of **induced destruction-polymerization transformations** or **bond-switching reactions –** one covalent bond is destroyed, but another one is formed instead of the former (distinguished by red color)

♣ are accompanied by **volume changes**

In principle could be studied with QEXAFS, but no data available…

QEXAFS: applications to Disordered Solids

T-induced phase transformations (crystallization)

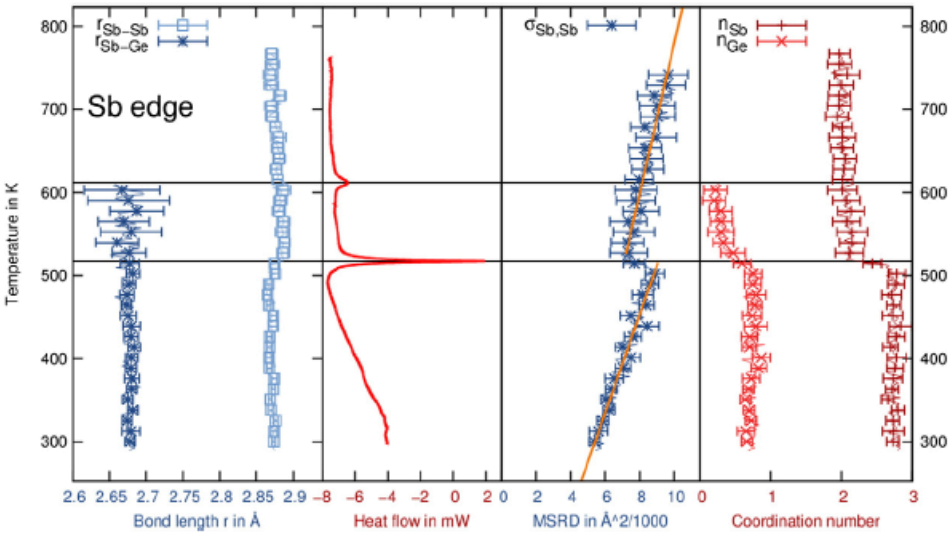


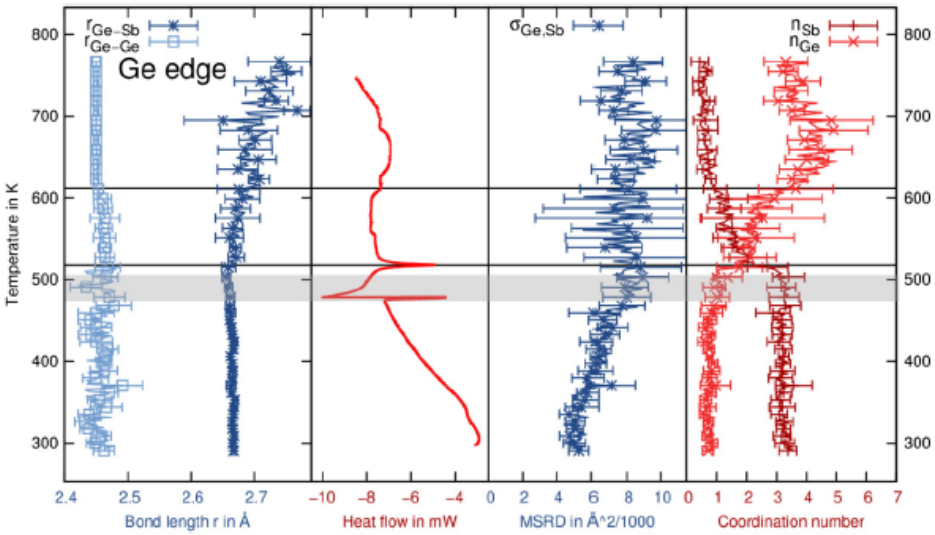
EXAFS oscillations kχ(k) at the Ge edge (left) and the Sb edge (right) together with the calorimetric signal obtained simultaneously with EXAFS measurements. Two exothermic peaks are observed in the calorimetric signal at 514 K and 604 K and correspond to clear changes in the EXAFS oscillations in its amplitude and frequency, thus suggesting a change in local order around both, Ge and Sb atoms.

P. Zalden et al, Journal of Non-Crystalline Solids 377 (2013) 30–33

QEXAFS: applications to Disordered Solids

Phase transformations (crystallization), cont.



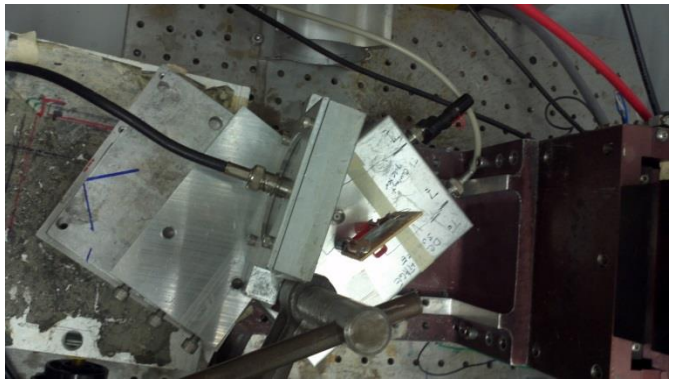


new insight on the crystallization process in phase-change memory materials:

- - the first crystallization at 514 K is related to the crystallization of an Sb-rich ($Ge_{11}Sb_{89}$) phase and simultaneously the Ge atoms partly segregate and form Ge-rich regions with an amorphous structure.
- - the as-formed amorphous Ge regions crystallize at 604 K upon heating
- - problem identified when using $Ge_{15}Sb_{85}$ as a phase change material due to possibility of irreversible changes in chemical composition with increasing number of cycles.

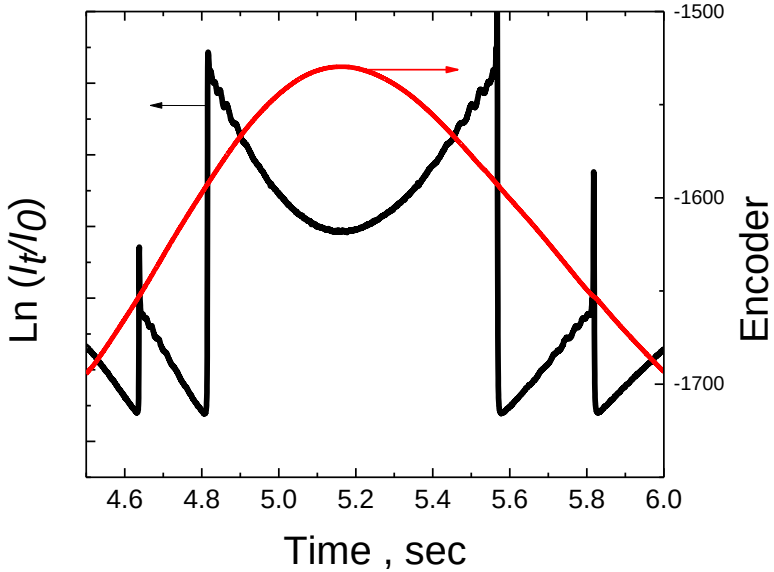
P. Zalden et al, Journal of Non-Crystalline Solids 377 (2013) 30–33

QEXAFS: data acquisition and treatment

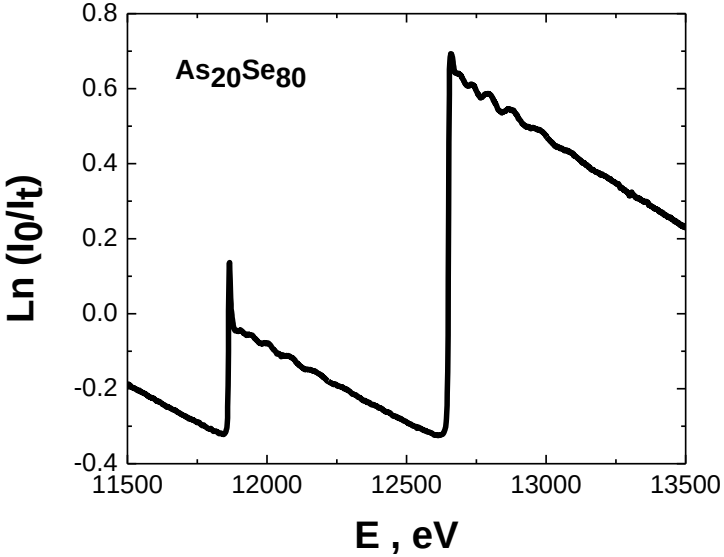


Design your experiment carefully taking into account speed of the reaction (other transformations)

Collect the data using control experiments and sufficient statistics

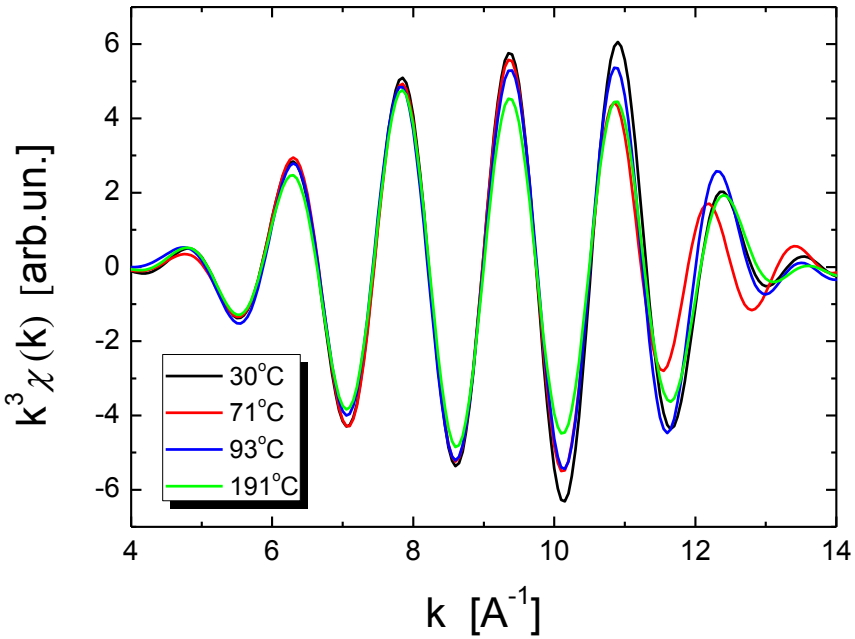


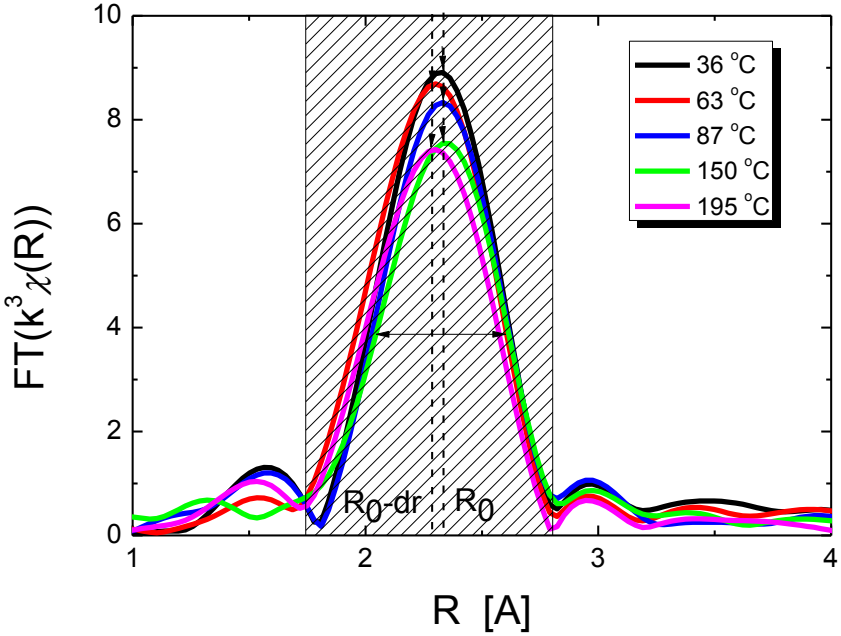
Separate scans using Crop-Chop software and convert encoder values into energy values



Import individual scans into Athena and perform regular EXAFS spectra pocessing for each scan

QEXAFS: data acquisition and treatment





Deglitch, remove background properly, etc.

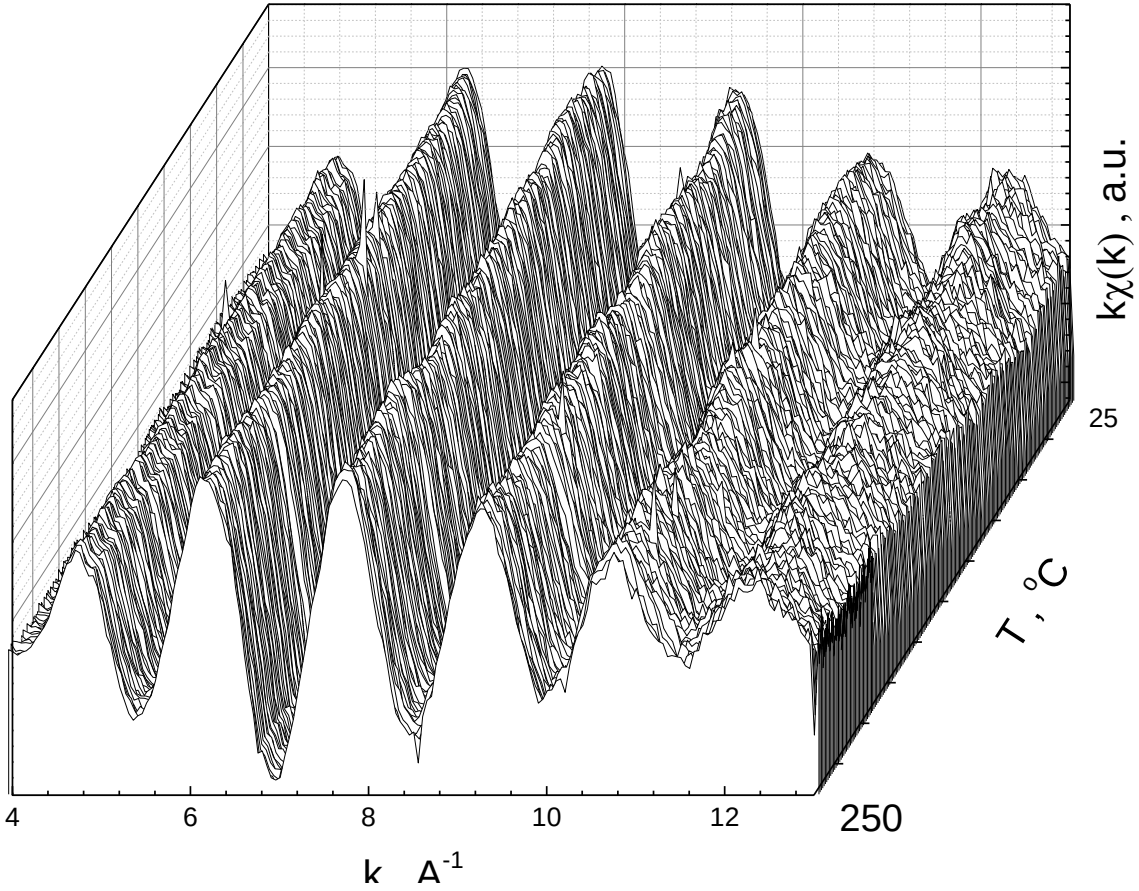
Fit with theory (in Artemis as an option)

Find from your fit N_j (number of neighbors in the *j*th shell) R_j, (average distance) and $\sigma_0{}^2{}_j$ (the Debye-Waller factor) dependences

Do appropriate error analysis

QEXAFS: applications to Disordered Solids

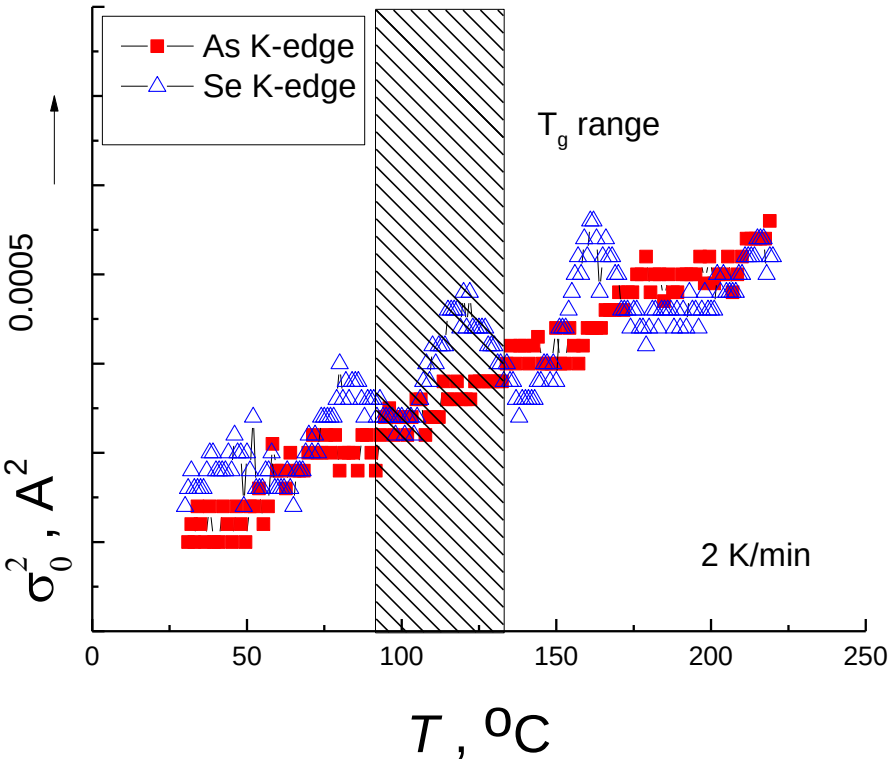
Temperature-induced changes (heating through glass transition)

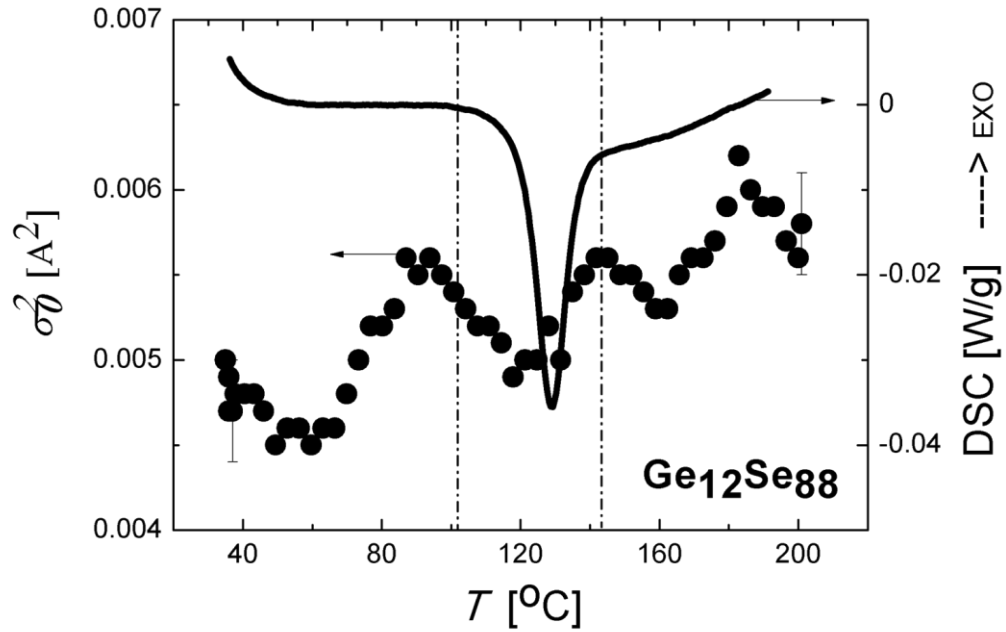


***k* weighted $\chi(k)$ oscillations at Se K-edge of $As_{20}Se_{80}$ glass recorded with 2 K/min heating rate.**

QEXAFS: applications to Disordered Solids

Temperature-induced changes (heating through glass transition)





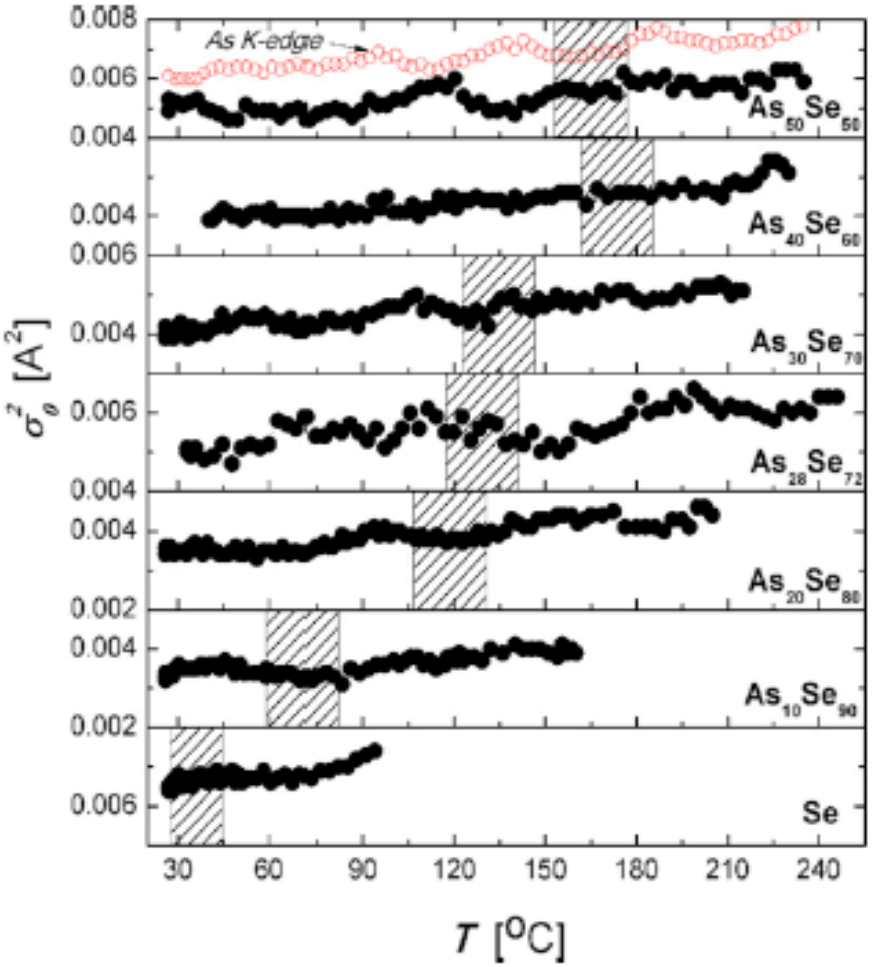
σ_0^2(T) dependences at Se and As K-edges of $As_{20}Se_{80}$ glass recorded with 2 K/min heating rate.

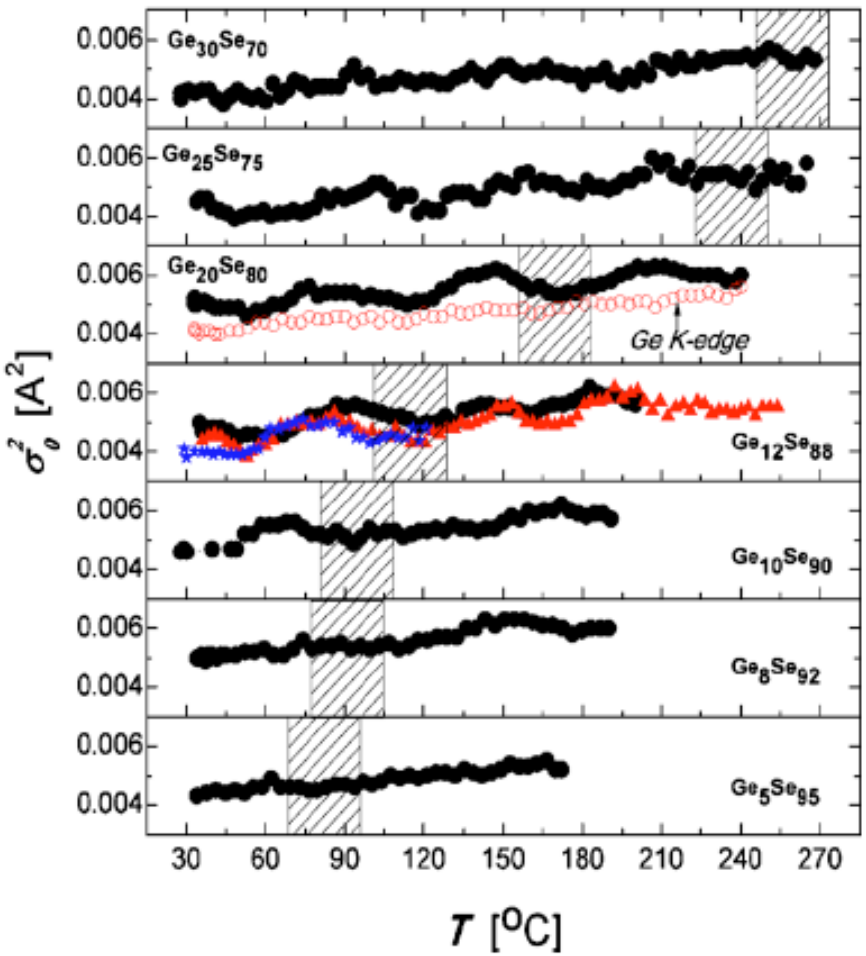
σ_0^2(T) dependences at Se K-edges of $Ge_{12}Se_{88}$ glass recorded with 4 K/min heating rate. DSC curve recorded with the same heating rate.

Nearest neighbor distance (R) and Debye-Waller factor (σ_0^2) are fitted, while the other two parameters *E_0* and *N* are fixed. Data for crystalline As_2Se_3 and $GeSe_2$ were used as input for FEFF calculations.

QEXAFS: applications to Disordered Solids

Temperature-induced changes (heating through glass transition)



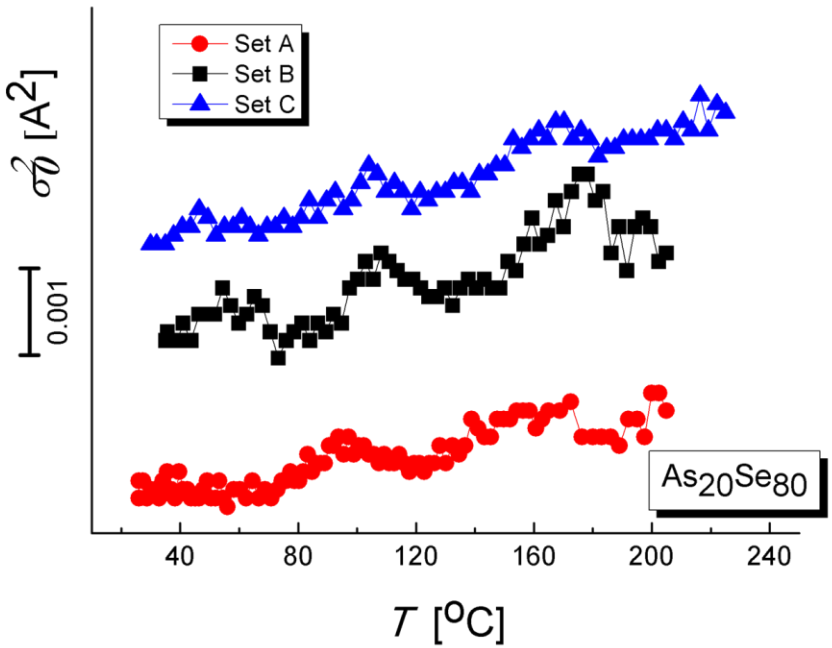


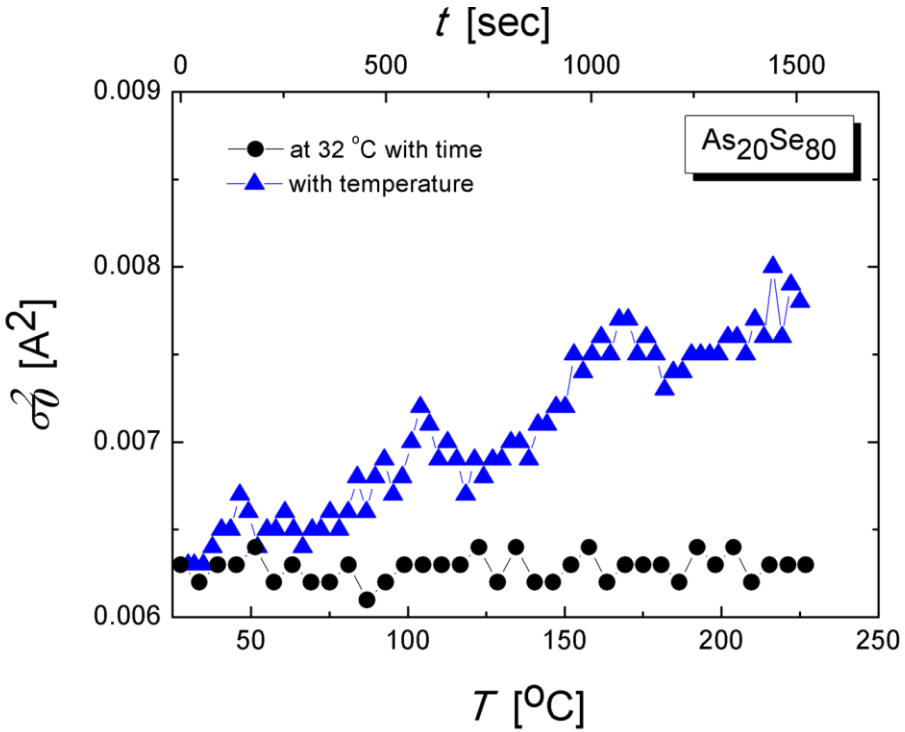
Compositional dependence of $\sigma_0^2(T)$ for Se K-edge of As_xSe_{100-x} and Ge_xSe_{100-x} glasses. T_g-range is cross-hatched. Reproducibility of the results is shown at the example of $Ge_{12}Se_{88}$ sample: $\sigma_0^2(T)$ curves are recorded at one year interval. For comparison, the $\sigma_0^2(T)$ for Ge K-edge is shown for $Ge_{20}Se_{80}$ composition..

R. Golovchak et al, Appl. Phys. Let. 98, 171905 (2011)

QEXAFS: applications to Disordered Solids

Temperature-induced changes (heating through glass transition)



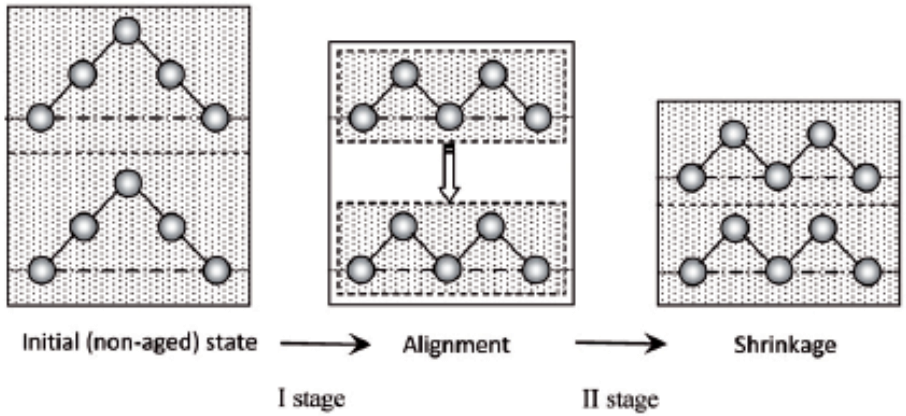


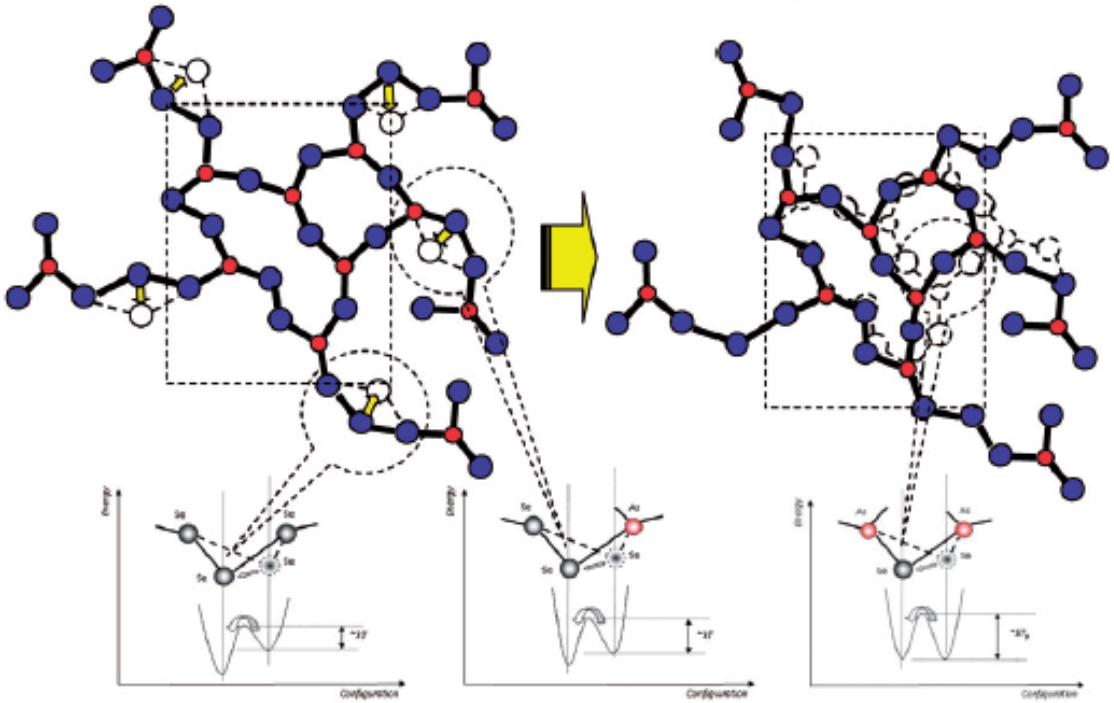
Comparison of Debye-Waller factor (left panel) obtained by fitting of QEXAFS data, recorded at Se K-edge of $As_{20}Se_{80}$ glass: 20 years aged samples (set A); 22 years aged samples (set B) – repeated in 2 years experiment with the samples of same thermal prehistory, as in set A; newly fabricated and then 5 years aged samples (Set C). The right panel shows temperature vs time dependence (4 K/min) of Debye-Waller factor for set C samples, the latter one showing the level of statistical error during measurements.

R. Golovchak et al, Appl. Phys. Let. 98, 171905 (2011)

QEXAFS: applications to Disordered Solids

Mechanism





Deviations from monotonic linear temperature dependence of $\sigma_0^2(T)$ for certain As_xSe_{100-x} and Ge_xSe_{100-x} glasses have been observed

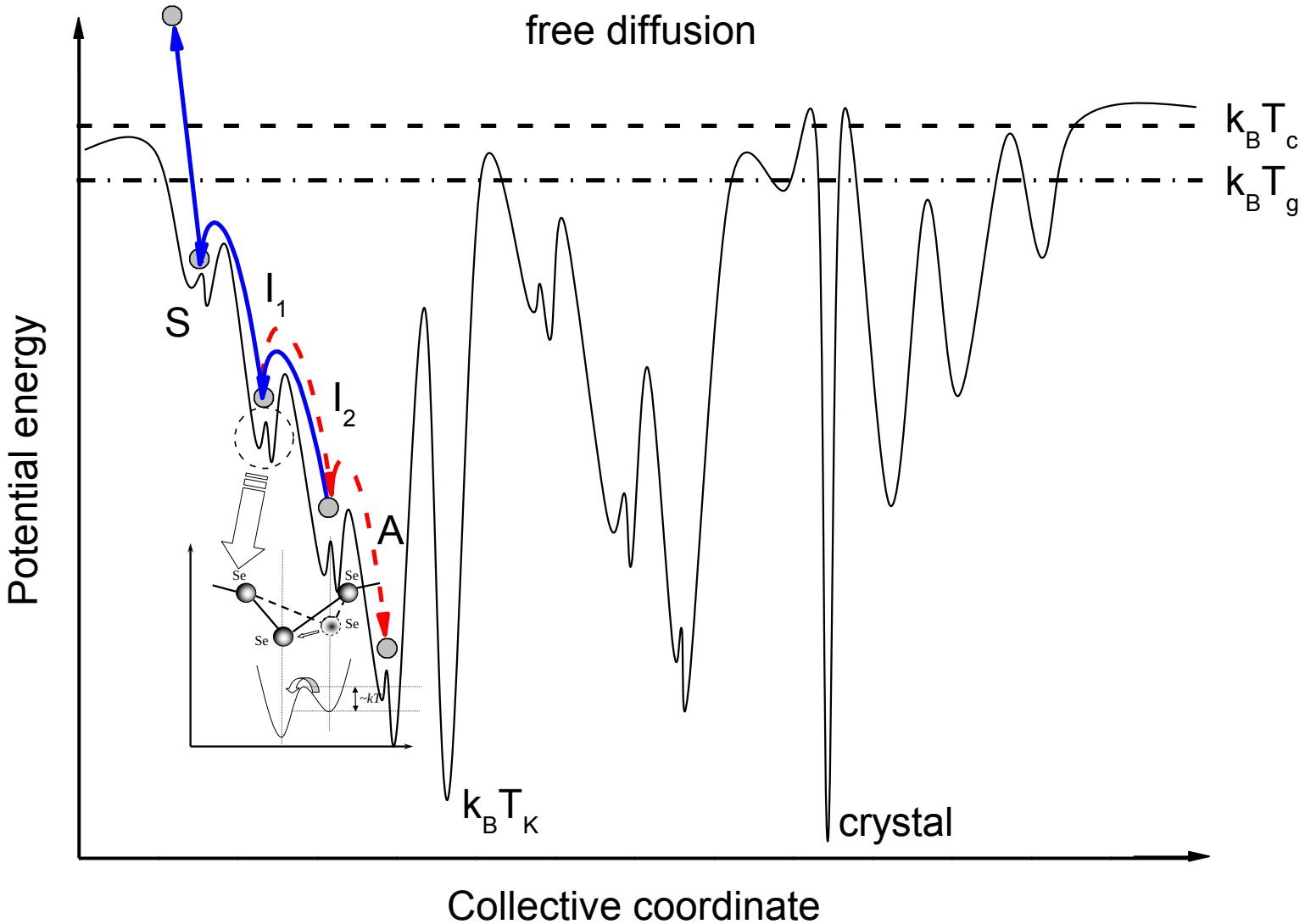
$\sigma_0^2(T)$ includes components related to thermal and structural disorder

Observed wiggles could be explained through the hierarchy of cooperative rearrangement processes and Energy/Enthalpy landscape diagram

R. Golovchak et al, Phil. Mag. 92, No. 33 (2012) 4182–4193

QEXAFS: applications to Disordered Solids

In the supercooled liquid state, the system's energy is determined by the exact positions of all *N* particles and can be qualitatively described by **"Landscape paradigm"** [**A. Angell, Nature 393 (1998) 521**].



Concluding remarks

- QEXAFS is considered as very informative technique to study various kinetic phenomena in disordered solids, however very scarce data are available in scientific periodic…

- Experiment should be carefully designed taking into account timing of the investigated phenomenon, statistical error (repeatability), stability of the samples under X-rays, other uncertainties related to the equipment and studied phenomenon

- Data should be analyzed with great care, especially in the case of subtle changes.