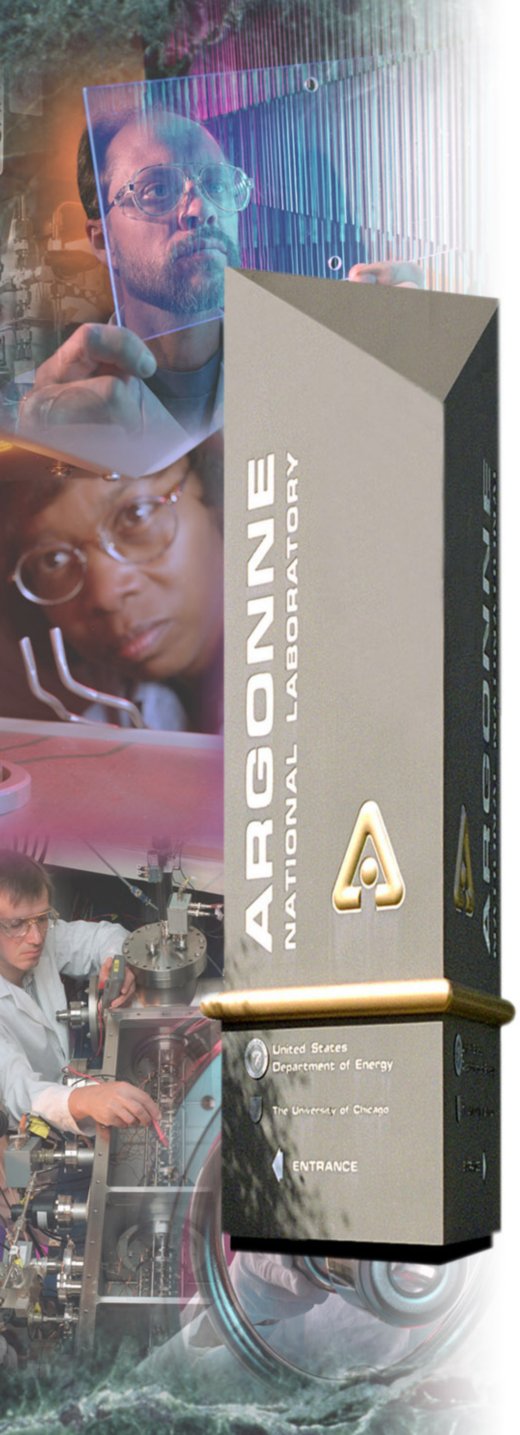

XAFS and other techniques:

A “4-footnote” lecture.

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Advanced Photon Source

XAFS Summer School, ANL July 2005

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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Why do you need this torture on the last day:

- **Because there are a variety of other probes that measure atomic positions, their disorder, their correlations, etc, in different ways, information that complements that obtained by XAFS.**

Neutron and x-ray diffraction (PDF analysis)
Mossbauer Spectroscopy, NMR, NQR
Electron Energy Loss Spectroscopy (EELS, EXELFS)

The different length and time scales probed in XAFS compared to other techniques can help you determine what really is going on.

Outline

- The length scales (short- or long-range order?).
- Some examples.
- The time scales (Static or dynamic?).
- Spatial resolution (in atomic positions).
- Atomic disorder (DWF’s).
- Orientation dependence (see NSLS User’s meetings, 2001).

The length scale

The Length scale: Short- versus long-ranged probes.

- **XAFS probes as far as the (*elastically-scattered*) photoelectron can reach all the while the core-hole is alive.**

- The mean-free path (λ) is determined by the core-hole lifetime (τ) and the inelastic losses. Both depend on p.e. energy k.

  The higher the k, the farthest the p.e. reaches within τ. But losses become more significant as more excitations become available.

$$p = \hbar k = mv$$

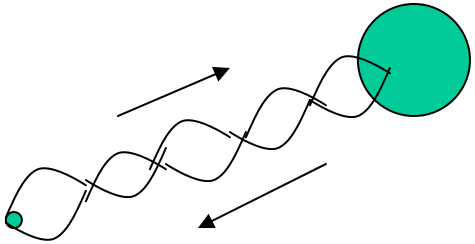
$$v = \frac{x}{\tau};\, x = \frac{\hbar k}{m}\tau$$

Near threshold (XANES): tens of Å.
EXAFS: ≈10 Å.

XAFS is an *excited* final state effect, so length and time scales are related ! (Einstein would have been proud…)

Length scales…

- Since XAFS is an interference effect between outgoing and backscattered p.e. waves, it needs a coherent final state. Inelastic scattering (losses) change the energy of the p.e. (and hence its phase kr), smearing the XAFS.



i.e., don't perturb the standing wave !

$$k = \frac{2\pi}{\lambda}$$

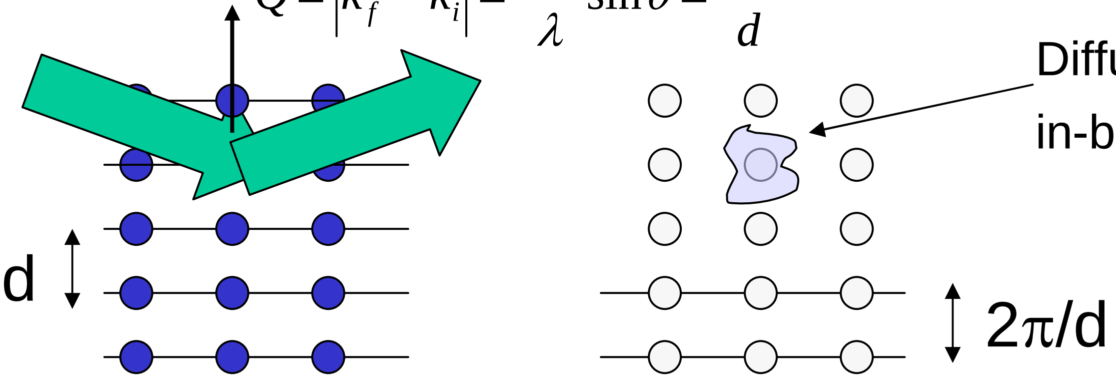
This is wavelength, not mean free path.

- XAFS doesn't require long range order, but it does require short-ranged correlations between atoms (e.g. liquids, amorphous solids).

Length scales…

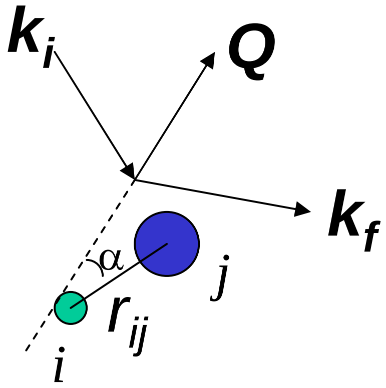
- **Diffraction probes a scale over which the scattering is coherent; i.e., well defined correlations in atomic positions. In good crystals this could be microns (i.e., much longer than XAFS).**
- Long-range periodic order (many unit cells) yields Bragg peaks at positions in reciprocal space corresponding to lattice planar spacings (given by the space group), while other correlated atomic displacements yield diffuse scattering (e.g. phonons, disorder).

$$Q = \left|\vec{k}_f - \vec{k}_i\right| = \frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{d}$$



Diffuse scattering under and in-between Bragg peaks.

PDF from powder diffraction (neutrons, x-rays)



$$I = \left|\sum_{i=1}^{N} f_i e^{i\vec{Q}\cdot\vec{r}_i}\right|^2 = \sum_i\sum_j f_i^* f_j e^{-i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)} = \sum_i\sum_j f_i^* f_j e^{iQr_{ij}\cos\alpha}$$

Powder: average over all orientations of r_{ij} :

$$\left\langle e^{iQr_{ij}\cos\alpha}\right\rangle = \frac{1}{4\pi}2\pi\int_{-1}^{1} d(\cos\alpha)e^{iQr_{ij}\cos\alpha} = \frac{\sin Qr_{ij}}{Qr_{ij}}$$

$$I(Q) = \sum_i\sum_j f_i^* f_j \frac{\sin Qr_{ij}}{Qr_{ij}}$$

From I(Q) one can obtain radial distribution functions from amorphous materials and liquids as well. However, for non-monatomic samples I(Q) probes *all correlated pairs* (AA, BB, AB for two atom types). XAFS measures partial RDF’s involving the absorbing atom.

Length scales: Some other techniques.

Other probes of short range order:

- Mossbauer spectroscopy, NMR, NQR
- Electron energy loss spectroscopy (EELS)

Mossbauer, NMR, NQR, use changes in nuclear energy levels and nuclear spins (chemical shift, quadrupole splitting, line width, relaxation times) to gain insight into the local structure (neighbors, symmetry, disorder).

Limited to selected isotopes.

EELS measures the energy loss of inelastically scattered electrons. Much like XAFS, *but only for thin films (1000 Å). Needs to worry about plasmon scattering.*

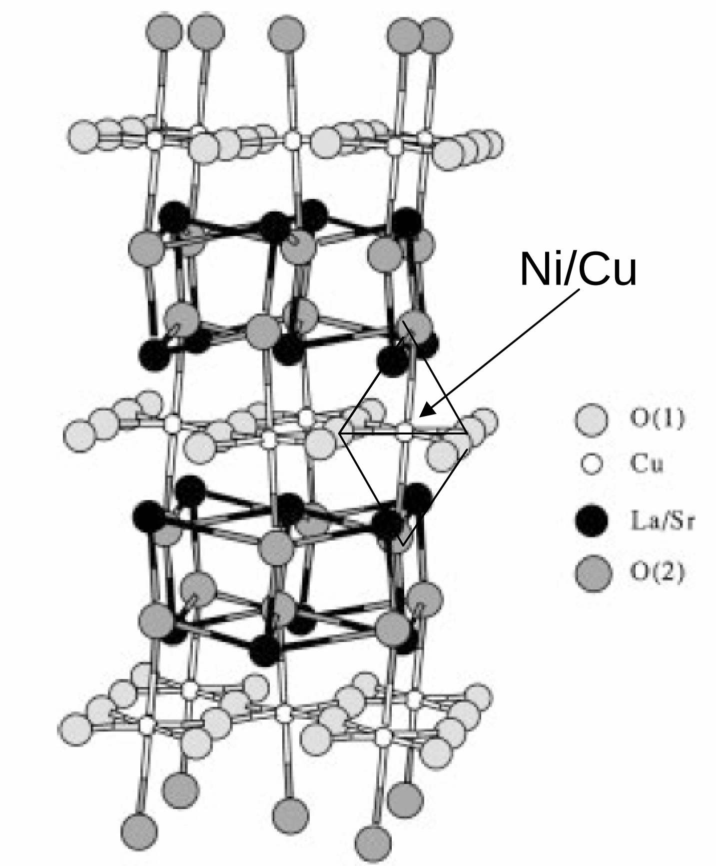
Footnote #1:

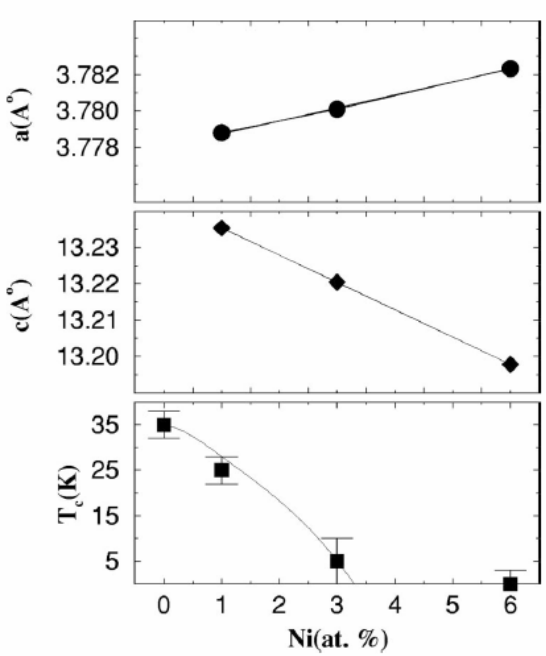
- **XAFS probes short-range ordering.**
- **Diffraction can probe *both* long-range, periodic ordering (Bragg scat, Q=G) and also short-range ordering (diffuse scat. Q≠G).**
- **The big advantage of XAFS is in its element specificity (PPDF) and direct measurement of 3-body correlations through MS. The big advantage of diffraction-PDF is that it can also probe intermediate order (10-50Å), if it exists.**

Examples

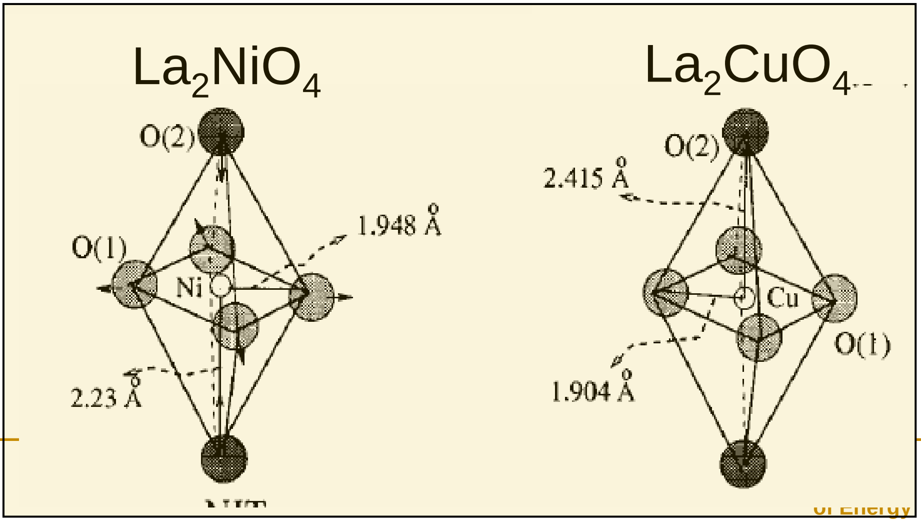
XAFS “K-B” when element of interest is few %

$La_{1.85}Sr_{0.15}Cu_{1-y}Ni_yO_4$

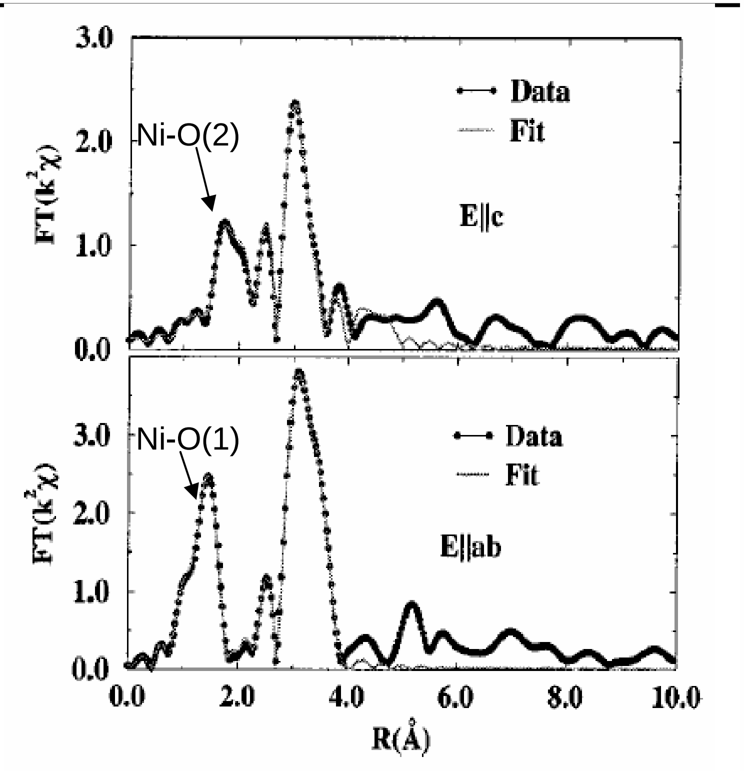


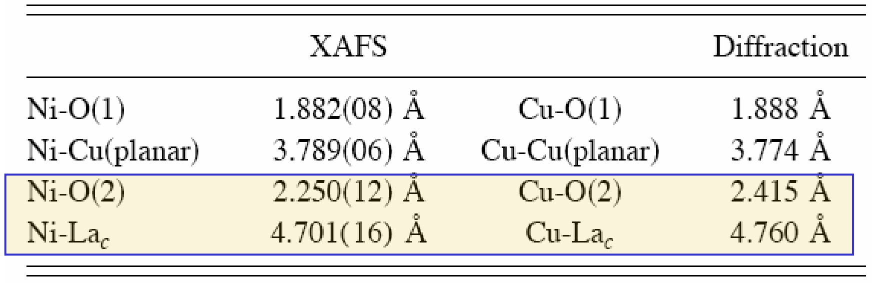


Diffraction shows Ni contracts *c*-axis, expands *a*-axis.



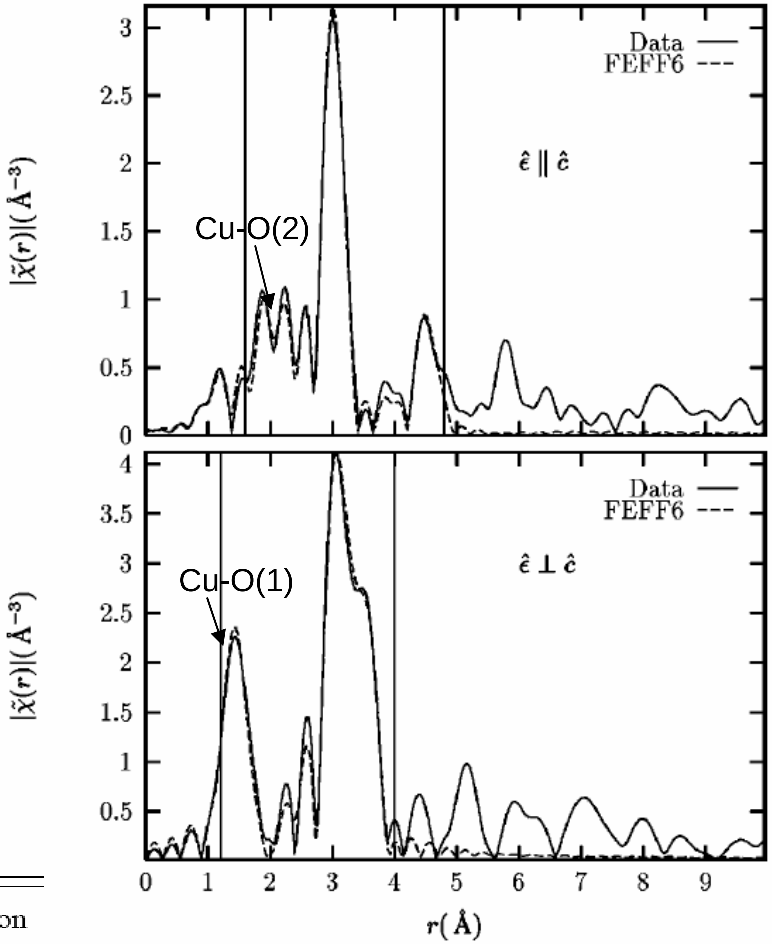
Ni XAFS





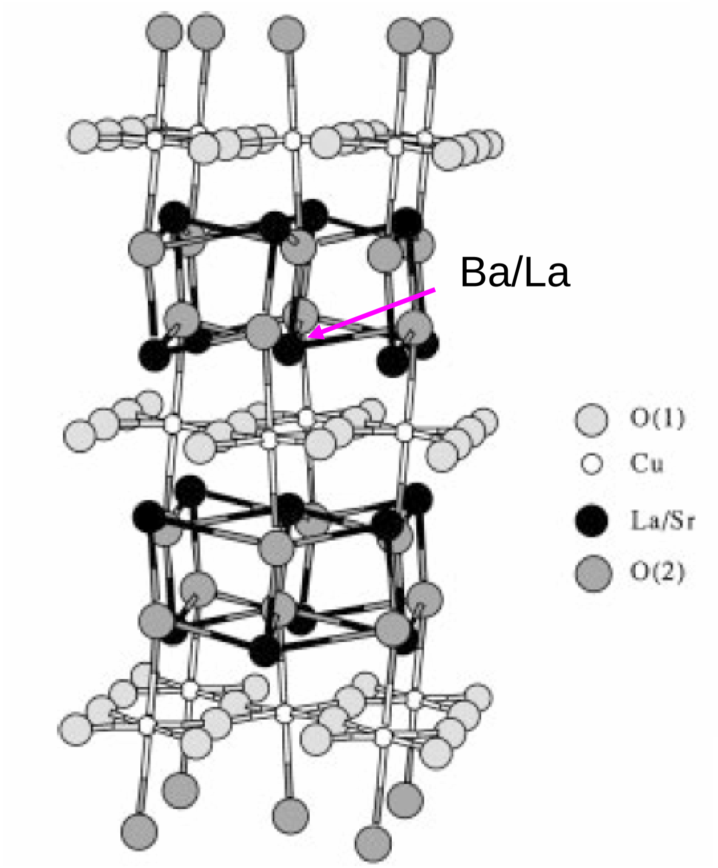
	XAFS		Diffraction
Ni-O(1)	1.882(08) Å	Cu-O(1)	1.888 Å
Ni-Cu(planar)	3.789(06) Å	Cu-Cu(planar)	3.774 Å
Ni-O(2)	2.250(12) Å	Cu-O(2)	2.415 Å
Ni-La_c	4.701(16) Å	Cu-La_c	4.760 Å

Cu XAFS

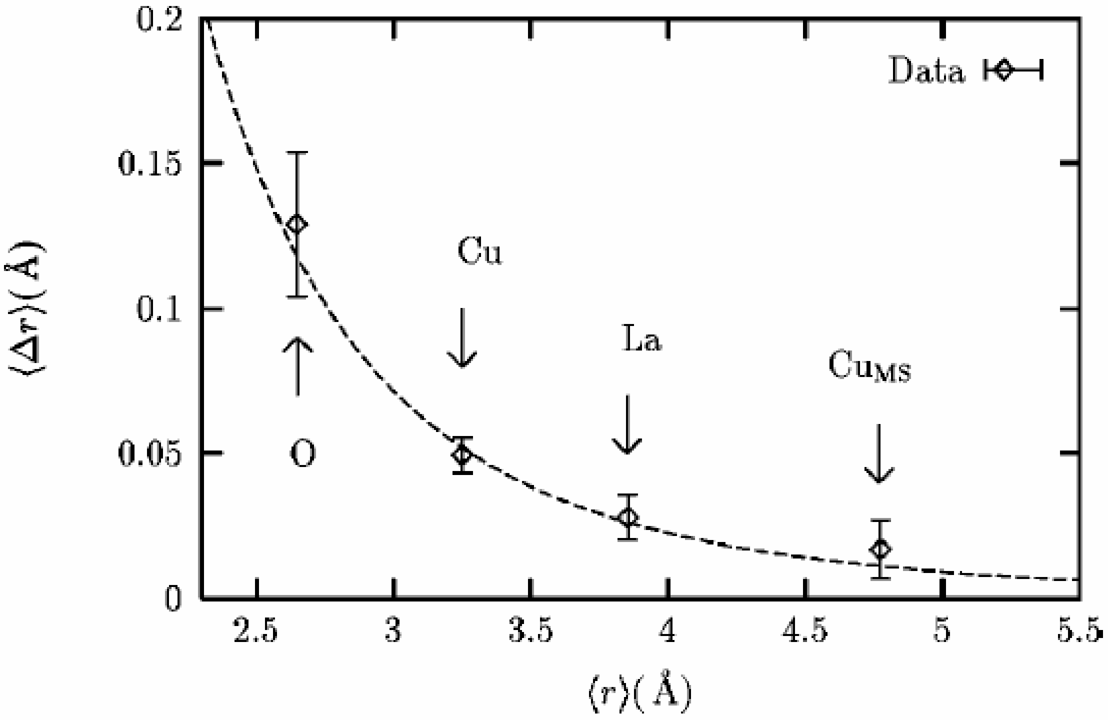


Ni distortion not periodic, so it only adds disorder to Bragg diffraction. PDF of diffraction not sensitive since few % Ni.

Local strain field around a large ion.



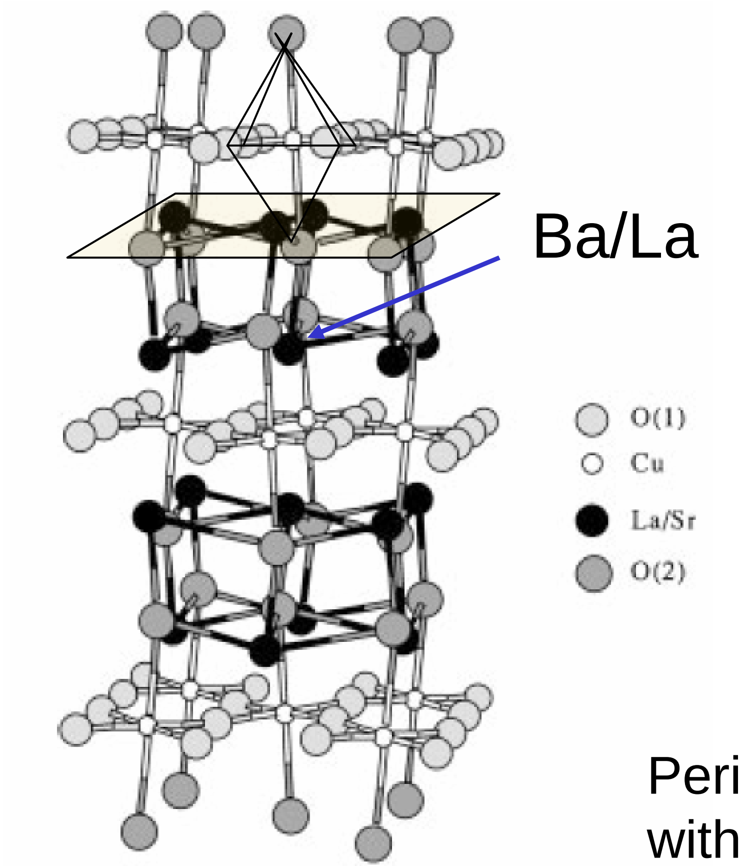
Ba XAFS

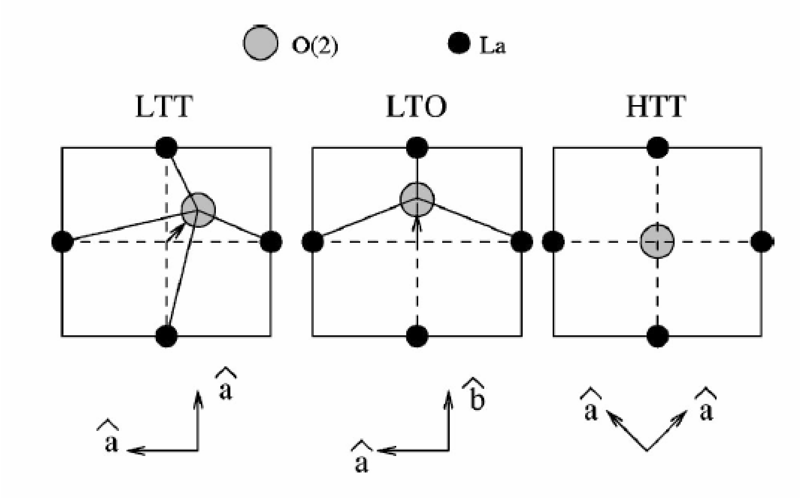


Strain field around Ba due to larger ionic size than La.

Again not periodic, few %: XAFS best for quantitative study.

Local (SRO) and average (LRO) structure can differ



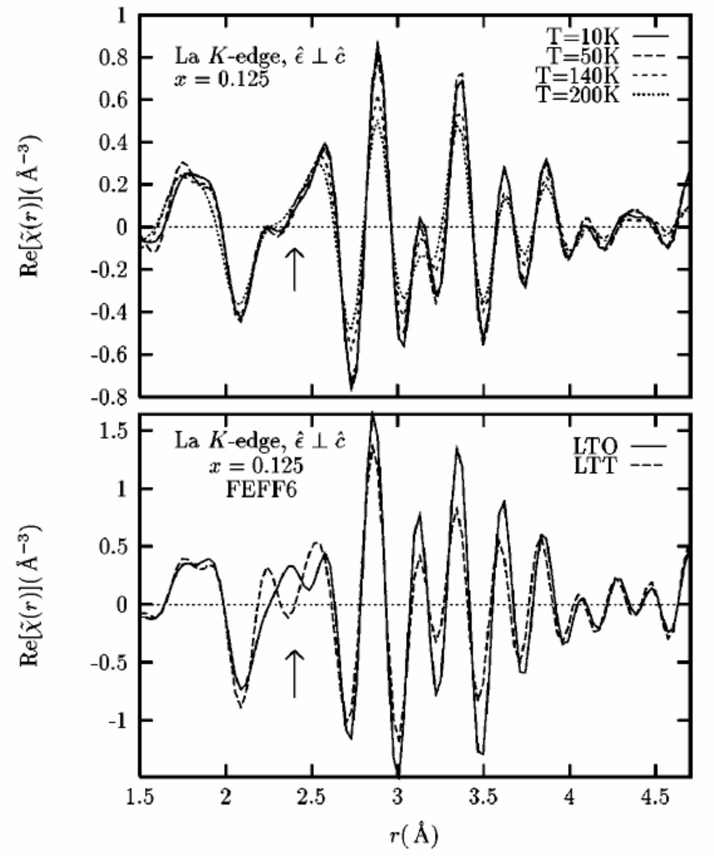


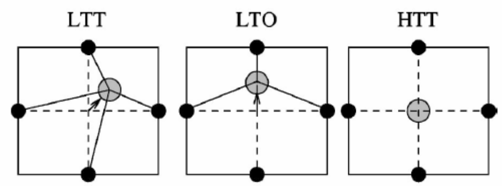
Bragg diffraction:
LTT→ LTO→ HTT
60K 200K

Periodic structure (LRO) shows changes, with T, in the direction of CuO_6 tilt. Easily probed in La-O(2) plane.

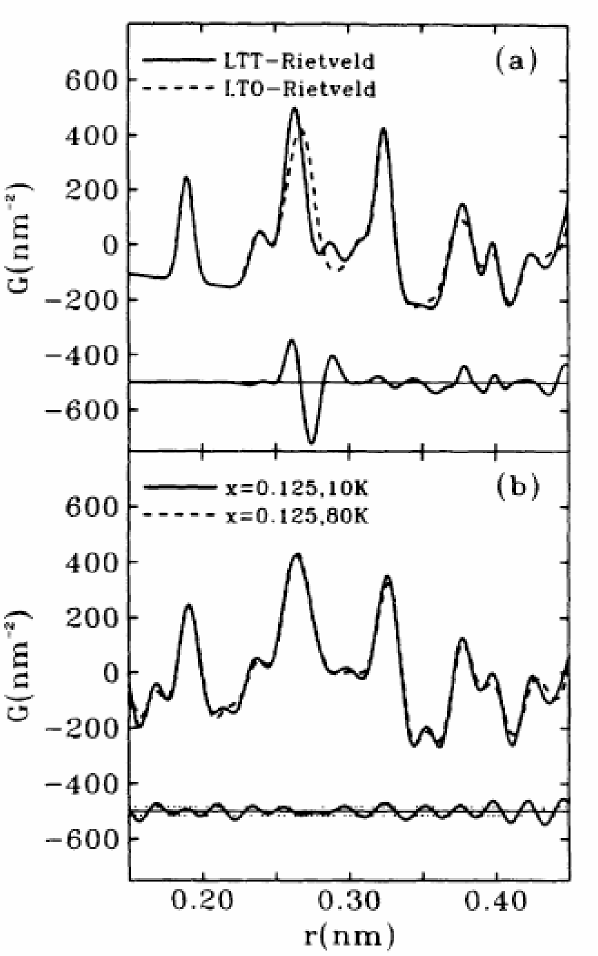
Expected changes at LTT→ LTO phase transition

La XAFS

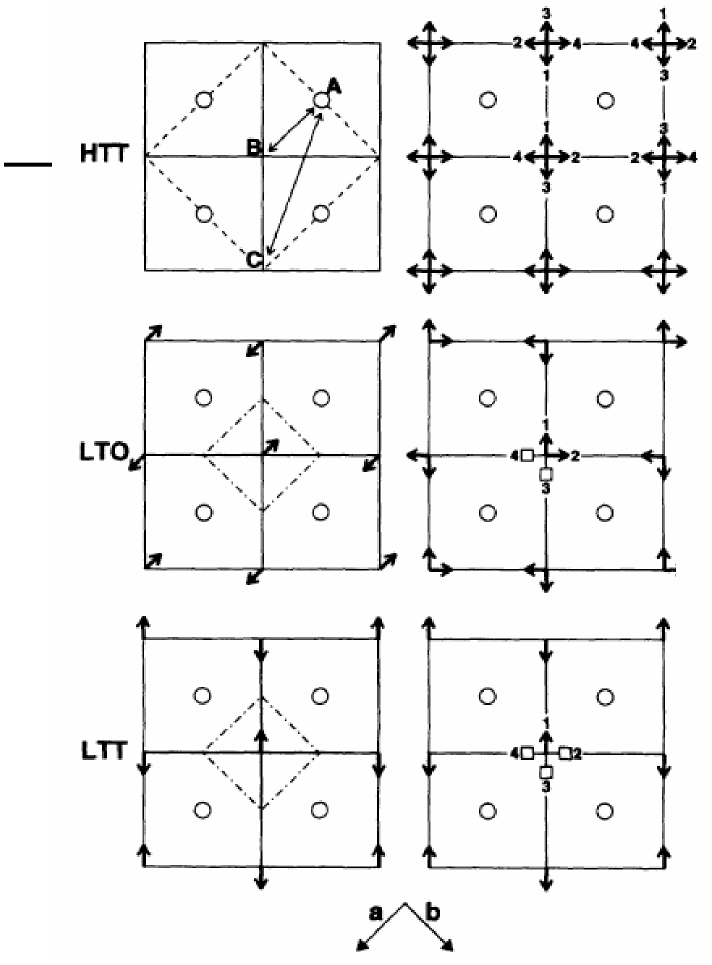


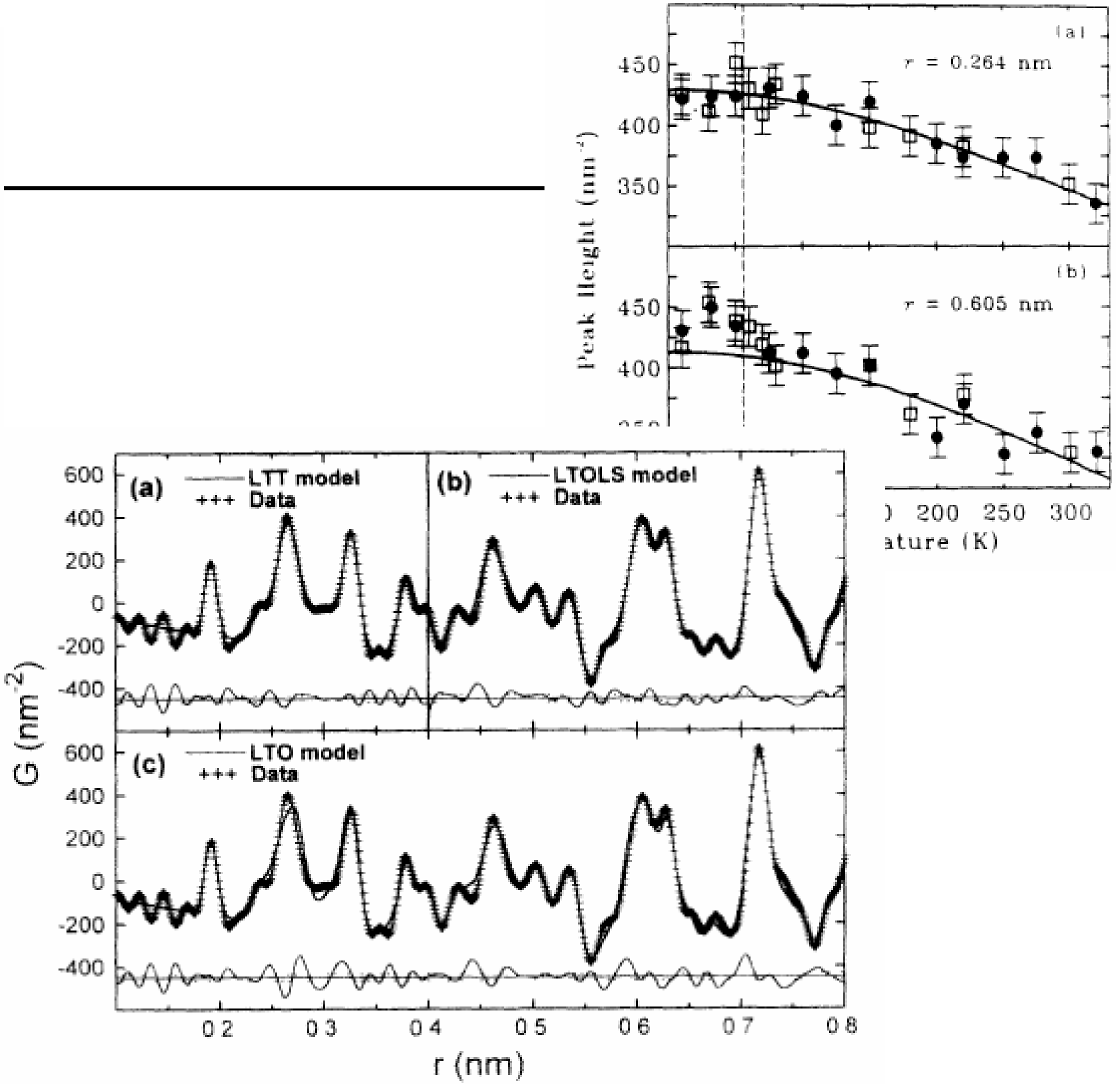


Neutron’s PDF



Octahedra do not change tilt direction !

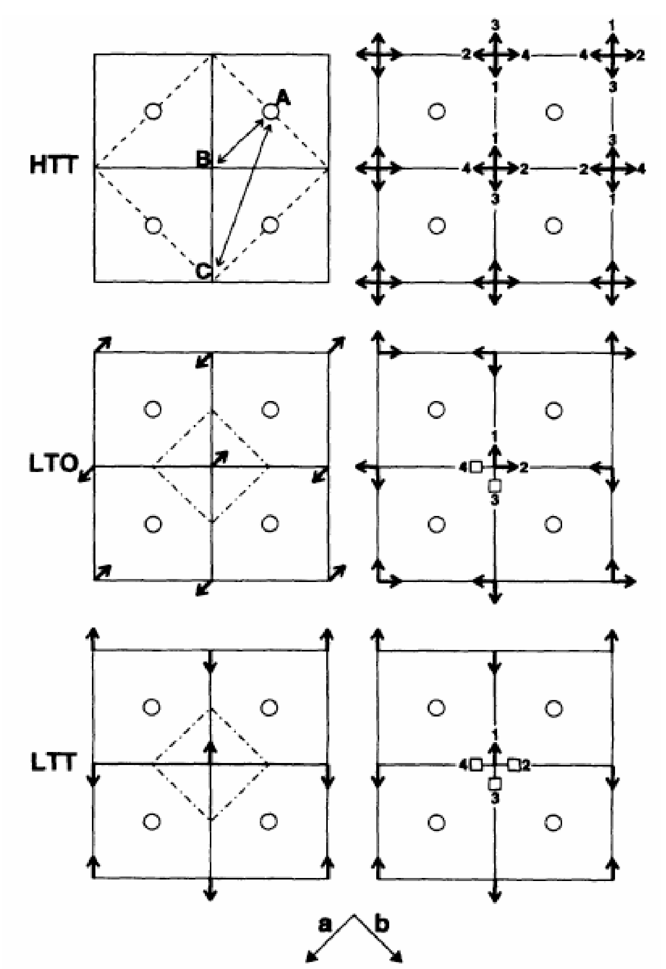


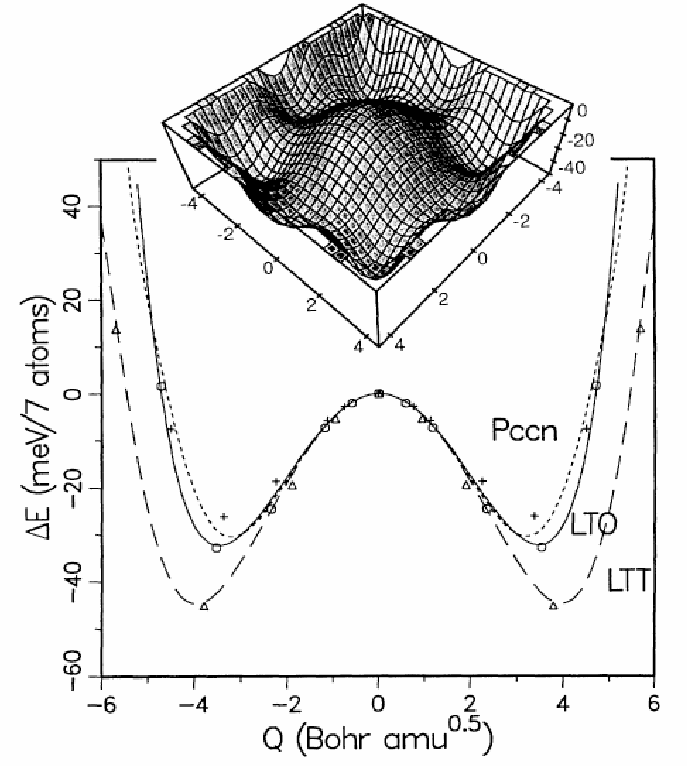


Billinge *et al*,
PRL **72**,2282 (1994).

Crystal structure (LRO) results from superposition of local LTT domains. Changes are not in direction of tilt, but in the correlations between O displacements in neighboring cells. PDF gets IRO.

Is the arrangement of tilts dynamic or static?





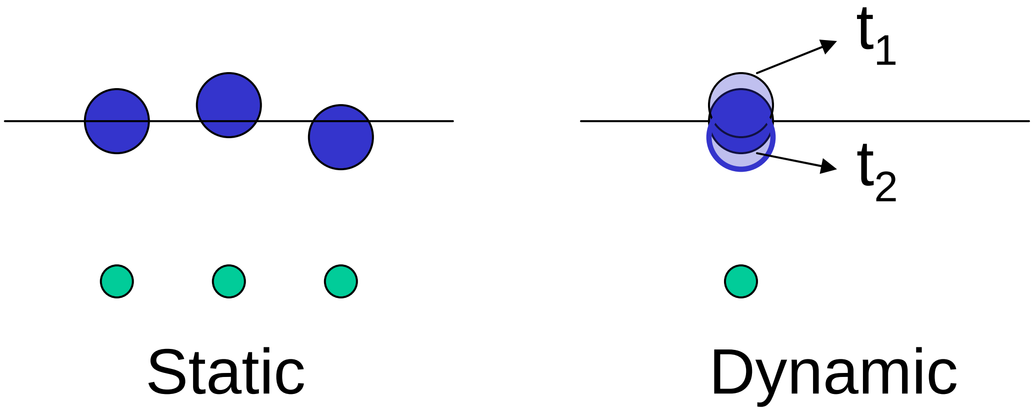
Pickett *et al*., **67**, 228 (1991)

XAFS and diffraction measure different length scales, but both take a very fast snapshot of the structure.

Time scales

Time scales

- XAFS time scale given by the core-hole lifetime, 10^{-15} sec, much faster than any atomic motion (phonons meV →10^{-13} sec).
- Each absorption event probes the instantaneous atomic positions. Since a measurement integrates over many snapshots and over many absorbers, it probes the distribution of atoms through spatial (static) and time (dynamic) averaging.

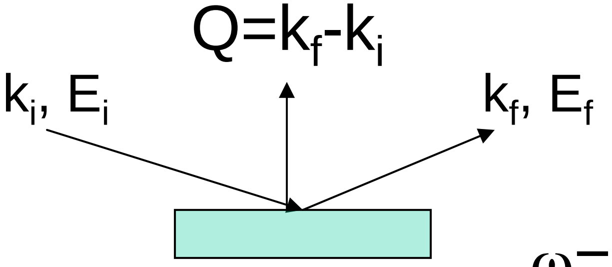


XAFS can't distinguish between static and dynamic displacements.

(However T dependence can be used to separate static from thermal disorder)

Time scales

The x-ray scattering cross section is related to S(Q, ω):



ω=E$_f$-E$_i$

$$S(Q,\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{j,l}\left\langle e^{-i\vec{Q}\cdot\vec{r}_j(0)}e^{i\vec{Q}\cdot\vec{r}_l(t)}\right\rangle_T$$

Diffraction with no energy discrimination integrates over ω,

$$\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t}=2\pi\,\delta(t)$$

… and results in S(Q) at t=0; *i.e*, the instantaneous correlation function.

- Energy discrimination (inelastic scattering) can be used to probe dynamics through choice of energy transfer.

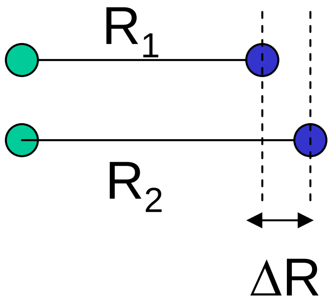
Footnote #2:

- **XAFS and diffraction measure the instantaneous distribution of atoms, averaged over their respective length scales.**
- **Inelastic scattering can be used to study dynamics.**
- **Nuclear techniques such as Mossbauer spectroscopy and NMR have much slower time scales (10^{-6}-10^{-9} sec) due to much longer lifetime/relaxation times of excited states.**

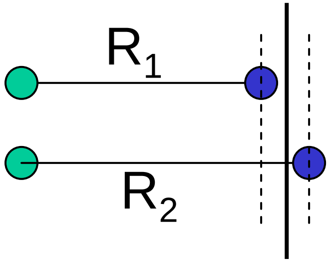
Spatial resolution

Spatial resolution

The ability to resolve two distances “close” to each other.



OR



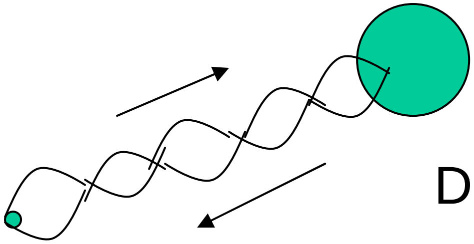
$$\langle R \rangle = (R_1 + R_2)/2$$

$$\sigma = \Delta R/2$$

Intuition: To resolve needs ΔR to be a significant fraction of smallest p.e. wavelength:

$$\Delta R \geq \frac{\lambda_{\min}}{4} = \frac{2\pi}{4k_{\max}} = \frac{\pi}{2k_{\max}}$$

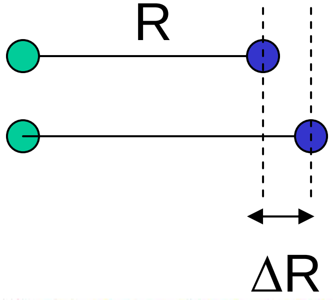
$$\boxed{k_{\max} \geq \frac{\pi}{2\Delta R}}$$



De Broglie λ

$$k = \frac{2\pi}{\lambda}$$

Spatial Resolution



A little more rigorous derivation:

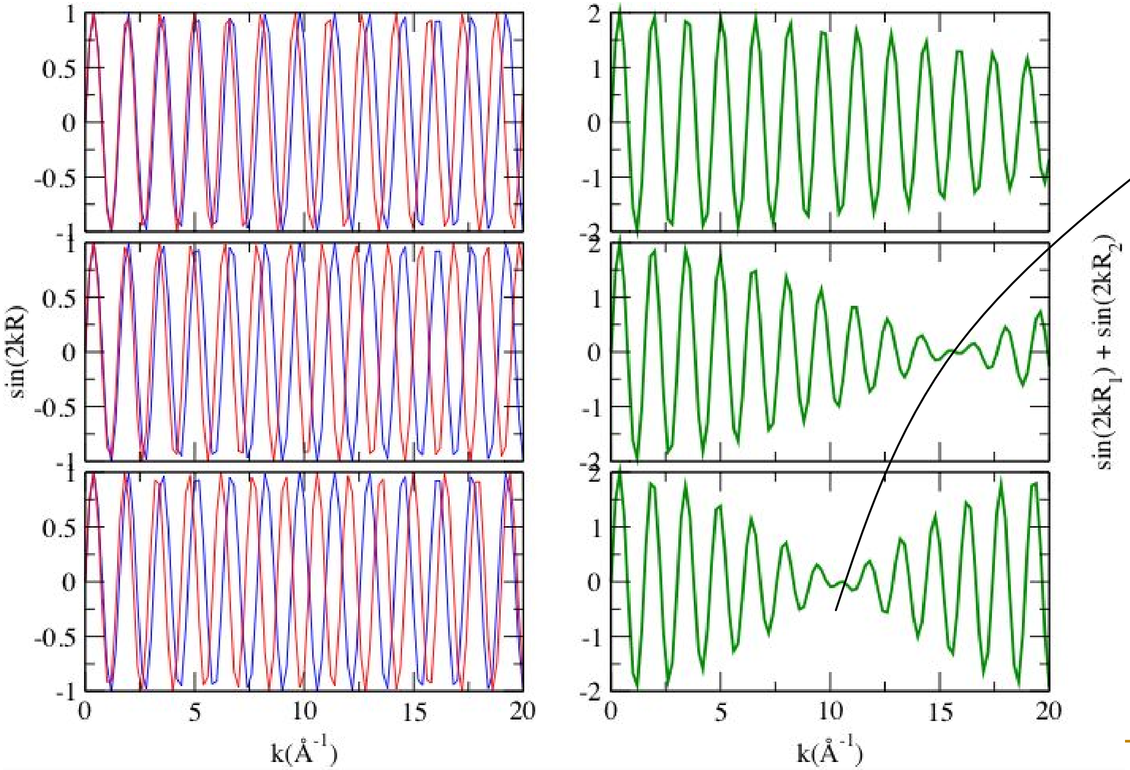
$$\sin 2kR + \sin[2k(R+\Delta R)] =$$

$$\sin 2kR + (\sin 2kR \cos 2k\Delta R + \cos 2kR \sin 2k\Delta R)$$

$$\sin 2kR[1+\cos 2k\Delta R]$$

Low "freq" modulation with beat at 2kΔR=π

$$k_{beat} = \frac{\pi}{2\Delta R}$$



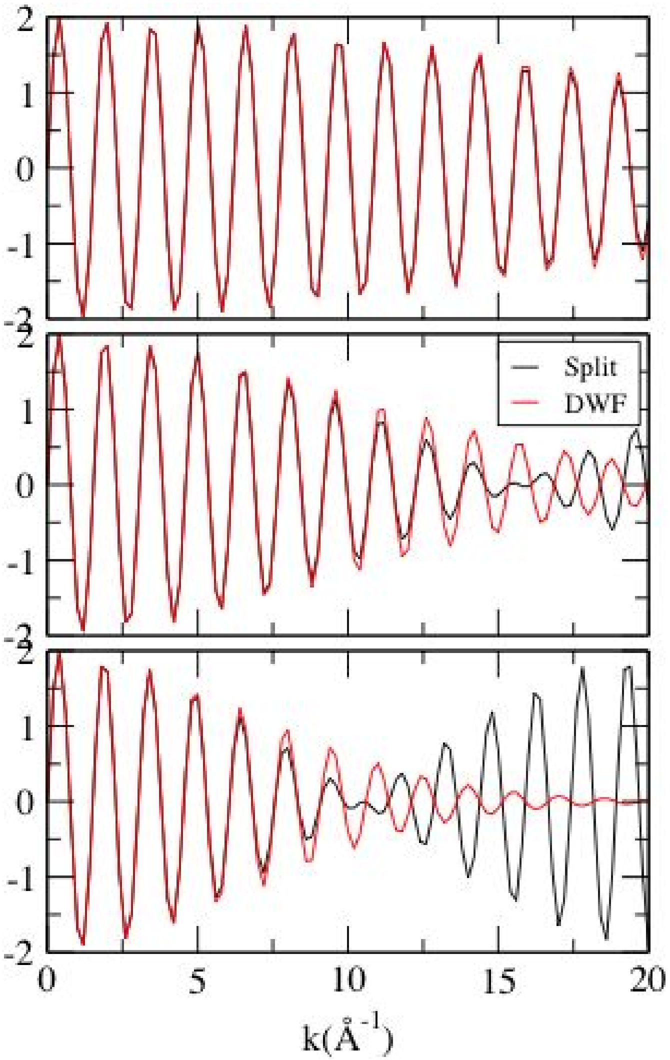
R=2.0Å

ΔR=0.05 Å

ΔR=0.1 Å

ΔR=0.15 Å

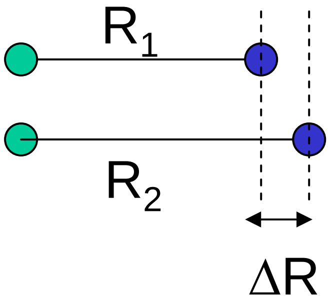
Spatial Resolution



σ=0.025Å

σ=0.05Å

σ=0.075Å



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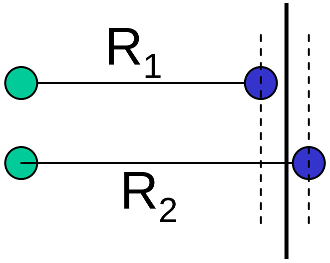
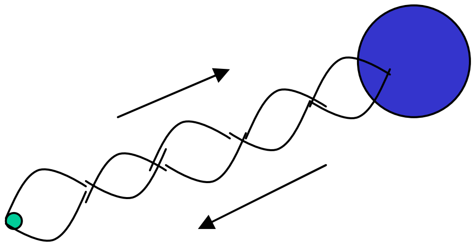


$$\langle R\rangle = (R_1 + R_2)/2$$

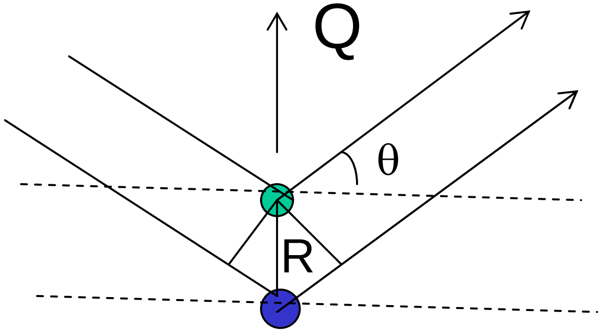
$$\sigma = \Delta R/2$$

Needs $k_{\mathrm{max}} > k_{\mathrm{beat}}$ to resolve ΔR

Spatial resolution



k, 2R



Q, R

In XAFS phase shift between outgoing and backscattered waves is given by 2R (optical path length).
In diffraction, phase shift between scattered waves given by some projection of R.

$$Q = \frac{4\pi}{\lambda}\sin\theta$$

$$k_{\max} \ge \frac{\pi}{2\Delta R}$$

$$Q_{\max} \ge \frac{\pi}{\Delta R}$$

$$Bragg: Q_{hkl} = \frac{2\pi}{d_{hkl}}; d_{hkl} = \sqrt{\frac{a^2}{h^2}+\frac{b^2}{k^2}+\frac{c^2}{l^2}}$$

k_{max}~20Å^{-1}, ΔR~0.08Å

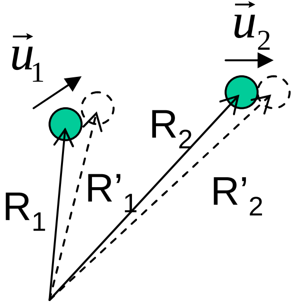
a~3Å, (10,0,0), Q~20Å^{-1}, ΔR~0.16 Å

Footnote #3:

- **In order to resolve a distance splitting of ΔR needs to measure XAFS at least up to $k_{max}=(\pi/2\Delta R)$, and diffraction up to $Q_{max}=(\pi/\Delta R)$.**
- **Other techniques, especially those sensitive to symmetry breaking (Raman, Bragg diffraction), could be more sensitive than XAFS to detect small distance splittings. Even if distances cannot be resolved by XAFS, small changes might be evidenced in anomalous T Dependence of DWF’s.**

Atomic Disorder (DWF's)

Debye-Waller factors



$$u_1^2 = \left\langle (\vec{R}_1' - \vec{R}_1)^2 \right\rangle; u_2^2 = \left\langle (\vec{R}_2' - \vec{R}_2)^2 \right\rangle$$

$$\sigma^2 = \left\langle [(\vec{R}_2' - \vec{R}_1') - (\vec{R}_2 - \vec{R}_1)]^2 \right\rangle =$$

$$= \left\langle [(\vec{R}_2' - \vec{R}_2) - (\vec{R}_1' - \vec{R}_1)]^2 \right\rangle =$$

$$= u_1^2 + u_2^2 - 2\langle(\vec{u}_1 \cdot \vec{u}_2\rangle = u_1^2 + u_2^2 - 2u_1u_2\langle \hat{u}_1 \cdot \hat{u}_2 \rangle$$

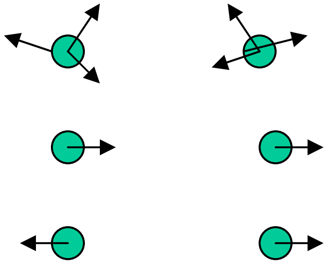
Diffraction: u^2
XAFS : σ^2

$$|u_1| = |u_2|$$

$$\sigma^2 = u_1^2 + u_2^2, \quad if \ C = 0$$

$$\sigma^2 = 0, \quad if \ C = 1$$

$$\sigma^2 = 4u^2, \quad if \ C = -1$$



Footnote # 4:

- **XAFS yields disorder in interatomic distances while Diffraction (as well as Mossbauer spectroscopy) yields disorder about crystal sites.**

- **Care must be exercised when comparing DWF’s amongst techniques. Such comparison, however, might be useful in determining correlations in atomic displacements.**

Orientation dependence (angular-resolved XAFS)

See http://www.aps.anl.gov/xfd/people/haskel/NSLS-meet_files/v3_document.htm

Thanks for listening.
Now is question/discussion time.