

XAFS and other techniques

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Advanced Photon Source

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Complementarity; strengths and weaknesses

- **Other probes of local structure also sensitive to atomic positions, disorder, dynamics.**
- **Information from other probes usually complements that obtained by XAFS (and vice versa)**
 - *Neutron and x-ray diffraction (PDF analysis)*
 - *Nuclear resonance (Mossbauer Spectroscopy, NMR, NQR)*
 - *Electron Energy Loss Spectroscopy (EELS)*
 - *Non-resonant inelastic x-ray scattering (e.g. X-ray Raman)*

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



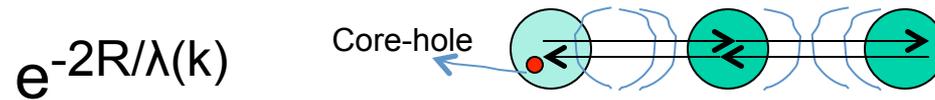
Outline

- **The length scales (short vs long-range order)**
- **The time scales (static vs dynamic)**
- **Spatial resolution (can I resolve these distances?)**
- **Atomic disorder**
- **The “Z problem” (can I distinguish between atoms?)**
- **Polarization dependence**

The length scale

The Length scale: Short versus long-ranged probes

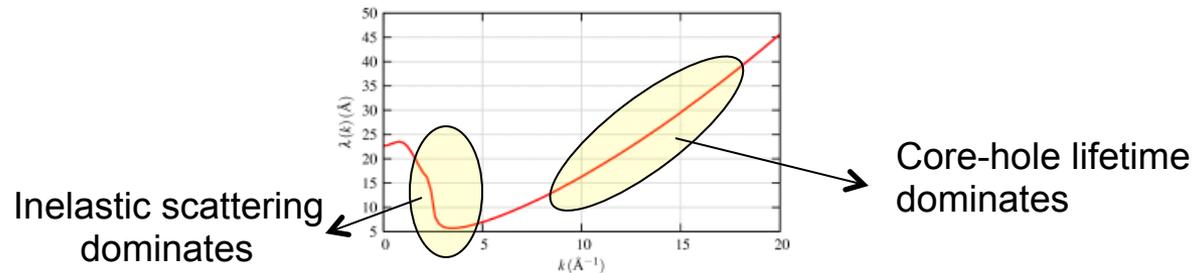
- XAFS probes as far as the **elastically-scattered** photoelectron can reach all the while the **core-hole is alive**.



- Mean-free path (λ) is determined by the core-hole lifetime (τ) and the inelastic losses. Both depend on p.e. wavenumber k .
The higher the k , the farthest the p.e. reaches within τ . Losses are strongly tied to available excitations (e.g. plasmons)

$$p = \hbar k = mv$$

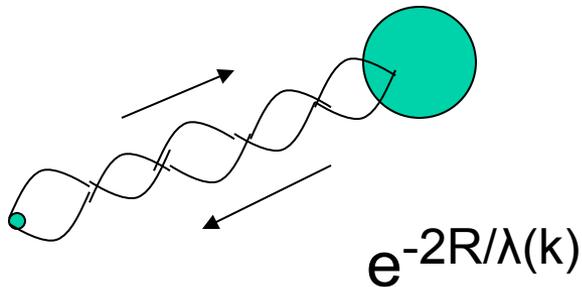
$$v = \frac{x}{\tau}; x = \frac{\hbar k}{m} \tau$$



XAFS is an *excited* final state effect, so length and time scales are related !

Length scales...

- Since XAFS is an interference effect between outgoing and backscattered p.e. waves, it needs a coherent final state. Inelastic scattering (losses) changes the p.e. wavenumber (energy) destroying coherence



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

$$k = \frac{2\pi}{\lambda_{p.e.}}$$

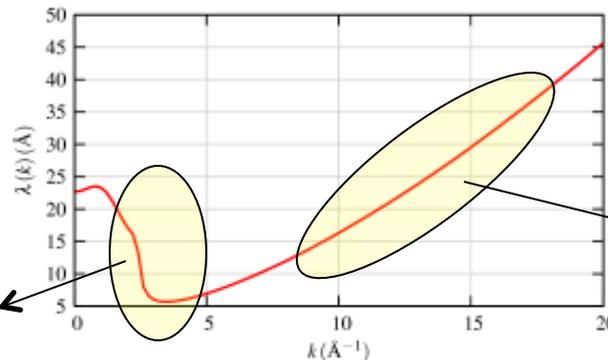
This is wavelength, not mean free path.

$$E = 3.81k^2$$

$$E = 30 \text{ eV at } 2.8 \text{ \AA}^{-1}$$

Length scale (k) $\sim 10 \text{ \AA}$

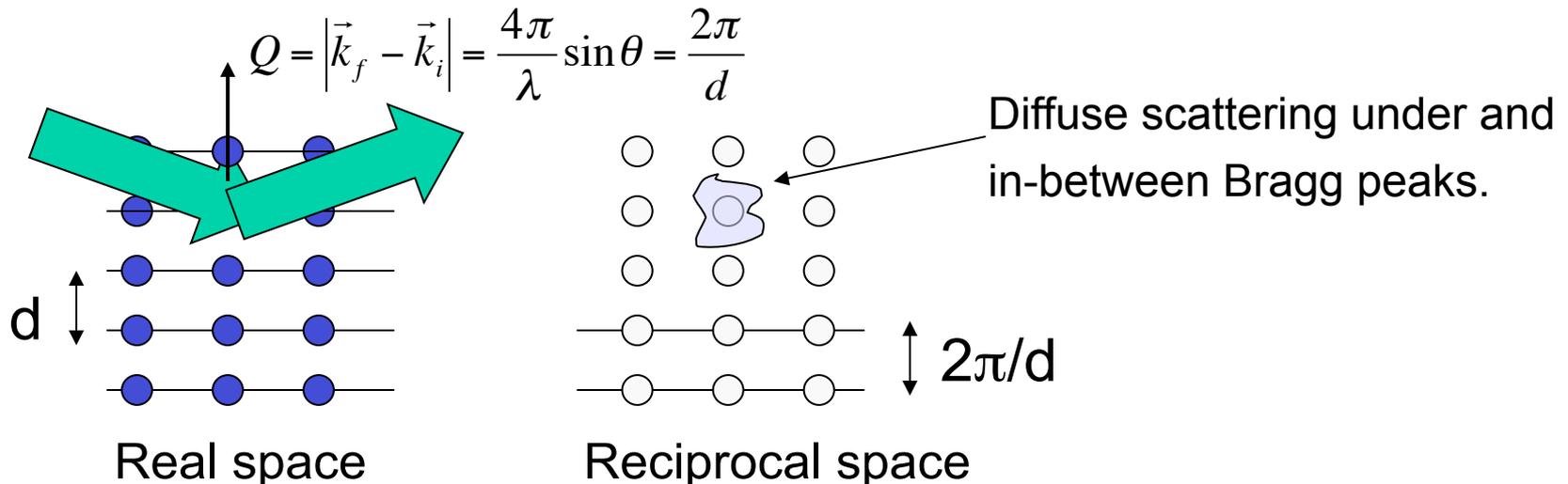
Inelastic scattering dominates



Core-hole lifetime dominates

Length scales...

- **Bragg 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).



PDF from scattering data (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} :

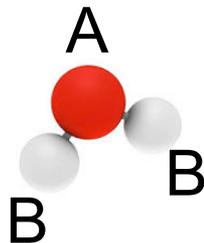
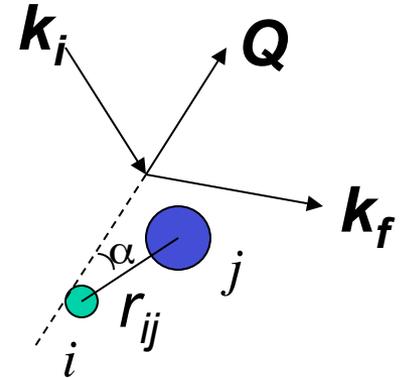
$$\langle e^{iQr_{ij} \cos \alpha} \rangle = \frac{1}{4\pi} 2\pi \int_{-1}^1 d(\cos \alpha) e^{iQr_{ij} \cos \alpha} = \frac{\sin Qr_{ij}}{Qr_{ij}}$$

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

oscillatory function of Q with r_{ij} frequency
here Q plays role of k in XAFS

$I(Q)$ can yield radial distribution functions in amorphous, liquid, crystalline samples. In 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.

- Resonant PDF can enhance selected pair correlations



Length scales: Some other techniques.

Other probes of short range order:

- Nuclear techniques: Mossbauer spectroscopy, NMR, NQR
- Electron techniques: Electron energy loss spectroscopy (EELS)
- X-ray techniques: Inelastic x-ray scattering (X-ray Raman)

Mossbauer, NMR, NQR

Nuclear energy levels and nuclear spin relaxation depends on local structure (neighbors, symmetry, disorder).

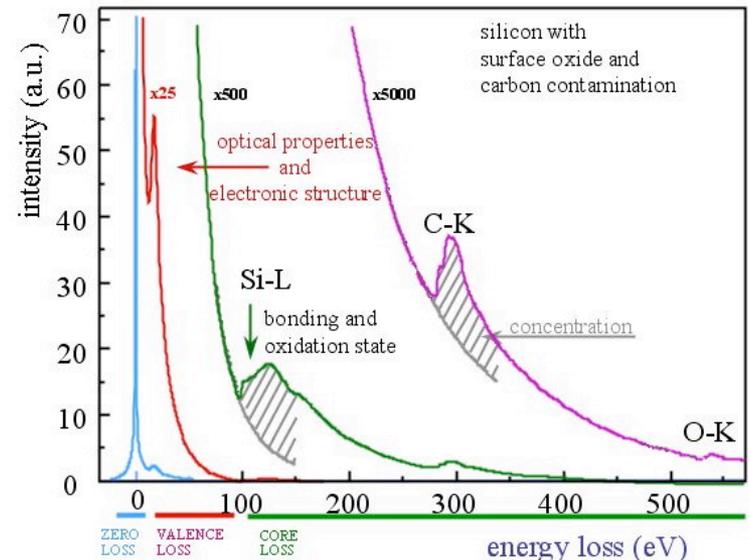
Limited to selected isotopes

EELS (X-ray Raman)

energy loss of inelastically scattered electrons (photons).

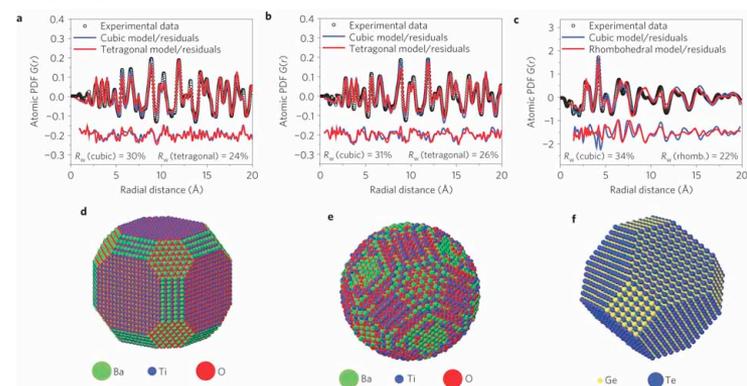
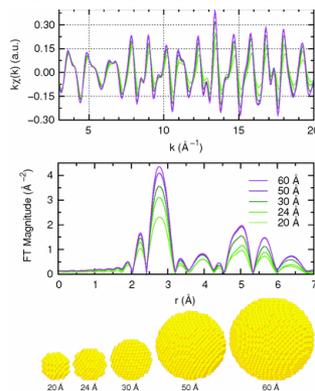
EELS: Limited to *thin films* (1000 Å).

X-ray Raman: Access to soft energy edges (e.g. for high pressure expts)

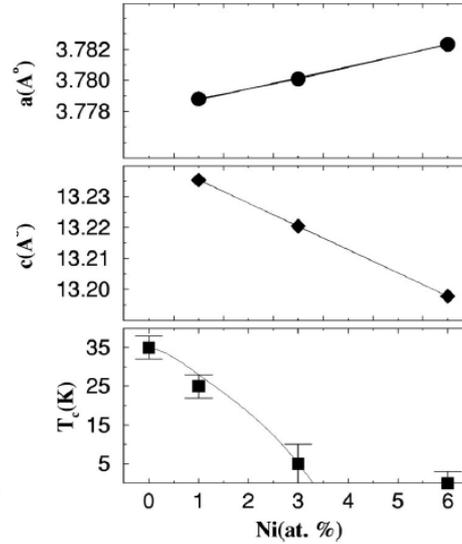
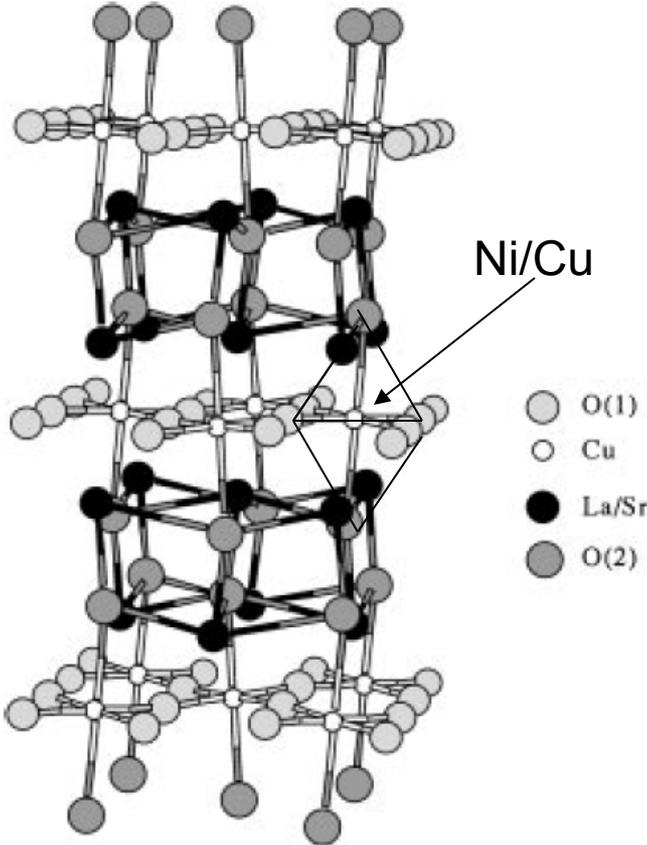


Summary: length scales

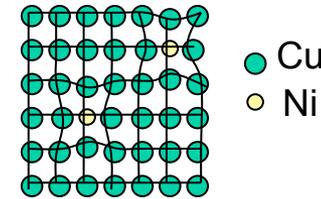
- XAFS (also EELS, X-ray Raman, Nuclear techniques) probes short-range order only ($\sim 10 \text{ \AA} = 1 \text{ nm}$)
- Scattering can probe *both* long-range ($\sim 1 \text{ }\mu\text{m}$), periodic ordering (Bragg scat, $Q=G$) and short-range ordering through PDF analysis (diffuse scat. $Q \neq G$).
- The big advantage of XAFS is in its element specificity (PPDF): e.g., diluted concentrations. Also allows direct measurement of 3-body correlations through multiple scattering. The big advantage of PDF-scattering is that it can also probe intermediate order (10-30 \AA), if it exists.



Example: Local structure vs average structure



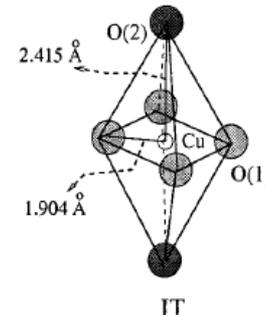
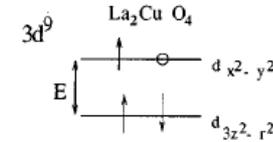
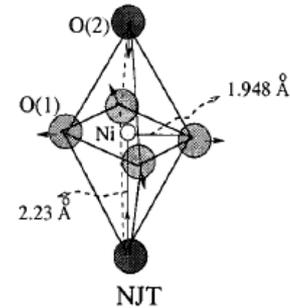
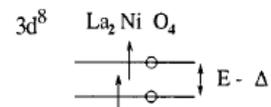
Diffraction: Ni doping contracts c-axis, expands a-axis, **uniformly**



Vegard's law

$$x \cdot c_{Ni} + (1-x) \cdot c_{Cu} = c_{macroscopic}$$

$$(\Delta V / V)_{Ni} > (\Delta V / V)_{macroscopic}$$

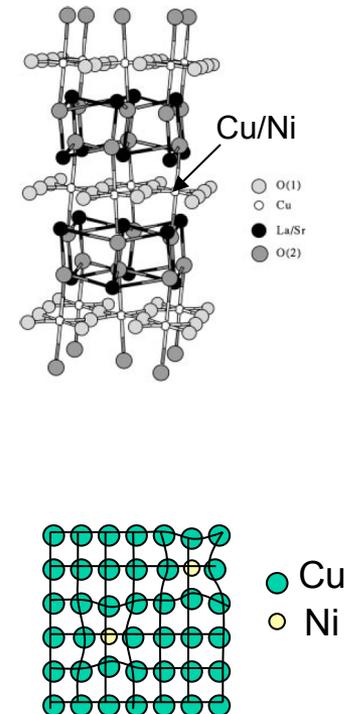
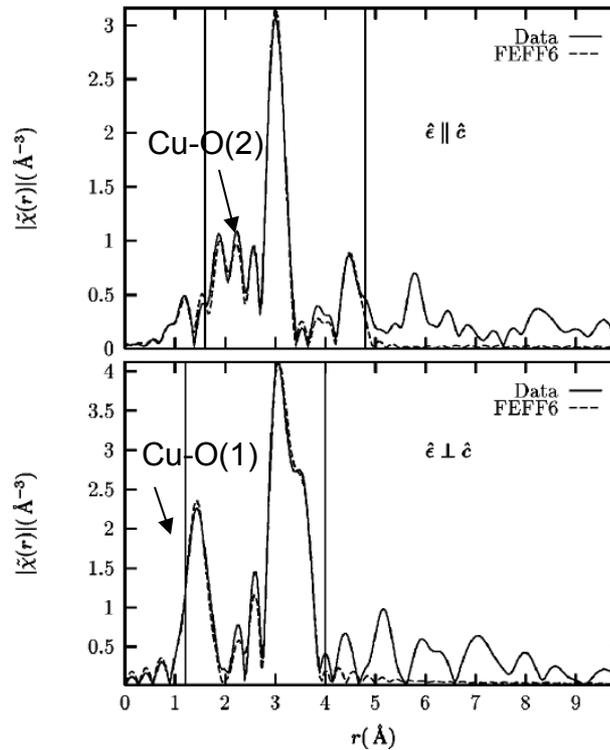
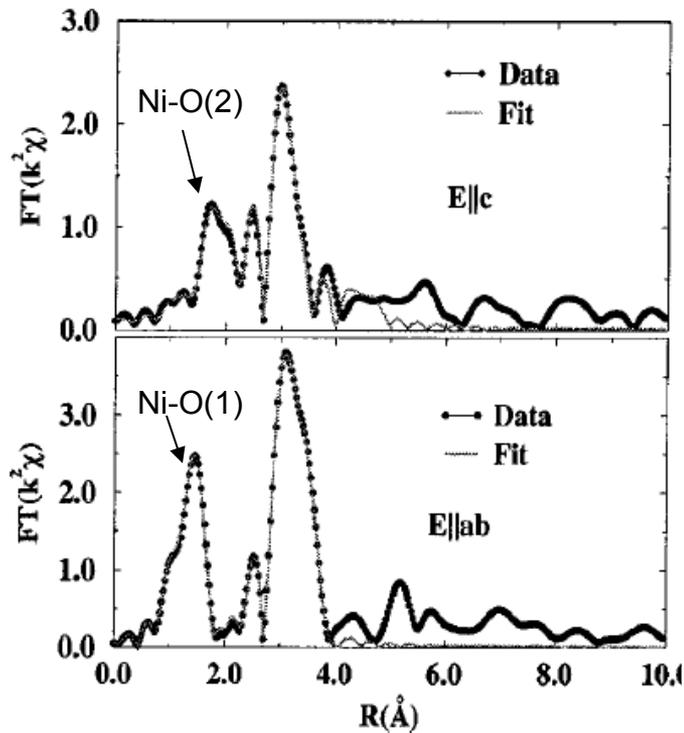


Cu²⁺: Jahn Teller
Ni²⁺: non JT



Ni XAFS

Cu XAFS



$$x \cdot a_{Ni} + (1-x) \cdot a_{Cu} = a_{macroscopic}$$

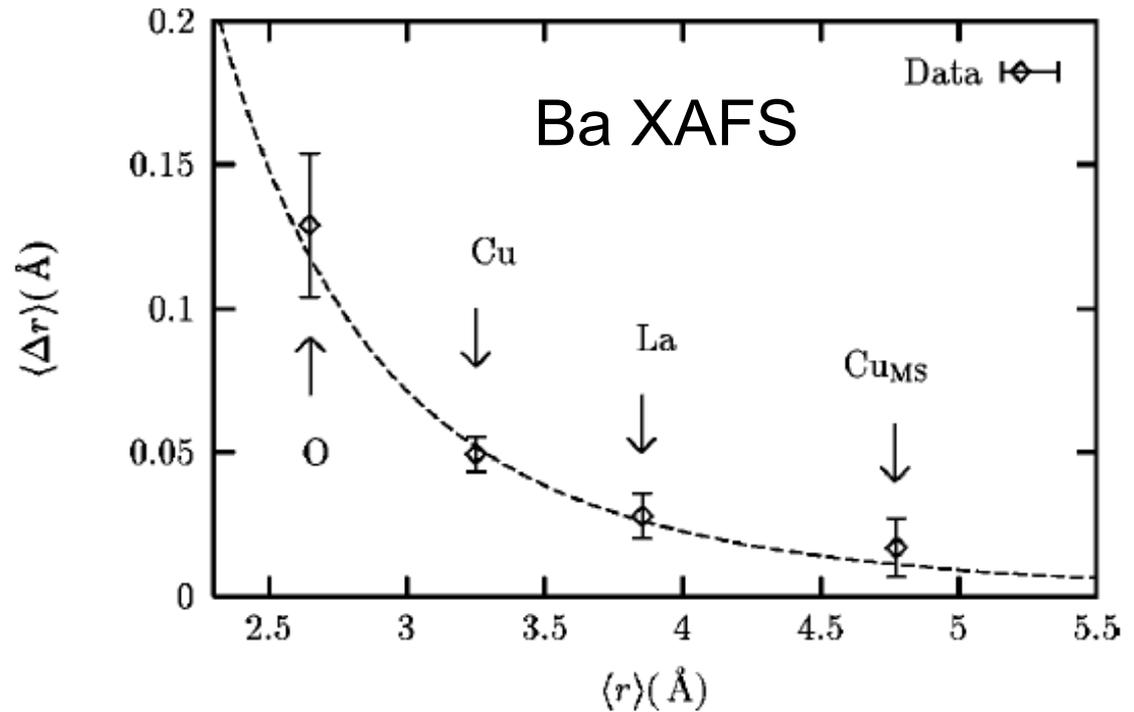
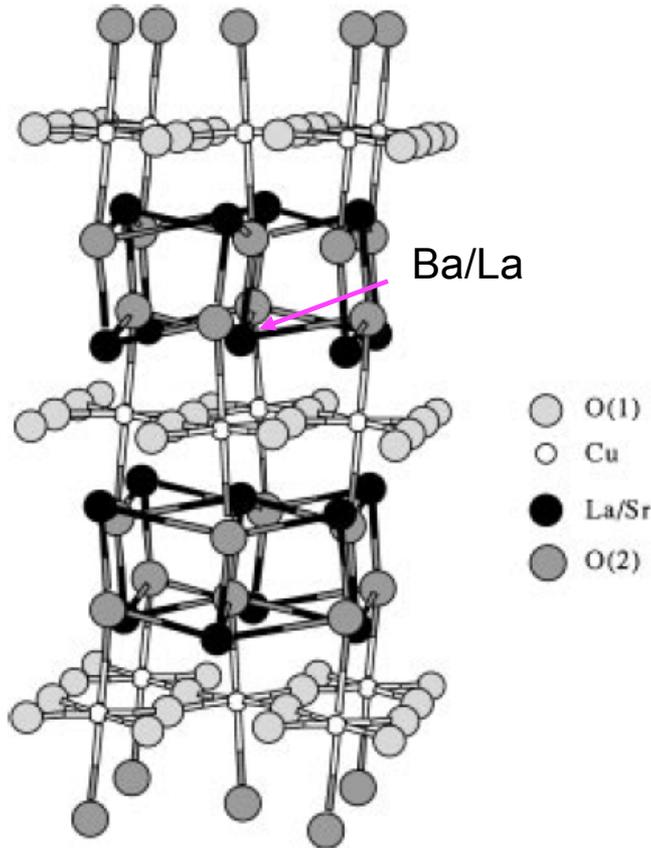
Ni distortion not periodic, only average lattice contraction seen by diffraction. Should yield diffuse scattering.

	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	

$$x \cdot c_{Ni} + (1-x) \cdot c_{Cu} = c_{macroscopic}$$



Local strain field around a large ion.



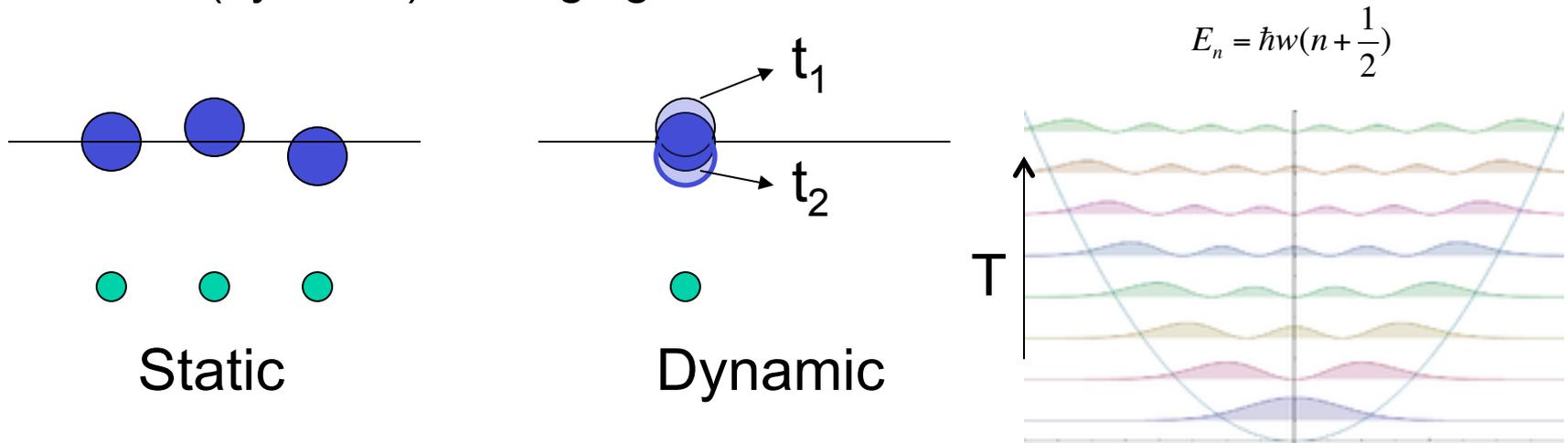
Strain field around Ba due to larger ionic size than La.

Non-periodic distortion easily seen/quantified with XAFS
Diffraction would show disorder, lattice expansion

Time scales

Time scale: XAFS

- XAFS time scale given by the core-hole lifetime, 10^{-15} sec, much faster than any atomic motion (phonons meV $\rightarrow 10^{-13}$ 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.

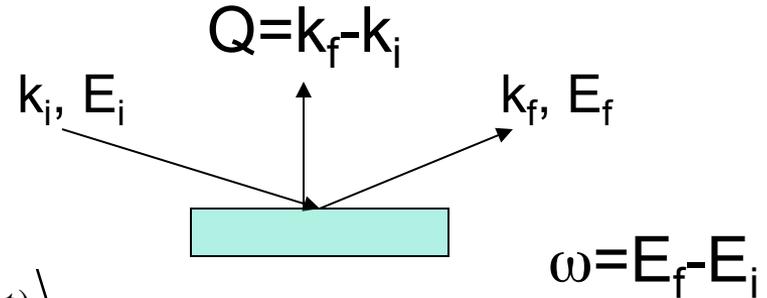


XAFS can't distinguish between static and dynamic displacements.
(However T dependence can be used to separate static from thermal disorder)

Time scale: Scattering/Diffraction

The x-ray and neutron scattering cross section is related to $S(Q, \omega)$:

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



Scattering with no energy discrimination (“quasi-elastic”) integrates over ω ,

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

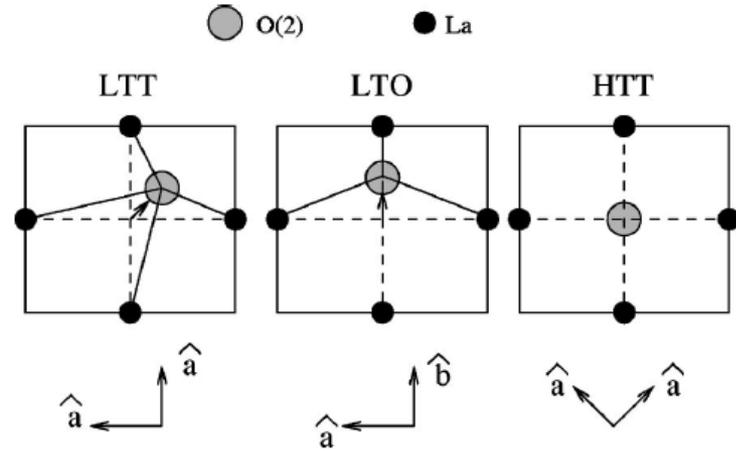
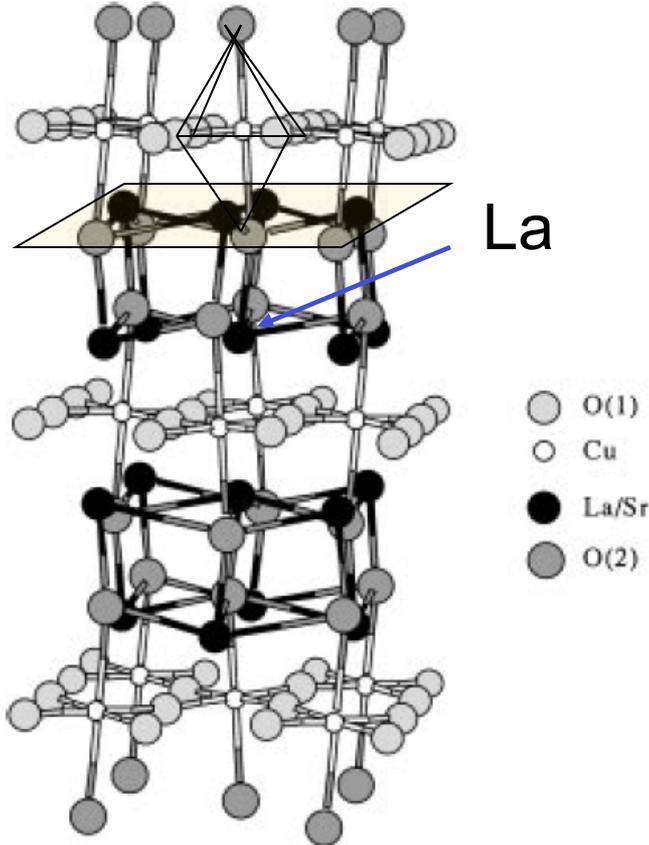
... and results in $S(Q)$ at $t=0$; *i.e.*, the instantaneous correlation function.

- Energy discrimination (inelastic scattering) can be used to probe dynamics

Time scales

- **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 nuclear states.**

Example: time scales

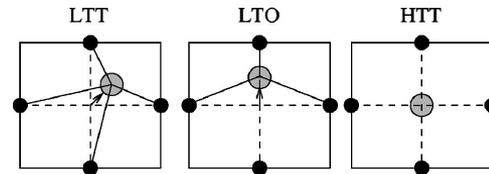
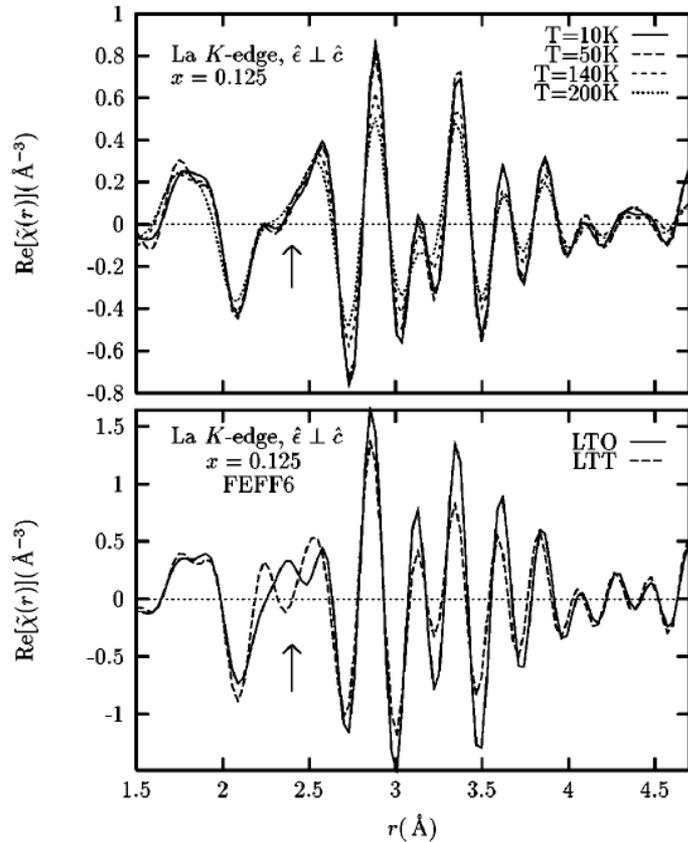


Bragg diffraction:
LTT → LTO → HTT
60K 200K

Change in tilt direction results in significant redistribution of La-O(2) distances; easily probed by XAFS

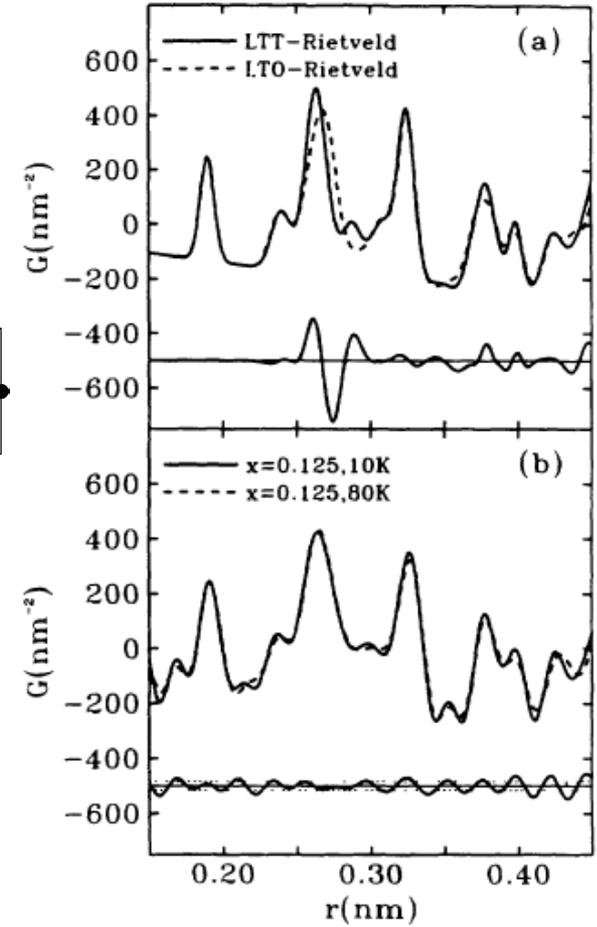
Expected changes at LTT → LTO phase transition

La XAFS



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

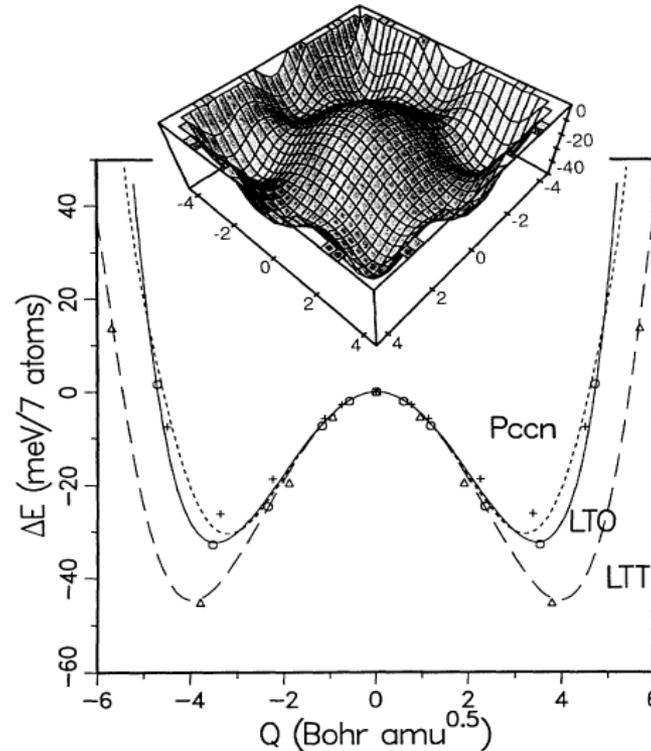
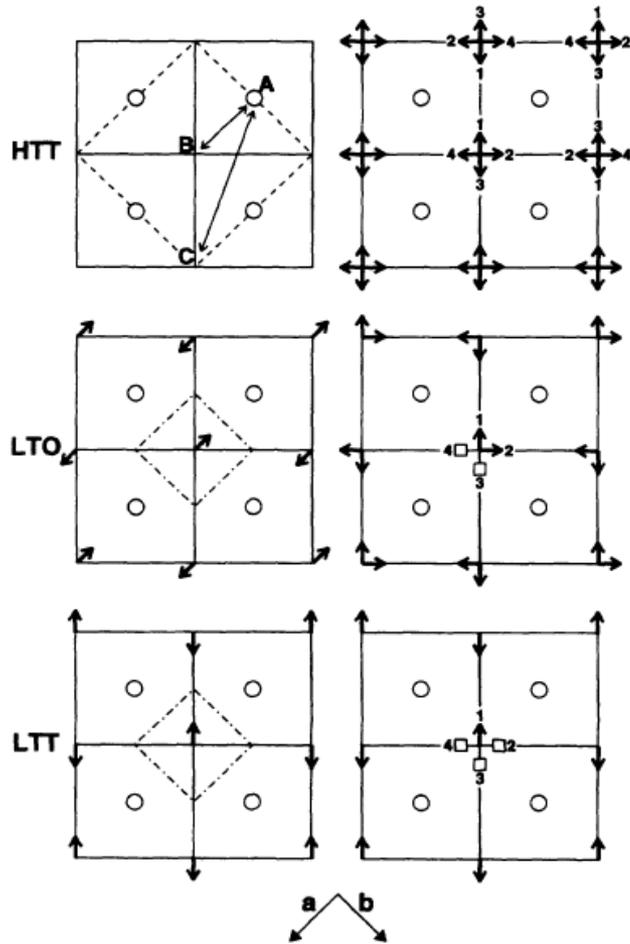
Neutron's PDF



Octahedra do not change tilt direction !



Orientational dynamical disorder

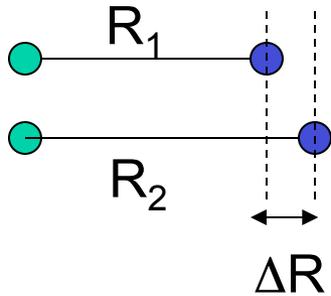


Slower probes (e.g. La NMR) or long-range probes will average over dynamic displacements, while XAFS only sees local tilt

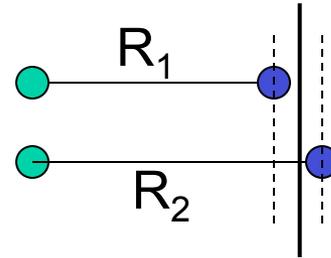
Spatial resolution

Spatial resolution

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



OR



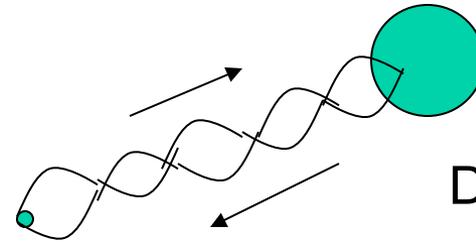
$$\langle R \rangle = (R_1 + R_2)/2$$

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

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

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

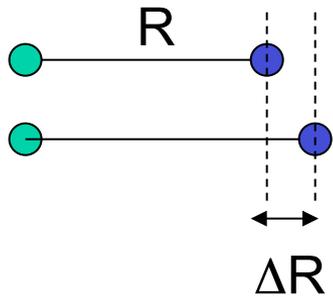
$$k_{\max} \geq \frac{\pi}{2\Delta R}$$



De Broglie λ

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

Spatial Resolution



A little more rigorous derivation:

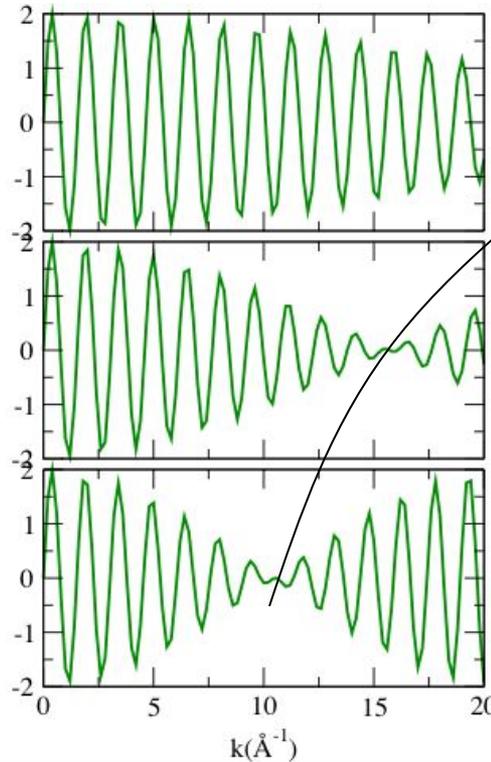
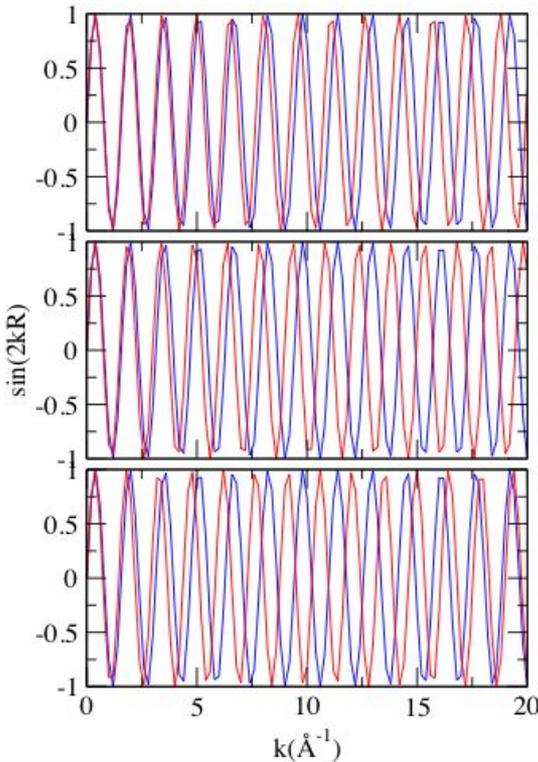
$$\sin 2kR + \sin[2k(R + \Delta R)] =$$

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

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

Low “freq” modulation
with beat at $2k\Delta R = \pi$

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



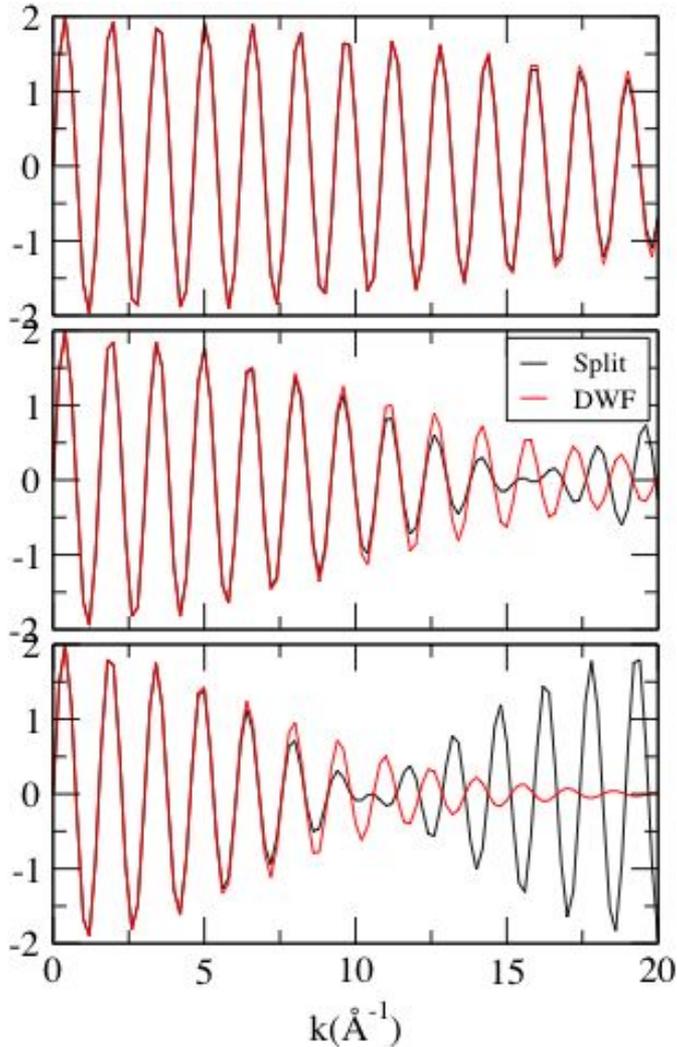
$\Delta R = 0.05 \text{ \AA}$

$\Delta R = 0.1 \text{ \AA}$

$\Delta R = 0.15 \text{ \AA}$

$R = 2.0 \text{ \AA}$

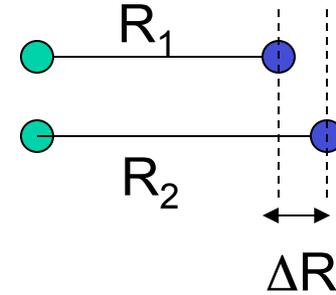
Spatial Resolution



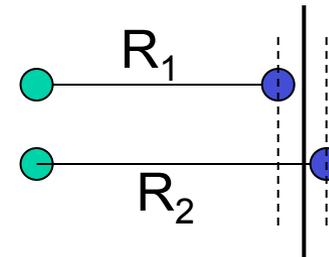
$\sigma = 0.025 \text{ \AA}$

$\sigma = 0.05 \text{ \AA}$

$\sigma = 0.075 \text{ \AA}$



OR

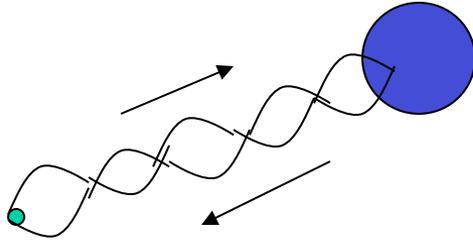


$$\langle R \rangle = (R_1 + R_2) / 2$$

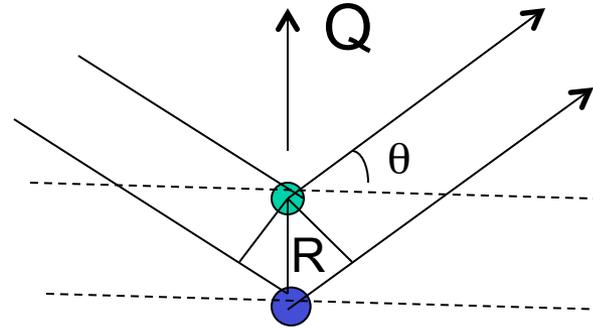
$$\sigma = \Delta R / 2$$

Needs $k_{\text{max}} > k_{\text{beat}}$ 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 .

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

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

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

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

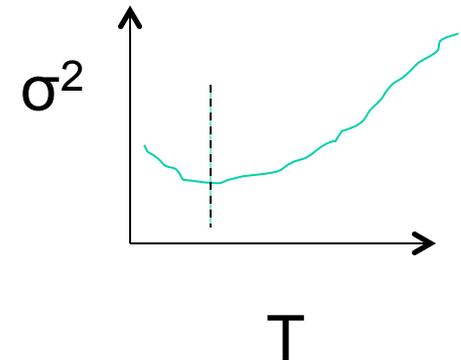
$$k_{\max} \sim 20 \text{ \AA}^{-1}, \Delta R \sim 0.08 \text{ \AA}$$

$$a \sim 3 \text{ \AA}, (10,0,0), Q \sim 20 \text{ \AA}^{-1}, \Delta R \sim 0.16 \text{ \AA}$$

Spatial resolution

- In order to resolve a distance splitting of ΔR needs to measure XAFS to at least $k_{\max}=(\pi/2\Delta R)$, 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.

e.g. unresolved distance splitting at low T
due to structural phase transition



Atomic Disorder (DWF' s)

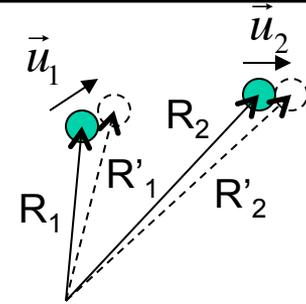
Debye-Waller factors

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

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

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

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



Diffraction:	u^2
XAFS	σ^2

$$|u_1| = |u_2|$$

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



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



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



Atomic Disorder

- XAFS yields disorder in interatomic distances while Diffraction (as well as Mossbauer spectroscopy) yields disorder about lattice site.
- Care must be exercised when comparing DWF' s amongst techniques. Such comparison, however, might be useful in determining correlations in atomic displacements.

$$|u_1| = |u_2|$$

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



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



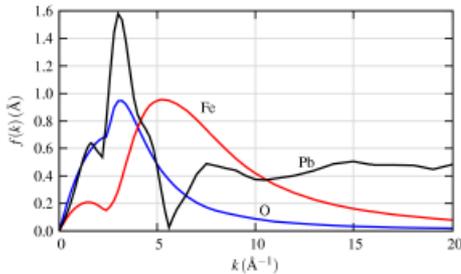
$$\sigma^2 = 4u^2, \quad \text{if } C = -1$$



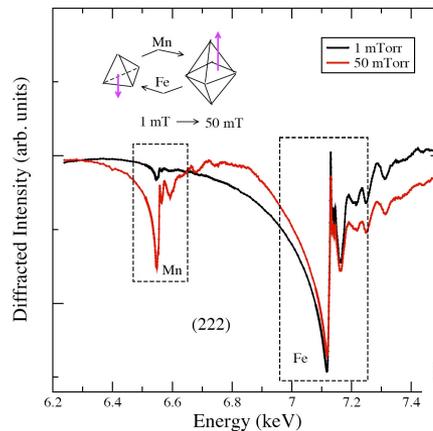
The “Z” problem

The Z problem and getting around it

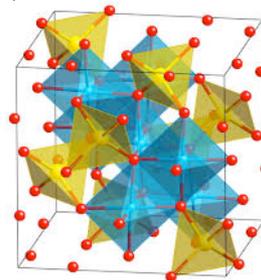
- Scattering amplitude depends on Z; XAFS can't distinguish neighbors only a few Z apart
- Non-resonant x-ray diffraction same problem ($f_0 \sim Z$)
- Resonant x-ray diffraction/PDF : $f_0 + f' + if''$
- Neutron diffraction scattering length: $b = b' - ib'' = b_c + \frac{2b_i}{\sqrt{I(I+1)}} s \cdot I$



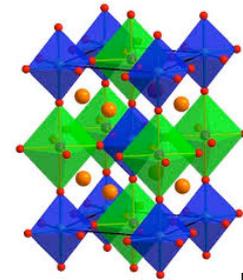
$F(k)$



$MnFe_2O_4$



	bc	bi
Mn	-3.73	1.8
56Fe	9.94	0
Co	2.49	-6.2
58Ni	14.4	0



Double Perovskite
e.g. La_2MnNiO_6

Polarization dependence

Polarization dependence

- You may be able to exploit the polarization dependence of XAFS to solve complex structures with overlapping distances
- Or to probe for orientational order in your sample

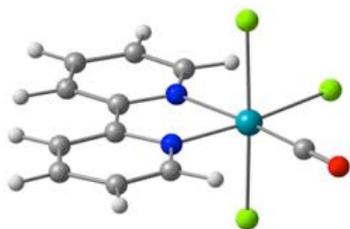
$$\mu(E) \approx |\langle f | e\vec{r} \cdot \vec{\varepsilon} | i \rangle|^2$$

Electric dipole linear polarization $\Delta l = \pm 1, \Delta m = 0$

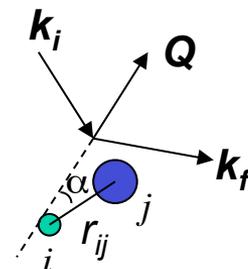
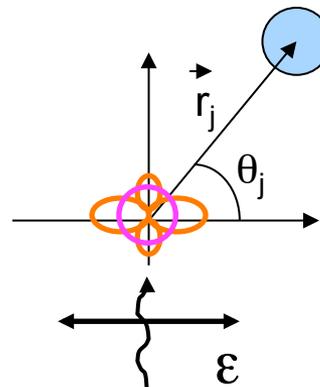
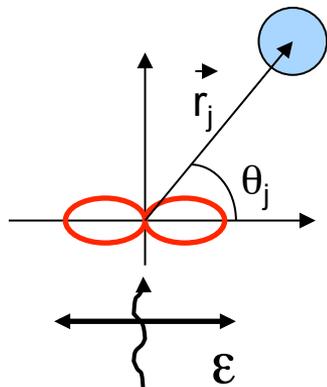
K-edge: $s \rightarrow p$

$L_{2,3}$ edges: $p \rightarrow d, p \rightarrow s$

Scattering probes:
 Q plays role of ε



mer-[Os^{II}(CO)(bpy)Cl₃]



$$I = \sum_i \sum_j f_i^* f_j e^{-i\vec{Q} \cdot (\vec{r}_i - \vec{r}_j)}$$

$$\chi(k) \propto 3 \cos^2 \Theta_j f(\pi)$$

$$\chi(k) \propto \langle 112 \rangle \langle 011 \rangle f(\pi) (1 - 3 \cos^2 \Theta_j) + \frac{| \langle 211 \rangle |^2}{2} f(\pi) (1 + 3 \cos^2 \Theta_j) + \frac{| \langle 011 \rangle |^2}{2} f(\pi)$$



Polarization dependence

- Dipole selection rules (and polarization dependence) a consequence of orthonormality of Spherical harmonics

$$\mu(E) \approx |\langle f | e\vec{r} \cdot \vec{\epsilon} | i \rangle|^2$$

$$Y_l^m(\theta, \varphi) \approx P_l^m(\cos\theta)e^{im\varphi}$$

$$\int_{-1}^1 P_l(x)P_l(x)dx = \frac{2}{2l+1}\delta_{ll} \quad \left\{ \begin{array}{l} P_0(x) = 1 \\ P_1(x) = x \\ P_2(x) = \frac{1}{2}(3x^2 - 1) \end{array} \right.$$

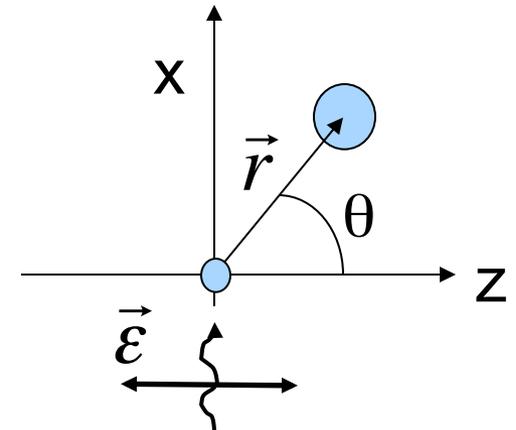
$x = \cos\Theta$

K-edge:

Y_1^0

$$\left\{ \begin{array}{l} |i\rangle = |s\rangle \quad \text{○} \quad (l = 0, P_0) \\ \vec{r} \cdot \vec{\epsilon} \approx \cos\Theta \quad (P_1) \end{array} \right.$$

$$|f\rangle = |p\rangle \approx \cos\Theta \quad \text{○○} \quad (l = 1, P_1)$$



Electric dipole
Linear polarization

$$\Delta l = \pm 1, \Delta m = 0$$

Polarization dependence

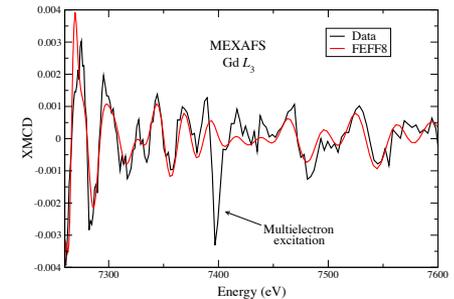
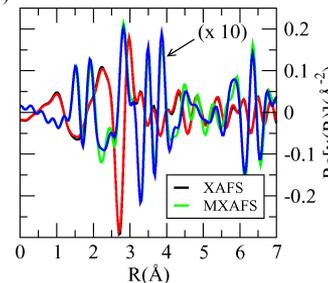
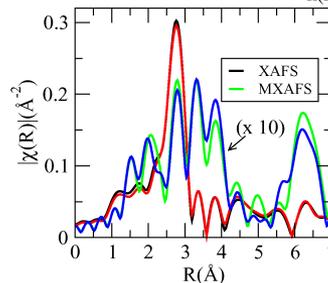
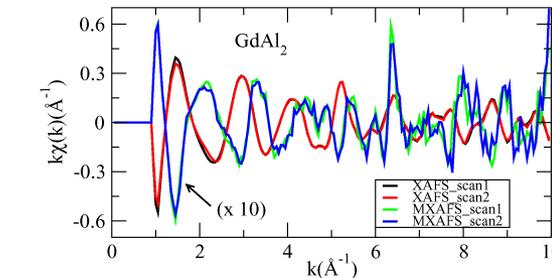
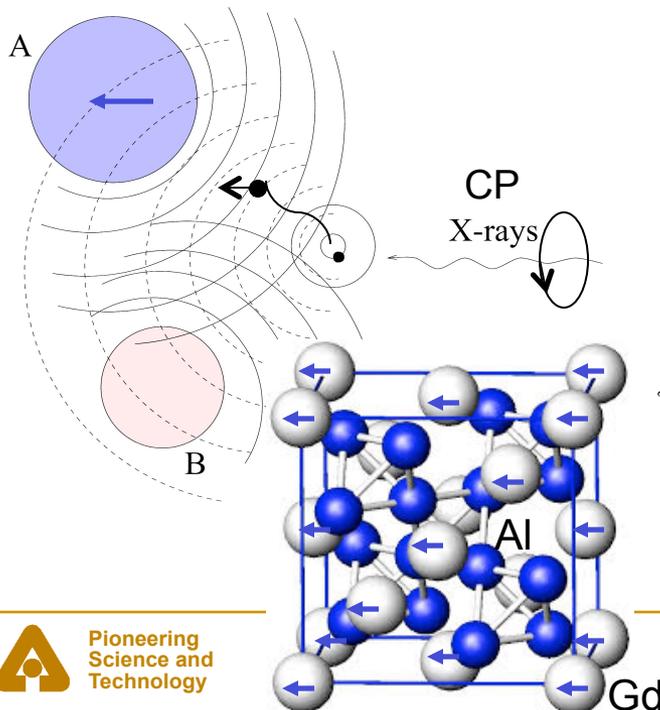
- When using circularly polarized x-rays, dipole selection rules (preservation of angular momentum) require that **excited photoelectrons carry projection of angular momentum** originally carried by the photon \rightarrow XMCD and MXAFS

$$\mu(E) \approx |\langle f | e\vec{r} \cdot (E\hat{x} \pm iE\hat{y}) | i \rangle|^2$$

$$Y_l^m(\theta, \varphi) \approx P_l^m(\cos\theta)e^{im\varphi}$$

$$\Delta l = \pm 1, \Delta m = \pm 1$$

$\downarrow Y_1^{\pm 1}$





International X-ray Absorption Society PORTAL

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XAFS16 1st Flyers
Satellite Meetings
DESY, Hamburg
Stuttgart
HZB, Berlin-Adlershof

NEWS

IXAS16 Awards Call for Nominations
November 4, 2014

International Conference on Electronic Structure and Spectroscopy (ICESS15)
October 21, 2014

4th Mexican Synchrotron Radiation Users Meeting
October 21, 2014

Revised timeline for XASF conference site selection
August 3, 2014

XASF16 Satellite Meetings
June 29, 2014

The 12th International School and Symposium on Synchrotron Radiation in Natural Science (ISSRNS 2014)
May 30, 2014

XAFS16 Satellite Meeting : Application of XAFS to the Study of magnetic Materials
May 17, 2014

German Conference for Research with Synchrotron Radiation, Neutrons and Ion Beams at Large Facilities 2014
May 8, 2014

XAFS16 Satellite Meeting : Data acquisition, treatment, storage-

IXAS Web Magazine
XAS Research Review

Volume 10

Facility Representative's Area
Facility Links
Info plaza for facilities & XAS users

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First Announcement

16th International Conference on X-ray Absorption Fine Structure



XAFS16

23 - 28 August 2015

Karlsruhe Institute of Technology Karlsruhe, Germany

Important dates :

2nd Announcement : mid 2014
Abstract submission : January 15, 2015
Registration : April 2015

International Scientific Advisory Committee

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Clemens Heske
Henning Lichtenberg
Stefan Mangold
Jörg Rothe
Ralph Steininger
Marika Vespa
Tomya Vitova

Satellite sessions at HZB (Berlin), DESY (Hamburg) and the MPI-IS (Stuttgart)

Ernst Fleck Aze (HZB)
Eberhard Goering (MPI-IS)
Edmund Weiler (DESY)

Details will be announced at the conference
website

Topics

- X-ray facilities, instrumentation, optics
- Materials science and energy-related materials
- Catalysis
- Radioactive and nuclear materials
- Life science, biology and biochemistry
- Earth and environmental sciences
- Cultural heritage
- Atoms and molecules
- Nanotechnology
- Surfaces and interfaces
- Magnetism
- Soft matter
- X-ray and electron spectroscopies (XES, RIXS, NEXS, HERFD, and XPS)
- Theoretical methods
- Software, data analysis
- Newer methods and combination of techniques
- Time-resolved and ultrafast techniques
- X-ray microscopy



Website : <http://www.xafs16.org>
E-Mail : info@xafs16.org

HZB Helmholtz
Zentrum Berlin

