

## **XAFS** and other techniques

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## **Complementarity with other techniques Gain awareness of strengths and limitations**

Other probes of local structure sensitive to bonding, symmetry, disorder, dynamics

- Neutron and x-ray scattering probes (Pair Distribution Function, Diffuse Scattering)
- Nuclear resonance probes (Mossbauer Spectroscopy, NMR, ...)
- Electron scattering probes (EELS, EXELFS, )
- Non-resonant inelastic x-ray scattering (X-ray Raman)
- Optical probes (Raman, IR, ...)



The different length and time scales probed by complementary techniques can provide a more holistic view of the structure and dynamics

### **Outline**

- The length scales (short vs long-range order)
- The time scales (static vs dynamic)
- Spatial resolution (can I resolve these distances?)
- Atomic disorder (DWFs)
- The "Z problem" (can I distinguish between atoms?)
- Directional information (beyond "radial" in RDF)
- Extensions of XAFS (site-specific DAFS, magnetic XAFS/DAFS)
- APS-U: nanoprobes, extreme conditions

# The length scale



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

 XAFS probes distances 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 contributions depend on p.e. wavenumber k.
  - The higher the k, the farthest the p.e. reaches within  $\tau$ . Losses are strongly tied to available excitations (e.g. plasmons)



XAFS is an excited final state effect (finite lifetime), 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 final state coherence



Other sources of damping and attenuation (DWFs at high k, spherical wave  $\chi(k) \sim R^{-2}$ ) lead to typical L < 10 Å

#### Length scales...

- Bragg diffraction probes a scale over which the scattering is coherent; i.e., well defined correlations in atomic positions. In high quality crystals this could be 1000 Å or longer (i.e., way 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. from phonons, or short-range order).



### PDF from total 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<sub>ij</sub> :

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

$$I(Q) = \sum_{i} \sum_{j} f_i^* f_j \frac{\sin Q r_{ij}}{Q r_{ij}}$$

Oscillatory function of Q with r<sub>ij</sub> fequency 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 pair correlations* (AA, BB, AB for two atom types)
- XAFS measures partial pair correlations involving absorbing atom
- XAFS goes beyond pair correlations when multiple scattering is included (3-body, 4-body...)
- Resonant PDF can enhance selected pair correlations

## Length scales: Some other techniques

Other probes of local structure

- Nuclear techniques: Mossbauer spectroscopy, NMR, NQR
- Electron techniques: Electron energy loss spectroscopy (EELS, EXELFS)
- 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 or photons. EELS: Limited to *thin films (1000 Å)* 









O K-edge Raman ( $E_i$ ~ 10 keV), Diamond anvil cell X-ray induced H<sub>2</sub>O cleavage and formation of O2-H2 molecular alloy W. Mao et al., Science 2006

X-ray Raman: Access to soft x-ray edges in opaque environments (e.g. high pressure expts) X-ray Raman and EELS: beyond E-dipole approximation at large Q values

## **Summary: Length scales**

- XAFS (also EELS/EXELFS, X-ray Raman, Nuclear techniques) sensitive to short-range order only (~ few Å to 10 Å= 1 nm)
- X-ray and Neutron scattering can probe *both* long-range (~ 1000 Å) periodic ordering (Bragg scat, Q=G) and short-range ordering through PDF analysis (diffuse scat. Q≠G).
- The big advantage of XAFS is in its elemental 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 Å), if it exists.



Roscioni et al., PRB 2011

Banerjee et al., J. Chem. Phys. C, 2018

### **Example: Local structure vs average structure**



## Local structure vs average structure

Polarization dependent XAFS on oriented powder, fluorescence detection (few % Ni)



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





- JT effect absent in Ni2+, large reduction in Ni-O(2) distance.
- Random distortion, so diffraction only sees
   average lattice contraction
- Distortion should produce diffuse scattering



Haskel et al, PRB 2001

### Local structure vs average structure Local strain field around a diluted (few at %), large ion



- Non-periodic distortion easily seen/quantified with XAFS
- Invisible to diffraction other than disorder, average lattice expansion.
- Should give diffuse scattering

## Time scales



## Time scale: XAFS

- XAFS time scale given by the core-hole lifetime, 10<sup>-15</sup> sec (fs), much faster than any atomic motion (meV phonons ~ 10<sup>-12</sup> sec).
- Each absorption event probes the instantaneous atomic positions. Since a measurement integrates over many snapshots (time averaging) and over many absorbers (spatial averaging), XAFS probes the distribution of atoms through both spatial and time averaging.
- XAFS cannot directly distinguish between static and dynamic displacements.
- However, temperature dependence can be used to separate static and thermal contributions to atomic disorder (DWFs)



## **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  $\omega$ ,

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

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

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



Niels Christensen, Technical U. Denmark

## **Summary: Time scales**

- XAFS and diffraction measure the instantaneous distribution of atoms, averaged over their respective length scales.
- Inelastic x-ray and neutron scattering can probe excitations within an energy window to deduce time scale of dynamics leveraging Heisenberg's uncertainty principle ( $\Delta E \Delta t \sim \hbar$ ): 1 meV ~ 1 ps; 100 meV ~ 10 fs
- Nuclear techniques such as Mossbauer spectroscopy have slower time scales (10<sup>-9</sup> sec) due to longer lifetime of excited nuclear states.

### **Example: Time scales**



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

#### Expected changes at LTT $\rightarrow$ LTO phase transition



Haskel et al, PRB 2000

Billinge et al, PRL 1994

### Temperature driven (dynamical) orientational disorder



Slower probes (e.g. <sup>139</sup>La NMR) or long-range probes (diffraction) will average over dynamic displacements, while XAFS only sees local tilts/displacements

# **Spatial resolution**



## **Spatial resolution: XAFS**

The ability to resolve two distances "close" to each other.



Intuition: To resolve needs  $\Delta R$  to be a significant fraction of smallest p.e. wavelength:



## **Spatial Resolution: XAFS**

A little more rigorous derivation:



## **Spatial Resolution: XAFS**



## **Spatial resolution: diffraction**



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<sub>max</sub>~20Å<sup>-1</sup>, ∆R~0.08Å

a~3Å, (10,0,0), Q~20Å<sup>-1</sup>, ∆R~0.16 Å

## **Summary: Spatial resolution**

- In order to resolve distances or interplanar spacings that differ by  $\Delta R$  needs to measure XAFS to at least k<sub>max</sub>=( $\pi/2\Delta R$ ) and diffraction up to Q<sub>max</sub>=( $\pi/\Delta R$ ).
- Other probes sensitive to point and space group symmetry (optical Raman, Bragg diffraction) could be more sensitive than XAFS for detection of small distance splittings and symmetry breakings, especially when k<sub>max</sub> is limited.
- XANES can provide high sensitivity to symmetry breaking (e.g. loss of inversion center, e.g. off-center displacements in titanates)
- Even if distance splittings cannot be resolved by XAFS, they may become evident in anomalous T Dependence of DWF's.





Shebanova et al, J. Solid State Chem., 2003



Unresolved distance splitting at low T due to a structural phase transition

#### Atomic Disorder (Debye Waller factors)



Image credit: https://www.stx.ox.ac.uk/event/happ-one-day-conference-order-and-chaos

## **Debye-Waller factors**

$$u_{1}^{2} = \left\langle (\vec{R}_{1}' - \vec{R}_{1})^{2} \right\rangle; u_{2}^{2} = \left\langle (\vec{R}_{2}' - \vec{R}_{2})^{2} \right\rangle$$
  

$$\sigma^{2} = \left\langle [(\vec{R}_{2}' - \vec{R}_{1}') - (\vec{R}_{2} - \vec{R}_{1})]^{2} \right\rangle =$$
  

$$= \left\langle [(\vec{R}_{2}' - \vec{R}_{2}) - (\vec{R}_{1}' - \vec{R}_{1})]^{2} \right\rangle =$$
  

$$= u_{1}^{2} + u_{2}^{2} - 2\left\langle (\vec{u}_{1} \cdot \vec{u}_{2}) \right\rangle = u_{1}^{2} + u_{2}^{2} - 2u_{1}u_{2}\left\langle \hat{u}_{1} \cdot \hat{u}_{2} \right\rangle$$

R: equilibrium position R': off-equilibrium, either thermal or static





XAFS is biased towards sensing optical versus acoustic phonon modes

## **Summary: Atomic Disorder**

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

$$|u_1| \models |u_2|$$
  

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

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

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

#### The "Z" problem



## The Z problem

- Photoelectron scattering amplitude f(k) and phase shift  $\delta(k)$  dictated by Z number, especially at high k
- XAFS can't distinguish scatterers that are next or few Z numbers apart
- Same goes for non-resonant x-ray diffraction: scattering length  $f_o(Q)r_o \sim Zr_o$  at low Q ( $r_o$  classical e radius)
- Neutron scattering length varies randomly with Z and isotope
- Light elements such as H are pretty much invisible to XAFS



Directional information Beyond "radial" in RDF



#### Polarized XAFS (related to natural dichroism)

- When symmetry lower than cubic, can exploit polarization dependence (natural dichroism) to selectively probe subsets of local structure
- Requires single crystal or highly textured samples. Rotate crystal or rotate polarization (with insertion devices or phase plates).
- A way to solve complex local structures (e.g., distances within resolution limit), and getting directional information (distances and atom types) relative to crystalline axes.



## **Example: Polarized XAFS at high pressure**



- La K-edge XAFS on single crystal sample (layered structure, tetragonal space group)
- Use XRD to align *a* or *c* axis with linear-H polarization (rotate pressure cell/crystal)
- XRD to measure charge order and tilt correlations
- XAFS to measure local tilts

La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub>

LTO

#### **Example: Polarized XAFS at high pressure**

average, XRD

Argonne



Even though correlation length of LTT tilts is strongly reduced beyond detection limit of XRD, local tilts persist as seen by XAFS. Local tilt evolution correlates with Tc(P)

Fabbris et al, High Pressure Research 36, 348 (2016)

# Single crystal PDF (3D-PDF) for orientation-dependent SRO



- scattering to measure atomic correlations (SRO) along different crystallographic directions
- High energy x-rays ~ 100 keV,  $-15\text{\AA}^{-1} < Q < 15\text{\AA}^{-1}$ , thousands of Brillouin zones, tens of thousands of Bragg peaks

## Single crystal PDF (3D-PDF) for orientation-dependent SRO



Na ions intercalate into two-legged ladders

Configuration of ions within partially occupied ladders cannot be determined by powder diffraction/PDF 3D-PDF: Na ions arrange in zig-zag structure within 2-leg ladders, in-phase with neighboring ladders

## **Extensions of XAFS: DAFS**

- Leverage structure factor at selected Bragg peaks for crystalline site selectivity
- Real and Imaginary parts of complex anomalous scattering factors related by K-K transformation
- Example: Cu(1) and Cu(2) sites in YBCO separated by combining multiple (00L) reflections



## **Extensions of XAFS: DAFS**

- Example: artificial Mn-ferrite films
- Mn and Fe both occupy  $T_d$  and  $O_h$  sites
- Can control site occupancies with non-equilibrium growth

 $F_{422} = f_{\rm Th} + 8(1 - N_A)f_{\rm Fe}(E) + 8N_A f_A(E),$ 

$$F_{222} = f_{\rm Th} - 32f_{\rm O}(E) + 16(2 - N_B)f_{\rm Fe}(E) + 16N_B f_B(E),$$

$$f_{A,B} = f_{A,B}' + i f_{A,B}''$$







## **Extensions of XAFS: Magnetic XAFS**

 With 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 helicity



## **Extensions of XAFS: magnetic DANES**

- Nd<sub>2</sub>Fe<sub>14</sub>B is best permanent magnet material
- 2 Nd sites, 6 Fe sites
- Magnetic "hardness" (coercivity) from Nd sites
- [001] magnetic easy axis

Site	(110)	(220)	(440)	<b>^</b> [110]
Nd ( <i>f</i> )	3%	96.4%	48.5%	$k_i \bigwedge \hat{k}_f \bigvee$
Nd <i>(g)</i>	97%	3.6%	51.5%	$\widehat{\qquad} \widehat{\qquad} \widehat{m}  \widehat{m}  H    [001]$



Haskel et al, PRL (2005)





#### **APS-U: extreme pressures, sub-micron imaging**



### APS-U: XAFS at extreme pressures (multiple Mbar)



#### APS-U: XAFS/XMCD/XRD at extreme pressures, sub-micron imaging

Small brilliant beams for extreme pressures and real-space mapping

- Nanopositioners and sample/mirror interferometry for sample/beam registration with 10 nm precision
- 3" magnet bore accommodates CuBe DAC with compression/decompression membranes
- 2x RT reentrant bores accept Raman objective and fluorescence detector
- XAFS/XMCD/XRD/Raman



