An Introduction to X-ray Absorption Spectroscopy

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What is XAFS
(X-ray Absorption Fine-Structure)

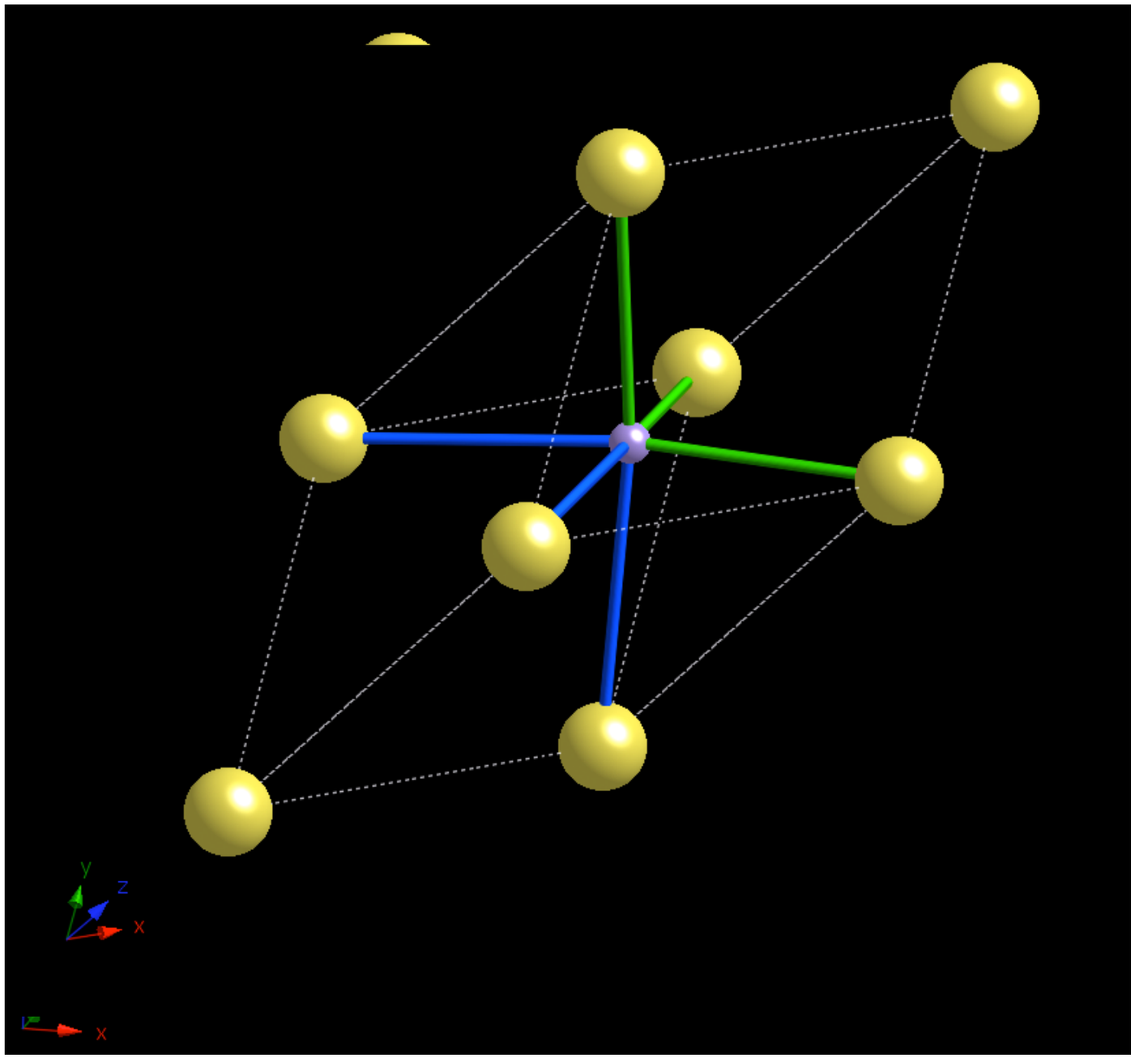
- XAFS (also XAS) refers to the modulation of the x-ray absorption coefficient near and above an absorption edge.
- XAFS is elementally selective and can explore the local atomic environment about the absorbing atom

XAFS Characteristics

- elementally selective
- local atomic coordination
- chemical / oxidation state
- applies to any element
- works at low concentrations
- small sample volumes (even monolayers)

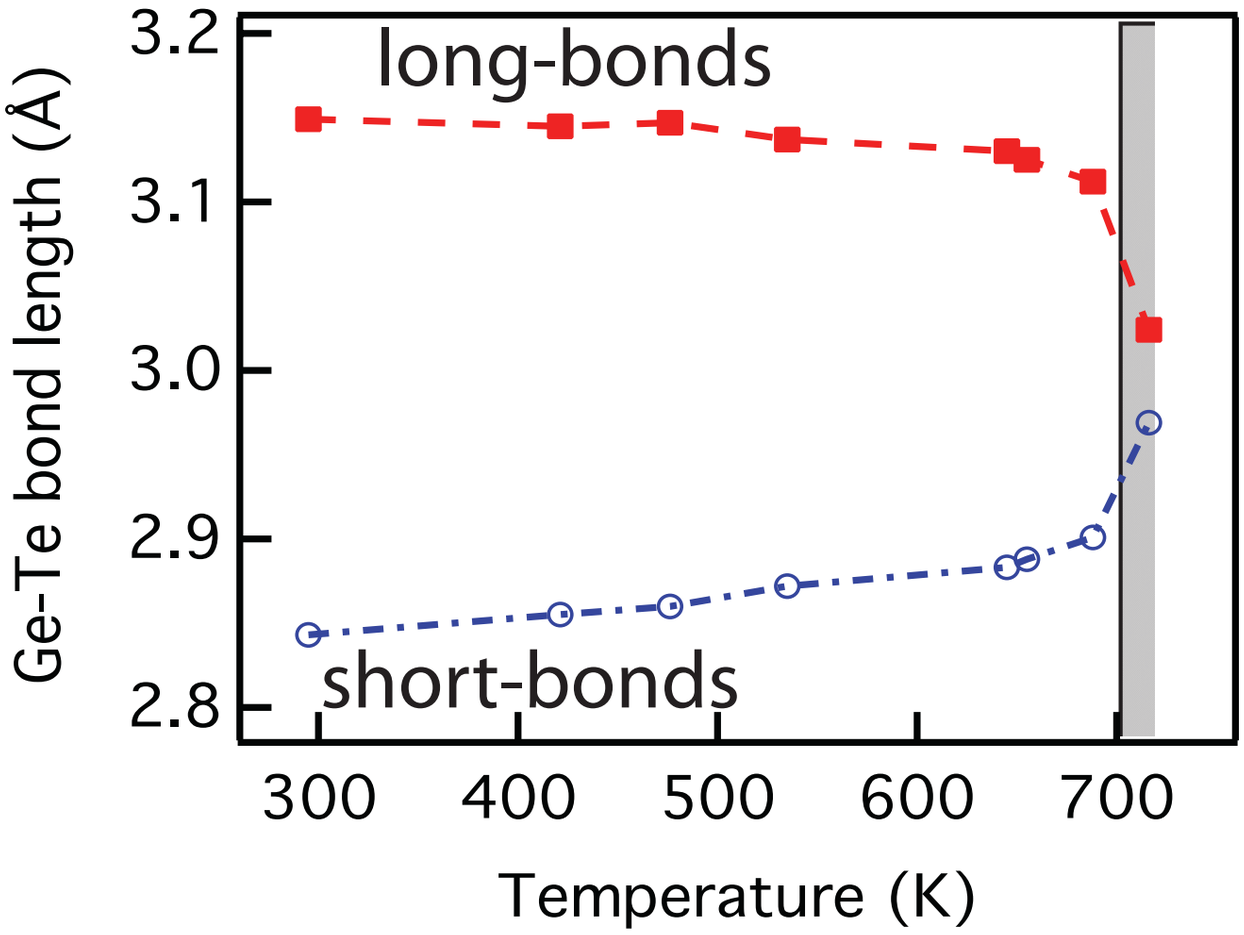
Local vs. Global Structure: An example

GeTe "ideal" Structure



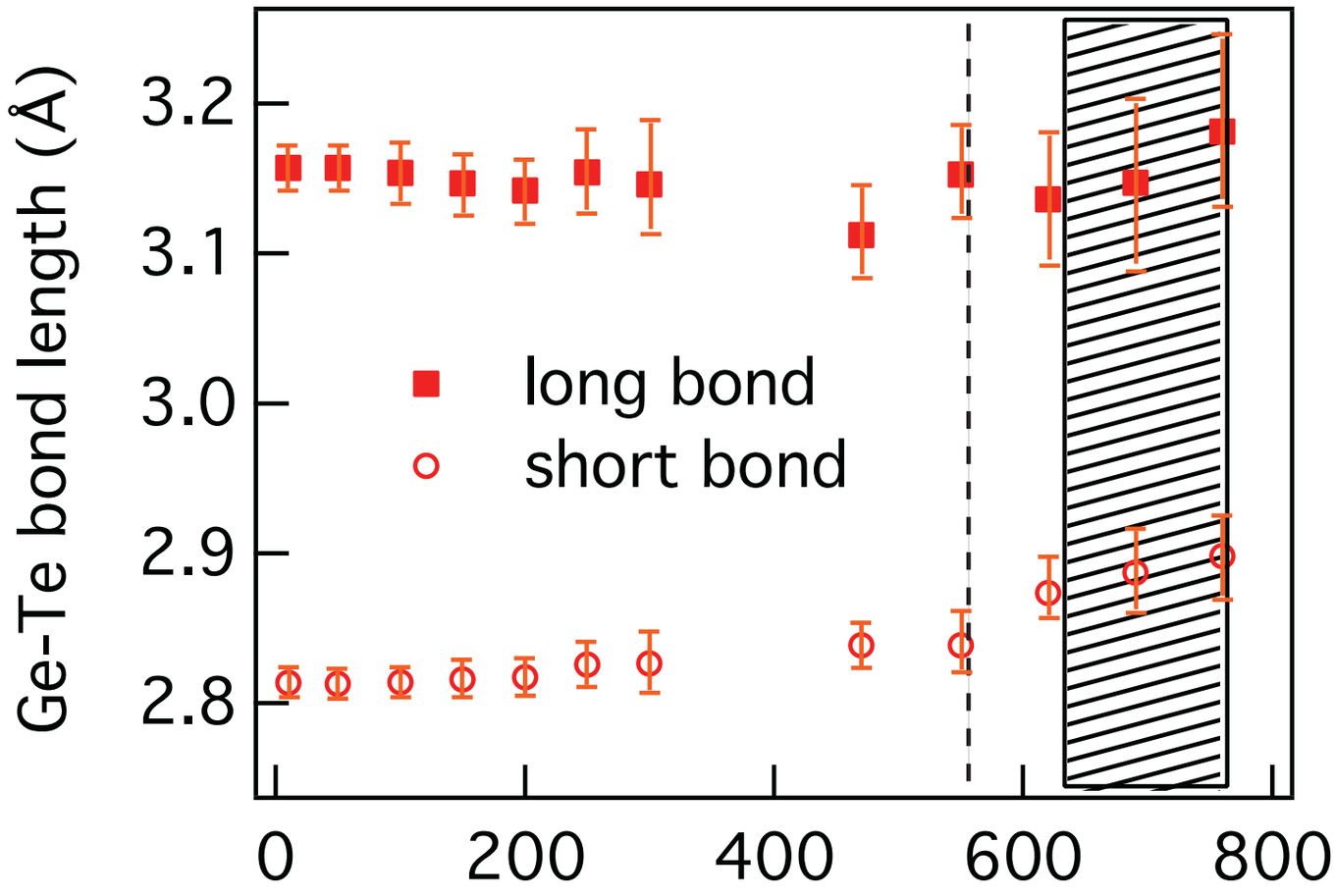
- Rhombohedral symmetry but more easily visualized as distorted rocksalt structure.

GeTe Diffraction



- Neutron powder diffraction shows long- and short-bonds calculated from average structure become equal at T_c

XAFS measurements



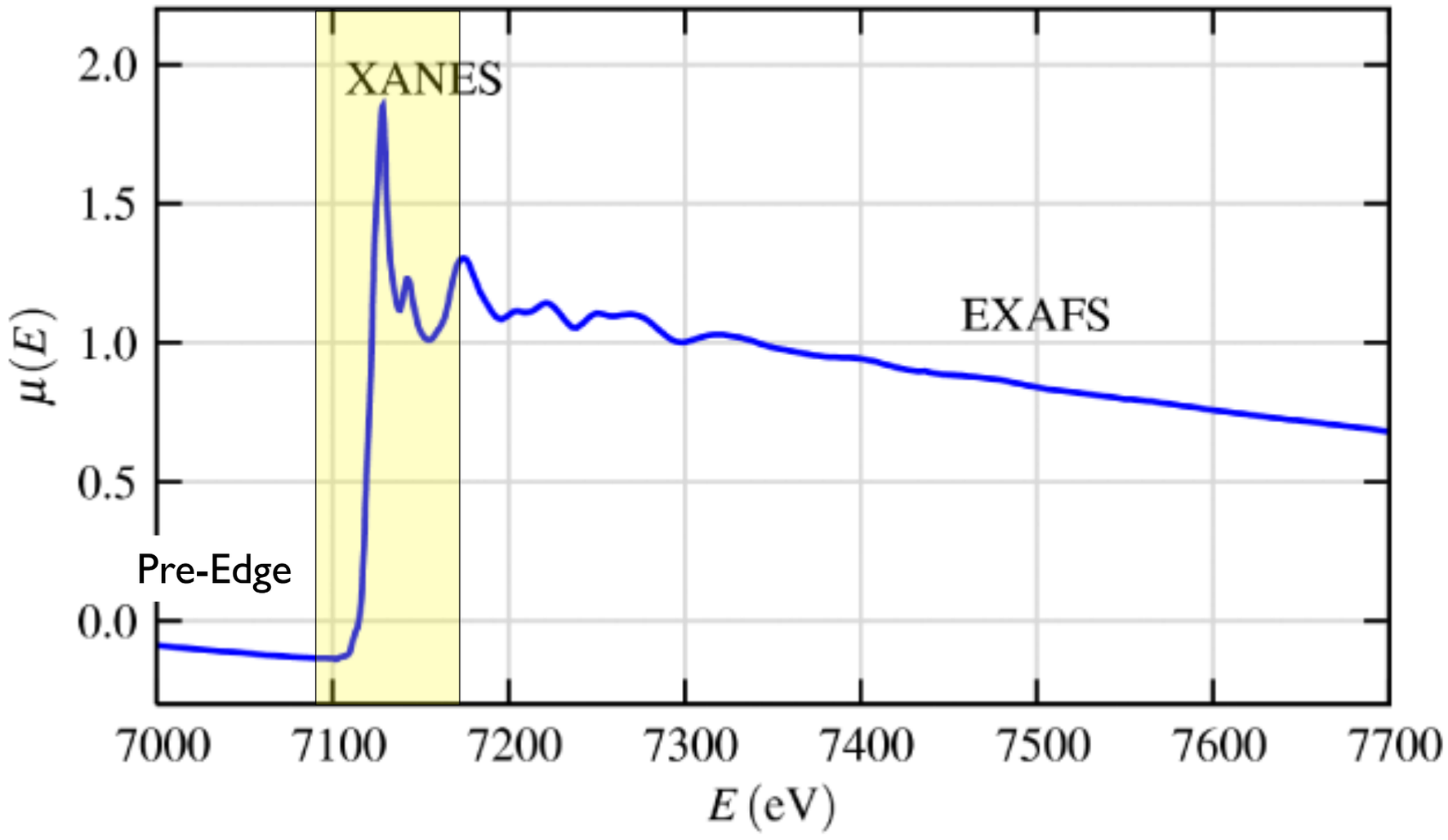
- Analysis showed that rhombohedral distortion existed up to and beyond T_c

XAFS is a local and Diffraction is a (longer) range probe

P. Fons, A. V. Kolobov, M. Krbal, J. Tominaga, K. Andrikopoulos, S. Yannopoulos, G. Voyiatzis, and T. Uruga. Phase transitions in crystalline GeTe: Pitfalls of averaging effects. Phys. Rev. B, 82(15):155209, 2010.

XAFS Example

Fe *K*-edge XAFS for FeO:



Modulation of the x-ray absorption above the edge constitutes the XAFS signal

XANES vs. EXAFS

- XANES X-ray Absorption Near-Edge Spectroscopy (0-40 eV)
- EXAFS Extended X-ray absorption Spectroscopy (40-1000 eV)

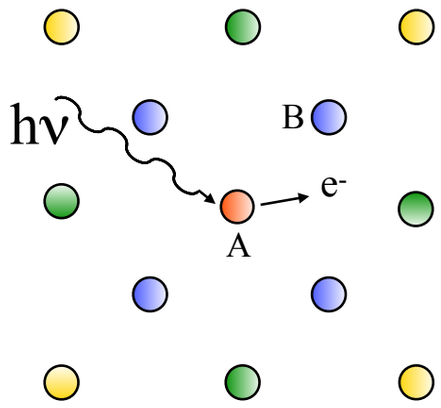
XANES and EXAFS are labels for two parts of the same spectra. They are distinguished due to the approximations used in the analysis of data

XANES region: The energy of the photoelectron (PE) is small, the mean free path long (nm) and PE interactions strong requiring more time consuming cluster calculations. XANES is a transition from a core into a bound state.

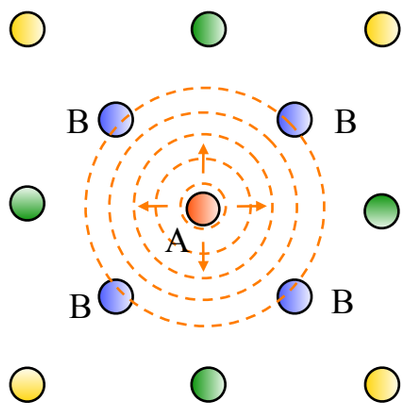
EXAFS region: The PE energy is higher and scattering can be treated as a finite series of interactions that can be well approximated by the the EXAFS equations we will encounter. EXAFS is a transition from a core to a continuum state

A visual interpretation of XAFS

Photon In

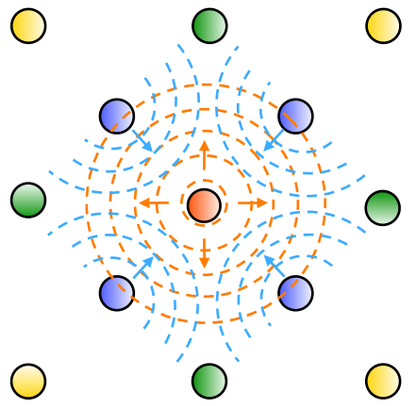


Photoelectron out



$$\left|f_0\right\rangle \propto \frac{e^{i\vec{k}\vec{r}+\delta_A}}{2kr}$$

For a s-state core level, an outgoing spherical wave moves out from the absorbing atom.



The outgoing spherical wave is scattered by the (coloumb) potentials of neighbor atoms causing interference with itself. The absorbing atom serves both as the source of the photoelectron and the detector. In other words, the XAFS signal reflects the local neighborhood about the absorbing atom.

Note that the photoelectron experiences a phase shift due to both distance traveled and interatomic potentials (which decreases the de Broglie wavelength λ as KE increases)