

X-RAY ABSORPTION SPECTROSCOPY (XAS)



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and X-ray Scattering

OUTLINE

- Background X-ray absorption spectroscopy (XAS)
- X-ray absorption near edge spectra (XANES) process
- XANES examples
- Extended X-ray absorption fine structure (EXAFS) fundamentals
- EXAFS examples

1920 PUBLISHED ABSORPTION EDGES

The K-Characteristic Absorption Frequencies for the
chemical elements magnesium to chromium

By Hugo Fricke

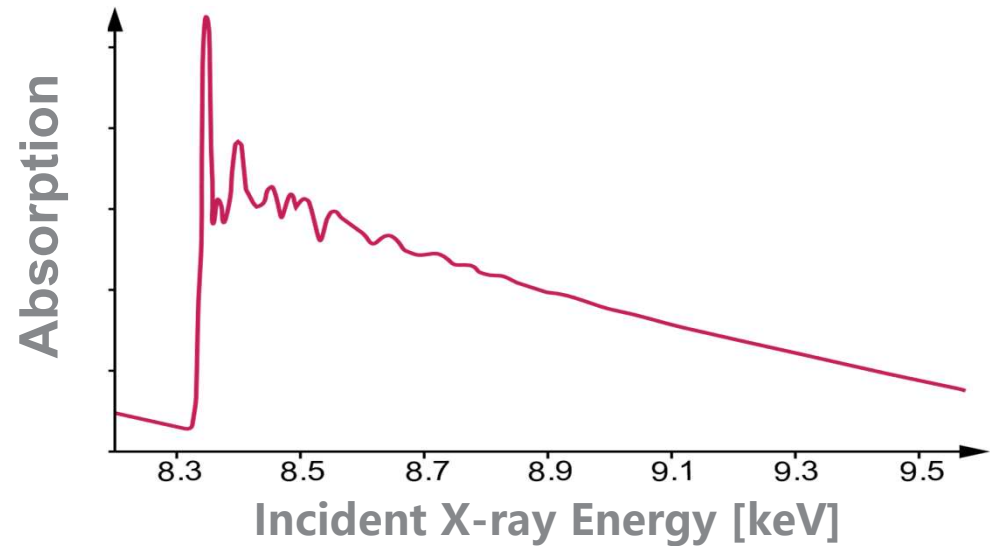
1971 UNDERSTANDING OF EXAFS

New Technique for Investigating Nanocrystalline Structures:
Fourier Analysis of the Extended X-ray-Absorption Fine
Structure

By Dale Sayers, Edward Stern and Farrel Lytle

ACRONYMS

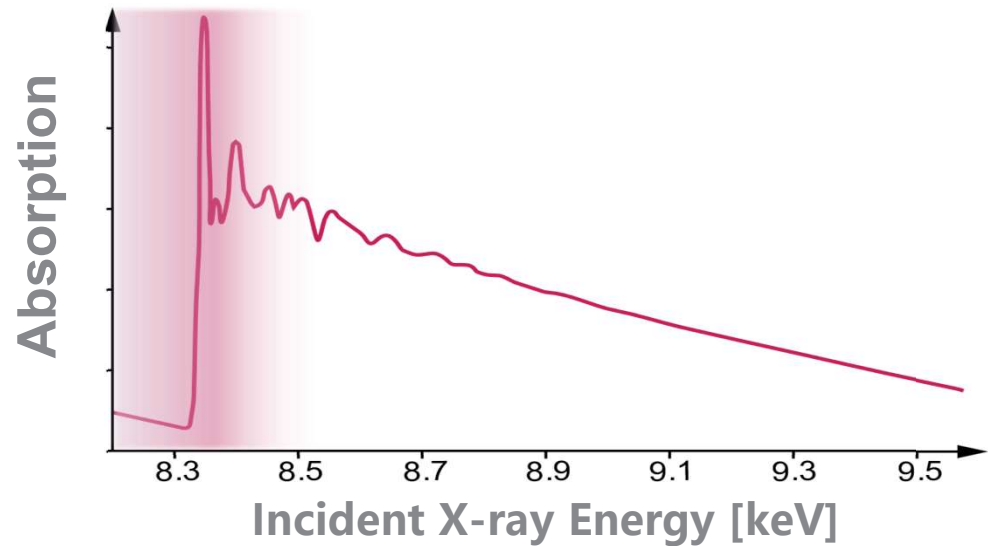
- General terms:
 - XAS: X-ray absorption spectroscopy
 - XAFS: X-ray absorption fine structure
- Specific terms:
 - XANES: x-ray absorption near edge structure
 - EXAFS: Extended x-ray absorption fine structure



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 - **XANES**: x-ray absorption near edge structure
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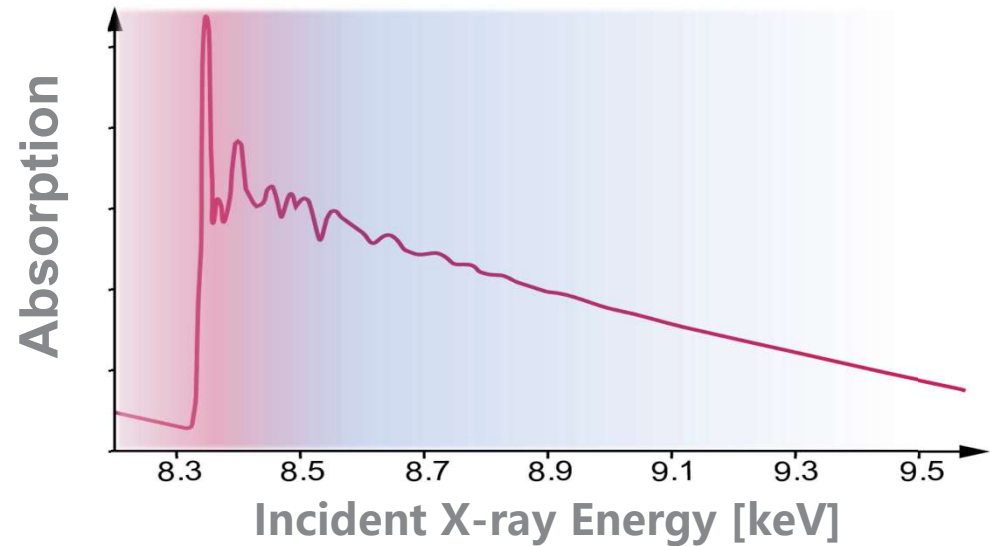
X-ray Absorption Near-Edge Structure



ACRONYMS

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Extended X-ray Absorption Fine Structure

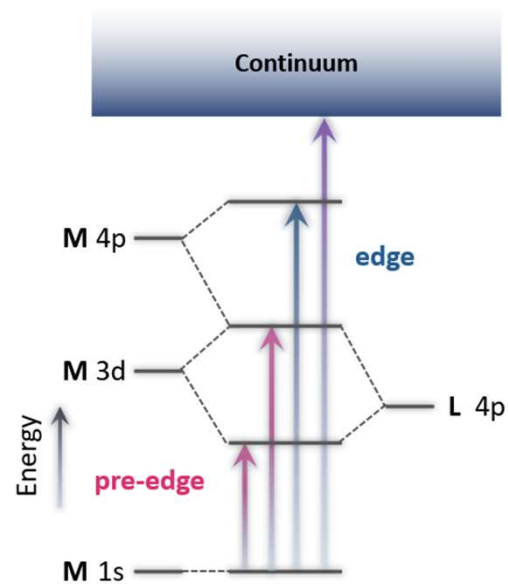
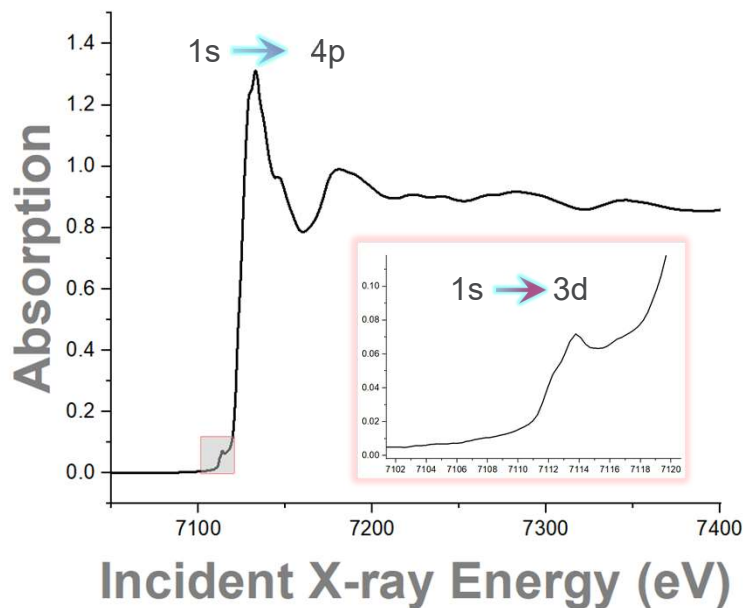


XANES: ELECTRONIC TRANSITIONS

- XANES directly probes the angular momentum of the unoccupied electronic states: these may be bound or unbound, discrete or broad, atomic or molecular.
- Dipole selection rules apply: $\Delta l = \pm 1$
- Primary transition will be:
 - $s \rightarrow p$ for K (1s core electron) and L₁ (2s core electron initial state) edges
 - $p \rightarrow d$ for L₂ (2p_{1/2}) and L₃ (2p_{3/2}) edges
- But.....final state usually not atomic-like and may have mixing (hybridization) with other orbitals. This is often the interesting part of the XANES!

*

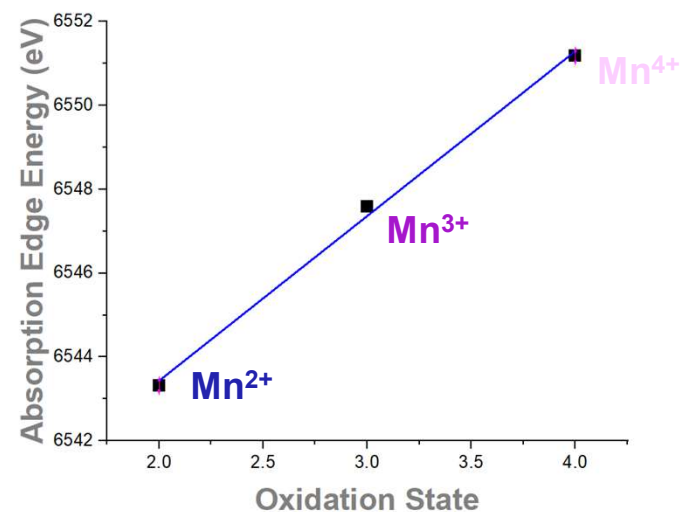
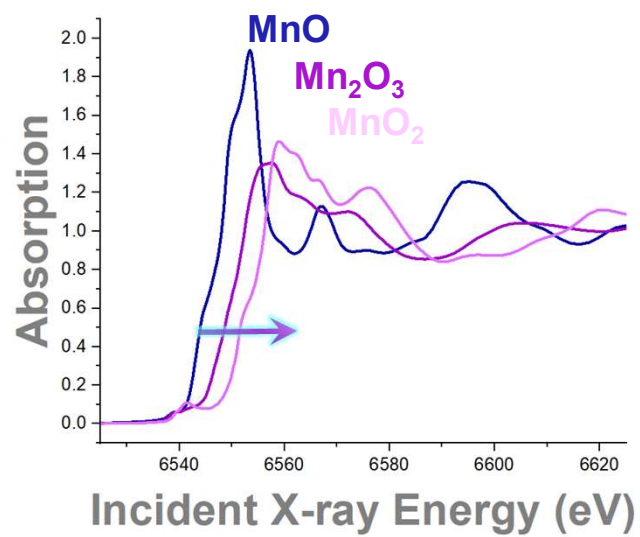
METAL K-EDGE XANES



- Absorption edge: dipole $1s \rightarrow 4p$ transition ($\Delta l = \pm 1$)
- Pre-edge: mixing of 3d-4p opens $1s \rightarrow 3d$ transition

OXIDATION STATE OF MN OXIDES

Mn K-edge XANES

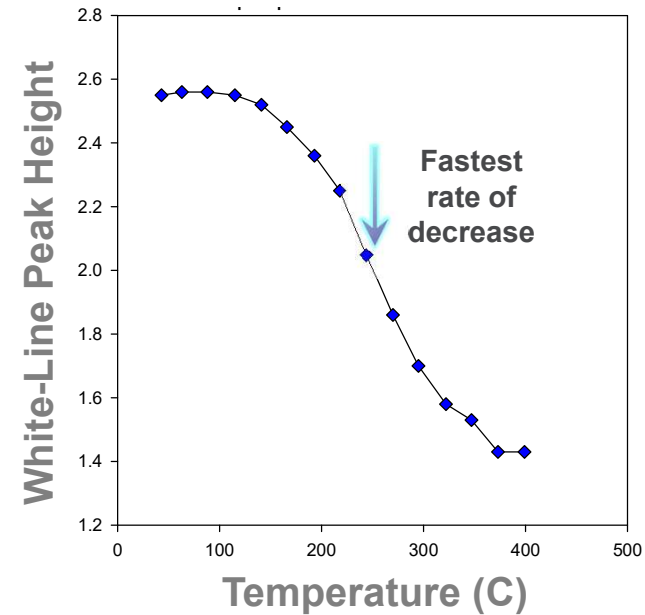
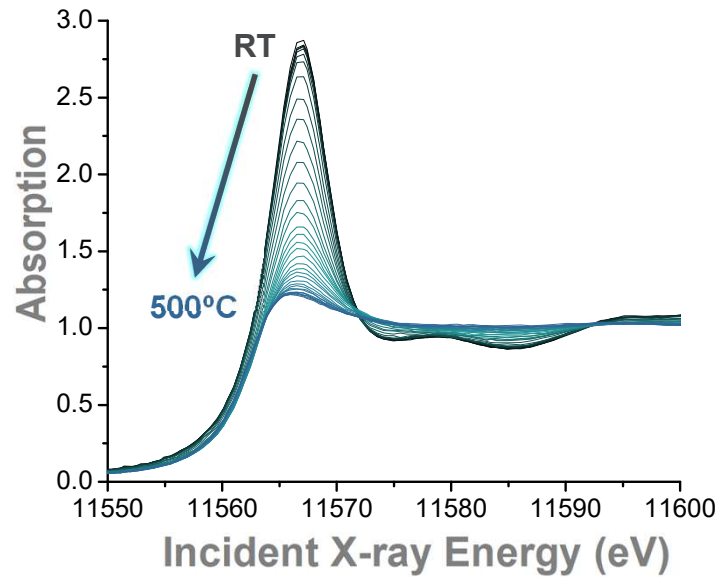


- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
- Early observation was by Berengren for phosphorus in 1920*!

*See "A history of X-ray absorption fine structure", R. Stumm von Bordwehr, Ann. Phys. Fr. 14 (1989) 377-466

PT XANES DURING IN SITU REDUCTION

Direct in situ measurement of Pt reduction



- Pt L₃-edge p→d transition
- Pt electrons: [Xe]4f¹⁴5d⁶s¹
- Pt white line intensity decreases as temperature increases due to 5d electrons filling
- Rate of decrease is fastest at ~270°C.

FAST-CHARGING LITHIUM-ION BATTERIES

Mechanism from XANES and DFT

Article

A disordered rock salt anode for fast-charging lithium-ion batteries

<https://doi.org/10.1038/s41586-020-2637-6>

Received: 16 December 2019

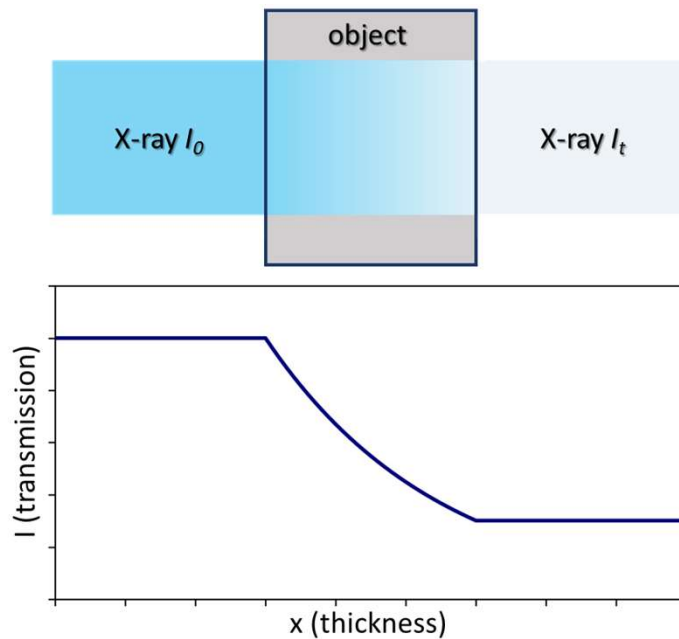
Accepted: 8 July 2020

Published online: 2 September 2020

Haodong Liu^{1,2}, Zhuoying Zhu^{1,2}, Qizhang Yan¹, Sicen Yu¹, Xin He², Yan Chen³, Rui Zhang⁴, Lu Ma⁵, Tongchao Liu⁶, Matthew Li⁶, Ruoqian Lin⁷, Yiming Chen¹, Yejing Li¹, Xing Xing¹, Yoonjung Choi⁸, Lucy Gao⁹, Helen Sung-yun Cho⁹, Ke An⁹, Jun Feng¹⁰, Robert Kostecki², Khalil Amine⁹, Tianpin Wu¹¹, Jun Lu^{6,12}, Huolin L. Xin^{4,12}, Shyue Ping Ong^{1,2,12} & Ping Liu^{1,2,12}

<https://doi.org/10.1038/s41586-020-2637-6>

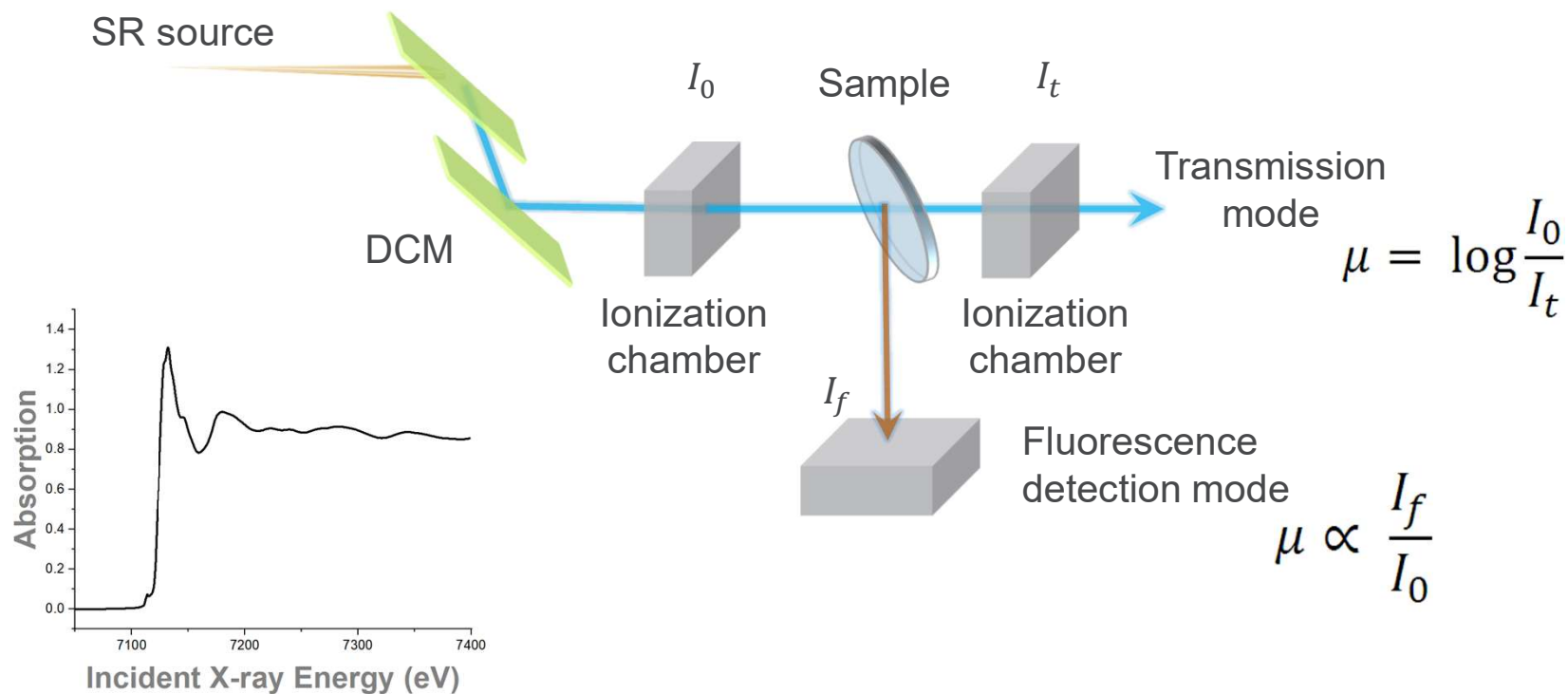
BEER'S LAW: ABSORPTION OF X-RAYS BY MATTER



$$I_t = I_0 e^{-\mu x}$$

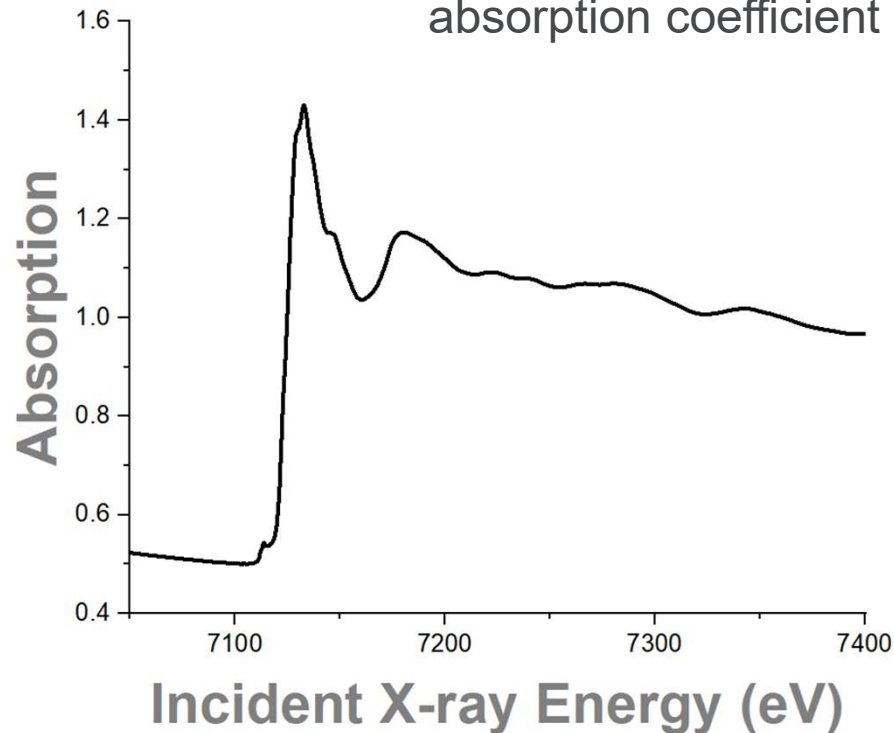
- μx : absorption length of a material
- One absorption length, $I_t = 37\% I_0$
- Two absorption lengths, $I_t = 13\% I_0$

MEASUREMENT OF X-RAY ABSORPTION COEFFICIENT



DEFINITION OF EXAFS $\chi(E)$

Normalized oscillatory part of the absorption coefficient

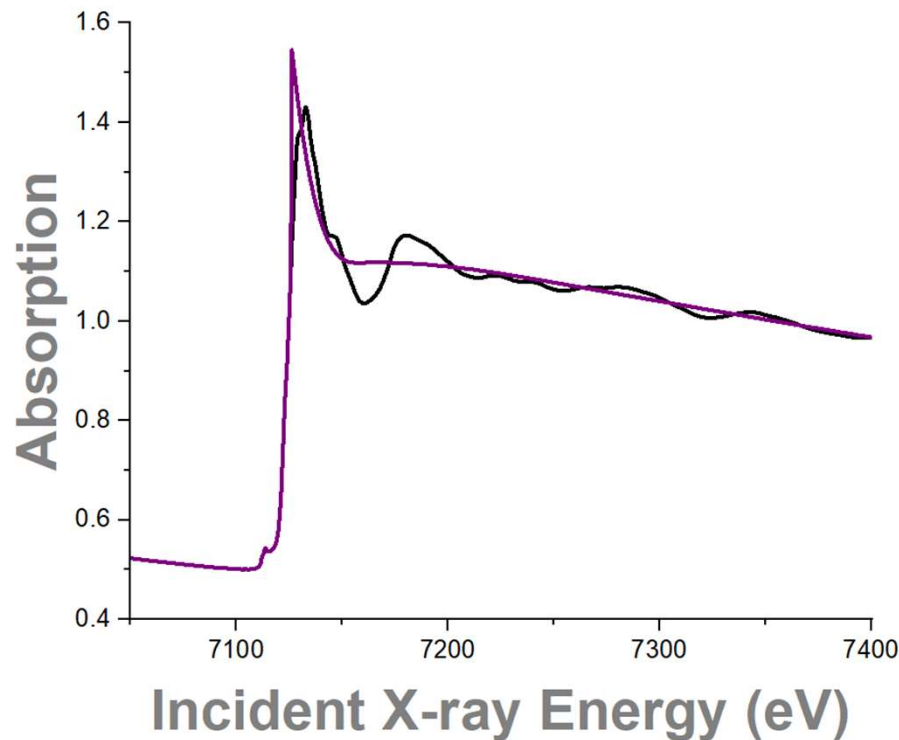


$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

Measured absorption coefficient in transmission or fluorescence

$$\mu = \log \frac{I_0}{I_t} \quad \mu \propto \frac{I_f}{I_0}$$

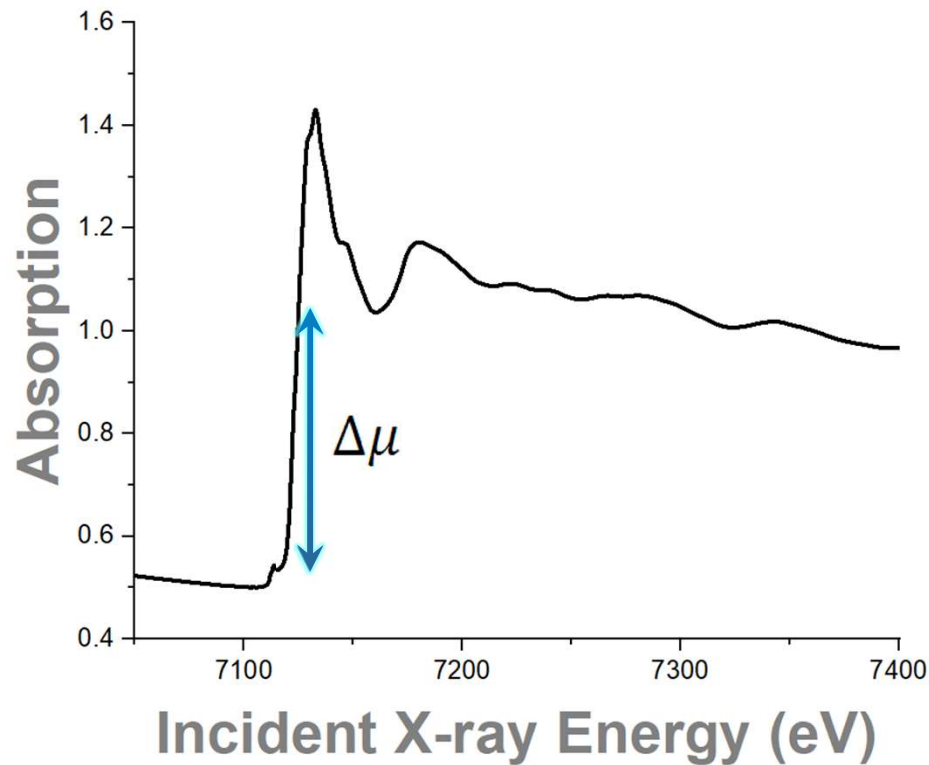
DEFINITION OF EXAFS



$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

Smoothly varying background function, representing the absorption without fine structure

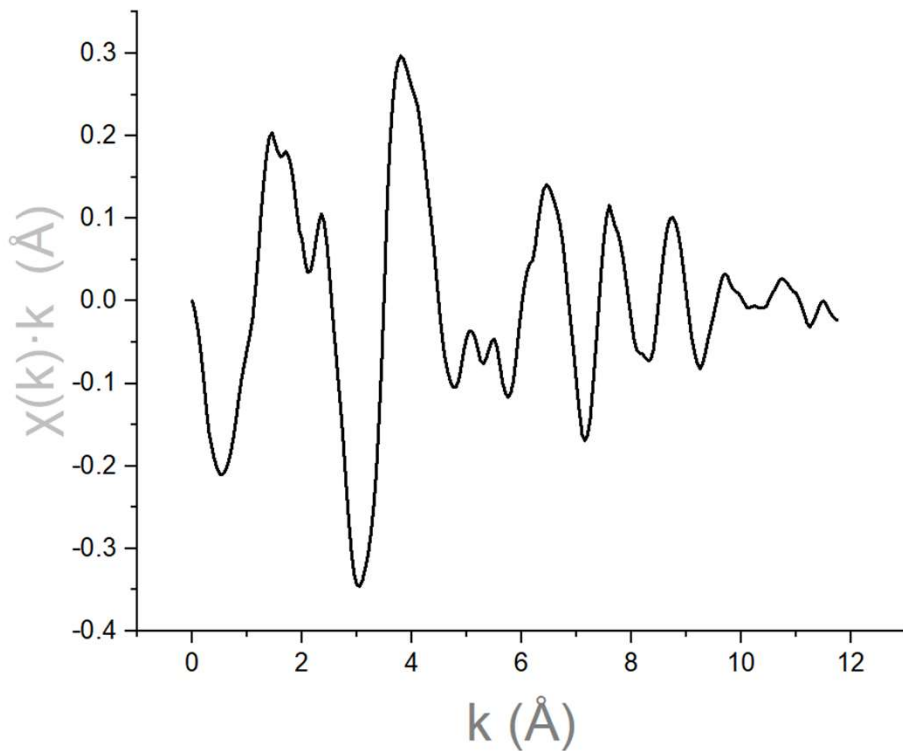
DEFINITION OF EXAFS



$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

Normalized by the edge step height

DEFINITION OF EXAFS



$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

$$k^2 = 2 m_e(E - E_0) / \hbar$$

FERMI'S GOLDEN RULE

$$\mu(E) \propto |\langle i | H | f \rangle|^2$$

$\langle i |$ Initial State: atom with core electron

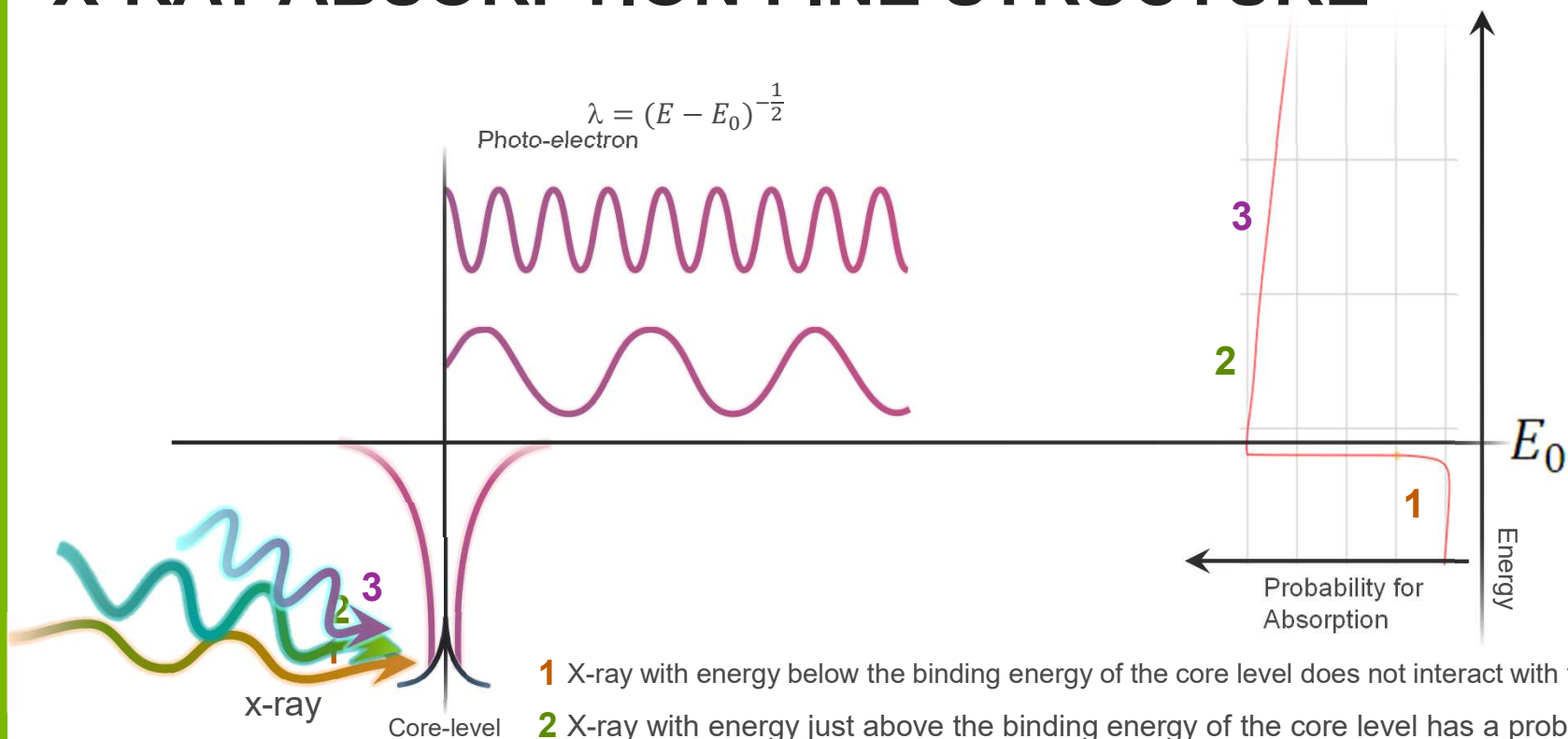
H Interaction term: incident x-ray

$|f\rangle$ Final State: atom with core hole, photo-electron

- Transition between two quantum states
- Initial state is well localized at the absorbing atom
- Final state is not, but can be written in terms of two parts

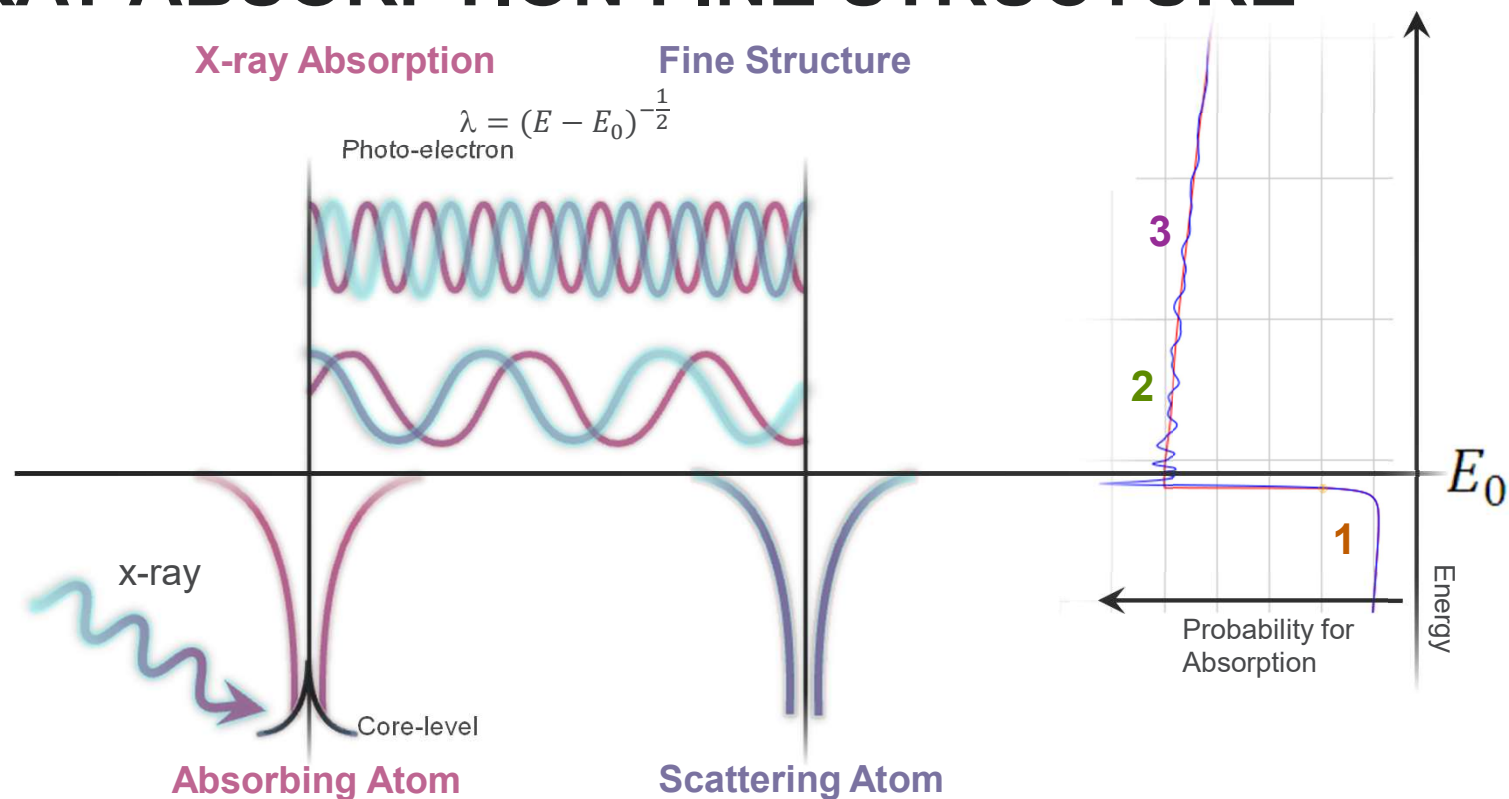
$$|f\rangle = \underbrace{|f_0\rangle}_{\text{adsorbing}} + \underbrace{|\Delta f\rangle}_{\text{neighboring}}$$

X-RAY ABSORPTION FINE STRUCTURE



- 1 X-ray with energy below the binding energy of the core level does not interact with the atom
- 2 X-ray with energy just above the binding energy of the core level has a probability of being absorbed producing a low energy photo-electron
- 3 X-ray with higher energy have a probability of being absorbed and producing higher energy photo-electron

X-RAY ABSORPTION FINE STRUCTURE



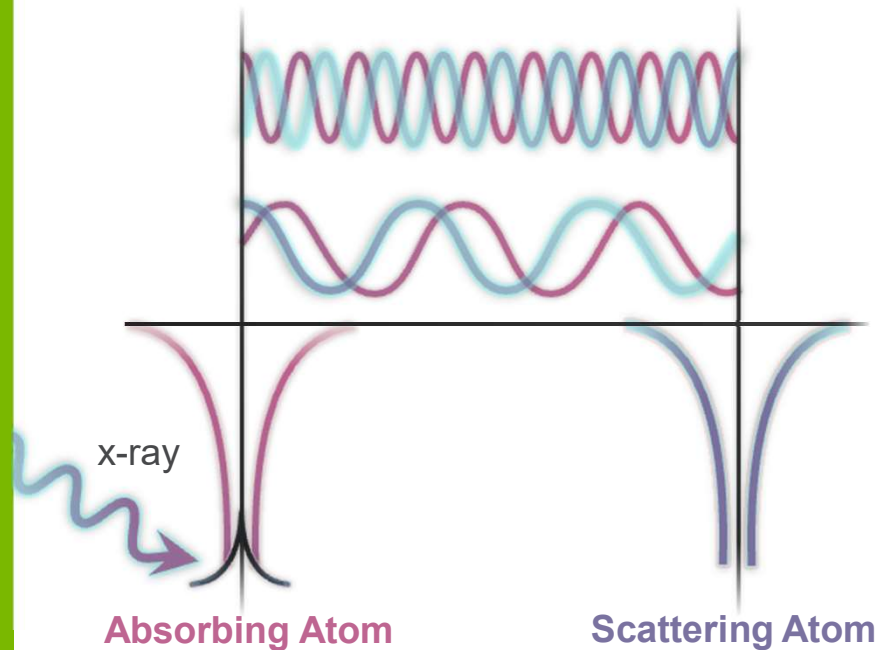
Interference between outgoing and scattered photoelectron at the absorbing atom causes modulations in the probability for absorption.

ATOMIC PHASE SHIFT $\delta(k)$

X-ray Absorption

Fine Structure

$$\lambda = (E - E_0)^{-\frac{1}{2}}$$



$$\chi(k) \propto \psi_{scatt}(k, r = 0)$$

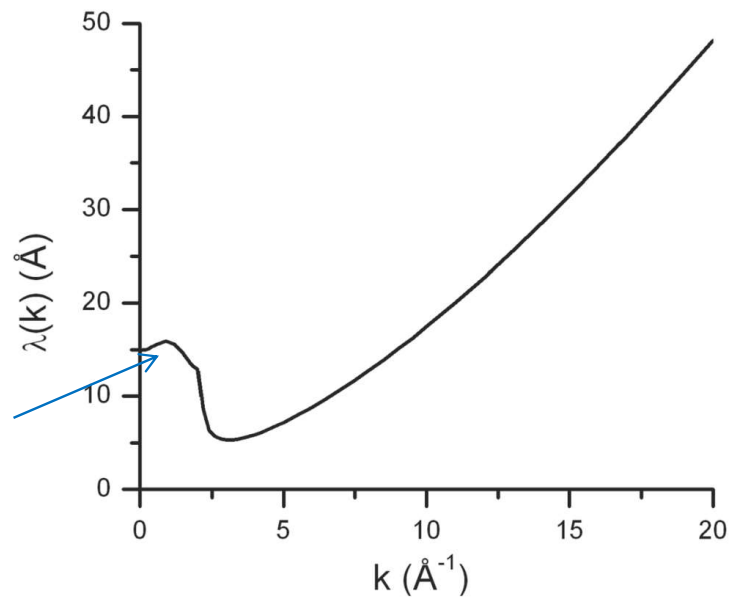
$$\propto \frac{e^{ikR}}{kR} [F(k)e^{-i\delta(k)}] \frac{e^{ikR}}{kR}$$

$$\chi(k) \propto \frac{F(k)}{k^2 R^2} \sin(2kR + \delta(k))$$

Atomic Phase shift has two parts. One part from the absorbing atom and another part from the scattering atom.

LIFETIME OF PHOTOELECTRON AND CORE HOLE

λ is large for low wave-numbers indicates that the XANES region contains contributions with long path lengths



Probability for a coherent photoelectron to travel the distance $2R$ is given by

$$e^{-\frac{2R}{\lambda_j}}$$

- X-ray absorption fine structure requires a core hole and a coherent photoelectron.
- The mean free path λ of the photoelectron limits the contributions to EXAFS to the first few neighbors

PASSIVE ELECTRON REDUCTION FACTOR

$$S_0^2 = \left| \langle \phi_f^{N-1} | \phi_i^{N-1} \rangle \right|^2$$

- The initial and final states include all the passive electrons of the absorbing atom.
- If the electrons do not react to the creation of the core hole, then there is no difference in these passive electrons and the initial and final states are identical giving $S_0^2 = 1$, indicating a screened potential.
- If the electrons do react (they only have 10^{-15} seconds to do so) then the final state will be slightly different from the initial state. The final state will have the electrons pulled in slightly due to the core hole and the value for S_0^2 can be as small as ~ 0.7 , indicating an unscreened potential.
- Value for S_0^2 depends only on the adsorbing atom and can be transferred from a standard material such as a foil.
- S_0^2 often contains experimental affects such as energy resolution so it is best to measure a foil under the same experimental conditions as the unknown sample.

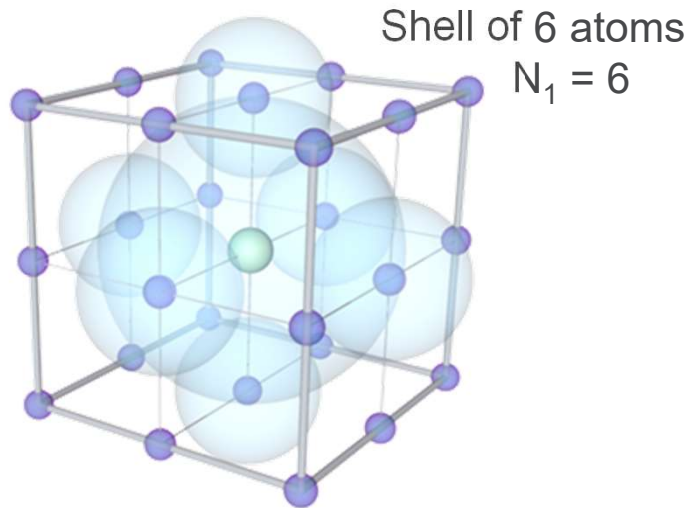
MANY SINGLE SCATTERING PATHS

Summing over scattering events

$$\chi(k) = \sum_j \chi_j(k)$$

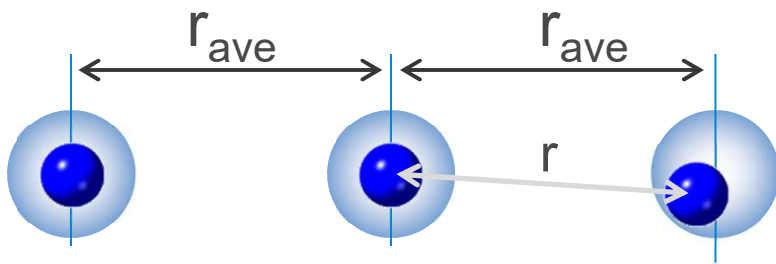
Summing over shells of atoms

$$\chi(k) = \sum_i N_i \chi_i(k)$$



- EXAFS signal is the sum of many individual scattering events j .
- It is convenient to group scattering events from shells of atoms, i , of the same type at the same radial distance from the adsorbing atom. Then we need to multiply the scattering contribution by the number of atoms in each shell (N_i).

MEAN SQUARE DISPLACEMENT



$$\int P(r) e^{i2k\Delta r} d\Delta r = \exp \left[\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} C_n \right]$$

$$= e^{2ik\Delta r} + e^{-2} \sigma^2 + e^{-\frac{4}{3}ik^3 C_3} + \dots$$

- Summing over shells introduces an error because not all of the atoms in a shell are at exactly the same radial distance from the adsorbing atom.
- The scattering process takes place in 10^{-15} seconds. Atomic vibrations occur in 10^{-12} to 10^{-13} seconds.
- Neighboring atoms are frozen at some position about their equilibrium position.

THE EXAFS EQUATION

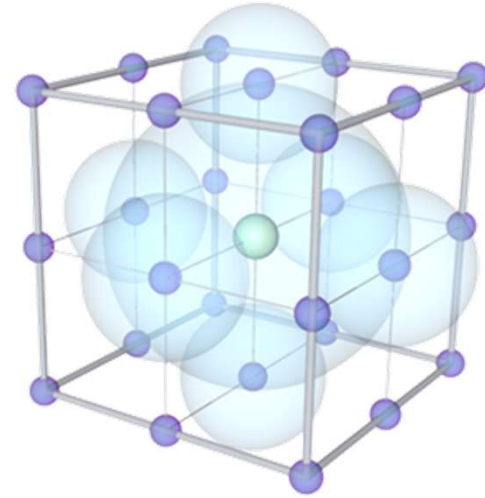
$$\chi(k) = \sum_i \chi_i(k)$$

with

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k) e^{-2k^2 \sigma_j^2} e^{-\frac{2R}{\lambda}}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 m_e(E - E_0) / \hbar$$



Theoretically calculated values

- $F_i(k)$ effective scattering amplitude
- $\varphi_i(k)$ effective scattering phase shift
- $\lambda(k)$ mean free path

Starting values

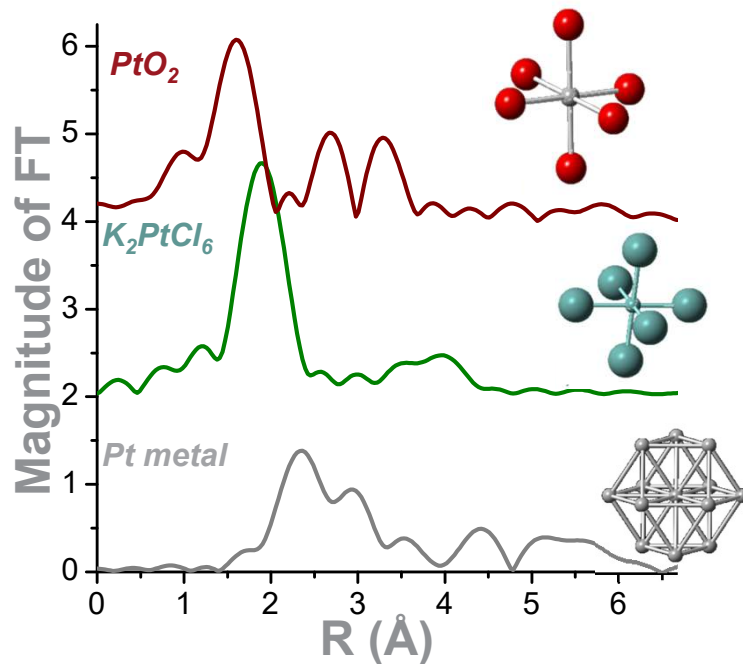
- R_0 initial path length

Parameters determined from a fit to data

- N_i degeneracy of path
- S_0^2 passive electron reduction factor
- σ_i^2 mean squared displacement of half-path length
- E_0 energy shift
- ΔR change in half-path length

PT EXAFS OF REFERENCE MATERIALS

Pt EXAFS: unique information about the average local atomic environment of Pt



PtO ₂		
Neighbor	Number	Distance (Å)
Pt-O	6	2.07
Pt-Pt	6	3.10

K ₂ PtCl ₆		
Neighbor	Number	Distance (Å)
Pt-Cl	6	2.32
Pt-K	4	4.22

Pt metal		
Neighbor	Number	Distance (Å)
Pt-Pt	12	2.77
Pt-Pt	6	3.92

Pt-O, Pt-Cl, and Pt-Pt signals are unique and are readily distinguished.

PLATINUM EXAFS: COMPARISONS WITH FOIL

3 nanometer
959 atoms
Pt-Pt1 CN 10.4

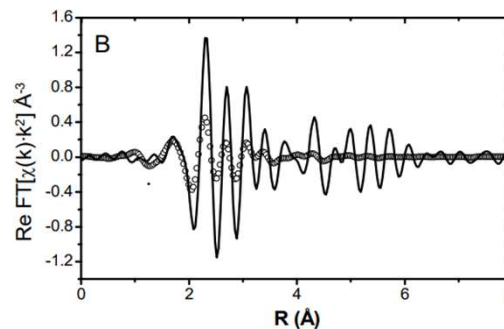
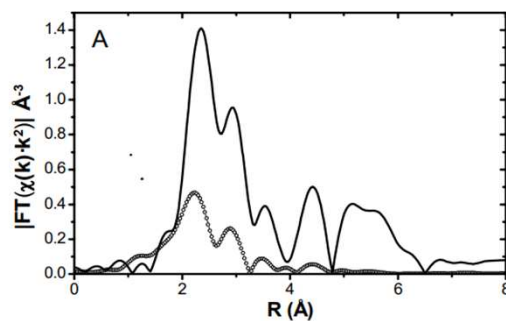
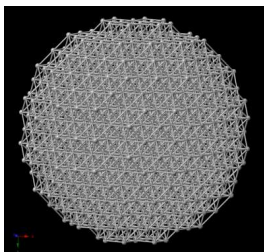
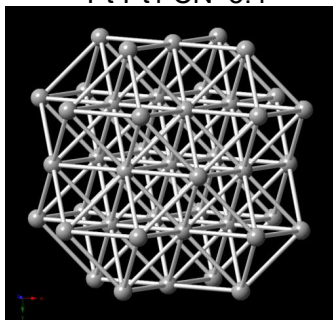
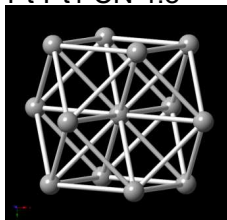


Figure 1. Magnitude (A) and real part of Fourier transform of 300C-reduced (symbols) and Pt foil (solid)

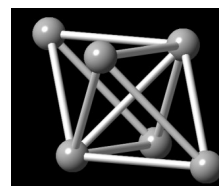
1.0 nanometer
43 atoms
Pt-Pt1 CN 5.4



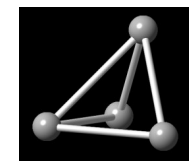
0.6 nanometer
13 atoms
Pt-Pt1 CN 4.8



6 atoms
Pt-Pt1 CN 4.0



4 atoms
Pt-Pt1 CN 3



<https://iopscience.iop.org/article/10.1088/1742-6596/430/1/012061/pdf>

EXAFS STUDY OF Nb₃Sn SUPERCONDUCTORS

Heald S. et al., *Scientific Reports* 2018; Tarantini C, et al. *Superconductor Science and Technology* 2019

Challenge

- Nb₃Sn proposed for future accelerator upgrades, but needs improved properties
- Doping can offer improvement, but optimization needs better understanding

EXAFS

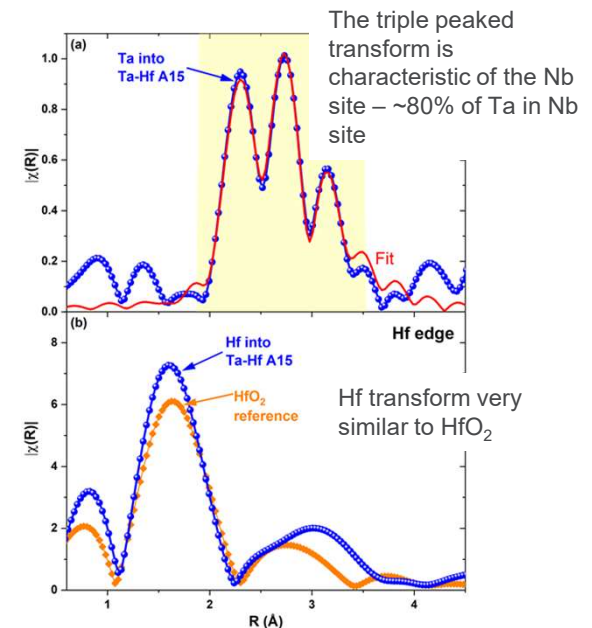
- Determine dopant lattice location.
- When combined with other results offered key insights into the role of dopants

Result

- Ti, Ta, and Hf dopants studied
- Determined Ta dopant increased antisite disorder with beneficial results
- Hf formed HfO₂ nanoparticle pinning sites
- Combined Ta and Hf doping offers promising route to meeting the needs of future accelerators.

Microprobe needed to measure narrow Nb₃Sn regions

Fourier Transformed EXAFS



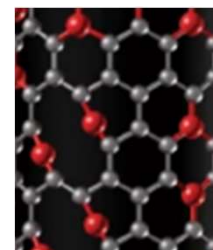
HIGH TEMPERATURE SHOCKWAVE STABILIZED SINGLE-ATOM CATALYSTS

Fourier transform comparisons

nature
nanotechnology

ARTICLES

<https://doi.org/10.1038/s41565-019-0518-7>



High temperature shockwave stabilized single atoms

Yonggang Yao^{1,8}, Zhennan Huang^{2,8}, Pengfei Xie^{3,8}, Lianping Wu^{4,8}, Lu Ma^{5,8}, Tangyuan Li^{1,8}, Zhenqian Pang⁴, Miaolun Jiao¹, Zhiqiang Liang¹, Jinlong Gao¹, Yang He⁶, Dylan Jacob Kline⁷, Michael R. Zachariah⁷, Chongmin Wang⁶, Jun Lu⁵, Tianpin Wu^{5*}, Teng Li^{4*}, Chao Wang^{3*}, Reza Shahbazian-Yassar^{2*} and Liangbing Hu^{1*}

<https://doi.org/10.1038/s41565-019-0518-7>

STRUCTURE OF LUMINESCENT PROTEIN-STABILIZED GOLD CLUSTERS

EXAFS with DFT interpretation

Chemical
Science



EDGE ARTICLE

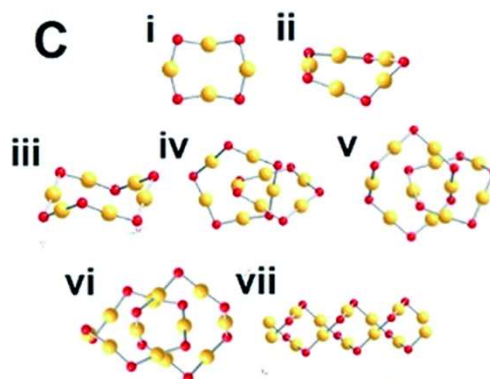
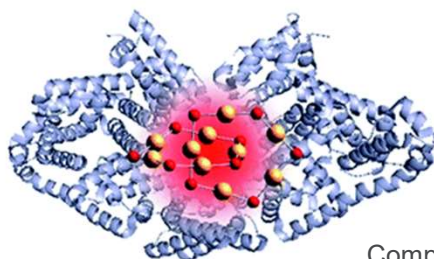
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Structure and formation of highly luminescent protein-stabilized gold clusters†

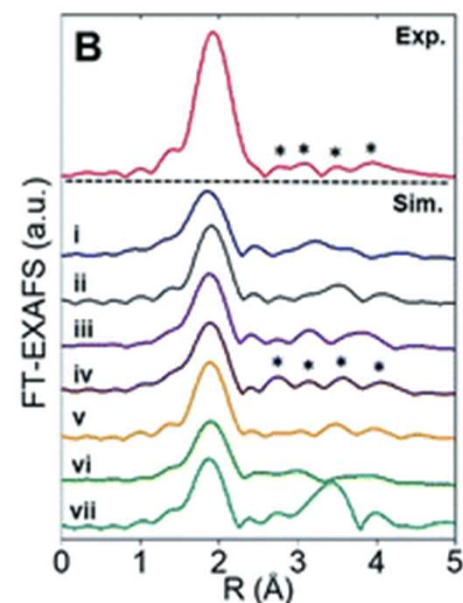
Cite this: *Chem. Sci.*, 2018, 9, 2782

D. M. Chevrier,^a V. D. Thanthirige,^b Z. Luo,^c S. Driscoll,^a P. Cho,^a M. A. MacDonald,^a Q. Yao,^c R. Guda,^d J. Xie,^c E. R. Johnson,^a A. Chatt,^a N. Zheng^d and P. Zhang^{a*}



Comparison between DFT simulated structure and measured spectra give insights into the gold cluster morphology

<https://doi.org/10.1039/C7SC05086K>



Q & A