X-RAY ABSORPTION SPECTROSCOPY (XAS)

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Advanced Photon Source

August 14, 2023
25th National School on Neutron
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

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1920 PUBLISHED ABSORPTION EDGES

THE K–CHARACTERISTIC ABSORPTION FREQUENCIES FOR THE CHEMICAL ELEMENTS MAGNESIUM TO CHROMIUM.

By Hugo Fricke.

SYNOPSIS.

Absorption of X-Rays.—This paper contains an account of an experimental investigation concerning the discontinuity in the X-ray absorption corresponding to the K-series for the chemical elements from magnesium to chromium inclusively. The method followed was the same as that devised and employed by de Broglie. A specially designed vacuum spectrograph was used.

Fine Structure of Absorption.—The spectrograms show that the discontinuity has a rather *complex structure*, a result in advance of those obtained by earlier investigators. A *photometric study* of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits.

Results. These are recorded in tables which give for each element the wavelengths of the different remarkable points in the structure of the discontinuities. The theoretical bearing of the new observations is briefly discussed.

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https://journals.aps.org/pr/pdf/10.1103/PhysRev.16.202

1971 UNDERSTANDING OF EXAFS

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of
the Extended X-Ray—Absorption Fine Structure*

Dale E. Sayers† and Edward A. Stern††

Department of Physics, University of Washington, Seattle, Washington 98105

and

Farrel W. Lytle

Boeing Scientific Research Laboratories, Seattle, Washington 98124
(Received 16 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption
fine structure to invert experimental data formally into a radial structure function with
determinable structural parameters of distance from the absorbing atom, number of
atoms, and widths of coordination shells. The technique is illustrated with a compari-
son of evaporated and crystalline Ge. We find that the first and second neighbors in
amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).

FIG. 2. Fourier transformation of the data of Fig. 1,
$\varphi(r)$, a radial structure function, compares amorphous
and crystalline Ge. Numbers over the peaks indicate
the measured distances in Å.

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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X-ray Absorption Near-Edge Structure

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Extended X-ray Absorption Fine Structure

Absorption

Incident X-ray Energy [keV]

8.3   8.5   8.7   8.9   9.1   9.3   9.5

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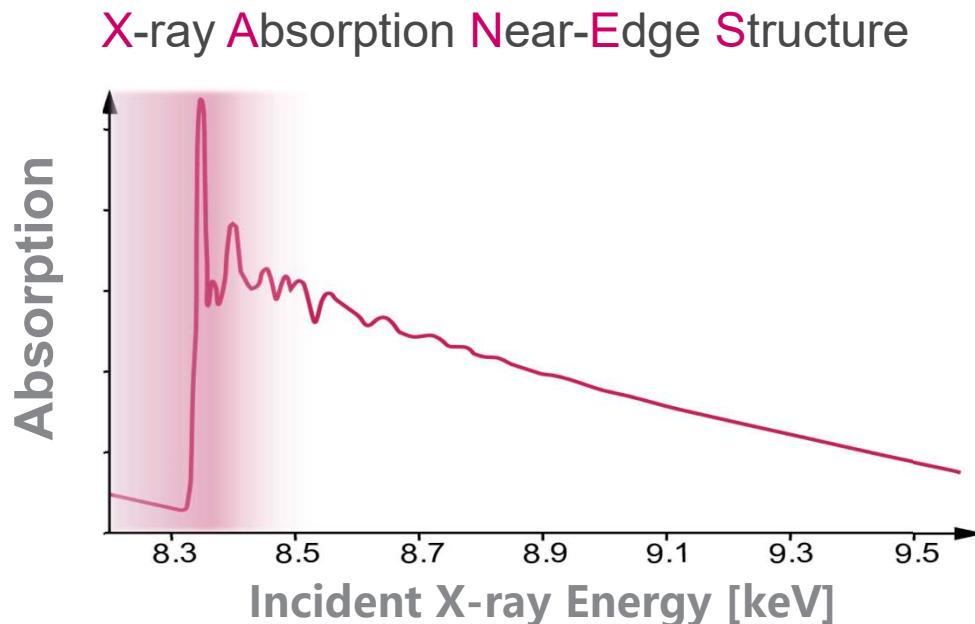
XANES: ELECTRONIC TRANSITIONS

- 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 L_1 (2s core electron initial state) edges

    - $p \rightarrow d$ for L_2 (2$p_{1/2}$) and L_3 (2$p_{3/2}$) 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
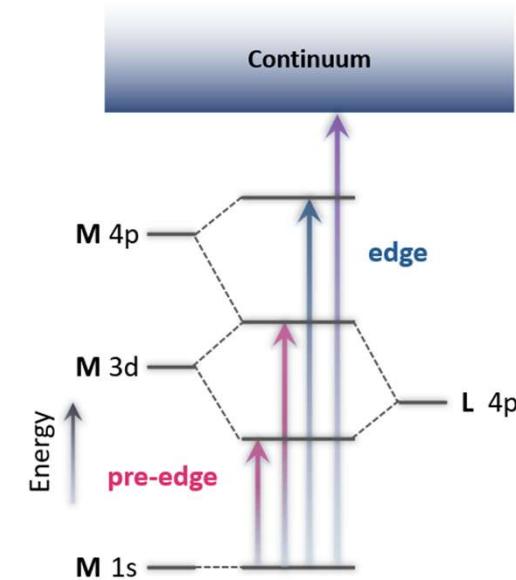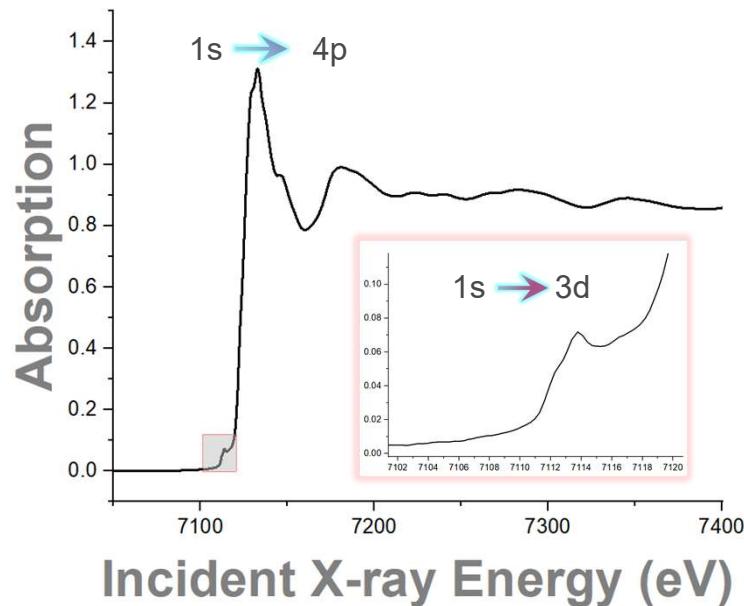
- Absorption edge: dipole 1s $\rightarrow$ 4p transition ($\Delta l = \pm 1$)
- Pre-edge: mixing of 3d-4p opens 1s $\rightarrow$ 3d transition

OXIDATION STATE OF MN OXIDES
Mn K-edge XANES
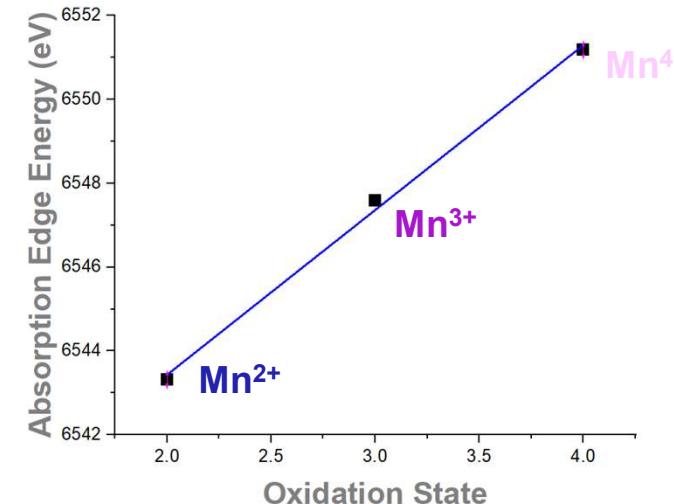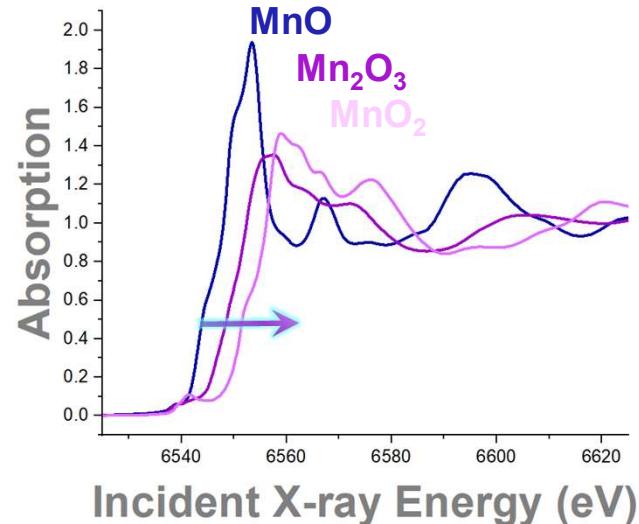
- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

- 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
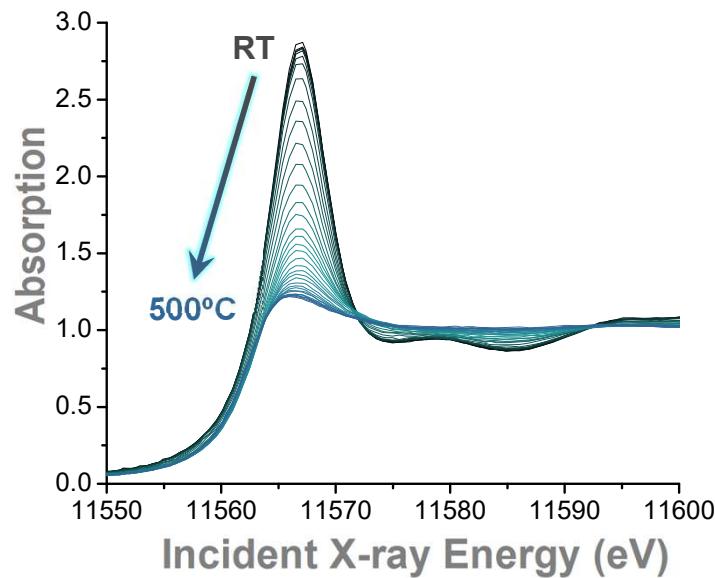
- Pt L_3-edge p->d transition
- Pt electrons: $[Xe]4f^{14}5d^{6}s^{1}$
- Pt white line intensity decreases as temperature increases due to 5d electrons filling
- Rate of decrease is fastest at ~270°C.
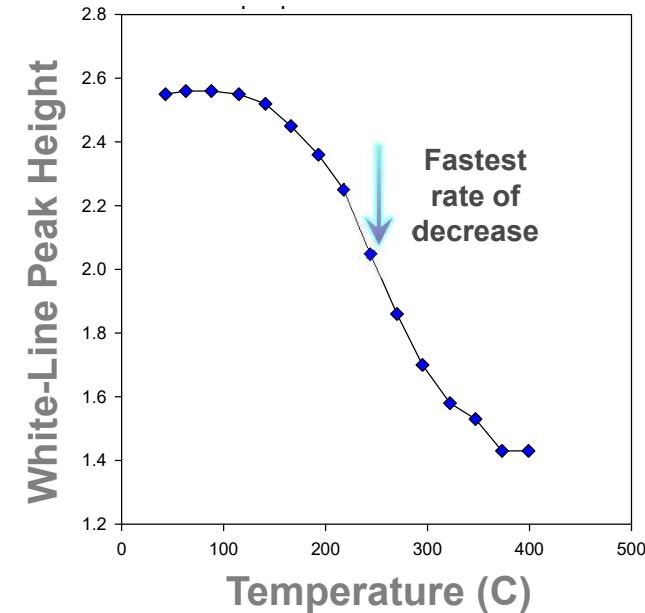
FAST-CHARGING LITHIUM-ION BATTERIES
Mechanism from XANES and DFT

Haodong Liu[1,13], Zhuoying Zhu[1,13], Qizhang Yan[1], Sicen Yu[1], Xin He[2], Yan Chen[3], Rui Zhang[4], Lu Ma[5], Tongchao Liu[6], Matthew Li[6], Ruoqian Lin[7], Yiming Chen[1], Yejing Li[1], Xing Xing[1], Yoonjung Choi[1], Lucy Gao[8], Helen Sung-yun Cho[9], Ke An[3], Jun Feng[10], Robert Kostecki[2], Khalil Amine[6], Tianpin Wu[11], Jun Lu[6,12], Huolin L. Xin[4,12], Shyue Ping Ong[1,12] & Ping Liu[1,12]

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

The team includes 26 authors with expertise in electrode chemistry, materials synthesis, neutron diffraction, in-situ XRD ICP-OES, STEM, XAS, SEM, XPS, and DFT.

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BEER'S LAW: ABSORPTION OF X-RAYS BY MATTER
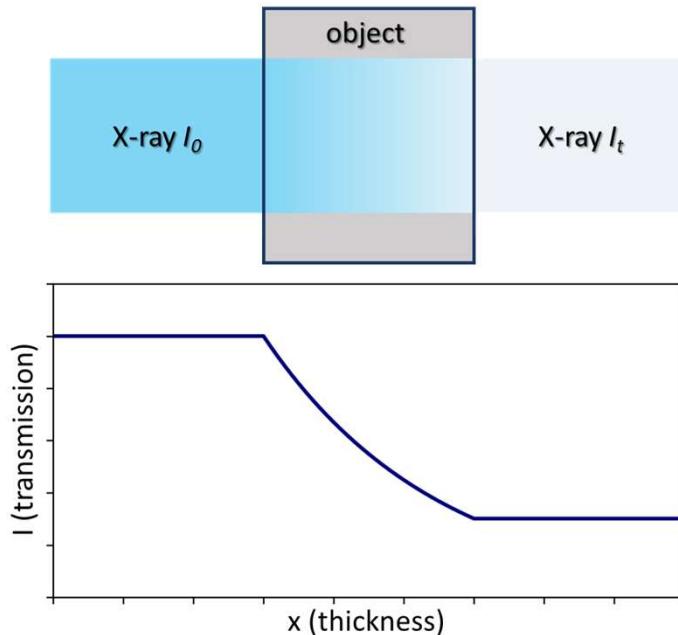
$$I_t = I_0 e^{-\mu x}$$

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

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MEASUREMENT OF X-RAY ABSORPTION COEFFICIENT

SR source

I_0

Sample

I_t

DCM

Transmission mode

$$\mu = \log\frac{I_0}{I_t}$$

Ionization chamber

Ionization chamber

I_f

Fluorescence detection mode

$$\mu \propto \frac{I_f}{I_0}$$

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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

$$\mu = \log\frac{I_0}{I_t} \qquad \mu \propto \frac{I_f}{I_0}$$
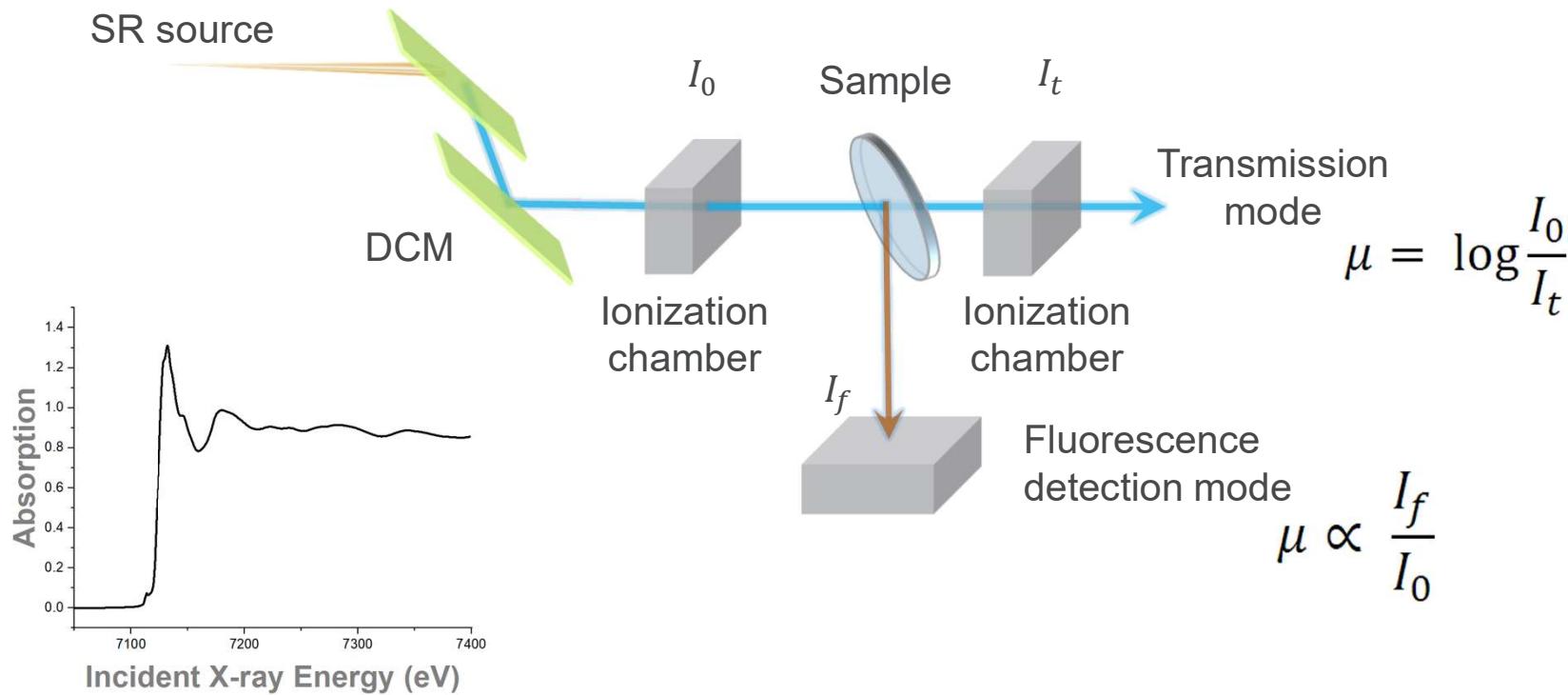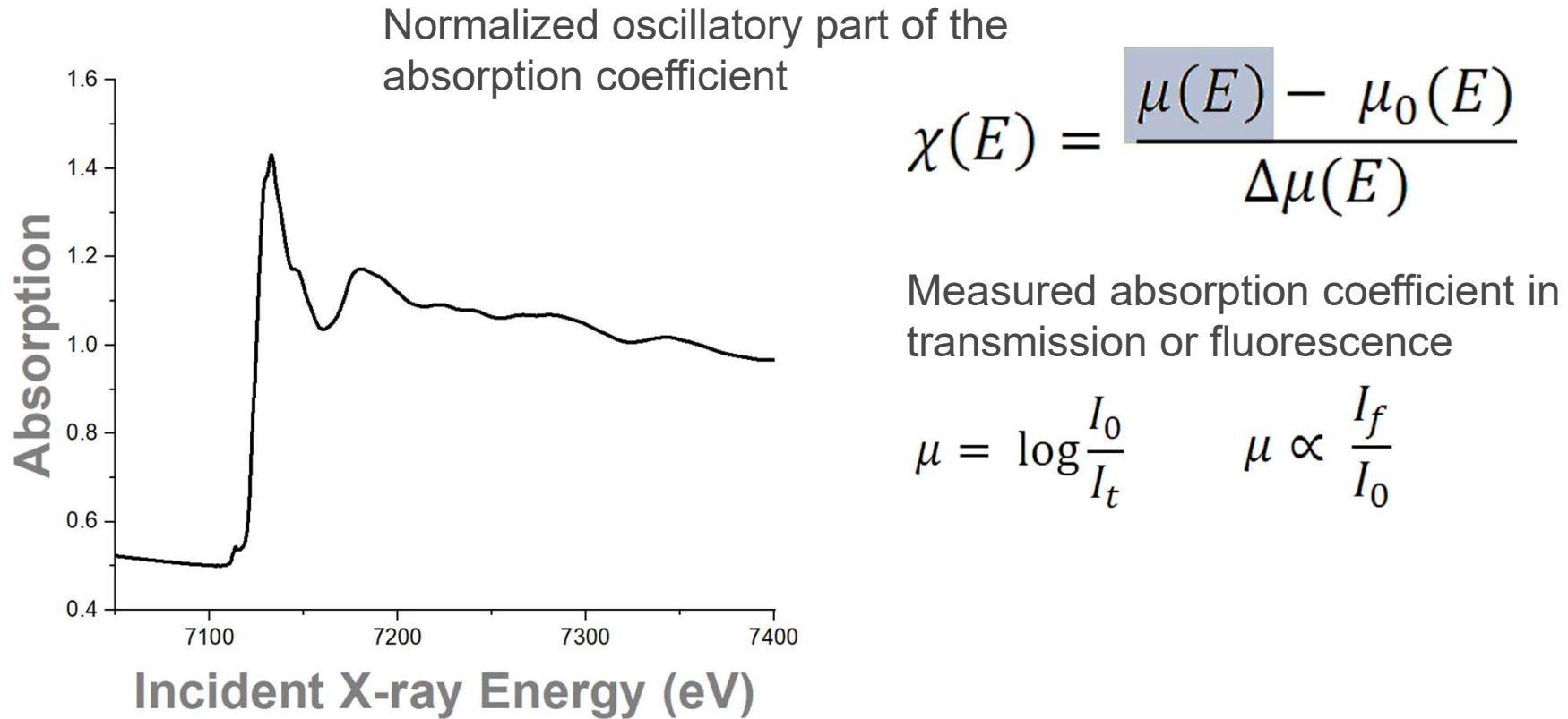
DEFINITION OF EXAFS
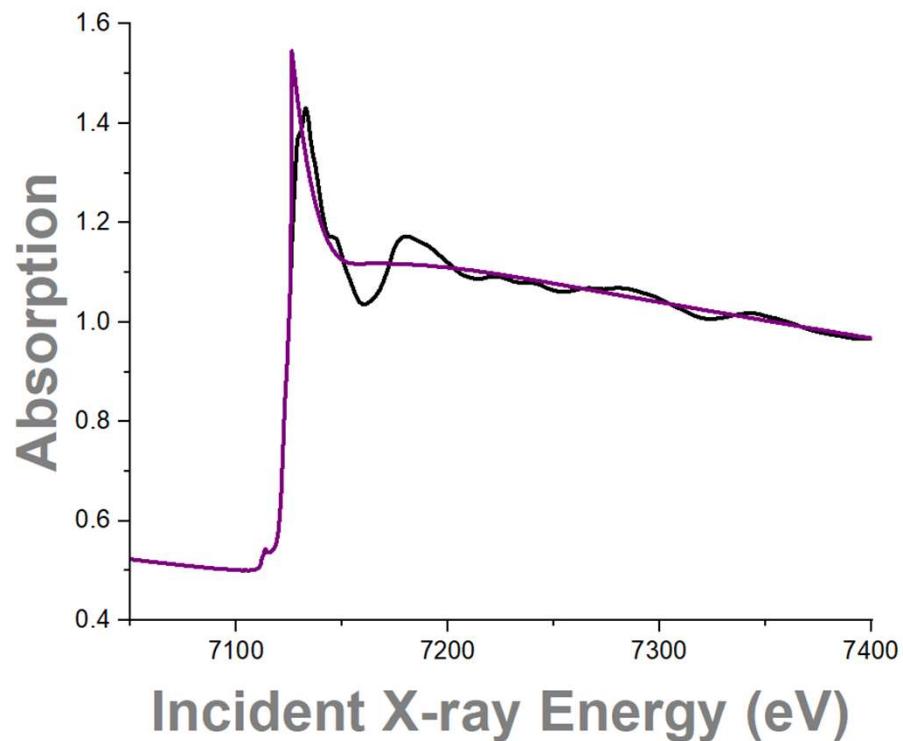
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)}$$

Smoothly varying background function, representing the absorption without fine structure

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DEFINITION OF EXAFS

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

Normalized by the edge step height

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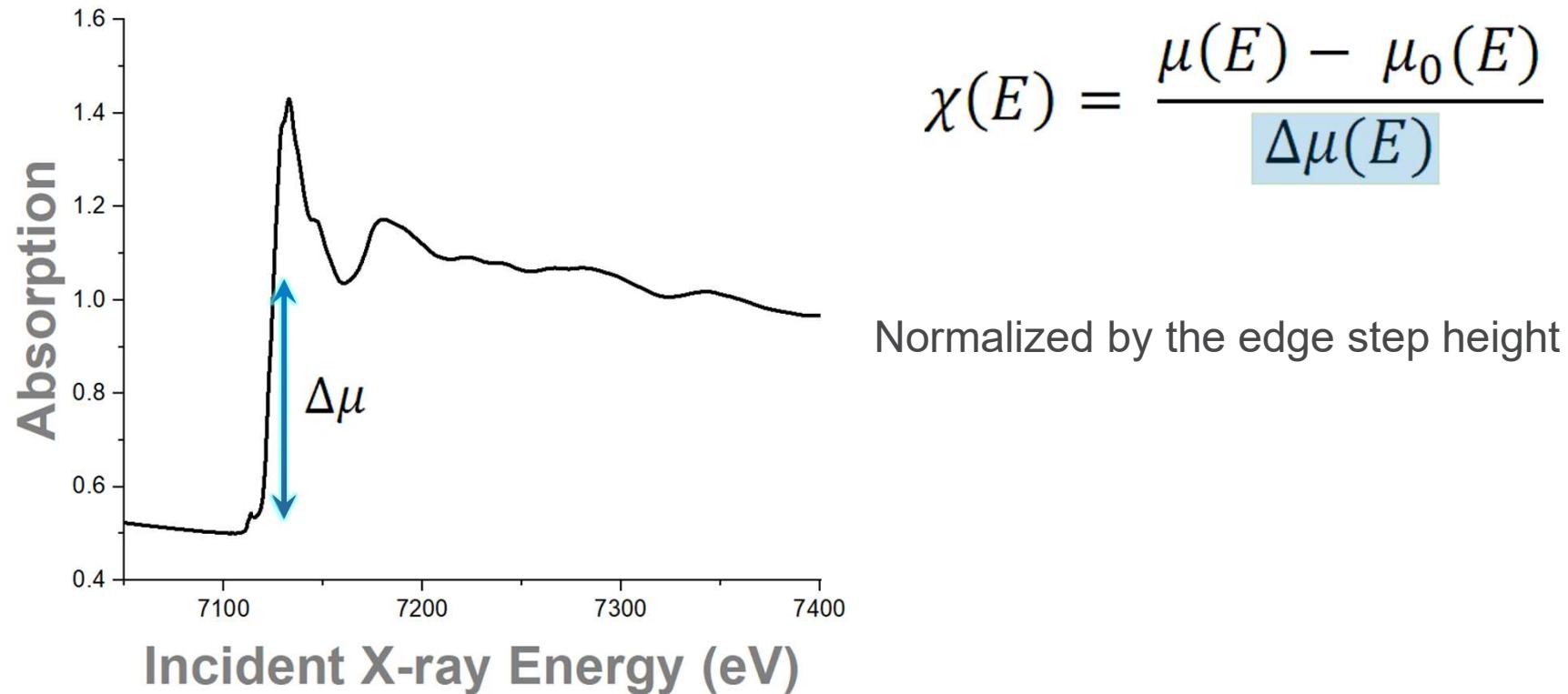
DEFINITION OF EXAFS

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

$$k^2 = 2\, m_e(E\text{-}E_0)/\, \hbar$$

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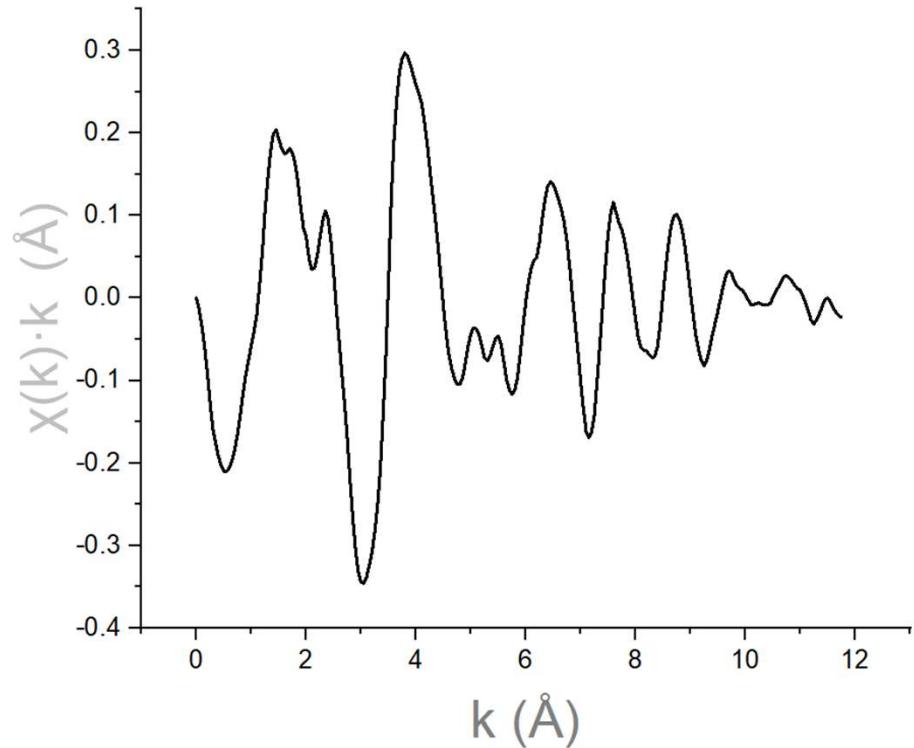
FERMI'S GOLDEN RULE

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

$\langle i|$ 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

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

adsorbing   neighboring

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X-RAY ABSORPTION FINE STRUCTURE

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

Photo-electron

E_0

Energy

Probability for Absorption

x-ray

Core-level

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

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X-RAY ABSORPTION FINE STRUCTURE

X-ray Absorption **Fine Structure**

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

Photo-electron

x-ray

Core-level

Absorbing Atom **Scattering Atom**

Probability for Absorption

Energy

E_0

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

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ATOMIC PHASE SHIFT $\delta(k)$

X-ray Absorption   **Fine Structure**

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

x-ray

Absorbing Atom   **Scattering Atom**
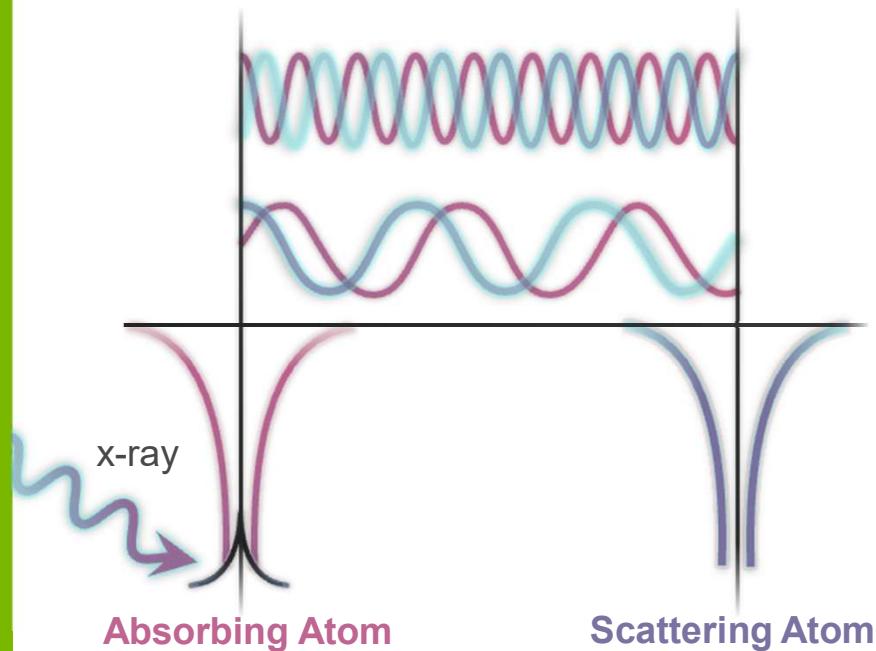
$$\chi(k) \propto \psi_{scatt}(k, \, r = 0)$$

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

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

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

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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

$$e^{-\frac{2R}{\lambda_j}}$$
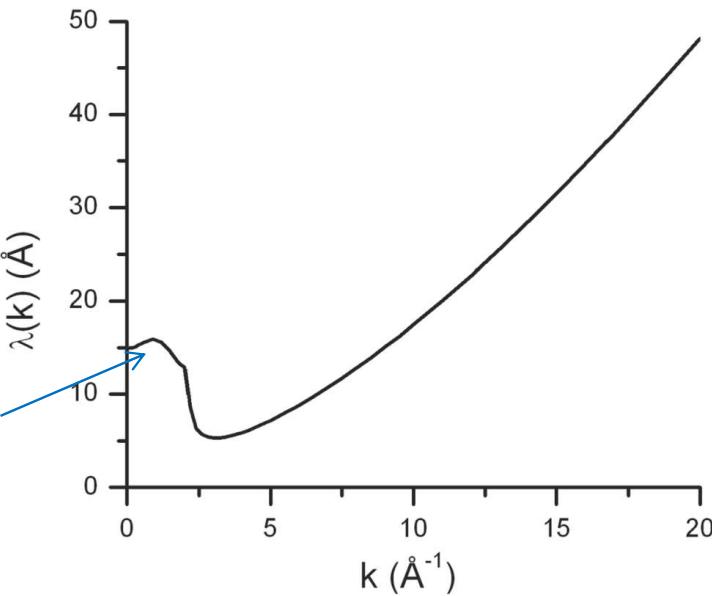
- X-ray absorption fine structure requires a core hole and a coherent photoelectron.

- The mean free path λ of the photoelectron limits the contributions to EXAFS to the first few neighbors

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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 scatting events

Shell of 6 atoms
$N_1 = 6$
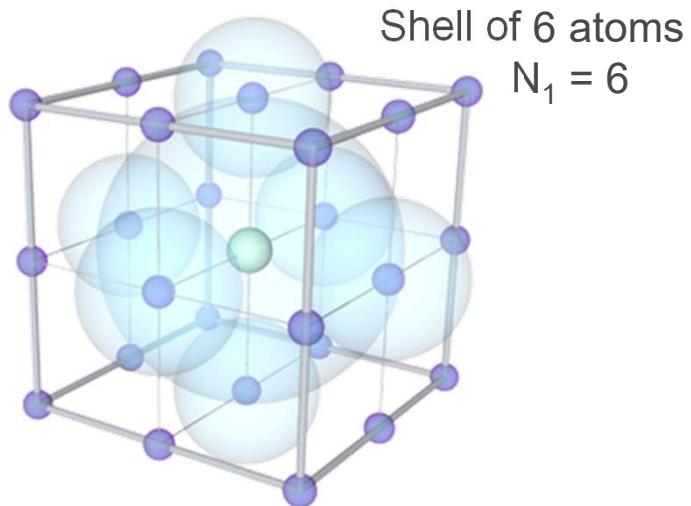
$$\chi(k) = \sum_j \chi_j(k)$$

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).

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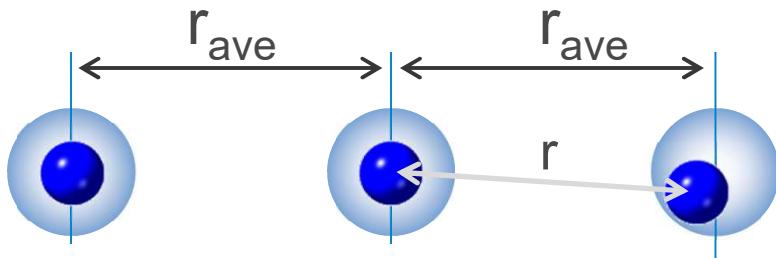
$$\int P(r)e^{i2k\Delta r}\, d\Delta r = exp\left[\sum_{n=1}^{\infty}\frac{(2ik)^n}{n!}C_n\right]$$

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

- 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

$$\chi(k) = \Sigma_i \; \chi_i(k)$$

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
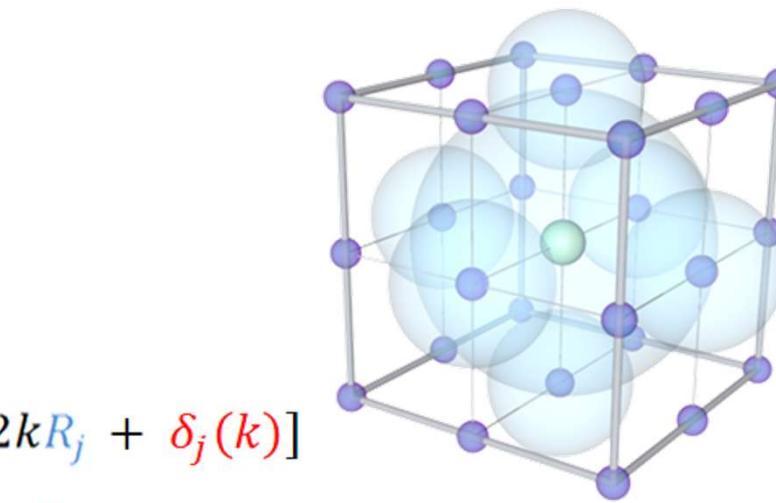
Parameters determined from a fit to data
N_i degeneracy of path
S_0^2 passive electron reduction factor
σ_i^2 mean squared displacement of half-path length
E_0 energy shift
ΔR change in half-path length

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PT EXAFS OF REFERENCE MATERIALS

Pt EXAFS: unique information about the average local atomic environment of Pt
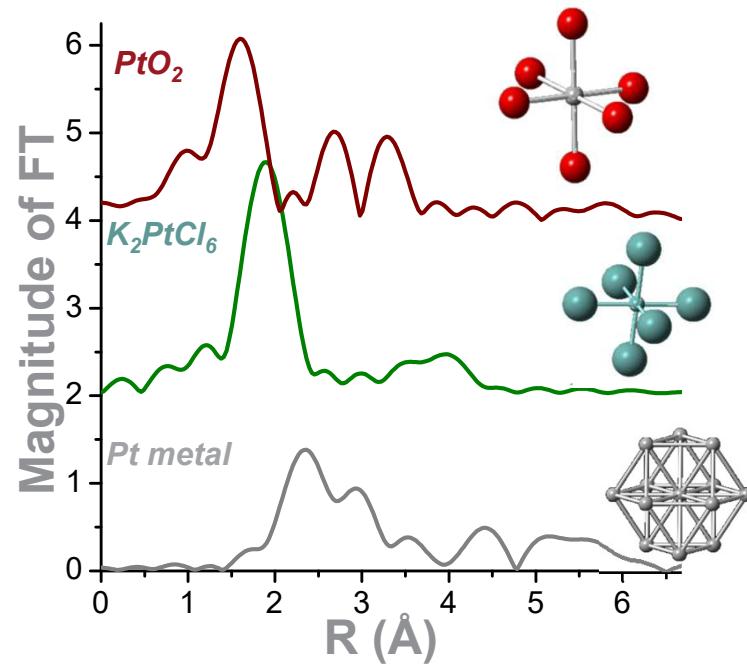
PtO$_2$		
Neighbor	Number	Distance (Å)
Pt-O	6	2.07
Pt-Pt	6	3.10

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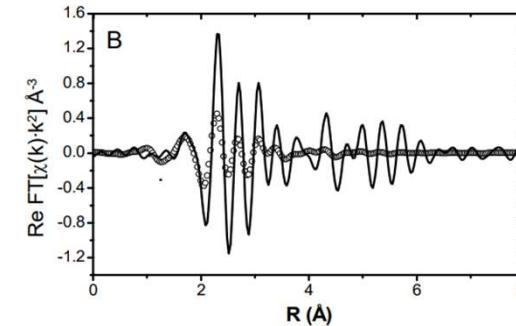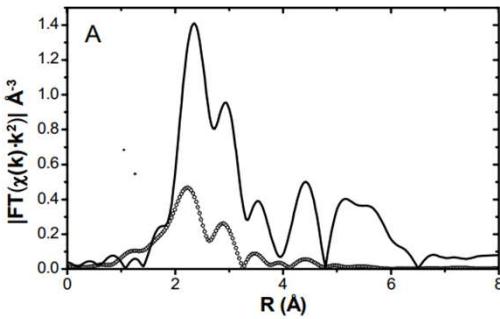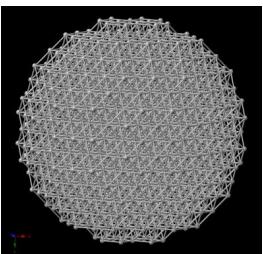
Figure 1. Magnitude (A) and real part of Fourier transform of 300C-reduced (symbols) and Pt foil (solid)

1.0 nanometer
43 atoms
Pt-Pt1 CN 5.4
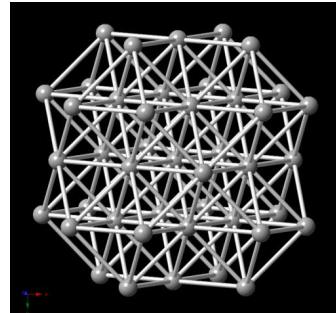
0.6 nanometer
13 atoms
Pt-Pt1 CN 4.8
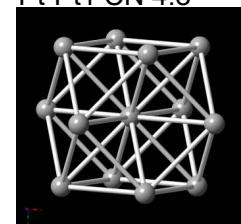
6 atoms
Pt-Pt1 CN 4.0

4 atoms
Pt-Pt1 CN 3

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

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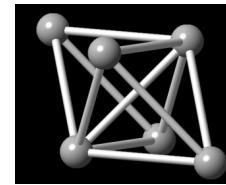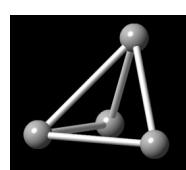
EXAFS STUDY OF NB$_3$SN SUPERCONDUCTORS

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

Challenge

- Nb$_3$Sn 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 HfO$_2$ nanoparticle pinning sites
- Combined Ta and Hf doping offers promising route to meeting the needs of future accelerators.

Microprobe needed to measure narrow Nb$_3$Sn regions
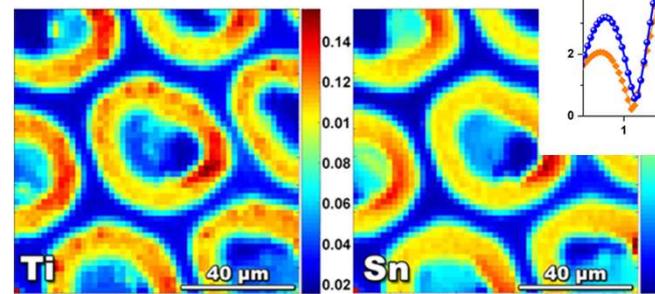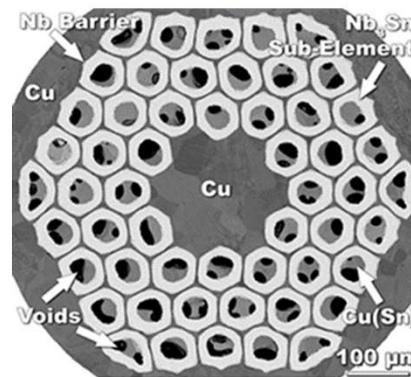
Fourier Transformed EXAFS

The triple peaked transform is characteristic of the Nb site – ~80% of Ta in Nb site

Hf transform very similar to HfO$_2$
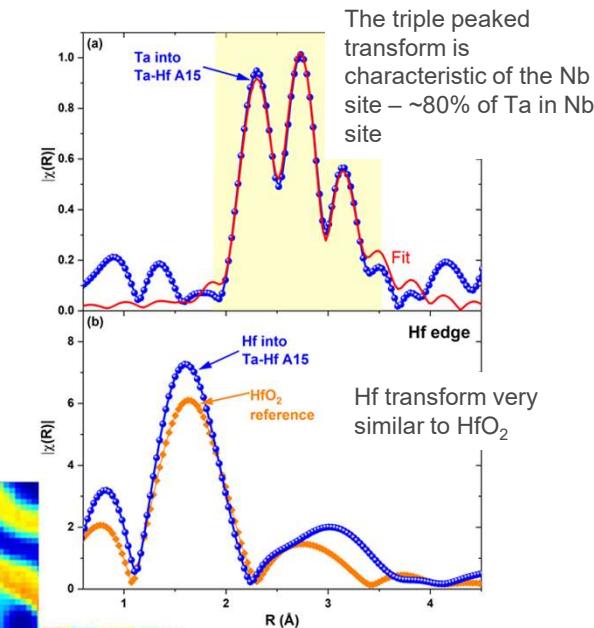
HIGH TEMPERATURE SHOCKWAVE STABILIZED SINGLE-ATOM CATALYSTS

Fourier transform comparisons
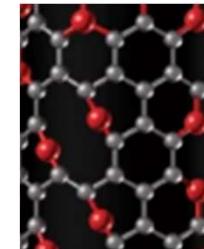
High temperature shockwave stabilized single atoms

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 Pang[4], Miaolun Jiao[1], Zhiqiang Liang[1], Jinlong Gao[1], Yang He[6], Dylan Jacob Kline [7], Michael R. Zachariah[7], Chongmin Wang [6], Jun Lu [5], Tianpin Wu [5]*, Teng Li [4]*, Chao Wang [3]*, Reza Shahbazian-Yassar [2]* and Liangbing Hu [1]*

# STRUCTURE OF LUMINESCENT PROTEIN-STABILIZED GOLD CLUSTERS

EXAFS with DFT interpretation

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

Q & A

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