Edward A. Stern

1930-2016

XAFS Short Course:
Principles and Applications

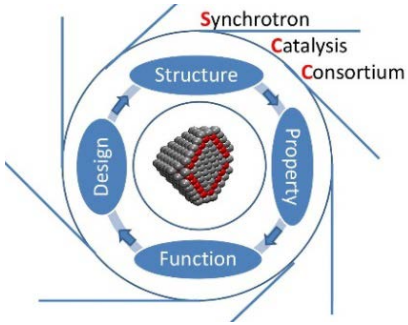
Instructors:

Klaus Attenkofer
Anatoly Frenkel
Shelly Kelly
Syed Khalid
Joshua Kas
Yuanyaun Li
Jing Liu
Nebojsa Marinkovic
Bruce Ravel
Eli Stavitski
Janis Timosenko
Qi Wang

BNL administrator:
Mercy Baez

Financial support

Brookhaven National Laboratory
and Synchrotron Catalysis Consortium



U.S. DEPARTMENT OF ENERGY

BNL/SCC Short Courses at BNL

2005

2006

2007

2008

2009

2010

2011

2012

2013

2014

2015

Agenda at a glance

Wednesday, Nov. 2

A. Frenkel, J. Kas, K. Attenkofer, S. Kelly,
B. Ravel, J. Timosenko

Coffee break	10:40 – 11am
Lunch	12 - 1:30pm
Coffee break	3:30 – 3:50pm
Dinner	6pm

Thursday, Nov. 3

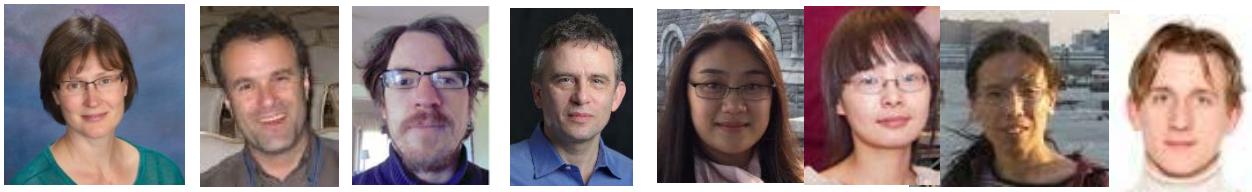
S. Khalid, B. Ravel, J. Kas, S. Kelly,
J. Timosenko, N. Marinkovic, A. Frenkel

Coffee break+photo	11 – 11:20am
Lunch	12:20 - 1:30pm
Coffee break	3:20 – 3:50pm
Dinner	6pm

Friday, Nov. 4

ISS beamline experiments: E. Stavitski, K. Attenkofer

Data analysis: B. Ravel, A. Frenkel, J. Kas,
J. Liu, J. Timosenko, S. Kelly, Q. Wang



Lunch 12 - 1 pm

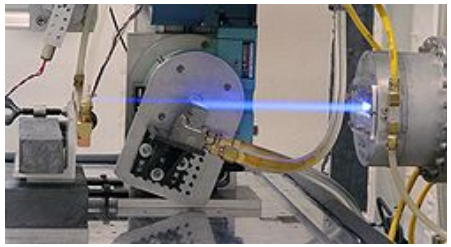
History of synchrotrons

Alfred-Marie LIENARD
(1869-1958)
The concept of retarded potentials in the calculation on the effects due to the motion of charged particles

Edwin Mattison McMillan
(1907 –1991)
Developed the first synchrotron at Berkeley;
Built in 1946

Vladimir Veksler
(1907 –1966)
Developed the principles of synchrotron design

Synchrotron radiation: 1947
GE synchrotron



History of XAFS

Ed Stern, Dale Sayers, Farrel Lytle

Absorption Coefficient and Fine Structure

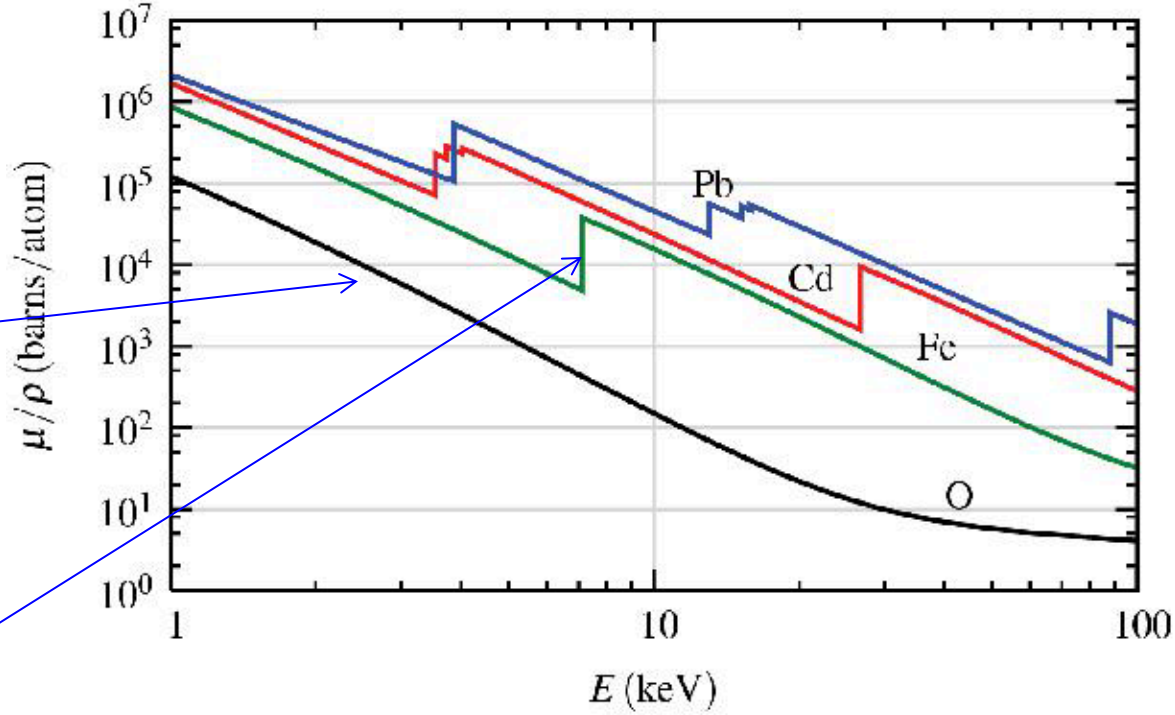
Beer – Lambert Law:

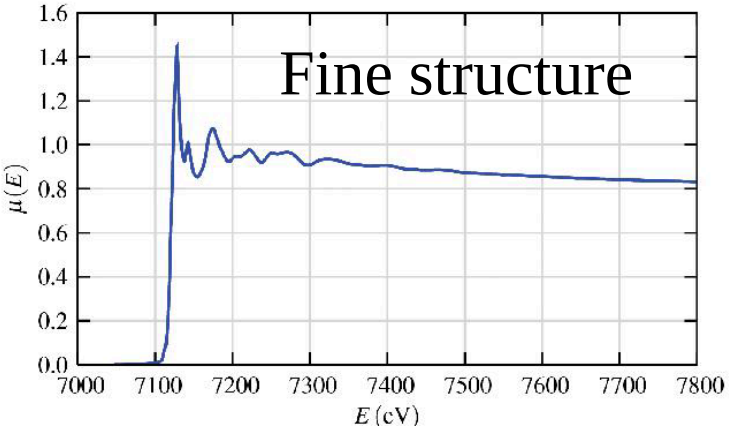
$$I = I_0 e^{-\mu x}$$

Victoreen formula:

$$\mu(E) = aE^{-3} + bE^{-4}$$

Absorption edges:
(M. de Broglie, 1913)





Frische and Hertz, 1920
(observed)
Kronig: LRO, 1931
Stern, Sayers, Lytle, SRO, 1971

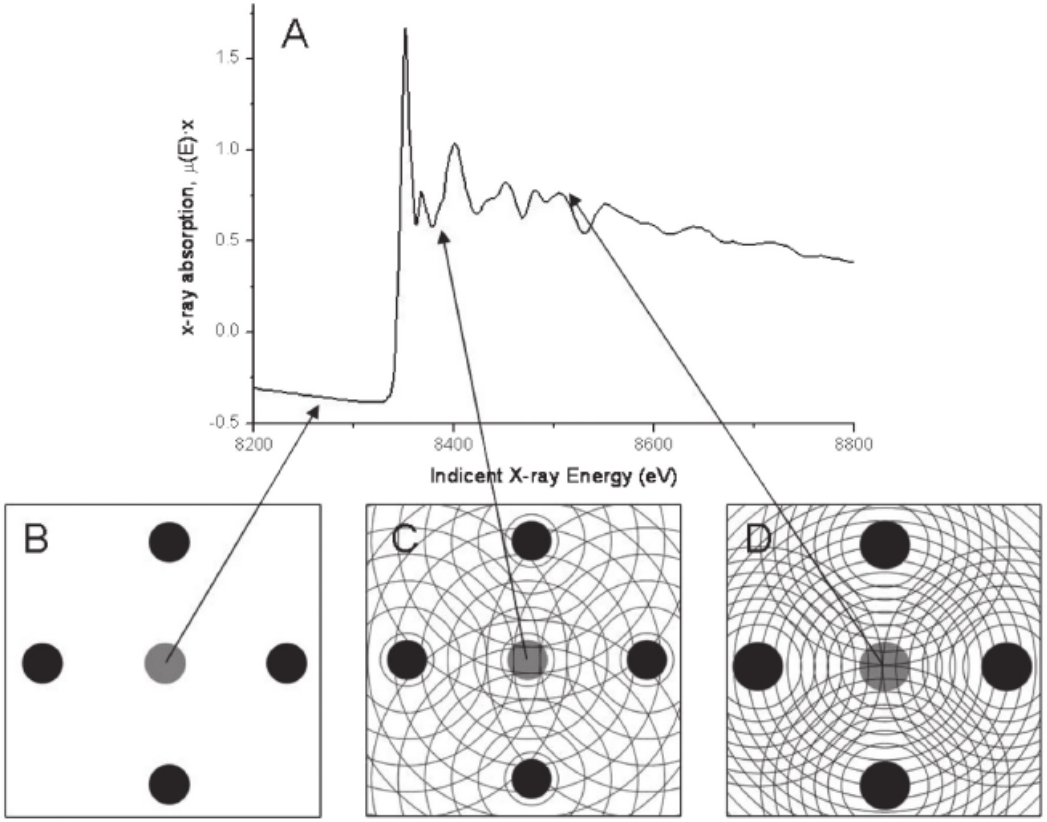


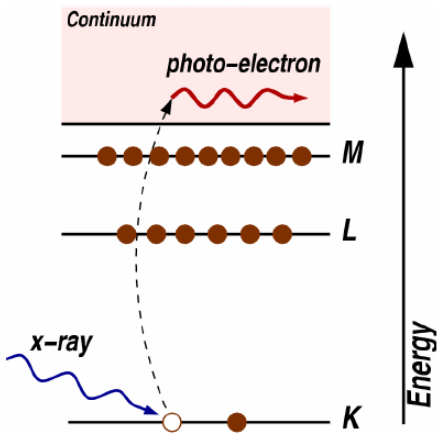
Fig. 14–7. Illustration of the X-ray absorption process. (A) Nickel K-edge X-ray absorption spectrum of NiO. (B–D) Nickel absorber atom (gray filled circle) and four of six neighboring oxygen atoms (black filled circles). The crests of photoelectron waves produced by X-ray absorption by the absorber atom (Ni) and by scattering from neighboring oxygen atoms are shown as concentric circles about Ni and O atoms, respectively. (B) At X-ray energies below the absorption edge no photoelectron is produced. (C) At energies close to but above the absorption edge, the photoelectron wavelength is longer than at higher energies. This particular wave produces a minimum in the oscillatory part of the absorption coefficient because the outgoing and scattered parts of the photoelectron meet at a minimum at the absorbing atom; that is, the peak crests are completely out of phase at the center of the absorber atom. (D) At higher X-ray energies the wavelength of the photoelectron is shorter than shown in C. This particular wave produces a maximum in the oscillatory part of the absorption coefficient because the outgoing and scattered parts of the photoelectron are in phase and meet at a maximum at the absorber atom.

S. Kelly, D. Hesterberg, B. Ravel,
In: Methods of Soil Analysis, 2008, Ch. 14, p. 394

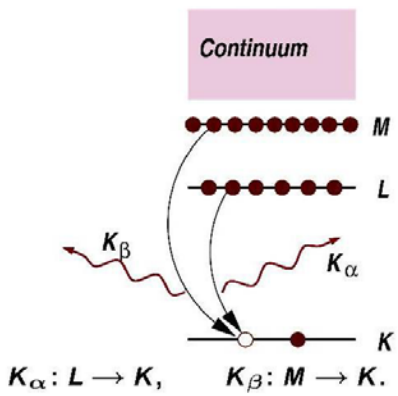
Theory of EXAFS and XANES

Fermi's Golden Rule
in one-electron approximation:

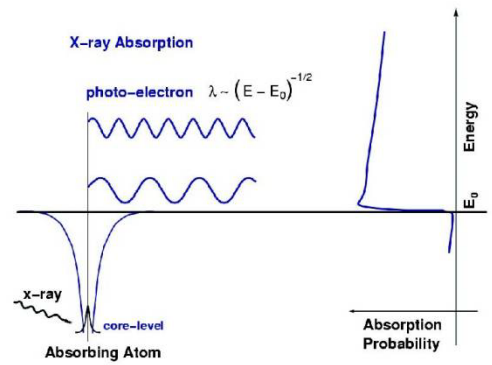
$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$$



Transmission mode



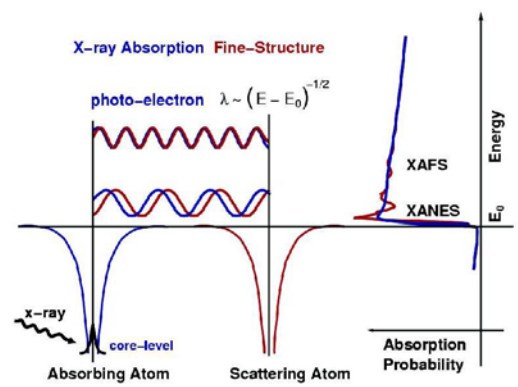
Fluorescence mode



$$E = E_0 + \frac{p^2}{2m}$$

$$p = \hbar k = \frac{h}{\lambda}$$

Absorption in the isolated atom



Absorption in the atom with neighbors

Information in XAFS data:

- Identities of nearest neighbors
- Coordination numbers of nearest neighbors
- Interatomic distances relative to the absorber
- Bond length disorder (static and dynamic)
- Charge states of elements

Materials properties

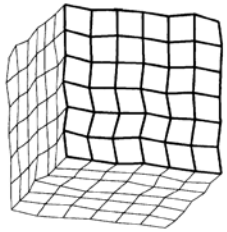
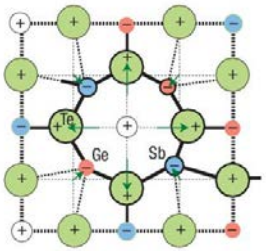


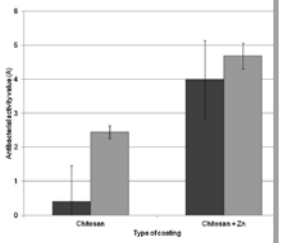
Fig. 2. Buckled structure of the $AgBr_{0.6}Cl_{0.4}$.

Physica B **208 & 209** , 334 (1995).



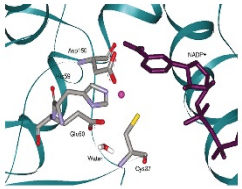
Nature Materials, **3**, 703-708 (2004).

J. Mater. Chemistry **22**, 7028-7035 (2012)

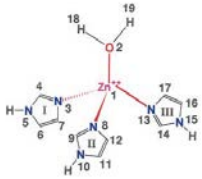


J. Mater. Chem. B **1**, 1968-1976 (2013)

Structural biology

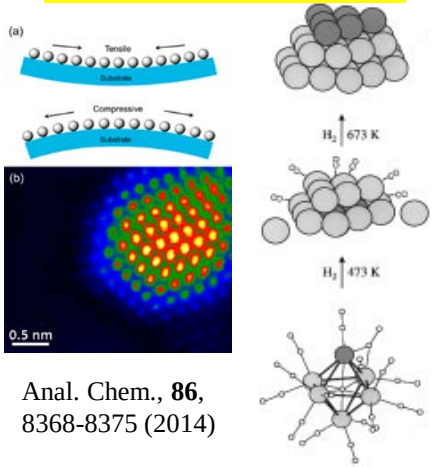


Nat. Struct. Biology, **10** , 98-103 (2003).



J. Biological Chemistry, **44** , 34335-34343 (2000).

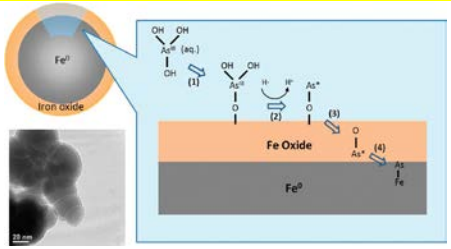
Catalytic mechanisms



Anal. Chem., **86**, 8368-8375 (2014)

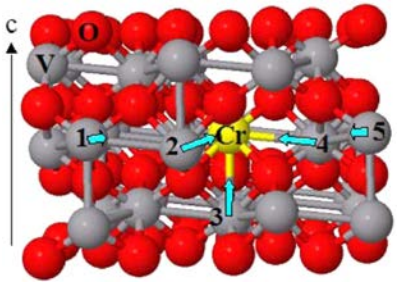
J. Am. Chem. Soc., 120, 1998

Environmental science



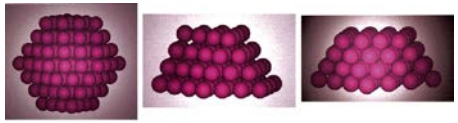
Environ. Sci. Technol. **46**, 7018-7026 (2012)

Phase transitions

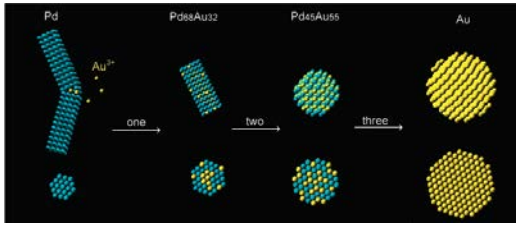


Phys. Rev. Lett. **97**, 195502 (2006).

Nanoparticles

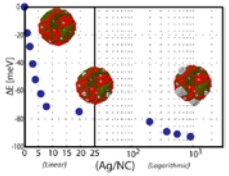


J. Phys. Chem. B, **105,** 12689-12703 (2001).

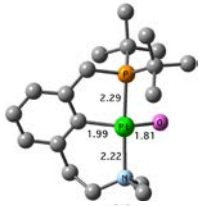


J. Am. Chem. Soc. **130**, 1093-1101 (2008).

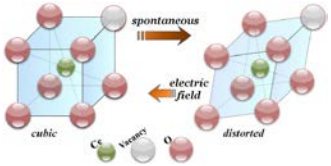
Novel materials



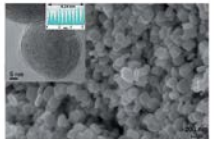
ACS Nano **9**, 10790-10800 (2015)



Nature **255**, 1093-1096, 2008.



App. Phys. Lett.**106**, 042904 (2015)



Angew. Chem. Int. Ed. **51**, 1148-1151 (2012)

Data analysis methods
1) Using analytical EXAFS equation

Amplitude

$$\chi_\Gamma(k) = \frac{NS_0^2}{kR^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin\left[2kR - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

FEFF

$$E_0 = E_0^{\text{bkg}} + \Delta E_0$$

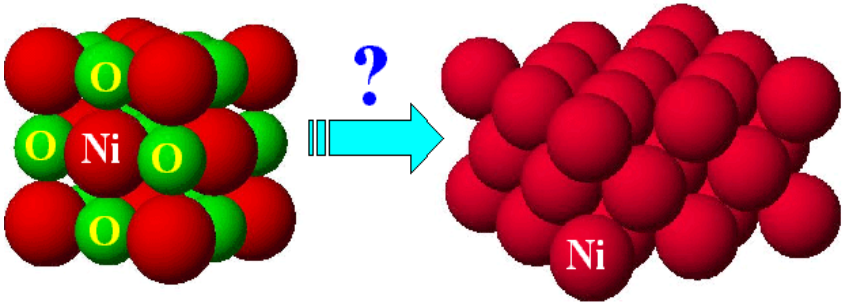
$$R = R_{\text{model}} + \Delta R$$

Same parameterization for single and multiple-scattering paths.

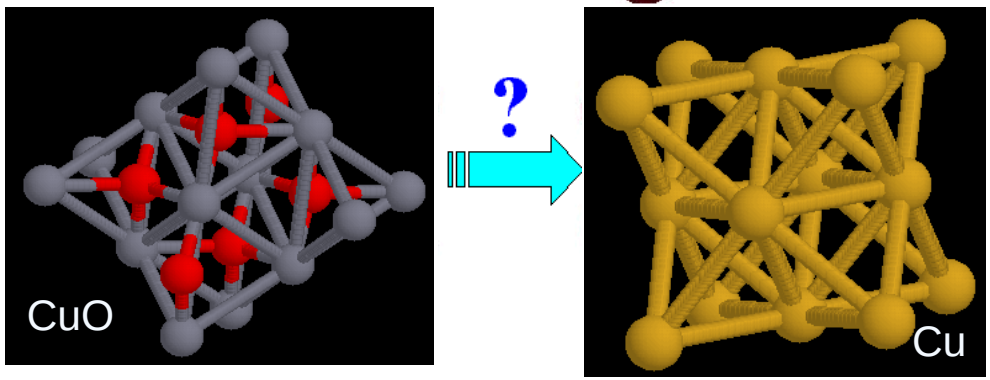
$$\chi(k) = \sum_\Gamma \chi_\Gamma(k)$$

- Parameterization of structural models for EXAFS data fitting
- FEFF theory
- Error analysis

2) Linear combination methods



$NiO + H_2 \rightarrow Ni + H_2O$



$CuO + H_2 \rightarrow Cu + H_2O$, or

$2CuO+CO \rightarrow Cu_2O+CO_2$
$Cu_2O+CO \rightarrow 2Cu+CO_2$

Fitting methods (using EXAFS theory) break down:

$$\mu = \sum_{i=1}^{N} x_i \mu(\mathrm{P}_i)$$

-too many variables,
-correlation of variables,
-nonlinear least squares methods $\Rightarrow$ multiple minima in parameter space

Alternative: linear methods:

Linear combination analysis (LCA)
Principal component analysis (PCA)
Multivariate Curve Resolution Alternating Least Squares (MCR-ALS)

Resources

International X-ray Absorption Society
http://www.ixasportal.net/ixas/

Tutorial materials:
XAFS.org (IXAS Wiki)

IFEFFIT mailing list
http://cars9.uchicago.edu/mailman/listinfo/ifeffit/