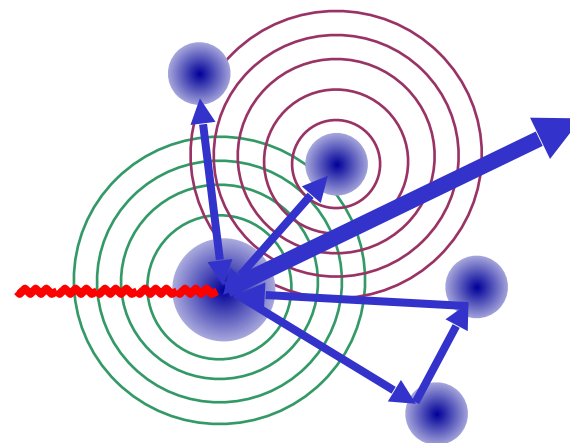




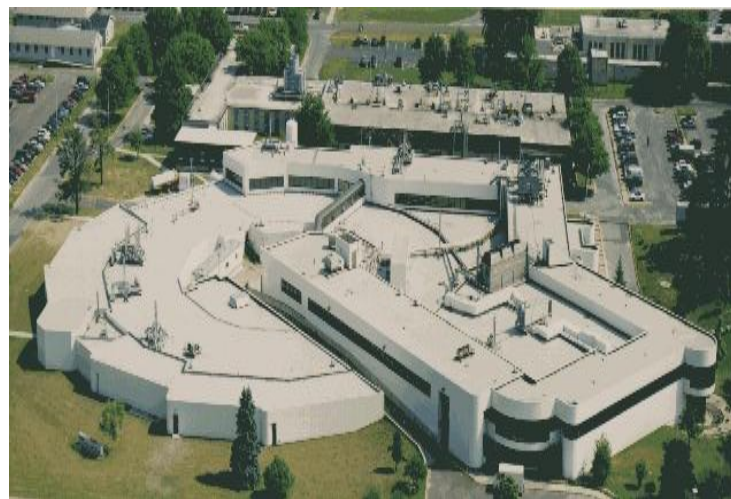
# *EXAFS of an Element with Multiple Absorbing Sites*

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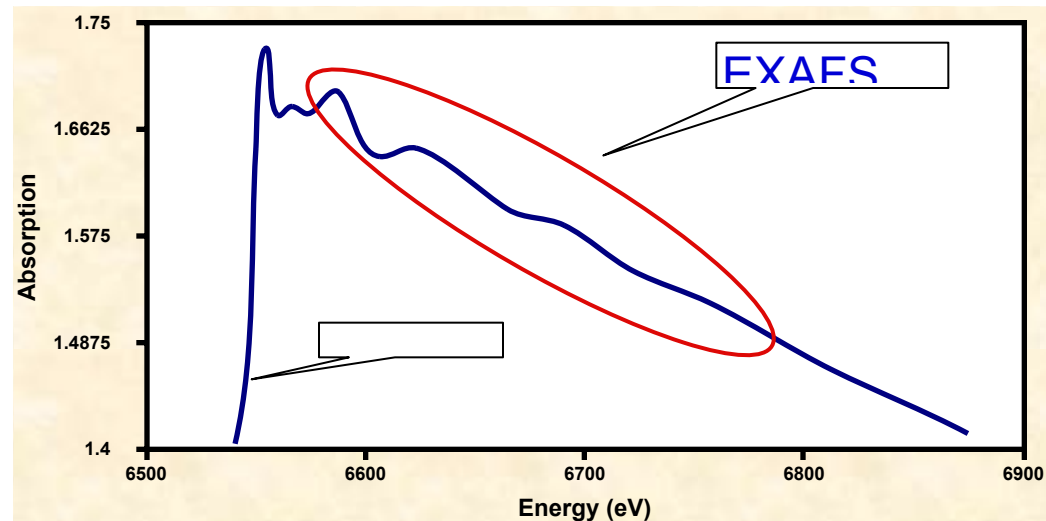
Data collected at beamline X23B of  
the National Synchrotron Light Source  
at Brookhaven National Laboratories



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## *Extended X-ray Absorption Fine Structure (EXAFS)*

- Oscillations caused by interference between outgoing and backscattered photoelectrons
- Provides information on local environment of specific heavy element
- Widely used to analyze materials with long-range order small or absent





# Methodology

## Model

## Data

Approximate atomic positions from x-ray diffraction data

Model EXAFS using FEFF Software (*ab initio* calculation)

Model of paths in  $k$  (momentum) - space (EXAFS is now periodic)

Collect and average data over all scans

Subtract background

Data in  $k$  space with background subtracted

Fourier transform data and model to  $r$ -space (distance)

Vary parameters to get least square fit

Check fit for stability and physical sense



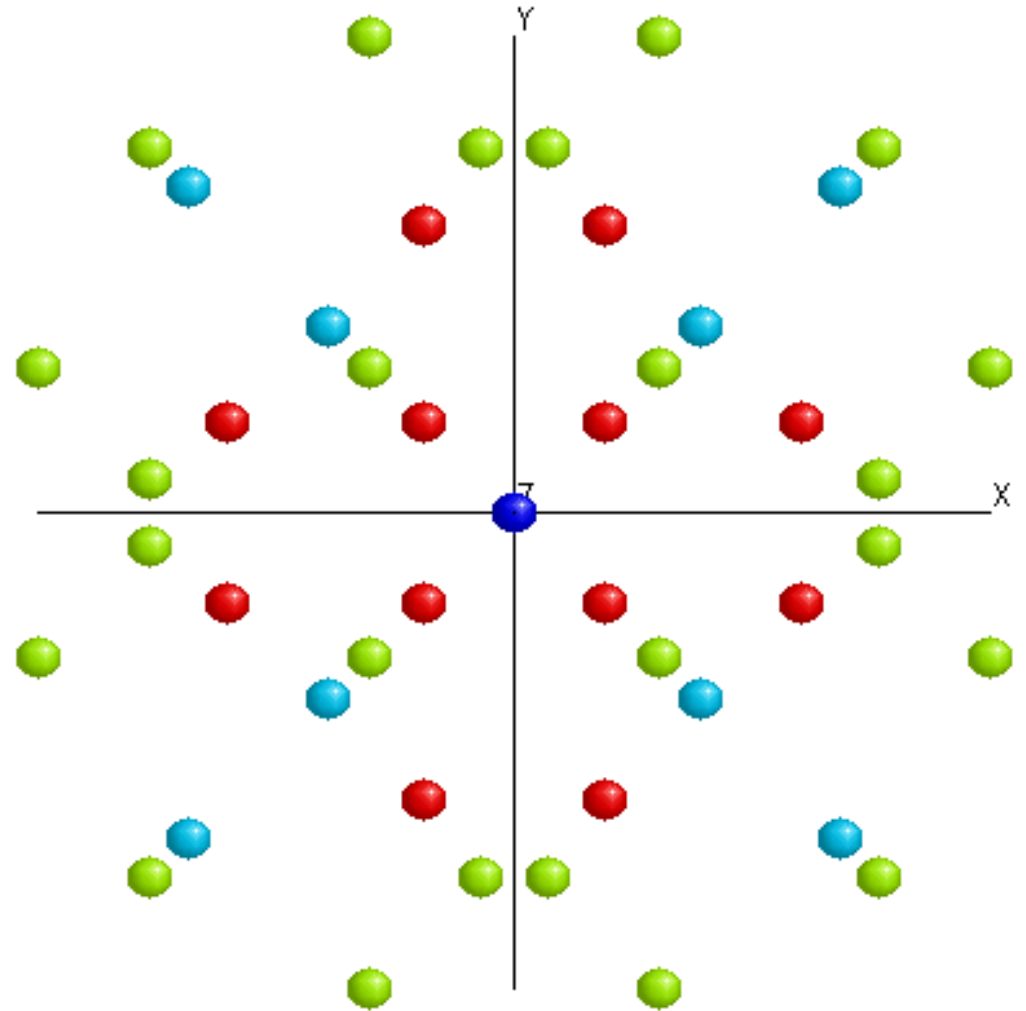


## *Materials with Multiple Absorbing Sites*

- Mixed materials
  - Partially cycled cathodes
  - Environmental samples
  - Advanced materials
- Pure materials with multiple crystallographic sites
  - Many transition-metal oxides
  - $\alpha$ -manganese

## *Local Structure of $\alpha$ -Manganese*

Site type	Number in unit cell
1	2
2	8
3	24
4	24

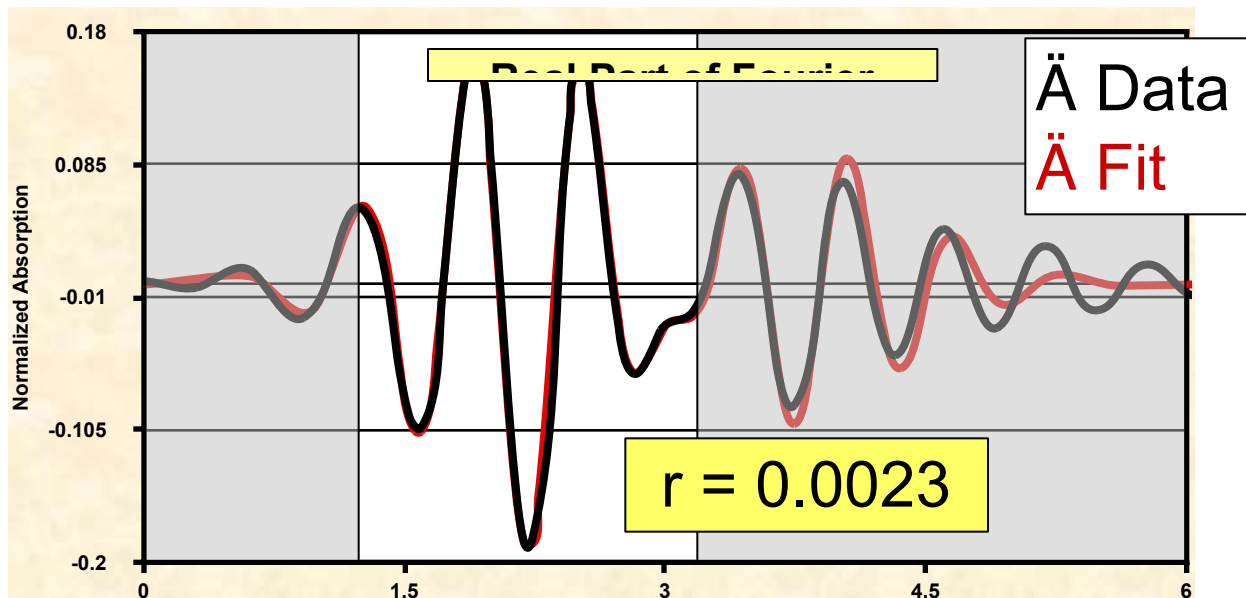




## *Model*

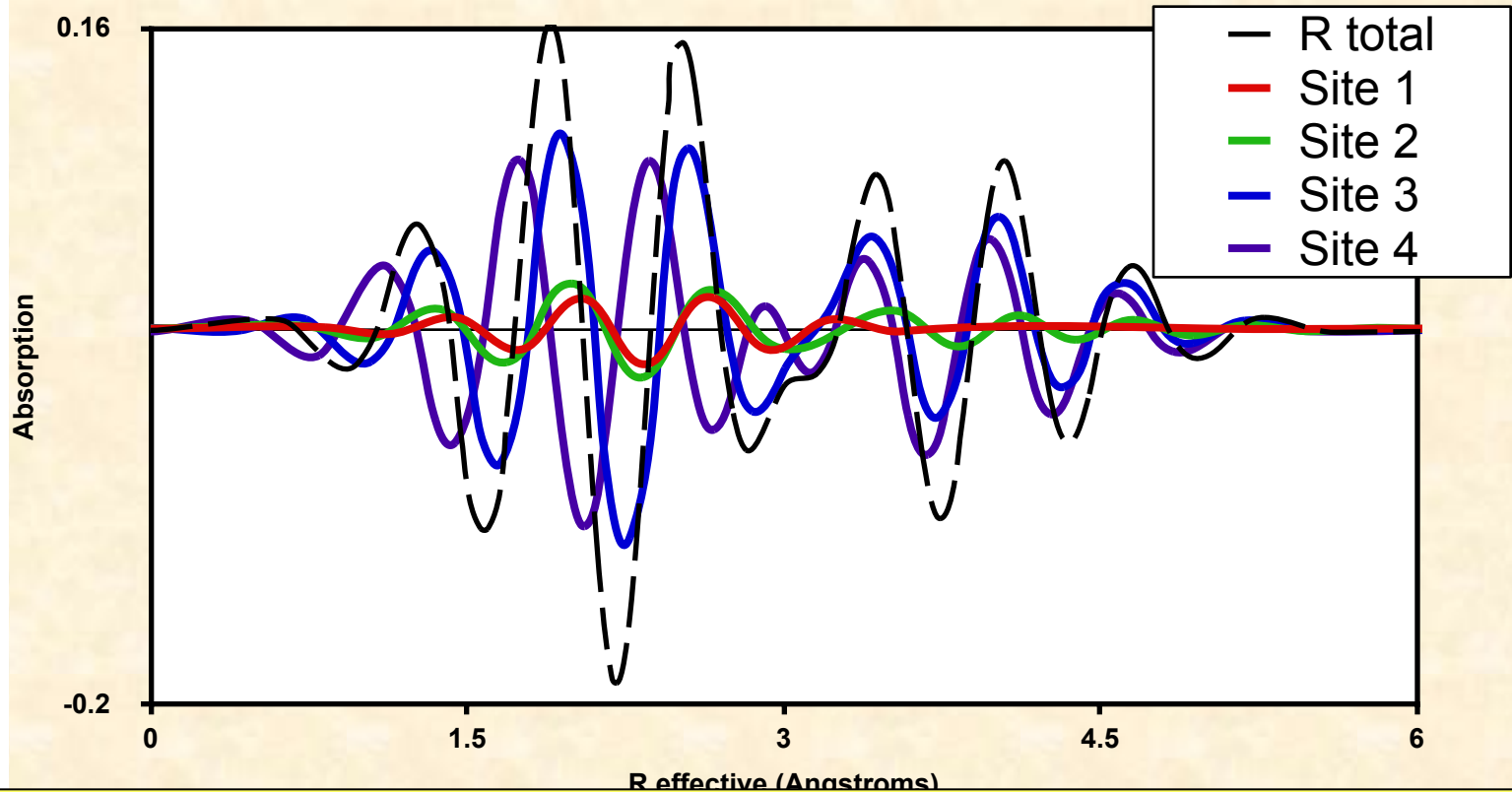
- Based on published x-ray diffraction (XRD) data
- Included paths out to 4.4 Å, but fit to only 3.2 Å (allows for spectral leakage)
- Included both direct and multiple scattering paths
- Constrained paths into two groups
  - Grouping did not affect best-fit values much, but did affect stability of fit
  - Chose grouping based on greatest stability and closest fit to data
  - Site 3 paths in one group, all other paths in second group
- Allowed  $\Delta E_0$  and  $S_0^2$  to vary

## Results



Paths	Bond lengths relative to XRD	Debye-Waller factor (Å)
Site 3	0.0% $\pm$ 1.5%	0.021 $\pm$ 0.009
All others	0.0% $\pm$ 4.4%	0.042 $\pm$ 0.029

## Contribution by Site

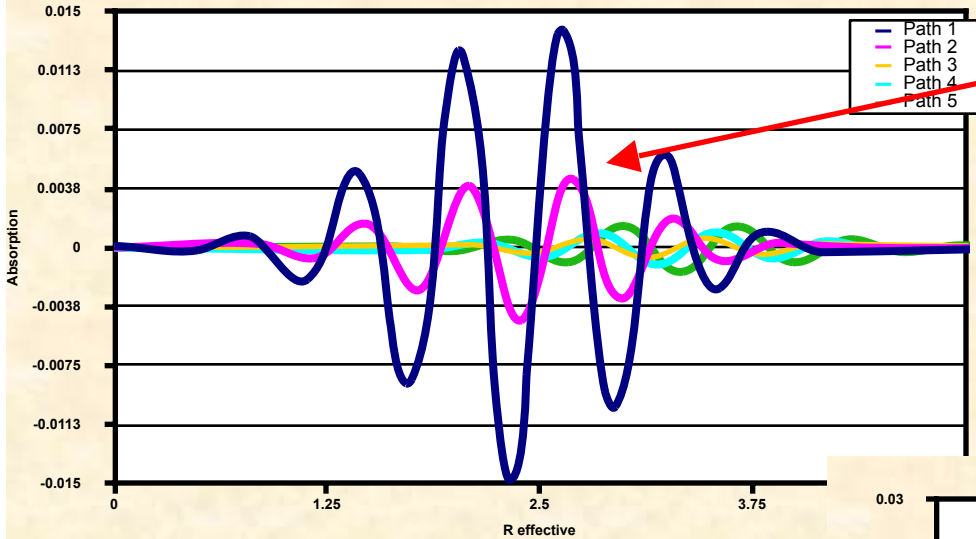


Note that sites of types 1 and 2 contribute almost equally, although sites of type 2 are four times as common!



## Interference at Sites 1 and 2

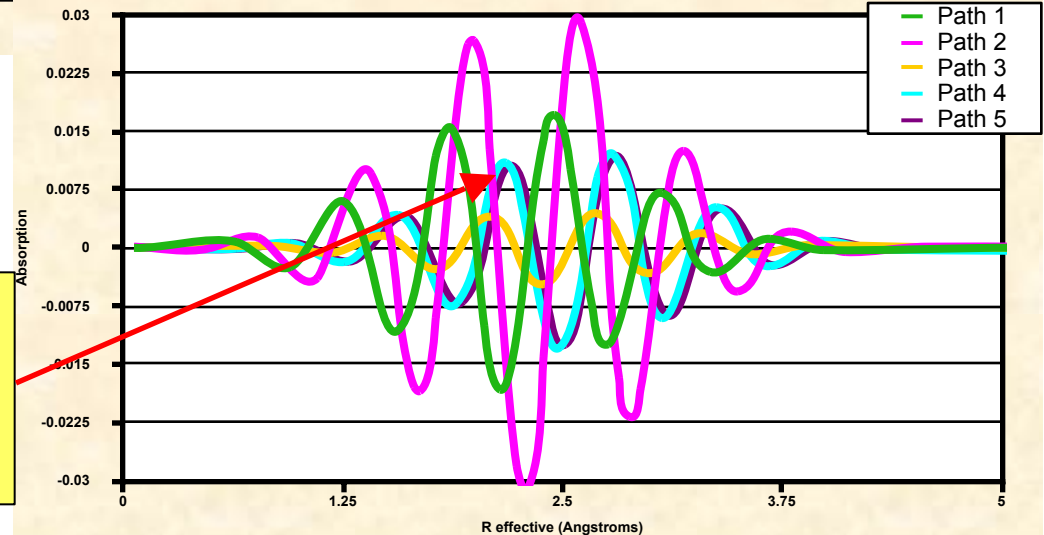
First Crystallographic Site



Note constructive interference between paths 1 and 2 of first site

Note destructive interference between paths 1 and 3+4 of second site

Second Crystallographic Site





## *Conclusions*

- Accurate EXAFS analysis on materials with multiple crystallographic sites is possible
- Relative contribution of a site type to the signal is not directly proportional to the number of sites of that type present, due to interference effects
- We plan to analyze a temperature series of manganese in order to determine the precision of the technique