The role of XAFS in a Research Program: Applied Magnetism and Magnetic Materials

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(and a host of others)

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Formally of NRL

Goals of this presentation

- Relax, do not take notes
- The role of XAFS in a research group
    - How to form an effective research team
    - Picking good problems
    - Using EXAFS as a supportive tool
    - Funding
- The role of EXAFS in magnetism and magnetic materials

My Research Team
(last few years, incomplete list)

Scott Calvin	(PD/XAFS)
Bruce Ravel	(PD/XAFS)
Julie Cross	(PD/XAFS)
Matt Newville	(XAFS)
Darius Fatemi	(PD/XAFS/Materials/XRD)
John Kirkland	(XAFS/beamline ops)
Aria Yang	(Student/XAFS/FMR/VSM/XRD)
John Snyder	(PD/Materials)
Everett Carpenter	(PD/Materials/XRD/DLS/SQUID)
Shannon Morrison	(Student/Materials/XRD)
Marc Raphael	(PD/Materials/XRD/SQUID/SEM/AFM)
Matt Willard	(PD/Materials/XRD/VSM)
Lynn Kurihara	(Materials/XRD)
Joe Christodoulides	(Materials/XRD/SQUID)
Taras Pokhil	(VSM/MFM/AFM)
Rhonda Stroud	(TEM)
Frances Hellman	(Materials/VSM/SQUID)
Zuo Xu	(PD/Materials)

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XAFS Research Activity
Hands on XAFS measurements
Problem solving
Education

1988 | 1990 | 1993 | 1996 | 2000 | 2003

Group Leader Activity
Funding
Team management
Identifying problems
Quality control

Student	NRC PD	NRL Staff	Section head (~15 Ph.D.s)	Branch Head (~40 Ph.D.s)	Professor

Building an effective research team

From a team member perspective

- Control materials synthesis
- Use supportive characterization techniques, not just XAFS
- Become an expert on materials of interest (not easy)

From a group leader perspective

- Surround yourself with youth and talent
- Control materials synthesis
- Use many supportive characterization techniques, not just XAFS
- Choose your problems wisely
- Funding

From a team member perspective

Control materials synthesis

-Materials optimization is essential (not left over samples in the dessicator)
-Fully characterized samples (signals quality)
-First series of XAFS measurements is often needed to dictate further materials optimization
-The growers call the shots

From a team member perspective

Use many supportive techniques

XAFS usually provides one piece of the puzzle (SRO chemistry, bond lengths, etc)

Supportive techniques are needed to provide verification and constraints to the XAFS model

- -XRD, ND (strong LRO information)
- -TEM/SEM (strong SRO information, morphology)
- -Magnetic (specialized information)
- -Transport (specialized information)

From a team member perspective

Educate yourself (constantly)

- Become and expert on materials of interest
- Determine key problems
- Do not do XAFS just because you can
- Talk to the experts
- Attend conferences
- Read review articles
- What are the outstanding issues, can XAFS help?

From a team member and leader perspective

Choose your problems wisely

Some problems are excellent XAFS problems that offer no new insight into the materials science, physics or chemistry of a material system

The XAFS problem should address an outstanding issue of fundamental importance to science and technology

Team leader or senior members should provide direction

From a team leader perspective

Surround yourself with talent and youth…

-Science and technology are changing so fast it is impractical to keep up with it all
-Know your limitations
-The students/PD know the latest and greatest
-Young talent is easy to find and cheap
-They work tirelessly

From a team leader perspective

Funding

- Do not try to fund XAFS or SR experiments – propose the solution to an outstanding problem
- Basic science vs mission driven funding (know your sources' needs)
- Trends are towards technological value, not science for science sake (even NSF)
- Proposals should address an S&T problem that when solved provides a tangible benefit
  - Improved performance
  - New use
  - Reduced size, etc

Magnetism and Magnetic Materials

Why?

Magnetic interactions are typically governed by exchange interactions and are particularly sensitive to NN and next NN chemistry, distances, and bond angles.

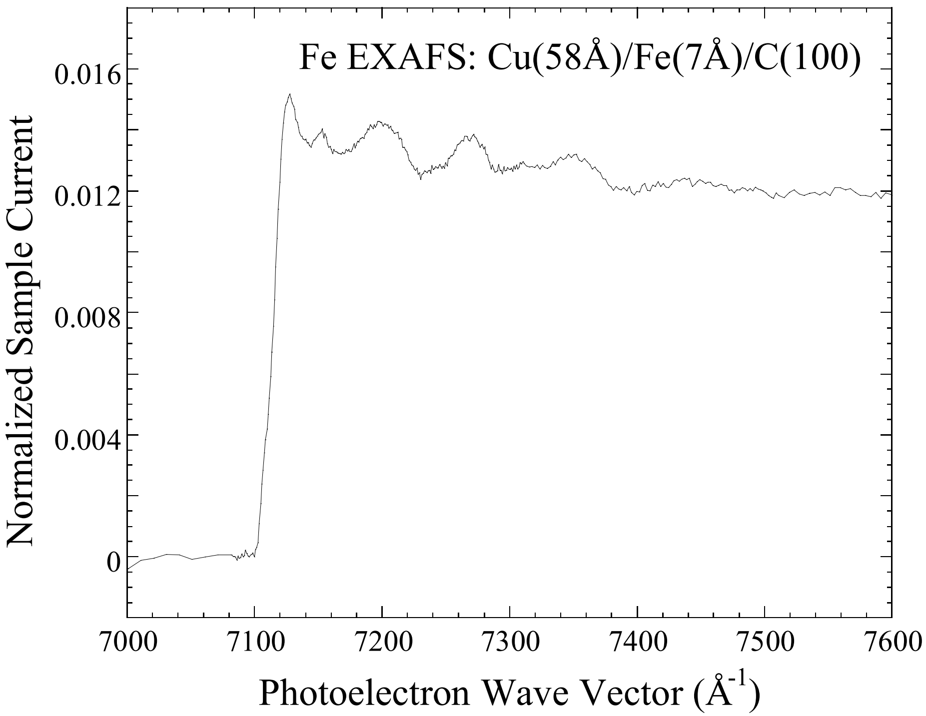
All magnetic interactions are sensitive to local chemistry and structure and therefore EXAFS can play a leading roll in characterization of materials.

To illustrate some interesting problems in magnetism that XAFS has played a key role:

3 examples

1. Heteroepitaxy of Fe on diamond
2. Measurement of amorphous to crystalline transition in thin films
3. Cation disorder in ferrites

Example 1: Ultrathin magnetic films: The case of epitaxial Fe on diamond
Motivation: Metallization of diamond by magnetic alloys is a precursor to advanced *spintronic* structures and devices



- Films are grown by MBE
- A few monolayers of Fe on (100) DLC
- Data collection is done using TEY
- Data shown is one scan of Fe of one spp
- Obviously some noise in the data but the fine structure is visible
- Is the noise a limiting factor?

(Measured mass is ~1 femtogram ($1x10^{-15}$ grams))

R.S. Swineford, D.P. Pappas, and V.G. Harris, PRB, 52, 11, 7890 (1995)

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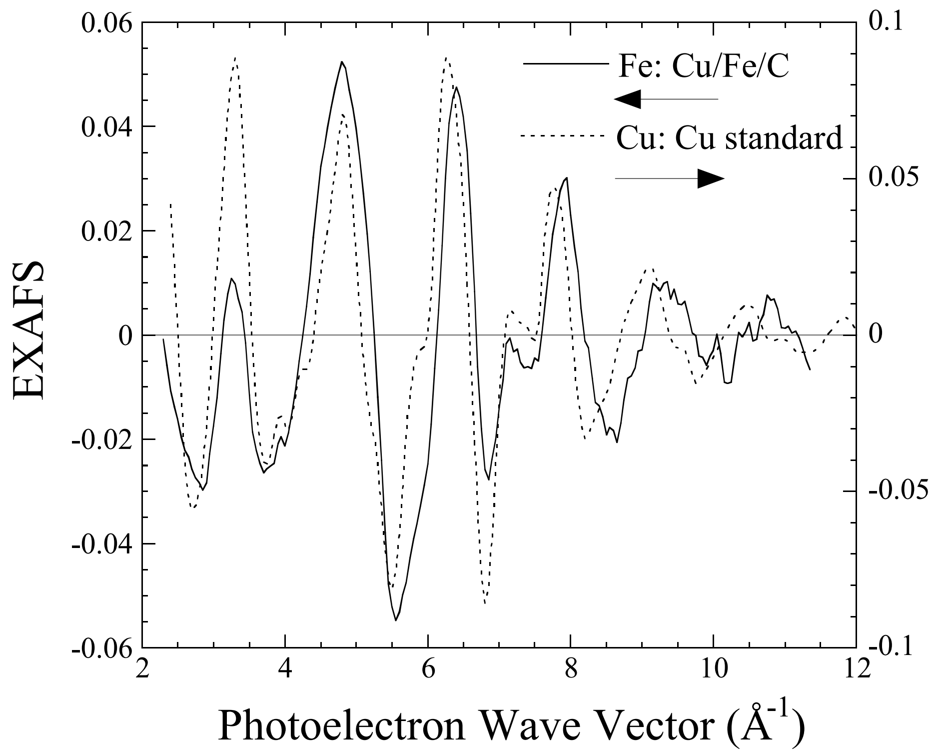
Qualitative k-space analysis



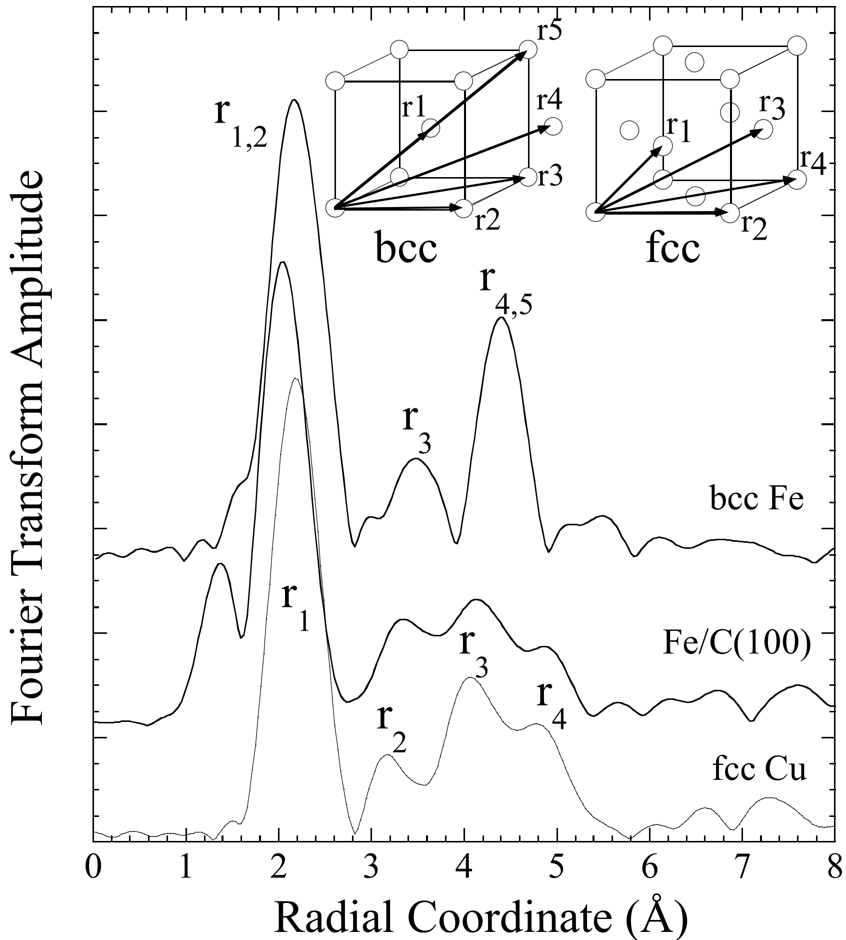
Comparing the Fe to Cu EXAFS in k-space is useful in identifying the crystal structure

Notice phase differences, signals change in bond distance

Many similarities exist between data sets in both phase and relative amplitudes

R.S. Swineford, D.P. Pappas, and V.G. Harris, PRB, 52, 11, 7890 (1995)

Qualitative r-space analysis



Comparison in r-space are more useful in that it identifies similarities in terms of short range and long range order, crystal symmetry.

Very useful in qualitative analysis

At this point-
-fcc vs bcc Fe/C
-Fe-C bond is observed

R.S. Swineford, D.P. Pappas, and V.G. Harris, PRB, 52, 11, 7890 (1995)

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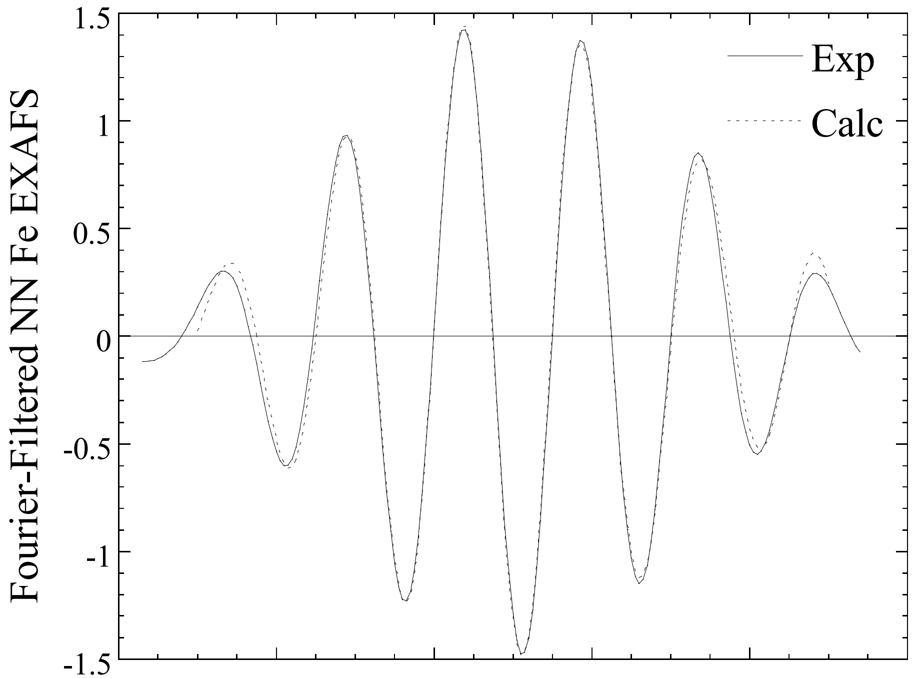
Quantitative FEFF analysis of FF FT data (single scattering)



R.S. Swineford, D.P. Pappas, and V.G. Harris, PRB, 52, 11, 7890 (1995)

Fe-Fe	2.50Ǻ
Fe-Cu	2.62Ǻ
Fe-C	1.84Ǻ
Lattice par.	3.55Ǻ

-Bond lengths, coordination, lattice parameter
-Up to 24 Å stabilized fcc-like structure
-C plays role in the stabilization of the Fe films
-Lattice constant of 3.55 Å, using LEED we measured an out of plane value of 3.59 Å.

Impact

First metallization of DLC by a ferromagnet

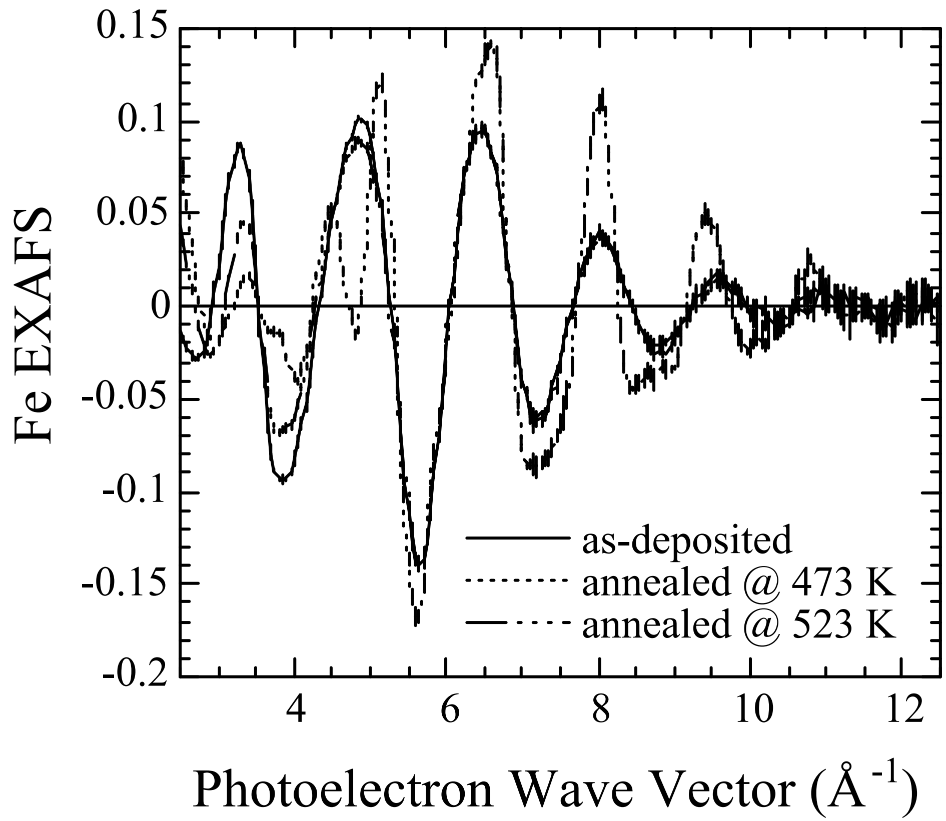
Confirmed heteroepitaxy of Fe/C

Paves the way for marriage between wide band gap materials and *spintronics**

**(http://www.sciam.com/article.cfm?articleID=0007A735-759A-1CDD-B4A8809EC588EEDF)*

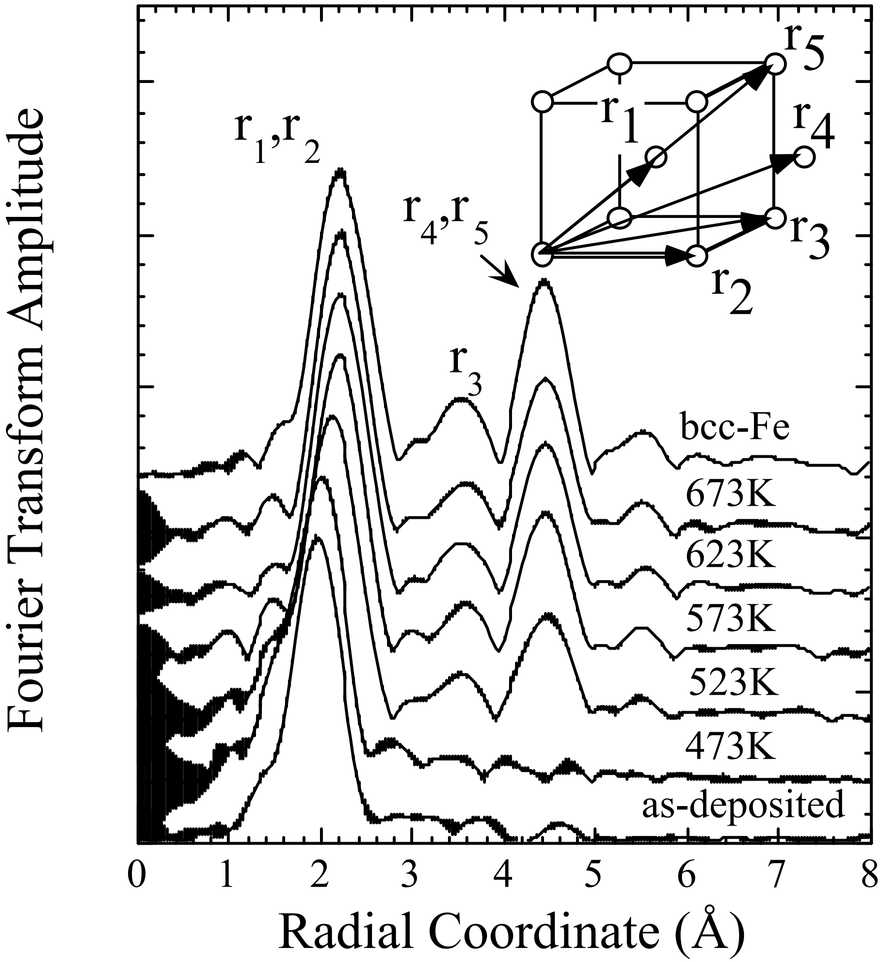
Technological impact…. 10-20 years

Example 2: Understanding amorphous to crystalline transition in solid state thin film systems ($Fe_{80}B_{20}$). Phase change media (rewritable disk technology).



V.G. Harris, et al., Appl. Phys. Lett., **68**(15), 2073 (1996).

- Data is collected from Fe edge using TEY cell
- Films are 15nm thick
- Annealed in sealed glass ampoules
- Goals are to deduce crystallization kinetics of thin films
- We see some high k noise
- No changes at 473K but changes seen in 523K
- Mass sampled is 26 femtograms



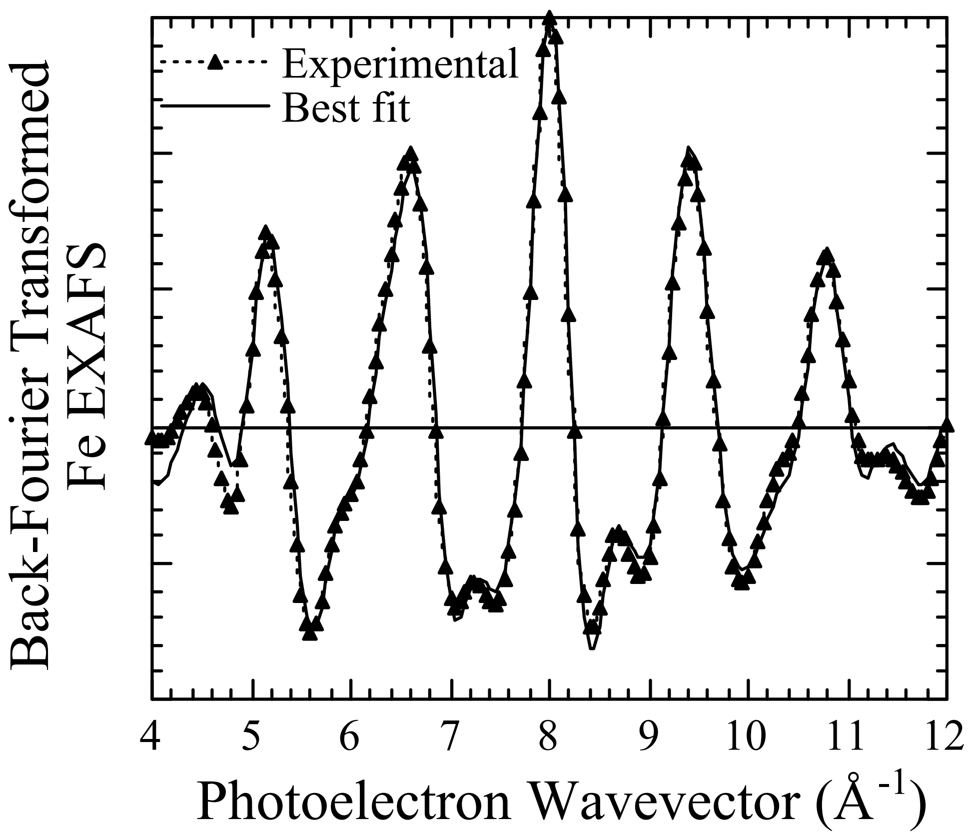
FT data illustrating the evolution of structure as a function of annealing temperature

Notice the shift in NN distance
At 523K we see evidence for bcc phase

The principle fingerprint of the crystalline phase is the bcc Fe

Are there other phases present?

V.G. Harris, et al., Appl. Phys. Lett., ***68****(15), 2073 (1996).*



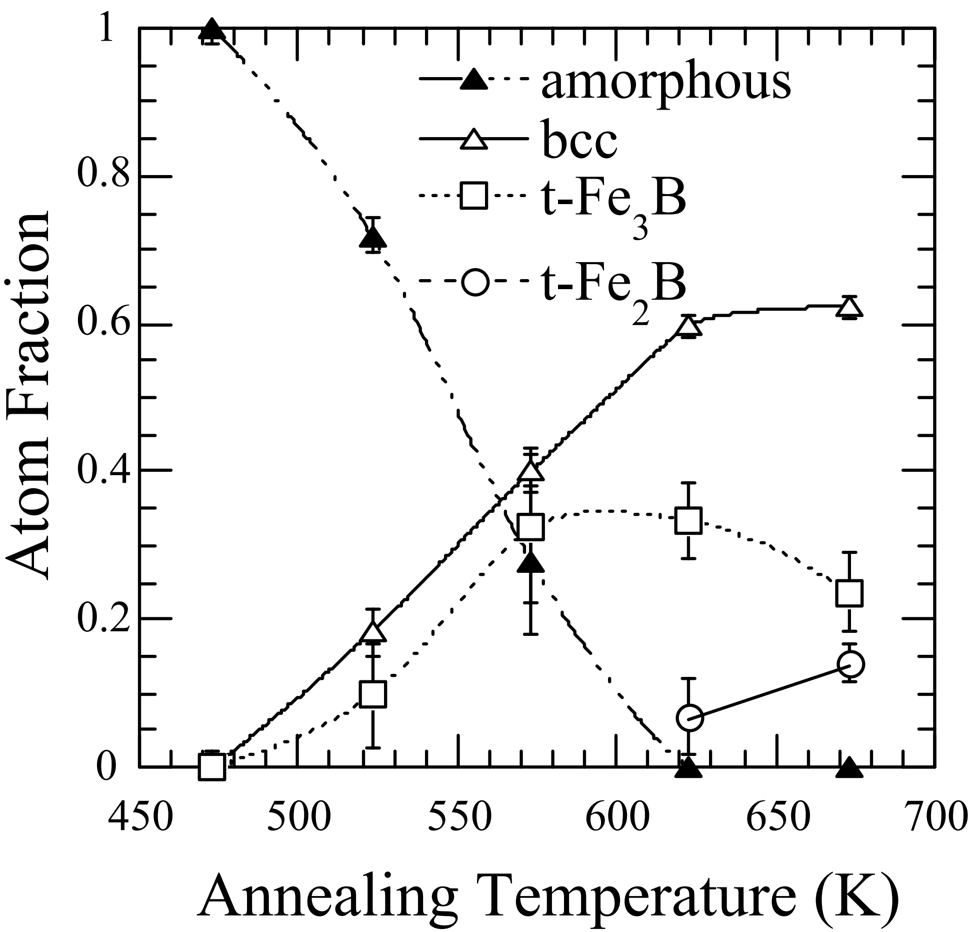
Unlike previous examples of FEFF fitting, here we use a linear combination of standards to fit the unknown data set

The whole spectrum is fit

The quality of fits are excellent

Error bars are deduced from fitting of mean +/- standard deviation

V.G. Harris, et al., Appl. Phys. Lett., ***68****(15), 2073 (1996).*



Crystallization phases are identified and their relative fractions determined

The products and their fractions are in exact agreement with the bulk phase diagram

However, primary crystallization occurs 250 K below bulk

Surface and substrate interface acts as early nucleation centers

*V.G. Harris, et al., Appl. Phys. Lett., **68**(15), 2073 (1996).*

Impact

First demonstration of crystallization studies of amorphous thin films

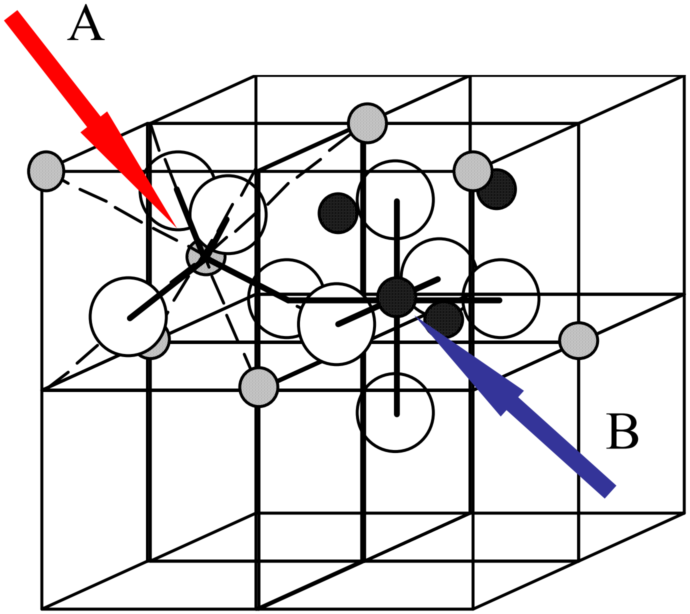
- Phase fractions are measured
- Temperature stability of thin amorphous films

Technological impact –

- Stability and dynamics of phase change media
- Thin film amorphous sensors

Precursor to PCA

Example 3: Cation disorder in spinel ferrites
Motivation: Control magnetic and electronic properties for wireless and radar applications



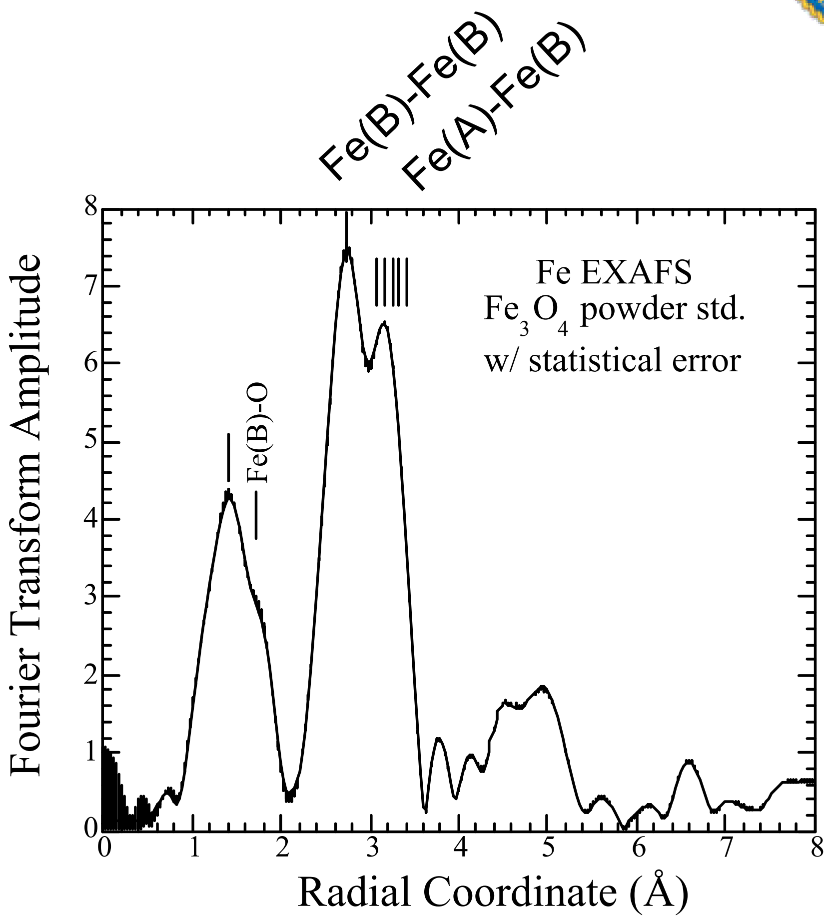
after E.W. Gorter, *Philips Res. Rep.*, **9**, 321 (1954).

Spinel Ferrites:

- 56 atoms/unit cell; AB_2O_4-type structure
- cations incompletely fill octahedral (16 of 32) and tetrahedral sites (8 of 64) in f.c.c. oxygen lattice
- valence and site filling determine ***magnetic*** and ***electronic*** performance

Goals:

- Determine cation distribution
- Determine valence of cations
- Tailor distribution and valence of cations to optimize magnetic & electronic properties.



Fourier transformed Fe EXAFS from Fe_3O_4 standard illustrating pair correlations leading to A- & B-site fingerprinting

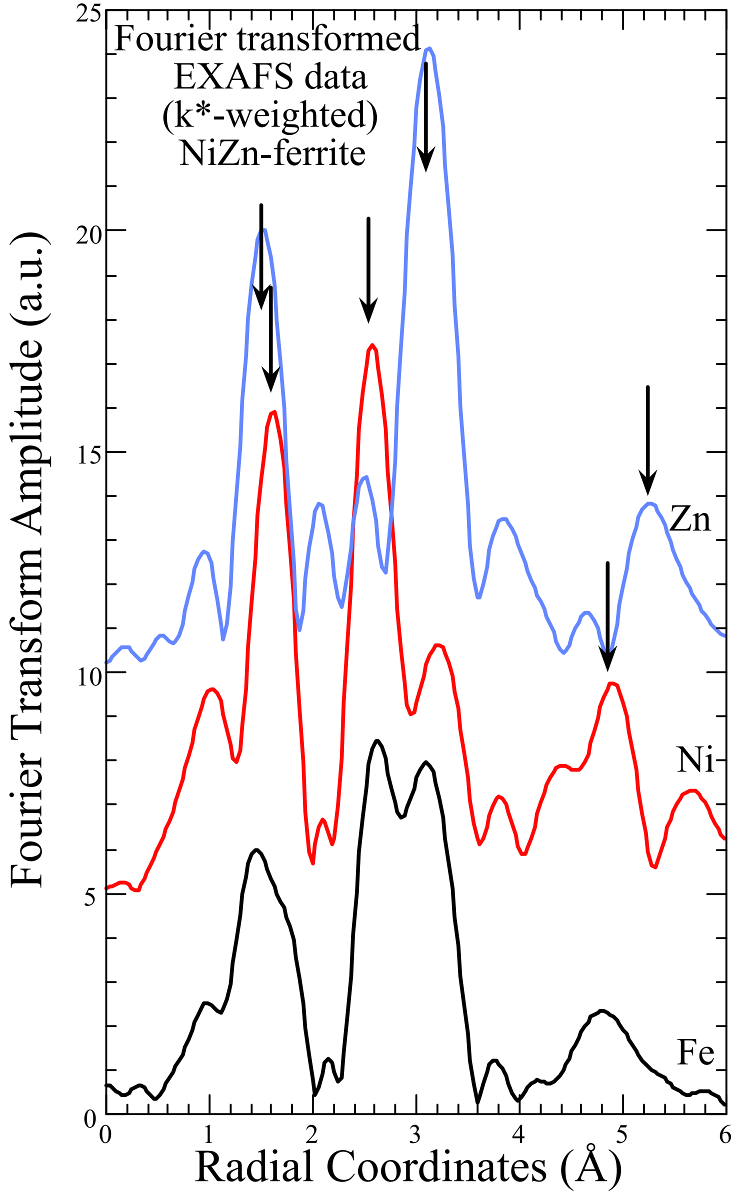
Partial Radial Distribution Function

Correlation		CN	r (Å)	Site of Backscatterers
Tetrahedral Environment:				
A1	A-O	4	1.8746	CPL
A2	A-B	12	3.4783	octahedral
A3	A-O	12	3.4889	CPL
A4	A-A	4	3.6330	tetrahedral
Octahedral Environment:				
B1	B-O	6	2.0645	CPL
B2	B-B	6	2.9663	octahedral
B3	B-A	6	3.4783	tetrahedral
B4	B-O	2	3.5748	CPL
B5	B-O	6	3.6528	CPL

A: metal ion occupying tetrahedral site; B: metal ion occupying octahedral site
CPL: close-packed lattice sites

Zn, Ni, and Fe FT EXAFS from a single NiZn-ferrite film

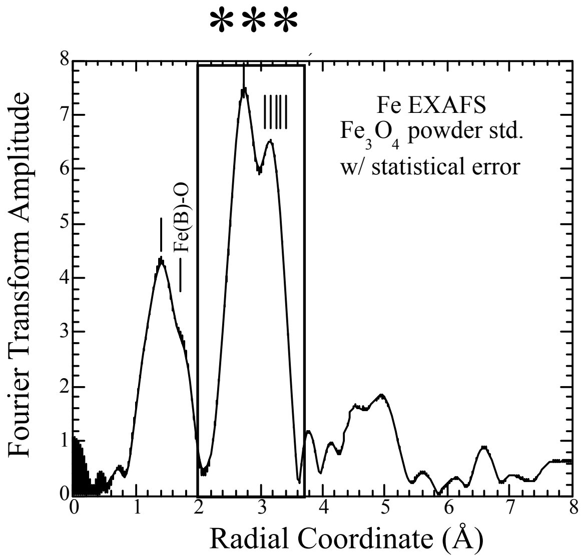
Data collected using TEY

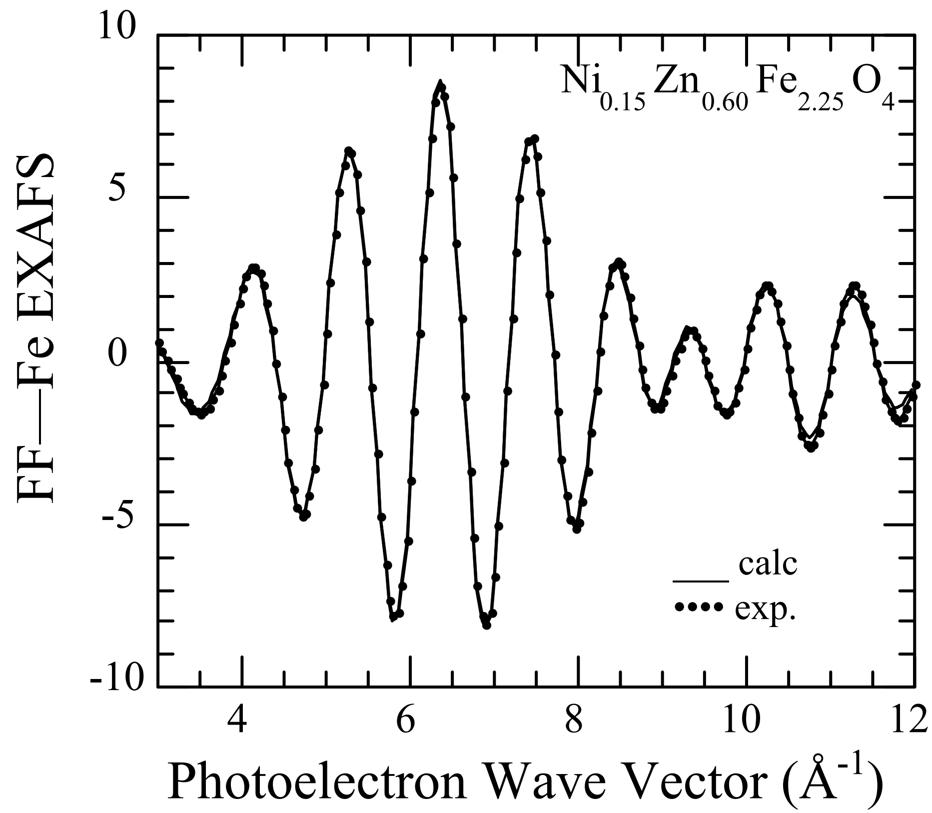


Notice anion and cation fingerprinting in both oxygen bonds and cation-cation bonds

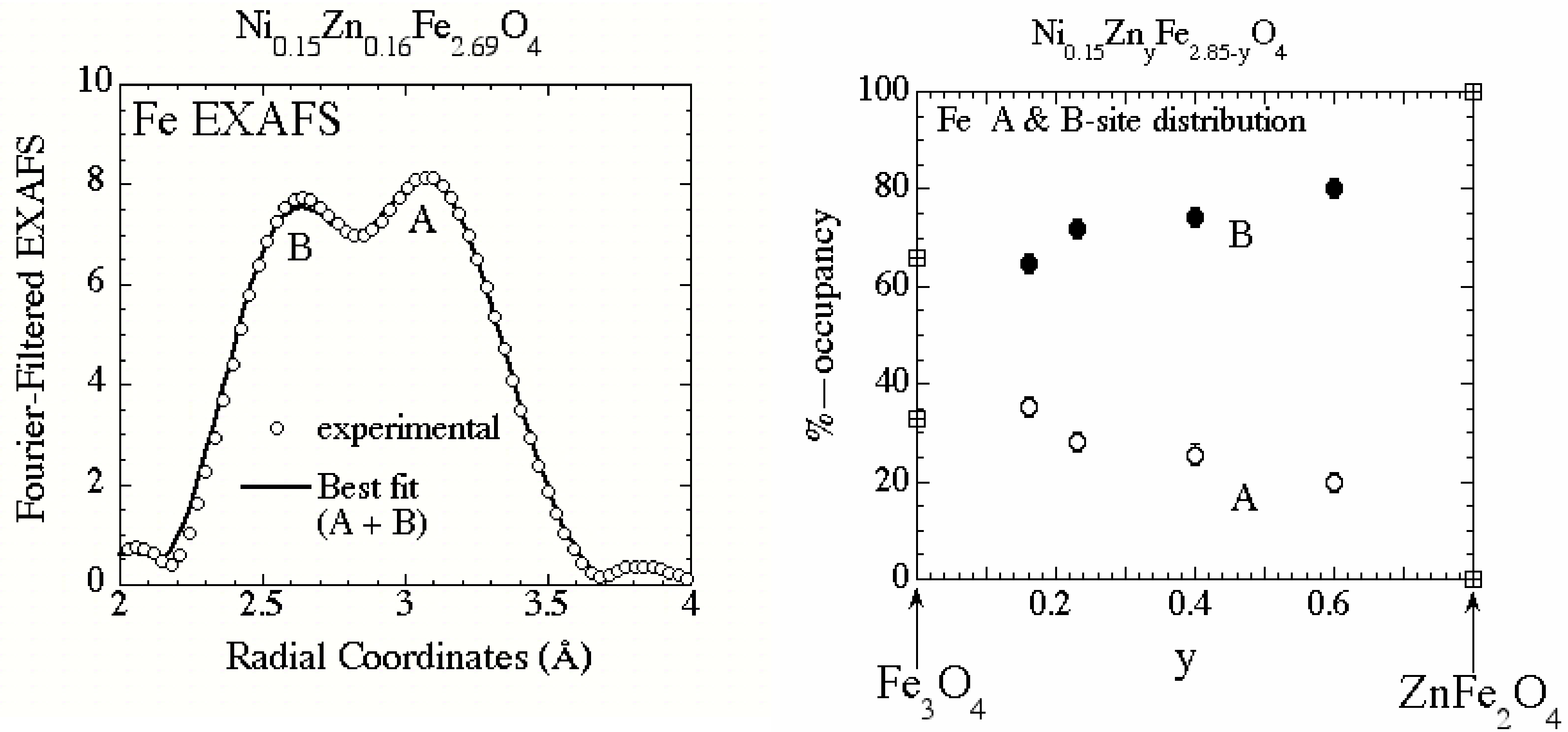
Cation fingerprinting in the 2-4 Ǻ range is particularly striking

May allow determination of cation site occupancy r(Å) → k


***
Fourier Transform Amplitude
Radial Coordinate (Å)
Fe EXAFS
Fe3O4 powder std.
w/ statistical error
Fe(B)-O

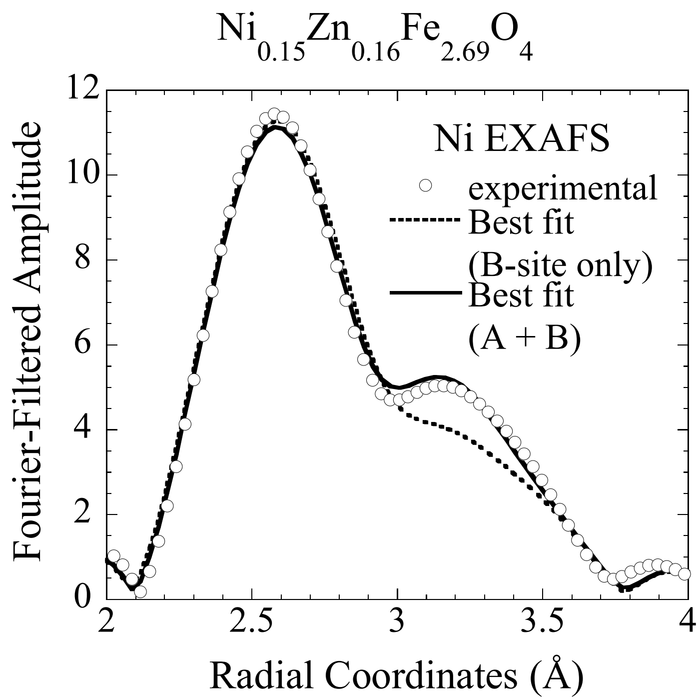

Ni0.15 Zn0.60 Fe2.25 O4
FF—Fe EXAFS
Photoelectron Wave Vector (Å-1)
calc
exp.

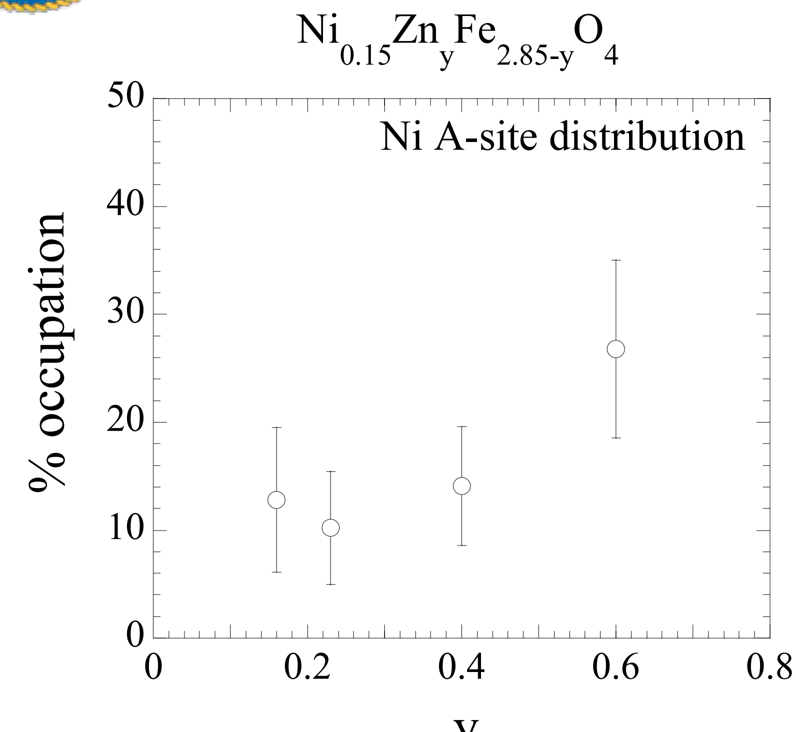
fitting



- Cation data are FF and fit in k-space
- Presented here in r-space
- Quantitative cation distribution is presented as a function of Zn substitution

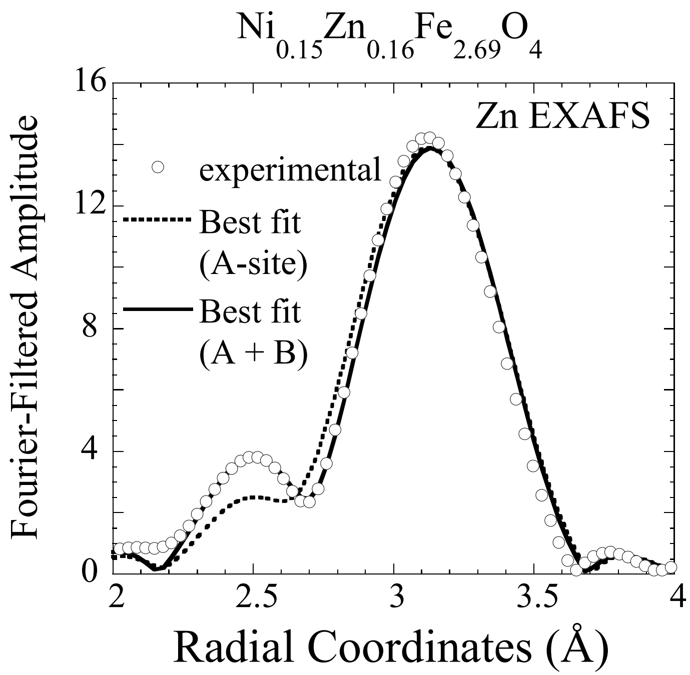
V.G. Harris, et al., "Cation distributions in spinel ferrites via EXAFS ," Appl. Phys. Lett., ***68****(15), 2082 (1996).*

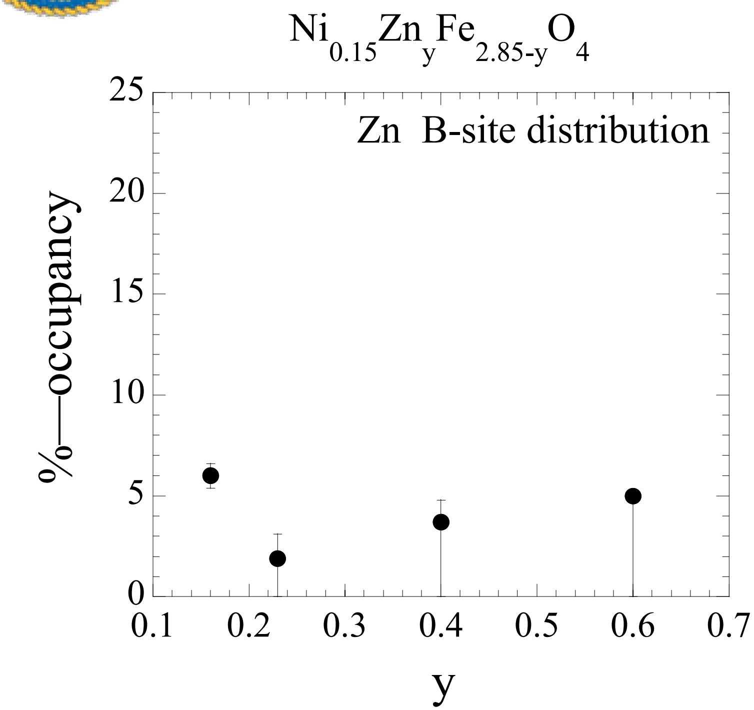




-Ni EXAFS is fit with only B-site FEFF (dashed)
-Compared to best fit with combination of B and A-site FEFF
-% occupation on A-site is shown as a function of Zn
-Error bars are determined by fitting the standard deviation of merged data sets

V.G. Harris, et al., "Cation distributions in spinel ferrites via EXAFS ," Appl. Phys. Lett., ***68****(15), 2082 (1996).*





-Zn EXAFS is fit with only A-site FEFF (dashed)

-Compared to best fit with combination of B and A-site FEFF

-% occupation on B-site is shown as a function of Zn

-Error bars are determined by fitting the standard deviation of merged data sets

V.G. Harris, et al., "Cation distributions in spinel ferrites via EXAFS ," Appl. Phys. Lett., ***68****(15), 2082 (1996).*

Impact

•Allows for characterization of ferrite grown far from equilibrium
•Thin films and nanoparticles
•Design of new ferrites

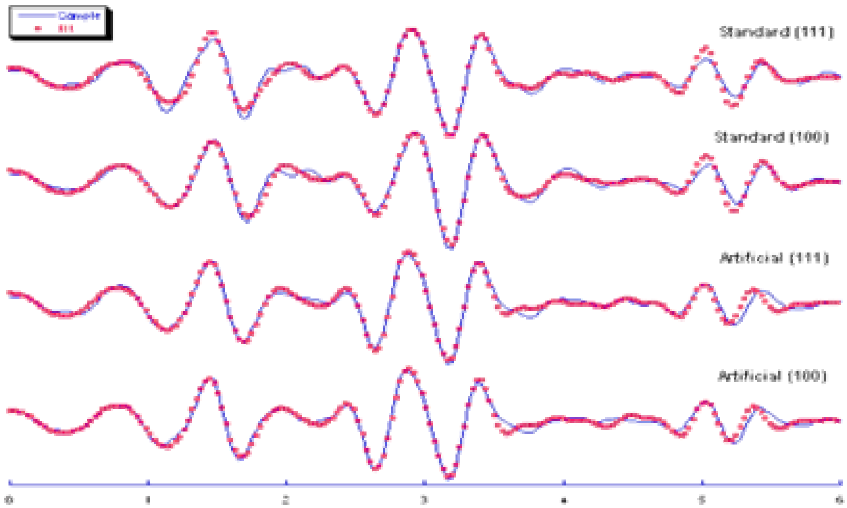
Technological impact-

Device technology basis of radar, microwave networking, wireless communication

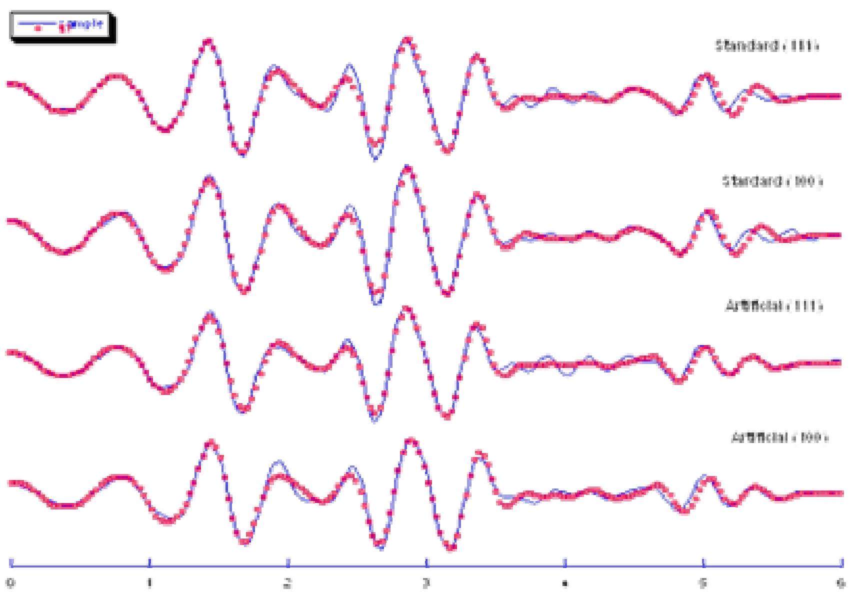
Next ten years

Real part of Fourier transform of EXAFS data and fits

Fe Edge:



Mn Edge:



Latest XAFS of ferrites

Ravel et al./ Calvin et al./ Yang et al.

- Multiedge refinement for improved statistics
- Cation site distribution
- Phase identification
- Particle size
- Lattice parameter and *u* parameter
- Local distortions

S. Calvin , et al., "Use of multiedge refinement of extended x-ray absorption fine structure of manganese zinc ferrite nanoparticles," Appl. Phys. Lett., ***81****(20), 3828 (2002).*

Summary

XAFS and the research team

- Control materials synthesis
- Educate, educate, educate
- Use multiple probes to compliment XAFS and verify model constraints
- Choose XAFS problems based on quality, not because it's a neat XAFS problem
- Funding- propose a solution