STRUCTURE-PROPERTY RELATIONSHIPS OF PHOTOMAGNETIC COORDINATION POLYMER HETEROSTRUCTURES

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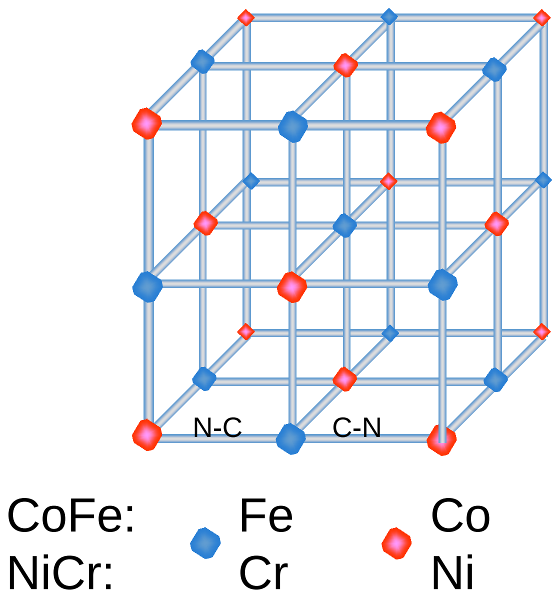
Overview

- Structure-Property Relationships of Photomagnetic Coordination Polymer Heterostructures?
  - Magnetic properties of a combination of molecules can be changed by light.
  - Our experiments aim to characterize the structure and structural changes which occur
- In this talk:
  - Prussian blue analogues – the specific molecules used
  - 3 main experiments performed
    - Infrared spectroscopy
    - X-ray diffraction
    - X-ray absorption spectroscopy

Prussian Blue & Analogues

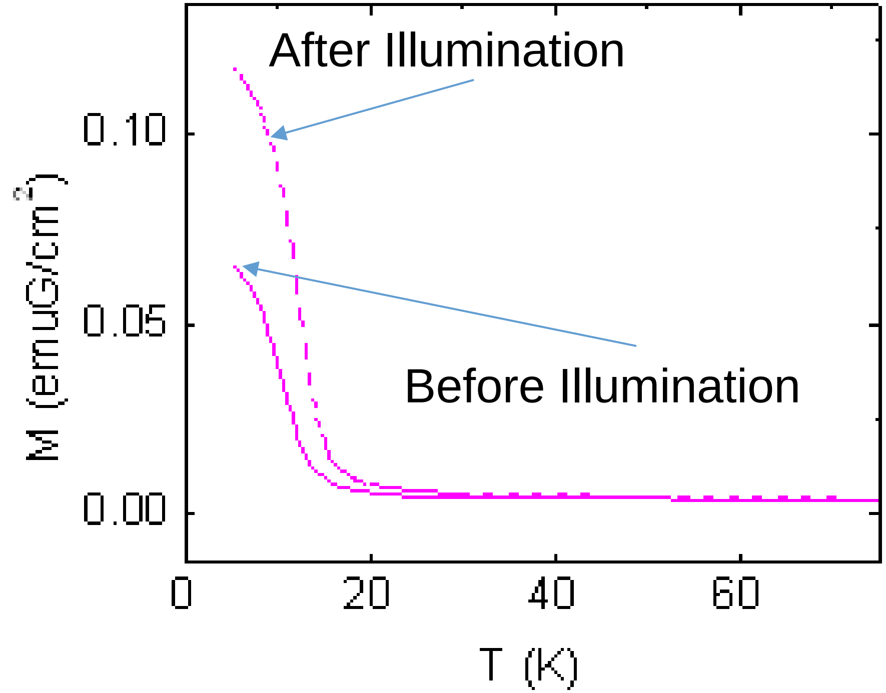
- Face centered cubic structure
  - Repeating pattern:
    Fe – CN – Fe
- Prussian Blue "Analogues" (PBAs)
  - Replace one or both Fe with other metals (M_1 – CN – M_2)
  - Examples:
    - Fe – CN – Co
    - Cr – CN – Ni
  - CoFe and NiCr - discussed in this talk
- Additional details (not shown): H_2O replaces some M-CN, interstitial ions found in crystal

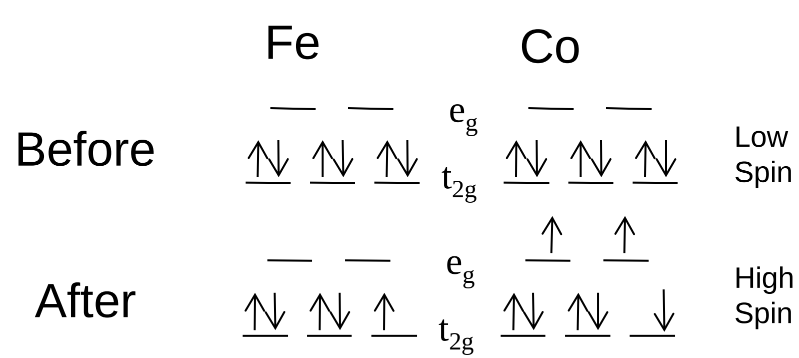


Source: Daniel Pajerowski

Cobalt Iron – Photomagnetic PBA

- CoFe PBA displays photomagnetic properties
- Below T=20K, CoFe ferromagnetic
- Red light illumination changes oxidation state
  - $Co^{III} – Fe^{II}$ to $Co^{II} – Fe^{III}$
  - Unpaired electrons leads to higher magnetization (see graph)[1]
- Above 20K, CoFe paramagnetic
  - Photoinduced transition still occurs, but no long range order
  - This effect persists to ~150K
- Transition causes size change[2]
  - Lattice constant increases by ~ 3 Å (9.97Å to 10.30Å)

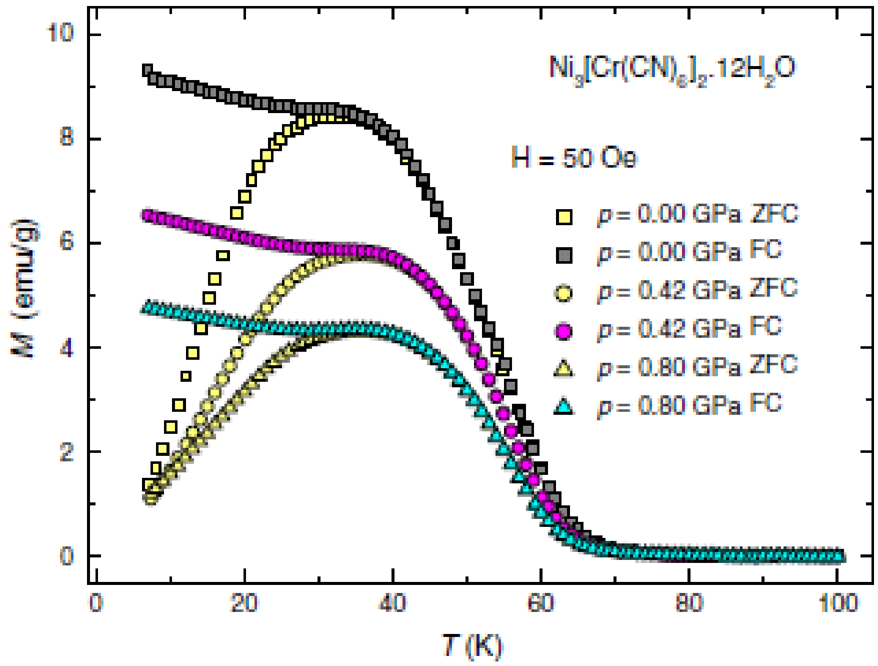




1. Photoinduced Magnetization of a Cobalt-Iron Cyanide: O. Sato et al., *Science Vol. 272*
2. Coherent Domain Growth under Photo-Excitation in a Prussian Blue Analogue: M. Hanawa et al., *J. Phys. Society of Japan Vol. 72*

Nickel Chromium – Different Properties

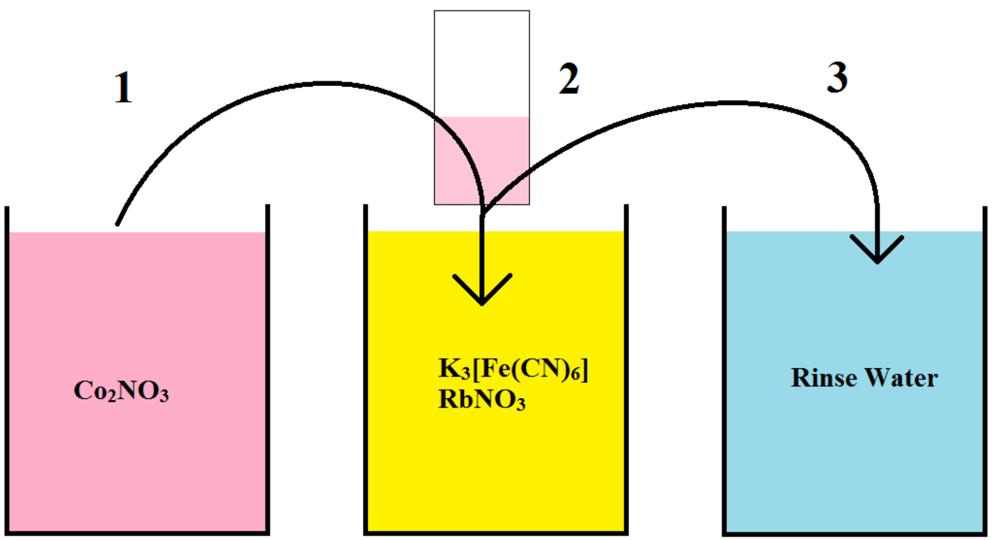
- Also exhibits magnetization changes
- Different stimulus: pressure
- Increased pressure = increased anisotropy = decrease in magnetization
- Effect present up to ~ 65K
- Different lattice constant from CoFe: a=10.43Å

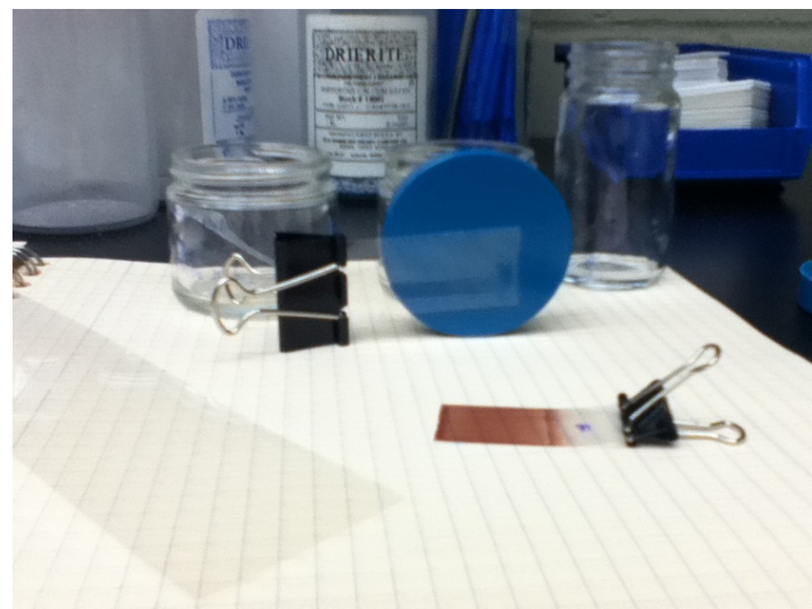


Source: Effect of pressure on the magnetic properties of $TM_3[Cr(CN)_6]_2 \cdot 6H_20$, M Zentková et al., *Phys.: Condens. Matter 2007, 19266217*

Creating PBA Films

- PBA are created as thin films using deposition
- Alternating deposition using metal nitrate and metal hexacyanide
  - Nitrates: Co, Ni; HexaCN: Fe, Cr
- Plastic (Melinex 550) used as solid support
- 40 cycles ~ 250nm thickness



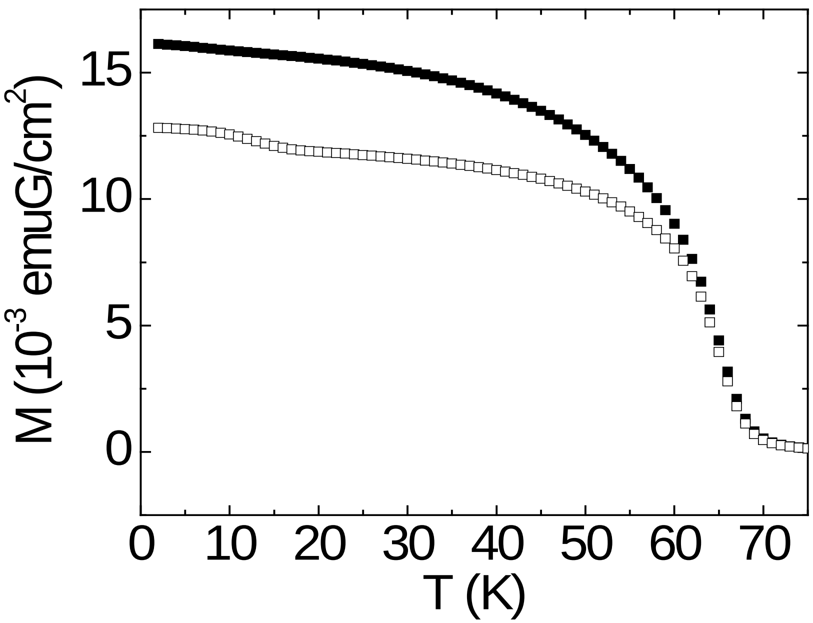


Film Creation Issues

- Dehydration – vacuum pumping of sample may be removing H_2O necessary for structure
- Rb concentration – Interstitial ion amount determines strength of magnetization effect
  - Deposition may also not be working properly
- Plastic substrate does not conduct heat well
  - Can lead to samples not cooling to necessary temperatures

PBA Trilayers and New Magnetic Properties

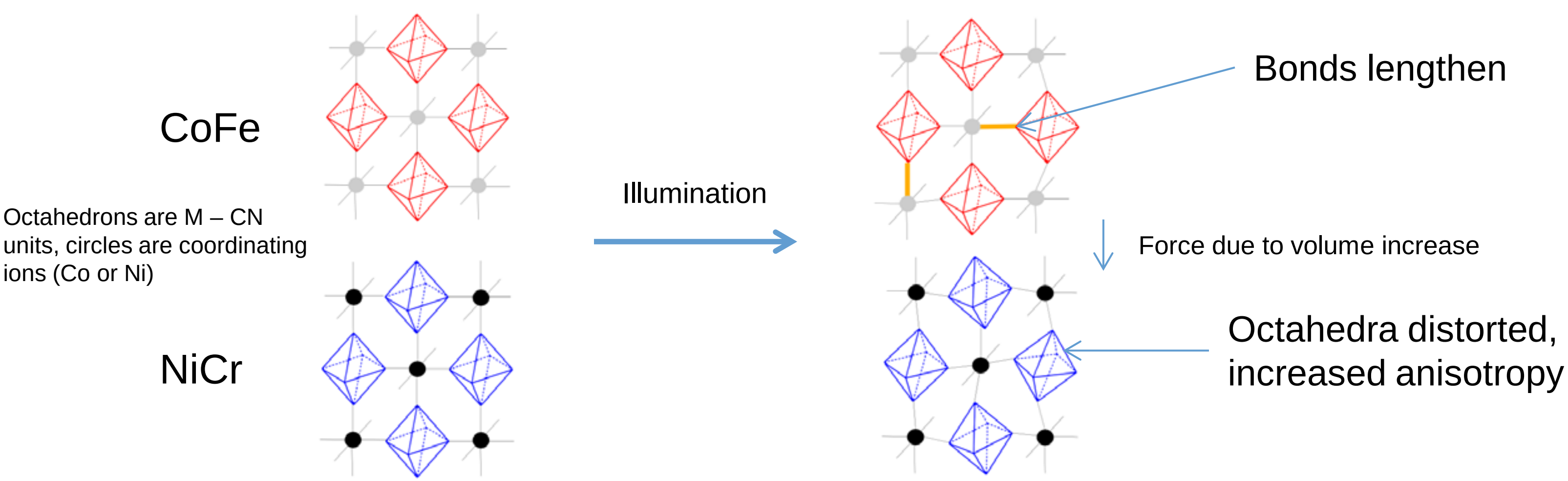
- Create PBA heterostructure: add different PBAs in layers
  - ABA structure: NiCr – CoFe – NiCr
  - Heterostructure displays magnetic properties at higher temperatures than previously possible for individual PBAs



Source: Daniel Pajerowski

Structure Property Hypothesis

- Hypothesis: Photoinduced change in CoFe affects NiCr layers, causing NiCr change
- Several steps:
  1. Illumination -> oxid. state change in CoFe
  2. State change -> bond length increase -> volume increase
  3. Volume incr. -> increased stress on NiCr layers
  4. NiCr decrease magnetization b/c increased pressure

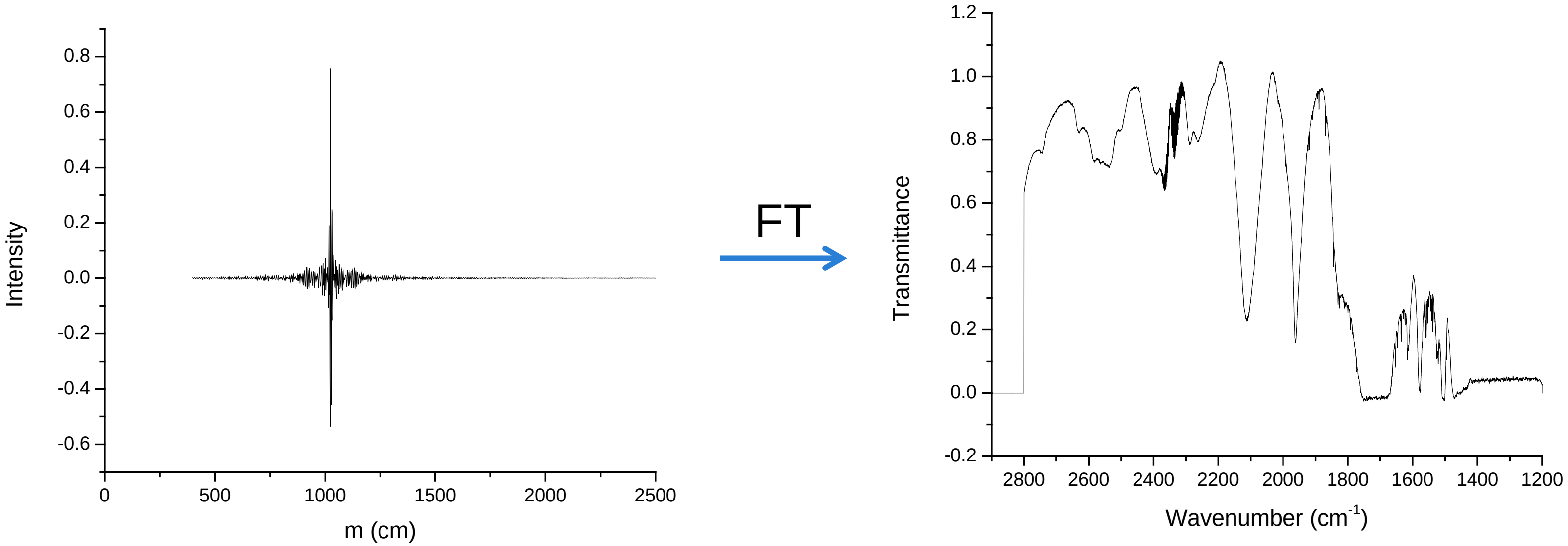


Experiment Plan

- 3 types of measurements employed:
  - Fourier-transform Infrared Spectroscopy (FTIR)
    - Infrared light absorbed by vibrational modes of PBA.
    - Measure vibrational energies, observe oxidation states
  - X-ray Diffraction (XRD)
    - Depends on long-range structure of samples
    - Allows determination of lattice constants for crystal structures
  - Extended X-ray Absorption Fine Structure (EXAFS) Spec.
    - Measures local structure
    - Can fit model of atom to atom distances to measured data

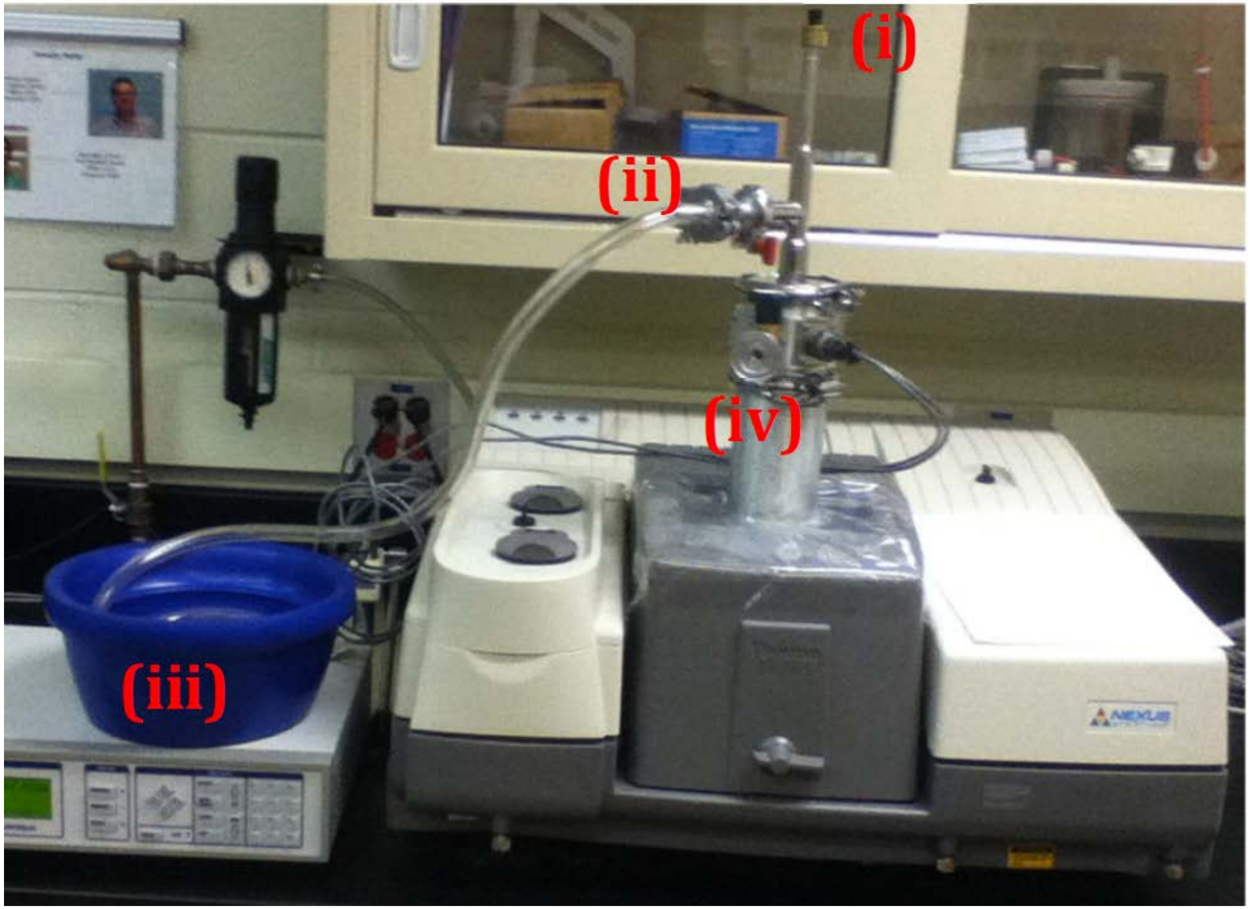
FTIR Spectroscopy: Vibrations

- Vibrations of atoms absorb discrete energies (like a harmonic oscillator) in IR
  - All energies measured simultaneously
  - Result is Fourier-transformed to give a transmission spectrum
  - Peaks are increased absorption



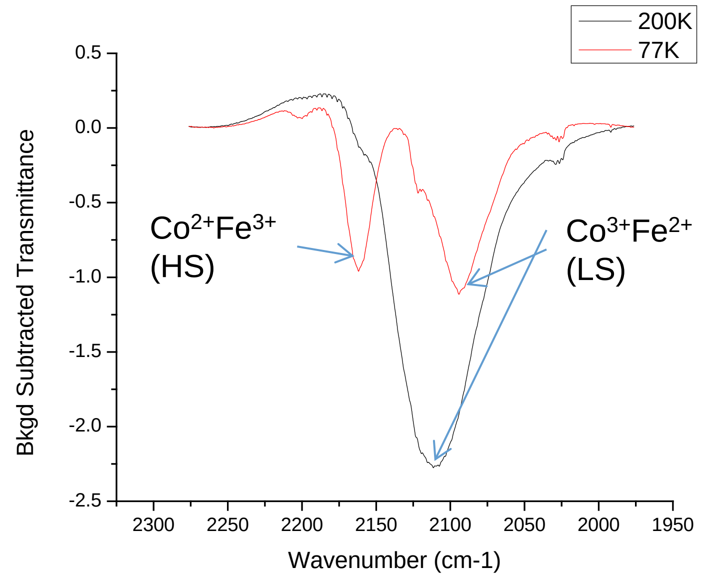
FTIR Setup

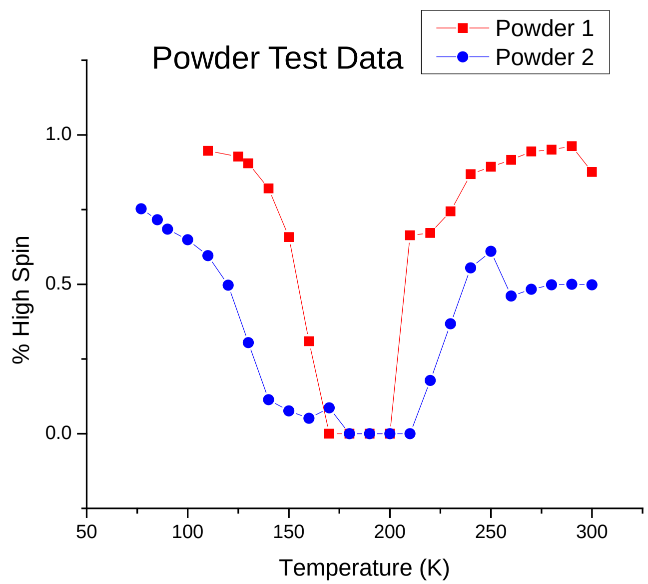
- We modified an existing FTIR setup to include a cryostat.
  - Our experiment requires liquid nitrogen (or lower) temperatures

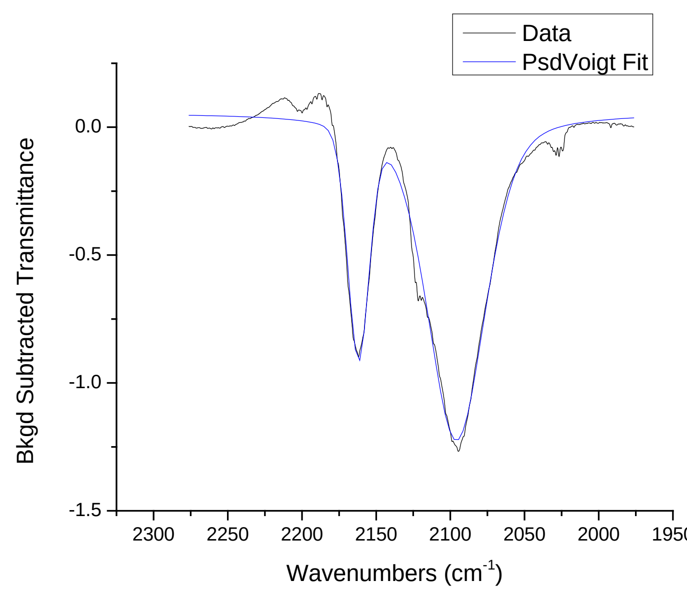


FTIR Data

- Able to replicate CoFe observations with powder
- Data for films is in progress, waiting on results

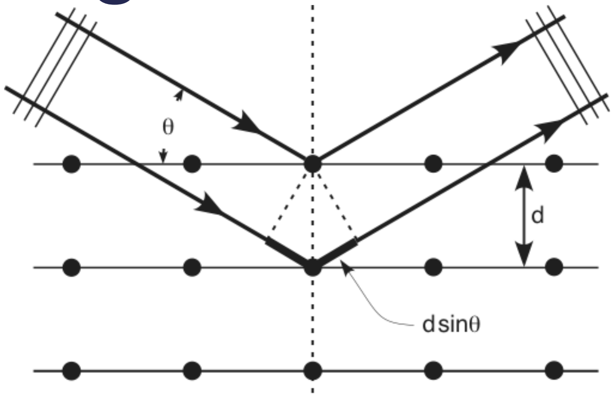




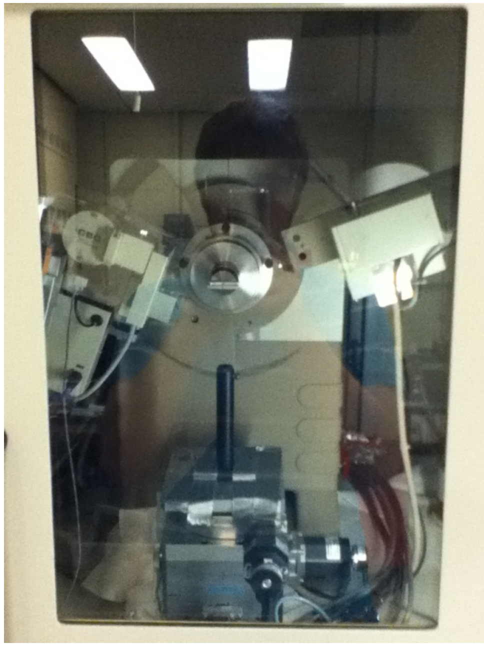


X-Ray Diffraction: Long Range Structure

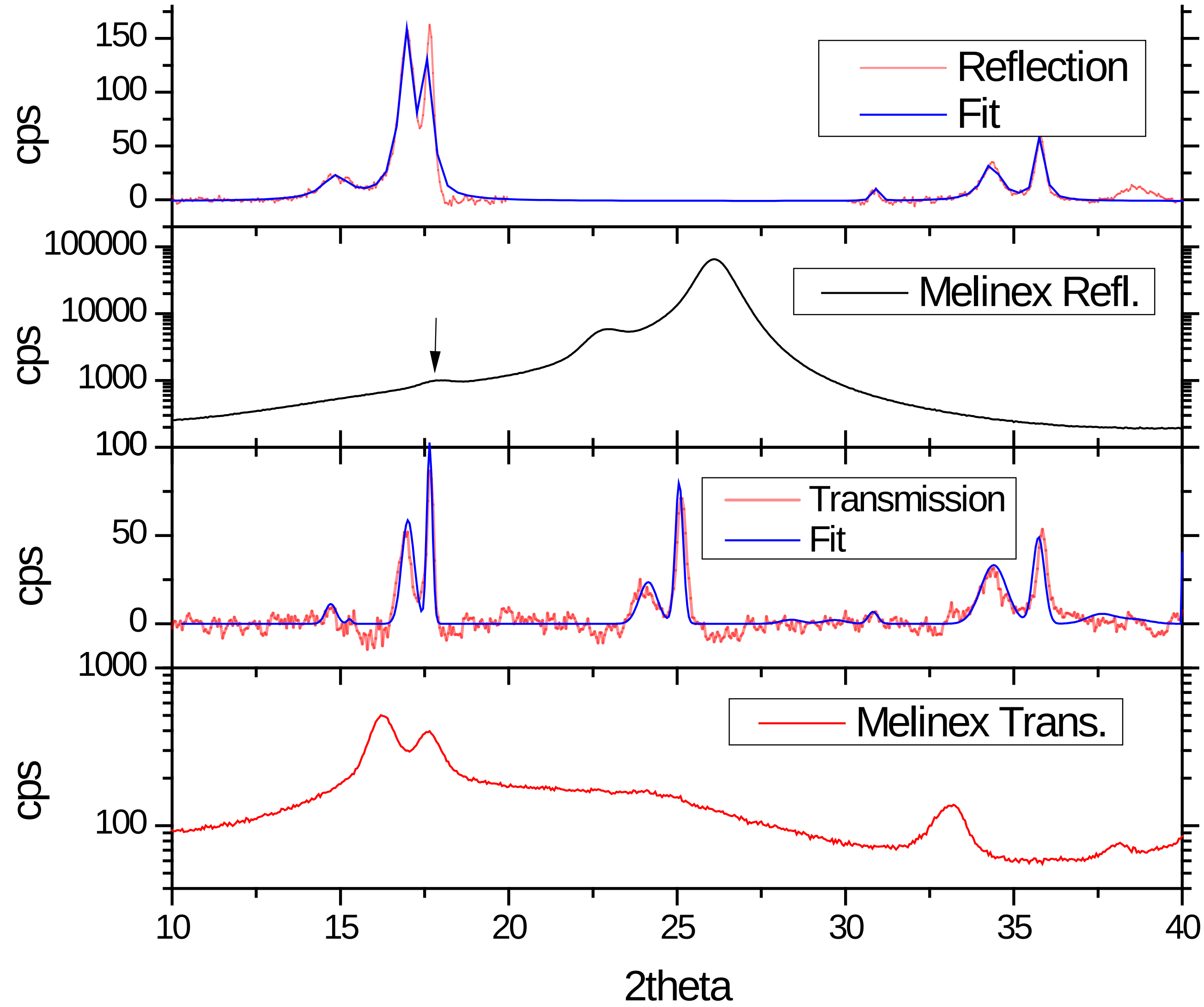
- Regular structure of crystals can be exploited for light scattering
- Depending on angle of scattering, parallel paths may be out of phase
  - Constructive interference when $n\lambda=2d*\sin\theta$
  - Peaks in intensity give values of θ for constructive interference, find d from above equation
  - Lattice constants obtained from d, based on type of reflection plane
- Different crystal planes will have sets of peaks



Source: wikipedia.org/wiki/X-ray_Crystallography



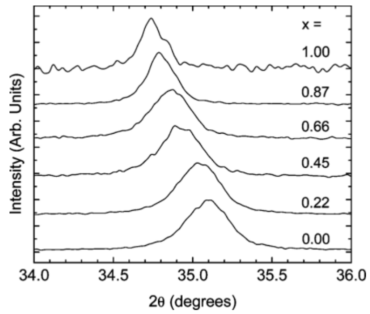
XRD Data



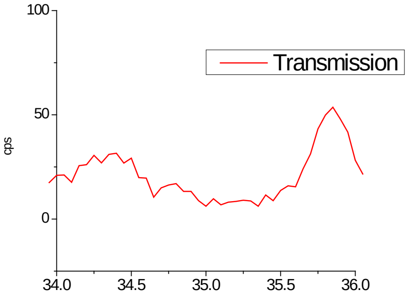
Reflection
Fit
Melinex Refl.
Transmission
Fit
Melinex Trans.
cps
cps
cps
cps
150
100
50
0
100000
10000
1000
100
50
0
1000
100
10
15
20
25
30
35
40
2theta

XRD and Lattice Constants

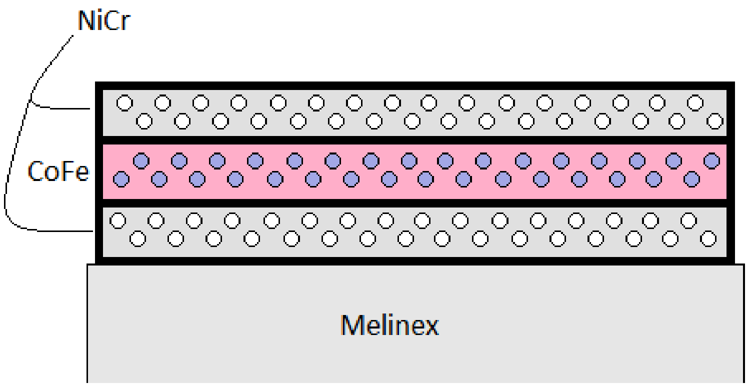
- Lattic constants obtained for both trans. and refl.
  - Two values: a=10.05 Å and a=10.43 Å. Same results regardless of film orientation
- Conclusion: CoFe and NiCr form polycrystalline, but separate, layers
  - Each PBA has different lattice constant
  - Compare with mixed solution, which has single peak



Mixed Sol'n

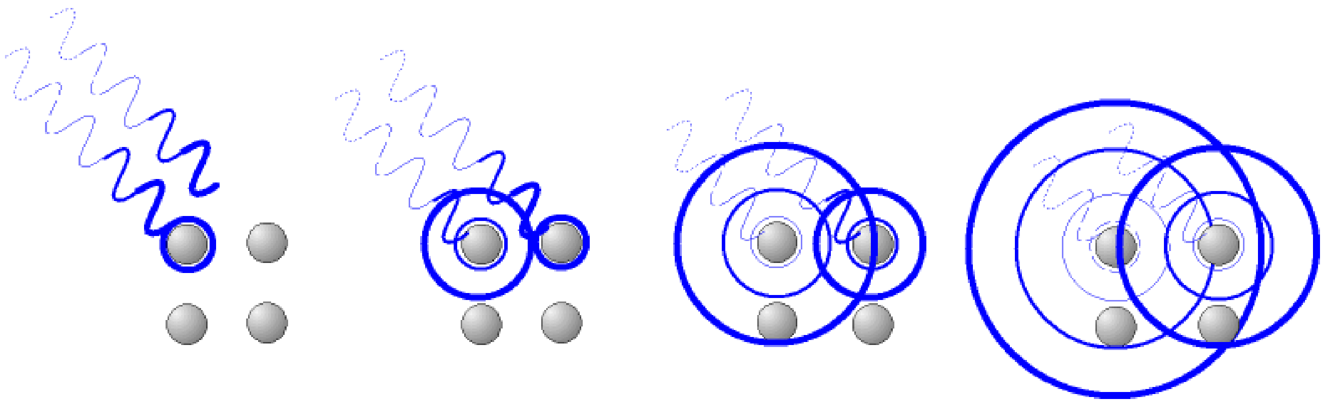


Trilayer Film



XAFS: Local Structure

- XAFS involves scattering x-rays off a central atom
  - Scattered wave can also scatter off neighboring atoms
- Resulting scattered wave composed of multiple waves with varying amplitudes.
  - Amplitudes are determined by path taken. In general, more scatterings = smaller amplitude
- By modeling a system and calculating the path amplitudes, parameters in the model can be fit to XAFS data, yielding local structure information



Source: wikipedia.org/wiki/File:Diffusion_rayleigh_et_diffraction.png

EXAFS at Brookhaven SNLS

- EXAFS requires x-rays from synchrotrons
- Our data was taken at the National Synchrotron Light Source at Brookhaven National Laboratory in New York
- Thanks to Bruce Ravel for taking this data

Brookhaven National Laboratory

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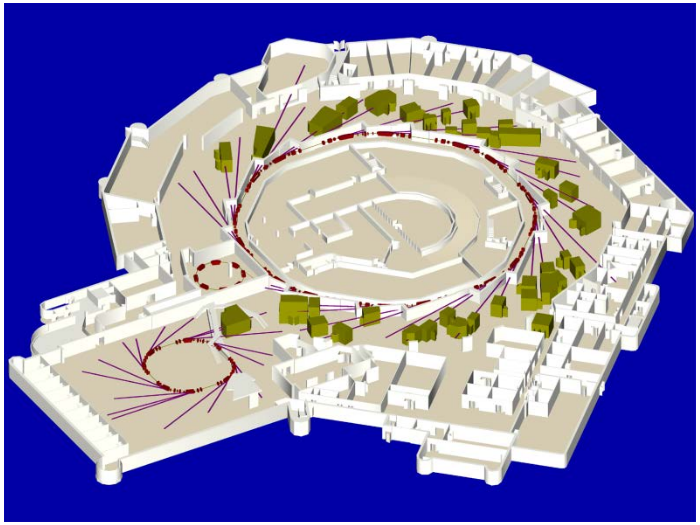
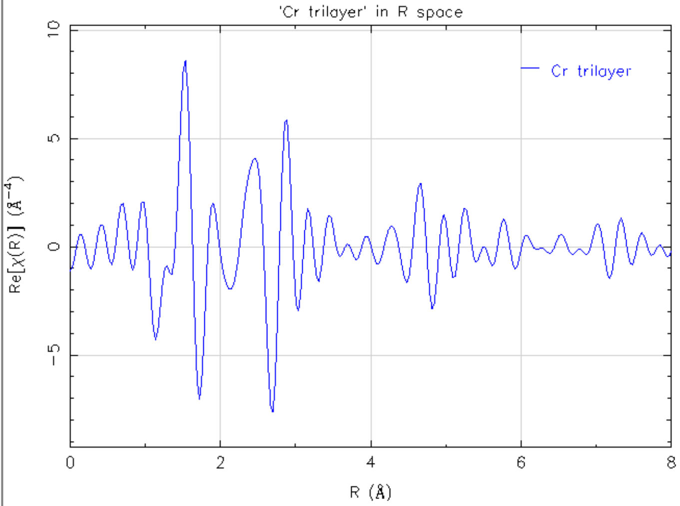
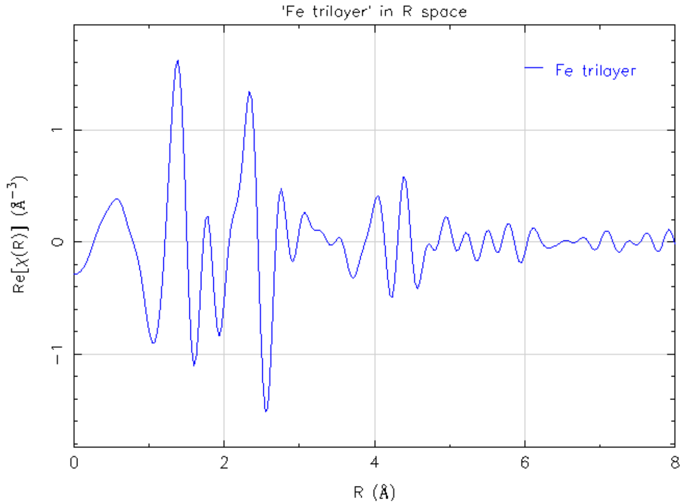
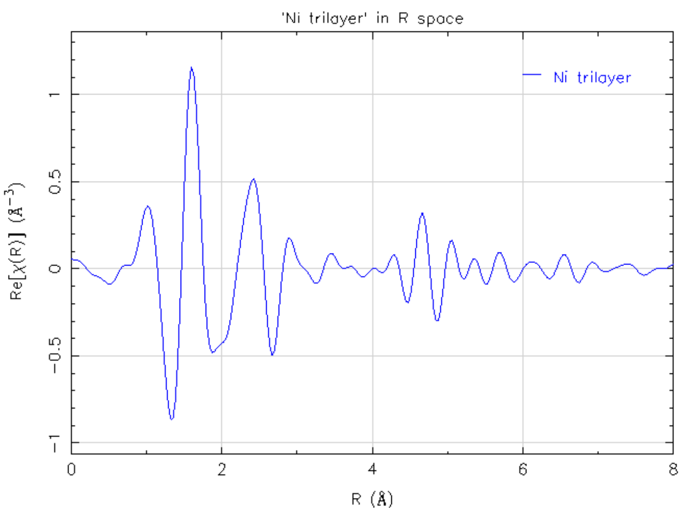
IR UV X

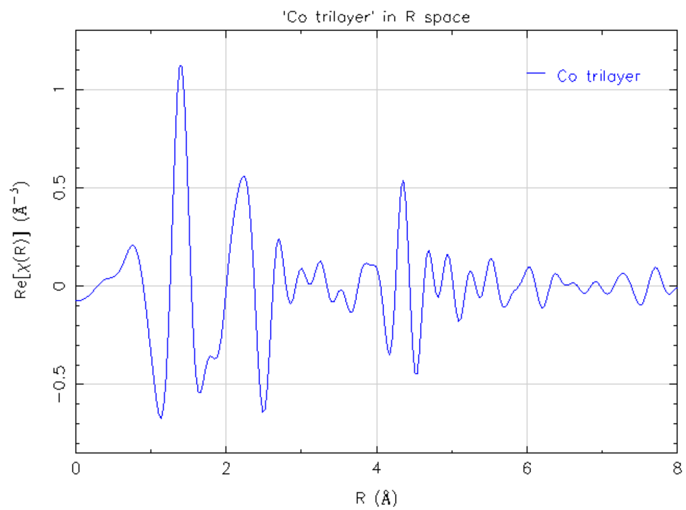


Room Temperature EXAFS Data

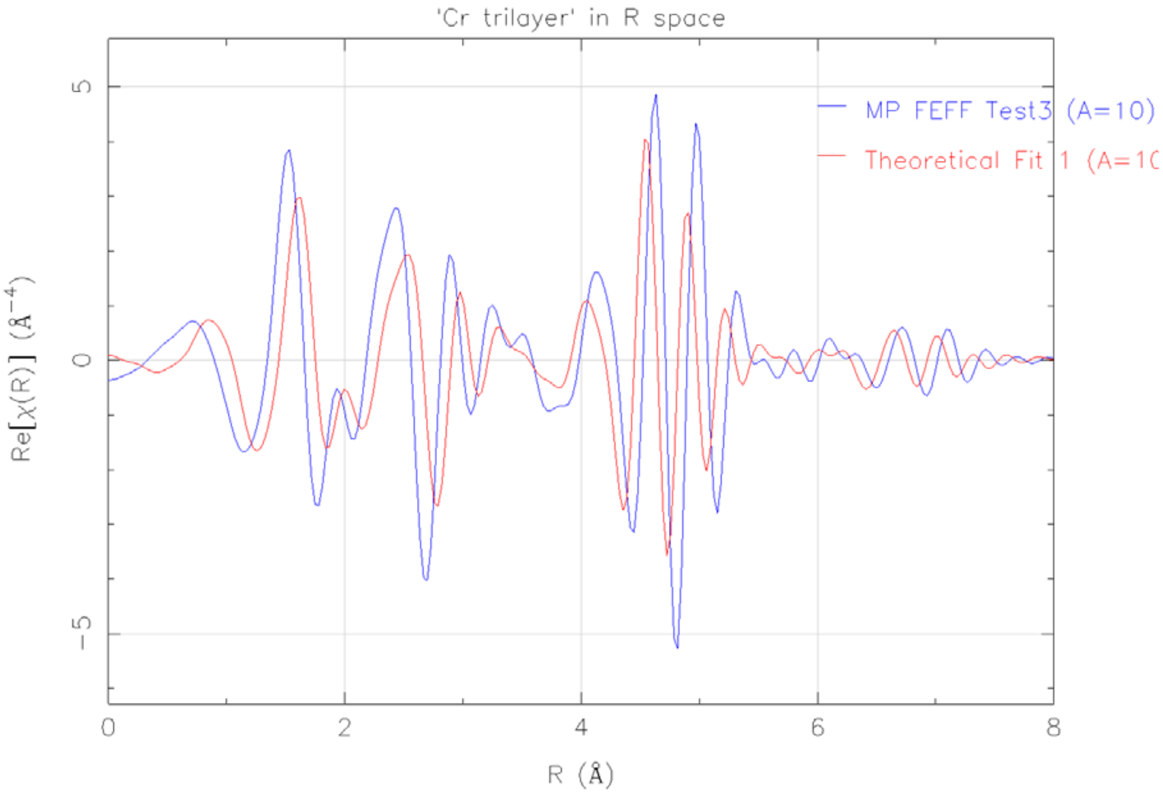


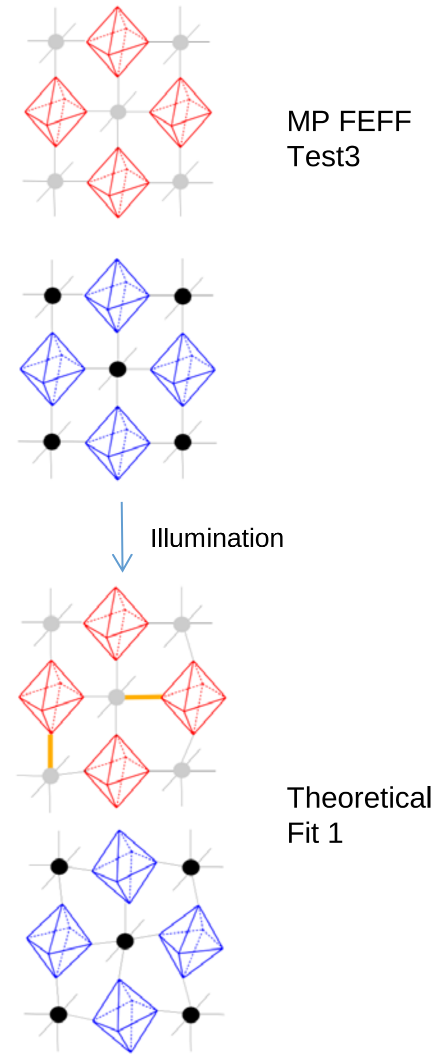






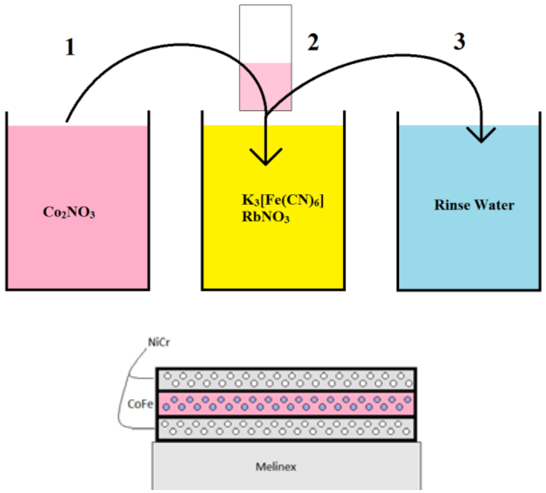
Sample EXAFS Prediction and Model

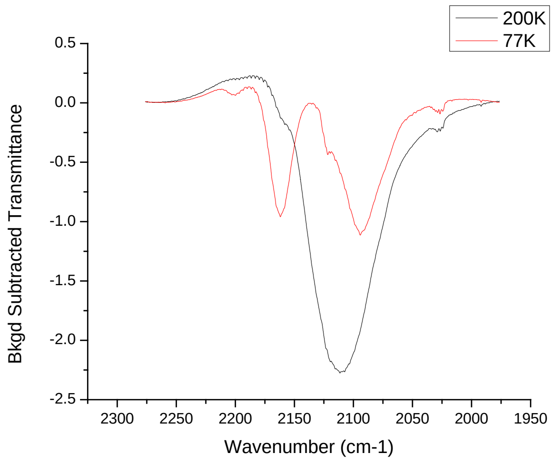




Conclusion

- Our PBA films, created by deposition, exhibit magnetization dependent on external stimuli
- Hypothesis – Light affects CoFe, which alters NiCr layers
- XRD data confirms that CoFe, NiCr layers are separate
- Room temp EXAFS have good signal and are consistent with structural measurements from XRD





Acknowledgements

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Ted Heilweil (for help with FTIR and liquid N/He)

Bruce Ravel (EXAFS Data)

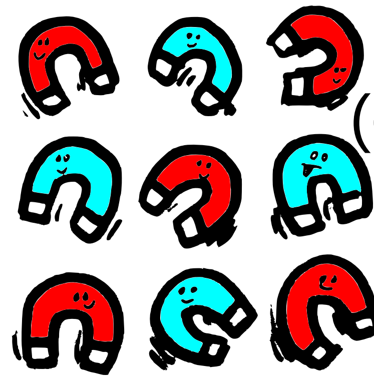
NSLS at Brookhaven

CHRNS

NIST/SURF

(a)

(b)



(c)