STRUCTURE-PROPERTY RELATIONSHIPS OF PHOTOMAGNETIC COORDINATION POLYMER HETEROSTRUCTURES

Brian Zakrzewski
Daniel Pajerowski (NCNR)
Ted Heilweil (Chemistry)
Bruce Ravel (NSLS)
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 (M₁ – CN – M₂)
  - Examples:
    - Fe – CN – Co
    - Cr – CN – Ni
  - CoFe and NiCr - discussed in this talk
- Additional details (not shown): H₂O 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
  - $\text{Co}^{III} – \text{Fe}^{II}$ to $\text{Co}^{II} – \text{Fe}^{III}$
  - 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)

---

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)$_6$]$_2$·6H$_2$O, 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 $\text{H}_2\text{O}$ 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

Octahedrons are M – CN units, circles are coordinating ions (Co or Ni)

Bonds lengthen

Force due to volume increase

Octahedra distorted, increased anisotropy
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 \( \theta \) 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

The diagrams show the XRD data for Reflection, Fit, Melinex Refl., Transmission, Fit, and Melinex Trans. The x-axis represents 2theta, while the y-axis represents cps. The data includes peaks at various 2theta values, indicating the crystalline structure of the samples.
XRD and Lattice Constants

- Lattic constants obtained for both trans. and refl.
  - Two values: $a=10.05\ \text{Å}$ and $a=10.43\ \text{Å}$. 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
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
Room Temperature EXAFS Data

- Cr trilayer in R space
- Fe trilayer in R space
- Ni trilayer in R space
- Co trilayer in R space
Sample EXAFS Prediction and Model

Re[X(R)] (Å^-1)

R (Å)

'Cr trilayer' in R space

- MP FEFF Test3 (A=10)
- Theoretical Fit 1 (A=10)

Illumination

Theoretical Fit 1

MP FEFF Test3
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

Daniel Pajerowski
Ted Heilweil (for help with FTIR and liquid N/He)
Bruce Ravel (EXAFS Data)
NSLS at Brookhaven
CHRNS
NIST/SURF