Materials for Magnetic Refrigeration

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What is magnetic refrigeration?

A Swiss research institute has developed an original patent-protected magnetic refrigeration system and is looking for a high-performance room temperature magnetocaloric material. Magnetic refrigeration is based on the magneto-caloric effect (MCE) of magnetic materials. The effectiveness of MCE depends mainly on the applied magnetic field. Gadolinium is used in low magnetic field (1 to 2 Tesla), but its MCE effect is small at room temperature. In order to develop a domestic refrigeration system, for room temperature application, a new magnetic material with large MCE is sought, which should be operated in a magnetic field of about 2 Tesla or less. Ideally the magneto-caloric material should present a large MCE: 10 to 15 Kelvin in 1- to 2-Tesla magnetic field.

The requested material can either be at the laboratory stage or fully developed. Technical Specifications / Specific technical requirements:

- Magnetic material other than Gadolinium
- Large MCE at room temperature: 10-15 Kelvin at 1 to 2 Tesla
- Less expensive than Gadolinium

Source: http://www.invenia.es/

NASA AMES Group: (left to right) Vitalij Pecharsky, David Jiles, and Karl Gschneidner are helping push the advancement of magnetic refrigeration. In 2001, the first room-temperature, permanent-magnet magnetic refrigerator was successfully tested by Astronautics Corporation of America, a research partner in the project with Ames Laboratory.

Order of magnitude estimate

$$Q = \Delta MH = (2\times10^{6} A\cdot m^{-1})(5J \times A^{-1}m^{-2}) = 10^{7} J/m^{3}$$

$$\rho = 8000 kg/m^{3}$$

$$Q = 1200 J/kg$$

$$\Delta S = Q/T = \frac{1200 J/kg}{300K} = 4 J/kg\cdot K$$

$$Q = 10 J/cm^{3}$$

$$\Delta S = Q/T = \frac{10 J/cm^{3}}{300K} = 33 mJ/cm^{3}\cdot K$$

- Magnetization of about the same as pure Fe or Gd is used.
- Field of 5 T (not realistic).
- This is an oversimplification and the actual values obtained are much higher (i.e. for Gd at ~300K the value is 110 $mJ/cm^{2}K$).
- Materials must have high-magnetization and the field change must also be large.
- Most studies use 5 T fields, this is not reasonable for energy applications.
- Compare to Freon:

$$L_v = 165 \text{ kJ/kg}$$

Maxwell Relation

$$\Delta S_M = \int_0^H \left[\frac{\partial M}{\partial T} \right]_H dH$$

$$approximate:$$

$$\Delta S_M(T,B) = -\Delta M \frac{dH_c}{dT}$$

- The entropy change can be 1-2 orders of magnitude higher if the critical field changes rapidly with temperature.
- Careful considerations must be made in order to properly evaluate the magnitude of the entropy change.
- Materials with first order magnetic transitions (FOMT) with associated structural transformations seem to have the largest magnetocaloric effects (MCE).

Read these first: W. Cui, et al., J. Appl. Phys. **96**,222509 (2010)
A. Giguère, et al., Phys. Rev. Lett. **83**, 2262 (1999).

Magnetocaloric Materials

- Most contain Rare Earths with the exception of MnAs-based materials.
- The alloy composition is chosen mainly to tune the bulk Curie temperature to the desired range around room temperature.
- High values of magnetic anisotropy are also necessary to have significant entropy changes.

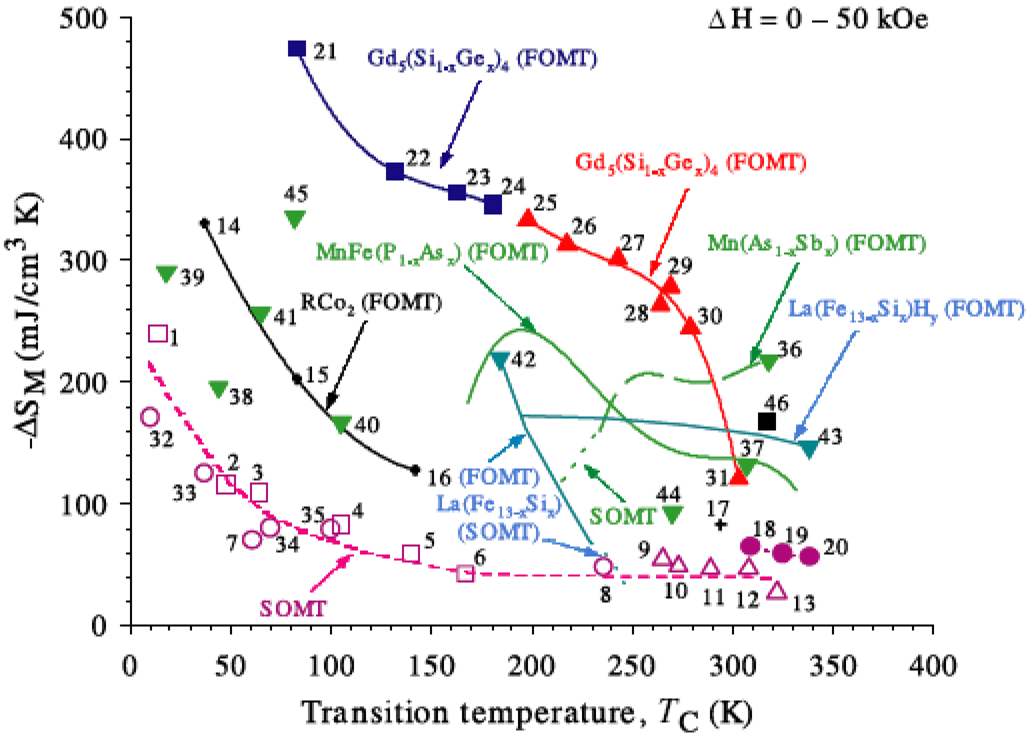


Figure from:
K .A. Gschneidner Jr., et al., Rep. Prog. Phys. **68** , 1479 (2005)

Summary of Basic Requirements (applications driven)

MCE Materials

- High magnetization.
- High anisotropy.
- Transition temperature near 300K.
- Broad phase transition to define the temperature difference of hot and cold reservoirs.
- The most studied materials for these applications normally have unusual phase transition behaviors.
- Non Toxic.
- Cheap.
- Bulk processing.

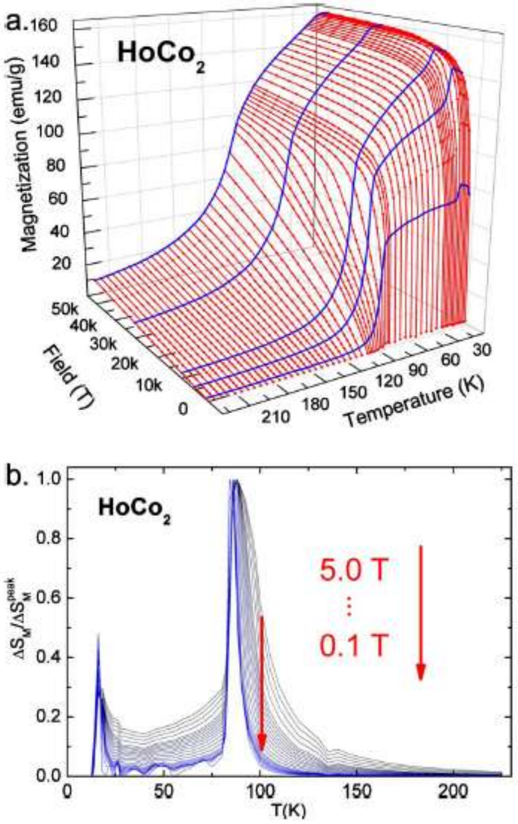
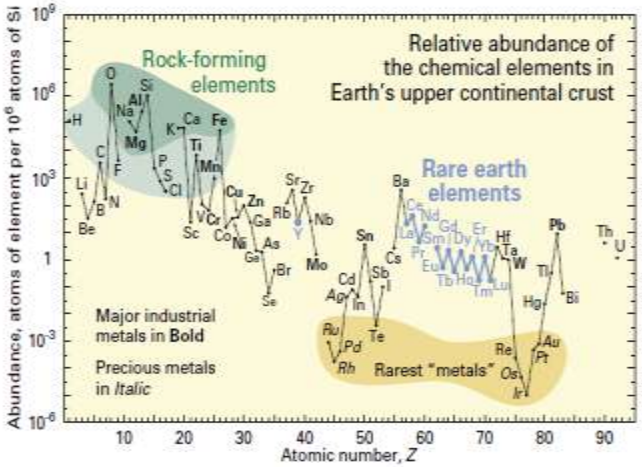
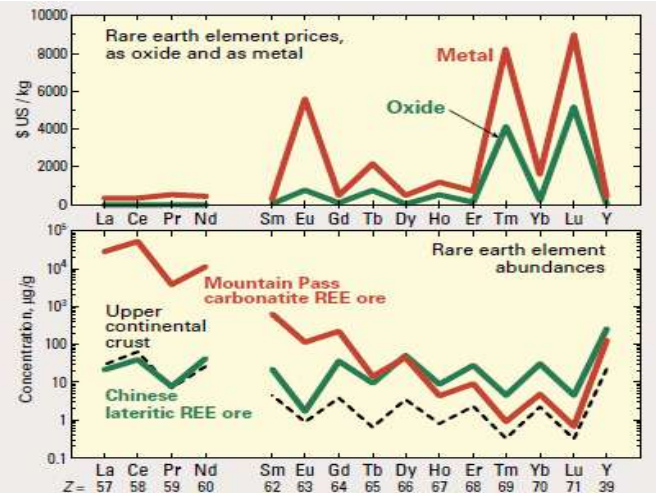


Figure from:
C.M. Bonilla et al., Phys. Rev. B 81, 224424 (2010)

How much does it cost?

- Green technology must be cost efficient.
- Use of Rare Earths or Platinum Group metals is prohibited.
- Also—Green implies non-toxic!
- Can Rock-forming elements to achieve the desired properties?
- The phase transition and magnetic anisotropy can be tuned by nanostructuring the materials.
- Our prior work has given us the experience and knowledge to tackle this task.
- Tools such as SNS and HFIR are necessary for smart materials design.





Idea #1

- Use nanostructuring to tune the transition temperature.
- Materials like Fe, Co and Ni can be used.
- Nanostructuring does dilute the magnetization, so careful design is necessary.
- GE is funded by DOE to use this approach in making Rare-Earth-free hard magnets.
- Design process is similar to hard disk drive media design where anisotropy, magnetization, thermal stability and grain size are controlled.

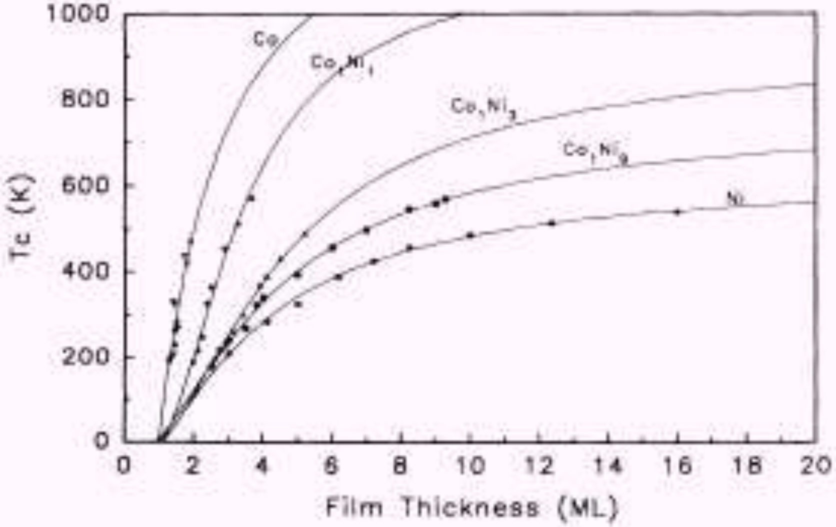
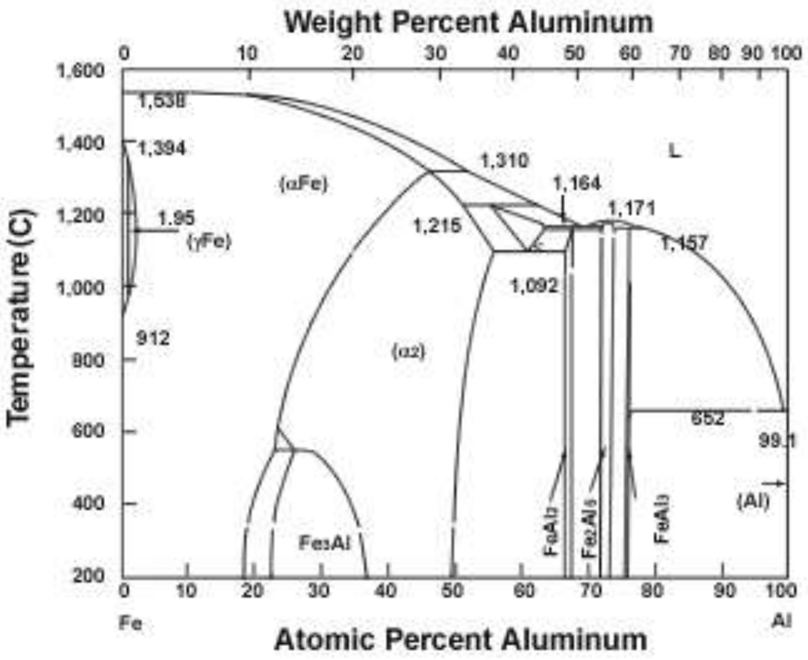


FIG. 5. Thickness dependence of T_C for Co-Ni alloy films with different compositions on Cu(100). The solid lines are finite-size scaling fits to Eq. (2) in text.

Figure from:
F. Huang, et al., Phys. Rev. B 49, 3962 (1994).

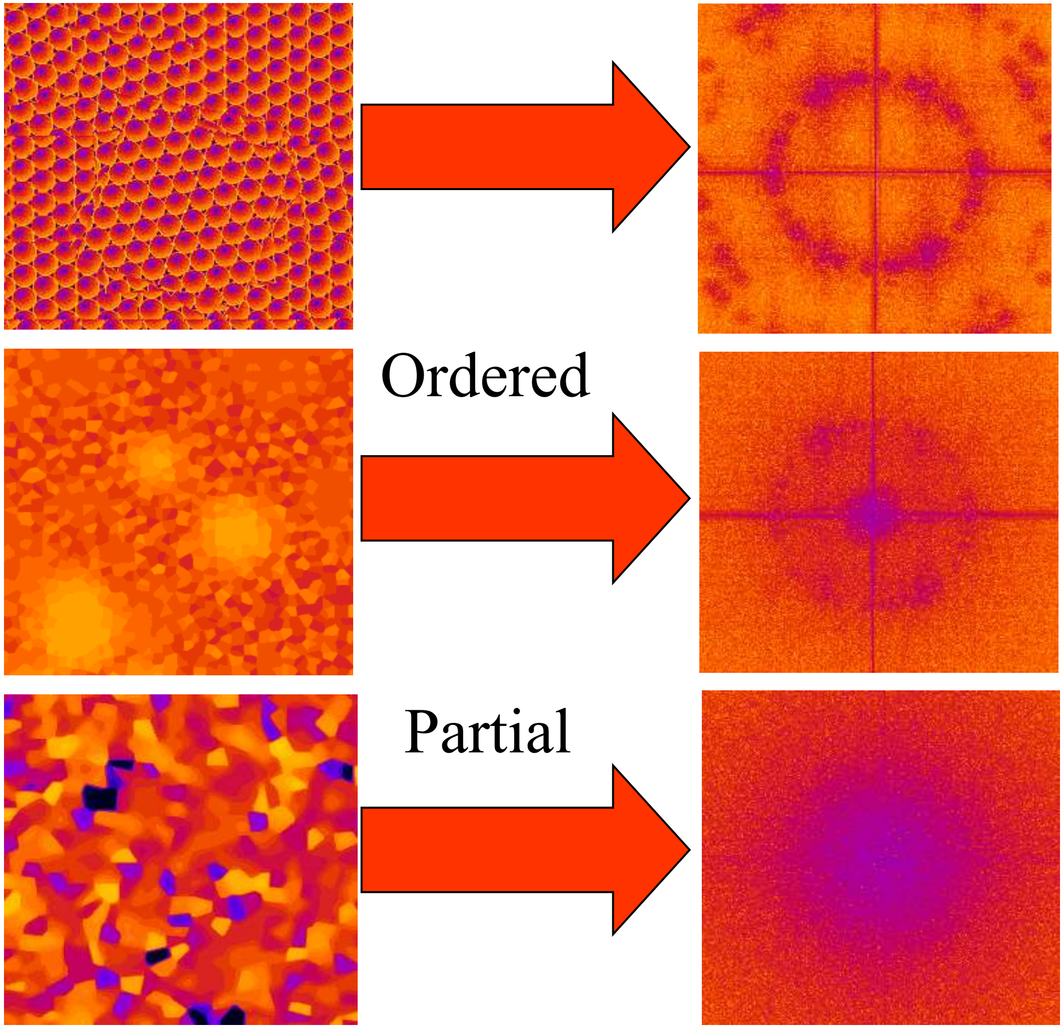
Idea #2

- Form alloys with 3d elements, aluminum and silicon that have desired properties.
- For example, Heusler alloys of these elements have antiferro, ferri ferro, helical and paramagnetic phases.
- The competition between different magnetic orderings may yield desired effects.
- Problems with cost and toxicity are solved--now focus on processing and characterization.



How can neutrons help?

Small Angle Neutron Scattering of FePtAu Nanoparticles

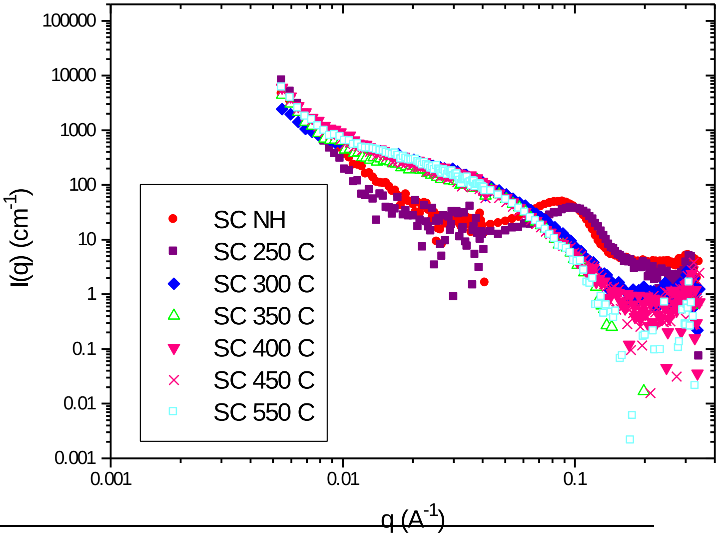


Ordered

Partial

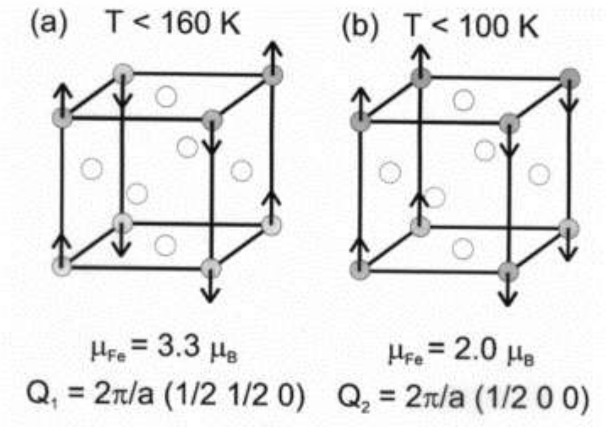
Sintered

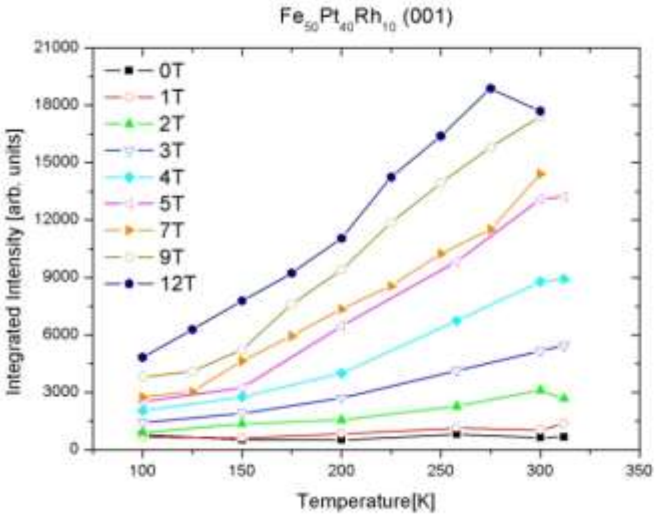
- A 500 ºC anneal is required to transform the nanoparticles into the desired metallurgical phase.
- The ring characteristic of long range order loses intensity in the partially sintered system.
- The sintered system has a single circular blob of intensity at low q and no ring.
- Salt-matrix annealing solved the problem.

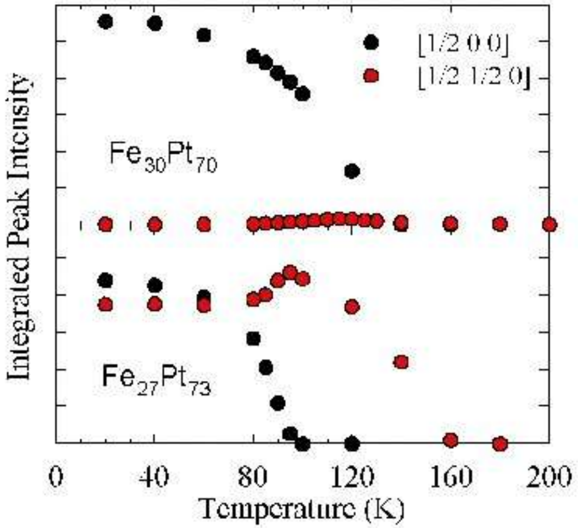


Neutron Diffraction: Spin Ordering Transitions in Films

- Neutrons measure the antiferromagnetic ordering and phase transition behavior.
- The origin of the magnetic behavior is probed with direct measurements of the magnetic ordering of the spins.
- Both ferromagnetic and antiferromagnetic arrangements of spins can be determined.







Inelastic Scattering: Spin Waves in Novel Superlattices

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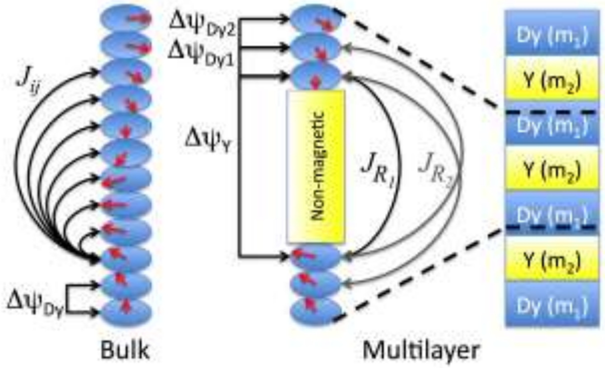
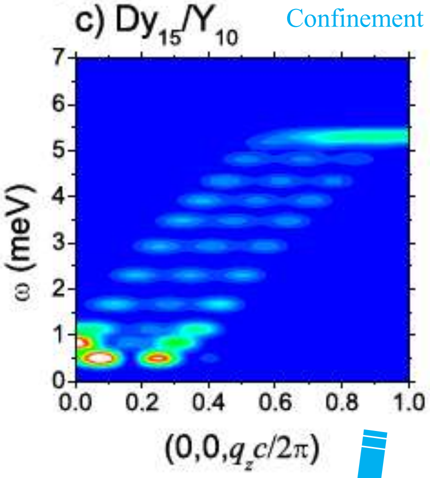
- We are studying the fundamental properties of spin waves in novel superlattices using neutron scattering.
- These studies require reproducible high quality crystalline samples with precise control of the nanoscale layer structure.
- Comparison of theory with experiment will quantify key materials parameters and enable further development of magnetic materials by design principles.

Theory

Atomic Spin Structure



Nanoscale Quantum Confinement

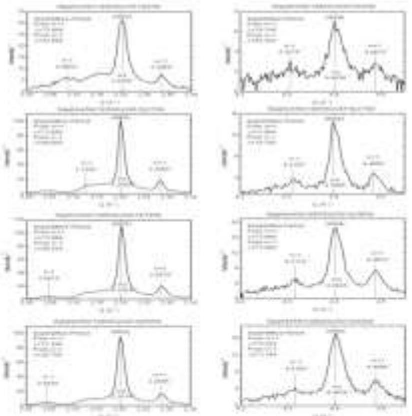


Elastic

Inelastic

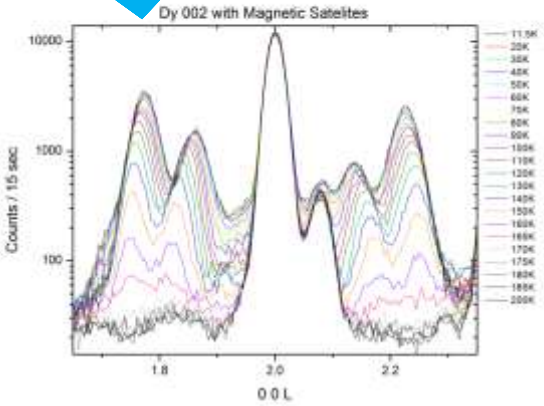
High-quality samples

Sub-angstrom control of Precise layer thickness

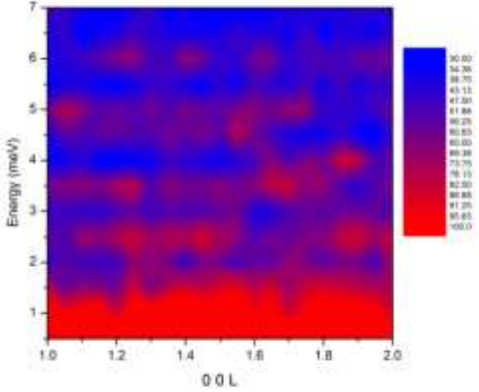


Experiment

Magnetic satellites



Quantized excitations



Polarized Neutron Reflectivity: Exchange Inversion Materials

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[2] Spallation Neutron Source, Neutron Scattering Science Division, Oak Ridge National Laboratory

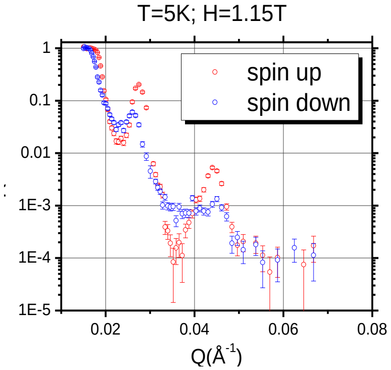
•Polarized neutron Reflectometry with off-specular scattering (PNROS) is applied to obtain 3D information about the internal structure, and magnetization vector distribution to probe key fundamental properties in new Exchange Inversion materials (EXIN).

•EXIN materials exhibit a first order magnetic transition form antiferro to ferromagnetic spin ordering structures.

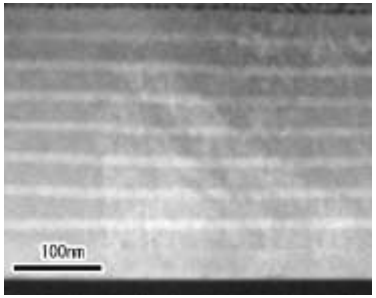
•Polarized neutron reflectivity was applied to gauge the layer magnetizations as a function of temperature in heterostuctures and films to pin down the nature of exchange interactions at interfaces.

•Tunable phase transition behavior makes EXIN films candidates for device and transducer applications in heat pumps, magnetic hard drive data storage and magnetic random access memory.

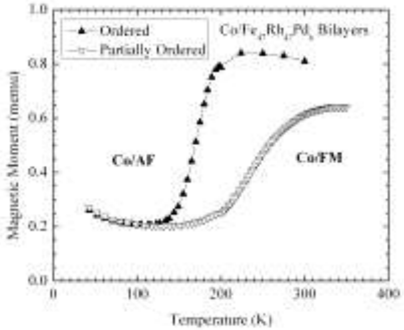
•Future studies will include materials such as MnAl and FeMnAl alloys.



Experimental polarized neutron reflectivity data taken in an external magnetic field of 1.15 Tesla. PNR probes how the magnetism is related to the structure.



Scanning electron microscopy image showing smooth layers with sharp interfaces.



Temperature-dependent magnetometry data showing the tunable EXIN ferromagnetic to antiferromagnetic phase transition.

Thank You!

Further Reading

✓Sintering behavior of spin-coated FePt and FePtAu nanoparticles, Kang SS, Jia Z, Zoto I, Reed D, Nikles DE, Harrell JW, Thompson G, Mankey G, Krishnamurthy VV, Porcar L, J. Appl. Phys. **99**, 08N704 (2006).

✓Antiferromagnetic phase transitions in an ordered $Pt_3Fe(111)$ film studied by neutron diffraction, V. V. Krishnamurthy, I. Zoto, G. J. Mankey, J. L. Robertson, S. Maat, Eric E. Fullerton, I. Nwagwu, and J. K. Akujieze, Phys. Rev. B **70**, 024424 (2004).

✓Antiferromagnetism in a $Fe_{50}Pt_{40}Rh_{10}$ thin film investigated using neutron diffraction, D. Lott, J. Fenske, A. Schreyer, P. Mani, G.J. Mankey, F. Klose, E. Schmidt, K. Schmalzl and E.V. Tatakovskaya, Phys. Rev. B **78**, 174413 (2008).

✓Chemical-order-induced magnetic exchange bias in epitaxial $FePt_3$ films, D. Lott, F. Klose, H. Ambaye, G. J. Mankey, P. Mani, M. Wolff, A. Schreyer, H. M. Christen, and B. C. Sales, Phys. Rev. B **77**, 132404 (2008).