Spring 2009 EE 710: Nanoscience and Engineering

Part 11: Magnetism in Nanomaterials

Text used (images not supplied on these charts):
C. Brechignac, P, Houdy, and M. Lachmani editors, *Nanomaterials and Nanochemistry*:
Chapter 5 by D. Givord, Springer NY, 2007 pp. 101-135

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Nanomagnetic Materials

- Two categories
  - Systems with nanometric dimensions
    - Clusters (nanoparticles)
  - Systems with macroscopic dimensions, but made up of crystallites with nanometric dimensions
    - Nanostructured or Nanopatterned materials
- Differ from bulk materials by
  - Intrinsic properties of isolated clusters
  - Coercively and remnant magnetization dependence on structure
  - Specific properties resulting from coupling between constitutive nanocrystallites

Magnetism in Matter

- Magnetic Moment, m
  - Atomic scale: magnetism results from electron motion
  - Orbital moment, m_l, due to motion of electron within its orbit
    - $m_l = -\mu_B l$, where l is the orbital angular momentum, and μ_B is the Bohr Magnetron. Values of l = 0,1, 2, and 3 are the s, p, d, and f shells respectively
  - The spin moment, m_s, $= -2\,\mu_B s$, due to the electron spin, s, is purely quantum mechanical and is characterized by $s = \pm \frac{1}{2}$
  - A different set of electrons rotating about the nucleus is associated with each element in the electronic table.
  - In a given electron shell there are 2l+1 states for each spin state, making a total of 2(2l+1) states possible.
  - The distribution of electrons over the available orbits in a given shell aims to minimize the energy associated with their mutual repulsion. This energy contains an exchange term which depends on the spin and for this reason is responsible for magnetism in matter

- Electron shells fill according to Hund's rules
    - The total spin S associated with all the electrons in the same electron shell is maximal (parallel to each other)
        - Remember to constrain this system to the Pauli exclusion principle
    - The total angular momentum L is maximal, with the restriction that the first rule takes precedence
- Viewed by the electrons, the motion of the nucleus creates a magnetic field acting on the spin moment. This field is the source of spin orbit coupling between orbital and spin moments
- Energy of the spin orbit coupling is

$$E_{spin\text{-}orbit}=\lambda LS$$

where λ is the spin-orbit coupling constant

- The orbital and spin contributions associated with all the electrons in a full shell tend to balance one another so that the resulting magnetic moment is zero.
- Magnetism is characterized only by partially filled electron shells

Magnetic Moments in Matter

- There are only two series of elements in which mixing of orbitals does not result in disappearance of the magnetic moment in solid state
  - The series of elements known as rare earths which go from cerium to lutetium corresponds to the progressive filling of the 4f shell.
    - Electrons localized in their atomic shells are essentially subject to the same exchange interactions present in isolated atoms, thus generating a magnetic moment when in solid form.
  - The second series of magnetic elements containing iron, cobalt, and nickel corresponds to the filling of the 3d shell.
    - In insulating systems such as oxides the 3d electrons are localized and the magnetic moment is still defined by Hund rules.
    - In metals, the 3d electrons are said to be itinerant, forming an energy band with width of the order of 5eV. The magnetic moment is no longer strictly on the atomic scale.
    - Stoner showed that an alternative approach can be used to describe most of the observed behavior
      - The whole set of electrons is considered to be distributed over two half bands. Each half contains 5N states where N is the total number of atoms and characterized by the value of the electron spins (up or down).
      - In the absence of exchange interactions, the minimal energy corresponds to the equal filling of two half bands and the system is nonmagnetic.
      - However one half band will be favored because of the tendency for the electron spins to line up. The state system is defined by competition between these two terms.
      - In the five elements Cr, Mn, Fe, Co and Ni, the minimum energy configuration is magnetic.
    - Many properties of 3d metals can be described by treating the magnetic moments as atomic
    - However, the distribution of moments considered at two different times will not be strictly the same since electrons can hop from one atom to another.

Magnetic Order

- Exchange interactions
- The exact nature of coupling between moments depends on:
  - Elements present
  - Crystallographic arrangement
- For this reason there are a whole range of magnetic structuring present in nature
- When all the moments are II the structure is said to be ferromagnetic.
  - The moment per unit volume of matter is called the spontaneous magnetization, M_s
- Antiferromagnetic structure
  - Moments within the sublattice are II but different sublattice elements cancel each other out resulting in zero magnetization
- Ferrimagnetic structure
  - The number of atoms or value of magnetic moments are not the same in each sublattice
  - Effect cancels most of the magnetic field but not completely and there remain spontaneous magnetization on the microscopic level.
- The exchange energy expressed for these systems is:

  where J is the exchange integral representing the coupling between spins, and S are the spins carried by two neighboring atoms
- The exchange energy is very short range and if all atoms are identical to their nearest neighbors then
- Positive J implies that the minimal energy configuration corresponds to II coupling → ferromagnetism
- Negative J favors antiparallel coupling

Magnetization Process

- External magnetic field Happ is applied to a ferromagnetic material
- Zeeman energy of coupling with the field is given per unit volume by
- Magnetization tends to occur along the field direction
  - Starting form the initial situation resulting from the division into different sublattice domains and characterized
  - Magnetization increases by displacement of domain walls in such a way that domains with magnetization along the field gro larger at the detriment of others
  - Wall displacement proceeds until a state is reached in which all the moments are aligned with the field. This happens at Happ = NM_s where N is the magnetization tensor
  - In stronger fields, the magnetization remains constant and the material is said to be saturated.

Coercivity

- A new field is now applied to the sample in the opposite direction
- According to our theory the magnetization should grow in the opposite direction in order to minimize the Zeeman energy.
- However, nucleation of the saturated domain requires the system to overcome an energy barrier
- In fact the moment taking part in the reverse magnetization must go through the perpendicular axis of magnetization (again using N). Thus for highly anisotropic N, the material must overcome a large energy barrier.
- We define the coercivity of a material as its capacity to resist the effect of an applied field.
- When the applied field is exactly antiparallel to the initial magnetization direction , z, then the coercive field, H_c, at which the magnetization swings into the field is equal to the anisotropic field

- As soon as the nucleation occurs, all moments reverse in phase in the process know as coherent rotation.

Magnetism in Small Systems

- Magnetic moments in clusters
- First measurements made on Iron and Cobalt clusters of 1-2 nm
  - For Iron, atomic moment was $2.2\mu_B$ equal to that of bulk solid
  - For Co, atomic moment was $2.08\mu_B$ where as bulk was $1.72\mu_B$

Ferromagnetism of certain metals that are Paramagnetic in Bulk

- Rhodium clusters of 32 atoms have a magnetic moment of 1 μ_B /atom
- Measured using Circular dichroism spectroscopy
- Circular dichroism using X-rays from a synchrtron on any nanocluster material indicates a magnetic moment at the atomic level.

Magnetic Anisotropy in Clusters

- Deviations from cubic symmetry add the overall anistropy of any lattice structure.
- For nanoparticles where the structure forms more of a spheroid the degree of directional anisotropy can be extremely high.
- Co anisotropy is $3*10^7$ J/m^3 which is two orders of magnitude greater than in bulk

Dependence on particle size

- For iron alloys the coercivity has been shown to depend on the size of the structure.
- Reduction in particle size is accompanied by an increase in overall coercivity
- Reduction in size below 1 um can produce coercivities , $\mu_o H_c = 0.5T$
- However an extremely fast drop in coercivity occurs at nanometric dimensions (10 nm)
- Since coercivity depends on anisotropy, then the result may be considered as a signature of a significant drop in effective anisotropy
- Indeed the coercivity drops as function of D^6

Residual Coercivity in Nanopatterned Structures

- Magnetostriction plays a dominant role as the size of the structure is reduced
- The material distorts to minimize the interactions of the crystalline field
- This deformation itself leads to anisotropy and a secondary coercivity. It is possible that the significant reduction in coercivity of NiFe below 10nm is due to such a realignment.