Nanomagnetism

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Dr. Ombretta Masala (Nanoco Technologies, Manchester)
Outline:

- Introduction to cooperative magnetism
- Size effects in magnetism
- Magnetic oxides
- Intermetallics
- Core/shell architectures
- Spontaneously formed magnetic composites
Diamagnetism: Very weak effect possessed by all bodies. Characterized by materials repelling magnetic field lines.

Water is diamagnetic, and hence most living beings are as well.

Frogs (and humans) can be floated by very strong magnetic fields [work done at the European High Field Magnet Lab, Nijmegen, Netherlands]
Paramagnetism: Associated with systems having unpaired electrons. Oxygen is a good example.

Electrons in atoms:

\[ \uparrow \quad \uparrow \quad \text{paramagnetic} \]

\[ \downarrow \quad \downarrow \quad \text{diamagnetic} \]

Paramagnetism is characterized by a weak attraction to a magnetic field. In the image, liquid oxygen is being held by an electromagnet.

Usually, dia- and paramagnetism are not cooperative.
Cooperative Magnetism

Ferromagnetism: Characterized by a very strong attraction to a magnetic field, and frequently by the material having a memory of being in a magnetic field.

Most materials that we refer to as “magnets” are actually ferromagnets, and specifically, hard ferromagnets.

Ferro comes from the phenomenon being associated with iron.
(some) materials are ferromagnetic below their Curie temperatures.

Curie temperature
For iron, it is 1043 K or 770°C.
**Domains** are collections of aligned spins (on electrons). They can be aligned (or magnetized) or misaligned (demagnetized).
Domains explain why two pieces of iron don’t normally attract each other; iron is a “soft” magnet, and its domains easily demagnetize.

“Hard” magnets such as ferrite, $\text{Fe}_3\text{O}_4$ can be demagnetized by heating.

Soft ferromagnets: $\text{CoS}_2$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{ZnFe}_2\text{O}_4$
Hard ferromagnets: $\text{SmCo}_5$, $\text{CoFe}_2\text{O}_4$, $\text{Nd-Fe-B}$, $\text{FePt}$
Domains also explain hysteresis, and the notion of magnetic memory:

- Magnetization $M$
- Magnetic field $H$
- Domain wall motion/nucleation
- Spin rotation (coherent/incoherent)
Cooperative Magnetism

Important terms associated with ferromagnetic hysteresis

- Saturation $M_s$
- Remanence $M_R$
- Coercivity $H_C$

$M$ vs. $H$ plot

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Cooperative Magnetism

Antiferromagnets:

Near-neighbor spins are antialigned. No hysteresis.
Examples: $MF_2$, $MO$ ($M = Mn, Fe, Co, Ni, Cu$), IrMn ...

Ferrimagnets:

Near-neighbor spins are antialigned, and are also not compensated (the spins don’t cancel). Hysteresis and magnetization like in a ferromagnet.
Examples: $Fe_3O_4$, $CoFe_2O_4$, $Y_3Fe_5O_{12}$, $BaFe_6O_{19}$ ...
Size effects

$H_c$  

Single Domain  

SP: Superparamagnetic  

Multi Domain  

Isotherm of $H_c$ as a function of particle diameter
Size effects

Single-domain ferrite ($\text{Fe}_3\text{O}_4$) nanoparticles in magnetotatic bacteria

Nature, March 2\textsuperscript{nd}, 2006
Size effects

Superparamagnetism and blocking

\[ T_B = \frac{KV}{25k_B} \]

Blocked
SP

\[ T_B \]

\[ M \]

\[ H/T \]
SYNTHESIS ROUTES FOR LARGE VOLUMES OF NANOPARTICLES

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Oxide nanoparticles

Oxides can be prepared by

**Hydrolysis:**

\[ 2M^{3+}(H_2O)_6 \rightarrow M_2O_3 + 9H_2O + 6H^+ \]  
[eg. \( \gamma \)-Fe\(_2\)O\(_3\)]

**Metathesis:**

\[ TiCl_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4RCl \]  

**Thermolysis:**

\[ Zn(acac)_2 \rightarrow ZnO + \text{products in refluxing dibenzylether} \]
Oxide nanoparticles

Example: CoFe$_2$O$_4$

Stoichiometric amounts of Co(acac)$_2$ and Fe(acac)$_3$ in benzyl ether

Oleylamine and oleic acid as capping agents

200°C and at reflux

Size control by using different amounts of capping agents and different reaction time
MnFe$_2$O$_4$ nanoparticles capped with oleic acid and oleyl amine prepared by decomposing Mn(acac)$_2$ and Fe(acac)$_3$ in refluxing dibenzyl ether at 300°C.

Oxide nanoparticles: $\text{MnFe}_2\text{O}_4$

No evidence for a magnetic “dead layer” in well-capped, crystalline nanoparticles.


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Oxide nanoparticles: $\text{CoFe}_2\text{O}_4$

X-ray diffraction data and Rietveld refinement: Inverse spinel structure $\text{Fe(2CoFe)O}_4$. $Fd-3m$ (227)
Oxide nanoparticles: $\text{CoFe}_2\text{O}_4$

Magnetic properties:

- **Powder**
- **Particles in Wax**
Oxide nanoparticles: $\text{CoFe}_2\text{O}_4$

Temperature effects:
Hysteresis at low temperature (5K) and at RT (300K)

Size effects:
Samples have sizes between 5 nm and 14 nm

Particle interaction effects:
Particles as pressed powder and dilute in wax
Oxide nanoparticles: $\text{CoFe}_2\text{O}_4$

- **Wax**
- **Powders**
  - 5 nm
  - 7.1 nm
  - 10.4 nm
  - 14 nm

- 300 K
- 5 K
Oxide nanoparticles: CoFe$_2$O$_4$
Oxide nanoparticles: CoFe$_2$O$_4$

- Temperature effects: Coercivity higher at low temperatures
- Size effects: Saturation magnetization does not change with size; coercivity changes with size; blocking temperature increases with size
- Interparticle interaction effect: Coercivity of non-interacting particles is higher. Record at 5 K (near 3 T)
- Shape of hysteresis loop distinct (powder vs. wax)
- Blocking temperature increases with dilution
- Remanence ratio increases with dilution
Oxide nanoparticles: CoFe$_2$O$_4$

7.9 ± 0.5 nm spheres

~9 nm cubes

~12 nm cube

Decomposing Co(acac)$_2$ in refluxing dibenzylether gives CoO in the wurtzite modification.

Intermetallics: FePt

Disordered, \textit{Fm-3m} (225), non-magnetic

Ordered, \textit{P4/mmm} (123), magnetic

Platinum, being heavy, induces spin-orbit coupling, resulting in high $K$
Films of nanoparticles annealed to up to 500°C to induce ordering and coercivity. 5 nm particles are coercive at RT.
Intermetallics: FePt

Stoichiometric amounts of Na$_2$Fe(CO)$_4$ and Pt(acac)$_2$

Oleylamine or oleylamine/oleic acid as surfactants

Stir at 70°C for 1 h, reflux in various solvents

<table>
<thead>
<tr>
<th>Educts</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>Time(min)</th>
<th>Phase</th>
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<tr>
<td>reagents</td>
<td>octyl ether</td>
<td>~270</td>
<td>60</td>
<td>fcc</td>
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<tr>
<td>reagents</td>
<td>nonadecane</td>
<td>~310</td>
<td>60</td>
<td>fct</td>
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<tr>
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<td>tetracosane</td>
<td>~335</td>
<td>120</td>
<td>fct</td>
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<td>~265</td>
<td>1200</td>
<td>fct</td>
</tr>
</tbody>
</table>
Intermetallics: FePt

Ordering of atoms in high temperature solvents without increasing particle size.
Oxides: Core/shell magnets; Soft and hard ferrites

Initial experiments:

Core grown first (from metal acetylacetonates) and then shell. The idea is to prepare interfaces, such as would be obtained by heteroepitaxy, from solution.

Many m$^2$ of interface rather than mm$^2$

Spinel CoFe$_2$O$_4$ is a hard ferrimagnet and ZnFe$_2$O$_4$ is soft. Lattice parameters are nearly the same.

Problem in the characterization: Co, Fe, Zn are nearly indistinguishable by x-rays and by electrons.
Oxides: Core/shell magnets; Soft and hard ferrites

Neutron data from NPDF, Los Alamos, fitted using a two-spinel model.
Single blocking temperature: The blocking temperature of the core/shell nanoparticles increases with the amount of hard magnetic material.
Oxides: Core/shell magnets; Soft and hard ferrites

How should the magnetic interface behave?

Oxides: Core/shell magnets; Soft and hard ferrites dispersed in wax

Smooth scaling of coercivity with increasing amounts of the soft component.


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Oxides: Core/shell magnets; ferri/antiferro

Co/CoO

Magnetoresistive angle sensor:

Modified from Grünberg, Phys. Today
54 (2001) 34

Meiklejohn, Bean, Phys. Rev. 102 (1956) 1413.

Hysteresis loops of fine oxide-coated particles of cobalt taken at 77°K. The dashed lines show the hysteresis loop when the material is cooled in the absence of a magnetic field. The solid lines show the hysteresis loop when the material is cooled in a saturating magnetic field.
Oxides: Core/shell magnets; ferri/antiferro

spins of FM are pinned to those of the AFM

additional energy (crystal anisotropy of AFM)
Oxides: Core/shell magnets; ferri/antiferro

Preparation:

CoFe$_2$O$_4$ (core), Mn(acac)$_2$

Oleylamine/oleic acid

200$^\circ$C and reflux in benzyl ether
Antiferomagnetic MnO grown over ferrimagnetic CoFe$_2$O$_4$.

The phases become visible by TEM because they are structurally distinct.

X-ray diffraction indicates the clear presence of two phases; rock salt MnO and spinel CoFe$_2$O$_4$.

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Oxides: Core/shell magnets; ferri/antiferro

CoFe$_2$O$_4$/MnO

Exchange biasing.

Oxides: Molten salt prepn. of complex oxides

Oxide prepared from nitrates in NaNO₃/KNO₃ flux

Refluxing in 2-pyrrolidone caps and disperses particles

Y. Tian, D. Chen, and X. Jiao, \(La_{1-x}Sr_xMnO_3\) (\(x = 0, 0.3, 0.5, 0.7\)) Nanoparticles nearly freestanding in water: Preparation and magnetic properties, Chem. Mater. 18 (2006) 6088-6090.

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Spontaneously formed magnetic nanocomposites

Spontaneously formed magnetic nanocomposites

- Phase segregation in block copolymers and polymer melts
- The formation of Raney Ni
- Spinodal decompositions
The key is tethering:
- Covalent (copolymers)
- Electrostatic (hybrid materials)
- Kinetic (metals, ceramics)

Spontaneously formed magnetic nanocomposites
Spontaneously formed magnetic nanocomposites

ZnMn$_2$O$_4$ (hæterolite) pellet in flowing H$_2$

- 700 K

Zn$_{0.33}$Mn$_{0.66}$O

- 900 K

Zn$_{0.1}$Mn$_{0.9}$O + Zn(g)

Toberer and Seshadri, Adv. Mater. 17 (2005) 2244
Spontaneously formed magnetic nanocomposites

9 ZnO / ZnMn$_2$O$_4$  →  ZnMn$_2$O$_4$  →  rock salt Zn$_{0.1}$Mn$_{0.9}$O
Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn

Macropore network remains intact and grains remain well-connected
Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn
Spontaneously formed magnetic nanocomposites

BET, SEM, and TEM suggest ~50 nm pores

Hierarchically Porous Mn

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Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn

TEM: Pore walls are \{100\} faces; lowest energy faces of rocks salt

Spontaneously formed magnetic nanocomposites

Hierarchically Porous Mn

Mn$_3$O$_4$  MnO

MnO  MnO

Sintered Mn$_3$O$_4$ reduced in 5% H$_2$/N$_2$

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Spontaneously formed magnetic nanocomposites

Titania is used in:
- photocatalysis
- Grätzel cells
- water purification
- sensing

$3 \text{ZnO/Zn}_2\text{TiO}_4 \rightarrow \text{Zn}_2\text{TiO}_4 \rightarrow \text{TiO}_2$
Spontaneously formed magnetic nanocomposites

Interesting morphologies in the intermediate stages of leaching.


Other early transition metal oxides (V, Nb, Cr W, ...)

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Spontaneously formed magnetic nanocomposites

Single-domain Ni nanoparticles on porous MnO, prepared by reducing $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$. (a) through (d) are increasing $x$.

$$\text{Mn}_{3-x}\text{Ni}_x\text{O}_4 \rightarrow (3-x)\text{MnO} + x\text{Ni}$$
Spontaneously formed magnetic nanocomposites

X-ray diffraction confirms the quantitative conversion.

\[ \text{Mn}_{3-x}\text{Ni}_x\text{O}_4 \rightarrow (3-x)\text{MnO} + x\text{Ni} \]
The Ni loops, after field cooling, are shifted on the field axis because of antiferromagnetic MnO.
The extent of exchange biasing (at 5 K) scales with the inverse diameter of the Ni particles.
Spontaneously formed magnetic nanocomposites

The coercivity (at 5 K) is increased as well, as the extent of exchange bias increases. A way of hardening soft magnets.
Spontaneously formed magnetic nanocomposites

Other systems: Co on MnO.

In progress: CoO and Cr₂O₃-based systems.
Summary

Much yet to be learned from even simple nanomagnetic systems: For example, size effects on antiferromagnets.

Simple ways of achieving complex magnetic nanoarchitectures
Questions ?