Designing Nanoscale Materials
Lecture Series by 2004 Debye Institute Professor
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Debye Lecture 6

Nanostructured Magnetic Materials for Information Technology

C. B. Murray
Magnetic Nanocrystals and Nanocrystal Superlattices

IBM T. J. Watson Research Center; Yorktown Heights, NY

(1) Synthesize, characterize and integrate nanostructured materials.
(2) Probe the limits conventional materials/device scaling.
(3) Harness mesoscopic properties for future technology.
(4) Explore the potential of self-assembly for nanofabrication.

Film Growth: Self-Assembly
Nanocrystal Superlattice
Annealed Superlattice
Patterning & addressing
Applications & Opportunities for High Energy Product magnets.

- Micro/Nano Devices
- Automotive and Avionic Components
- Medical diagnostic system
- Hard disk drives
- Head actuators
- Various actuators in acoustic systems
Disk Technology

- Lubricant
- C:Nx Overcoat
- CoPtCrB
- Magnetic Layer
- Cr
- Underlayer
- Glass
- Substrate
Advanced Technologies To Delay Superparamagnetism

1. AFC media - implemented 1Q2001

2. Perpendicular recording

Reduces demagnetizing influence of adjacent bit fields, minimizes transition parameter. Involves new head configuration, return path soft underlayer, as NiFe, in media.

3. Reduce BAR (Bit aspect ratio) 20 ----> 4

4. Patterned media

5. Thermally assisted writing

Required because of increased media coercivity (increases $K_u$ to compensate for a reduced $V$). Involves new magnetic materials

Ed Grochowski at Almaden
Superparamagnetism

- Single magnetic domain particles.
- Orientation determined by anisotropy energy, $K$.
- Energy barrier, $\Delta E = KV / k_BT$.
- Remnant magnetization, $M_{rem}$:
  \[ M_{rem}(t) = M_{sat}e^{-t/\tau} \text{ where } \tau = \tau_o e^{-KV/k_BT} \]
- Blocking temperature, $k_BT_B \approx 25\Delta E$.
- At $T >> T_B$, particles are superparamagnetic.
- Zero hysteresis – Langevin equation
  \[ M(H) = \coth(\mu H / k_BT) - k_BT / \mu H \]
- At $T << T_B$, particles are ferromagnetic.

\[
\begin{align*}
\text{Energy} & \quad \Delta E \\
\text{Orientation} & \quad \\
\end{align*}
\]
Magnetization - size dependence

10nm fcc-Co particles

2-2.5nm fcc-Co particles
Read Head Design Technologies

Spin Valve (GMR) Read Head
CIP

Shield 1

Antiferromagnetic Exchange Film
Current Flow
Contact
Hard Bias
Contact
Hard Bias
NiFe GMR Free Film
Co GMR Pinned Film
Cu Spacer

Magnetic Tunnel Junction (MJT) Read Head
CPP

Bottom Contact
Tunnel Barrier
Tunnel Valves Films
Current Flow
Hard Bias

Shield 1

Ed Grochowski at Almaden
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Evolution of Magnetic Read/Write Sensors

Ferrite Inductive MnFe
Read/Write Head
Wire wound coil
Machined Pole Pieces
Gap Width Controlled
By Films And Assembly
Tolerances

Thin Film Inductive Write
MR Read Head
Write Wide-Read Narrow
Four Contact Structure
SAL
NiFe MR Film

Thin Film Inductive Write
GMR Read Head
Write Wide-Read Narrow
Four Contact Structure
Pinned, Free Films
Antiferromagnetic Exchange Film
CIP Operation

Thin Film Inductive Write
Tunnel Junction Read Head
CPP Operation

IBM
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IBM HDD Roadmap

- 1 inch profile 10K RPM
- 73 GB Server
- 75 GB Desktop
- 48 GB
- 36GB 15K RPM
- 32 GB
- 25.3 GB
- 8.1 GB
- 5.1 GB
- 1.2 GB
- 1.0 inch consumer based
- 0.34 GB Microdrive
- 1 GB Microdrive
- 9.1 GB
- 4.5 GB
- 2.5 inch

HDD Capacity, GBytes

Availability Year

Ed Grochowski at Almaden
AFC media magnetization response to magnetic field

M_{rt_{\text{top}}} = 0.31
M_{rt_{\text{bottom}}} = 0.09

CoPtCrB
Ru
CoPtCrB
Cr
underlayers
Glass substrate

35 Gb/in² media
M_{rt} = 0.35 memu/cm²

AFC media
M_{rt} = 0.22 memu/cm²

H (kOe)

Synthesis and Self-assembly of Co nanoparticles

- High temperature (200 °C), solution phase synthesis.
- Rapid nucleation – growth controlled by coordinating ligands.
- Size distribution improved by size selective precipitation.
Synthesis of Transition Metal Nanocrystals

Co^{2+} + (Et)_3BH + R_3P + C_{17}H_{19}COOH
250°C Na^+ Napth^-

Co^{2+} + C16(OH)_{2}+R_3P + C_{17}H_{19}COOH

Sequential reduction of metals Core/Shell

Co_{2}(CO)_8 + R_3P + C_{17}H_{19}COOH

Simultaneous reduction of metals alloys

Co^{2+} + M^{n+}

Ni 9 nm
Co 8 nm
Co/Ni 9 nm
FePt 4 nm

Co/Ni 9 nm
Crystal phases of Cobalt

3 crystal phases are studied.

Fcc and hcp differ only in stacking sequence of close-packed layers.

fcc: ABCABC…

hcp: ABABAB...

• Cubic unit cell
• Complex internal structure

Set I - 8 atoms
Set II - 12 atoms

XRD modeling of cobalt nanoparticles

- Better fits obtained by including
  - Stacking faults
  - Twin faults
- Introduction of stacking faults generates mixed fcc/hcp structures.
- Leads to the inter conversion of fcc and hcp phases
XRD Modeling of hcp nanoparticles

- TEM images show that hcp Co nanoparticles are slightly prolate.
- XRD fitting show extensive faulting/disorder.
  - Approximately one fault every 2.5 stacking planes.
  - Consistent across a variety of particle sizes.
XRD Modeling of fcc nanoparticles

- TEM images show that fcc Co nanoparticles are spherical in shape.
- XRD fitting - one fault every 4 planes.
  - Bad fits at higher angles.
- Dark regions in TEM imply “multiple twinned” (MT) structures.
XRD Modeling of MT polyhedra

- Better fits have been reported for MT polyhedra
  - Highly faceted structures
  - Icosahedral, cubeoctahedral and decahedral structures suggested
- HR-TEM images also suggest the presence of multiple domains
  - Consistent with multiple twinning

TEM images show that ε-Co forms as spherical nanoparticles with narrow size distributions.

XRD fits - perfect crystalline internal structure.

Supported by HR-TEM images of individual nanoparticles.
Modeling of the magnetization of Co nanoparticles

• Equilibrium partition function of nanoparticles in applied magnetic field.

\[
\langle M \rangle = \int dKp(K) \int dVp(V) \int dH_0 \int dH_0 \frac{d\mu_0}{d\mu_0} M_{sat} \left( \hat{\mu} \cdot \hat{H} \right) e^{-\frac{E(\hat{H}, \hat{p}, V)}{k_B T}} \int d\mu_0 e^{-\frac{E(\hat{H}, \hat{p}, V)}{k_B T}}
\]

\[
E / V = -M_{sat} \hat{\mu} \cdot \hat{H} - KS_z^2
\]

\[
M_{rem}(t) = \int dKp(K) \int dVp(V) [\alpha M_{sat} e^{-t/\tau}] \quad \text{where} \quad \tau = \tau_o e^{-KV/k_B T}
\]
Magnetic modeling of MT Co nanoparticles

- TEM analysis - 7 nm diameter
- Magnetic fitting
  - Diameter $6.2 \pm 0.5$ nm
  - $K = 7.0 \times 10^5 \pm 3.5 \times 10^5$ ergs cm$^{-3}$
- Smaller “magnetic” diameter accounted for by the presence of oxide layer.
- Anisotropy close to bulk fcc value
- Remnant magnetization is half saturation magnetization at low temperatures
  - Implies uniaxial symmetry.
Magnetic modeling of MT Co nanoparticles

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- Smaller “magnetic” diameter accounted for by the presence of oxide layer.
- Anisotropy close to bulk fcc value
- Remnant magnetization is half saturation magnetization at low temperatures
  - Implies uniaxial symmetry
    - Predicted for MT polyhedra

For 0.1 T, only $T>170$ K in equilibrium

Expt.

Fit

Saturation Magnetization (1 Tesla)

Remnant Magnetization (120 s)

M (emu)

T (K)
Magnetic modeling of \( \varepsilon \)-Co nanoparticles

- TEM analysis - diameter of 9.5 nm
- Magnetic fitting
  - Diameter 8.4 ± 0.9 nm
  - Anisotropy 7.1x10^5 ± 4.0x10^5 ergs cm\(^{-3}\)
- Anisotropy also close to bulk fcc value
- Remnant magnetization is half saturation magnetization at low temperatures
  - Implies uniaxial symmetry.
Materials Selection: $K_u V >> kT$

- **Cubic**
  - Ni
  - NiO$._2$Fe$._3$O$._7$
  - Fe
  - CoOFe$._2$O$._3$
  - BaO$._6$Fe$._2$O$._3$
  - Co
- **Hexagonal**
  - MnAl
  - CoPt
  - FePt
- **Tetragonal**
  - Fe$._{14}$Nd$._2$B
  - YCo$._5$
  - SmCo$._5$
  - SmFe$._{11}$Ti

- **Hard magnets**

- $K_u V >> kT$
- $K_u V < kT$

Crystal Anisotropy
Shape Anisotropy
Exchange Anisotropy
Strain Anisotropy

CoPt $L_{10}$ structure (tetragonal)
Shape ?
Solution phase synthesis

Example: FePt nanoparticles

Starting Materials

\[
\begin{align*}
\text{FeCl}_2 \\
\text{Pt(acac)}_2 \\
\text{COOH (acid)} \\
\text{NH}_2 \text{ (amine)} \\
\text{LiBEt}_3\text{H (Superhydride)}
\end{align*}
\]

Mixing

200-260°C

Particle dispersion

\[
\text{Pt(acac)}_2 =
\]

S. Sun, C. B. Murray, IBM Yorktown
Nanoparticles for magnetic storage

- Narrow size distribution → higher thermal stability
- Smaller particles → narrower transition widths

35 GBit/in\(^2\) prototype media
8.5 nm grains
\(\sigma_{\text{area}} \cong 0.6\)

Nanoparticle arrays
4 nm FePt particles
\(\sigma_{\text{area}} \cong 0.05\)

Magnetic properties

- Annealing leads to formation of ordered, ferromagnetic phase

Annealing at 550°C

Chemically disordered fcc structure
Superparamagnetic

Chemically ordered fcc structure
Ferromagnetic

Pt Fe

C axis
Magnetic properties

- Order parameter and coercivity increase with annealing temperature and duration

3 layer samples of 6 nm FePt particles

XRD data M. Toney, IBM Almaden
VSM Hysteresis loops

3 layers, annealed in N₂ at 580 C for 30 min, FePt samples from FeCl₂

“3D” random assembly of 4nm particles
Chemical analysis

- Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy shows iron oxide fraction that is reduced upon annealing
- NEXAFS more sensitive to particle surface - averaged ratio may be different

Special thanks to Robin Farrow for providing iron oxide reference samples.
Structural properties

- X-ray scattering and TEM used to study structural properties

TEM images of 6 nm particles
(a) as synthesized
(b) 530 °C for 60 min in vacuum
(c) 600 °C for 60 min in vacuum

TEM images courtesy of Zu-Rong Dai

- X-ray scattering and TEM used to study structural properties

3 layers of 4 nm particles annealed in N₂

XRD data M. Toney, IBM Almaden
Polymer-mediated self assembly

- Substrate surface is functionalized
- Dipped into dispersion of stabilized nanoparticles
- Ligand exchange leads to formation of strongly bound layer of nanoparticles
- New layer of functional molecule replaces stabilizer
- Repeat process to form multilayers

S. Sun, C. B. Murray, IBM Yorktown
Magnetic recording

X-Y Piezo Scanning Stage

Computer → V → I

Servo Electronics

Slider

Sample

to piezos

Suspension

Reading

Writing

 MR signal [mV]

x [µm]

500 fc/mm

1040 fc/mm

2140 fc/mm

5000 fc/mm

4

2

0

-2

-4

-6

-8

-10

-12

-14

-16

-18

-20

0

5

10

15

20

2.5

Electronic components and their roles in magnetic recording are illustrated. The computer outputs a voltage (V), which is converted to current (I) for controlling the servo electronics. The slider is positioned on the sample surface by the X-Y piezo scanning stage. The MR signal, measured in millivolts, varies across different spatial frequencies (fc/mm) shown in the graph. The graph indicates the reading process for different spatial frequencies.
Size control of nanocrystals in the absence of Ostwald ripening

Factors influencing the nucleation rate

- reaction temperature
- concentrations of precursors
- concentrations of surfactants

Factors influencing the nucleation rate

- fast
- slow

precursors

nucleation

growth

until all monomer is consumed

CoPt$_3$ nanocrystals

Fe$_2$O$_3$ nanocrystals

220 °C

200 °C

170 °C

145 °C

307 °C

255 °C

245 °C

200 °C

5 nm

30 nm
Cobalt Nanocrystal Superlattices (T. Betley et al)

Hexagonal packing

10 nm Cobalt NCs

Cubic packing
Three-dimensional colloidal supercrystals of CoPt$_3$ nanocrystals

Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany
Photon penetration depth 50 nm

Electron escape depth 5 nm

sample surface

vacuum

secondary electrons

Photon penetration depth 50 nm

sample

FePt

Fe2O3

polymer
For the unannealed particles the ratio in the spectra can be estimated as 20% Fe, 80% Fe2O3 (I am still not sure what oxide we have, maybe a mixture). On the left is the contribution to the spectra as a function of radius. A 3nm diameter FePt metal core with a 0.5nm thick oxide shell would produce such a spectrum.
For the annealed particles the metal ratio is much higher, here an example for 650C/5min anneal. On the left is the contribution to the spectra as a function of radius. A 3.6 nm diameter FePt metal core with a 0.2nm thick oxide shell would produce such a spectrum.
Fe3O4 sample from Robin
XMCD in 500 Oe, 20 degrees incidence
along easy axis
run 20125013

Polar Kerr
Fe₃O₄ sample from Robin
XMCD in 500 Oe, 20 degrees incidence along easy axis
test reproducibility - is very good
Three layers of PEI-E066 on Si(110) annealed under Ar + H(5%) for 30 min. The samples have been immersed into acetone for 1 min and dried.

030902-A, 400°C
030902-B, 450°C
030902-C, 500°C
030902-D, 530°C
030902-E, 560°C
030902-F, 580°C
And here the comparison between 8nm, 6nm, and 4nm.
From Mike Toney, XRD
From Mike Toney, XRD
Hello,
Here the data from the latest ALS run. Jan made two samples for comparison, sample #4 is 50 nm Fe55Pt45 without cap layer, sample #5 is 50 nm Fe55Pt45 with 2 nm Pt cap layer.
Here the Fe spectra for comparison. The one without cap layer is much more oxidized as expected.
This graph shows sample #5 with respect to a clean Fe reference, and the best fit to the spectrum I got with assuming 70\% Fe and 30\% FeO.
And the contribution to the spectra of Fe and Fe3O4 for 8nm, 6nm, and 4nm. If I put this into the model the oxide layer for the 6 and 8 nm particles seems to be thinner (2Å) than for the 4 nm particles (4Å).
The 8nm sample has very high coercivity.
This is a comparison of the films made 030101. They are all just after the onset of being ferromagnetic, the spectra are all very similar.
030101-A  Hc=1.2 kOe

030101-C  Hc=0.14 kOe

030101-B  Hc=2.4 kOe

030101-D  Hc=1.2 kOe

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<td>E068, ~8nm FePt</td>
<td>SiO₂/Si</td>
<td>PEI-FePt, 1 layer</td>
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Hi all,
I did a calculation of the signal one would expect in total yield detection for the following geometry:
This is basically a particle of 40A diameter with 32A FePt core surrounded by one monolayer Fe3O4. It is embedded in the polymer (for the calculation I assumed just carbon) with 60A particle distance, that gives about 10A carbon on top.
Synthesis and Characterization of Iron Oxide Nanoparticle

\[ \text{Fe(CO)}_5 \xrightarrow{\text{octyl ether oleic acid}} \text{Fe-NC} \xrightarrow{(\text{CH}_3)_3\text{N-O}} \gamma\text{-Fe}_2\text{O}_3\text{-NC} \]

\[ \text{FeO} \xrightarrow{\Delta T} \text{Fe} + \text{Fe}_3\text{O}_4 \]

narrow sizedistribution of maghemite particle tuning of physical (e.g. magnetic) properties.
RF & Microwave
Bio applications.
Fe3O4 Nanocrystals
(Sun and Zeng)

Figure 1. TEM bright field image of 16-nm Fe3O4 nanoparticles deposited from their dodecane dispersion on amorphous carbon surface and dried at 60 °C for 30 min: (A) a monolayer assembly, (B) a multilayer assembly, (C) HRTEM image of a single Fe3O4 nanoparticle. The images were acquired from a Philips EM 430 at 300 KV.
$\text{Fe(acac)}_2$ or $\text{Fe(acac)}_3$

TOE or DOE
OA (and tributylphosphine)

$\text{FeO}$

$\text{Fe} + \text{Fe}_3\text{O}_4$

$\text{TOA or DOE}$
OA, 350 C

TOA, OA

$\text{Fe(CO)}_5$

$\text{armorphous Fe-NC}$

$\text{Ox in air}$

$>300 \text{ C}$
Shape selective synthesis of wuestite

Substitute trimethylamine N-oxide with pyridin N-oxide

\[
\begin{align*}
\text{Fe(CO)}_5 & \quad \text{oleic acid dioctyl ether or trioctylamine} \\
\Delta T & \quad \text{FeO-NC}
\end{align*}
\]
FeO Nanoparticles

Right a) TEM image of a single cubic superlattice built of cubic FeO nanocrystals with 11 nm edge length. b) TEM image of a larger superlattice oxidized or decomposed after storage. c) SAED of the cubic superlattice in b) showing reflections for magnetite and orientational ordering in the superlattice.

Right: a) LRTEM image of a quadratic subunit of a TEM grid showing nearly cubic superlattice built up of cubic wuestite nanocrystals. b) SAED of a selected superlattice with uneven but symmetric intensity distribution caused by preferred alignment of the particles (orientational ordering). c) TEM image of aligned superlattices arising during deposition of cubic FeO nanocrystals in a magnetic field parallel to the substrate. d) TEM image of aggregated superlattices deposited without external magnetic field.
Figure 6: a) TEM image of wustite nanocrystals with seeds of magnetite inside. b) SAED of the material showing a speckled pattern for FeO reflections and diffuse rings for magnetite reflections. c) Dark-field image of the region in Figure 5a (shown as negative); a part of the magnetite reflections were selected with the objective aperture. d) Dark-field image of the region in Figure 5a (shown as negative); a part of the wustite reflections were selected with the objective aperture.
Fe₃O₄ nanoparticles

Shape induce crystal alignment
(14 nm MnFe₂O₄ nanoparticles)
Dark Field Imaging of the Fe3O4 and FeO in TEM.

Figure 6: a) TEM image of wuestite nanocrystals with seeds of magnetite inside. b) SAED of the material showing a speckled pattern for FeO reflections and diffuse rings for magnetite reflections. c) Dark-field image of the region in Figure 5a (shown as negative); a part of the magnetite reflections were selected with the objective aperture. d) Dark-field image of the region in Figure 5a (shown as negative); a part of the wuestite reflections were selected with the objective aperture.
Bimagnetic Core/Shell Nanoparticles

Figure 1. TEM bright field images of core/shell Fe$_{58}$Pt$_{42}$/Fe$_3$O$_4$ nanoparticles with core/shell being (A) 4 nm/0.5 nm and (B) 4 nm/2 nm; (C) HRTEM of a single Fe$_{58}$Pt$_{42}$/Fe$_3$O$_4$ particle with 4 nm core and 2 nm shell; and (D) EDX spectrum of a group of Fe$_{58}$Pt$_{42}$/Fe$_3$O$_4$ nanoparticles with 4 nm core and 1 nm shell. The shell thickness is measured statistically with standard deviation at around 11%.

GMR Head Structure

Inductive Write

Spin Valve/GMR Read

Integrated Lead Suspension/ Pico Slider

Copper Write Coils

Inductive Write Head P2 Layer

Head/Slider Section

Lower P1-Shield 2

Antiferromagnetic Exchange Film 150 Å

Ta Contact

CoPtCr Hard Bias

Cu Spacer 25 Å

NiFe29 GMR Free Film 50 Å

CoFe GMR Pinned Film 30 Å

Shield 1

IBM

ED GROCHOWSKI et ALMADEN
Spin-dependent tunneling in Nanocrystal arrays

Chuck Black, Bob Sandstrom, Chris Murray, Shouheng Sun

- shortest current path ~ 8 nanocrystals

$G_{V=0}$ follows simple thermal-activation

$$\ln(G_{V=0}) = \text{const.} - \frac{E_C}{k_B T}$$

- from fit to data, measure $E_C \approx 10$ meV
- for all devices measured, $10 \text{ meV} < E_C < 14 \text{ meV}$
Fe₃O₄ Nanocrystals
(Sun and Zeng)

\[ \text{Fe(acac)}_3 + \text{ROH} + \text{RCOOH} + \text{RNH}_2 + \text{Ph}_2\text{O} \]

Figure 1. TEM bright field image of 16-nm Fe₃O₄ nanoparticles deposited from their dodecane dispersion on amorphous carbon surface and dried at 60 °C for 30 min: (A) a monolayer assembly, (B) a multilayer assembly, (C) HRTEM image of a single Fe₃O₄ nanoparticle. The images were acquired from a Philips EM 430 at 300 KV.
Potential for spintronic device applications
AFC media magnetization response to magnetic field

M_{rt, top} = 0.31
M_{rt, bottom} = 0.09

CoPtCrB
Ru
CoPtCrB
Cr
underlayers
Glass substrate

Nanoparticle synthesis from self-assembled polymer templates

- Diblock copolymer system PS/PMMA
- Self-assembly promoted by heating
- Removal of PMMA

Metal deposition

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