Chemically Synthesized FePt Nanoparticles

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Motivation

• Chemically synthesized FePt nanoparticles are promising materials for ultra-high density media

• As-made: $d=3.5 \text{ nm, } \Delta d/ d \sim 0.1$, disordered fcc, superparamagnetic.

• High-anisotropy $L1_0$ phase requires annealing above $500^\circ \text{C}$.

• Major issues: easy-axis alignment, particle agglomeration/ sintering during annealing
Solution Annealing
(a possible pathway to easy axis alignment)

- FePt nanoparticle arrays are typically annealed in a furnace at high temperatures.
- Additive Au reduces the chemical ordering temperature and allows for the possibility of annealing in dispersion.
- Our approaches to solution annealing:
  - Heat dispersion of FePtAu particles in phenol ether in pressurized vessel to achieve high temperature
  - Heat FePtAu particles in high boiling point silicone oil at atmospheric pressure.
Effect of additive Au on chemical ordering

- Additive Au reduces ordering temperature by ~100-150°C.

- Coercivity enhancement and superlattice (L1₀) XRD peaks at T(anneal) ~ 350°C.
FePtAu nanoparticles annealed in phenyl ether

Partial chemical ordering is obtained by heating a dispersion of FePtAu nanoparticles in phenyl ether in a pressure vessel at 500°C and 250 psi for 60 min. (Boiling point = 260°C at atmospheric pressure.)
TEM after annealing in phenyl ether (500°C, 250 psi)

- $d \sim 5$-10 nm
- Particle growth and increase in size distribution
- Core-shell structure
(FePt)$_{76}$Au$_{24}$ nanoparticles annealed in high-temperature silicone oil (Dow Syltherm) at atmospheric pressure

- Weak ordering after annealing at 400°C [(001), (110),…]
- Further, but incomplete, ordering after post annealing in a furnace at 600°C.
- Au segregation during annealing [(111), …]

![Graph showing X-ray diffraction patterns](image)

Annealed in oil at 400°C, then furnace annealed at 600°C

Annealed in oil at 400°C for 4 hrs
Dynamic coercivity of FePtAu nanoparticles annealed in silicone oil

\[
H_{cr}(t) = H_0 \left\{ 1 - \left[ \frac{k_B T}{K u V} \ln(f_0 t)^n \right] \right\}
\]

\[n = \frac{2}{3}, \quad f_0 = 10^9 \text{ Hz}\]

\[H_0 \sim \frac{1}{2} H_k \sim K / M_s\]

Assuming \(M_s \sim 1000 \text{ emu/ cc},\)

\(K \sim 8.5 \times 10^6 \text{ erg/ cc}\)

\(V \sim 191 \text{ nm}^3 (d \sim 7.2 \text{ nm})\)

Note: For fully ordered FePt, 
\(K \sim 7 \times 10^7 \text{ erg/ cc}\)
TEM of FePtAu(24%) annealed in silicone oil

- d ~ 1-5 nm
- broad size distribution
- Annealing in silicone oil gives less average particle growth than annealing in phenol ether.
Effect of Metal Additives on Sintering

- Additive Au and Ag significantly lowers the ordering temperature in nanoparticles.
- There is evidence that large particles order more easily than small particles.
- What is the correlation between sintering and chemical ordering?
Effect of additives on grain growth and chemical ordering - XRD

- Additive Au lowers the ordering temperature and lowers the temperature for grain growth.
- Additive Cu raises the ordering temperature and raises the temperature for grain growth.
Effect of additives on grain growth during annealing

• Scherrer analysis:

\[ t = \frac{0.9 \lambda}{B \cos \theta}, \; B = 2\theta \text{ linewidth} \]

• Additives have a strong effect on the increase in grain size during annealing.

• Grain growth and the onset of chemical ordering are strongly correlated.

(Note: Strain contributions are small size since B is roughly independent of θ.)
Summary

• Partial chemical ordering has been obtained by annealing ~4 nm FePtAu nanoparticles in solution. Solution annealing increases size distribution.

• Dispersions of chemically ordered particles may be useful for preparing films with aligned easy axes.

• The effect of metal additives on chemical ordering and on grain growth during annealing is correlated.

• The dependence of chemical ordering on particle size is an important issue that is being addressed experimentally and theoretically (Butler).
Theoretical Studies of Size Effect on Equilibrium Order-Disorder Transformation in FePt Nanoparticles

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Introduction

• Recent reports suggest that FePt nanoparticles below a critical size cannot be chemically ordered by thermal annealing.

• We use a lattice gas model to calculate the size dependence of the equilibrium order-disorder phase transition.

• Fe and Pt atoms occupy sites on a crystal lattice and interact through a lattice potential (mixing potentials).

• Atoms can exchange positions based on Gibbs statistics: \( W(\text{state}) \propto \exp[-E(\text{state})/kT] \)

• Computation done using Monte-Carlo procedure.
Phases of FePt

The diagram shows the phase diagram for the FePt system, indicating the different phases and their transition temperatures.

- **L** (liquid) phase
- **(αFe)** phase at 1538°C
- **(γFe,Pt)** phase at 1394°C
- **(γFe,Pt)** phase at 1769°C
- **γ1 (Fe3Pt)** at ~1300°C
- **γ2 (FePt)** at ~1350°C
- **γ3 (FePt3)** at ~65°C

The diagram also includes structures of the phases **L10 (FePt)** and **L12 (FePt3, Fe3Pt)**.
Calculation of mixing potentials

- The energies of 21 structures (infinite periodic system of 6-18 atoms) were calculated using 1st principles methods (VASP) starting from a fully ordered state.

- Mixing potentials for 1st, 2nd, and 3rd nearest neighbor atoms were numerically determined to give good agreement with VASP calculations for the energies of the small structures.

- Mixing potentials were used in Monte-Carlo model for large number of atoms.

![Graph showing energies of structures (eV) with relative and absolute average errors]
Calculated equilibrium order-disorder phase transition

\[ LRO = C^Fe_1 - C^Fe_2 = \frac{N^Fe_1}{N_1} - \frac{N^Fe_2}{N_2} \]
PHASE TRANSITION TEMPERATURES

Equilibrium order-disorder temperature decreases with particle size.

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>To (bulk)</td>
<td>1510 K</td>
<td>1572 K</td>
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<tr>
<td>To (d=5.94 nm)</td>
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<td>To (d=3.5 nm)</td>
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<td></td>
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<tr>
<td>T_Curie (bulk)</td>
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Conclusions

• Results show that small particles (3.5 nm) can have long-range order at room temperature; however, results suggest the driving force from disordered to ordered phase decreases with decreasing size.

• Kinetic disorder-order calculations are needed to determine the time scale and feasibility of ordering small particles.