Magnetization dynamics in colloidal magnetic nanocrystals

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Acknowledgment

Graduate students

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Ultrafast manipulation of magnetization

Demagnetization

Magnetization

Spin switching

by fast electric current, magnetic field or optical pulse with applications data storage and switching devices
Magnetic properties in nanometer scale

• Critical temperature, $T_c(d)$, of magnetic ordering

\[
\frac{T_c(d) - T_c(\infty)}{T_c(\infty)} = \pm \left( \frac{d}{d_0} \right)^{-\lambda}
\]

$d$: diameter

Lang et al, PRB, 73, 224444 (2006)

• Size-dependent magnetization of superparamagnetic NCs

\[
M(T, H, V) = M_s \left[ \coth \left( \frac{\mu_v VH}{kT} \right) - \frac{kT}{\mu_v VH} \right]
\]

$M_s$: saturation magnetization, $\mu_v$: volume magnetization
$V$: volume of nanocrystal, $H$: magnetic field, $T$: temperature

Unpublished Result

• Superparamagnetic relaxation time ($\tau$)

\[
\tau = \tau_0 \exp \left( \frac{E_a}{kT} \right)
\]

$E_a$ (magnetic anisotropy energy)

\[
E_a = K_{eff} V \sin^2 \theta
\]

$\theta$: angle between easy axis and $\vec{\nabla}$
Focus of this study

• Size effect on ultrafast optically induced magnetization dynamics

• Chemical and structural tuning of magnetization dynamics

• Surface and medium effect on magnetization dynamics

Material and technique used

1. Chemically synthesize colloidal superparamagnetic nanocrystals

2. Time-resolved Faraday rotation
Colloidal nanocrystals as model nanoscale magnets

- Size, shape and compositional control

- Core/shell structure with hetero interface

- Surface modification with organic molecules

\begin{align*}
\text{Fe}_3\text{O}_4 & \quad \text{MnFe}_2\text{O}_4 \\
\text{J. Crystal Growth} & \quad \text{J. Am. Chem. Soc.} \\
2004, 263, 616 & \quad 2004, 126, 11458 \\
\text{CoFe}_2\text{O}_4@\text{MnO} & \quad \text{PtFe}@\text{MnO} \\
\text{J. Am. Chem. Soc.} & \quad \text{J. Am. Chem. Soc.} \\
2005, 127, 9354 & \quad 2006, 128, 1042. \\
\text{NC} & \quad \text{NH}_2 \\
\text{CH}_3\text{(CH}_2\text{)}_N\text{NH}_2 & \quad \text{Metallophorphyrin} \\
\end{align*}
Chemical synthesis of colloidal magnetite nanocrystals

- Fe(acac)₃ is heated (250-300°C) in the mixture of amines, diols in high boiling point liquid.
- Spherical nanocrystals with diameter of >5nm can be made with narrow size dispersion (<5%)
- Surface is coated with organic molecules for solubility in liquid

(Left) Schlenk line for atmosphere control during the reaction.  
(Right) Flask with temperature controlled heater (right)
Faraday rotation as a tool for probing magnetization (M)

Faraday rotation, \( \theta \)

\[ \theta \propto M \cdot k \]

Linearly polarized light
Magnetic field

\( \mathbf{k} \)

\[ \mathbf{M} \]

\[ \left( \begin{array}{ccc} \varepsilon_1 & ig & 0 \\ -ig & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_2 \end{array} \right) \]

\( E = E_0 \left( (g''+ig'') \frac{1}{2cn_0} \right) \exp \left[ -i \omega \left( t - \frac{n_0 z}{c} \right) - \frac{\omega k_e z}{c} \right] \)

\[ \tilde{\theta} = \frac{\omega g}{2cn_0}, \quad \tilde{\theta} : \text{specific complex Faraday rotation} \]

Phenomenologically, magnetooptic effect measures off-diagonal element of dielectric tensor, which carries information on magnetization.

In simple cases (uniaxial crystal, B//z)
Pump-probe time-resolved Faraday rotation

Pros

- Sub-picosecond time resolution of transient magnetization with a relatively inexpensive setup
- Example: Mossbauer ~ns resolution
- XMCD ~ps resolution, but requires ps synchrotron x-ray source

Cons

- Indirect (magneto-optic) probe of magnetization.
- Optical artifact can complicate interpretation of the signal.
Structure and magnetism of magnetite nanocrystals (NCs)

Lattice structure of magnetite

Tetrahedral A site

Octahedral B site

Adapted from Magnetism, J. Stöhr & H.C. Siegmann

Static magnetic properties of bulk magnetite

Saturation magnetization \( (M_s) = 4.1 \, m_B/ \text{f.u} \)
Curie temperature \( (T_C) = 858 \, \text{K} \)
Magnetocrystalline anisotropy \( (K_A) = 4.5 \times 10^4 \, \text{J/m}^3 \)

Exchange coupling constants

\[ J_{A-A} = -18.1 \, \text{K} \]
\[ J_{A-B} = -27.6 \, \text{K} \]
\[ J_{B-B} = 3.0 \, \text{K} \]

Fe\(^{2+}(d^6)\): \( \uparrow \uparrow \uparrow \uparrow \)
Fe\(^{3+}(d^5)\): \( \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \)

\( S=2, \)
\( m=4m_B \)

\( S=5/2, \)
\( m=5m_B \)

Antiferromagnetic coupling between A- and B-site.
Ferromagnetic coupling between two B sites.
Static optical and magnetic properties of magnetite NCs

**UV-Vis-NIR spectrum and TEM image**

- **Static absorption has no significant size dependence.** – optical transitions seems local in nature, although band-like electronic structure describe the real situation.

**Size-dependent Faraday rotation**

- **Superparamagnetic colloids**
Time-resolved Faraday rotation of magnetite NCs

\[ \Delta \theta \propto M(t) \cdot k \]

Measurement geometry

- Fractional changes in magnetization \((\Delta M(t) / M_0)\) is measured for all the samples.
- Recirculating jet samples at low concentration are used to prevent accumulated thermal effect and interparticle interaction.

Nano Letters 8, 571, (2008)
Comparison with transient absorption

True response of spins or indirect reflection of electronic response?

- Immediate sub-ps demagnetization following excitation.
  → probably not mediated by slow spin-lattice coupling ($\tau \sim 100\text{ps}$).
  Demagnetization occurs probably via excitation of magnon by fast relaxing electrons.

- Early time dynamics of $\Delta M/M_0$ is distinctly different from transient absorption.
  → Measured $\Delta M/M_0$ is a not an electronic artifact.
Pump intensity dependence of $\Delta M(t)/M_0$

- Degree of demagnetization scales linearly with excitation density. At higher excitation fluence, $\Delta M/M_0$ exhibits nonlinear behavior due to multiphoton transitions.

- Saturation of $\Delta M/M_0$ occurs at the excitation density of $\sim 10\%$.

- Recovery of $\Delta M/M_0$ occurs on distinct multiple time scales.
Size dependence of $M(t)/M_0$

**Size-dependent $\Delta M/M_0$**

Larger NC exhibits larger amplitude of demagnetization on the slower time scale. Recovery of $\Delta M/M_0$ is slower in larger nanocrystals.

**Lack of Size-dependent $\Delta OD$**

No significant size dependence on transient absorption – electronic response is insensitive to the size.

Finite-size effect *directly on spin* degrees of freedom

Size-dependent spin correlation?
Transient lattice temperature of photo excited NCs

Transient lattice temperature can be estimated from the period of coherent acoustic phonon

\[ \tau(T) = \frac{2\pi r}{\eta c_L(T)} , \quad \eta \cot(\eta) = 1 - \left( \frac{\eta c_L(T)}{2 c_T(T)} \right)^2 \]

\[ c_L = \sqrt{\frac{C_{11}}{\rho}}, \quad c_T = \sqrt{\frac{C_{44}}{\rho}} \]

\( t \): period, \( r \): radius, \( T \): temperature
Young’s moduli (\( C_{11} \) and \( C_{44} \)) and density (\( \rho \))
\( c_L, c_T \): longitudinal & transverse speed of sound

\( \tau \) increases approximately linearly with increasing temperature

\( \tau = 1.1 \text{ ps (for 4.8 nm)} \)
Transient lattice temperature of photo excited NCs

Fluence dependent lattice temperature

Time-dependent lattice temperature

Average lattice temperature during the first 5 ps after excitation.

Size-dependent temperature decay in NPs roughly $\tau \propto r^2$

Effect of lattice temperature on magnetization of NCs

Langevin function

\[ M(T, H, V) = M_s \left[ \coth \left( \frac{\mu_v VH}{kT} \right) - \frac{kT}{\mu_v VH} \right] \]

- \( M_s \): saturation magnetization,
- \( \mu_v \): volume magnetization (434 emu/cm\(^3\))
- \( V \): volume of nanocrystal,
- \( H \): magnetic field (3000 Oe)
- \( T \): temperature

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>% demagnetization with ( \Delta T = 100K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>4.2</td>
</tr>
<tr>
<td>7.5</td>
<td>3.6</td>
</tr>
<tr>
<td>11</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Heating of spin by hot lattice is not responsible for the observed size dependence of \( \Delta M/M_0 \) under the experimental condition employed.

More likely the size effect directly on spin degrees of freedom
Effect of average spin orbit coupling on $M(t)$

Substitution of Fe$^{2+}$ with Co$^{2+}$ increases average spin-orbit coupling strength → faster spin relaxation is expected.

Faster recovery of $M$ with increasing Co content

Rate of spin-lattice relaxation via Raman mechanism has been correlated with magnetocrystalline anisotropy energy, which is also related to spin-orbit coupling.

Anisotropy constant $K_1$ (J/m$^3$)

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_1$ (J/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>$4.5 \cdot 10^4$</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>$22.3 \cdot 10^4$</td>
</tr>
</tbody>
</table>
Effect of average spin orbit coupling on $M(t)$

Correlation between magnetocrystalline anisotropy and relaxation time

Rate of slow demagnetization by photoexcitation in a series of ferrimagnetic solids was also correlated with spin-orbit coupling
Importance of interface in magnetization

**In (anti)ferromagnetic solids**

- Exchange bias device
- Memory device based on exchange bias
- Metalloporphyrin on Ni/Co
- Spin ordering of magnetic molecules on ferromagnetic substrate
- Control of ferromagnetic order at ferromagnetic/multiferroic interface


**In molecular radicals in solution**

- Solvent molecules around the radical plays a critical role determining e- spin relaxation time
- Solvent can provide
  1. fluctuating potential and spin orbit coupling
  2. Phonon bath for spin-lattice relaxation

**In nanocrystals**

- Intermediate between bulk solid and molecular radicals?
Effect of surrounding organic medium on $M(t)$

Is nanocrystals small enough to be affected by the solvent?

- Overlap of Raman spectrum with spin excitation spectrum
- Viscosity

Potential factors of solvent affecting $M(t)$ of nanocrystals
Summary

• Strong size effect on recovery dynamics of magnetization following optical demagnetization

• Spin-orbit coupling strength vs. magnetization recovery dynamics in ferrite nanocrystals

• Effect of surrounding solvent molecules on the magnetization recovery dynamics

• Surface-passivation effect