Faraday Rotation Enhancement in Magnetic Core/Gold Shell Nanoparticles

> Condensed Matter Seminar Kansas State University October 29, 2010

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Gary Wysin collaboration with Viktor Chikan, chemistry

wysin@phys.ksu.edu www.phys.ksu.edu/personal/wysin Nanoparticle Electromagnetics

- Gold plasmonic responses in spherical NPs.
- What is and what causes Faraday Rotation?
- Dielectric response, absorption, and FR.
- Gold shell effects on magnetic core.
- Response of a collection of NPs.

ABSTRACT

We report enhanced optical Faraday rotation in gold-coated maghemite (γ-Fe₂O₃) nanoparticles. The Faraday rotation spectrum measured from 480 – 690 nm shows a peak at about 530 nm, not present in either uncoated maghemite nanoparticles or solid gold nanoparticles. This
peak corresponds to an intrinsic electronic transition in the maghemite nanoparticles and is consistent with a near-field enhancement of
Faraday rotation resulting from the spectral overlap of the surface plasmon resonance in the gold with the electronic transition in maghemite. This demonstration of surface plasmon resonance-enhanced magneto-optics (SuPREMO) in a composite magnetic/plasmonic nanosystem may enable design of nanostructures for remote sensing and imaging of magnetic fields and for miniaturized magneto-optical devices.

Surface Plasmon Resonance Enhanced Magneto-Optics (SuPREMO): Faraday Rotation Enhancement in Gold-Coated Iron Oxide Nanocrystals

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Received January 1, 2009; Revised Manuscript Received March 2, 2009 (Nanoletters)

gold-coated γ -Fe₂O₃ nanoparticles





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The Faraday rotation spectra of uncoated and gold-coated γ -Fe₂O₃ nanoparticles are compared in Figure 3b. The goldcoated γ -Fe₂O₃ nanoparticles show an overall similar Faraday rotation spectrum to the uncoated particles, with the exception of a sharp peak that appears around 530 nm. The uncoated γ -Fe₂O₃ nanoparticles show only a weak shoulder in this region; no well-resolved resonant feature can be discerned. A simple "non-interacting" mixture of γ -Fe₂O₃ nanoparticles and colloidal gold nanospheres (green curve in Figure 3b) with an absorbance matched to that of the goldcoated γ -Fe₂O₃ nanoparticle sample also does not show the sharp Faraday rotation peak at 530 nm. This demonstrates that the rotation peak is not due merely to the presence of the gold component, but rather is a consequence of the close proximity of the gold and the γ -Fe₂O₃ in the composite γ -Fe₂O₃ /gold nanostructure.

The origin of the Faraday rotation peak at 530 nm can be traced to the electronic structure of the γ -Fe₂O₃, specifically the crystal field transitions of Fe³⁺ 3d⁵ electrons that dominate the visible spectrum of iron oxides.^{59,60} The crystal field

gold-shell on maghemite (Fe_2O_3) cores (from Viktor Chikan's lab)



Figure 3 (b) Variation of color change when the thickness of gold onto the surface of the nanoparticles is increased.

Viktor Chikan's core/shell particles



Figure 3 (a) UV-vis absorption spectrum of 3rd batch synthesis of gold coated Fe₂O₃ nanoparticles. The initial peak position is indicated by an arrow at 606 nm and shifts to 532 nm with increasing thickness of gold shell.

Viktor Chikan's core particles



Figure 2 (a) TEM image of Fe_2O_3 nanoparticles used in the experiment.

Viktor Chikan's core/shell particles, at $\lambda = 632$ nm



Figure 4 (b) Experimental Verdet constant of gold coated Fe_2O_3 nanoparticles only (normalized by the volume fraction of the particles) as a function of gold shell thickness



A nearly uniform polarization is induced in the NP. Its amplitude depends on the dielectric function $\epsilon(\omega)$. How to describe effects on the light? **Bulk Plasma oscillations**





$$E = -\frac{\sigma}{\epsilon_0}$$

n = electron number density z = electron gas displacement

newtonian mechanics:

 $QE = M\ddot{z}$

$$-\left(enV\right)\left(-\frac{\sigma}{\epsilon_0}\right) = \left(mnV\right)\ddot{z}$$

$$-\left(\frac{ne^2}{\epsilon_0}\right)z = m\ddot{z}$$

$$\ddot{z} = -\frac{ne^2}{m\epsilon_0} \ z = -\omega_p^2 \ z$$

About electric polarization P



Spherical conductor, plasma oscillations

$$\omega_s = \sqrt{\frac{ne^2}{3m\epsilon_0}} = \frac{\omega_p}{\sqrt{3}}$$

z = electron gas displacement



Geometry affects the resonance frequency

bulk gold: $n = 5.90 \times 10^{28} / m^3$ $\omega_p = 1.36 \times 10^{16} \text{ rad/s}$ $\lambda_p = 138.5 \text{ nm}$ $n = 5.90 \times 10^{28} / m^3$ spherical gold: $\omega_{s} = 7.85 \times 10^{15} \text{ rad/s}$ $\lambda_s = 240 \text{ nm}$

Sphere in a host medium, Laplace eqn. solution. dielectric response



$$\Phi_{\text{outside}} = -\left[r - \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)\frac{a^3}{r^2}\right]E_0\cos\theta$$

$$\vec{E}_{\text{outside}} = \vec{E}_0 + \frac{\vec{p}\cdot\vec{r}}{4\pi\epsilon_a r^3}$$

induced electric dipole:
$$\vec{p} = \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)\left(4\pi a^3\epsilon_a \vec{E}_0\right)$$

Resonance of a conducting sphere



divergence when:

$$2\epsilon_a + \epsilon_b = 0$$

Drude model, free electron gas:

$$\epsilon_b(\omega) = \epsilon_0 \left[1 - \frac{\omega_p^2}{\omega^2} \right]$$

resonance:
$$\implies 2\frac{\epsilon_a}{\epsilon_0} + 1 - \frac{\omega_p^2}{\omega^2} = 0 \implies \omega_{\rm SP} = \frac{\omega_p}{\sqrt{2\frac{\epsilon_a}{\epsilon_0} + 1}}$$

for gold

What about electron response and Faraday rotation?

Use circular polarization, and magnetic field **B** along **k**=k**n**.

EM waves approaching you, the observer:



LEFT circular polarization CCW rotation positive helicity $\boldsymbol{\sigma} \cdot \boldsymbol{n}$

$$\hat{u}_L = \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y}) \ e^{-i\omega t}$$

RIGHT circular polarization CW rotation negative helicity $\boldsymbol{\sigma} \cdot \boldsymbol{n}$

$$\hat{u}_R = \frac{1}{\sqrt{2}} (\hat{x} - i\hat{y}) \ e^{-i\omega t}$$

Free electron response, at frequency ω :

LEFT circular polarization



$$F_{\text{net}} = eE_0 + evB_z = m\omega^2 r$$
$$r = \frac{eE_0}{m\omega^2 - e\omega B_z} = \frac{eE_0}{m\omega(\omega - \omega_B)}$$

cyclotron frequency:

$$\omega_B = \frac{eB_z}{m}$$

RIGHT circular polarization



larger induced electric dipole

Effect on electric permittivity ϵ

permittivity ϵ :polarization:electric dipole: $\epsilon \vec{E} = \vec{D} = \epsilon_0 \vec{E} + \vec{P}$ $\vec{P} = n \vec{p}$ $\vec{p} = -e \vec{r}$

$$\epsilon = \frac{D_0}{E_0} = \frac{\epsilon_0 E_0 + P}{E_0} = \epsilon_0 + \frac{P}{E_0} \qquad \Longrightarrow \qquad \epsilon = \epsilon_0 - \frac{ne^2}{m\omega(\omega \pm \omega_B)}$$

$$k = \frac{2\pi}{\lambda} = \sqrt{\epsilon\mu} \ \omega \qquad \qquad k = \frac{\omega}{c} \sqrt{1 - \frac{\omega_p^2}{\omega(\omega \pm \omega_B)}} \quad \Longrightarrow \quad \lambda_R < \lambda_L$$

Why is there Faraday rotation, and how large is it?

Incident linear polarization, at a single frequency ω : $\vec{E}_{1} = E_{1} \hat{x} - E_{2} \frac{1}{(\hat{w}_{1} + \hat{w}_{2})}$

$$E_{\text{inc}} = E_{\text{inc}} x = E_{\text{inc}} \sqrt{2} (u_R + u_L)$$

$$\text{red} = \lambda_L \quad \hat{u}_L = \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y})$$

$$\text{blue} = \lambda_R \quad \hat{u}_R = \frac{1}{\sqrt{2}} (\hat{x} - i\hat{y})$$

$$\textbf{B} \quad \textbf{k} \quad \textbf{k} \quad \textbf{z} \quad \textbf{z}$$

After propagation through z:

$$\vec{E}(z) = \frac{E_{\rm inc}}{\sqrt{2}} \left[\hat{u}_R e^{ik_R z} + \hat{u}_L e^{ik_L z} \right]$$

$$\vec{E}(z) = E_{\rm inc} \left[\hat{x} \cos\left(\frac{\Delta k}{2}z\right) + \hat{y} \sin\left(\frac{\Delta k}{2}z\right) \right] e^{i\bar{k}z}$$

Faraday rotation: $\Delta \phi = \frac{\Delta k}{2} z$

$$\bar{k} \equiv \frac{1}{2}(k_R + k_L)$$
$$\Delta k \equiv k_R - k_L$$

Faraday rotation: Connection to dielectric matrix E

An electron is affected by several forces:

$$\vec{F} = -m\omega_0^2 \vec{r} - e\vec{E} - e\vec{r} \times \vec{B} - m\gamma \dot{\vec{r}} = m\ddot{\vec{r}}$$

electric Lorentz

harmonic motion:

binding

$$\vec{r}(t) = \vec{r_0} e^{-i\omega t}$$
 incident waves

F₀

$$m\left(\omega^{2}-\omega_{0}^{2}+i\omega\gamma\right)\vec{r}-i\omega e\vec{B}\times\vec{r}=e\vec{E}$$
electron response

damping

$$\begin{pmatrix} m(\omega^2 - \omega_0^2 + i\omega\gamma) & i\omega eB_z \\ -i\omega eB_z & m(\omega^2 - \omega_0^2 + i\omega\gamma) \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}$$

form is: $M \cdot \vec{r} = e\vec{E}$ solution is: $\vec{r} = \begin{pmatrix} x \\ y \end{pmatrix} = M^{-1} \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}$

Result for electric permittivity ϵ

$$\epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P} \qquad \vec{P} = -ne\vec{r} \qquad \vec{r} = M^{-1} \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}$$

Then magic happens and

$$\epsilon = \begin{pmatrix} \epsilon_{xx} & i\epsilon_{xy} \\ -i\epsilon_{xy} & \epsilon_{xx} \end{pmatrix}$$

$$\epsilon_{xx} = \epsilon_0 - \frac{\left(ne^2/m\right)\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)}{\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)^2 - \left(\omega eB_z/m\right)^2}$$
$$\epsilon_{xy} = \frac{\left(ne^2/m\right)\left(\omega eB_z/m\right)}{\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)^2 - \left(\omega eB_z/m\right)^2}$$

What's important: The eigenstates of \in are the RIGHT/LEFT circular polarization states!

$$\lambda_{1} = \epsilon_{R} = \epsilon_{xx} + \epsilon_{xy} \qquad \hat{u}_{1} = \hat{u}_{R} = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y}) \qquad \text{RIGHT circular}$$
$$\lambda_{2} = \epsilon_{L} = \epsilon_{xx} - \epsilon_{xy} \qquad \hat{u}_{2} = \hat{u}_{L} = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y}) \qquad \text{LEFT circular}$$

for the propagating eigenstates:

$$\epsilon_{R/L} = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\omega\gamma \pm \omega\omega_B} \right)$$

$$\Rightarrow \begin{array}{c} k_R = \sqrt{\epsilon_R \mu_0} \ \omega \\ \Rightarrow \\ k_L = \sqrt{\epsilon_L \mu_0} \ \omega \end{array}$$

Faraday rotation:

$$\Delta \phi = \frac{1}{2}(k_{R}-k_{L})z \quad \Rightarrow \qquad \Delta \phi = \frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z$$
This could be complex.

$$\theta_{F} = \operatorname{Real}\left\{\frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z\right\} = \operatorname{rotation}$$

$$\chi_{F} = \operatorname{Imag}\left\{\frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z\right\} = \operatorname{ellipticity}$$
waves approaching

observer

Faraday rotation at $\omega_{\rm B} \ll \omega$

cyclotron frequency at B=1.0 T $\omega_{\rm R}$ = eB/m = 1.8×10¹¹ rad/s

optical frequency at λ =600 nm $\omega = 2\pi c/\lambda$ =3.1x10¹⁵ rad/s

Then the Faraday rotation is proportional to B:

$$\theta_{\rm F} = \upsilon B z$$

 υ = Verdet constant

Viktor Chikan's core/shell particles, at $\lambda = 632$ nm



Figure 4 (b) Experimental Verdet constant of gold coated Fe_2O_3 nanoparticles only (normalized by the volume fraction of the particles) as a function of gold shell thickness



maghemite core, superparamagnetic gold shell surrounded by host medium, ϵ_a

polarization: $\vec{P} = \frac{\vec{p}}{4\pi a^3/3} = \alpha_s \vec{E}_0$

induced electric dipole (from Laplace eqn. solution):

$$\vec{p} = 3\epsilon_a \frac{\left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right) + \left(\frac{b}{a}\right)^3 \left(\frac{2\epsilon_b + \epsilon_a}{2\epsilon_a + \epsilon_b}\right) \left(\frac{\epsilon_c - \epsilon_b}{2\epsilon_b + \epsilon_c}\right)}{1 + 2\left(\frac{b}{a}\right)^3 \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right) \left(\frac{\epsilon_c - \epsilon_b}{2\epsilon_b + \epsilon_c}\right)} \left(\frac{4\pi a^3}{3}\right) \vec{E_0}$$

$$NP \text{ polarizability } \mathbf{\alpha}_s$$

core/shell NP electrostatics:

$$\langle \vec{E}_{in} \rangle = \underbrace{\begin{pmatrix} 3\epsilon_a \\ 2\epsilon_a + \epsilon_b \end{pmatrix}}_{\{z_{ca} + \epsilon_b \end{pmatrix}} \frac{\left(\frac{3\epsilon_b}{2\epsilon_b + \epsilon_c}\right)}{\left(\frac{3\epsilon_b}{2\epsilon_b + \epsilon_c}\right)} \vec{E}_0$$

$$\langle \vec{E}_{in} \rangle = \underbrace{\begin{pmatrix} 3\epsilon_a \\ 2\epsilon_a + \epsilon_b \end{pmatrix}}_{\{z_{ca} + \epsilon_b \end{pmatrix}} \frac{1 + \left(\frac{b}{a}\right)^3 \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)}{\left(\frac{2\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)} \vec{E}_0$$

$$\langle \vec{E}_{in} \rangle = \underbrace{\begin{pmatrix} 3\epsilon_a \\ 2\epsilon_a + \epsilon_b \end{pmatrix}}_{\{z_{ca} + \epsilon_b \end{pmatrix}} \frac{1 + \left(\frac{b}{a}\right)^3 \left(\frac{\epsilon_b - \epsilon_c}{2\epsilon_a + \epsilon_b}\right)}{\left(\frac{2\epsilon_b - \epsilon_c}{2\epsilon_a + \epsilon_b}\right)} \vec{E}_0$$

$$\Rightarrow \langle \vec{E}_{in} \rangle = F_s \vec{E}_0$$

$$F_s$$

But scattering is from a collection of NPs. Use some kind of effective medium theory.

What are this sample's averaged ϵ_R , ϵ_L ? N=# of NPs

simple averaging (Maxwell Garnet theory): $\langle \vec{E} \rangle = (1 - f)\vec{E}_{0} + f\langle \vec{E}_{in} \rangle = [(1 - f) + fF_{s}]\vec{E}_{0} \implies \vec{E}_{0} = \frac{\langle \vec{E} \rangle}{[(1 - f) + fF_{s}]}$ $\langle \vec{D} \rangle = \langle \epsilon_{eff} \rangle \langle \vec{E} \rangle = \epsilon_{a} \langle \vec{E} \rangle + f\vec{P} = \epsilon_{a} \langle \vec{E} \rangle + f\alpha_{s}\vec{E}_{0} \not\Leftarrow \qquad \checkmark$ $\langle \vec{D} \rangle = \langle \epsilon_{eff} \rangle \langle \vec{E} \rangle = \left[\epsilon_{a} + \frac{f\alpha_{s}}{1 - f + fF_{s}}\right] \langle \vec{E} \rangle \implies \qquad \checkmark$

 $\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & &$

Find this for RIGHT/LEFT polarizations

gold parameters



Gold shell has extra scattering. This increases the effective damping of free electrons.

scattering time

 $\tau = 9.1$ fs.



/ intrinsic scattering

 $\gamma_p = \frac{1}{\tau} + \frac{v_F}{d}$

\ surface scattering



The superparamagnetic Fe_2O_3 core:

fit ϵ_{eff} via absorption: $(v=\pm 1 \text{ for } R/L)$ assumption: $\varepsilon = 1 - \frac{g_0^2}{\omega^2 - \omega_0^2 + i\gamma_0\omega - \nu\omega\omega_B}$ $\alpha = \frac{\omega}{c} \operatorname{Im}\left\{\sqrt{\varepsilon_{\text{eff}}}\right\}_{1}$ (single resonance, bound e) 1.5 smoothed exptl data Fe_2O_3 particles in water, raw exptl data b=4.85 nm radius absorption over 1 cm distance single resonance fit $g_0 = 2.76 \ \mu m^{-1} = 5.20 \ x \ 10^{15} \ rad/s$ $\alpha (cm^{-1})$ $\omega_0 = 2.686 \,\mu\text{m}^{-1} = 5.06 \,\text{x} \, 10^{15} \,\text{rad/s}$ (372 nm) Fits the primary $\gamma_0 = 1.532 \ \mu m^{-1} = 2.886 \ x \ 10^{15} \ rad/s \ (0.347 \ fs)$ resonance near



Fits the primary resonance near 350 nm, that is responsible for faraday rotation.

The superparamagnetic Fe_2O_3 core:

radius b = 4.85 nmvolume $V = 4\pi b^3/3 = 478 \text{ nm}^3$



saturation magnetization M=414 kA/m uniaxial anisotropy $K_A = 4700 \text{ J/m}^3$

anisotropy energy $K_A V=14 \text{ meV}$ (thermal energy $k_B T=26 \text{ meV}$)

magnetic moment $m = MV \approx 21000 \mu_B$

internal field $B_{in} \approx 5.5B_{external}$ (cyclotron freq. $\omega_B = eB_{in}/m_e$)

enhanced compared to the gold











Viktor's core/shell particles, at $\lambda = 632$ nm



Figure 4 (b) Experimental Verdet constant of gold coated Fe_2O_3 nanoparticles only (normalized by the volume fraction of the particles) as a function of gold shell thickness

Summary

- A model for $\epsilon(\omega)$ was developed to calculate Faraday rotation in core/shell NPs.
- The gold shell has a plasmonic resonance that depends on thickness.
- Absorption and Faraday rotation are driven by this resonance.
- Clustering of particles needs to be accounted for.