Enhanced Nonlinear Optical Response from Nano-Scale Composite Materials

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with special thanks to:
Nick Lepeshkin, Giovanni Piredda, Aaron Schweinsberg,
John Sipe, David D. Smith, and many others.

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The Promise of Nonlinear Optics

Nonlinear optical techniques hold great promise for applications including:

- **Photonic Devices**
- **Quantum Imaging**
- **Quantum Computing/Communications**
- **Optical Switching**
- **Optical Power Limiters**
- **All-Optical Image Processing**

But the lack of high-quality photonic material is often the chief limitation in implementing these ideas.

Composite Materials for Nonlinear Optics

Want large nonlinear response for applications in photonics

One specific goal:

Composite with $\chi^{(3)}$ exceeding those of constituents

Approaches:

- Nanocomposite materials
  Distance scale of mixing $<< \lambda$
  Enhanced NL response by local field effects
- Microcomposite materials (photonic crystals, etc.)
  Distance scale of mixing $\approx \lambda$
  Constructive interference increase E and NL response

Material Systems for Composite NLO Materials

All-dielectric composite materials

Minimum loss, but limited NL response

Metal-dielectric composite materials

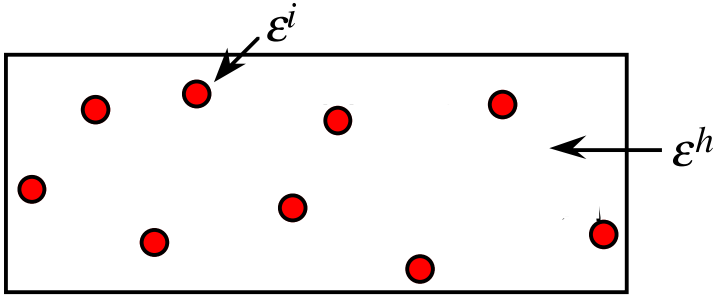
Larger loss, but larger NL response

Note that $\chi^{(3)}$ of gold $\approx 10^6\ \chi^{(3)}$ of silica glass!

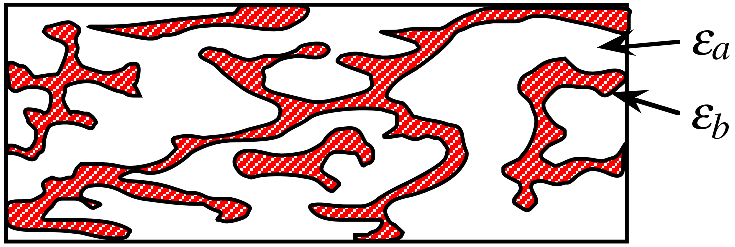
Also, metal-dielectric composites possess surface plasmon resonances, which can further enhance the NL response.

Nanocomposite Materials for Nonlinear Optics

- Maxwell Garnett

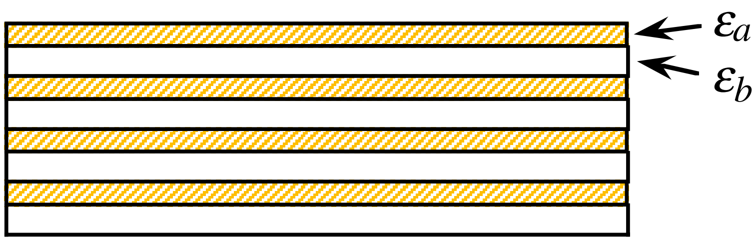


- Bruggeman (interdispersed)



- Fractal Structure

- Layered



scale size of inhomogeneity << optical wavelength

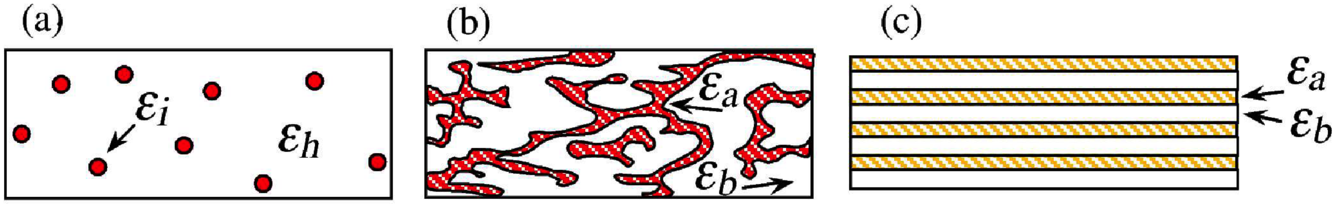
Composite Optical Materials for Photonics

Our approach is to fabricate nanocomposite materials with specialized optical properties.

Motivation: Composite material can possess best properties of each constituent. And can perhaps even exceed properties of each constituent.

Example: Form a composite material for which $\chi^{(3)}$ exceeds those of its constituents. This can occurs because of local-field effects.

We have significant experience in this field (Fischer, Gehr, Nelson), and have achieved a factor of 3 enhancement in $\chi^{(3)}$.



Enhancement of the NLO Response

Under very general conditions, we can express the NL response as

$$\chi_{\mathrm{eff}}^{(3)} = f\, L^2 |L|^2 \chi^{(3)}$$

where *f* is the volume fraction of nonlinear material and *L* is the local-field factor.

For a homogeneous material

$$L = \frac{\varepsilon + 2}{3}$$

For a spherical particle of dielectric constant ε_m embedded in a host of dielectic constant ε_h

$$L = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h}$$

Under appropriate conditions, the product $f\, L^2 |L|^2$ can exceed unity.

Gold-Doped Glass: A Maxwell-Garnett Composite

Developmental Glass, Corning Inc.

Red Glass Caraffe
Nurenberg, ca. 1700

Huelsmann Museum, Bielefeld

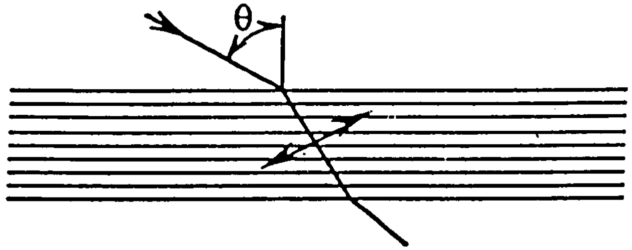
gold volume fraction approximately 10^{-6}
gold particles approximately 10 nm diameter

- Composite materials can possess properties very different from those of their constituents.
- Red color is because the material absorbs very strong in the blue, at the surface plasmon frequency

Demonstration of Enhanced NLO Response

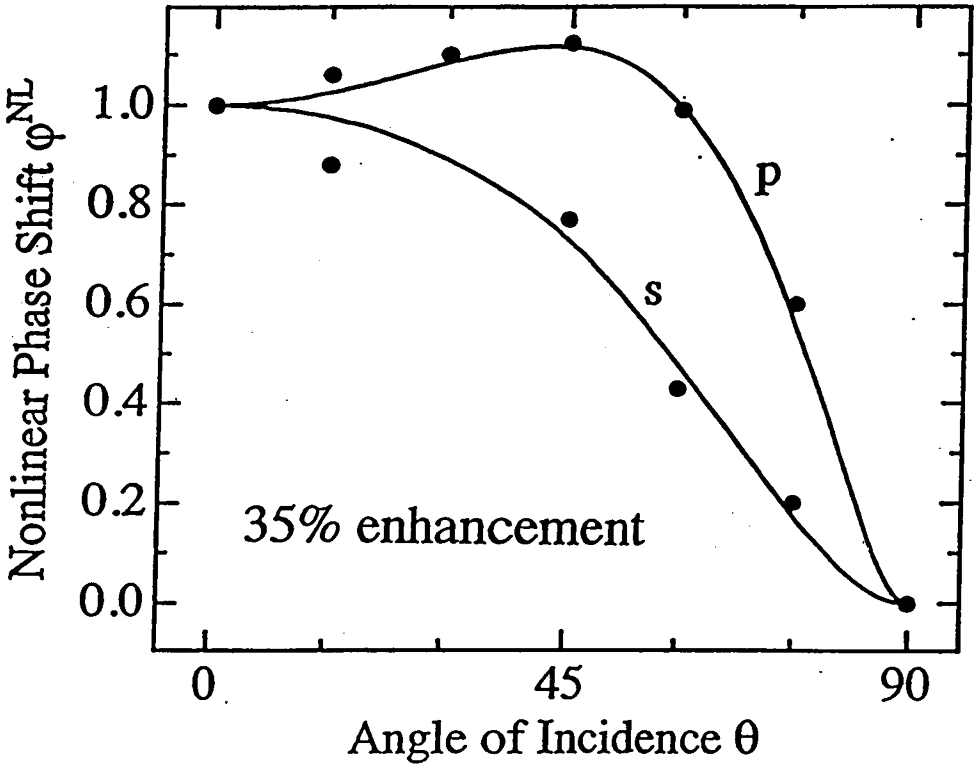
- Alternating layers of TiO_2 and the conjugated polymer PBZT.

- Measure NL phase shift as a function of angle of incidence



$\nabla \cdot \mathbf{D} = 0$ implies that $(\varepsilon \mathbf{E})_\perp$ is continuous.

Thus field is concentrated in *lower* index material.

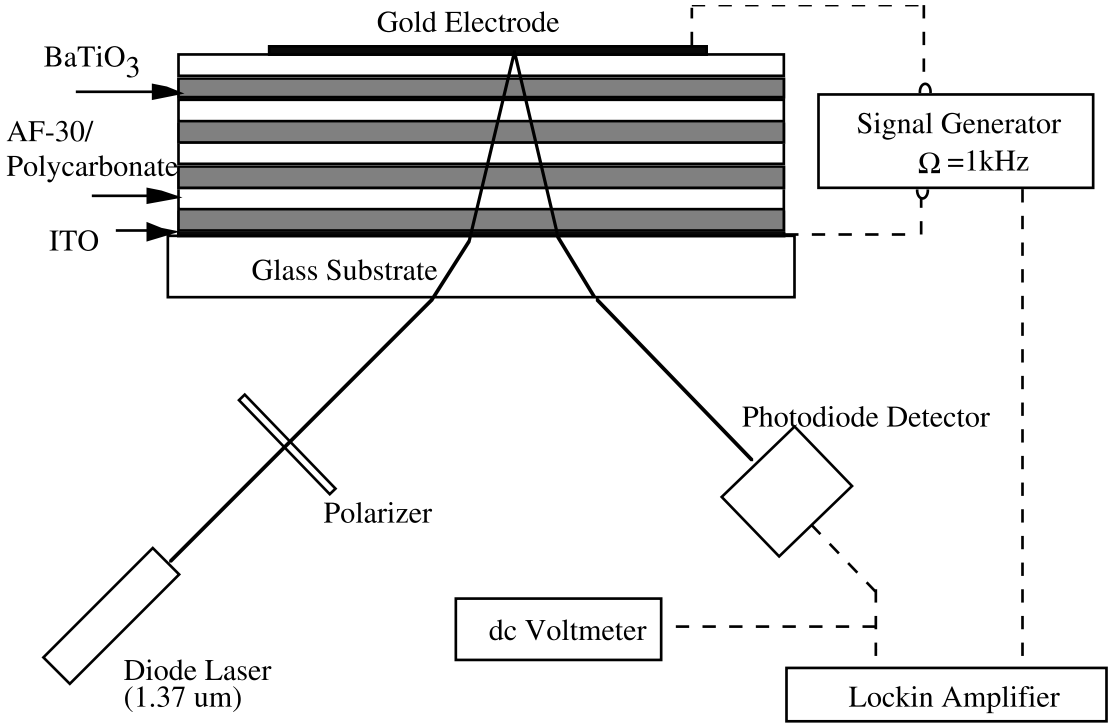


35% enhancement

Fischer, Boyd, Gehr, Jenekhe, Osaheni, Sipe, and Weller-Brophy, Phys. Rev. Lett. 74, 1871, 1995.

Gehr, Fischer, Boyd, and Sipe, Phys. Rev. A 53, 2792 1996.

Enhanced EO Response of Layered Composite Materials



$$\chi^{(eff)}_{ijkl}(\omega';\omega,\Omega_1,\Omega_2) = f_a \left[\frac{\varepsilon_{eff}(\omega')}{\varepsilon_a(\omega')}\right]\left[\frac{\varepsilon_{eff}(\omega)}{\varepsilon_a(\omega)}\right]\left[\frac{\varepsilon_{eff}(\Omega_1)}{\varepsilon_a(\Omega_1)}\right]\left[\frac{\varepsilon_{eff}(\Omega_2)}{\varepsilon_a(\Omega_2)}\right]\chi^{(a)}_{ijkl}(\omega';\omega,\Omega_1,\Omega_2)$$

- AF-30 (10%) in polycarbonate (spin coated)
  n=1.58 ε(dc) = 2.9
- barium titante (rf sputtered)
  n=1.98 ε(dc) = 15

$$\chi^{(3)}_{zzzz} = (3.2 + 0.2i) \times 10^{-21}\ (m / V)^2 \pm 25\%$$

$$\approx 3.2\ \chi^{(3)}_{zzzz}(\text{AF-30 / polycarbonate})$$

3.2 times enhancement in agreement with theory

R. L. Nelson, R. W. Boyd, Appl. Phys. Lett. 74, 2417, 1999.

Role of Metals in Composite NLO Materials

All-dielectric composite materials

- Minimum loss, but limited NL response

Metal-dielectric composite materials

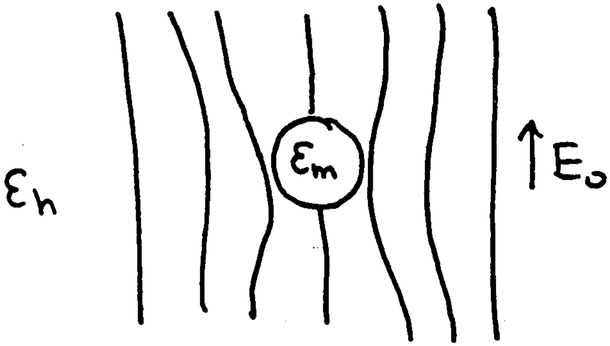
- Larger loss, but larger NL response
- Note that $\chi^{(3)}$ of gold $\approx 10^6$ $\chi^{(3)}$ of silica glass!
- Also, metal-dielectric composites possess surface plasmon resonances, which can further enhance the NL response.

How to minimize loss

- minimize attenuation by dilution (in liquid colloids)
- minimimze attenuation through metal-dielectric PBG structures

Metal / Dielectric Composites

Very large local field effects



$$E_{in} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_0$$

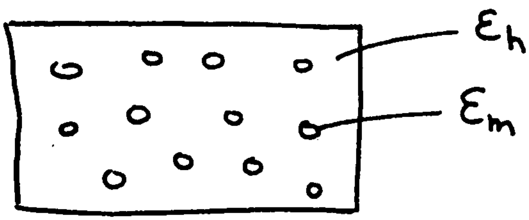
$$\equiv \mathcal{L} E_0$$

(ε_m is negative!)

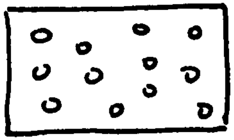
At resonance

$$\mathcal{L} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} \longrightarrow \frac{3\varepsilon_h}{i\varepsilon_m''} \approx (3 \text{ to } 30)\, i$$

$$\chi_{eff}^{(3)} = f \mathcal{L}^2 |\mathcal{L}|^2 \chi_m^{(3)} + (1-f)\, \chi_h^{(3)}$$



Counterintuitive Consequence of Local Field Effects



gold nanoparticles in a liquid dye solution (HITCI)

Both constituents are reverse saturable absorbers $\Longrightarrow$ $\text{Im}\,\chi^{(3)} > 0$

Effective NL susceptibility of composite

$$\chi^{(3)}_{\text{eff}} = f\,\mathcal{L}^2|\mathcal{L}|^2\,\chi^{(3)}_{\text{Au}} + (1-f)\,\chi^{(3)}_{\text{dye sol'n}}$$

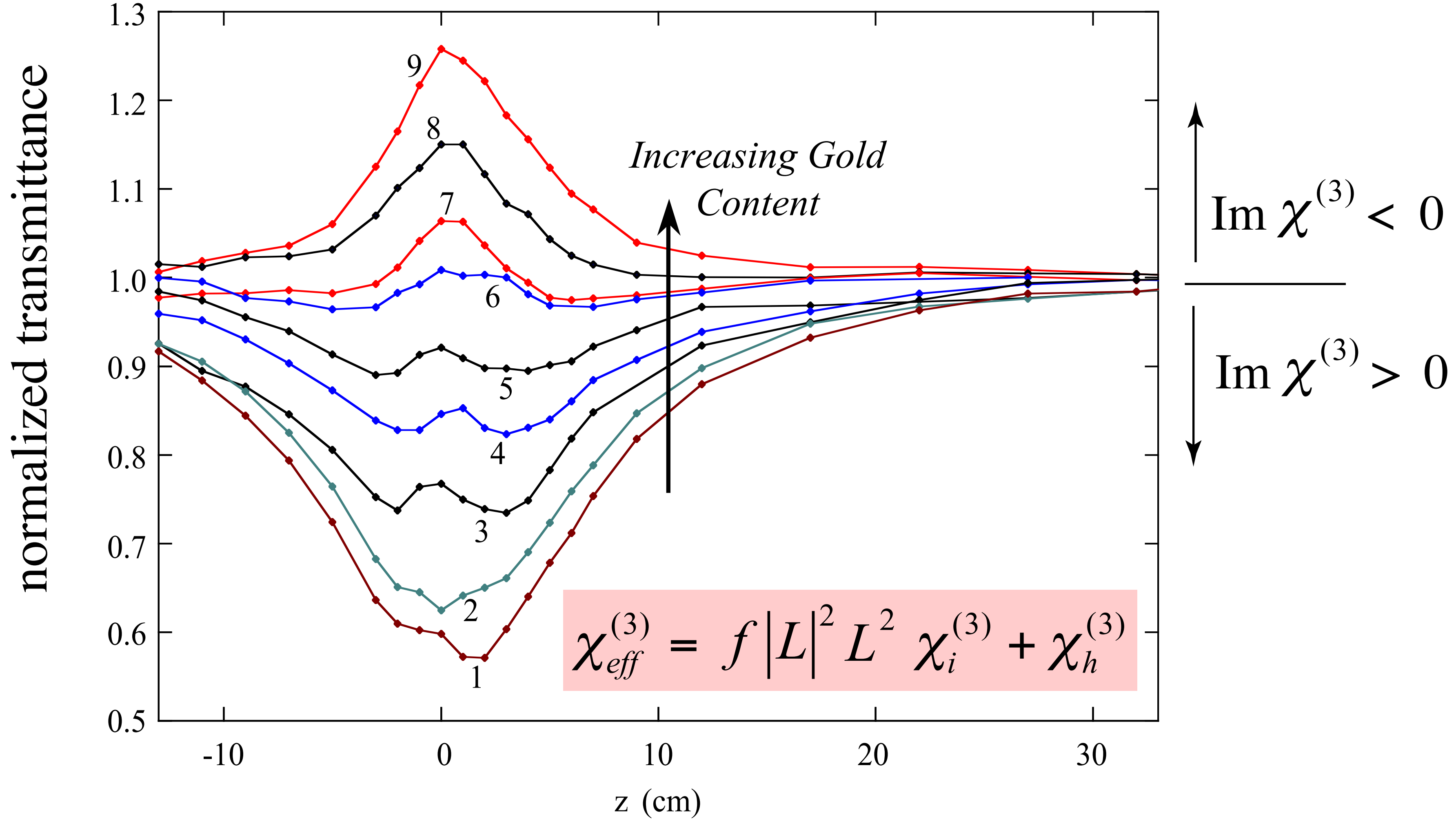
$$\mathcal{L} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} = \text{pure imaginary at resonance!}$$

A cancellation of the two contributions to $\chi^{(3)}$ can occur, even though they have same sign.

Counterintuitive Consequence of Local Field Effects

Cancellation of two contributions that have the same sign

Gold nanoparticles in a saturable absorber dye solution (13 μM HITCI)

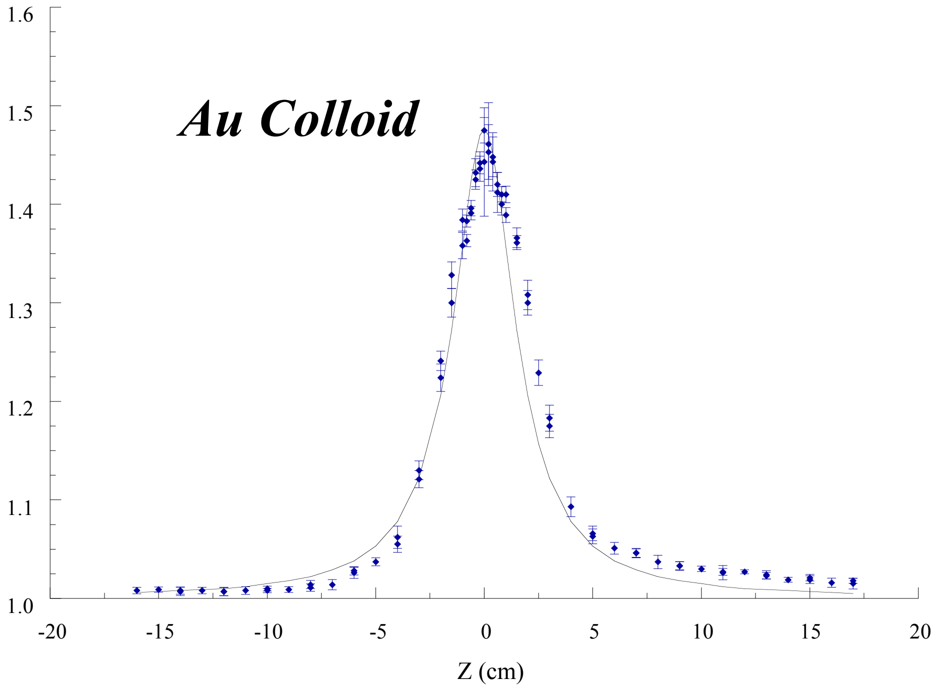


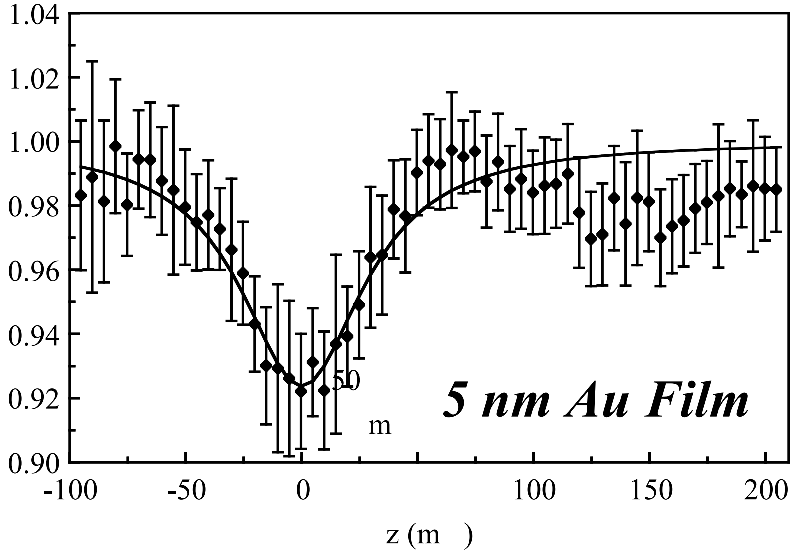
$$\chi_{eff}^{(3)} = f\left|L\right|^2 L^2 \chi_i^{(3)} + \chi_h^{(3)}$$

D.D. Smith, G. Fischer, R.W. Boyd, D.A.Gregory, *JOSA B* **14**, 1625, 1997.

Comparison of Bulk and Colloidal Gold

Open Aperture Z-Scans of Gold Colloid and Au film at 532nm



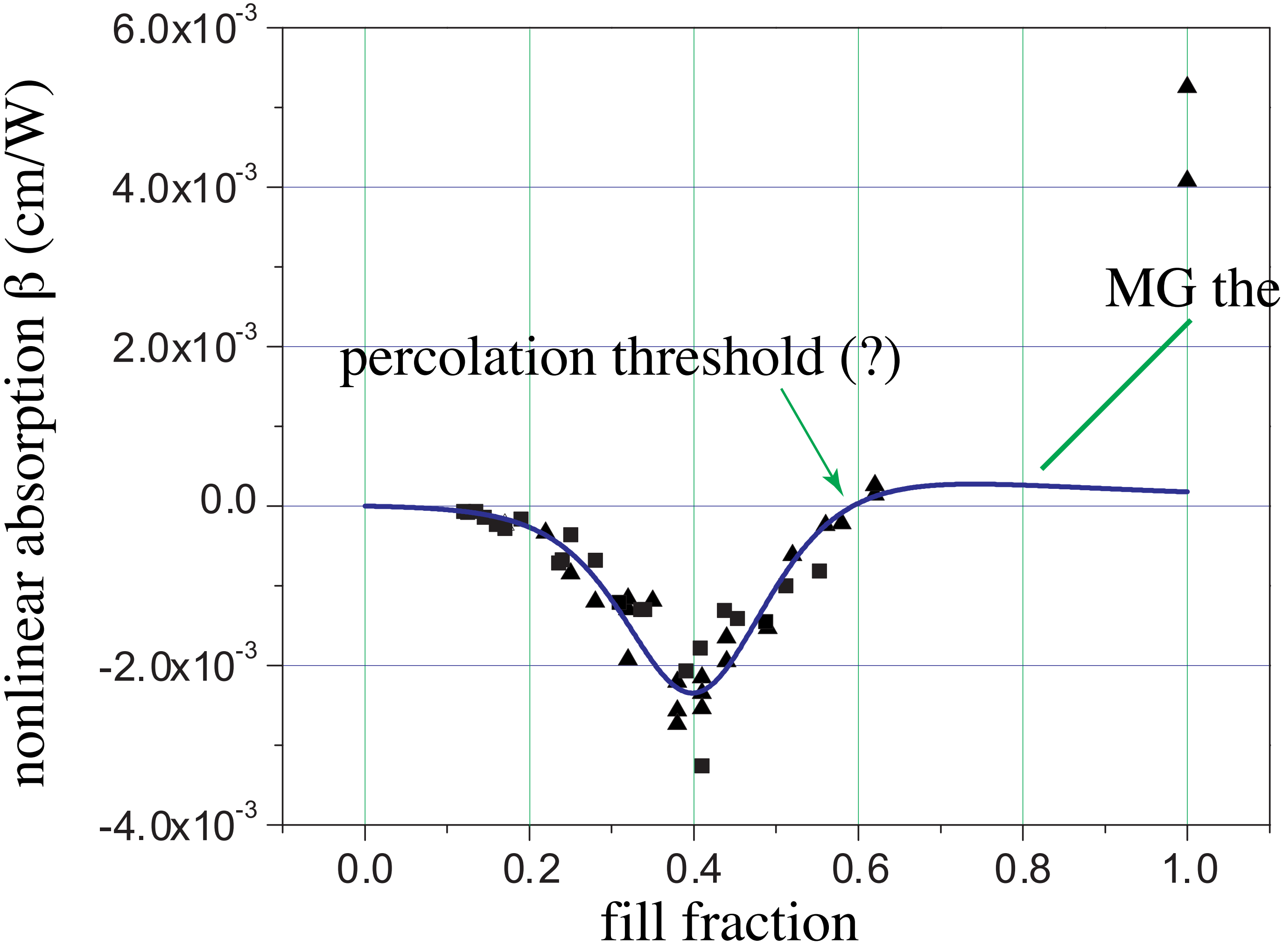


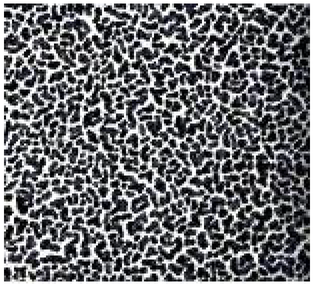
- ➢ Nonlinearities possess opposite sign!

Nonlinear Optical Response of Semicontinuous Metal Films

Measure nonlinear response as function of gold fill fraction

Note: Maxwell Garnett theory not valid at high fill fractions!

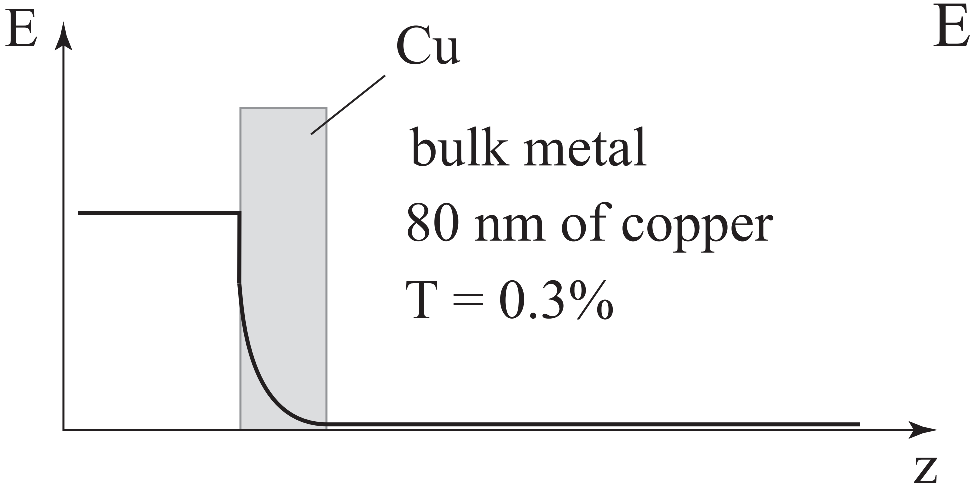




(with D. D. Smith and G. Piredda)

Accessing the Optical Nonlinearity of Metals with Metal-Dielectric Photonic Crystal Structures

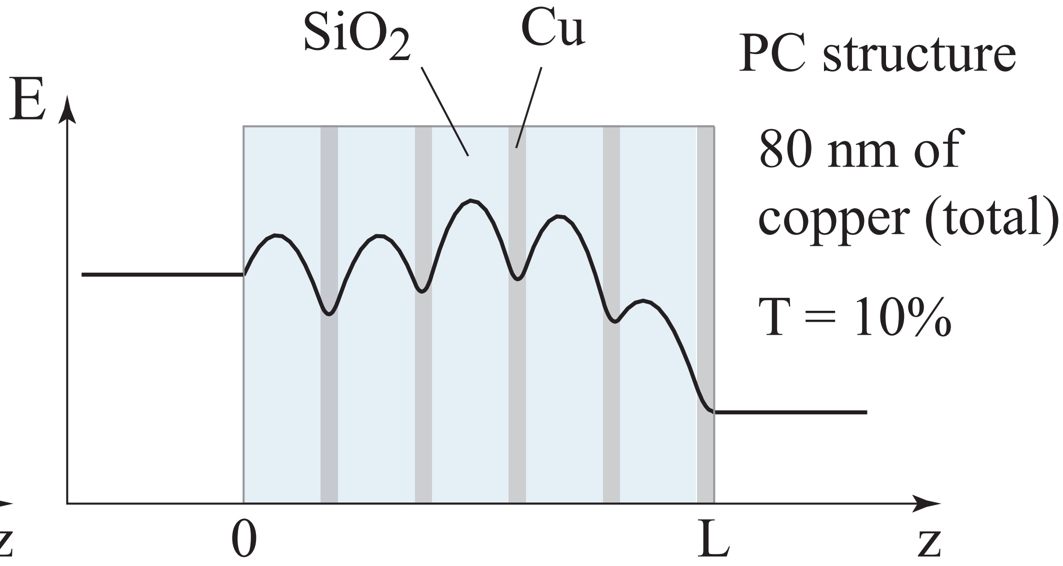
- Metals have very large optical nonlinearities but low transmission
- Low transmission is because metals are highly reflecting (not because they are absorbing!)
- Solution: construct metal-dielectric photonic crystal structure (linear properties studied earlier by Bloemer and Scalora)



bulk metal

80 nm of copper

T = 0.3%



PC structure

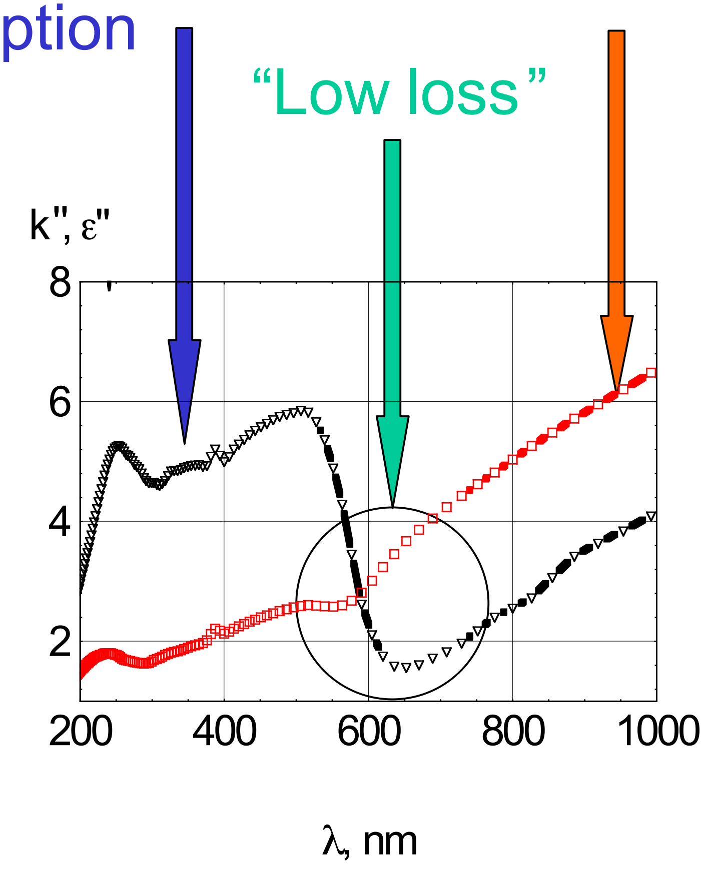
80 nm of copper (total)

T = 10%

Greater than 10 times enhancement of NLO response is predicted!

R.S. Bennink, Y.K. Yoon, R.W. Boyd, and J. E. Sipe, Opt. Lett. 24, 1416, 1999.

“Loss” mechanisms in copper



Intraband (d-p) absorption

“Low loss”

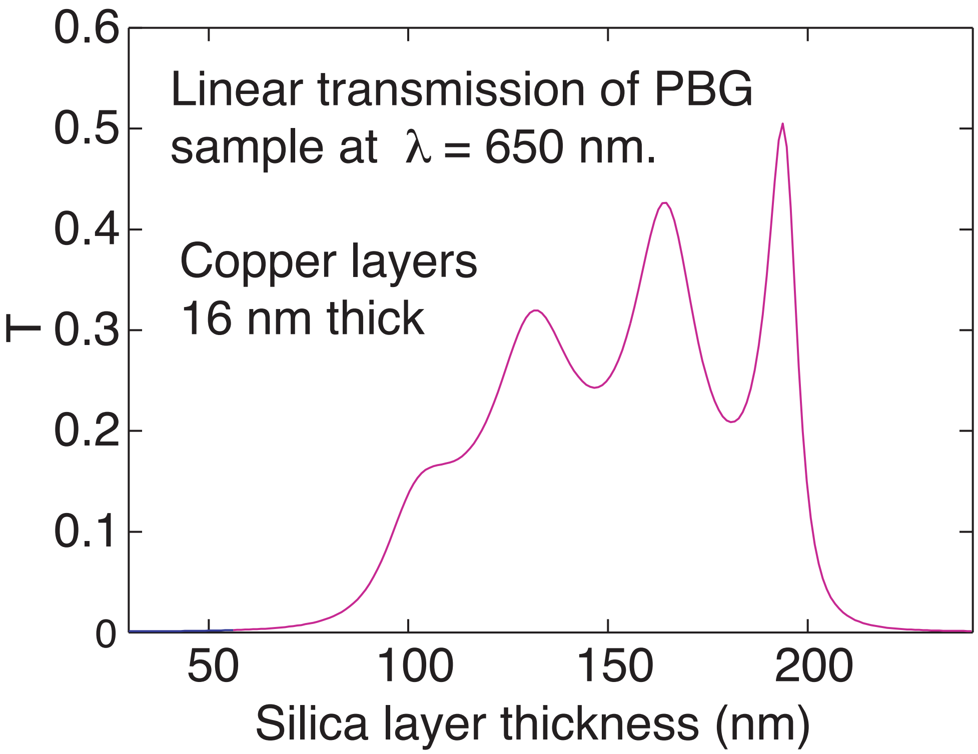
Drude reflection region

Cu

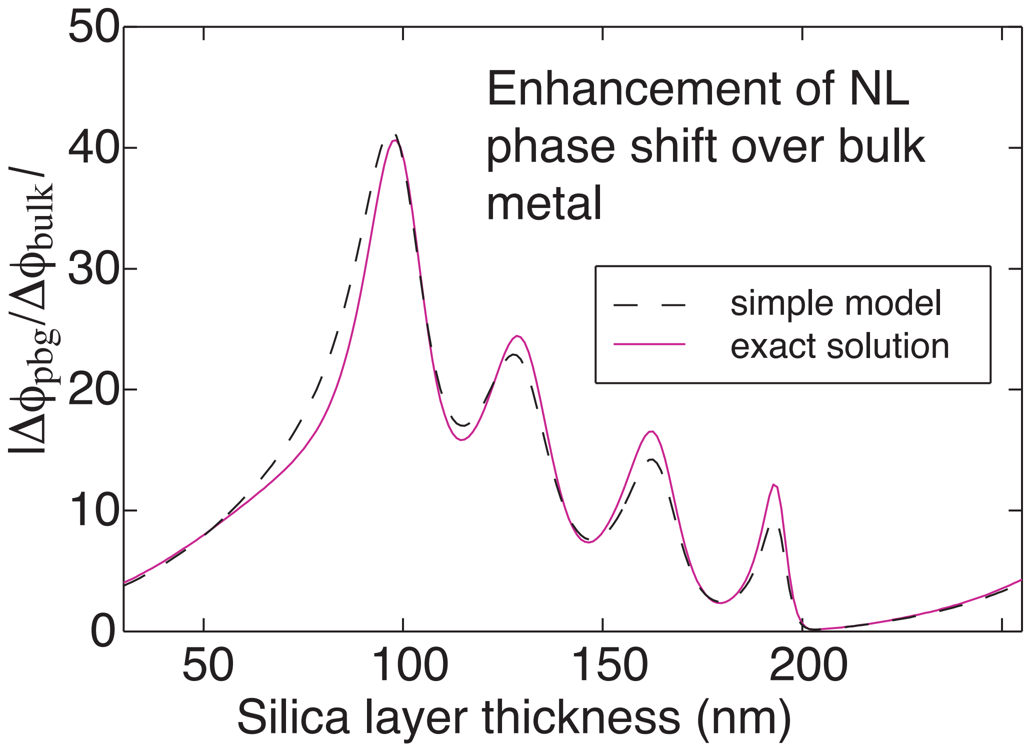
We work at 650 nm.

Accessing the Optical Nonlinearity of Metals with Metal-Dielectric Photonic Crystal Structures

- Metal-dielectric structures can have high transmission.



- And produce enhanced nonlinear phase shifts!

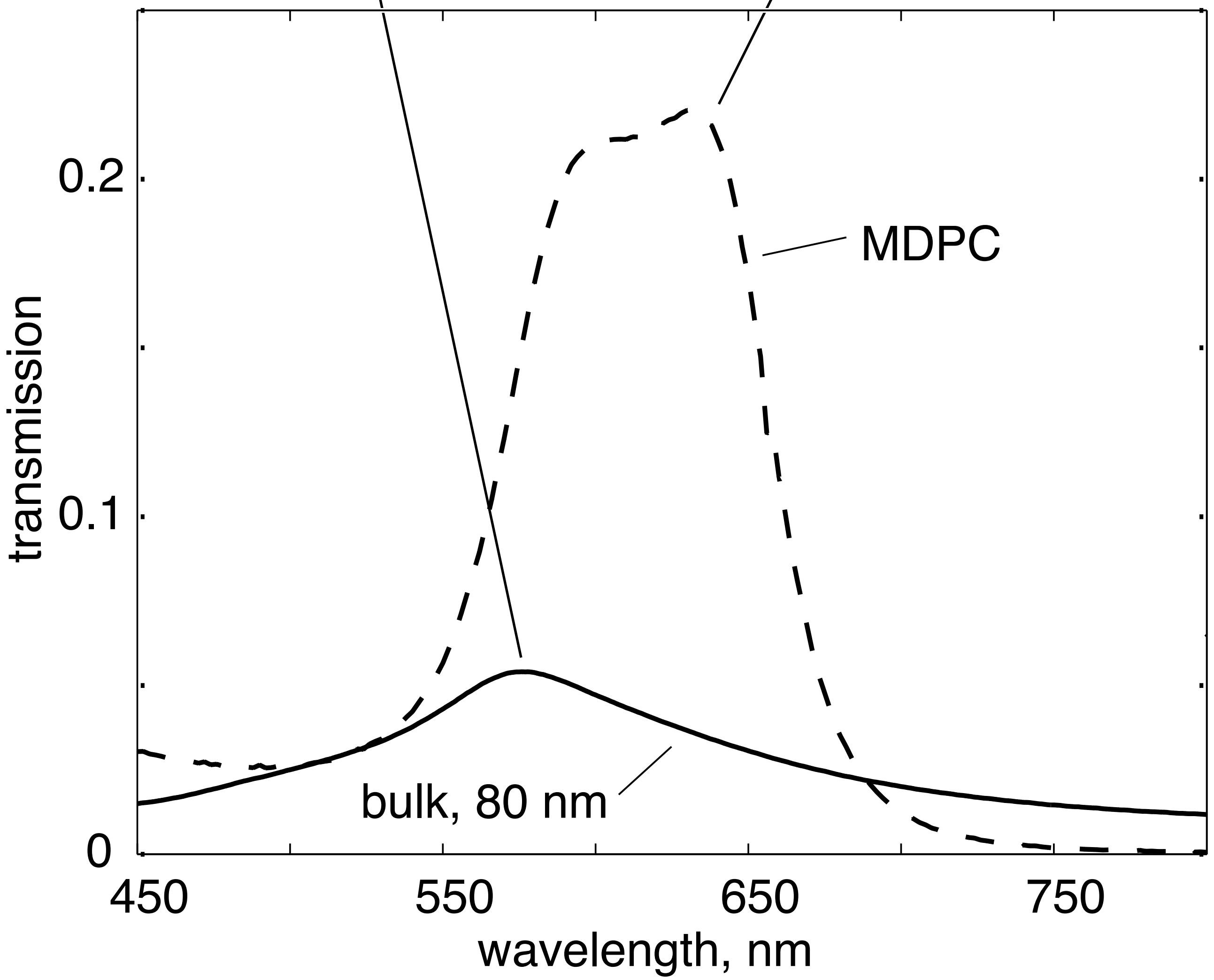


- The imaginary part of $\chi^{(3)}$ produces a nonlinear phase shift! (And the real part of $\chi^{(3)}$ leads to nonlinear transmission!)

Linear Transmittance of Samples

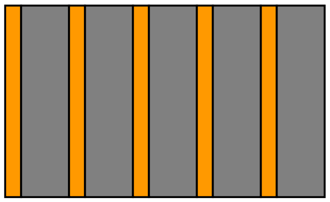
Material (interband) feature

Structural (M/D PC) feature



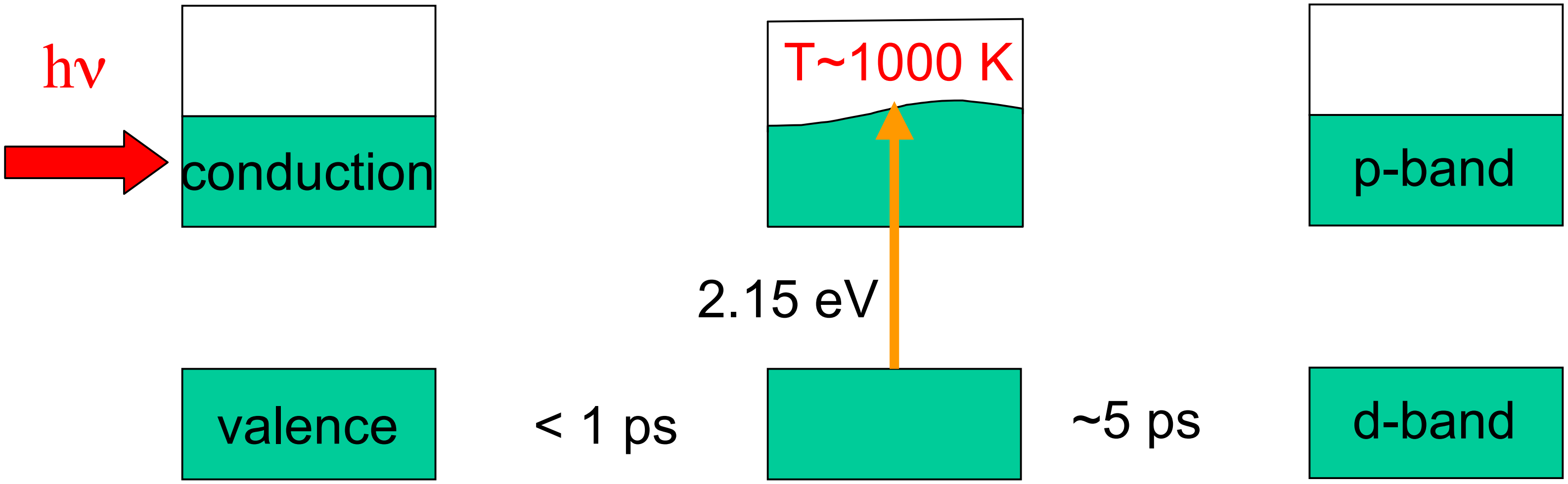
Cu: 40 nm film

M/D PC: Cu / silica



5x16/98 nm
(80 nm total Cu)

Mechanism of nonlinear response: "Fermi smearing"



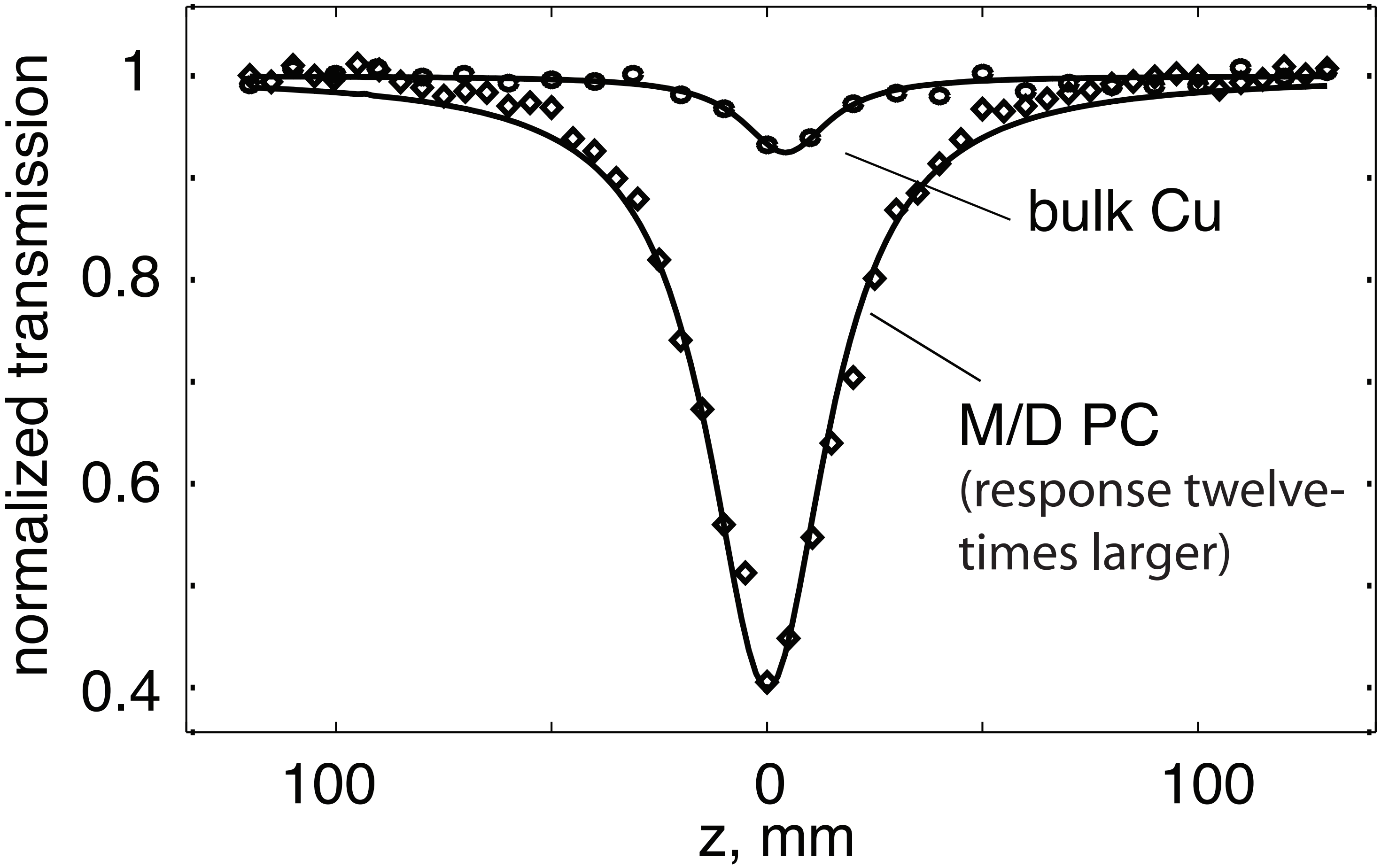
$$\Delta \mathrm{T} \rightarrow \Delta\varepsilon(E_{\mathrm{IB}}) \rightarrow \text{change in optical properties}$$

Near the interband absorption edge, "Fermi smearing" is the dominant nonlinear process

$\chi^{(3)}$ is largely imaginary

G. L. Eesley, Phys. Rev. B33, 2144 (1986)
H. E. Elsayed-Ali et al. Phys. Rev. Lett. 58, 1212 (1987)

Z-Scan Comparison of M/D PC and Bulk Sample



I = 500 MW/cm^2

λ = 650 nm

- We observe a large NL change in transmission
- But there is no measurable NL phase shift for either sample ☹

Lepeshkin, Schweinsberg, Piredda, Bennink, Boyd, Phys. Rev. Lett. 93 123902 (2004).

Current Project: Composite Materials for Laser Systems

Motivation: Design lasers with superior performance based on the use of composite materials.

Specific Goals:

(1) Design a laser host material with a very small n_2 to prevent laser beam filamentation

(2) Control key laser parameters by means of local field effects
- Einstein A coefficient
- laser gain coefficient
- gain saturation intensity

Example: Control laser properties through Einstein *A* coefficient

Why?
- long lifetime gives good energy storage
- short lifetime produces high gain

How to modify the Einstein *A* coefficient

$$A = A_{\text{vac}}\, n_{\text{eff}}\, |L|^2$$

volume averaged

local-field factor of immediate vicinity of emitter

Dependence of Laser Parameters on Properties of Host Material

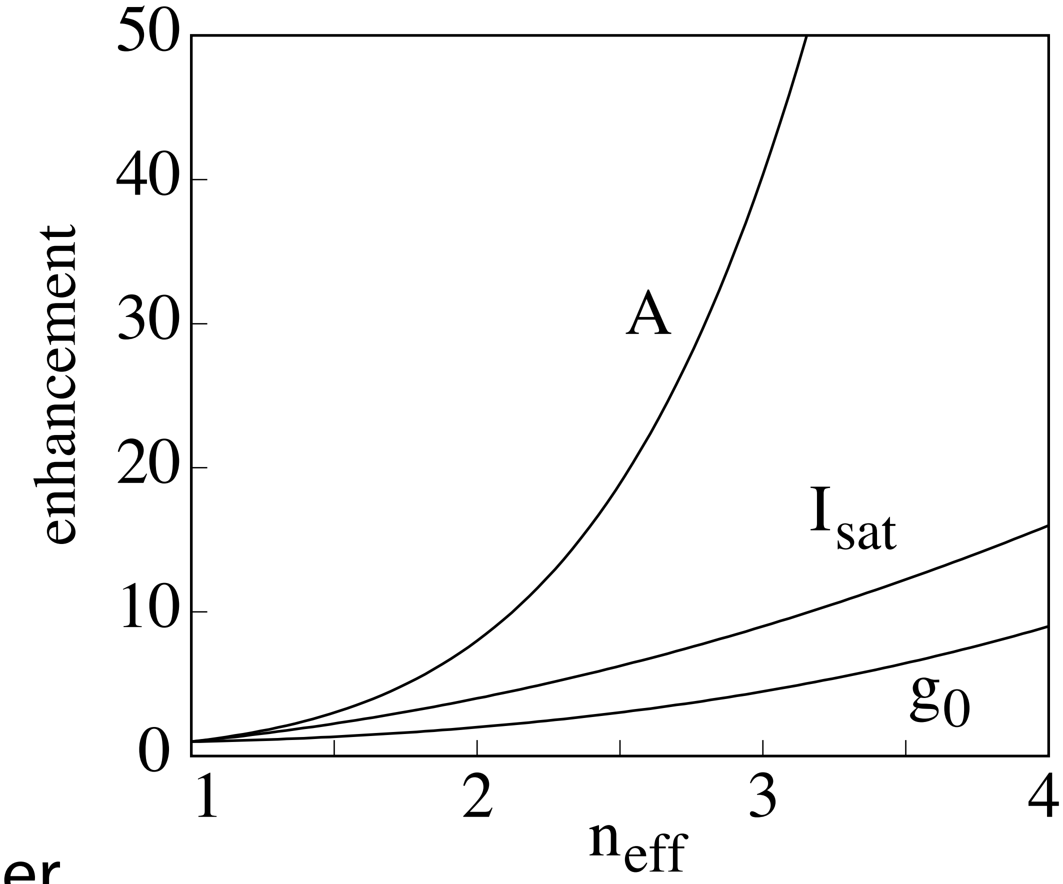
In simplest approximation, laser parameters depend only on effective refractive index of material.

$$A = A_{vac}\, n_{eff} |L|^2$$

$$g_0 = \frac{|L|^2}{n_{eff}} g_{0,\, vac}$$

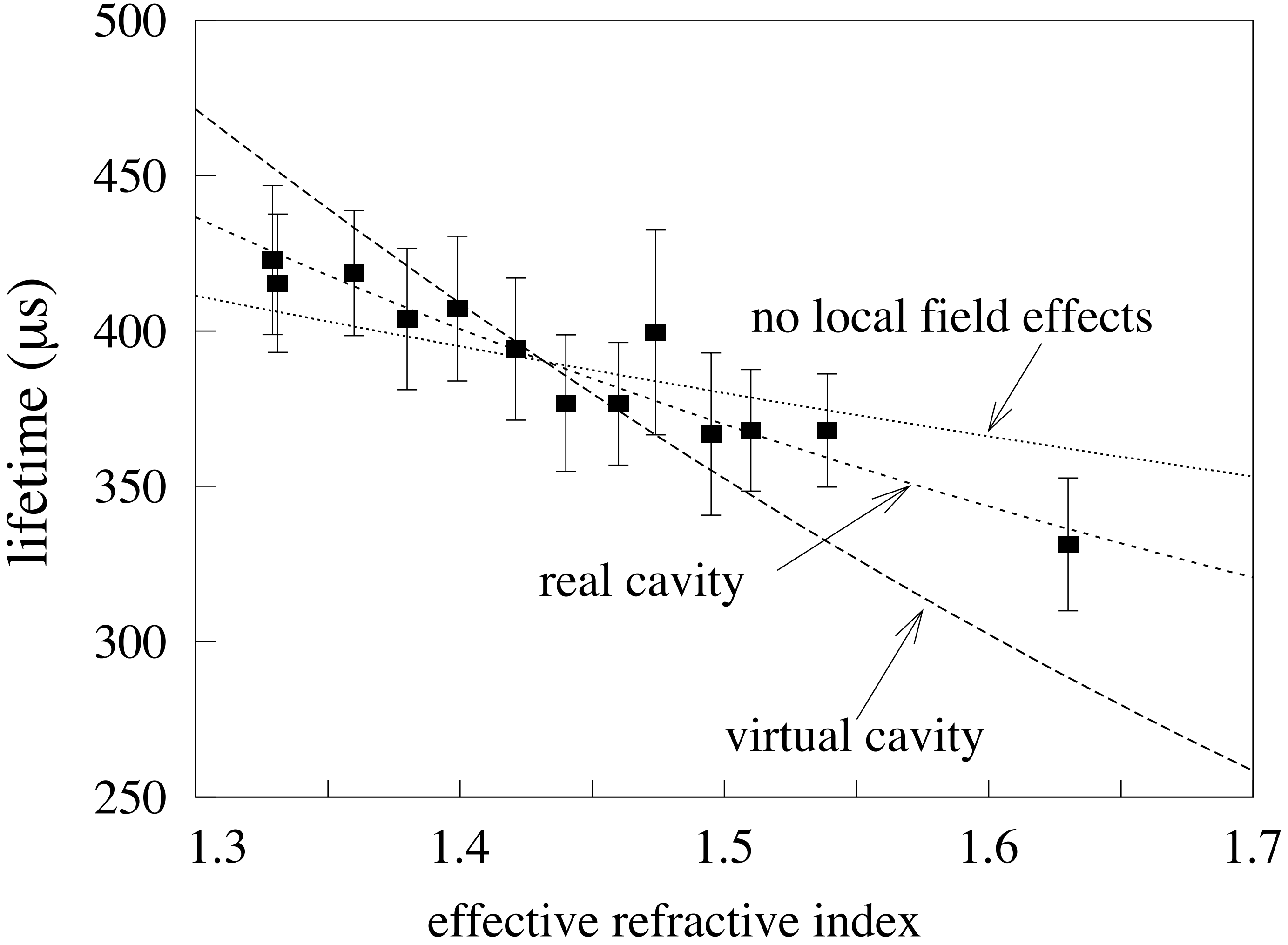
$$I_{sat} = n_{eff}^2 I_{sat,\, vac}$$

$$\text{where} \quad L = \frac{n_{eff}^2 + 2}{3}$$

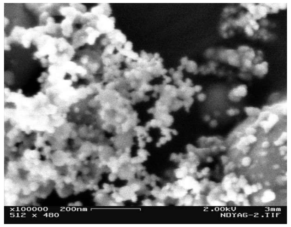


Note that great control of laser properties is possible by this approach

Dependence of Radiative Lifetime on Refractive Index of Host



Nd:YAG nanoparticles
(20 nm) suspended in
a variety of liquids



Real Cavity Model

$$A^{(\mathrm{diel})} = \frac{A^{(\mathrm{vac})}}{n\left(\frac{3n^2}{2n^2+1}\right)^2}$$

Lorentz (Virtual Cavity) Model

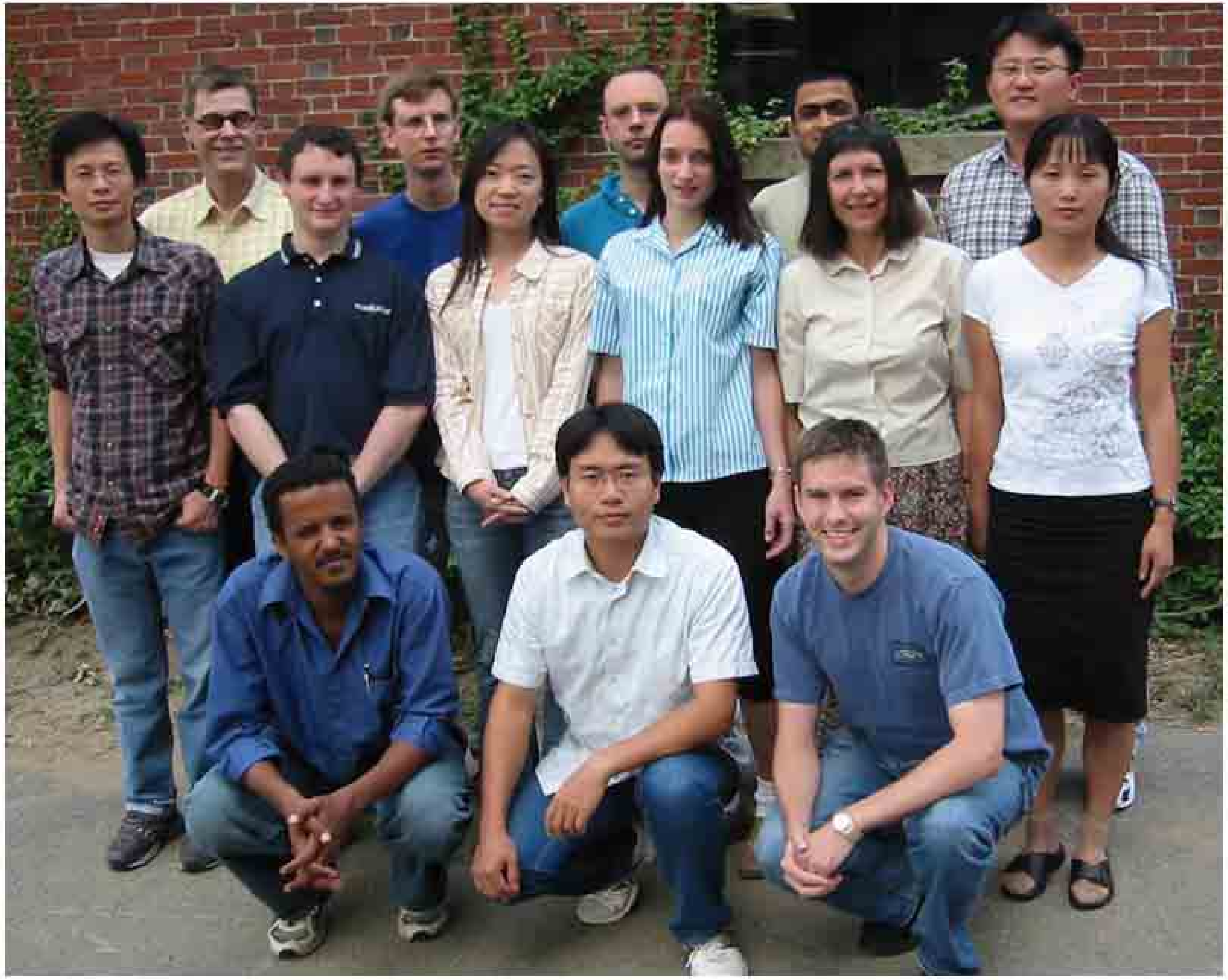
$$A^{(\mathrm{diel})} = \frac{A^{(\mathrm{vac})}}{n\left(\frac{n^2+2}{3}\right)^2}$$

Dolgaleva, Boyd, Milonni, JOSA B 211 516 (2007).

Conclusions

- Both nano-scale and microscale structuring can lead to enhanced nonlinear optical effects
- Influence of nano-scale structuring can be understood in terms of local field effects
- Nano-scale structuring can lead to enhancement (layered results) or cancellation (dye/colloid) of NLO response
- Influence of microscale structuring can be understood in terms of properties of photonic crystals
- Metal / dielectric photonic crystals can be designed to allow access to the large nonlinearity of metals
- We hope that nanocomposite materials will lead to new opportunities in the engineering of laser systems

Special Thanks to My Students and Research Associates



Aloha!

And thank you for your attention.

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