Enhanced Nonlinear Optical Response from Nano-Scale Composite Materials

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with special thanks to:
Ksenia Dolgaleva, 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

Boadly speaking: composites can (at very least) provide best properties of each constituent and can (at best) provide properties exceeding those of its constituents.

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

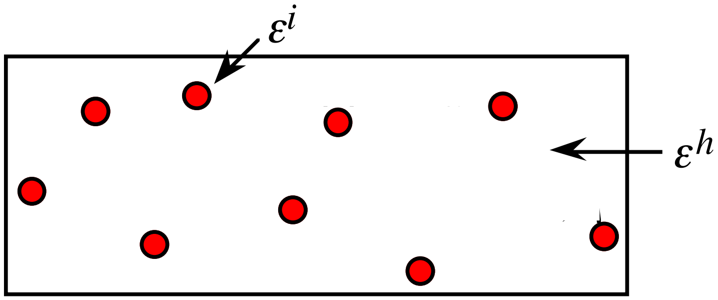
- Minimum loss, but limited NL response

Metal-dielectric composite materials

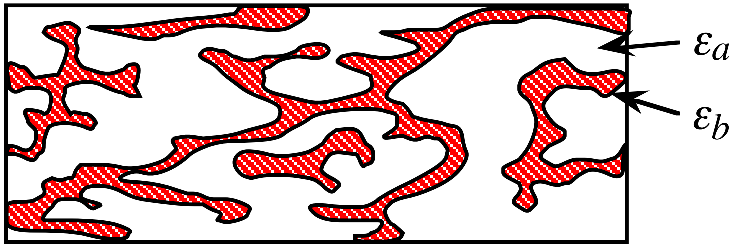
- Larger loss, but larger NL response
- Note that $\chi^{(3)}$ of gold $\approx 10^6 \ \chi^{(3)}$ of silica glass!
- Also, metal-dielectric composites possess surface plasmon resonances, which can further enhance the NL response.

Nanocomposite Materials for Nonlinear Optics

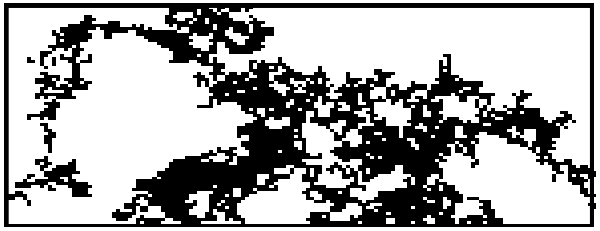
- Maxwell Garnett



- Bruggeman (interdispersed)



- Fractal Structure



- Layered

- In each case, scale size of inhomogeneity << optical wavelength

- Thus all optical properties, such as n and $\chi^{(3)}$, can be described by effective (volume averaged) values

Gold-Doped Glass: A Maxwell-Garnett Composite

Red Glass Caraffe
Nurenberg, ca. 1700

Huelsmann Museum, Bielefeld

Developmental Glass, Corning Inc.

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

Enhancement of the NLO Response

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

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

where f is the volume fraction of nonlinear material and L is the local-field factor, which is different for each material geometry.

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

- For a homogeneous material $L = \dfrac{\varepsilon + 2}{3}$

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

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

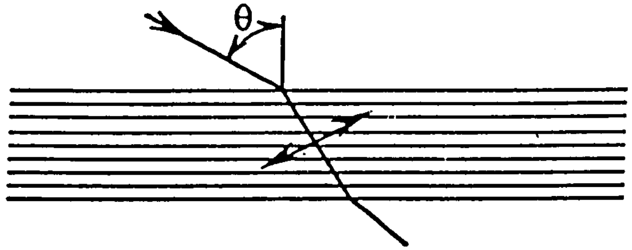
- For a layered geometry with the electric field perpendicular to the plane of the layers, the local field factor for component a is given by

$$L = \frac{\varepsilon_{\text{eff}}}{\varepsilon_{\text{a}}} \qquad \frac{1}{\varepsilon_{\text{eff}}} = \frac{f_{\text{a}}}{\varepsilon_{\text{a}}} + \frac{f_{\text{b}}}{\varepsilon_{\text{b}}}$$

Demonstration of Enhanced NLO Response

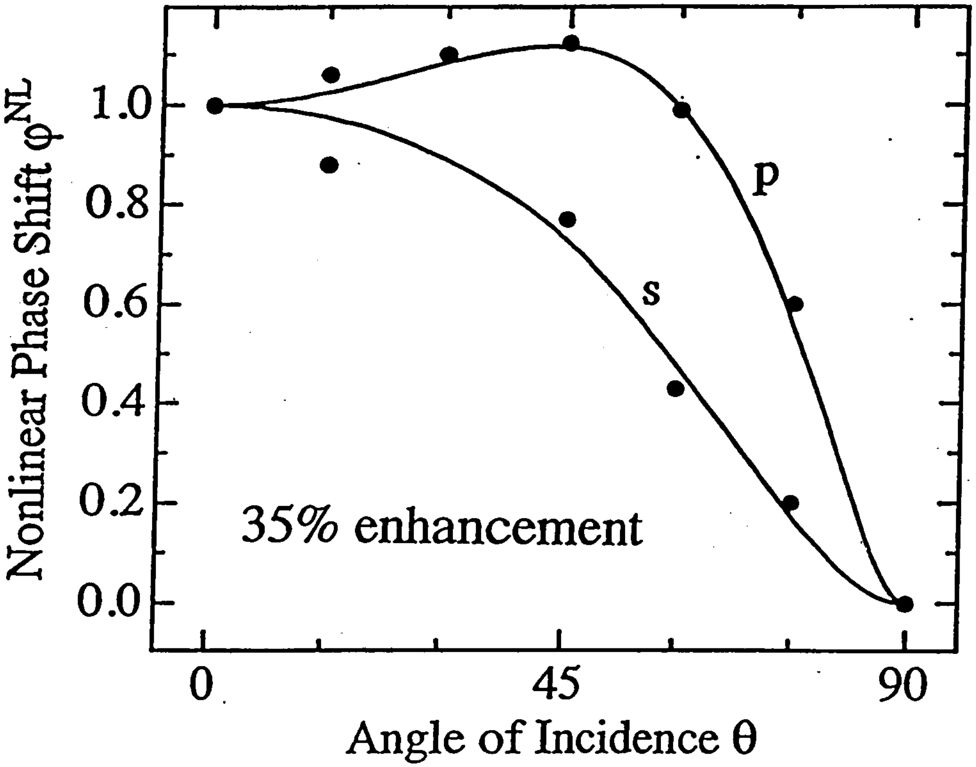
- Alternating layers of TiO_2 and the conjugated polymer PBZT.

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



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

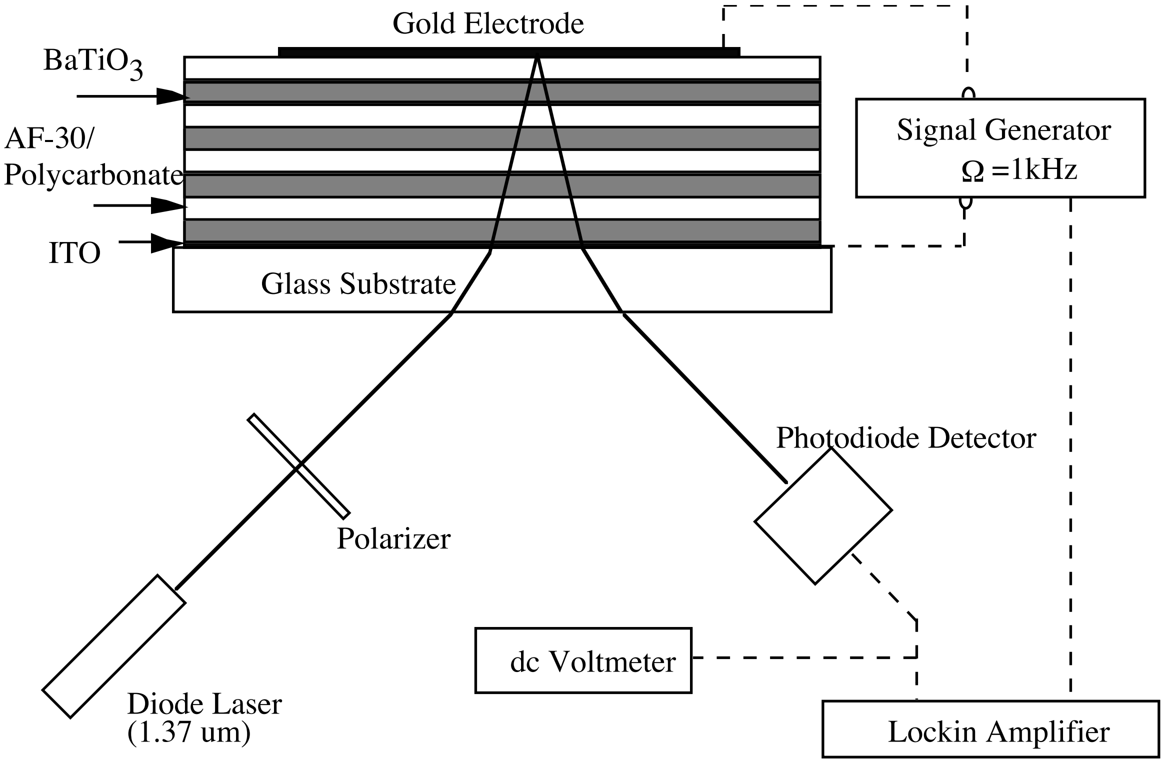
Thus field is concentrated in *lower* index material.



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



- quadratic electrooptic effect
- AF-30 (10%) in polycarbonate (spin coated)

  n=1.58 ε(dc) = 2.9
- barium titante (rf sputtered)

  n=1.98 ε(dc) = 15

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

$$\chi_{zzzz}^{(3)} = (3.2+0.2i)\times 10^{-21}\,(m/V)^2 \pm 25\% \quad \approx 3.2\,\chi_{zzzz}^{(3)}(\text{AF-30 / polycarbonate})$$

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 ≈ 10^6 $\chi^{(3)}$ of silica glass!

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

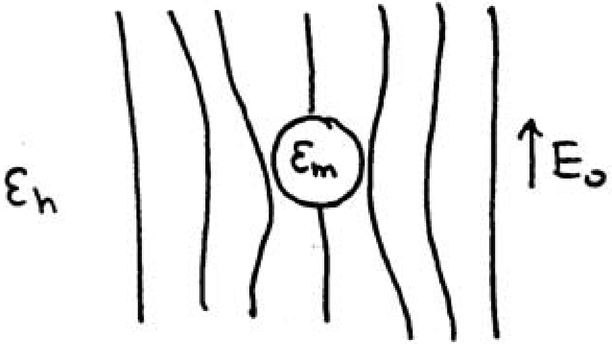
How to minimize loss

  minimize attenuation by dilution (in liquid colloids)

  minimimze attenuation through metal-dielectric PBG structures

Metal / Dielectric Composites

Very large local field effects



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

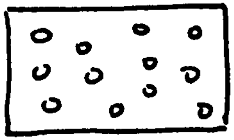
$$\equiv \alpha E_0$$

(ε_m is negative !)

At resonance

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

Counterintuitive Consequence of Local Field Effects



gold nanoparticles in a liquid dye solution (HITCI)

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

Effective NL susceptibility of composite

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

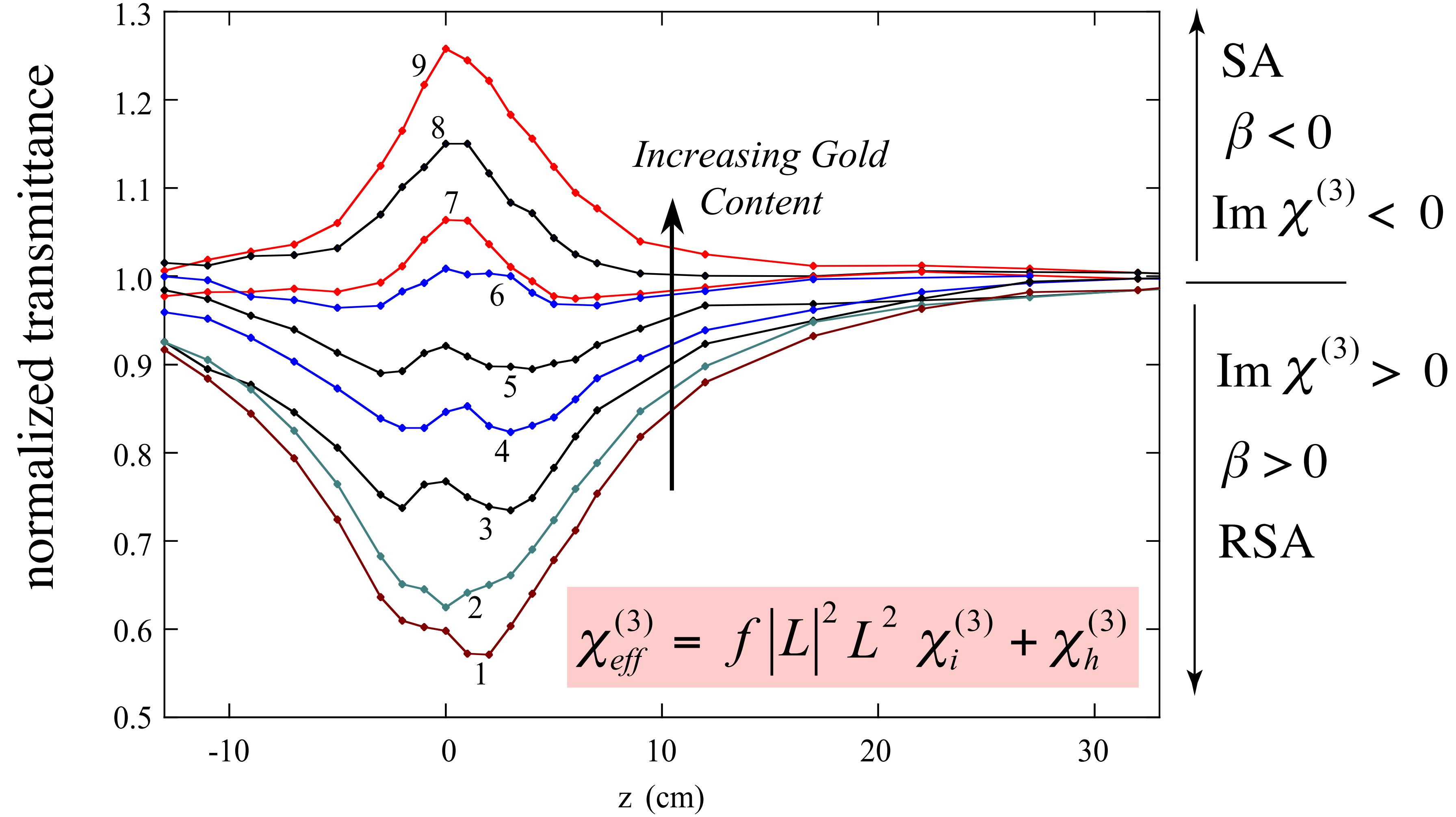
$$\mathcal{L} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} = \text{pure imaginary at resonance!}$$

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)



SA

$\beta < 0$

$\mathrm{Im}\,\chi^{(3)} < 0$

$\mathrm{Im}\,\chi^{(3)} > 0$

$\beta > 0$

RSA

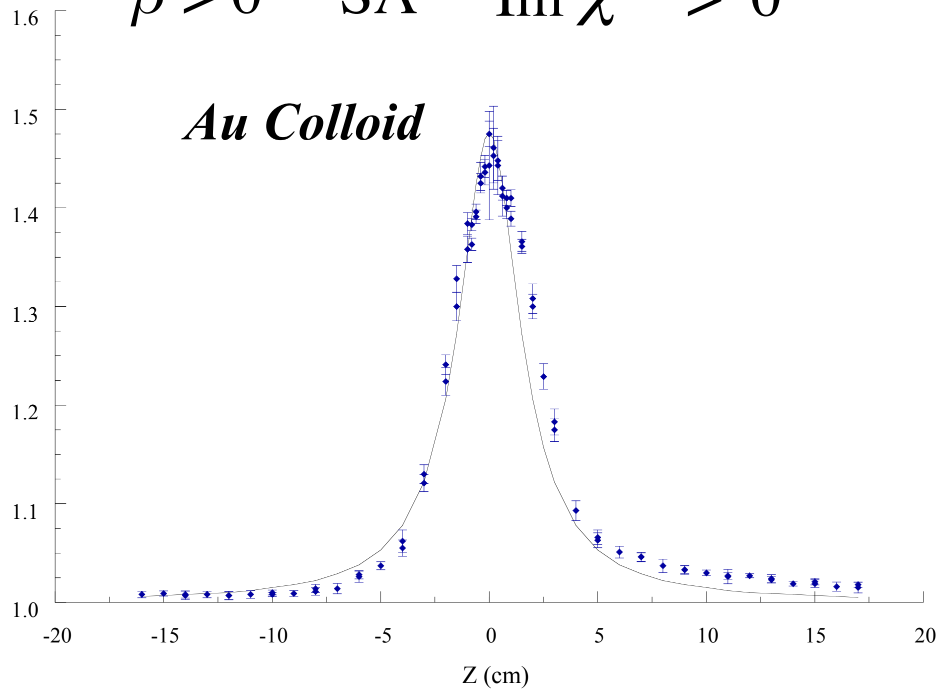
$$\chi_{eff}^{(3)} = f\left|L\right|^2 L^2\,\chi_i^{(3)} + \chi_h^{(3)}$$

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

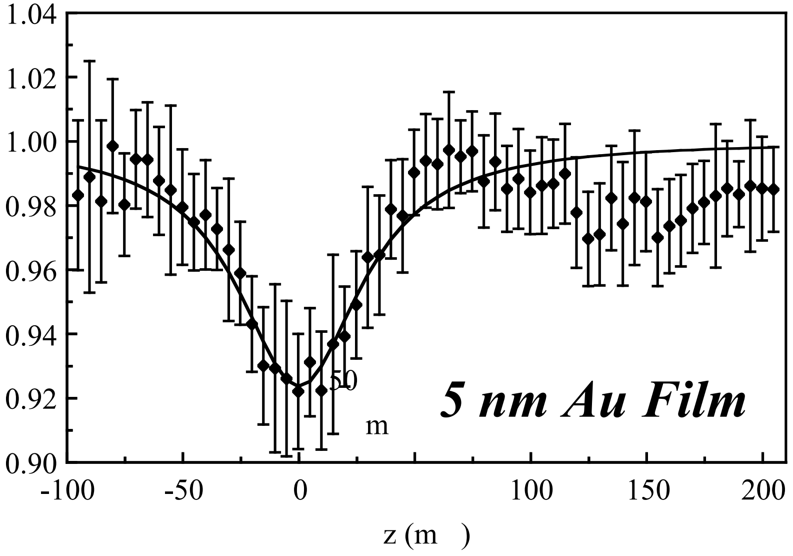
Comparison of Bulk and Colloidal Gold

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

$\beta > 0$ SA $\mathrm{Im}\,\chi^{(3)} > 0$



$\beta < 0$ RSA $\mathrm{Im}\,\chi^{(3)} < 0$

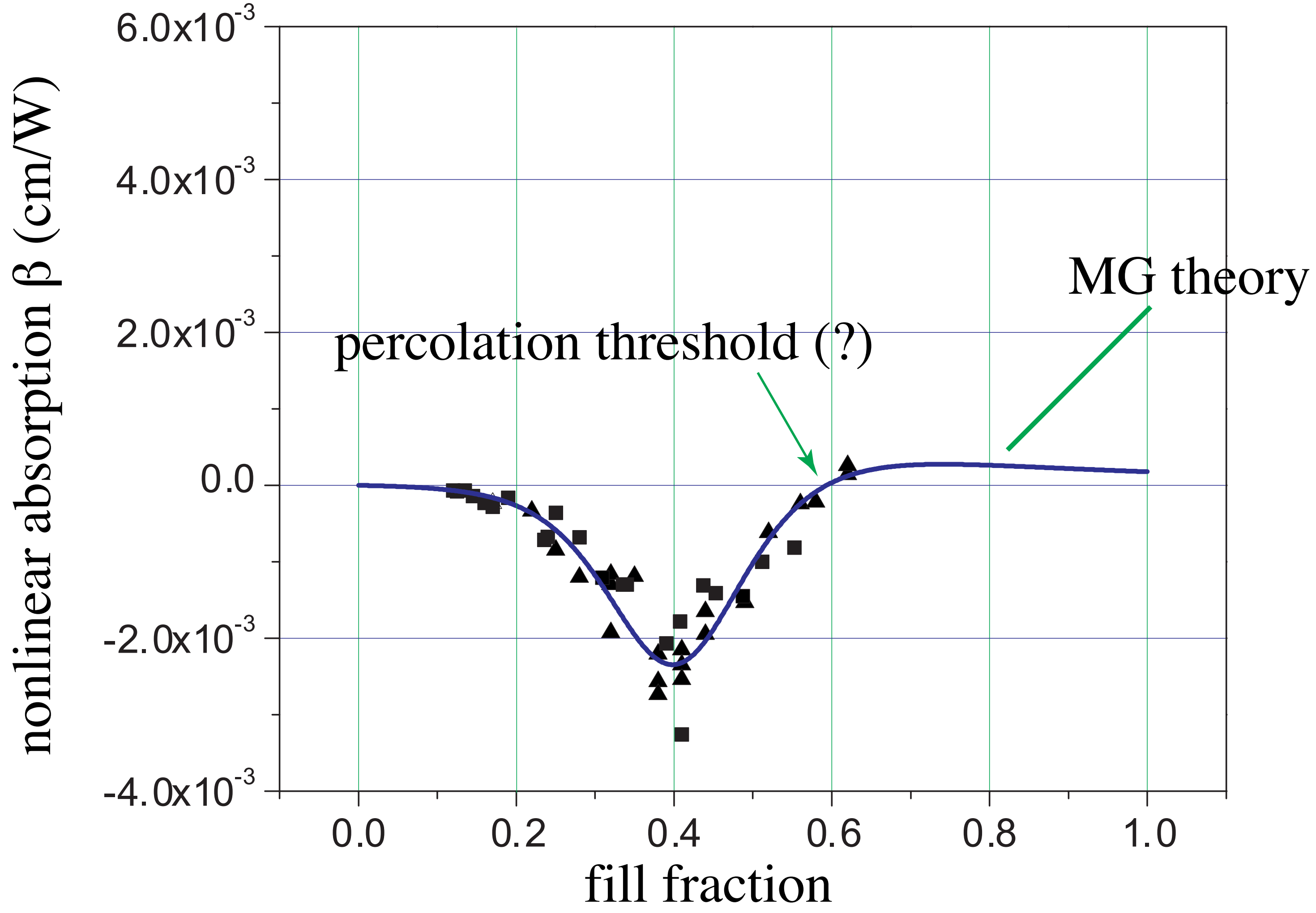


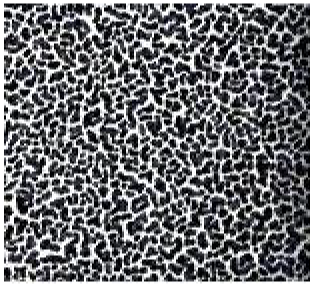
- ➢ Nonlinearities possess opposite sign!

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!



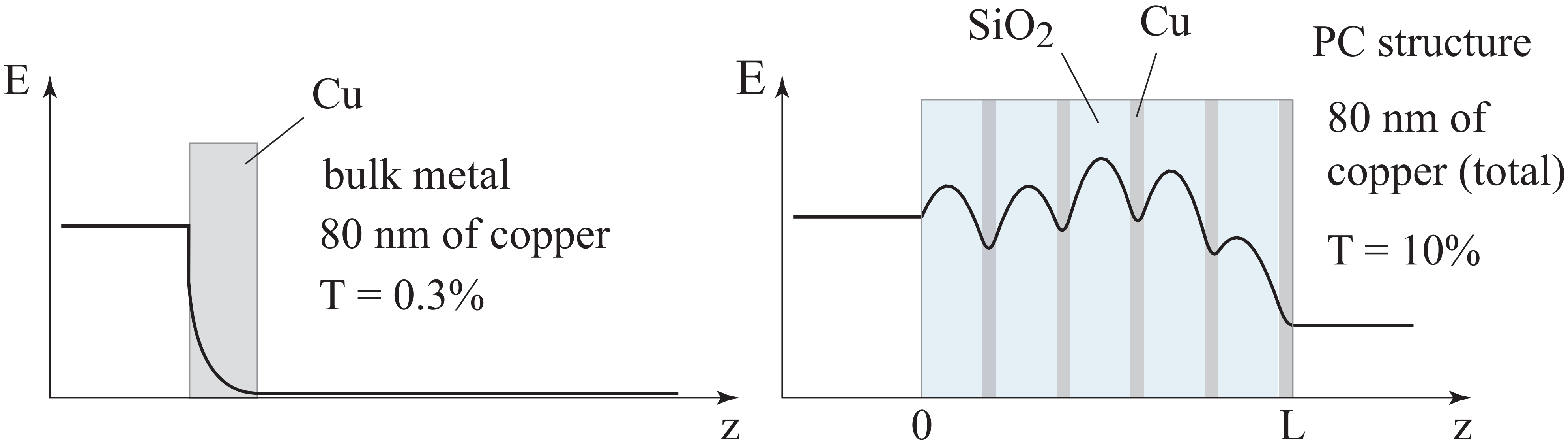


gold-silica
nanocomposite
(SEM)

(with D. D. Smith and G. Piredda. JOSA B, 2008)

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

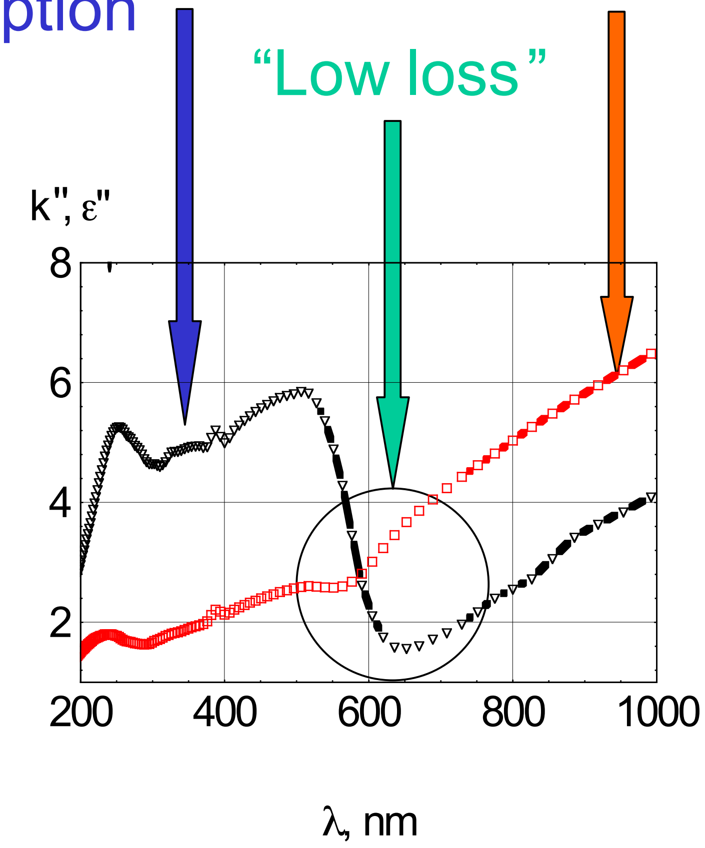
- Metals have very large optical nonlinearities but low transmission
- Low transmission is because metals are highly reflecting (not because they are absorbing!)
- Solution: construct metal-dielectric photonic crystal structure (linear properties studied earlier by Bloemer and Scalora)



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”

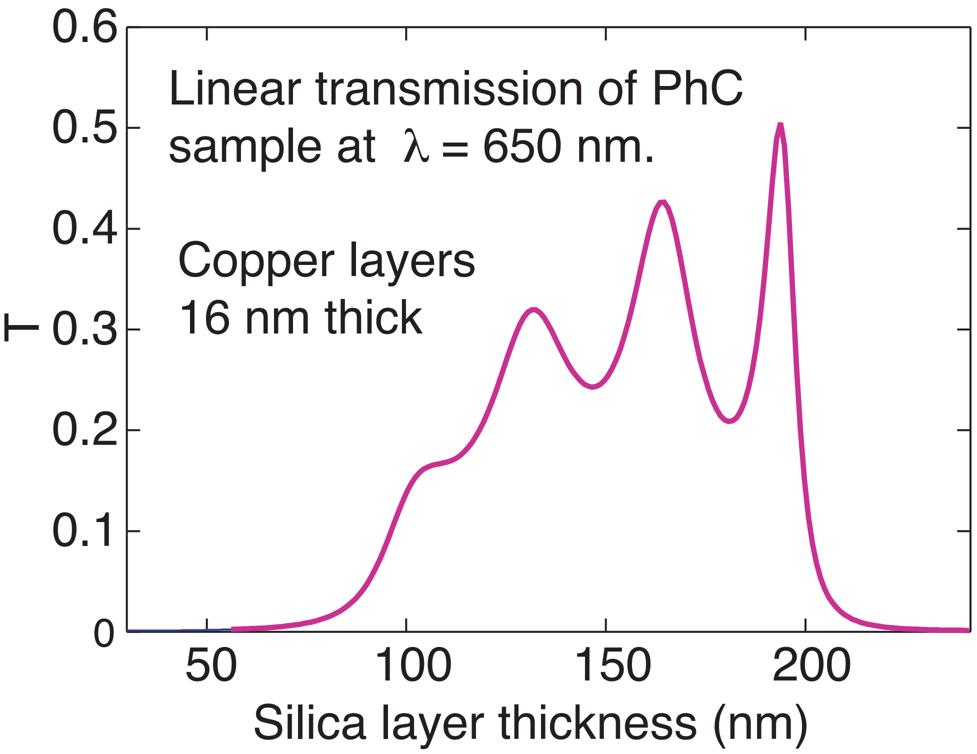
Drude reflection region

Cu

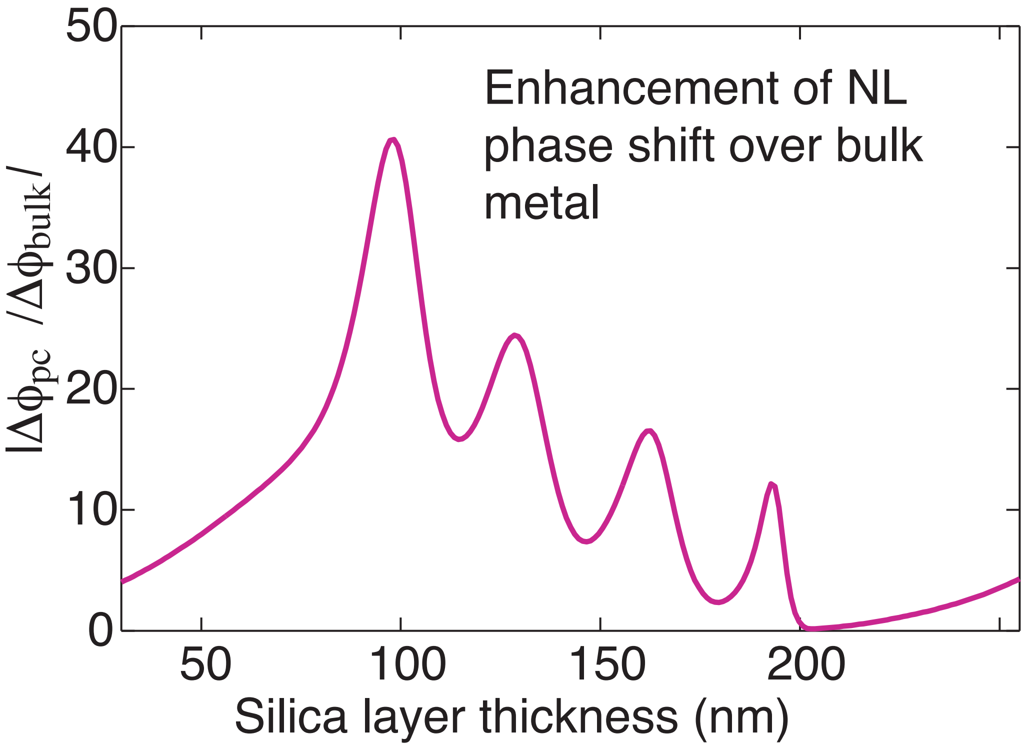
We work at 650 nm.

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

- Metal-dielectric structures can have high transmission.

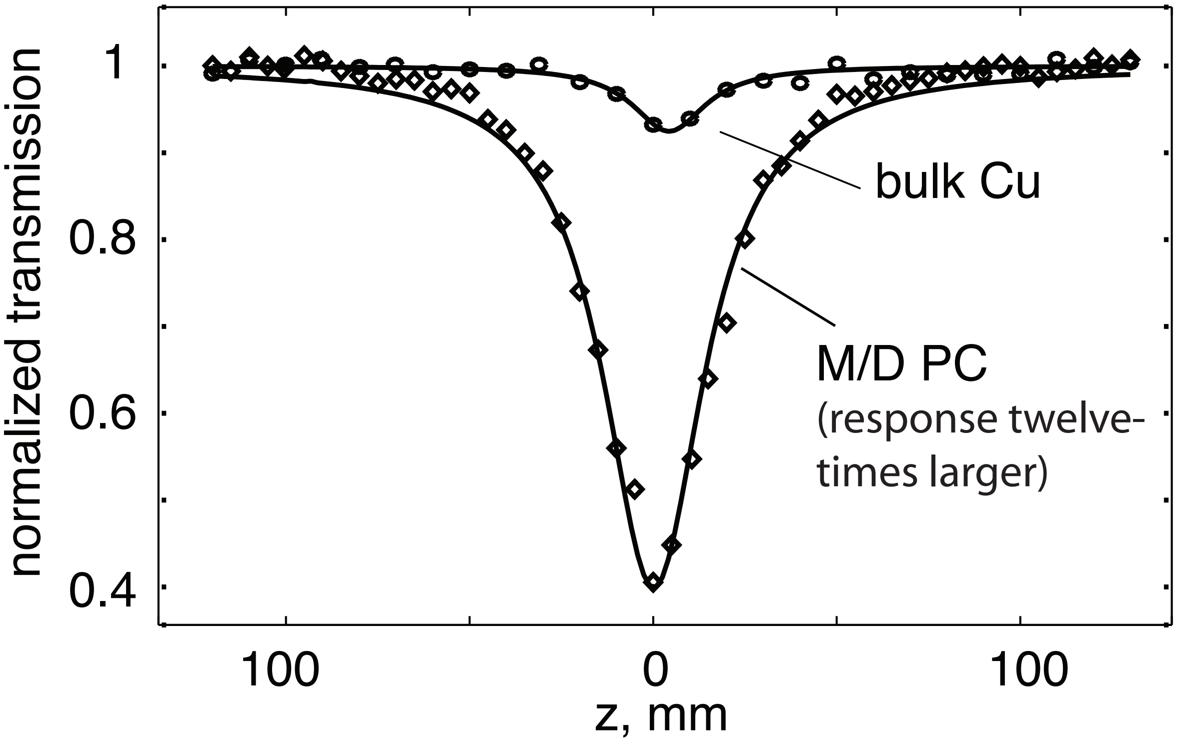


- And produce enhanced nonlinear phase shifts!



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

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



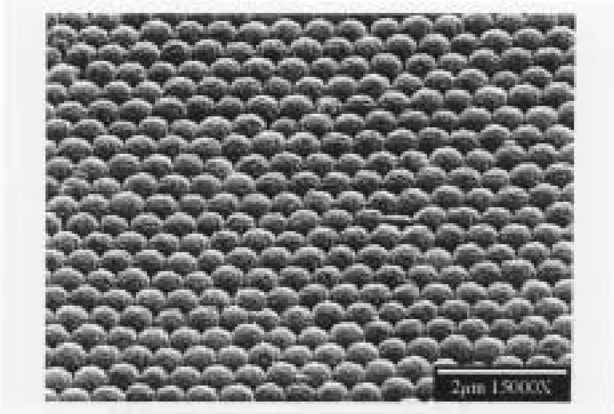
$I = 500\ \mathrm{MW/cm^2}$

$\lambda = 650\ \mathrm{nm}$

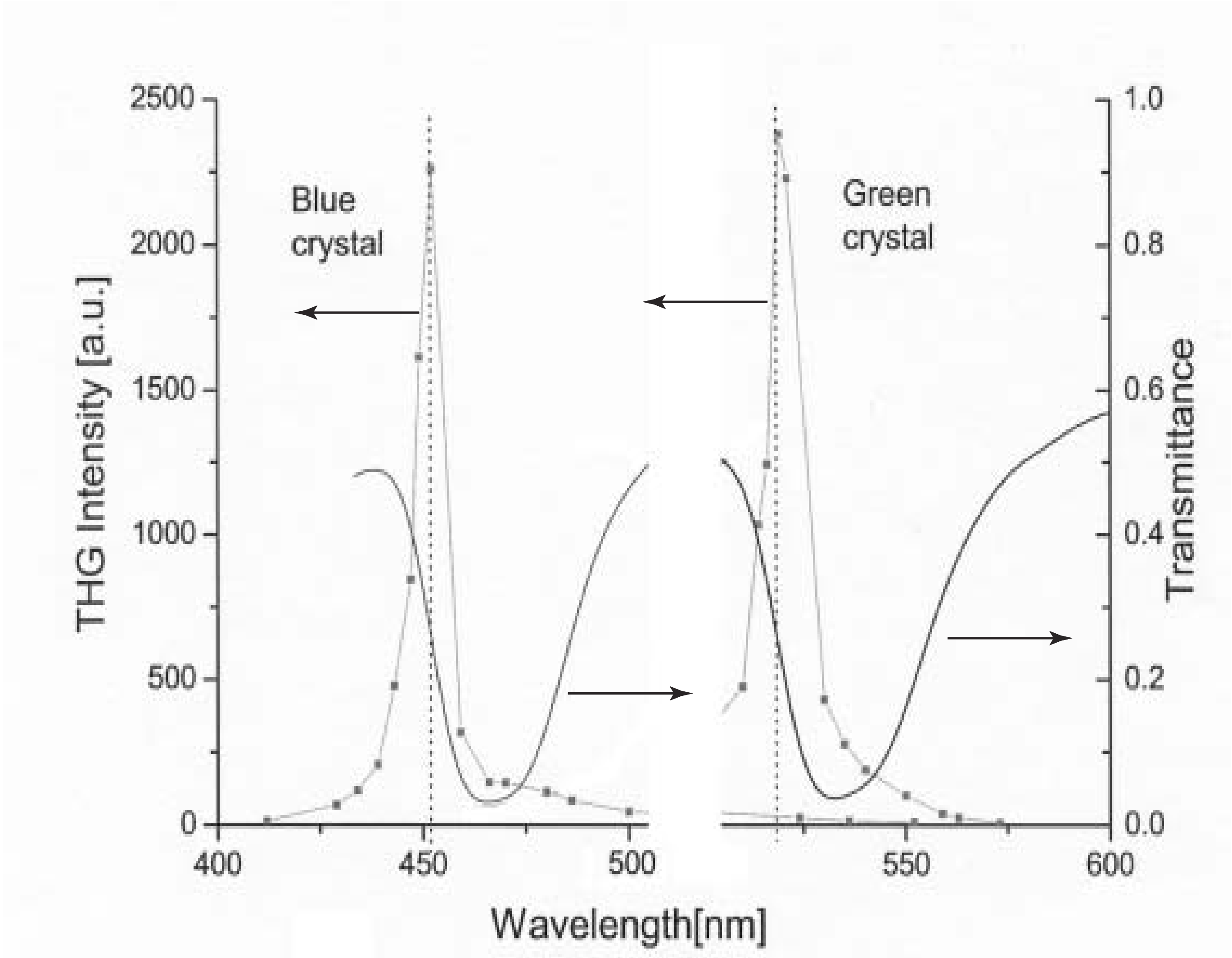
- We observe a large NL change in transmission
- But there is no measurable NL phase shift ☹
- Next steps (?)
  - design new structure optimized to show NL phase shift
  - develop device applications of metal/dielectric composites

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

Third-Harmonic Generation in a 3D Photonic Crystal



polystyrene photonic crystal



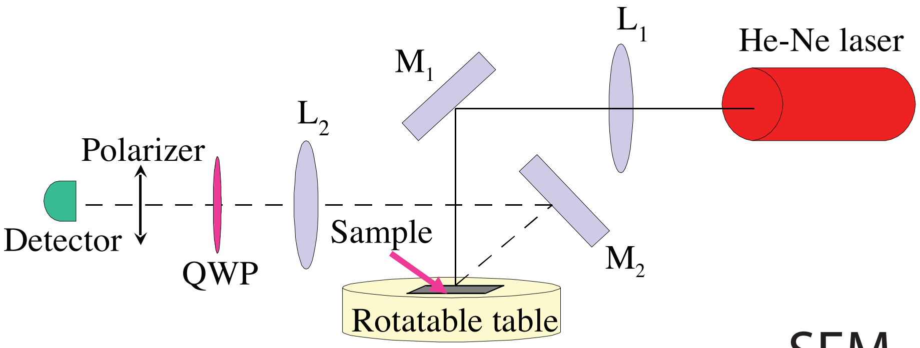
Phase matching provided by PBG structure.

Direct THG visible by eye!

P. P. Markowicz, V. K. S. Hsiao, H. Tiryaki, A. N. Cartwright, P. N. Prasad, K. Dolgaleva, N. N. Lepeshkin, and R. W. Boyd, Appl. Phys. Lett. 87, 051102 (2005)

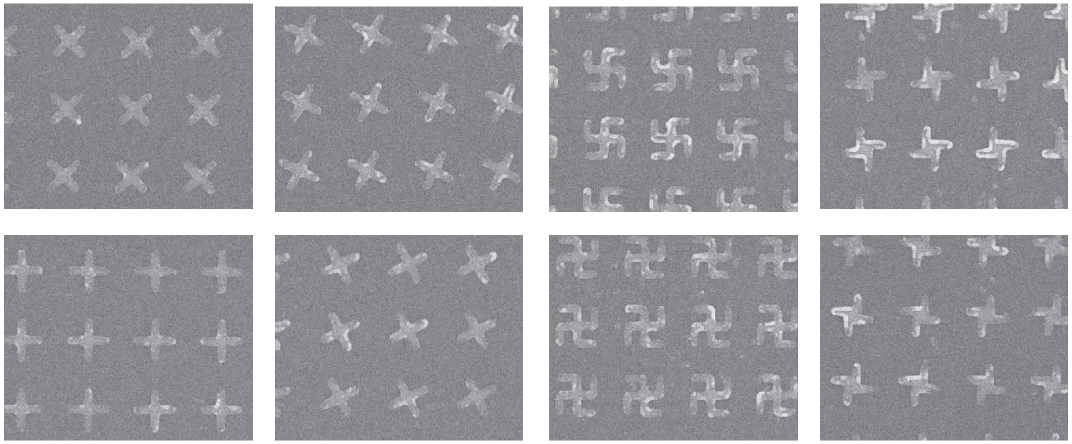
Optical Properties of Artificial Chiral Materials

- Use nanofabrication to create planar structures with strong polarization properties
- Induce large optical activity by means of planar chiral structures
- Which is more important: “molecular” or structural chirality?



Samples are patterned in 30 nm gold layer and have 800 nm period

SEM

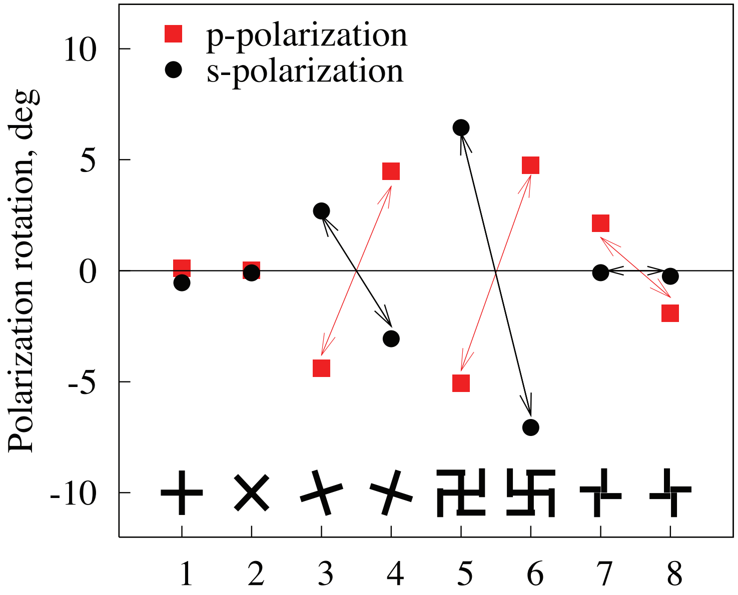


achiral

structural chirality

strong molecular chirality

weak molecular chirality



Tentative conclusion: structural chirality is dominant effect

S. N. Volkov, K. Dolgaleva, R.W. Boyd, K.Jefimovs, J.Turunen, Y. Svirko, B. Canfield, and M. Kauranen, to be published.

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

K. Dolgaleva R. W. Boyd and P. W. Milonni, J. Opt. Soc. Am. B, 24 516 2007.

K. Dolgaleva and R. W. Boyd, J. Opt. Soc. Am. B, 24 A19 2007.

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

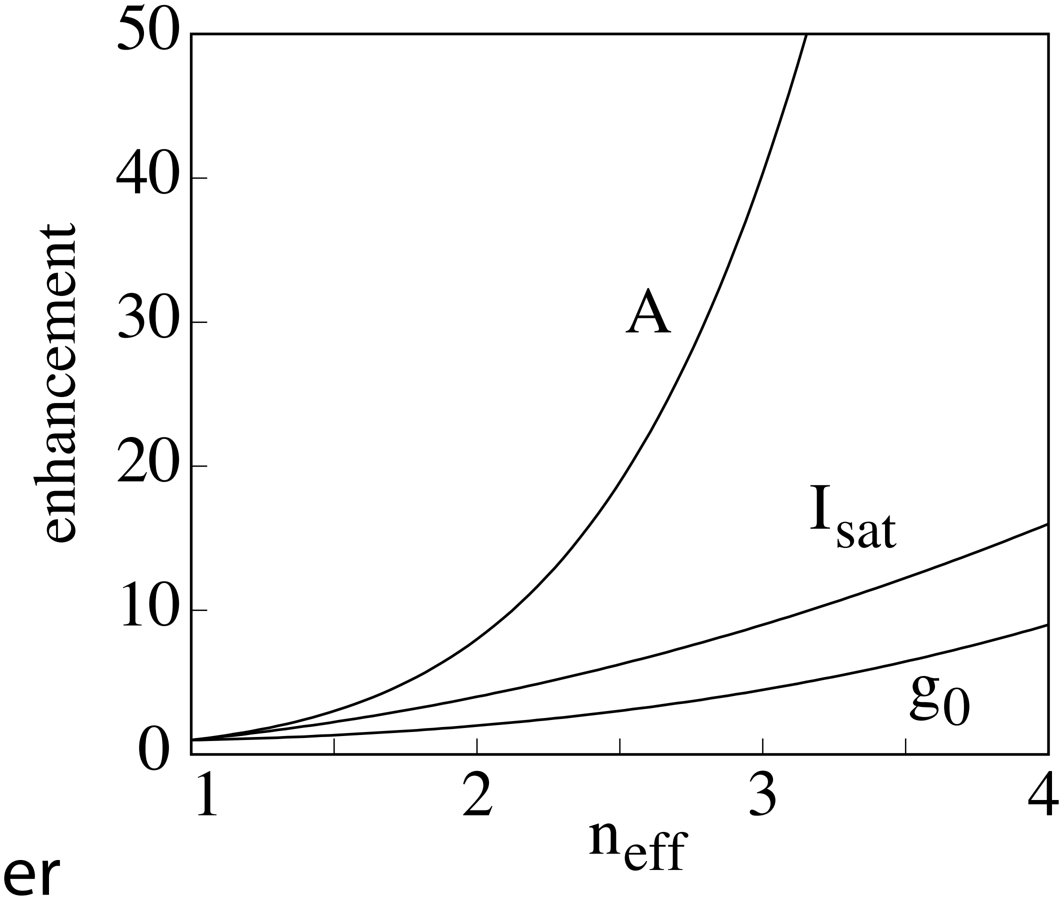
In simplest approximation, laser parameters depend only on effective refractive index of material.

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

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

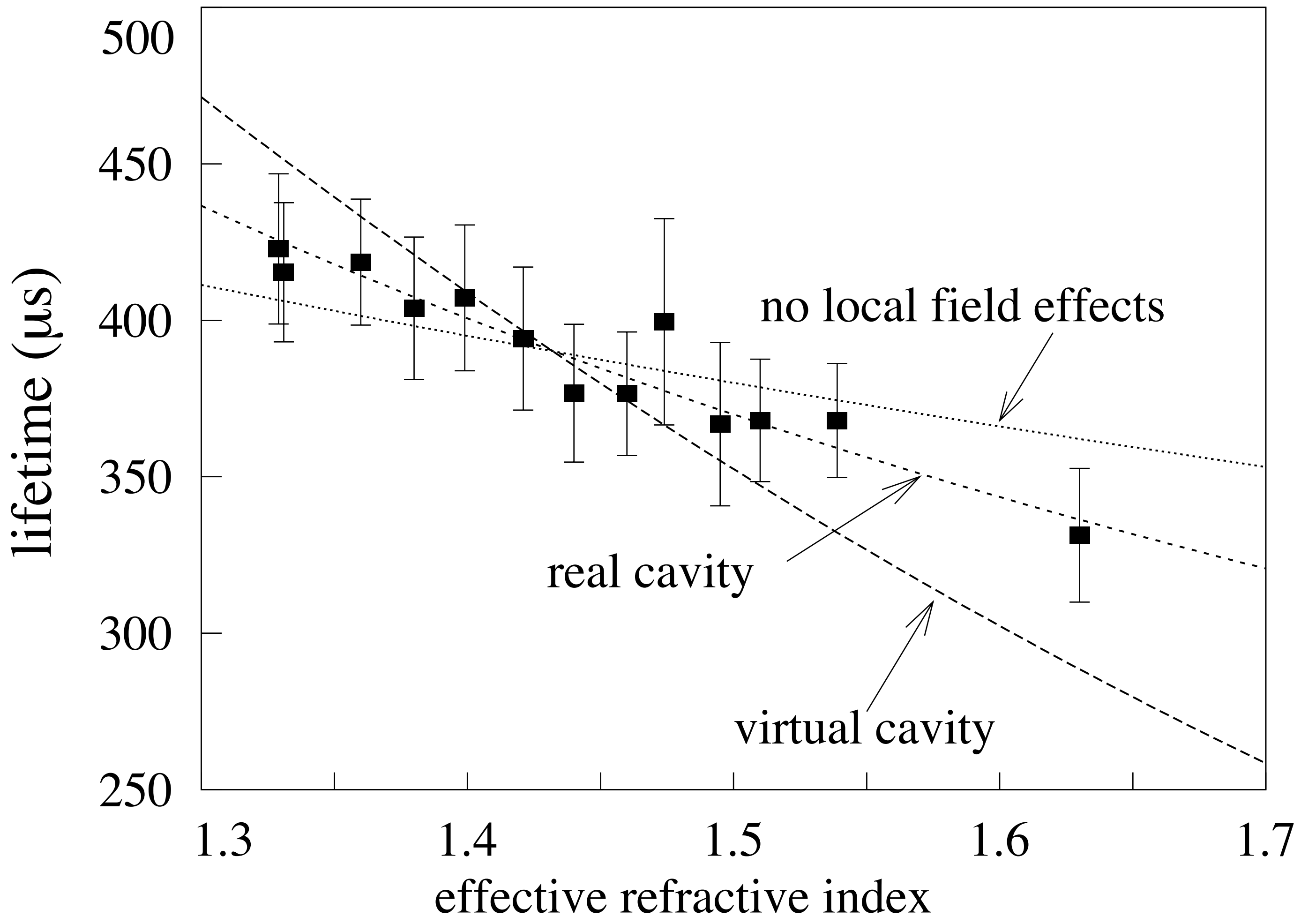
$$I_{sat} = n_{eff}^2\, I_{sat,\,vac}$$

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

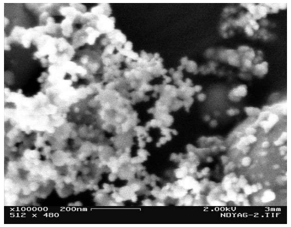


Note that great control of laser paramters is possible

Dependence of Radiative Lifetime on Refractive Index of Host



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



Real Cavity Model

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

Lorentz (Virtual Cavity) Model

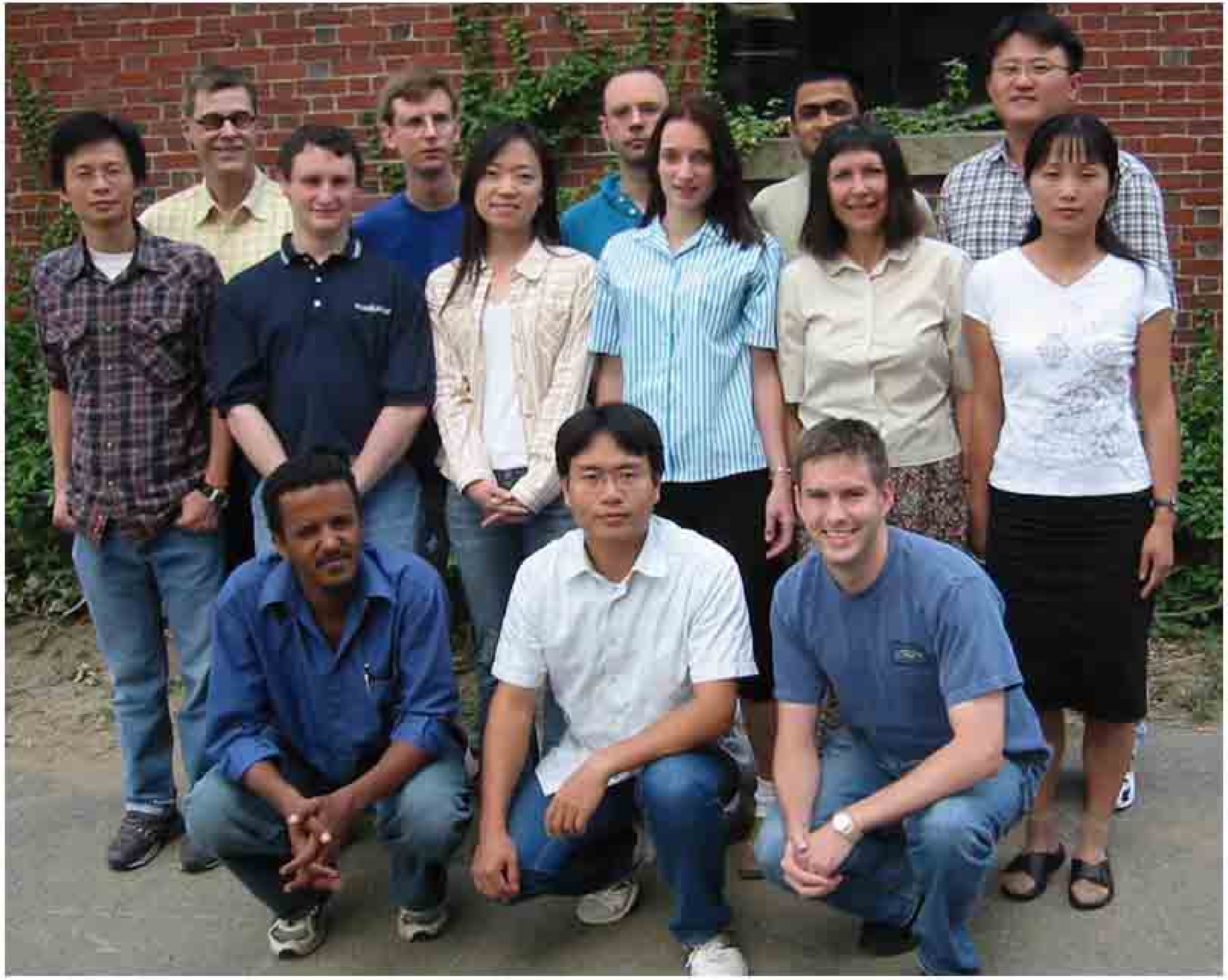
$$A^{(diel)} = \frac{A^{(vac)}}{n\left(\frac{n^2+2}{3}\right)^2}$$

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



Thank you for your attention!