The Institute of Optics
Nonlinear Optics
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# Influence of Local Field Effects on the Radiative Properties of Nd:YAG Nanoparticles in a Liquid Suspension

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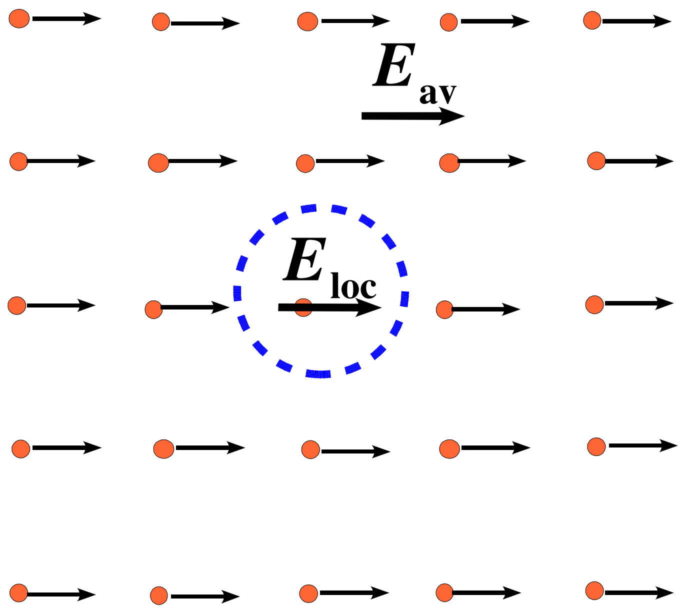
# Motivation

- Radiative properties of nanocomposites differ from those of constituent materials.
- Practical interest for application in photonics and laser engineering
- It motivated our investigation of radiative lifetime in Nd:YAG nanoparticles suspended in different liquids.

# Outline

- Radiative lifetime in a dielectric
- Local-field effects: different models
- Previously-conducted experiments
- Sample preparation
- Data analysis

# Local-field effects




$$\boldsymbol{E}_{\mathbf{loc}} \neq \boldsymbol{E}_{\mathbf{av}}$$

Local-field correction factor:

$$L = \frac{E_{\mathrm{loc}}}{E_{\mathrm{av}}}$$

# Radiative lifetime in a dielectric

$$\frac{1}{\tau_{\mathrm{rad}}}=\frac{2\pi}{\hbar}\left|V_{12}(\omega_0)\right|^2\rho(\omega_0)$$

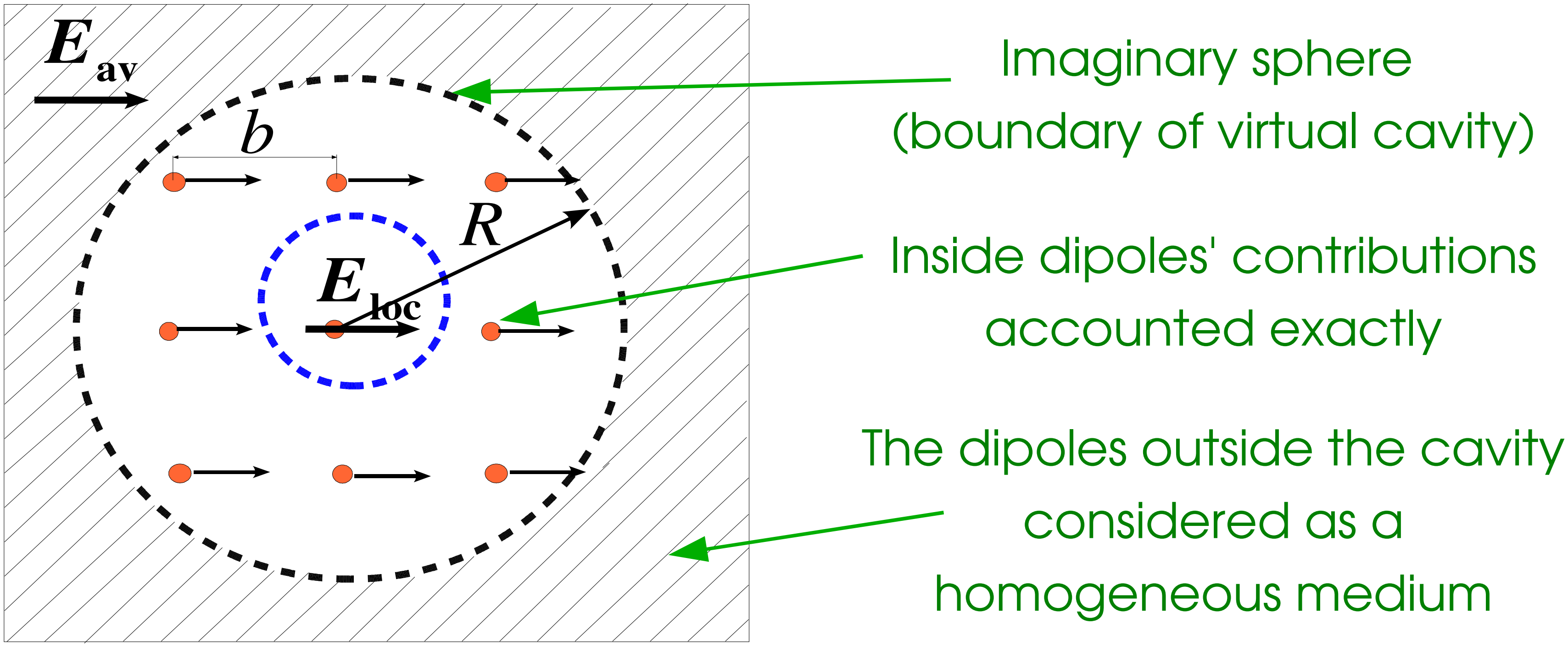
In a dielectric:

Density of states $\rho(\omega_0)\propto n^2$

Coupling coefficient $V_{12}(\omega_0)\propto\frac{L}{\sqrt{n}}$

$$\tau_{\mathrm{rad}}^{(\mathrm{diel})}=\frac{\tau_{\mathrm{rad}}^{(\mathrm{vac})}}{nL^2}.$$

# Local-field-correction factor: Virtual-cavity (Lorentz) model

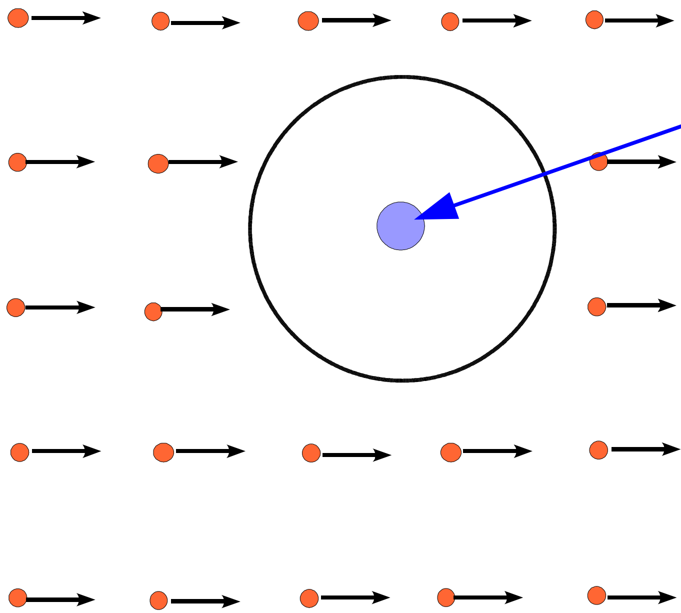



$$b \ll R \ll \lambda$$

Lorentz local-field correction factor

$$L = \frac{n^2 + 2}{3}$$

# Local-field-correction factor:
# Real-cavity model



Emitters replace part of the volume of the medium

Real-cavity local-field correction factor

$$L = \frac{3n^2}{2n^2+1}$$

# The two models describe different experimental situations

## Lorentz model

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

Dopants in hosts:

- Rare-earth ions in different crystallic lattices and glasses
- Homogeneous dielectrics

## Real-cavity model

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

Inclusions in suspensions:

- Dye droplets suspended in different liquids
- $Eu^{3+}$ organic complexes suspended in liquids and gases
- Quantum dots suspended in different backgrounds

# The two models describe different experimental situations

**Lorentz model**

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

**Real-cavity model**

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

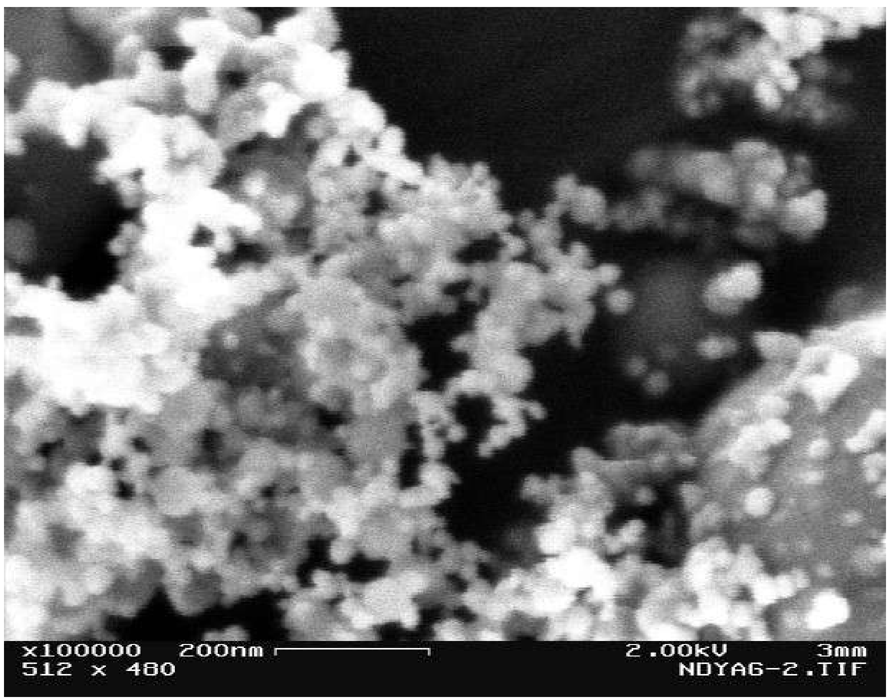
Nanoparticles???

- R. S. Meltzer, S. P. Feofilov, B. Tissue, and H. B. Yuan, "Dependence of fluorescence lifetimes of $Y^2O^3$:$Eu^{3+}$ nanoparticles on the surrounding medium", *Phys. Rev. B* **60**, R14012 (1999).

One would expect nanoparticles to be here

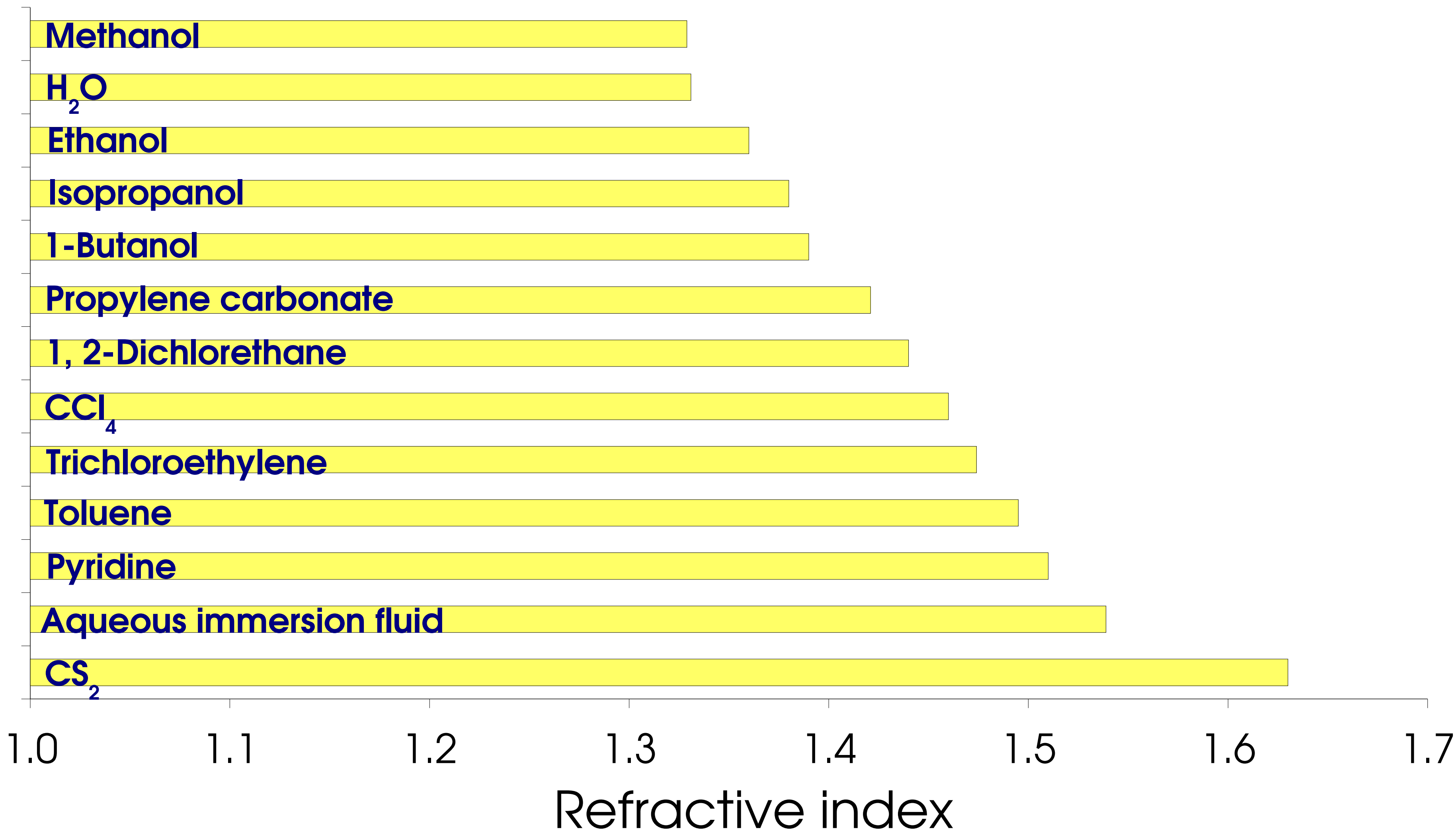
# Sample preparation

Nd:YAG nanopowder
(SEM picture)

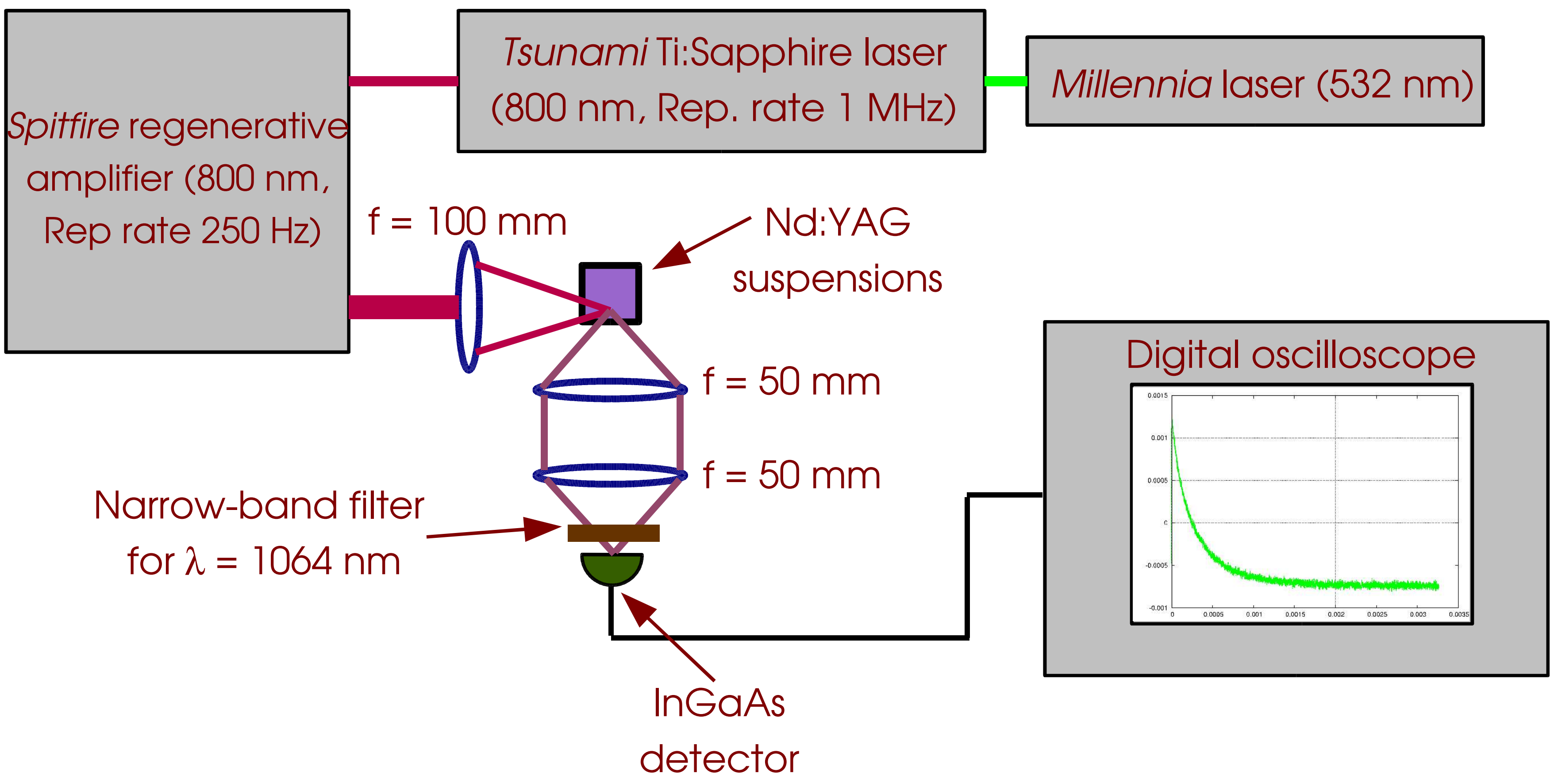



- $Nd^{3+}$:YAG nanoparticles (manufactured by ***TAL Materials***).
- Nd concentration **0.9 at. %**.
- Average particle size **~20 nm**.
- The particles were suspended in different organic and inorganic liquids.
- Nd:YAG nanopowder volume fractions in suspensions were **0.11%**.

# Liquid backgrounds

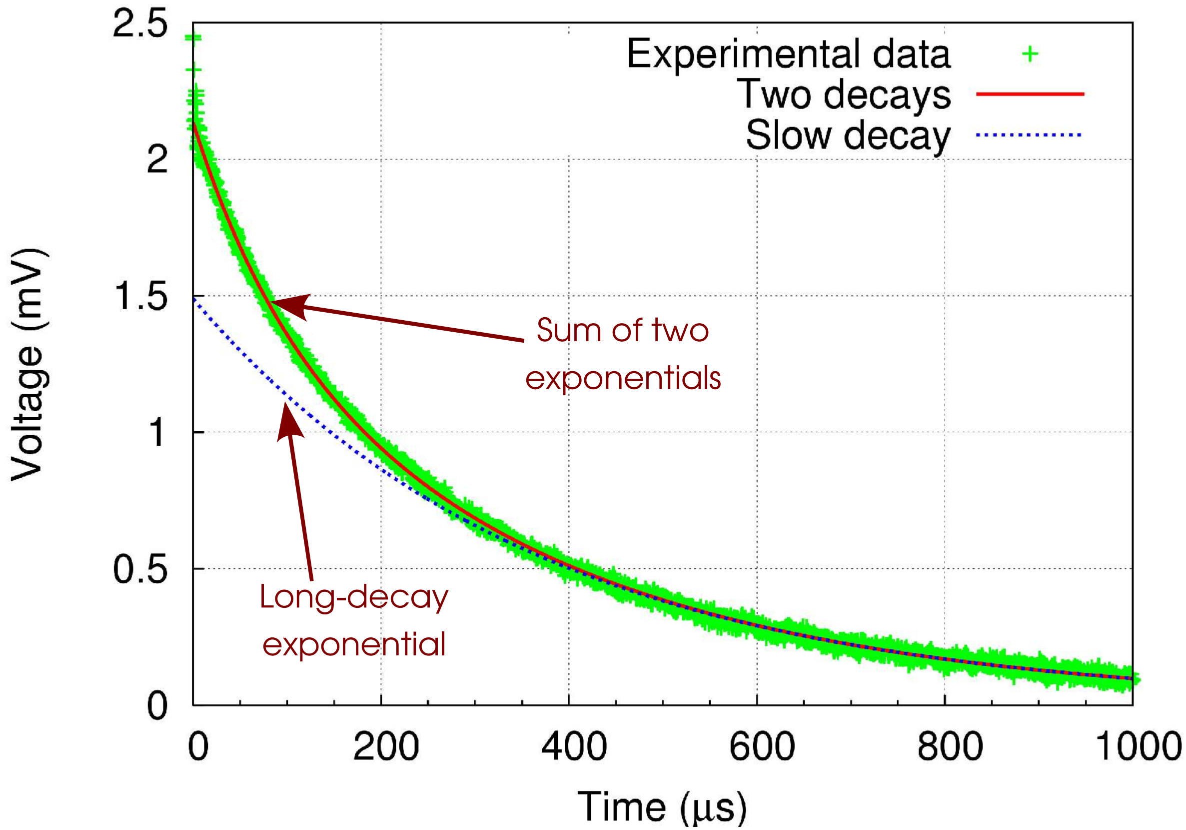


# Experimental setup



# Data analysis

Typical Nd:YAG fluorescence decay




- Bi-exponential decay: $\tau_{long}$ : $\tau_{short}$ = 4 : 1
- The longer decay is the one that agrees with the theory.
- The shorter decay is due to the contribution from the surface ions.

# Quantum yield

- Quantum yield tells what fraction of energy decays through the radiative channel.

$$\eta = \frac{A_{\text{rad}}^{(\text{YAG})}}{A_{\text{rad}}^{(\text{YAG})} + A_{\text{nonrad}}}$$

- If quantum yield is close to unity, the fluorescence decay is purely radiative.

$$\eta \approx 1 \longrightarrow \boxed{\frac{1}{\tau_{\text{measured}}} \approx \frac{1}{\tau_{\text{rad}}}}$$

- If quantum yield is less than unity, non-radiative transitions affect the dynamics of the fluorescence decay.

$$\eta < 1 \longrightarrow \boxed{\frac{1}{\tau_{\text{measured}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nonrad}}} = \frac{nL^2}{\tau_{\text{rad}}^{(\text{vac})}} + \frac{1}{\tau_{\text{nonrad}}}}$$

# Quantum yield in Nd:YAG

Theoretical calculations: $\eta \approx 0.92$

- W. F. Krupke, *IEEE J. Quantum Electron.* **7**, 153 (1971).

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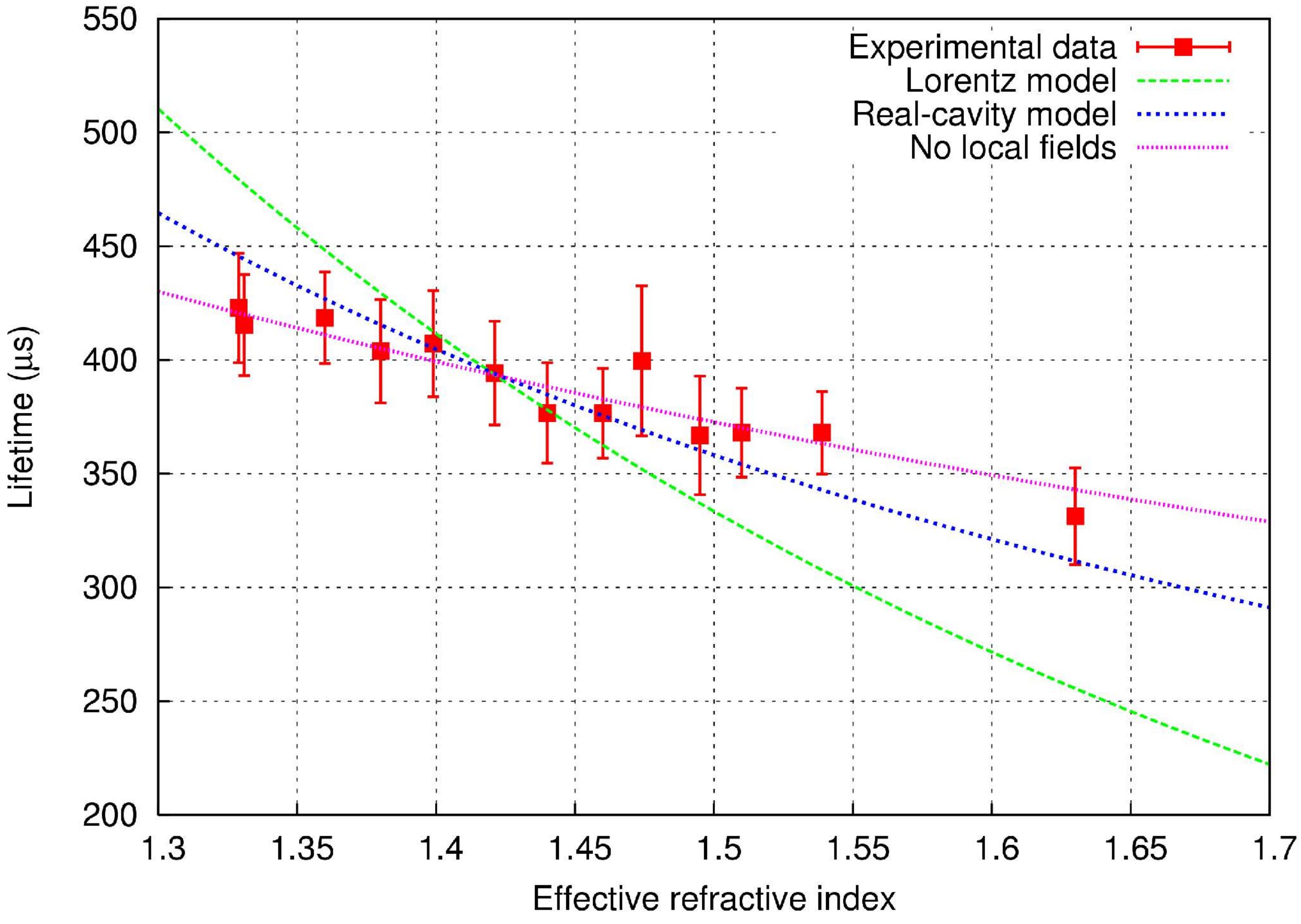
Experimental measurements:

$$0.47 \leq \eta \leq 0.99$$

- T. S. Lomheim and L. G. DeShazer, *J. Opt. Soc. Am.* **68**, 1575 (1978).
- C. J. Kennedy and J. D. Barry, *Appl. Phys. Lett.* **31**, 91 (1977).
- T. Kushida and J. E. Geusic, *Phys. Rev. Lett.* **21**, 1172 (1968).

# Radiative decay time as a function of the refractive index ($\eta \approx 1$)

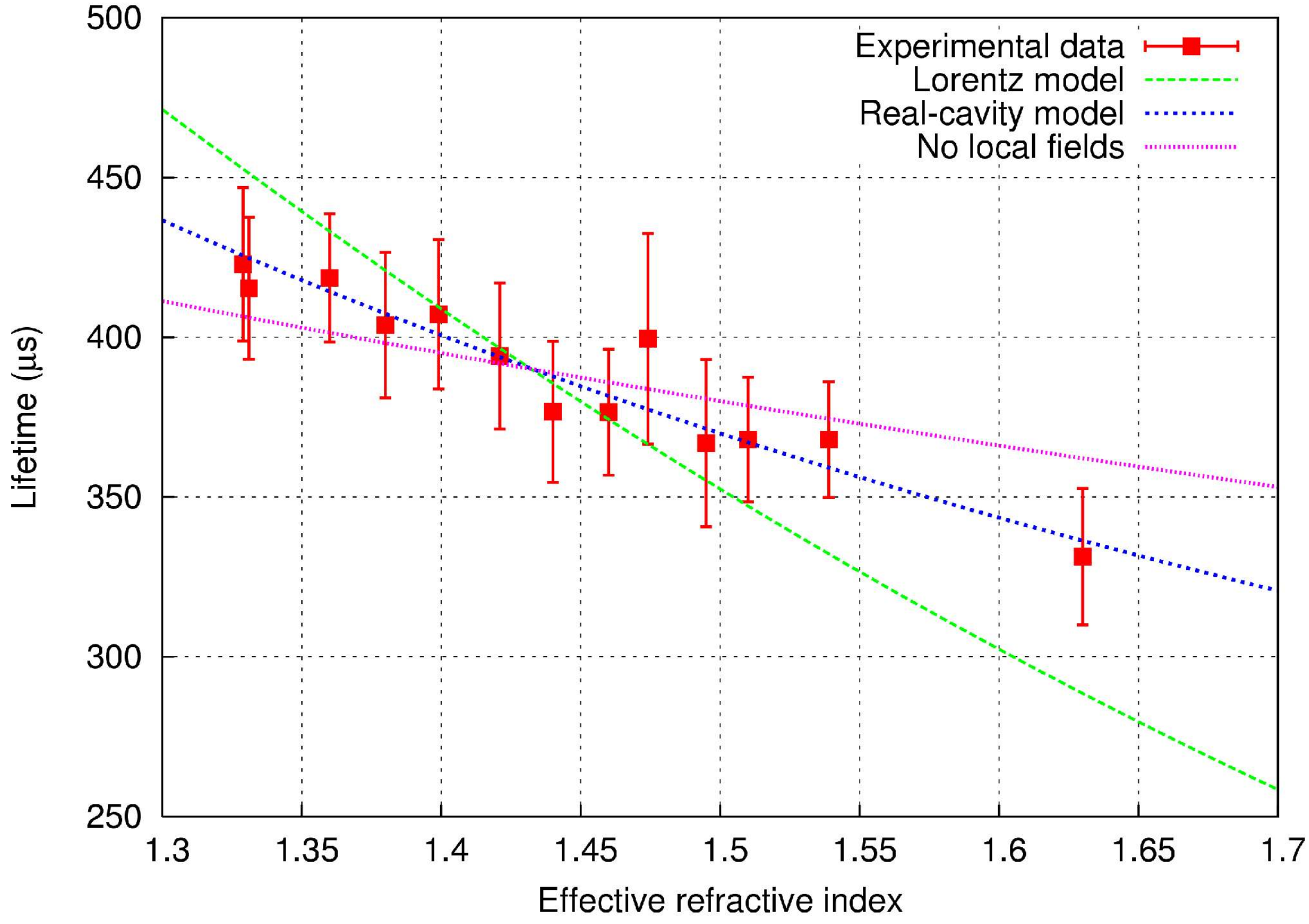
Data Fit in the Assumption of $\eta \approx 1$




- Experimental data were fitted to different local-field models.
- Both the no-local-field-effects and real-cavity models describe the experimental results (with the bias towards the no-local-field-effects model.)

# Radiative decay time as a function of the refractive index ($\eta \approx 0.47$)

Data Fit in the Assumption of $\eta \approx 0.47$




- Real-cavity model yields the best least-square fit.
- Lorentz model can be ruled out.
- No-local-field-effects model lies pretty close to the experimental points.

# Conclusions

- Radiative lifetimes of Nd:YAG nanoparticles suspensions in different liquid backgrounds were measured.
- A two-exponential decay dynamics was observed with the slower exponent corresponding to the theory.
- Real-cavity model gives the best least-square fit to the experimental points (in the assumption that the quantum yield of the Nd:YAG nanopowder is 47%).

# Many thanks to:

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