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13. ABSTRACT *(Maximum 200 words)*

This report describes the results of a theoretical investigation into the nonlinear optical response of granular composites. In particular, we have investigated the degree to which the cubic nonlinear response can be enhanced in such composites, relative to the same response in pure materials. Cubic nonlinear response is potentially of great practical importance in developing novel materials with a strongly intensity-dependent transmission coefficient, index of refraction, etc. We find that there are many types of composite geometries which give rise to such strong enhancements. These include composites near the percolation threshold, composites in which one of the components is arranged in the form of a fractal cluster, and nonlinear coatings (such as dyes) adsorbed onto the surface of particles which have a resonant optical response at an appropriate frequency. We have carried out this investigation using both analytical approximations and a variety of approximate numerical techniques, including large-scale computer simulations. Finally, we briefly describe some work in progress, in which a composite composed of materials with a purely quadratic response can exhibit an enhanced cubic response.

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DAVID G. STROUD

October 19, 1994

U. S. ARMY RESEARCH OFFICE

GRANT DAAL03-92-G-0263

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STATEMENT OF THE PROBLEM

ARO Grant DAAL03-92-G-0263 ran from February 1. 1993 to January 31. 1994. The central goal of this project was to carry out a theoretical investigation of ways to increase the cubic nonlinear susceptibility of composite materials. A large cubic nonlinearity is equivalent to a material with a strongly intensity-dependent dielectric function. Such materials have obvious practical potential, as intensity-dependent filters, for example. In addition, they are of basic interest as materials with unusual nonlinear optical properties.

It has recently been discovered that cubic nonlinearities of this kind are greatly enhanced in composite materials. The central reason for this enhancement is that the local electric field can be greatly enhanced in a composite material. Hence, a susceptibility which depends on a higher power of the electric field, such as a cubic nonlinear susceptibility, can be increased even more than a linear susceptibility. The goal of this project was to investigate various ways of increasing this enhancement. Of particular interest was the nonlinear response of certain dyes coated on a substrate with a resonant surface plasmon excitation. In particular, we wanted to show that this response is greatly enhanced at frequencies close to this excitation (this expectation has been realized; see below).

SUMMARY OF MOST IMPORTANT RESULTS

Our most important results are summarized in the publications which emerged from this grant. For convenience, we also summarize these results briefly in the next several paragraphs, which consist of abstracts of the publications generated with support from the ARO grant.

1. "Cubic Nonlinearities in Small-Particle Composites: Local-Field Induced Giant Enhancements," by D. Stroud and X. Zhang (Physica **A207**, pp. 55-64 (1994)). In this paper, we discuss methods for enhancing the cubic nonlinear susceptibility χ_e of a composite material, starting from an exact relation between χ_e and the fourth moment of the electric field in the related linear composite. At zero frequencies, in

a random metal-insulator composite, χ_e can be greatly enhanced near a percolation threshold. Similar enhancement is obtained when a linear fractal is embedded in a nonlinear host. In a random Drude metal/insulator composite χ_e is greatly enhanced near surface-plasmon resonances; the enhancement shows very strong structure which is nearly undetectable in the linear response. In a suspension of spheres coated with a nonlinear material, $\chi_e/\chi_{coat} \gg 1$ near the surface-plasmon resonance frequency of the core particle.

2. "Numerical Studies of the Nonlinear Properties of Composites," by X. Zhang and D. Stroud (Phys. Rev. **B49**, 944 (1994)). In this paper, we use both numerical and analytical techniques to investigate various ways of enhancing the cubic nonlinear susceptibility χ_e of a composite material. We start from the exact relation $\chi_e = \sum_i p_i \chi_i < (\vec{E} \cdot \vec{E})^2 >_{i,lin} / E_0^4$, where χ_i and p_i are the cubic nonlinear susceptibility and volume fraction of the i^{th} component, E_0 is the applied electric field, and $< E^4 >_{i,lin}$ is the expectation value of the electric field in the i^{th} component, calculated in the linear limit where $\chi_i = 0$. In our numerical work, we represent the composite by a random resistor or impedance network, calculating the electric field distributions by a generalized transfer-matrix algorithm. Under certain conditions, we find that χ_e is greatly enhanced near the percolation threshold. We also find a large enhancement for a linear fractal in a nonlinear host. In a random Drude metal/insulator composite χ_e is hugely enhanced especially near frequencies which correspond to the surface-plasmon resonance spectrum of the composite. At zero frequency, the random composite results are reasonably well described by a nonlinear effective-medium approximation. The finite-frequency enhancement shows very strong reproducible structure which is nearly undetectable in the linear response of the composite, and which may possibly be described by a generalized nonlinear effective-medium approximation. The fractal results agree qualitatively with a new nonlinear differential effective-medium approximation. Finally, we consider a suspension of coated spheres embedded in a host. If the

coating is nonlinear, we show that $\chi_e/\chi_{coat} \gg 1$ near the surface-plasmon resonance frequency of the core particle.

3. "Effective Linear and Nonlinear Response of Fractal Clusters," by P. M. Hui and D. Stroud (Phys. Rev. **B49**. 11729 (1994))/ In this paper, we generalize a differential effective medium approximation previously developed for the effective linear response of a fractal cluster, to treat the effective nonlinear response. We consider a material having a nonlinear **J**-**E** characteristic which forms a cluster in another, possibly nonlinear material. A differential equation for the cluster-size-dependent nonlinear susceptibility is derived and a general solution is obtained. Numerical examples are given for two special cases: a cluster of a nonlinear material in a linear host, and a cluster of a linear material in a nonlinear host. An enhancement in the nonlinear response due to clustering is found for the case of clustering of a nonlinear material in a linear host.

4. "Theory of Optical Bistability in a Weakly Nonlinear Composite Medium," by David J. Bergman, Ohad Levy, and D. Stroud (Phys. Rev. **B49**, 129 (1994). This paper presents a new variational approach to discuss bistable behavior in composite media where one component is a nonlinear dielectric while the other has a field independent complex dielectric constant with a negative real part. Under certain conditions, the physical parameters may be adjusted so that bistability appears even though the nonlinear behavior is everywhere weak, thus allowing it to be treated as a small perturbation to the leading linear behavior.

5. "Effective Dielectric Response of Nonlinear Composites," by K. W. Yu, P. M. Hui, and D. Stroud (Phys. Rev. **B47**, 14150 (1993)). In this paper, a perturbative approach is developed to compute the local field for the case of a nonlinear inclusion embedded in a linear host. The result is applied to nonlinear composites. General formulas for calculating the effective nonlinear susceptibility up to the case of fifth-order nonlinearity are given. The formulation is applied to problems in two and three dimensions (2D

and 3D). For 2D problems, we study cylindrical and concentric cylindrical inclusions. By means of an exact mapping, the concentric cylinder problem can mapped onto that of an elliptic cylinder. A general expression is derived for the effective nonlinear susceptibility of a dilute composite of randomly oriented elliptic cylinders embedded in a linear host. For 3D problems, we study the cases of spherical and coated spherical inclusions. General expressions for the effective nonlinear susceptibility are derived in the dilute limit up to the case of fifth order nonlinearity. For composites consisting of spherical inclusions coated by a nonlinear material and embedded in a linear host, it is possible to enhance the nonlinear response of the composite by tuning material parameters such as the linear dielectric constants of the host, coating, and core materials, and by adjusting the thickness of the coating.

6. "Scaling Behavior and Surface-Plasmon Resonances in a Model Three-Dimensional Metal-Insulator Composite," by X. Zhang and D. Stroud (Phys. Rev. **B48**, 6658 (1993)). In this paper, we calculate the a. c. dielectric function of a model Drude metal/insulator composite, using a three-dimensional transfer-matrix algorithm. The real part of the effective conductivity, Re $g_e(\omega)$, reveals (i) a Drude peak which appears only above the percolation threshold p_c; and (ii) a broad spectrum of surface plasmon resonances whose lower edge approaches zero frequency at p_c. Sufficiently near p_c, the dielectric function is consistent with an expected scaling form previously verified in two dimensions. The surface plasmon spectrum resembles effective-medium predictions except for a weak but persistent peak near $0.4\omega/\omega_p$.

WORK IN PROGRESS.

Even though funding has expired, we are continuing work along the lines described above. A number of new and fascinating lines of research have opened up for possible future study. We summarize two of these below.

Second-Harmonic Generation and Induced Cubic Nonlinearities in Composite Media. This is a joint project with Prof. David J. Bergman and Ohad Levy of Tel Aviv University. We have shown that, even if none of the components of the composite have a cubic nonlinearity, such a cubic nonlinearity can be indirectly produced in a medium with second-order nonlinearity (i. e. second-harmonic-generation, or a nonzero $\chi^{(2)}$). This induced cubic nonlinearity can be even larger than the enhanced cubic nonlinearities analyzed in most of the present work. Thus, this mechanism would be an additional means of producing an intensity-dependent index of refraction in a composite material.

Induced Cubic Nonlinearities in a Linear Material. An even more intriguing possibility is that cubic nonlinearities can be generated in a material which, in bulk form, is strictly linear, just due to the finite size of the particles involved. We have just begun to investigate this possibility, which arises from the failure of the quasistatic approximation in composites. If opportunity arises, we will continue this work in the coming year.

LIST OF PUBLICATIONS AND TECHNICAL REPORTS

PUBLICATIONS IN REFEREED JOURNALS

1. "Cubic Nonlinearities in Small Particle Composites: Local-Field- Induced Giant Enhancements," D. Stroud and X. Zhang, Physica **A207**, pp. 55-64 (1994).

2. "Effective Linear and Nonlinear Response of Fractal Clusters," P. M. Hui and D. Stroud, Phys. Rev. **B49**, 11729 (1994).

3. "Effective Dielectric Response of Nonlinear Composites," K. W. Yu, P. M. Hui, and D. Stroud, Phys. Rev. **B47**, 14150 (1993).

4. "Theory of Optical Bistability in a Weakly Nonlinear Composite Medium," D. J. Bergman, O.Levy, and D. Stroud, Phys. Rev. **B49**, 129 (1994).

5. "Numerical Studies of the Nonlinear Properties of Composites," X. Zhang and D. Stroud, Phys. Rev. **B49**, 944 (1994).

6. "Scaling Behavior and Surface Plasmon Resonances in a Model Three- Dimensional Metal-Insulator Composites," X. Zhang and D. Stroud, Phys. Rev. **B48**, 6658 (1993).

INVITED AND CONTRIBUTED PRESENTATIONS

1. "Numerical Studies of the Nonlinear Properties of Composites," X. Zhang and D. Stroud, presented at the March meeting of the American Physical Society, Pittsburgh, PA, Mar;ch 21-25, 1994.

2. "Nonlinear Optical Properties of Composite Media," General Colloquium to be presented at New Mexico State University, December 8, 1994.

3. "Nonlinear Optical Properties of Composite Media," to be presented at Wright-Patterson AFB, Dayton, OH, October 21, 1994 (invited seminar).

4. "Nonlinear Optical Properties of Composite Media," at the III International Conference on the Electrical and Optical Properties of Inhomogeneous Media (ETOPIM III), Guanajuato, Mexico, August 9-13, 1993 (invited).

5. "Theory of Nonlinear Optical Properties of Composite Materials," at White Sands Missile Range, White Sands, New Mexico, February 16, 1993.

6. "Optical Properties of Random Composites," at Xerox Webster Research Laboratories, Webster, NY, January 5, 1993 (invited seminar).

LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

1. Mr. Xifeng Zhang, Department of Physics, Ohio State University. Ph. D. degree (expected, Spring, 1995).

2. Prof. Pak-Ming Hui, Department of Physics, Chinese University of Hong Kong.

3. Prof. David J. Bergman, Department of Physics, Tel-Aviv University.

4. Mr. Ohad Levy, Graduate Student, Department of Physics, Tel-Aviv University.

5. Prof. Kin-Wah Yu, Department of Physics, Chinese University of Hong-Kong.

REPORTABLE INVENTIONS

No reportable inventions have resulted from work supported under this Grant.