Nonlinear optical properties of a gold-silica composite with high gold fill fraction and the sign change of its nonlinear absorption coefficient

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We study the intensity-dependent absorption coefficient of gold-silica composites as a function of fill fraction at frequencies near the plasmon resonance. The samples we have studied act as saturable absorbers at all wavelengths and all fill fractions, whereas pure gold is an optical limiter. We provide an explanation based on the intensity-dependent damping of the surface plasmon for this reversal of the sign of the nonlinear absorption.

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1. INTRODUCTION

The optical properties of metal-dielectric composite materials are dominated by the presence of the plasmon resonance. At the plasmon resonance frequency the electric field inside the metal becomes large in comparison to the applied field; this increased field strength leads to an increased absorption of light and to the enhancement of the nonlinear optical properties of the composite.

The theoretical description of the plasmon resonance is well established for composite materials in which the metal is present in very low volume concentrations. The Maxwell Garnett effective-medium theory [1] satisfactorily predicts the linear optical properties. In the Maxwell Garnett theory each metal particle is modeled as a dipole that does not interact with the other particles. Experimental studies of the application of Maxwell Garnett and other formulas for the effective index of composite materials are given in [2,3], and this theory has been extended to the nonlinear case [4,5].

At a higher fill fraction the Maxwell Garnett theory is inadequate. The metal particles become close to each other and begin to interact. Moreover, the nanoparticles can aggregate, and in order to model the response of the structures that they form it is necessary to take into account electric multipole orders higher than dipole. There is not yet an accurate and experimentally confirmed theory for high-fill-fraction composites. Many of the proposed theories that treat composites in which the fill fraction of each component may be large are effective-medium calculations [6–8]. A theory by Sheng [9,10] takes into account some features of the microstructure, and numerical methods permit one to go beyond the effective-medium approximation [11–13]. Experimental studies of the nonlinear optical properties of metal-rich composite materials are few. The optical nonlinearities of gold-silica samples at high fill fractions have been studied by Liao and coworkers using degenerate four-wave mixing [14,15]; similar studies have been performed on other composite materials [16,17]. These studies have found that the magnitude of the nonlinear susceptibility of metal-dielectric composites grows with the metal fill fraction up to a fill fraction of approximately 0.40 and then decreases.

In this paper we examine a range of fill fractions between 0.05 and 0.55 at frequencies around the plasmon resonance. We find that the composite material acts as a saturable absorber at all fill fractions and at all frequencies for which we have collected data. The negative sign of the nonlinear absorption coefficient for gold nanoparticle systems (that indicates saturable absorption) is a fact that is well established for dilute composites. It is a consequence of the phase relation between the field inside the nanoparticles and the incident field. This argument [18] is reviewed in detail herein in the discussion of our data. The fact that the sign of the nonlinear absorption coefficient remains negative even at high fill fractions indicates that at high fill fractions the local field maintains characteristics similar to those that it has at low fill fractions. We propose as well a complementary view, based on the damping of the surface plasmon resonance, of the origin of the negative sign of the nonlinear absorption coefficient.

2. EXPERIMENT

The samples are approximately 200 nm thick films prepared by cosputtering gold and SiO_2 onto a quartz substrate using a multitarget magnetron sputtering system. The targets and substrate were inclined with respect to each other, and as a result the concentration of gold varies on the samples from 0.05 to 0.55.

The deposition rates of gold and silica were calibrated by separately depositing each of them onto a grating and measuring the thickness with a profilometer. The sample was placed in the same position as the calibration gratings for cosputtering, and the fill fraction was calculated at each point from the known deposition rates. The thickness of the resulting film was determined by profilometry. We studied the structure of the sample using electron microscopy. Two of the micrographs, obtained using a Zeiss SUPRA 40 VP scanning electron microscope (SEM), are shown in Fig. 1; the clear features in these images represent gold. Figure 1(a) is the sample at fill fraction $f=0.05$; at this low fill fraction the diameter of most nanoparticles can be estimated as $\lesssim 10\,\text{nm}$. Figure 1(b) is the sample at $f=0.55$; even at this high fill fraction the sample consists of isolated gold nanoparticles. Three representative linear attenuation spectra of the sample at three different fill fractions are shown in Fig. 2. The plasmon resonance at $f=0.05$ is barely recognizable; it is quite prominent at $f=0.23$, centered at 520 nm, and slightly shifted to the red at $f=0.41$.

We performed wavelength-resolved measurements of the nonlinear absorption coefficient β at five different fill fractions ($f=0.05$, 0.23, 0.31, 0.41, and 0.55) and performed measurements at the fixed wavelength of 532 nm over all the range of fill fraction using the open-aperture z-scan technique [19]. The nonlinear absorption coefficient β is defined by the formula $\alpha(I)=\alpha(0)+\beta I$ and determines the lowest order of the dependence of the absorption coefficient α on the intensity.

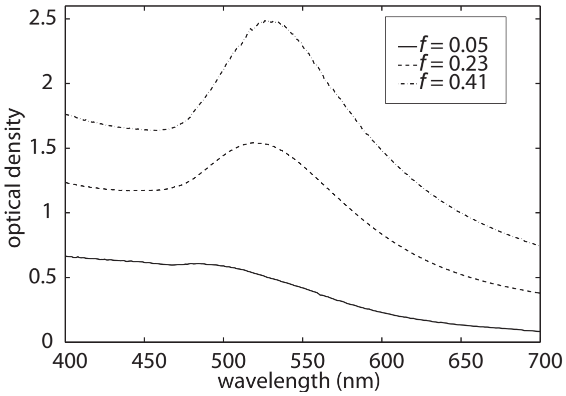

Fig. 2. Linear attenuation spectra of the gold-silica composite samples for various fill fractions.

In the open-aperture z-scan technique the transmittance through the sample is measured as a function of position as the sample is translated through the focus of a Gaussian beam. The transmission profile shows an increase or decrease in the proximity of the focus according to the sign of the nonlinear absorption coefficient β. For pulses with a Gaussian temporal profile, a material with an instantaneous nonlinearity, small changes in transmission, and using integrating detectors to measure the transmitted energy for each pulse, the transmission normalized to its linear value can be fitted by the approximate expression

$$T(z)=1-\frac{q_0(z,0)}{2^{3/2}}, \tag{1}$$

where z is the sample position and $q_0(z,0)=\beta I_0(0)L_{\text{eff}}$ with $I_0(0)$ the on-axis intensity at the peak of the pulse and L_{eff} an effective thickness of the sample that depends on the linear absorption coefficient.

For our measurements we used 25 ps pulses at a 10 Hz repetition rate produced by an optical parametric amplifier (OPA) (EKSPLA PG401 VIR); the low repetition rate renders any thermal contribution to the nonlinearity negligible. The waist diameter of the Gaussian beam is approximately 100 μm.

We display our results for fill fractions of 0.05, 0.23, and 0.41 in Fig. 3. The frequency-resolved data at other

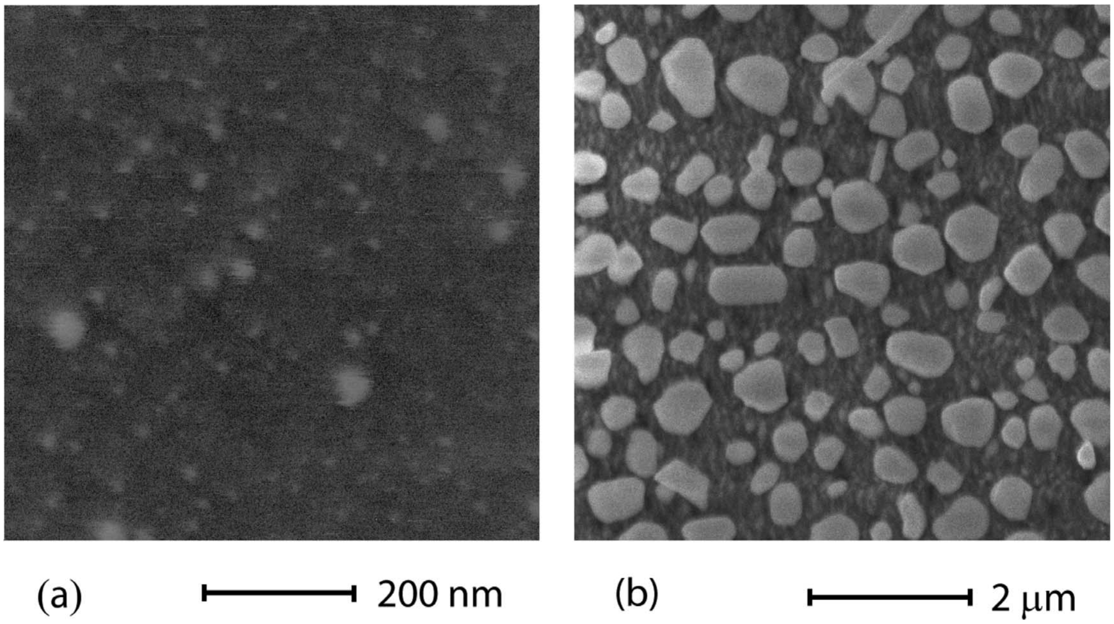

Fig. 1. SEM micrographs of the gold-silica composite. The clear areas of the micrograph represent gold. (a) Sample at $f=0.05$; the diameter of most nanoparticles can be estimated as $\lesssim 10\,\text{nm}$. (b) Sample at $f=0.55$; even at this high fill fraction the sample consists of isolated gold nanoparticles.

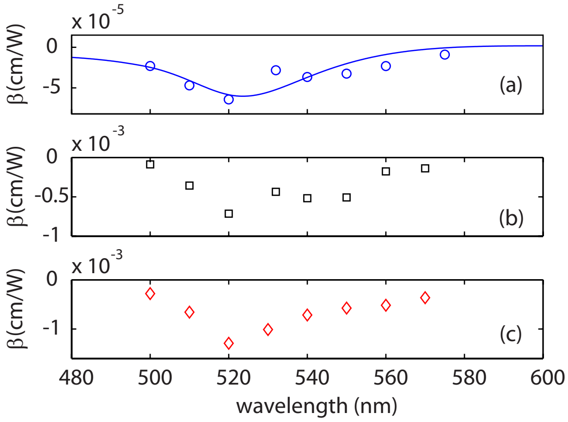

Fig. 3. (Color online) Nonlinear absorption coefficient of the gold-silica composite film at fill fraction (a) $f=0.05$, (b) $f=0.23$, and (c) $f=0.41$, respectively. A fit to the Maxwell Garnett theory with $D=2.40$ is shown for the data for $f=0.05$. The Maxwell Garnett theory is not valid at the higher fill fractions.

fill fractions do not add any significantly different information. We have plotted a fit to the Maxwell Garnett theory for the data at $f=0.05$; we discuss the fit in Section 3.

The composite material is found to act as a saturable absorber (that corresponds to having a negative value of β) for all fill fractions and at all wavelengths for which a measurement was performed. The nonlinearity first grows and then decreases as a function of fill fraction; this behavior can clearly be seen in Fig. 4, where we plot the nonlinear absorption coefficient against the fill fraction at a fixed wavelength. Similar results have been reported in other papers [14,16,17]. We also observe from Fig. 3 that the peak of the nonlinear response as a function of wavelength does not shift much as the fill fraction is varied.

We obtain a useful insight into the nature of the optical response by noting that the nonlinear response (Fig. 3) peaks at approximately the same wavelength as the linear response (Fig. 2). The link between the linear and nonlinear properties is of course the plasmon resonance; we shall examine this link in more detail in Section 3 and show how it determines the sign of the nonlinear absorption coefficient.

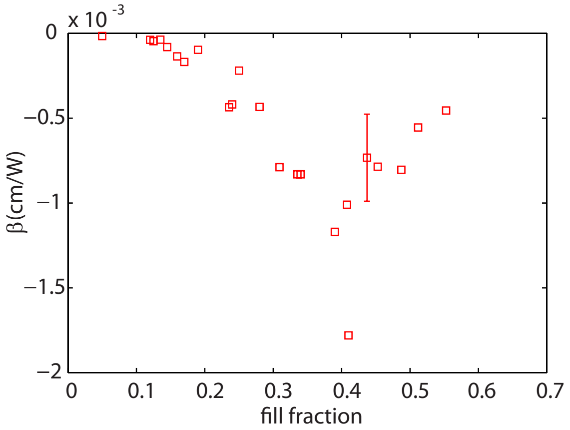

Fig. 4. (Color online) Nonlinear absorption coefficient of a gold-silica composite film plotted as a function of fill fraction at a wavelength of 532 nm. An error bar is shown for one data point; the estimated error is 35% for all data points.

3. DISCUSSION

It is possible to understand the experimental results at low fill fractions through the use of a modified version of the Maxwell Garnett theory, which retains its spirit and all of its fundamental approximations.

The need for modifications of the Maxwell Garnett theory comes from the fact that we want a formula that we can apply to very thin samples. The standard Maxwell Garnett theory calculates the local field in a composite sample at the location of a specified nanoparticle assuming that the nanoparticle is surrounded by an isotropic distribution of dipole density; this condition is not completely fulfilled for a sample that is only 200 nm thick.

We proceed in two steps. First we develop a theory valid for a planar (two-dimensional) sample. We then note that the formulas for the two-dimensional and the usual three-dimensional cases can be written in the same form using a parameter D (for dimension) that takes the values of 2 and 3, respectively. We then let the parameter D vary freely between 2 and 3 to represent the case of a sample that is neither truly two- nor three-dimensional. Details of the derivation of the two-dimensional Maxwell Garnett theory are given in Appendix A. The effective dielectric constant ϵ of a D-dimensional Maxwell Garnett composite medium is thereby found to be given by the relation

$$\frac{\epsilon-\epsilon_h}{\epsilon+(D-1)\epsilon_h}=f\frac{\epsilon_i-\epsilon_h}{\epsilon_i+(D-1)\epsilon_h}, \tag{2}$$

where ϵ_h is the dielectric constant of the host and can be considered purely real while $\epsilon_i=\epsilon_i'+i\epsilon_i''$ is the dielectric constant of the metallic inclusions. For small fill fractions when the dielectric constant of the composite material is very close to the dielectric constant of the host, the dielectric constant of the composite material can be approximated by

$$\epsilon\approx\epsilon_h\left[1+Df\frac{\epsilon_i-\epsilon_h}{\epsilon_i+\epsilon_h(D-1)}\right]. \tag{3}$$

In these small-fill-fraction conditions the approximate expression for the linear absorption coefficient,

$$\alpha=\frac{\omega}{c}\,\mathrm{Im}\sqrt{\epsilon}\approx 2\frac{\omega}{c}Df\sqrt{\epsilon_h}\,\mathrm{Im}\left\{\frac{\epsilon_i-\epsilon_h}{\epsilon_i+\epsilon_h(D-1)}\right\}, \tag{4}$$

greatly simplifies for a host with no loss to the following expression:

$$\alpha\approx\frac{\omega}{c}D^2f\epsilon_h^{3/2}\frac{\epsilon_i''}{[\epsilon_i'+(D-1)\epsilon_h]^2+\epsilon_i''^2}. \tag{5}$$

Equation (5), which is only valid in the limit of very small fill fractions, leads to the reversal of the sign of the induced absorption with respect to that of pure gold for the following reason. Near resonance, that is, for $[\epsilon_i'+(D-1)\epsilon_h]^2\approx 0$, α is inversely proportional to ϵ_i''. Thus, as ϵ_i'' increases the overall absorption α decreases. The bulk properties of gold are such that $\mathrm{Im}\,\chi^{(3)}$, the imaginary part of the third-order nonlinear susceptibility, is positive, meaning that gold itself acts as a reverse saturable absorber, that is, as an optical limiter. As the optical field strength E increases, the effective value of ϵ_i'' thus increases by an amount equal to 3 Im $\chi^{(3)}|E|^2$, and the overall absorption decreases. Thus the composite material acts as a saturable absorber. We observe that this is similar to what happens in the case of a forced harmonic oscillator: at resonance it is the most damped oscillator that dissipates the least power because an oscillator at resonance oscillates with an amplitude inversely proportional to the damping constant.

The simple explanation just presented for the sign reversal, or that presented in [18], cannot be applied to a situation in which the fill fraction of the metallic component becomes large. In this case we can suggest the following more heuristic explanation. It has previously been established [20] that the surface plasmon resonance becomes broadened in the presence of intense optical radiation. The broadening of the resonance implies an increased damping for the surface plasmon. Thus the field enhancement within each nanoparticle is decreased and consequently the overall absorption is decreased. Thus, by this mechanism the composite material is once again expected to act as a saturable absorber.

The explanation that we just presented complements, for the case of the imaginary part of the nonlinearity, the reasoning based on the local-field effects that was presented in [18]. We briefly review that reasoning here. An expression for the nonlinear susceptibility of a Maxwell Garnett composite has been derived in [5] for the case of spherical inclusions. In Appendix A we give a brief derivation of the nonlinear susceptibility for the case of cylindrical inclusions that is valid when the inclusions only are nonlinear. The result for D dimensions is

$$\chi^{(3)} = f|q_i|^2 (q_i)^2 \chi_i^{(3)}, \tag{6}$$

where q_i is the local-field factor in the metal inclusions. The local-field factor for D dimensions is

$$q_i = \frac{\epsilon + (D-1)\epsilon_h}{\epsilon_i + (D-1)\epsilon_h}. \tag{7}$$

Equation (6) displays the sign-reversal effect that we have discussed starting from Eq. (5). At the plasmon resonance the condition $\epsilon_i' + 2\epsilon_h = 0$ is approximately satisfied (exactly satisfied in the limit of a very small fill fraction); the local-field factor therefore becomes $q_i \approx 3\epsilon_h / i\epsilon_i''$, which is imaginary. Thus q_i^2 is mainly real negative and the nonlinear susceptibility of the composite material is opposite in sign to that of the metal inclusions.

A comparison of the predictions of Eq. (6) and the experimental data is given in Fig. 3(a). To obtain good agreement with the data we took the parameter D to have a value of 2.38. Moreover we took into account that collisions of the free electrons with the boundaries of the nanoparticles modify the dielectric function of gold. We assume that this process only influences the imaginary part of the dielectric function. The relaxation time τ of the conduction electrons in the nanoparticles is taken to be described by the relation $1/\tau = 1/\tau_{\text{bulk}} + v_F/l$, where v_F is the Fermi velocity and l is the average mean path between two points on the surface of the nanoparticle, which for a sphere of radius R is $4R/3$ [21]. The imaginary part of the dielectric function of gold is therefore given by

$$\epsilon_i'' = \epsilon_{i(\text{bulk})}'' + \frac{3\omega_p^2 v_F}{4\omega_p^3 R}. \tag{8}$$

We use the value 1.36×10^{16} Hz for the plasma frequency ω_p and 1.40×10^{8} cm/s for the Fermi velocity v_F [22] of bulk gold.

The fit of Fig. 3 is realized using a radius of 3 nm for the nanoparticles, which is supported by the (SEM) micrograph in Fig. 1(a); it is reached assuming a third-order susceptibility for gold $\chi^{(3)} = (-2+10i) \times 10^{-8}$ esu, which is compatible with the value found in [23].

The Maxwell Garnett theory, and therefore Eq. (6), cannot quantitatively describe the sets of our data that have fill fractions f equal or larger than 0.23, but the concept described using Eq. (5) is still valid: the nonlinearity of the composite results from an intensity-dependent damping of the resonance and it makes sense from a physical point of view that the nonlinear behavior of the composite material at high fill fractions is similar to the behavior at lower fill fractions if the character of the resonance is not drastically modified.

In other words, the fact that the nonlinear behavior of our sample is rather uniform at all fill fractions is an indication that the local fields are similar to the low fill fractions' local fields in all conditions; they are concentrated inside the nanoparticles or their aggregates and there are no complicated field distributions with hot spots. As a confirmation, all of the SEM micrographs that we collected show that the sample consists of isolated gold nanoparticles; Fig. 1(b) shows the structure of the sample at the highest fill fraction at which we took measurements. The heuristic considerations that we present should not be valid for composite materials with a more complicated morphology as for example the films investigated by Seal *et al.* [24].

4. CONCLUSIONS

We have performed frequency-resolved measurements of the nonlinear absorption coefficient of gold-silica composite materials for a large range of fill fractions. The films are found to act as saturable absorbers at all fill fractions and all wavelengths, although gold itself is an optical limiter. We have presented a simple model for the change of sign of the nonlinear absorption that we have observed, which can be interpreted in terms of the intensity-dependent damping of the surface plasmon resonance.

APPENDIX A

The Maxwell Garnett theory for the effective dielectric constant of a medium consisting of a collection of nanoparticles of dielectric constant ε_i immersed in a host of dielectric constant ε_h is developed in the same way as the Clausius–Mossotti theory for the dielectric constant of a rarefied gas. To obtain the polarization density of the composite medium one has to add the polarization of the host material and the polarization of the nanoparticles; the polarization of the nanoparticles is calculated from their polarizability taking into account that each of them is subject to the Lorentz local field rather than the macroscopic field.

We model the two-dimensional composite as a collection of infinitely long cylinders whose axis is perpendicular to the applied field immersed in a host medium (Fig. 5). In other words, we approximate the two-dimensional medium as a three-dimensional medium with translational symmetry along one axis; this approximation allows us to easily obtain the expression for the third-order susceptibility.

If a cylinder of radius R and dielectric constant ε_i immersed in a medium of dielectric constant ε_h is subject to an electric field $\mathbf{E}$ perpendicular to its axis, it acquires a polarization per unit length

$$\mathbf{\Pi}_{\mathrm{cyl}} = \varepsilon_h \frac{R^2}{2}\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + \varepsilon_h}\mathbf{E} = \alpha_{\mathrm{cyl}}\mathbf{E}. \tag{A1}$$

The polarization density of the medium, when the macroscopic electric field is $\mathbf{E}$, is

$$\mathbf{P} = \mathbf{P}_h + N\mathbf{\Pi}_{\mathrm{cyl}} = \chi_h \mathbf{E} + N\alpha_{\mathrm{cyl}}\mathbf{E}_{\mathrm{loc}}, \tag{A2}$$

where N is the number of cylindrical inclusions per unit area and $\mathbf{E}_{\mathrm{loc}}$ is the Lorentz local field.

The Lorentz local field is the field to which each inclusion is subject, that is, the macroscopic field minus the field generated by the inclusion itself. It can be calculated by eliminating the inclusions from a cylindrical region, creating in this way a cylindrical cavity, and leaving all the rest (in particular the polarization of the other inclusions) unchanged; in this cavity the Lorentz field is uniform and given by

$$\mathbf{E}_{\mathrm{loc}} = \mathbf{E} + \frac{2\pi\mathbf{\Pi}}{\epsilon_h}, \tag{A3}$$

where $\mathbf{\Pi} = N\mathbf{\Pi}_{\mathrm{cyl}}$ is the polarization density per unit volume due to the inclusions.

Inserting Eq. (A3) into Eq. (A2) we obtain the following expression for the susceptibility χ of the composite medium:

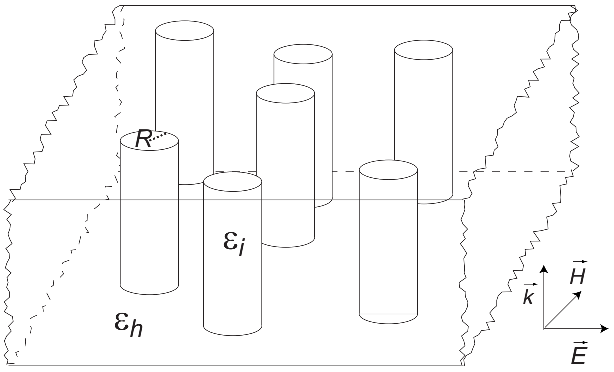

Fig. 5. Section of the model for a Maxwell Garnett two-dimensional composite, a host with infinitely long cylindrical inclusions.

$$\chi = \chi_h + \frac{N\alpha_{\mathrm{cyl}}}{1 - \dfrac{2\pi N\alpha_{\mathrm{cyl}}}{\epsilon_h}}. \tag{A4}$$

Rewriting Eq. (A4) in terms of the dielectric constants we obtain for the two-dimensional Maxwell Garnett composite the following relation:

$$\frac{\epsilon - \epsilon_h}{\epsilon + \epsilon_h} = f\frac{\epsilon_i - \epsilon_h}{\epsilon_i + \epsilon_h}. \tag{A5}$$

The local field $\mathbf{E}_i$ inside the cylindrical inclusions is given by

$$\mathbf{E}_i = q_i \mathbf{E}, \tag{A6}$$

where

$$q_i = \frac{\epsilon + \epsilon_h}{\epsilon_i + \epsilon_h} \tag{A7}$$

is the local-field factor.

Comparing Eq. (A5) to the Maxwell Garnett result for spherical inclusions we see that both the two- and three-dimensional relations have the form

$$\frac{\epsilon - \epsilon_h}{\epsilon + (D-1)\epsilon_h} = f\frac{\epsilon_i - \epsilon_h}{\epsilon_i + (D-1)\epsilon_h}, \tag{A8}$$

where D is the dimensionality of the system. In an analogous way we have for the local-field factor

$$q_i = \frac{\epsilon + (D-1)\epsilon_h}{\epsilon_i + (D-1)\epsilon_h}. \tag{A9}$$

In Eqs. (A8) and (A9) the dimensionality D can be treated as a free parameter ranging between 2 and 3 to represent composite media whose characteristics are intermediate between the two- and three-dimensional cases.

An expression for the effective third-order nonlinearity for the Maxwell Garnett composite in the case in which only the inclusions are nonlinear can be obtained considering that the Maxwell Garnett expression must remain valid as the electric field increases and the dielectric constant of the inclusions change. We can then equate the variation in both sides of Eq. (A8) obtaining

$$\frac{\partial}{\partial\epsilon}\left(\frac{\epsilon - \epsilon_h}{\epsilon + (D-1)\epsilon_h}\right)\Delta\epsilon = f\frac{\partial}{\partial\epsilon_i}\left(\frac{\epsilon_i - \epsilon_h}{\epsilon_i + (D-1)\epsilon_h}\right)\Delta\epsilon_i, \tag{A10}$$

and after a few simplifications we obtain a concise expression for the change of the effective dielectric constant ϵ as a function of the change of the dielectric constant of the inclusions ϵ_i:

$$\Delta\epsilon = f q_i^2 \Delta\epsilon_i. \tag{A11}$$

If the inclusions have a Kerr nonlinearity then $\Delta\epsilon_i$ can be written as a function of the local field in the inclusions as $\Delta\epsilon_i = 4\pi\chi_i^{(3)}|E_i|^2 = 4\pi\chi_i^{(3)}|q_i|^2|E|^2$. Inserting this last expression into Eq. (A11) we obtain the effective nonlinearity of the composite as

$$\chi^{(3)} = f\chi_i^{(3)} q_i^2 |q_i|^2. \tag{A12}$$

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