Nonlinear optical susceptibilities of layered composite materials

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Received November 17, 1992; revised manuscript received July 27, 1993

We present a theoretical description of composite nonlinear optical materials having the form of a layered structure of two or more components that differ both in their linear and nonlinear optical properties. We assume that the thickness of each layer is much smaller than an optical wavelength. We present explicit predictions for the second-order nonlinear optical susceptibilities describing second-harmonic generation and the Pockels effect and for the third-order susceptibility describing the nonlinear index of refraction. We find that under experimentally realizable conditions the nonlinear susceptibility of such a composite can exceed those of its constituent materials.

INTRODUCTION

Composite optical materials are an important class of materials for use in nonlinear optics and electro-optics. Interest in composite materials stems in part from the fact that the optical properties of a composite material can differ significantly from those of its constituent components. In fact, one of the first theoretical studies of composite materials was that of Maxwell Garnett,[1] who considered the linear response of metallic inclusion particles suspended in glass or in aqueous solutions and thereby was able to explain the colors of metallic colloids. Recent work has extended this analysis to the nonlinear optical case[2–10] for both the limit in which nonlinear inclusion particles are suspended in a linear host[2–6,8,9] and the more general case in which both the inclusion particles and the host can respond nonlinearly.[7,10] In our recent investigation[10] we found that, because of local field effects, there are many conditions under which a composite can possess a nonlinear susceptibility that is significantly greater than those of its constituent components. Other recent studies have shown that metallic composites with fractal structures can have large nonlinear susceptibilities.[11–13]

In the present paper we present a theoretical analysis of the nonlinear optical properties of a composite material having a layered geometry of the form shown schematically in Fig. 1. The composite is formed of alternating layers of two different materials possessing linear dielectric constants ϵ_a and ϵ_b and nonlinear susceptibilities χ_a^{NL} and χ_b^{NL}, respectively. (The order of the nonlinearity and the frequency dependence of the nonlinear susceptibilities is specified below within the context of each specific case that is treated.) We assume that the thickness of each layer is much smaller than an optical wavelength and consequently that the propagation of light through the structure can be described in terms of effective linear and nonlinear optical susceptibilities. In general the thicknesses of the layers of materials a and b can be different, and in fact only the volume fractions f_a and f_b of the two components enter into our final results. Although our analysis is restricted to the case of a composite that is composed of only two different materials, generalization to more than two components is straightforward.

Before beginning the detailed mathematical description of the optical properties of such a composite, we point out that the results of the analysis depend critically on the directions of polarization of the interacting light waves. In particular, if the electric field is polarized in the plane of the layers (i.e., $\mathbf{E} \perp \hat{z}$ in the notation of Fig. 1), then the electric field is spatially uniform within the composite material (because of the boundary condition that states that the tangential component of $\mathbf{E}$ must be continuous at an interface); consequently the optical constants of the composite become simple averages of those of the constituent materials, that is,

$$\epsilon_{\mathrm{eff}} = f_a\epsilon_a + f_b\epsilon_b\,, \tag{1a}$$

$$\chi_{\mathrm{eff}}^{\mathrm{NL}} = f_a\chi_a^{\mathrm{NL}} + f_b\chi_b^{\mathrm{NL}}\,. \tag{1b}$$

On the other hand, if the electric field is polarized perpendicular to the plane of the layers (i.e., $\mathbf{E} \parallel \hat{z}$), then the electric field becomes nonuniformly distributed between the two components of the composite (because the normal component of $\mathbf{D}$ and not that of $\mathbf{E}$ is continuous at the boundary); a simple calculation shows that the effective linear dielectric constant is given by

$$\frac{1}{\epsilon_{\mathrm{eff}}} = \frac{f_a}{\epsilon_a} + \frac{f_b}{\epsilon_b}\,, \tag{2}$$

whereas the effective nonlinear susceptibility is given by a different expression for each specific process. A consequence of the fact that the electric field is nonuniformly distributed between the two components is that under certain circumstances the effective susceptibility of the composite can exceed those of its constituent materials.

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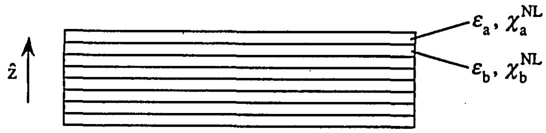

Fig. 1. Composite optical material with a layered geometry. The thickness of each layer is assumed to be much smaller than an optical wavelength.

MESOSCOPIC AND MACROSCOPIC FIELDS

Let us now turn to a more detailed description of the fields within each layer of the composite material. Using lowercase letters to designate quantities measured at the mesoscopic level (i.e., within one of the layers), we relate the mesoscopic field $\tilde{\mathbf{e}}(\mathbf{r}, t) = \mathbf{e}(\mathbf{r}, \omega)\exp(-i\omega t)$ + c.c. to the corresponding macroscopic field $\mathbf{E}$ through

$$\mathbf{E}(\mathbf{r}, \omega) = \int \Delta(\mathbf{r} - \mathbf{r}')\mathbf{e}(\mathbf{r}', \omega)\,\mathrm{d}\mathbf{r}', \tag{3}$$

where $\Delta(\mathbf{r}) = \Delta(|\mathbf{r}|)$ is a smoothly varying weighting function normalized to unity[14] and extending over a range R. Previously[10,15] we showed that, for $R \ll \lambda$, where λ is the vacuum wavelength of light, we have

$$\begin{aligned}\mathbf{e}(\mathbf{r}, \omega) = \mathbf{E}(\mathbf{r}, \omega) &+ \frac{4\pi}{3}\mathbf{P}(\mathbf{r}, \omega) \\ &+ \int \overleftrightarrow{\mathbf{T}}^0(\mathbf{r} - \mathbf{r}')c(|\mathbf{r} - \mathbf{r}'|) \cdot \mathbf{p}(\mathbf{r}', \omega)\mathrm{d}\mathbf{r}' \\ &- \frac{4\pi}{3}\mathbf{p}(\mathbf{r}, \omega),\end{aligned} \tag{4}$$

where $\mathbf{p}(\mathbf{r}, \omega)$ and $\mathbf{P}(\mathbf{r}, \omega)$, respectively, are the mesoscopic and macroscopic polarizations, $c(r)$ is a spherically symmetric cutoff function of range $\approx\mathbf{R}$, and $\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})$ is the static dipole tensor cutoff near the origin, that is

$$\overleftrightarrow{\mathbf{T}}^0(\mathbf{r}) = \begin{cases} (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \overleftrightarrow{U})/\mathbf{r}^3 & \mathbf{r} > \eta\,, \\ 0 & \mathbf{r} < \eta \end{cases} \tag{5}$$

with $\eta \to 0^+$, $\overleftrightarrow{U}$ the unit dyadic, and $\hat{\mathbf{r}} = \mathbf{r}/r$. For our case of interest, where a typical thickness l of a layer satisfies $l \ll R$, we indicate the range of $c(r)$ by the circle in Fig. 2(a). Suppose now that point $\mathbf{r}$ lies in a layer of medium a. Then part of the contribution to the integral in Eq. (4) is the layer in which the point $\mathbf{r}$ lies, minus the small sphere at the origin [Fig. 2(b)]. The two terms representing these components may easily be evaluated through use of the laws of electrostatics [recall that $\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})$ refers to the static dipole tensor], and we have

$$-4\pi\hat{z}\hat{z} \cdot \mathbf{p}_a(\omega) - \left[-\frac{4\pi}{3}\mathbf{p}_a(\omega)\right], \tag{6a}$$

where $\mathbf{p}_a(\omega)$ is the polarization in a medium near point $\mathbf{r}$. Here near refers to distances on the order of R, since $R \ll \lambda$. Since $l \ll R$, in evaluating the rest of the integral in Eq. (4) we may replace the remaining layers by a uniform polarization equal to $\mathbf{P}$; the electrostatic field is then that of a sphere minus the contribution from the missing layer [see Fig. 2(c)],

$$-\frac{4\pi}{3}\mathbf{P}(\omega) - [-4\pi\hat{z}\hat{z} \cdot \mathbf{P}(\omega)]. \tag{6b}$$

Using the sum of expressions (6a) and (6b) for the integral in Eq. (4), we find that

$$\mathbf{e}_a(\omega) = \mathbf{E}(\omega) + 4\pi\hat{z}\hat{z} \cdot \mathbf{P}(\omega) - 4\pi\hat{z}\hat{z} \cdot \mathbf{p}_a(\omega), \tag{7}$$

where $\mathbf{e}_a$ denotes the mesoscopic field in medium a; a similar equation holds for $\mathbf{e}_b$. Throughout we drop the dependence on position in the notation, since all these quantities may be taken as uniform over distances of the order of R; thus we also have

$$\mathbf{P}(\omega) = f_a\mathbf{p}_a(\omega) + f_b\mathbf{p}_b(\omega). \tag{8}$$

From Eq. (7) we see that the x and the y components satisfy $e_{ax}(\omega) = e_{bx}(\omega) = E_x(\omega)$, $e_{ay}(\omega) = e_{by}(\omega) = E_y(\omega)$ [see the discussion above Eq. (1)], while

$$e_{az}(\omega) = E_z(\omega) + F_z(\omega) - 4\pi p_{az}(\omega), \tag{9a}$$
$$e_{bz}(\omega) = E_z(\omega) + F_z(\omega) - 4\pi p_{bz}(\omega), \tag{9b}$$

where for convenience we have introduced

$$F_z(\omega) = 4\pi f_a p_{az}(\omega) + 4\pi f_b p_{bz}(\omega). \tag{10}$$

It is this nontrivial case of a z-polarized field that will be of interest to us below.

Note that Eq. (4) follows directly from the Maxwell equations and the assumption that $R \ll \lambda$ without our requiring any condition on $\mathbf{p}(\mathbf{r}, \omega)$. Thus Eqs. (7)–(10), which also require $l \ll R$ for their validity, also hold for linear or nonlinear optics. Once a model for a relation between $\mathbf{p}$ and $\mathbf{e}$ is adopted (see below), linear and nonlinear constitutive relations can be derived. We note that we may derive Eqs. (7)–(10) from a careful application of the laws of electrostatics by imagining that the medium is placed between two capacitor plates [see discussion after Eq. (1)]. The derivation given here, although longer, is

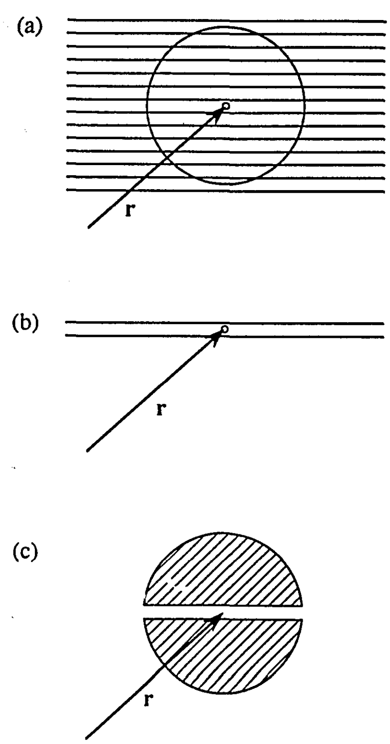

Fig. 2. Calculation of the mesoscopic and the macroscopic fields.

the one that we prefer: in an experimental geometry of interest in optics, the quantities in Eqs. (7)–(10) need not be uniform over a distance of the order of the thickness of the sample, and they certainly can vary in the xy plane over distances much smaller than the length of the sample. Thus the artifice of capacitor plates and a field that is assumed to be uniform throughout the sample is somewhat suspect. In the derivation leading to Eq. (7) we had to assume only that the field was uniform in the z direction within each layer, of typical thickness $1 \ll R$, and in the xy plane over lengths $R \ll \lambda$; typically R is much smaller than the size of the sample.

LINEAR RESPONSE

We first specialize the results of the previous section to the case of a material with linear response by assuming that the mesoscopic polarizations are given by

$$p_{az}(\omega) = \chi_a^{(1)}(\omega) e_{az}(\omega), \qquad p_{bz}(\omega) = \chi_b^{(1)}(\omega) e_{bz}(\omega). \quad (11)$$

If these expressions are substituted into Eqs. (9) and (10), we find that the mesoscopic electric fields are given by the expressions

$$e_{az}(\omega) = \frac{1}{\epsilon_a(\omega)} \frac{E_z(\omega)}{\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]}, \quad (12a)$$

$$e_{bz}(\omega) = \frac{1}{\epsilon_b(\omega)} \frac{E_z(\omega)}{\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]}. \quad (12b)$$

Through use of Eqs. (11) and (12) the macroscopic polarization $P_z(\omega) = f_a p_{az}(\omega) + f_b p_{bz}(\omega)$ can be calculated. This result can then be expressed in terms of a linear susceptibility through use of the standard relation $P_z(\omega) = \chi^{(1)}(\omega) E_z(\omega)$ or in terms of an effective dielectric constant through use of the standard definitions $\epsilon(\omega) = 1 + 4\pi\chi^{(1)}(\omega)$. Such a procedure yields the result

$$\frac{1}{\epsilon_{\text{eff}}(\omega)} = \frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}, \quad (13)$$

in agreement with Eq. (2), which was quoted above without proof. Figure 3 shows the dependence of the effective dielectric constant on the fill fraction f_b of component b for several different values of the ratio $\epsilon_b(\omega)/\epsilon_a(\omega)$ of linear dielectric constants. Equations (12) for the mesoscopic electric field can be rewritten in terms of the effective dielectric constant as

$$e_{az}(\omega) = \frac{\epsilon_{\text{eff}}(\omega)}{\epsilon_a(\omega)} E_z(\omega), \qquad e_{bz}(\omega) = \frac{\epsilon_{\text{eff}}(\omega)}{\epsilon_b(\omega)} E_z(\omega). \quad (14)$$

Note that the ratio $\epsilon_{\text{eff}}(\omega)/\epsilon_a(\omega)$ can be interpreted as the local-field enhancement factor for component a, that is, the factor by which the mesoscopic field within region a exceeds the macroscopic electric field. The ratio $\epsilon_{\text{eff}}(\omega)/\epsilon_b(\omega)$ can similarly be interpreted as the local-field enhancement factor for component b. Note that one of these factors will necessarily be greater than unity. If the component for which the local-field enhancement factor exceeds unity displays a nonlinear response, the effective nonlinear susceptibility of the composite material can be enhanced with respect to that of the pure nonlinear material. Several examples of such behavior are presented below.

SECOND-HARMONIC GENERATION

Next we consider the process of second-harmonic generation in a layered composite material. We assume that in the general case each of the components possesses a second-order nonlinear susceptibility given by $\chi_a^{(2)} = \chi_a^{(2)}(2\omega = \omega + \omega)$ and $\chi_b^{(2)} = \chi_b^{(2)}(2\omega = \omega + \omega)$. For this and the other nonlinear processes that we consider below, we work out only the susceptibility components involving z-polarized light, e.g., $\chi_a^{(2)}(2\omega = \omega + \omega) = \chi_{azzz}^{(2)}(2\omega = \omega + \omega)$. It is these terms that generally will exhibit the largest enhancement. These terms would be relevant, for example, for the case of TM light propagating along the layers of the structure. The effective medium coefficients for susceptibility components involving solely x and y follow from Eq. (1b), while the effective medium coefficients for susceptibility components involving z as well as x or y can be derived as indicated below but with the general Eq. (7) used in place of its z component, Eqs. (9) and (10).

In the present case of second-harmonic generation the total polarization within component a, correct to second order in the electric field, can be written as

$$p_{az}(2\omega) = \chi_a^{(2)} e_{az}^{\,2}(\omega) + \chi_a^{(1)}(2\omega) e_{az}(2\omega), \quad (15)$$

where $e_{az}(\omega)$ and $e_{az}(2\omega)$ represent the electric fields within component a at the fundamental and the second-harmonic frequencies, respectively. In evaluating this expression we take $e_{az}(2\omega)$ to be given by the general expressions (9). However, it is adequate to take $e_{az}(\omega)$, which appears in the first term, to be given by Eq. (12a), which was derived with the assumption that the medium possesses only a linear response. The reason why this is adequate is that the first term on the right-hand side of Eq. (15) is explicitly second order in the mesoscopic field $e_{az}(\omega)$, and hence only the linear contribution to $e_{az}(\omega)$ need be used. On the other hand, the second term in Eq. (15) is linear in $e_{az}(2\omega)$, and hence for consistency we must include the nonlinear contribution to $e_{az}(2\omega)$, which is contained in the factor $p_{az}(\omega)$ of Eq. (9). We thus obtain the result

$$p_{az}(2\omega) = \chi_a^{(2)} \left\{ \frac{E_z(\omega)}{\epsilon_a(\omega)\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]} \right\}^2 + \chi_a^{(1)}(2\omega) \times [E_z(2\omega) + F_z(2\omega) - 4\pi p_{az}(2\omega)]. \quad (16)$$

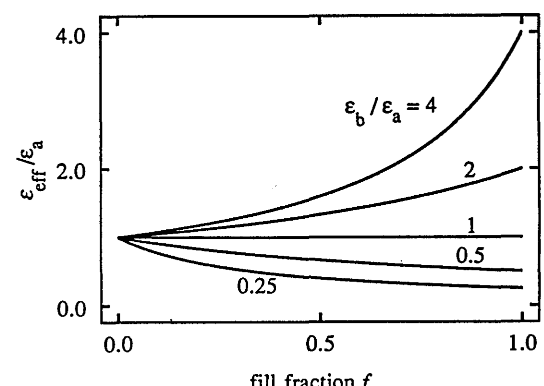

Fig. 3. Dependence of the effective dielectric constant on the fill fraction f_b of component b.

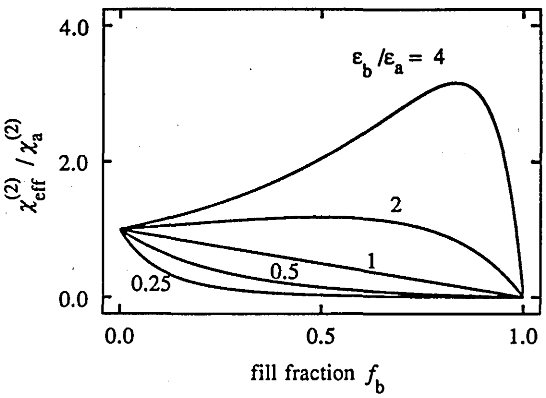

Fig. 4. Effective nonlinear susceptibility for second-harmonic generation plotted versus the fill fraction of component b with the assumption that only component a possesses a second-order nonlinear optical response.

This equation can now be solved for $p_{az}(2\omega)$ to yield

$$p_{az}(2\omega) = \frac{\chi_a^{(2)}}{\epsilon_a(2\omega)} \left\{ \frac{E_z(\omega)}{\epsilon_a(\omega)\left[\frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}\right]} \right\}^2 + \frac{\chi_a^{(1)}(2\omega)}{\epsilon_a(2\omega)}[E_z(2\omega) + F_z(2\omega)]. \qquad (17)$$

A similar equation holds for $p_{bz}(2\omega)$ through the interchange of subscripts a and b. We next calculate the macroscopic polarization at the second-harmonic frequency by performing the volume average of the mesoscopic polarizations as $P_z(2\omega) = f_a p_{az}(2\omega) + f_b p_{bz}(2\omega)$. We introduce Eqs. (10) and (11) in order to evaluate the term $F_z(2\omega)$, and we find through explicit calculation that

$$P_z(2\omega) = \chi_{\rm eff}^{(2)}(2\omega = \omega + \omega)E_z{}^2(\omega) + \chi_{\rm eff}^{(1)}(2\omega)E_z(2\omega), \qquad (18)$$

where $\chi_{\rm eff}^{(1)}(2\omega)$ is now given by $[\epsilon_{\rm eff}(2\omega) - 1]/4\pi$, with $\epsilon_{\rm eff}$ given by Eq. (2), and where the effective nonlinear susceptibility for second-harmonic generation is given by

$$\chi_{\rm eff}^{(2)}(2\omega = \omega + \omega) = \frac{\frac{f_a\chi_a^{(2)}}{\epsilon_a(2\omega)\epsilon_a(\omega)^2} + \frac{f_b\chi_b^{(2)}}{\epsilon_b(2\omega)\epsilon_b(\omega)^2}}{\left[\frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}\right]^2\left[\frac{f_a}{\epsilon_a(2\omega)} + \frac{f_b}{\epsilon_b(2\omega)}\right]}. \qquad (19)$$

As is generally true for a second-order susceptibility, this expression displays a third-order dependence on the local field enhancement factor ($\epsilon_{\rm eff}/\epsilon_a$ for medium a, $\epsilon_{\rm eff}/\epsilon_b$ for medium b). Figure 4 shows the predicted dependence of the effective nonlinear susceptibility for second-harmonic generation on the fill fraction of component b with the simplifying assumptions that only component a possesses a second-order linear response and that the linear dielectric constants are not frequency dependent, that is, that $\epsilon_a(\omega) = \epsilon_a(2\omega)$ and $\epsilon_b(\omega) = \epsilon_b(2\omega)$. Note that under realistic conditions the nonlinear susceptibility of the composite can exceed that of the nonlinear component by a factor of approximately 3. Enhancement of the nonlinear susceptibility occurs when the nonlinear component of the composite (i.e., component a) possesses a linear dielectric constant that is smaller than that of the other component, because according to Eq. (14) it is under this condition that the field within the nonlinear component exceeds the macroscopic field.

POCKELS EFFECT

We next consider the Pockels electro-optic effect in a layered composite material. The calculation proceeds along the same lines as that of the second-harmonic response. We assume that each of the components possesses a second-order nonlinear susceptibility given by $\chi_a^{(2)} = \chi_a^{(2)}(\omega = \omega + 0)$ and $\chi_b^{(2)} = \chi_b^{(2)}(\omega = \omega + 0)$; we assume that charging effects that are due to free carriers are negligible. We denote the dc fields in media a and b and the macroscopic dc field by $e_{az}(0)$, $e_{bz}(0)$, and $E_z(0)$, respectively. The total polarization within component a, correct to second order in the electric field, can then be represented as

$$\begin{aligned} P_{az}(\omega) &= 2\chi_a^{(2)}e_{az}(\omega)e_{az}(0) + \chi_a^{(1)}(\omega)e_{az}(\omega) \\ &= \frac{2\chi_a^{(2)}E_z(\omega)E_z(0)}{\epsilon_a(\omega)\left[\frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}\right]\epsilon_a(0)\left[\frac{f_a}{\epsilon_a(0)} + \frac{f_b}{\epsilon_b(0)}\right]} \\ &\quad + \chi_a^{(1)}(\omega)[E_z(\omega) + F_z(\omega) - 4\pi p_{az}(\omega)], \end{aligned} \qquad (20)$$

where, as in Eq. (16), we have included the nonlinear contribution to the mesoscopic field in the second term in this expression but not in the first in order that both contributions be correct to second order in the applied field amplitude. We now solve the second form of this equation for $p_{az}(\omega)$ to obtain

$$\begin{aligned} p_{az}(\omega) = \frac{2\chi_a^{(2)}}{\epsilon_a(\omega)} &\frac{E_z(\omega)}{\left[\frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}\right]} \\ &\times \frac{E_z(0)}{\epsilon_a(0)\left[\frac{f_a}{\epsilon_a(0)} + \frac{f_b}{\epsilon_b(0)}\right]} \\ &+ \frac{\chi_a^{(1)}(\omega)}{\epsilon_a(\omega)}[E_z(\omega) + F_z(\omega)]. \end{aligned} \qquad (21)$$

A similar equation holds for $p_{bz}(\omega)$ through the interchange of subscripts a and b. We next calculate the macroscopic polarization at the optical frequency by performing the volume average to obtain $P_z(\omega) = f_a p_{az}(\omega) + f_b p_{bz}(\omega)$. We find through explicit calculation that

$$P_z(\omega) = 2\chi_{\rm eff}^{(2)}(\omega = \omega + 0)E_z(\omega)E_z(0) + \chi_{\rm eff}^{(1)}(\omega)E_z(\omega), \qquad (22)$$

where the effective nonlinear susceptibility describing the Pockels effect is given by

$$\chi_{\rm eff}^{(2)}(\omega = \omega + 0) = \frac{\frac{f_a\chi_a^{(2)}}{\epsilon_a(0)\epsilon_a(\omega)^2} + \frac{f_b\chi_b^{(2)}}{\epsilon_b(0)\epsilon_b(\omega)^2}}{\left[\frac{f_a}{\epsilon_a(\omega)} + \frac{f_b}{\epsilon_b(\omega)}\right]^2\left[\frac{f_a}{\epsilon_a(0)} + \frac{f_b}{\epsilon_b(0)}\right]}. \qquad (23)$$

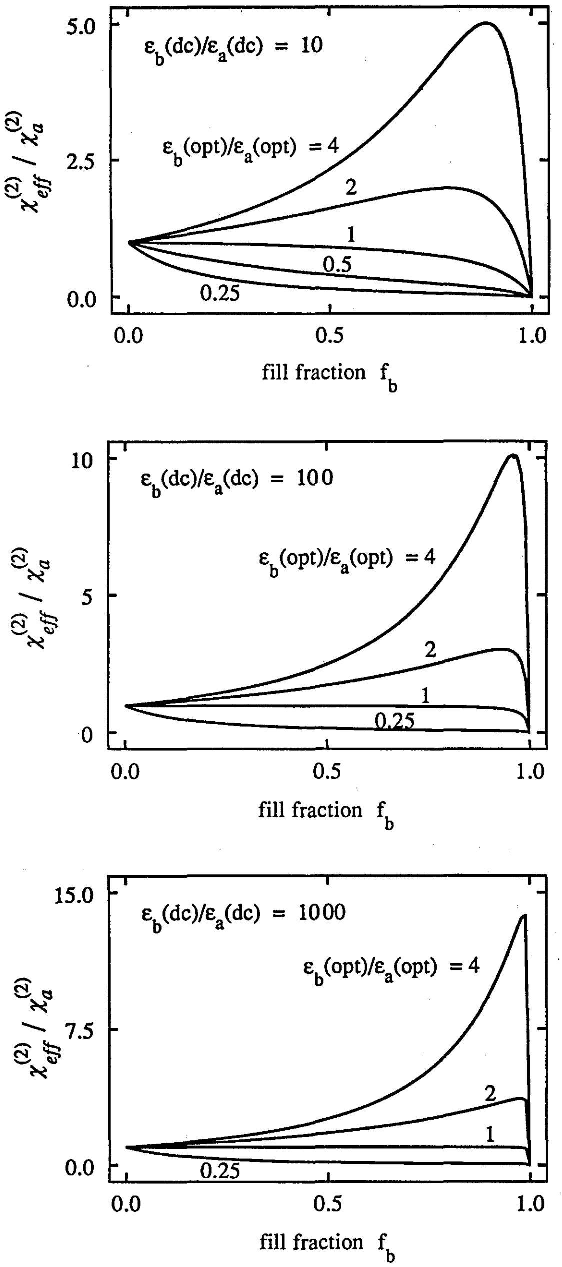

Fig. 5. Effective nonlinear susceptibility for the Pockels effect plotted versus the fill fraction of component b, with the assumption that only component a possesses a second-order nonlinear optical response.

If we make the simplifying assumptions that only component a responds nonlinearly and that the dc and the optical-frequency linear dielectric constants are equal, that is, that $\epsilon_a(0) = \epsilon_a(\omega)$ and $\epsilon_b(0) = \epsilon_b(\omega)$, then the predictions of Eq. (23) are identical to those displayed in Fig. 4 for second-harmonic generation. However, in practice dc dielectric constants span a much larger range than optical-frequency dielectric constants, and for this reason it generally is not a good approximation to ignore the frequency dependence of the linear dielectric constant. Figure 5 shows the dependence of the effective nonlinear susceptibility on the fill fraction of component b for this more general case. Note that the much larger enhancements in the effective susceptibility are possible in this case.

NONLINEAR REFRACTIVE INDEX

Similar reasoning can be used for calculating the nonlinear optical susceptibility that describes the nonlinear refractive index. In this case we assume that each component of the composite is described by a third-order nonlinear susceptibility of the form $\chi_a^{(3)} = \chi_a^{(3)}(\omega = \omega + \omega - \omega)$ and $\chi_b^{(3)} = \chi_b^{(3)}(\omega = \omega + \omega - \omega)$. The total polarization within component a, correct to third order in the electric field, can then be represented as

$$P_{az}(\omega) = 3\chi_a^{(3)} \times \frac{|E_z(\omega)|^2 E_z(\omega)}{\left|\epsilon_a(\omega)\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]\right|^2 \left\{\epsilon_a(\omega)\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]\right\}} + \chi_a^{(1)}(\omega)[E_z(\omega) + F_z(\omega) - 4\pi p_{az}(\omega)], \tag{24}$$

where, as in Eqs. (16) and (20), we have included the nonlinear contribution to the mesoscopic field in the second term in this expression but not in the first, in order that both contributions be correct to third order in the applied field amplitude. We now solve this equation for $p_{az}(\omega)$ to obtain

$$P_{az}(\omega) = \frac{3\chi_a^{(3)}}{\epsilon_a(\omega)} \times \frac{|E_z(\omega)|^2 E_z(\omega)}{\left|\epsilon_a(\omega)\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]\right|^2 \left\{\epsilon_a(\omega)\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]\right\}} + \frac{\chi_a^{(1)}(\omega)}{\epsilon_a(\omega)}[E_z(\omega) + F_z(\omega)], \tag{25}$$

A similar equation holds for $p_{bz}(\omega)$ through the interchange of subscripts a and b. We next calculate the macroscopic polarization by performing a volume average of the mesoscopic polarization as $P_z(\omega) = f_a p_{az}(\omega) + f_b p_{bz}(\omega)$. We then find through explicit calculation that the macroscopic polarization can be represented as

$$P_z(\omega) = 3\chi_{\text{eff}}^{(3)}(\omega = \omega + \omega - \omega)|E_z(\omega)|^2 E_z(\omega) + \chi_{\text{eff}}^{(1)}(\omega)E_z(\omega), \tag{26}$$

where the effective nonlinear susceptibility describing the nonlinear refractive index is given by

$$\chi_{\text{eff}}^{(3)}(\omega = \omega + \omega - \omega) = \frac{\dfrac{f_a\chi_a^{(3)}}{|\epsilon_a(\omega)|^2\epsilon_a(\omega)^2} + \dfrac{f_b\chi_b^{(3)}}{|\epsilon_b(\omega)|^2\epsilon_b(\omega)^2}}{\left|\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right|^2\left[\dfrac{f_a}{\epsilon_a(\omega)} + \dfrac{f_b}{\epsilon_b(\omega)}\right]^2}. \tag{27}$$

As is generally true for a third-order susceptibility, this result shows a fourth-order dependence on the local-field enhancement factor. The predictions of this equation are presented in Fig. 6 with the assumption that only component a possesses a third-order nonlinear optical response. Note that nearly an order-of-magnitude enhancement of

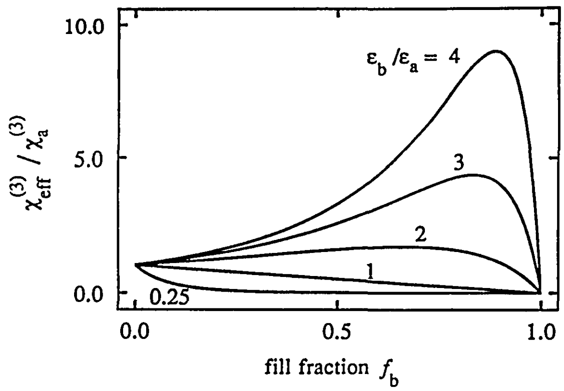

Fig. 6. Effective nonlinear susceptibility describing the nonlinear refractive index plotted versus the fill fraction of component b with the assumption that only component a possesses a third-order nonlinear optical response.

the nonlinear optical susceptibility is predicted under realistic experimental conditions.

For some purposes it is more convenient for us to describe the nonlinearity in the refractive index in terms of the parameter n_2, which is defined through the relation $n = n_0 + n_2 I$ and which is related to the third-order susceptibility through the relation

$$n_2 = \frac{12\pi^2}{n_0^2 c} \chi^{(3)}(\omega = \omega + \omega - \omega). \tag{28}$$

Note that n_2 increases with the fill fraction f_b less rapidly than does $\chi^{(3)}$ because of the factor n_0^2 [which is equal to ϵ_{eff} of Eq. (2)] that appears in the denominator of this expression. In fact, we can see by comparison of Eqs. (2), (19), (27), and (28) that the dependence of n_2 on f_b is identical to that of $\chi^{(2)}$. Thus Fig. 4 can also be used to predict the enhancement of n_2

DISCUSSION

The analysis presented in this paper can be applied to any layered composite structure, such as those formed by vacuum evaporation, by Langmuir–Blodgett techniques, or by spin coating. The analysis predicts that the effective nonlinear susceptibility of the composite can, under proper circumstances, exceed those of the constituent materials. Such an enhancement occurs if the component with the larger nonlinear response possesses the smaller linear dielectric constant. An example of such a situation is that of a composite material formed of layers of a nonlinear optical polymer alternating with layers of an inorganic oxide, such as titanium dioxide, the refractive index of which can be as large as 2.8, depending on the crystal structure and porosity of the layer.

We emphasize that the enhancements predicted here are not interference effects, at least not in the usual sense of that term. In particular, they do not require a regular spacing of the layers, nor indeed do they depend on the thicknesses of the individual layers (as long as they are much smaller than the wavelength of light), but only on the fill fractions of the individual components. Indeed, even if the layers were to vary in thickness, but over lengths on the order of many wavelengths of light, we would expect the effective medium parameters to be uniform if the fill fractions were.

Nonetheless, it is of course true that the techniques of thin-film optics can be applied to calculation of the nonlinear response of a multilayer film (see e.g., the work of Bethune[16]). In such a calculation the fields must be determined by the solution of a set of transfer-matrix equations, with the field calculated in any given layer for the specific incident field at hand. Such an approach is necessary if the layer thicknesses are of the order of the wavelength of light; true interference effects then become important. But if the layer thicknesses are much less than the wavelength of light then the approach that we take here, that of treating the multilayer structure as a uniform effective medium, is possible and of course simplifies any calculation. Still, we may use the transfer-matrix solutions to investigate when the approximations that we rely on break down. Taking as our criterion the condition that the actual phase change across a layer of thickness l be $\leq 1/4(2\pi)$, for a normally incident field we require that $l \leq \lambda/4n$, where λ is the wavelength of light in vacuum at any of the frequencies of interest and n is the refractive index of the layer. The condition is somewhat less stringent for nonnormal incidence or for a guided wave. The same length scale sets the distance over which effects that are due to surface roughness would lead to strong light scattering.

In our previous publication[10] we presented a theoretical analysis of a composite having the Maxwell Garnett geometry, that is, a material composed of spherical inclusion particles embedded in a host material. We note that the layered geometry possesses an anisotropic optical response and that for fields polarized perpendicular to the plane of the layers we obtain a larger enhancement than in the Maxwell Garnett case, whereas for fields polarized along the layers we obtain no enhancement at all. Another difference is that the validity of our Maxwell Garnett calculation was restricted to fill factors much less than unity, whereas for the simpler geometry of the layered structure we obtain results that are valid for all possible values of the fill factors of the two components.

ACKNOWLEDGMENTS

We gratefully acknowledge useful discussions of this material with P. Günter and J. T. Yardley. The portion of this work performed at the University of Rochester was supported by a U.S. Army Research Office University Research Initiative and by the New York State Center for Advanced Optical Technology. The portion of the work performed at the University of Toronto was supported by the National Science and Engineering Research Council of Canada.

REFERENCES AND NOTES

1. J. C. Maxwell Garnett, Philos. Trans. R. Soc. London **203**, 385 (1904); Ser. A **205**, 237 (1906).
2. K. C. Rustagi and C. Flytzanis, Opt. Lett. **9**, 344 (1984).
3. D. Ricard, Ph. Roussignol, and C. Flytzanis, Opt. Lett. **10**, 511 (1985).
4. F. Hache, D. Ricard, and C. Flytzanis, J. Opt. Soc. Am. B **3**, 1647 (1986).
5. Ph. Roussignol, D. Ricard, J. Lukasik, and C. Flytzanis, J. Opt. Soc. Am. B **4**, 5 (1987).
6. G. S. Agarwal and S. Dutta Gupta, Phys. Rev. A **38**, 5678 (1988).

7. J. W. Haus, R. Inguva, and C. M. Bowden, Phys. Rev. A **40,** 5729 (1989).
8. J. W. Haus, N. Kalyaniwalla, R. Inguva, M. Bloemer, and C. M. Bowden, J. Opt. Soc. Am. B **6,** 797 (1989).
9. N. C. Kothari, Phys. Rev. A **41,** 4486 (1990).
10. J. E. Sipe and R. W. Boyd, Phys. Rev. A **46,** 1614 (1992).
11. V. M. Shalaev and M. I. Stockman, Z. Phys. D **10,** 71 (1988); A. V. Butenko, V. M. Shalaev, and M. I. Stockman, Z. Phys. D **10,** 81 (1988).
12. A. V. Butenko, W. M. Shalaev, and M. I. Stockman, Sov. Phys. JETP **7,** 60 (1988).
13. A. V. Butenko, P. A. Chubakov, Yu. E. Danilova, S. V. Karpov, A. K. Popov, S. G. Rautian, V. P. Safonov, V. V. Slabko, V. M. Shalaev, and M. I. Stockman, Z. Phys. D **17,** 283 (1990).
14. J. van Kranendonk and J. E. Sipe, in *Progress in Optics XV,* E. Wolf, ed. (North-Holland, New York, 1977), p. 245.
15. Note that in the notation of Ref. 10 we have set $\epsilon_n = 1$ in writing Eq. (4) of the present paper, that is, in the present paper we do not treat one medium as the host and the other as the inclusion; both are formally treated as inclusions embedded in vacuum.
16. D. S. Bethune, J. Opt. Soc. Am. B **8,** 367 (1991).