PERGAMON

Solid State Communications 115 (2000) 347–352

solid state communications

www.elsevier.com/locate/ssc

Temperature effect on nonlinear optical response of metal–dielectric composite with interfacial layers

J.P. Huang[a,*], L. Gao[a], Z.Y. Li[a,b]

[a]*Department of Physics, Suzhou University, Suzhou 215006, People's Republic of China*
[b]*CCAST (World Laboratory), P.O. Box 8730, Beijing 100080, People's Republic of China*

Received 6 January 2000; accepted 26 April 2000 by R.C. Dynes

Abstract

The dependence of nonlinear optical response on temperature is investigated theoretically for a metal–dielectric composite with interfacial layers in a dilute limit. We show that the effect of interfacial layers on the nonlinear optical response of such composites is more prominent at low temperatures than at high temperatures, that the interfacial factor depends on the volume fraction of metallic particles and the frequency of the incident wave, and that an optimal interfacial layer is found for which the nonlinear optical response is able to be enhanced to a maximal. It is shown that weak nonlinearity can be greatly enhanced if the interfacial factor, frequency and volume fraction are chosen appropriately.

Keywords: A. Disordered systems; D. Electron–electron interactions; D. Electron–phonon interactions; D. Optical properties

1. Introduction

The nonlinear optical properties of disordered nonlinear metal–dielectric composites have received much attention because of their potential application to optical correlator device and phase-conjugator as well as thresholding device [1–3]. A typical system is composed of nonlinear (or linear) metallic particles randomly embedded in a linear (or nonlinear) dielectric host. A detailed analysis of the properties of a metal–dielectric composite reveals the existence of many interesting phenomena such as optical bistability [4] and optical percolation threshold [5]. Many authors have devoted themselves to the discussion of the nonlinear optical properties of such composite media. However, most of these theoretical studies [6,7] and experimental reports [8,9] on the effective nonlinear response were limited to room temperature. As far as elevated temperature is concerned, the preponderance of previous work on optical responses has treated the cases in which the phases are linear [10] and nonlinear [11] materials.

All the previous works are of particular interest, but they neglect the effect of the interfaces separating the metallic particles and the dielectric matrix. The goal of the present paper is to discuss the temperature effect on the nonlinear optical response of a metal–dielectric composite in a dilute limit, by incorporating interfacial-layer information. Our model, in the following, is based upon two experimental facts: (1) Transmission electron microscope (TEM) analysis of some samples shows the metal nanoclusters to be approximately spherical in shape and to be uniformly dispersed in the dielectric host [12]. (2) The third-order nonlinearity of metallic particles is about several orders of magnitude larger than that of the dielectric host in general, and the contribution of matrix to the effective nonlinear susceptibility is small enough to be neglected [13]. The discussion of this problem will be made by combining a Drude model with the interfacial factor [14,15] that is introduced to characterize the interfacial layer. Our results show that the weak nonlinearity can be enhanced greatly if the interfacial factor, frequency of incident wave and volume fraction of metallic particles are chosen appropriately, and give us some instructive information on how to get enhanced nonlinearity from the material with weak nonlinearity.

2. Formalism

We start by considering a kind of nonlinear composite in which nonlinear spherical metallic particles with concentric coating shells of dielectric constant ϵ_s are randomly

* Corresponding author.

0038-1098/00/$ - see front matter
PII: S0038-1098(00)00199-X

embedded in a linear host of dielectric constant ϵ_m. The radii of the core and the shell are r_0 and $r_0 + t$, respectively, with t being the thickness of the coating layer. The dielectric function of the metal core satisfies the displacement-electric field relation

$$\vec{D} = \epsilon_c(\vec{E}_c)\vec{E}_c = \epsilon_c^{(0)}\vec{E}_c + \chi_c^{(3)}|\vec{E}_c|^2\vec{E}_c, \tag{1}$$

where $\epsilon_c^{(0)}$ is the linear dielectric function and $\chi_c^{(3)}$, the third-order nonlinear susceptibility.

Throughout the work, the nonlinear term is assumed to be weak, $\chi_c^{(3)}|\vec{E}_c|^2 \ll \epsilon_c^{(0)}$. The same assumption was successfully made previously and such cubic nonlinearity is the lowest-order nonlinearity in a material with inversion symmetry or macroscopic isotropy [6,7,13].

For finite frequency ω, $\vec{D}$ and $\vec{E}$ are complex quantities, and dependent on position and frequency, in general. They satisfy the Maxwell equations $\nabla \times \vec{E} = i\omega\vec{B}$ and $\nabla \times \vec{D} = 0$, with $\vec{B}$ being the magnetic induction. However, if the sizes of the metallic particles are much less than the wavelength of the incident light, we can adopt a quasi-static approximation, namely, $\nabla \times \vec{E} = 0$ and $\nabla \times \vec{D} = 0$, neglecting the induction term $i\omega\vec{B}$ in Faraday's law. Then we can get the simpler case that the metallic particles are immersed in a uniform but time-dependent field. Also, such retardation can be neglected. Accordingly, the electric potentials ϕ for the dilute system are given by the solution of the Laplace equations,

$$\begin{aligned} &\phi_c = -AE_0 r\cos\theta \qquad r < r_0 \\ &\phi_s = -E_0(Br - Fr^{-2})\cos\theta \qquad r_0 < r < r_0 + t \\ &\phi_m = -E_0(r - Cr^{-2})\cos\theta \qquad r > r_0 + t, \end{aligned} \tag{2}$$

where $\vec{E}_0$ is the external applied field and, A, B, F and C, four parameters, can be determined under boundary conditions. The expression of the dipolar polarizability of the coated sphere, C, is given as follows

$$C = \frac{\rho(2\epsilon_s + \epsilon_m)x + (\epsilon_s - \epsilon_m)}{2\rho(\epsilon_s - \epsilon_m)x + (\epsilon_s + 2\epsilon_m)}(r_0 + t)^3 \tag{3}$$

where $\rho \equiv [r_0/(r_0 + t)]^3$ and

$$x = \frac{\epsilon_c(\vec{E}_c) - \epsilon_s}{\epsilon_c(\vec{E}_c) + 2\epsilon_s} \tag{4}$$

We now consider the effect of the interfacial layer through the limit, $t \to 0$, that is to say, the interfacial property is concentrated on a surface of approximate zero thickness. Only $t\epsilon_s$ can be seen as a significant quantity, $\tilde{\imath} = t\epsilon_s$. Then we take a dimensionless quantity as

$$I = \frac{\tilde{\imath}}{r_0\epsilon_m} \tag{5}$$

to characterize the interface separating the metallic particles and the dielectric host, and I is just called the interfacial factor. A similar description has been made to discuss the bounds on the effective linear thermal conductivity of composite media with imperfect interfaces and the third-order nonlinear optical response of such a composite [14,15]. Generally speaking, for a sharp and smooth interface, i.e. $I = 0$, there are no jumps in the normal component of the electric displacement D_n across the metallic-dielectric interface; for imperfect interface, i.e. $I \neq 0$, D_n jumps across the interface. In addition, I can be taken as a positive or negative value, which is reasonable because the dielectric function of metallic particles is made up of real and imaginary parts. The real part can be a negative large number, while the imaginary part is a positive small one; for simplicity, the small imaginary part can be neglected. When I is taken as a negative (or positive) value, the interface is shown to be metal-like (or dielectric-like). The value of ϵ_m in Eq. (5) can be taken as a constant number in that its dependence on the frequencies of incident waves (e.g. $\omega = 1.5$, 2.4, 3.5 ev) is very small (e.g. MgF_2). As for r_0, we often take an average value due to experimental data in theoretical analysis. Thus, different values of I denote different interfacial layers.

Considering this definition, Eq. (3) can be rewritten as

$$C = \frac{\dfrac{\epsilon_c(\vec{E}_c)}{\epsilon_m} - 1 + 2I}{\dfrac{\epsilon_c(\vec{E}_c)}{\epsilon_m} + 2 + 2I}(r_0 + t)^3 \tag{6}$$

According to the Clausius–Mosotti relation, the effective optical response can be expressed as

$$\epsilon_e(\vec{E}_c) = \epsilon_m + \frac{12\pi NC}{3 - 4\pi NC}\epsilon_m, \tag{7}$$

with N being the number of spherical metallic particles per unit volume. Substituting Eq. (6) into Eq. (7), we have the effective optical response such that

$$\epsilon_e(\vec{E}_c) = \epsilon_m + 3p\epsilon_m\frac{\epsilon_c(\vec{E}_c) + (2I - 1)\epsilon_m}{\epsilon_c(\vec{E}_c)(1 - p) + [2(1 + I - p(2I - 1)]\epsilon_m} \tag{8}$$

with the volume fraction of metallic particles $p \equiv (4/3)\pi N r_0^3$. By means of the Taylor expansion method for weak nonlinearity, Eq. (8) is given by

$$\epsilon_e(\vec{E}_c) = \epsilon_m + 3p\epsilon_m\frac{\epsilon_c^{(0)} + (2I - 1)\epsilon_m}{Q} \times\left(1 + \frac{\chi_c|\vec{E}_c|^2}{\epsilon_c^{(0)} + (2I - 1)\epsilon_m}\right) \times\left(1 - \frac{(1 - p)\chi_c|\vec{E}_c|^2}{Q}\right), \tag{9}$$

where $Q \equiv \epsilon_c^{(0)}(1 - p) + [2(1 + I) - p(I - 1)]\epsilon_m$.

In principle, the local field $\vec{E}_c$, uniform in metallic particles, can be solved exactly. Here, we only represent the local

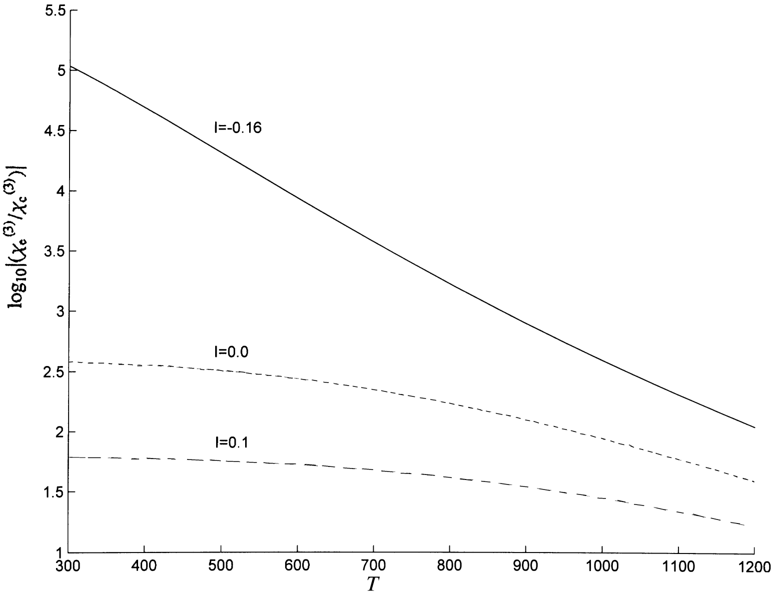

Fig. 1. The normalized effective nonlinear optical response $\log_{10}|(\chi_e{}^{(3)}/\chi_c{}^{(3)})|$, as a function of the temperature at invariant volume fraction $p = 0.05$ and frequency $\omega = 3.5$ ev for three values of $I(-0.16, 0.0, 0.1)$.

field in the weak nonlinearity limit

$$\vec{E}_c = \frac{3\epsilon_m}{\epsilon_c(\vec{E}_c)(1-p) + [2(1+I) - f(2I-1)]\epsilon_m}\vec{E}_0. \quad (10)$$

Due to the dependence of effective third-order nonlinear susceptibility on the linear part of $\vec{E}_c$, we may obtain

$$\vec{E}_c \approx \frac{3\epsilon_m}{Q}\vec{E}_0. \quad (11)$$

The macroscopic effective linear optical response $\epsilon_e{}^0$ and third-order nonlinear susceptibility $\chi_e{}^{(3)}$ could be defined as [16–18]

$$\epsilon_e = \epsilon_e{}^0 + \chi_e{}^{(3)}\left|\vec{E}_0\right|^2. \quad (12)$$

Consequently, $\epsilon_e{}^0$ and $\chi_e{}^{(3)}$ can be determined by the expressions

$$\epsilon_e{}^0 = \epsilon_m + 3p\epsilon_m \frac{\epsilon_c{}^{(0)} + (2I-1)\epsilon_m}{Q} \quad (13)$$

and

$$\chi_e{}^{(3)} = p\chi_c{}^{(3)}\left(\frac{3\epsilon_m}{Q}\right)^2\left|\frac{3\epsilon_m}{Q}\right|^2. \quad (14)$$

As for the metal component, the Drude model is often applied to describe the linear dielectric functions of noble metals, which causes such dielectric functions to exhibit a dependence on temperature. Then the linear dielectric function can be written as

$$\epsilon_c{}^{(0)} = 1 + \Delta\epsilon - \frac{\omega_p{}^2}{\omega(\omega + i\omega_c)} \quad (15)$$

where $\Delta\epsilon$, the contribution of the bound electrons, can be evaluated if compared with experimental data [19], and ω_p is the plasma oscillation frequency given by

$$\omega_p = \left(\frac{Ne^2}{m\epsilon_0}\right)^{1/2} \quad (16)$$

where N and m are the density and the effective mass of the electron, respectively. In principle, both N and m should depend on the change of temperature, however, we may assume this change in ω_p is so small that it can be negligible [20]. Such an assumption has been made to discuss surface-enhanced Raman scattering at an elevated temperature [21]. Thus the temperature effect on $\epsilon_c{}^{(0)}$ only lies in the collision frequency ω_c, which can be divided into two parts

$$\omega_c = \omega_{cp} + \omega_{ce}, \quad (17)$$

where ω_{cp} and ω_{ce} denote the contributions from the phonon–electron [20,21] and electron–electron scattering [19]. Here ω_{cp} has the following expression

$$\omega_{cp} = \frac{\omega_p{}^2\epsilon_0}{\sigma} \frac{\frac{2}{5} + 4\left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^4}{e^z - 1}\,dz}{4\left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^5}{(e^z-1)(1-e^z)}\,dz} \quad (18)$$

where θ and σ are the Debye temperature and d.c. conductivity, respectively, while the expression ω_{ce} can be obtained

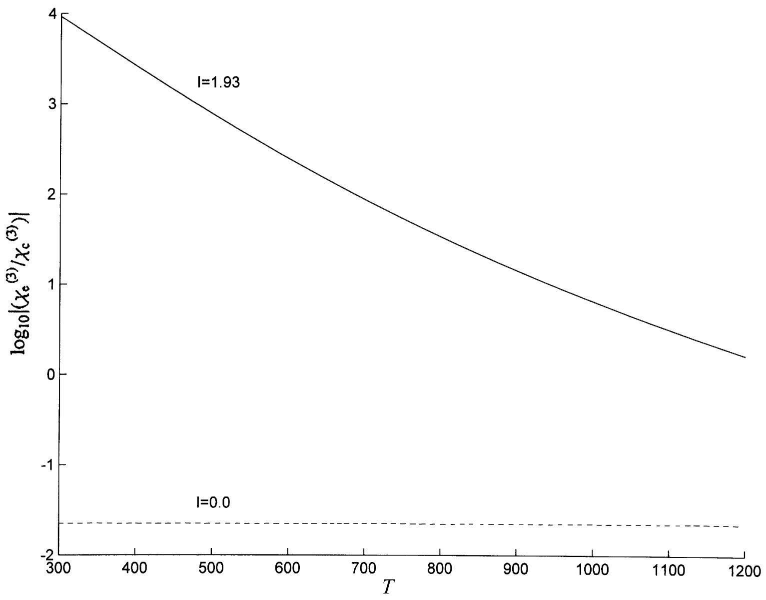

Fig. 2. The normalized effective nonlinear optical response $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$, as a function of the temperature at invariant volume fraction $p = 0.05$ and frequency $\omega = 2.4$ ev for three values of I(0.0, 1.93).

in terms of the Fermi energy E_F of the metal component [10,19],

$$\omega_{ce} = \frac{1}{12}\pi^3 \frac{SF}{\hbar E_F}\left[(k_B T)^2 + \left(\frac{\hbar\omega}{2\pi}\right)^2\right], \qquad (19)$$

where S and F denote two constants giving the average over the Fermi surface of the scattering probability and the fractional unklapp scattering. Eqs. 15–19 determine the dependence of the linear optical response of metallic particles on the temperature.

General speaking, the linear dielectric function of the dielectric component has a negligible dependence on the temperature, compared with that of the metal component. For example, MgF_2, used in the following numerical calculation, has temperature dependence with a linear coefficient of 10^{-6} and its linear dielectric function is referred to [22].

3. Numerical calculation and discussion

So far, the temperature effect on nonlinear optical response $\chi_e^{(3)}$ has been formulated in detail with interfacial factor I considered. Substituting Eqs. (15)–(19) into Eq. (14), we get detailed information on the temperature effect. This is investigated in the following by choosing Ag/MgF_2 as the numerical illustration. The parameters, listed in Refs. [10,11], for the temperature variation of ϵ_e^0 are well available in the present paper.

If we take $I = 0$, and pay no attention to the interfacial layer separating metallic particles and dielectric host, we will get all curves just similar to those from the Maxwell–Garnett theory in Ref. [11] where many explanations can be found.

In Fig. 1, the normalized effective nonlinear optical response $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$ is plotted as a function of temperature T for three different interfacial layers ($I = -0.16,\ 0,\ 0.1$) at volume fraction $p = 0.05$ and frequency $\omega = 3.5$ ev, which is easily obtained from various laser sources. It is shown that, given the volume fraction and frequency, these curves for different I are different from each other, and that the interfacial effect on enhanced nonlinear optical response is more dominant at low temperatures than at high temperatures. For the case of the metal-like interfacial layer, i.e. the value of I is taken as a negative number, the enhanced nonlinear optical response can be obtained, inversely, for the case of the dielectric-like interfacial layer, the enhanced nonlinearity cannot be obtained.

In Fig. 2, the normalized effective nonlinear optical response $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$ is plotted as a function of temperature T for two values of I(0.0,1.93) at $p = 0.05$ and $\omega = 2.4$ ev. For different I, the different curves are obtained, the framework of which is very similar to that in Fig. 1, so we can get some similar information. However, it should be noticed that the enhanced nonlinear optical response is obtained for the case of a dielectric-like interfacial layer, i.e. the interfacial factor I is taken as a positive value.

Comparing Fig. 2 with Fig. 1, we find that the properties of the interfacial layers are related to the frequencies. The interfacial layer is shown to be dielectric-like at low frequency and to be metal-like at high frequency. It is well known that the metallic response to frequency is

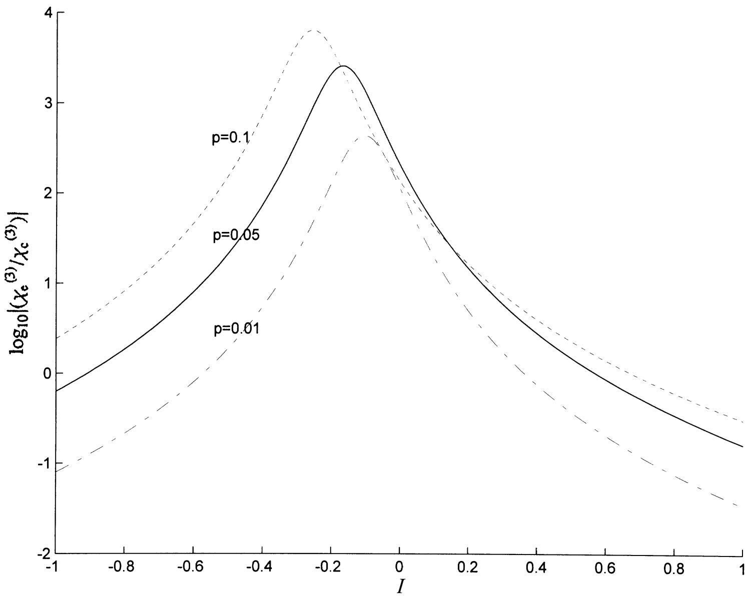

Fig. 3. The function of the normalized effective nonlinear optical response $\log_{10}|(\chi_e{}^{(3)}/\chi_c{}^{(3)})|$ versus I, for different volume fractions (0.1, 0.05, 0.01) at $\omega = 3.5$ ev and $T = 750$ K.

more dominant than the dielectric response. Consequently, even though the same volume fraction is chosen, the magnitudes of such enhanced nonlinear optical response are quite different from each other, such as shown in Figs. 1 and 2.

In Fig. 3, the normalized effective nonlinear optical response $\log_{10}|(\chi_e{}^{(3)}/\chi_c{}^{(3)})|$ is plotted as a function of the interfacial factor I for different volume fractions at $\omega = 3.5$ ev and $T = 750$ K. It is shown that I has an optimal value which makes the nonlinear optical response reach a maximum (such I will be denoted by I_{max} in the following). The result shows that an optimal interfacial layer exits for which enhanced nonlinear optical response can be obtained, which is reasonable in our discussed system. Fig. 3 also shows that, for different volume fractions, different curves are given even though their framework is similar. I_{max} depends on the volume fractions at high frequency; the

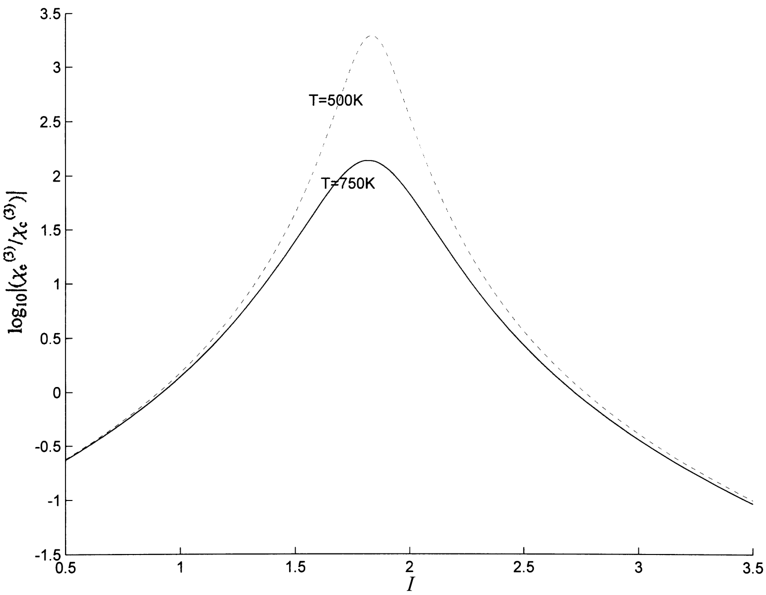

Fig. 4. The function of the normalized effective nonlinear optical response $\log_{10}|(\chi_e{}^{(3)}/\chi_c{}^{(3)})|$ versus I, at $\omega = 2.4$ ev and $p = 0.1$, for two temperatures (500 and 750 K).

absolute value of I_{max} and the corresponding value of $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$ are larger for high volume fraction than for low, which is due to the fact that the metallic property within the interfacial layer is more dominant at high volume fraction than at low. Also, I_{max} is nearly independent of volume fractions at low frequency (e.g. 2.4 ev), the reason for which lies in the fact that, at low frequency, the dielectric property within the interfacial layer is more dominant than the metallic property even though the volume fractions of metallic particles increase a little.

In Fig. 4, the normalized effective nonlinear optical response $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$ is plotted as a function of the interfacial factor I for two temperatures, at $\omega = 2.4$ ev and $p = 0.1$. For different temperatures, different curves are shown where the value of $\log_{10}|(\chi_e^{(3)}/\chi_c^{(3)})|$ is higher at low temperature (e.g. 500 K) than at high temperature (e.g. 750 K). The values of I_{max} at different temperatures are nearly the same. This is consistent with our definition of the interfacial factor I where I is not a convex function of temperature. From this figure, as far as this point is concerned, it can be determined that the temperature has almost no effect on I_{max}.

Comparing Fig. 3 with Fig. 4, we also find that the effect of I on the nonlinear response is increasingly dominant with the increasing frequencies at given temperature and volume fraction, i.e. the effect of I is more dominant at high frequency than at low. This conclusion has been made from Figs. 1 and 2. The explanation has been put forward therein because of the different response of the metal-like or dielectric-like interfacial layer to different frequencies.

Thus, we can get the enhanced nonlinear optical response of such a composite from the component with weak nonlinearity if a proper interfacial factor is chosen at a suitable frequency of incident wave and volume fraction of metallic particles.

4. Conclusion

In this paper, the dependence of nonlinear optical response on temperature is investigated theoretically for the metal–dielectric composite containing the interfacial layers in a dilute limit. Effective nonlinear optical response can be greatly enhanced even though the nonlinear component takes on a weak nonlinearity. It is shown that the interfacial effect on the nonlinear optical response of such a composite is more dominant at low temperatures than at high, that I depends on the volume fraction of metallic particles and frequency of incident wave, and that an optimal interfacial layer, I_{max}, is found for which nonlinear susceptibility may reach a maximum. Such results are particularly interesting and valuable in applications because they make it known that the weak nonlinearity can be enhanced greatly as well, if interfacial layer, frequency of incident wave and volume fraction of metallic particles are chosen properly. Also it gives us much instructive information on how to get enhanced nonlinearity from weak nonlinear optical response under certain conditions.

Acknowledgements

This project was supported by the National Natural Science Foundation of China under Grant no. 19774042.

References

[1] A.E. Neeves, M.H. Birnboim, Opt. Lett. 13 (1988) 1087.
[2] A.E. Neeves, M.H. Birnboim, J. Opt. Soc. Am. B 6 (1989) 7.
[3] J.J. Sakai (Ed.), Phase Conjugate Optics, McGraw-Hill, Singapore, 1992.
[4] D.J. Bergman, O. Levy, D. Stroud, Phys. Rev. B 44 (1994) 129.
[5] F. Brouers, J.P. Clerc, G. Giraud, Phys. Rev. B 44 (1991) 5299.
[6] G.S. Agarwal, S.D. Gupta, Phys. Rev. A 38 (1988) 5678.
[7] D. Stroud, V.E. Wood, J. Opt. Soc. Am. B 6 (1989) 778.
[8] R.J. Gehr, G.L. Fisher, R.W. Boyd, J. Opt. Soc. Am. B 14 (1997) 2310.
[9] H.B. Liao, R.F. Xiao, J.S. Fu, P. Yu, G.K.L. Wong, P. Sheng, Phys. Rev. Lett. 70 (1997) 1.
[10] H.P. Chiang, P.T. Leung, W.S. Tse, Solid State Commun. 101 (1997) 45.
[11] L. Gao, Z.Y. Li, Solid State Commun. 107 (1998) 751.
[12] S. Moto, T. Kubo, Y. Kurokawa, K. Suzuki, Thin Solid Films 322 (1998) 233.
[13] D. Stroud, P.M. Hui, Phys. Rev. B 37 (1988) 8719.
[14] S. Torquato, M.D. Rintoul, Phys. Rev. Lett. 75 (1995) 4067.
[15] L. Gao, Z.Y. Li, J. Appl. Phys. 87 (2000) 1620.
[16] P.M. Hui, J. Appl. Phys. 68 (1990) 3099.
[17] P.M. Hui, J. Appl. Phys. 33 (1993) 4072.
[18] D.L. Johnson, J. Koplik, L.M. Schwartz, Phys. Rev. Lett. 57 (1986) 2564.
[19] R.T. Beach, R.W. Christy, Phys. Rev. B 16 (1977) 5277.
[20] K. Ujihara, J. Appl. Phys. 43 (1972) 2376.
[21] P.T. Leung, M.H. Hinder, E.J. Sanchez, Phys. Rev. B 53 (1996) 12659.
[22] N.A. Nicorovici, D.R. Mckenzie, R.C. McPhedran, Opt. Commun. 117 (1995) 151.