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Optical Response of Metal-Dielectric Composite Containing Interfacial Layers*

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Abstract *A phenomenological approach to investigate the effect of interfacial layers on the absorption of metal-dielectric composite at elevated temperatures is put forward by making use of a model in which weakly nonlinear spherical metallic particles with linear concentric shells are randomly embedded in a linear host. Corresponding formulae in terms of the interfacial factor are derived in detail by incorporating Taylor expansion and Drude model. We take Ag/MgF$_2$ composite as numerical calculation. It is concluded that such absorption is dependent not only on the temperature, but also on the properties of interfacial layers. Many other interesting phenomena are shown.*

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1 Introduction

The nonlinear optical properties in 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.[1,2] A typical system is composed of nonlinear (or linear) metallic particles randomly embedded in a linear (or nonlinear) dielectric host. Detailed analysis of the dielectric properties of such composite reveals the existence of many interesting phenomenon such as optical bistability[3] and optical percolation threshold.[4] Many authors have studied the nonlinear optical response of such composite media. But most of such theoretical[5,6] and experimental[7,8] reports are limited at room temperature. As far as elevated temperature is concerned, absorption and refraction of such composite are discussed,[9] and recently, the nonlinear optical responses are investigated as well.[10,11]

All the previous works are of particular interest, but most of them neglect the existence of the interface as separating metallic particles from dielectric matrix. Many other works[12−15] have shown that the effective conductivity within the interfacial zone is often much higher than the bulk matrix conductivity, as shown that the interfacial effect plays an important role in determining effective conductivity. Conductivity and dielectric function both are two physical parameters for describing the property of material. Different optical responses are just up to different dielectric functions. The purpose of this paper is to discuss elevated-temperature effect on absorption of metal-dielectric composite containing interfacial layers. Refractive index of Bi (or Sb)-silica composite is large due to the interfacial layers.[16] Such interfacial layers are formed by the presence of nanosized metal particles, observed by transmission electron microscopy (TEM).[16] It is shown in the present paper that the absorption depends strongly on the properties of interfacial layers. Our model used in the following is based on two experimental facts: TEM analysis of some samples shows the metal nanoclusters to be approximately spherical in shape and to be uniformly dispersed in the dielectric host;[17] on the other hand, in general, the third-order nonlinearity of metallic particles is about several orders of magnitude larger than that of dielectric host, and thus the contribution of matrix to the effective nonlinear optical response is small enough to be neglected.[18] This problem will be dealt with by combining Taylor expansion and Drude model with the interfacial factor I considered. As far as the interfacial factor is concerned, it is introduced to characterizing interfacial layer[19] and has been developed to discuss nonlinear optical response of such the composite.[11,20] Here we extend first the interfacial factor to denote different properties (e.g., metal-like or dielectric-like) of interfacial layer by different values of I. Then Ag/MgF$_2$ is taken as sample for numerical calculation. Many interesting phenomena are found. It is shown finally that absorption is related not only to the temperature and applied field, but also to the interfacial layer.

2 Formalism

Let us consider first a certain nonlinear composite in

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which nonlinear spherical metallic particles with linear concentric shells are randomly embedded in a linear host. The radii of core and shell are r_0 and r_0+t, respectively, where t is just the thickness of coating layer. The dielectric functions of shell and dielectric host are denoted by ϵ_s and ϵ_m, while within the metal core the local constitutive relation has the following form

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

here $\vec{D}$ and $\vec{E}_c$ are, respectively, the displacement and electric field inside the core, and ϵ_c^0 and χ_c are linear dielectric function and cubic nonlinear susceptibility, respectively.

Throughout the work, the nonlinear term is assumed to be weak. 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.[5,6,18]

If the wavelength of the incident electromagnetic wave is larger in comparison with both particle size and mean distance between them, retardation effects can be neglected and quasi-static approximation can be applied. Solving Laplacian equations yields the dipolar polarizability of the coated sphere C,

$$C = \frac{\rho(2\epsilon_s+\epsilon_m)(\epsilon_c(\vec{E}_c)-\epsilon_s)+(\epsilon_s-\epsilon_m)(\epsilon_c(\vec{E}_c)+2\epsilon_s)}{2\rho(\epsilon_s-\epsilon_m)(\epsilon_c(\vec{E}_c)-\epsilon_s)+(\epsilon_s+2\epsilon_m)(\epsilon_c(\vec{E}_c)+2\epsilon_s)}(r_0+t)^3\,, \tag{2}$$

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

Now, we consider the effect of interfacial layer through the limit $t \to 0$, namely the interfacial property is concentrated on a surface of approximate zero thickness; then only $t\epsilon_s$ can be seen as a significant quantity. We take

$$I = \lim_{t\to 0,\epsilon_s\to\infty} t\epsilon_s \tag{3}$$

to characterize the interfaces separating metallic particles from dielectric host.[19,20] Here I is just called the interfacial factor. Generally speaking, for sharp and smooth interface denoted by $I=0$, there is no jump in the normal component of the electric displacement D_n across the interface, i.e. there are no interfacial layers; whereas, for imperfect interface denoted by $I \neq 0$, D_n jumps across the interface. We further remark[11] that I can be taken as positive or negative values, which is reasonable because the dielectric function of metallic particles is made up of a large negative real and a small positive imaginary parts. When I is taken as negative (or positive) value, the interface exhibits metal-like (or dielectric-like) behavior. The larger the positive value of I (or the absolute value of I as $I<0$), the stronger the dielectric (or metal) property within the interfacial layer. Consequently, different values of I represent different interfacial layers.[11]

According to the Clausius–Mossotti relation, we have the effective dielectric function

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

where N is the number of spherical metallic particles per unit volume. Considering Eqs (2) and (3), we can express Eq. (4) as

$$\epsilon_e(\vec{E}_c) = \epsilon_m + 3p\epsilon_m\frac{\epsilon_c(\vec{E}_c)+(2I/r_0\epsilon_m-1)\epsilon_m}{\epsilon_c(\vec{E}_c)(1-p)+[2(1+I/r_0\epsilon_m)-p(2I/r_0\epsilon_m-1)]\epsilon_m} \tag{5}$$

with the volume fraction of metallic particles $p \equiv 4/3\pi N r_0^3$. Making use of Taylor expansion method and noticing weak nonlinearity, we can write Eq. (5) as

$$\epsilon_e(\vec{E}_c) = \epsilon_m + 3p\epsilon_m\frac{\epsilon_c^0+(2I/r_0\epsilon_m-1)\epsilon_m}{Q}\Big[1+\frac{\chi_c|\vec{E}_c|^2}{\epsilon_c^0+(2I/r_0\epsilon_m-1)\epsilon_m}\Big]\Big[1-\frac{(1-p)\chi_c|\vec{E}_c|^2}{Q}\Big] \tag{6}$$

with

$$Q \equiv \epsilon_c^0(1-p)+[2(1+I/r_0\epsilon_m)-p(2I/r_0\epsilon_m-1)]\epsilon_m\,.$$

In principle, the local field $\vec{E}_c$, uniform in metallic particles, can be solved exactly by incorporating the appropriate boundary conditions. Here, we only represent the local field in the weak nonlinearity limit

$$\vec{E}_c = \frac{3\epsilon_m}{\epsilon_c(\vec{E}_c)(1-p)+[2(1+I/r_0\epsilon_m)-p(2I/r_0\epsilon_m-1)]\epsilon_m}\vec{E}_0\,, \tag{7}$$

where $\epsilon_c(\vec{E_c})$ also depends on $\vec{E_c}$. After iterating and keeping terms to first order in χ_c, we have

$$\vec{E_c} = \frac{3\epsilon_m}{Q}\vec{E_0} - \chi_c(1-p)\Big|\frac{3\epsilon_m}{Q}\Big|^2\frac{3\epsilon_m}{Q^2}|\vec{E_0}|^2\vec{E_0}\,. \tag{8}$$

The macroscopic effective linear dielectric function ϵ_e^0 and third-order nonlinear susceptibility χ_e can be introduced as follows:[21,22]

$$\epsilon_e = \epsilon_e^0 + \chi_e|\vec{E_0}|^2\,. \tag{9}$$

We therefore obtain explicit expressions for ϵ_e^0 and χ_e,

$$\epsilon_e^0 = \epsilon_m + 3p\epsilon_m\frac{\epsilon_c^0 + (2I/r_0\epsilon_m - 1)\epsilon_m}{Q} \tag{10}$$

and

$$\chi_e = p\chi_c\Big(\frac{3\epsilon_m}{Q}\Big)^2\Big|\frac{3\epsilon_m}{Q}\Big|^2\,. \tag{11}$$

We divide ϵ_e into real and imaginary parts, similar to the dielectric function of metal, i.e.,

$$\epsilon_e = \Gamma + \mathrm{i}\Sigma\,, \tag{12}$$

in which Γ and Σ are both real quantities. ϵ_e can also be written as

$$\epsilon_e = (n + \mathrm{i}k)^2\,, \tag{13}$$

where the quantity n is the refractive index of the medium, and k is the absorption coefficient.[23] The absorption coefficient gives the rate of damping of the wave during its propagation. And it is noticed that dissipation of energy occurs when dielectric function is complex, so the damping of the wave is due to absorption. A comparison between Eq. (12) and Eq. (13) yields the expression for k,

$$k = \frac{1}{\sqrt{2}}(\sqrt{\Gamma^2 + \Sigma^2} - \Gamma)^{1/2}\,. \tag{14}$$

As to metal component, the Drude model is often used to describe the linear dielectric functions of certain noble metals (e.g., Au and Ag), which causes such dielectric functions to own the dependence on temperature. Such a linear dielectric function can be written as

$$\epsilon_c^0 = 1 + \triangle\epsilon - \frac{\omega_p^2}{\omega(\omega + \mathrm{i}\omega_c)}\,, \tag{15}$$

where $\triangle\epsilon$, the contribution of the bound electrons, can be evaluated if compared with experimental data,[24] and ω_p is the plasma oscillation frequency given by

$$\omega_p = \Big(\frac{Ne^2}{m\epsilon_0}\Big)^{1/2} \tag{16}$$

with N and m being the density and the effective mass of the electron, respectively. Both N and m should vary with the change of temperature, however, such variance in ω_p is small enough to be negligible.[25] Such the assumption has been used to discuss surface-enhanced Raman scattering at elevated temperature.[26] Thus the temperature effect on ϵ_c^0 only lies in the collision frequency ω_c, as divided into two parts

$$\omega_c = \omega_{\rm cp} + \omega_{\rm ce}\,, \tag{17}$$

where $\omega_{\rm cp}$ and $\omega_{\rm ce}$ represent the contributions from phonon-electron and electron-electron scattering.[24] $\omega_{\rm cp}$ has the following expression

$$\omega_{\rm cp} = \frac{\omega_p^2\epsilon_0}{\sigma}\frac{\dfrac{2}{5} + 4\Big(\dfrac{T}{\theta}\Big)^5\displaystyle\int_0^{\frac{\theta}{T}}\frac{z^4}{\mathrm{e}^z - 1}\mathrm{d}z}{4\displaystyle\int_0^1\frac{z^5}{(\mathrm{e}^z - 1)(1 - \mathrm{e}^{-z})}\mathrm{d}z}\,, \tag{18}$$

where θ is the Debye temperature and σ is d.c. conductivity, while $\omega_{\rm ce}$ can be obtained in terms of the Fermi energy E_F of the metal component[24]

$$\omega_{\rm ce} = \frac{1}{12}\pi^3\frac{SF}{\hbar E_F}\Big[(k_BT)^2 + \Big(\frac{\hbar\omega}{2\pi}\Big)^2\Big]\,, \tag{19}$$

where S and F represent two constants giving the average over the Fermi surface of the scattering probability and the fractional unklapp scattering. The above equations (10), (15) $\sim$ (19) determine the dependence of linear optical response of metal component on the temperature.

In general, the linear dielectric function of dielectric component is much less dependent on temperature than the metal component. For example, MgF_2, used for the following numerical calculation, has temperature dependence with a linear coefficient of 10^{-6}, and its linear dielectric function is referred to Ref. [27].

3 Numerical Calculation and Discussion

So far, the temperature effect on the optical response has been formulated in detail, in terms of the interfacial factor I. Due to the fact that our system lies in the condition of quasi-static approximation, we choose the region of $\hbar\omega$ from 2.5 eV to 4.5 eV for numerical calculation. During the whole process, $|E_0|$ and χ_c are taken as 0.1 and 1, respectively, with arbitrary units, and we have ignored the tiny fluctuation of the applied field. In addition, during the whole calculation, we take the volume fraction of metallic particles as 0.05 because of two facts: (i) Clausius–Mossotti relation holds only for low volume fraction; (ii) absorption will be enhanced obviously by increasing volume fraction of metal component.

Paying no attention to the effect of the interfacial layer, i.e. $I = 0$, we can get the same results as those obtained through Maxwell–Garnett theory in Ref. [9].

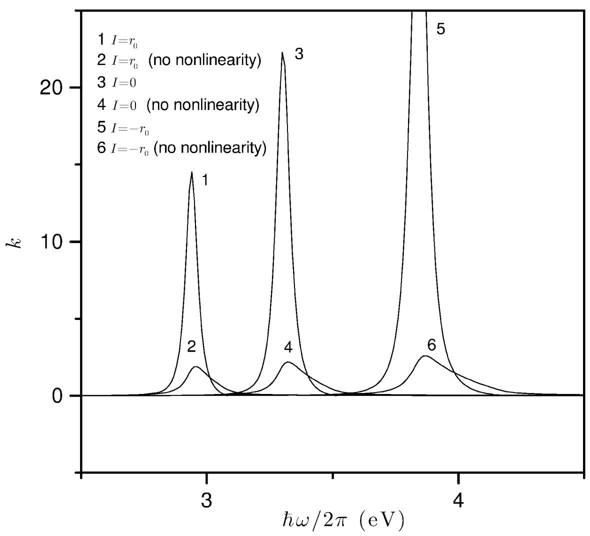

Fig. 1 Absorption coefficient k as a function of frequency $\hbar\omega$ for $T = 500$ K.

In Fig. 1, the absorption coefficient is plotted as a function of frequency. At plasma resonant frequency, the composite absorption can reach a maximum. For given volume fraction and temperature, different properties of interfacial layer have different effects on the location of plasma resonant frequency due to the change of local field. As the interfacial layer is changed from dielectric-like to metal-like, the plasma resonant frequency is increased, meanwhile, the corresponding absorption peak is enhanced.

If there is no nonlinear effect on absorption, i.e. we just consider the linear effect, with the second term in ϵ_e (Eq. (9)) drowned out, the absorption peak is reduced. It is shown qualitatively that nonlinearity plays a role in composite absorption. And it is noticed that such role is more important for metal-like interfacial layer than for dielectric-like one.

In Fig. 2 the absorption coefficient is plotted as a function of the temperature for $\omega = 2.4$ eV. If the volume fraction of metal component and the frequency of incident wave are given, the effect of the temperature on composite absorption is more prominent at high temperature than at low. And the effect of the interfacial layer on absorption only affects the absorption amplitude, exactly speaking, it is more sensitive to the temperature for dielectric-like than for metal-like.

Only when linear effect is considered, can nonlinearity enhance somewhat the effect of temperature on absorption for the case of dielectric-like interfacial layers. However, almost no nonlinear effect is shown for the case of metal-like (or without) interfacial layers.

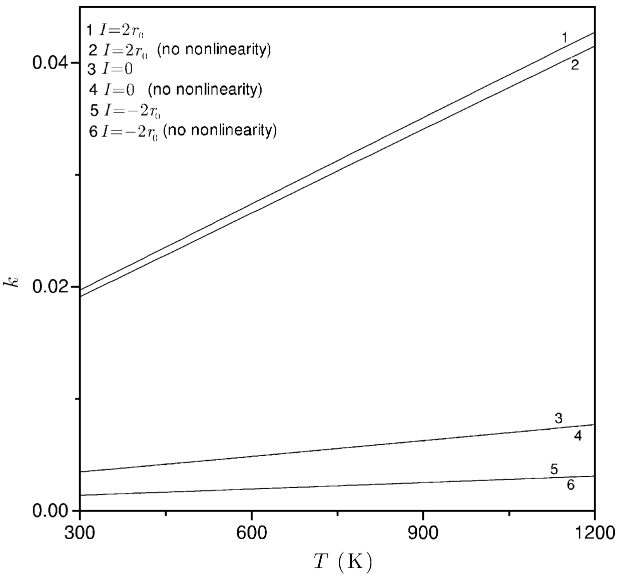

Fig. 2 Absorption coefficient k as a function of temperature T for $\hbar\omega = 2.4$ eV.

In Fig. 3 the absorption coefficient is plotted as a function of the interfacial factor. For different applied fields, there always exits an optimum interfacial factor, making the appearance of the absorption peak.

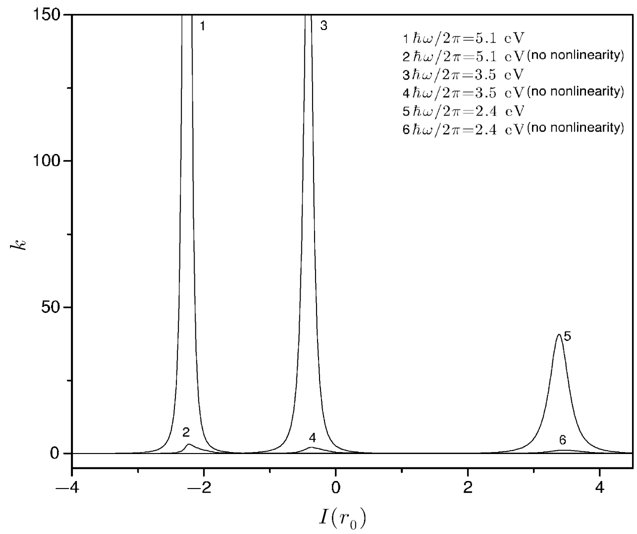

Fig. 3 Absorption coefficient k as a function of the interfacial factor I for $T = 750$ K.

If the composite lies in the circumstance with constant temperature, the increasing energy of applied field can enhance the absorption peak, at the same time, within the special interfacial layer corresponding to which the absorption reaches a maximum, the interfacial layer is changed bit by bit from dielectric-like to metal-like.

Without nonlinear influence, the absorption is decreased. It is determined again that nonlinearity can enhance composite absorption. Also, such an enhancement is more important at high frequency than at low frequency.

4 Conclusion

A weakly nonlinear composite has been investigated by a model in which weakly nonlinear spherical metal particles with linear concentric coating shells are randomly embedded in a linear dielectric host. We have discussed the absorption of such the composite with Drude model together with Taylor expansion. The effects of the interfacial layer, nonlinearity and the temperature on composite absorption, are discussed qualitatively. Several interesting phenomena are found in this work.

Firstly, we show the effects of the interfacial layer.

(i) Paying no attention to the interfacial layer yields the same results as those obtained in Ref. [9].

(ii) For a given temperature, the plasma resonant frequency is increased, meanwhile the corresponding absorption peak is enhanced when the interfacial layer is changed from dielectric-like to metal-like, as shows that the absorption peak corresponding to metal-like interfacial layer can be enhanced strongly.

(iii) For a given applied field, the effect of dielectric-like interfacial layer on absorption is more sensitive to temperature than metal-like (or without) interfacial layer.

(iv) For a given temperature, an optimum interfacial layer always exits at certain applied field making the absorption peak appear, and at high (or low) frequency, such the optimum interfacial layer exhibits metal-like (or dielectric-like) property.

Secondly, we show the effects of nonlinearity.

i) For a given temperature, nonlinearity can enhance absorption and such the enhancement is more important for metal-like interfacial layer than for dielectric-like one.

ii) If the applied field is given, nonlinearity can enhance a little temperature effect on absorption for the case of dielectric-like interfacial layer; however, almost no nonlinear effect is shown for other cases (e.g., metal-like or no interfacial layer).

iii) For a given temperature, nonlinear effect enhances material absorption, and such the enhancement is more important at high frequency than at low frequency. Thirdly, we give the effects of the temperature. For given applied field, the effect of the temperature on composite absorption is more prominent at high temperature than at low temperature.

Former experimental reports are limited at low temperatures. Our work, a phenomenological study, has discussed the optical absorption at elevated temperature. We expect that it will stimulate the development of experiments.

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