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OPTICAL PROPERTIES OF COMPOSITE MATERIALS AT HIGH TEMPERATURES

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The optical properties of composite materials are studied theoretically as a function of temperature via a phenomenological model for temperatures up to the melting points of the materials. Both the Maxwell-Garnett and Bruggeman models are considered and the temperature variation of the optical constants of the metallic particles is obtained with an account of the dependence of both the electron–phonon and electron–electron scattering on temperature. The results show that the extinction coefficient of the composite generally increases with temperature and that the Maxwell-Garnett and Bruggeman models can give very different results at certain optical frequency. Transmittance through a thin composite film is calculated providing a means for a simple experimental study of the various modeling results. Copyright © 1996 Elsevier Science Ltd

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INTRODUCTION

The optical properties of composite materials such as cermet have been studied intensively for the past two decades [1]. Most of these materials contain a metal–insulator composite which have interesting properties in the infrared and optical frequencies. Theoretically, there exists many models which can describe these properties adequately under different structural conditions of the composite. These include, for example, various mean field [2–4] and fractal-cluster [5] theories as well as computational approach via various simulation schemes [6]. Nevertheless, most of the previous experimental and theoretical studies were limited to room temperature condition and thus optical properties of such composite materials at elevated temperatures are rarely reported in the literature [7]. On the other hand, it is not unrealistic to expect that there are technological applications of these materials under which the composite system will be subject to high temperatures. It is the purpose of the present communication to study the temperature dependence of the optical constants of a metal–insulator composite via a simple phenomenological model. To begin, it is reasonable to assume that such dependence originates mainly from change in the metallic optical properties and those for the insulating host medium can be assumed to be constant with temperature change [8]. Hence, we shall first briefly review and adapt an adequate model for describing the temperature dependence of the metallic optical constants which accounts for both the electron–phonon and electron–electron collision processes in the metal. We shall then apply it to calculate the optical properties of the composite as a function of temperature. For the purpose of model calculations here, we shall adopt the simple existing effective medium theories including the Maxwell-Garnett and Bruggeman models for the optical functions of the composite.

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TEMPERATURE DEPENDENCE OF OPTICAL CONSTANTS

For simplicity, we shall assume a Drude model metal which will be adequate for certain simple and noble metals within the appropriate ranges of light frequencies. Hence we write the metal dielectric function as:

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

where ω_c is the collision frequency and ω_p the plasma frequency given by:

$$\omega_p = \sqrt{\frac{4\pi N e^2}{m^*}}, \tag{2}$$

with N and m^* the density and effective mass of the electrons, respectively. Here we shall assume that the main variation of the dielectric function with temperature comes from the temperature dependence of ω_c. Thus the relatively minor temperature dependence of N and m^* are neglected in the following. To describe the temperature dependence of ω_c, we shall separate the contribution from phonon–electron scattering and that from electron–electron scattering and write ω_c into two parts:

$$\omega_c = \omega_{cp} + \omega_{ce}. \tag{3}$$

To model the temperature dependence of the phonon part, we shall adapt the Debye model as first formulated by Holstein [9, 10]:

$$\omega_{cp}(T) = \omega_0 \left[\tfrac{2}{5} + 4\left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^4\,dz}{e^z - 1}\right], \tag{4}$$

where θ is the Debye temperature and ω_0 is a constant to be determined from the static limit of the above expression together with the knowledge of the d.c. conductivity $\sigma(0)$ in the following form [10, 11]:

$$\omega_{cp}(T, \omega \to 0) = \frac{\omega_p^2}{4\pi\sigma(0)} = \omega_0 \left[4\left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^5\,dz}{(e^z - 1)(1 - e^{-z})}\right]. \tag{5}$$

Previously, we have made use of a simpler version of ω_{cp} due to Ujihara [12] in our study of surface enhanced Raman scattering at elevated temperatures [13]. However, the determination of the constant ω_0 using tabulated empirical data in our earlier approach was not made in a way consistent as the present one.

Next we consider the electron–electron scattering frequency. To this end, we apply the result obtained by Lawrence [14] who used the Born approximation and Thomas–Fermi screening of the Coulomb interaction to improve an earlier result obtained by Gurzhi [15]. The result can be obtained in terms of the Fermi energy E_F of the metal as follows:

$$\omega_{ce} = \tfrac{1}{12}\pi^3 \frac{\Gamma\Delta}{\hbar E_F}\left[(k_B T)^2 + \left(\frac{\hbar\omega}{2\pi}\right)^2\right], \tag{6}$$

where Γ is a constant giving the average over the Fermi surface of the scattering probability and Δ the fractional umklapp scattering [11, 14]. Thus equation (1) together with equations (3)–(6) completely specify the temperature dependence of the dielectric function of the metal. Beach and Christy [11] have found that, with a correction term ($\delta\epsilon_1$) associated with the absorption peaks at higher frequencies to the real part of ϵ, the above scheme has been able to yield a reasonable fit to their experimental data for silver up to optical frequencies of 5 eV at room temperature. For elevated temperatures, there is some limitation in the above determination of ω_0 due to the possible anisotropy of the Fermi surface [11].

NUMERICAL MODELING OF COMPOSITE SYSTEMS

We shall consider the two well known models from mean field approximation for the effective dielectric constant of a metal–insulator composite. Assuming the dielectric host is nonabsorptive and being characterized by a real dielectric function ϵ', the Maxwell-Garnett (MG) model gives the average dielectric function of the composite from solving the following:

$$\frac{\bar{\epsilon}_{MG} - \epsilon'}{\bar{\epsilon}_{MG} + 2\epsilon'} = f\frac{\epsilon - \epsilon'}{\epsilon + 2\epsilon'}, \tag{7}$$

where f is the volume fraction of the metal particles. It is well known that the MG model is valid only for very small values of f and there is no percolation threshold associated with this model [4]. On the other hand, the Bruggeman (BR) model which is valid also for large value of f, has a percolation threshold of $f = 1/3$ and is obtained by solving the following equation:

$$\frac{f(\epsilon - \bar{\epsilon}_{BR})}{\epsilon + 2\bar{\epsilon}_{BR}} = \frac{(f-1)(\epsilon' - \bar{\epsilon}_{BR})}{\epsilon' + 2\bar{\epsilon}_{BR}}. \tag{8}$$

As mentioned before, there are many other models accounting for different aspects of the composite such as clustering of particles and higher percolation thresholds which in some cases fit better experimental results. However, here we shall limit ourselves to the above two simple models for the sake of model calculations in the present work. We have thus used equations (1), (3), (4) and (6) into both equations (7) and (8) to study the temperature variation of the optical constants of a cermet system, taken as Ag/MgF_2 for numerical illustrations [16]. The constants for MgF_2 as the host are well available in the literature and is known to have a negligible temperature dependence with a linear coefficient of

Table 1. Parameters used in the temperature dependence model

$m^* = 0.99\,\mathrm{m}$	$\delta\epsilon_1 = 2.4$
$N = 5.9 \times 10^{22}\,\mathrm{cm}^{-3}$	$E_F = 5.48\,\mathrm{eV}$
$\Gamma = 0.55$	$\Delta = 0.73$
$\theta = 220\,\mathrm{K}$	$1/\sigma(0) = 1.16 \times 10^{-6}\,\Omega\,\mathrm{cm}$ at $T = \theta$

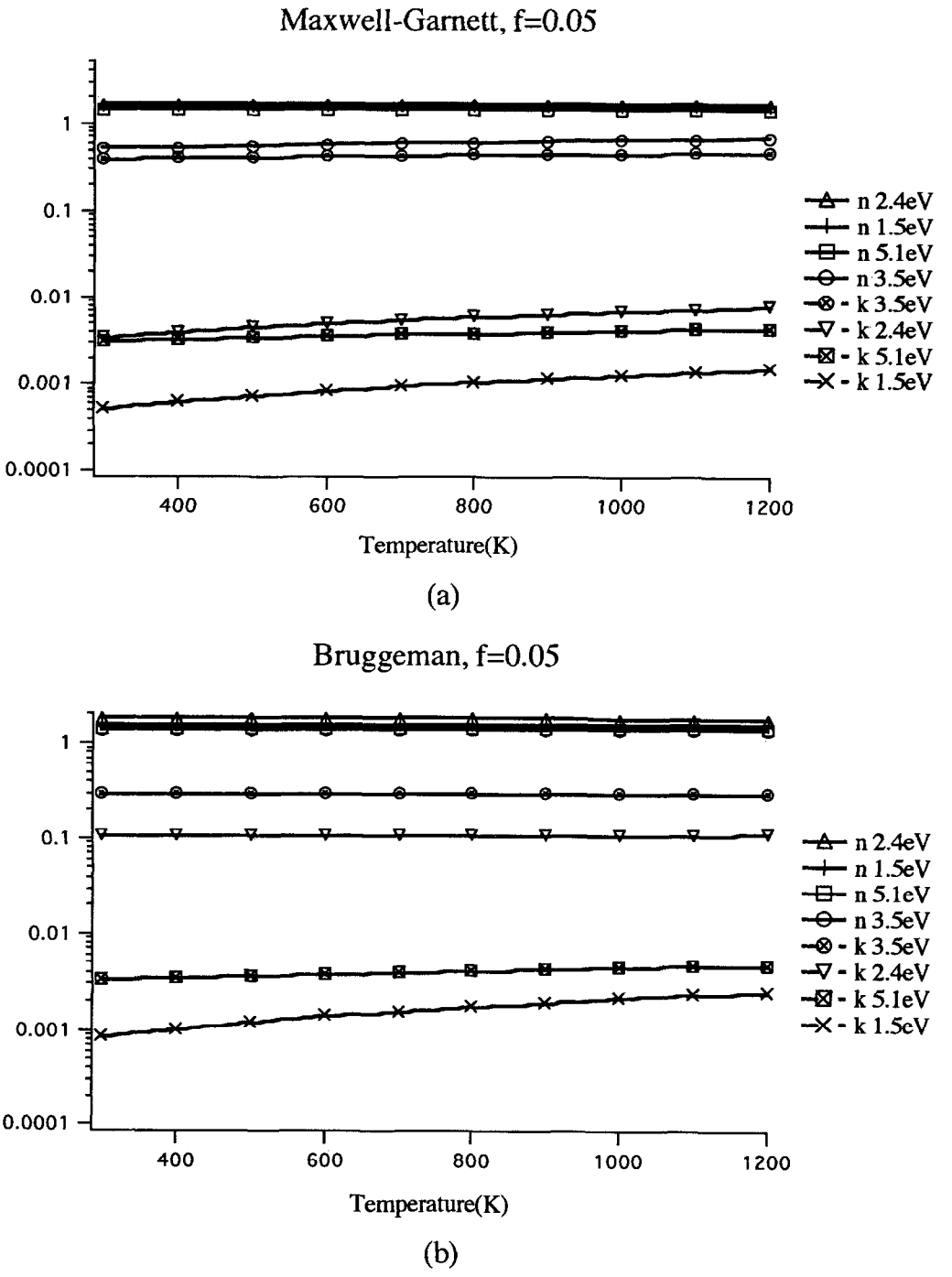
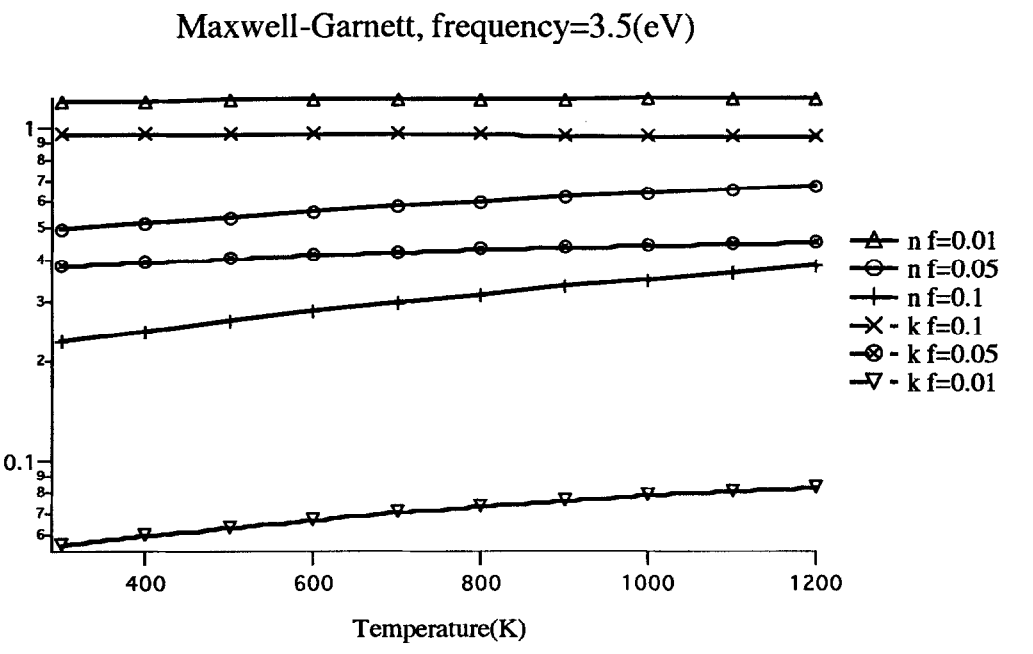


Fig. 1. Calculated optical constants (n, k) for a Ag/MgF_2 composite as a function of temperature at different optical frequencies for a fixed volume fraction of Ag at $f = 0.05$. Results from both the Maxwell-Garnett and the Bruggeman models are shown.

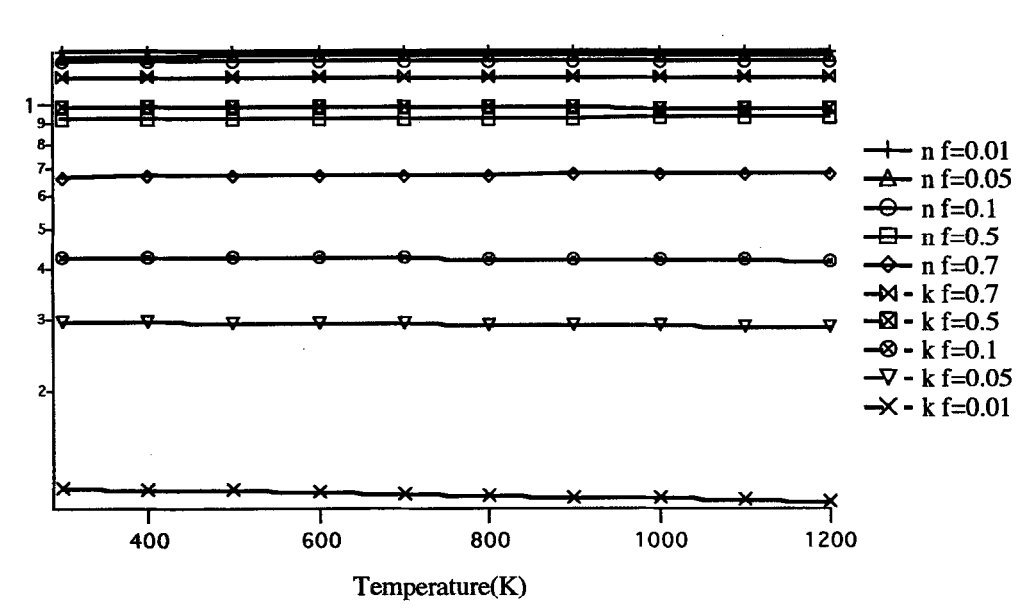
10^{-6} [17]. The thermal expansion of both the materials are neglected for the sake of optical property calculations. The parameters for the temperature dependence calculation were given in [11] and re-listed in Table 1. We report the computed optical constants (n, k) of the composite as a function of temperature which can be obtained from

$$\bar{\epsilon} = (n + ik)^2. \tag{9}$$

Figure 1 shows the results for n and k for a fixed volume fraction of Ag particles at frequencies easily obtainable from various laser sources. It is seen that both



(a)



(b)

Fig. 2. Same as in Fig. 1, except that the frequency is fixed at 3.5 eV and the volume fraction is varied.

the MG and BR models give very similar results at such a low volume fraction of metal. The n values stay relatively constant with temperature while the k values rise gradually, showing trends similar to those obtained previously from a less rigorous model for pure metal [13]. The k values are relatively low for such a small presence of metal in the composite. We also note that at 3.5 eV which is closed to the surface plasmon resonance of the Ag particles, k takes relatively large values and increases only mildly with temperatures. Figure 2 shows the results as a function of volume fraction at a fixed frequency of 3.5 eV. We limit f not to exceed 0.1 for the MG model. First we note that the MG model yields more appreciation of temperature variation

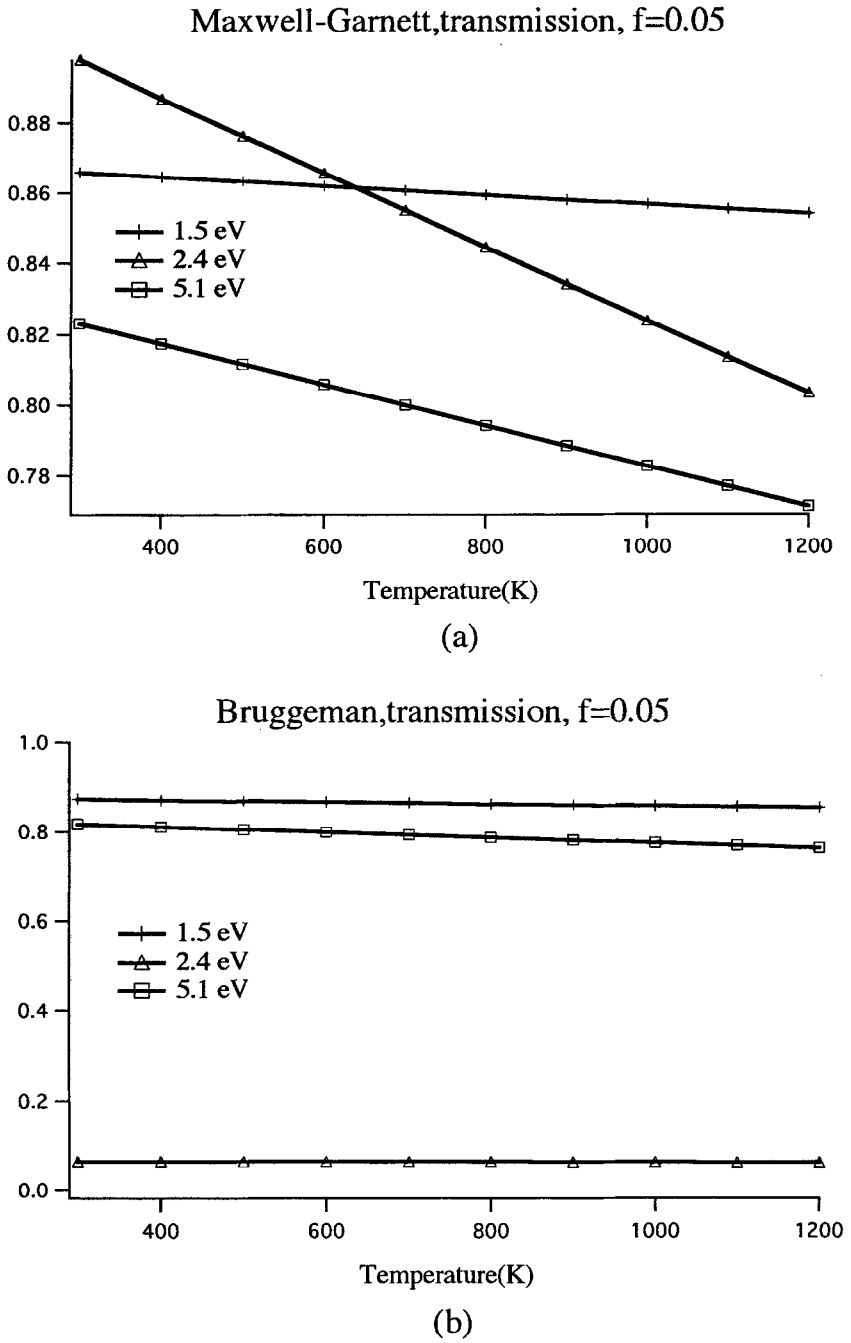


Fig. 3. Transmittance at normal incidence through a Am/MgF_2 film of 1 μm thick at different frequencies as a function of temperature. The volume fraction is fixed at 0.05.

in both n and k than the BR model does at this frequency. In fact, at very low volume fraction ($f = 0.01$), the BR model shows a slight *drop* in the values of k compared to an almost 50% rise in k for the full range of temperature rise as shown in the figure. In order to demonstrate some observable consequence of our modeling results, we have used the above (n, k) values to compute the transmittance at normal incidence through a free standing Ag/MgF_2 film of a micron thick as a function of temperature. Figure 3 shows the results from which we can see that the transmittance generally decreases as temperature increases due to the increase in metallic absorption. The results at 3.5 eV are much smaller and are not shown, this is again consistent with strong absorption at frequency close to surface plasmon resonance of the particles. Furthermore, one sees that at optical frequency

when the MG and BR models give sharply different results at room temperature (at $\omega = 2.4$ eV), the difference sustains for all higher temperatures by exhibiting a very different rate of decrease in transmittance through the film. This later result thus provides a means of checking the various models for both the effective dielectric function as well as the temperature dependence of these functions.

CONCLUSIONS

In this communication we have proposed a simple phenomenological description of the temperature dependence of the optical properties for composite materials. We have shown that simple transmittance experiments can be carried out to study the various modeling results. While it is apparent that many further improvements can be carried out in both the effective medium modeling (e.g. the probabilistic growth and fractal cluster modeling [4, 5]) and the temperature descriptions (e.g. account of diffusely scattering of electrons at the metal surface [11]), we certainly hope this work will stimulate experimentalist to seriously study the optical properties of these composites beyond the condition of room temperatures.

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