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The Lorentz model applied to composite materials

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Abstract. The dielectric functions of composite materials consisting of free-electron-type metal particles (Ag or Cu) and a dielectric host material with $\epsilon_h = 1.0$, 2.99 or 6.0 are calculated using the Maxwell-Garnett model. These function present an anomalous region when the interband transitions of the metal particles occur at frequencies above the resonance frequency ($2\epsilon_h = -\epsilon_m$). In this case the Lorentz oscillator model is used to analyse the optical behaviour of the composite material. The Lorentz parameters are calculated and discussed.

1. Introduction

The study of metal–insulator composites has been of interest from both experimental and theoretical points of view. The Maxwell-Garnett (MG) theory [1–5] is an effective medium theory that has been widely used to describe the optical properties of such systems, when one component predominates in concentration. It is assumed that the metal particles are small spheres, randomly immersed in the dielectric medium. The electric field ($\boldsymbol{E}_{\rm in}$) inside the spheres and that ($\boldsymbol{E}_{\rm out}$) in the host material are linearly related as given in [6]:

$$\boldsymbol{E}_{\rm in} = [3\epsilon_h/(2\epsilon_h + \epsilon_m)]\boldsymbol{E}_{\rm out} \tag{1}$$

where ϵ_h and ϵ_m are the dielectric functions of the host material and of the metal particles, respectively. In the MG model the mean electric field ($\boldsymbol{E}_{\rm MG}$), the mean dipole moment ($\boldsymbol{P}_{\rm MG}$) and the effective dielectric function ($\epsilon^{\rm MG}$) of the composite material are defined as follows:

$$\boldsymbol{E}_{\rm MG} = f\boldsymbol{E}_{\rm in} + (1-f)\boldsymbol{E}_{\rm out} \tag{2}$$

$$\boldsymbol{P}_{\rm MG} = f\boldsymbol{P}_{\rm in} + (1-f)\boldsymbol{P}_{\rm out} \tag{3}$$

$$4\Pi\boldsymbol{P}_{\rm MG} = (\epsilon^{\rm MG} - 1)\boldsymbol{E}_{\rm MG} \tag{4}$$

where f is the volume fraction occupied by the metal particles. From the above relations, the dielectric function of the composite material can be written in the form

$$\epsilon^{\rm MG} = \epsilon_h[\epsilon_m(1+2f) + 2\epsilon_h(1-f)]/[\epsilon_m(1-f) + \epsilon_h(2+f)]. \tag{5}$$

In this paper the Lorentz oscillator model [7] is considered in order to analyse the calculated MG effective dielectric function ($\epsilon^{\rm MG}$) for a composite medium consisting of a dielectric and free-electron-type metal particles (Ag or Cu), using the experimental values of the dielectric functions of the metals given in [8]. Usually this model is used to describe the optical properties of homogeneous materials, but in the present paper its applicability to the composite materials considered is verified, and an interpretation of the parameters that, in the Lorentz model, characterize the material is given.

2. Dielectric functions of the composite materials

The behaviour of the dielectric function of metal–insulator composite materials calculated using (5) for two different metal particles, Ag and Cu, for three values of the filling factor (f) and for $\epsilon_h = 1$ and 6 is presented in figures 1–4. The values of the dielectric functions of the small metal particles were obtained from the experimental data [8], as described in the appendix.

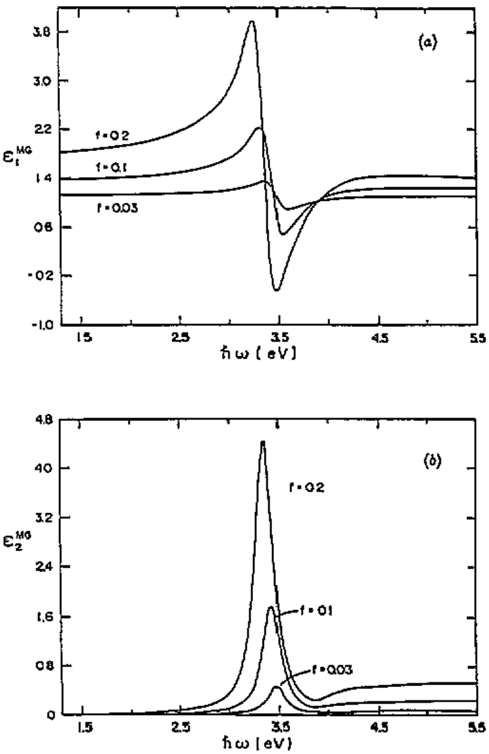

Figure 1. (a) Real (ϵ_1^{MG}) and (b) imaginary (ϵ_2^{MG}) parts of the dielectric function of the composite material: $\epsilon_h = 1.0$; Ag metal particles ($r = 50$ Å); $f = 0.03$, 0.1, 0.20.

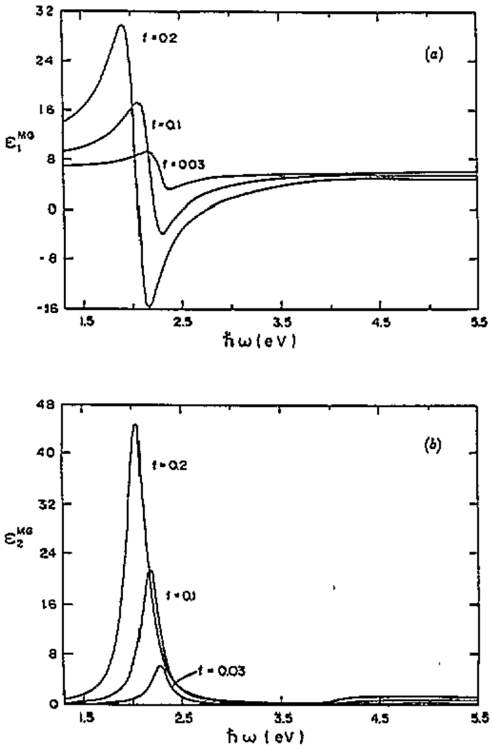

Figure 2. (a) Real (ϵ_1^{MG}) and (b) imaginary (ϵ_2^{MG}) parts of the dielectric function of the composite material: $\epsilon_h = 6.0$; Ag metal particles ($r = 50$ Å); $f = 0.03$, 0.1, 0.20.

The main characteristics of the dielectric function of the composite materials observed in these figures can be summarized as follows.

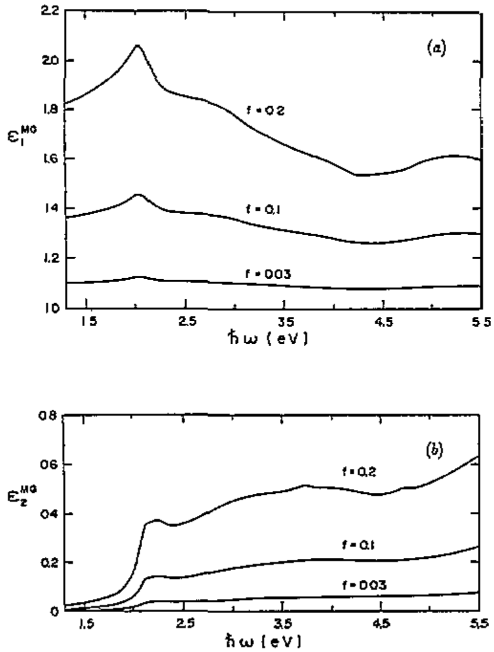

Figure 3. (*a*) Real (ϵ_1^{MG}) and (*b*) imaginary (ϵ_2^{MG}) parts of the dielectric function of the composite material: $\epsilon_h = 1.0$; Cu metal particles ($r = 50$ Å); $f = 0.03, 0.1, 0.20$.

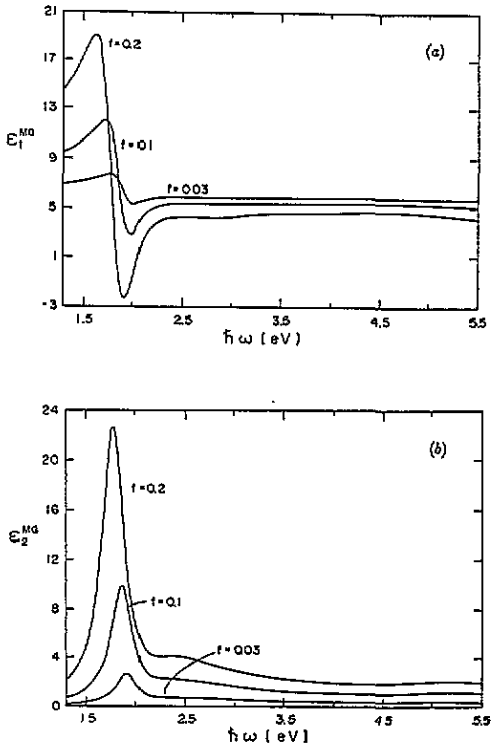

Figure 4. (*a*) Real (ϵ_1^{MG}) and (*b*) imaginary (ϵ_2^{MG}) parts of the dielectric function of the composite material: $\epsilon_h = 6.0$; Cu metal particles ($r = 50$ Å); $f = 0.03, 0.1, 0.20$.

(1) The existence of a resonance frequency (ω_0) where ϵ_2^{MG} (Im ϵ^{MG}) is maximum and where ϵ_1^{MG} (Re ϵ^{MG}) has a sharp decline (anomalous region).

(2) The anomalous region is observed for the composite materials containing Ag particles, and in this region the ϵ_1^{MG} function is symmetric relative to a value $\epsilon_h + \delta$, where δ tends to zero when f tends to zero. The same behaviour is observed for composite materials containing Cu particles when $\epsilon_h = 6$.

(3) When f and ϵ_h increase there is a red shift of the resonance frequency (ω_0) and an increase of the magnitude of ϵ^{MG}.

(4) For low values of ω, ϵ_1^{MG} tends to a constant value, which increases as f increases and tends to ϵ_h as f tends to zero.

3. The Lorentz oscillator model

The calculated (MG) dielectric functions for composite materials with $\epsilon_h = 1.0$, 2.99 or 6.0 (Ag particles) and with $\epsilon_h = 6.0$ (Cu particles) present a general behaviour similar to that predicted by the Lorentz oscillator model. In this model, the optical properties of a homogeneous material are expressed by the following Lorentz parameters: ω_0 (the resonance frequency), ϵ_0 (the value of the dielectric function at low frequencies compared to the electronic excitation frequencies); ω_p (the plasma frequency) and γ (the damping factor) [7]. The dielectric function in Lorentz model is expressed as

$$\epsilon = \epsilon_0 + \omega_p^2/(\omega_0^2 - \omega^2 - i\gamma\omega) \tag{6}$$

where $\epsilon = \epsilon_1 + i\epsilon_2$.

ϵ_1 presents a maximum and a minimum at the frequencies

$$\omega^2_{\substack{1,\max\\1,\min}} = \omega_0^2 \mp \gamma\omega_0 \tag{7}$$

with the maximum and minimum values

$$\epsilon_{\substack{1,\max\\1,\min}} = \epsilon_0 \pm \omega_p^2/(2\gamma\omega_0 + \gamma^2). \tag{8}$$

ϵ_2 presents a maximum, which for $\gamma^2 \ll \omega_0^2$ occurs at the frequency

$$\omega^2_{2,\max} \cong \omega_0^2 - \gamma^2/4 \tag{9}$$

where it has the value

$$\epsilon_{2,\max} \cong \omega_p^2/\omega_0\gamma. \tag{10}$$

From the above expressions the Lorentz parameters can be written in the form

$$\omega_0^2 = (\omega^2_{1,\max} + \omega^2_{1,\min})/2 \tag{11}$$

$$\gamma = (\omega^2_{1,\min} - \omega^2_{1,\max})/2\omega_0 \tag{12}$$

$$\omega_p^2 = \epsilon_{2,\max}\gamma\omega_0 \tag{13}$$

$$\epsilon_0 = (\epsilon_{1,\min} + \epsilon_{1,\max})/2. \tag{14}$$

The loss energy function ($L = -\mathrm{Im}1/\epsilon$), for $\gamma^2 \ll \omega_0^2$, is maximum at

$$^{\mathrm{L}}\omega^2_{\max} \cong \omega_0^2 + \omega_p^2/\epsilon_0 \tag{15}$$

and can be given at this point by the expression

$$L_{\max} = (\omega_p^2/\epsilon_0^2)/\gamma(\omega_0^2 + \omega_p^2/\epsilon_0)^{1/2}. \tag{16}$$

Table 1 presents the values of the Lorentz parameters for some of the composite materials analysed, calculated through expressions (11)–(14), where the values of $\omega_{1,\min}$, $\omega_{1,\max}$, $\epsilon_{1,\max}$, $\epsilon_{1,\min}$ and $\epsilon_{2,\max}$ are obtained from the ϵ^{MG} functions.

In order to test the consistency of the Lorentz model for composite materials the values of $^{\mathrm{L}}\omega_{\max}$ and $L_{\max}$ calculated from (15) and (16), using the Lorentz parameters, are presented in table 2 together with the values obtained from L^{MG} (the MG loss energy function).

Table 1. The Lorentz model parameters for some composite materials, with three values of the filling factor (f).

Composite material	f	$\hbar\omega_0$ (eV)	$\hbar\gamma$ (eV)	$\hbar\omega_p$ (eV)	ϵ_0
Ag particles	0.03	3.48	0.21	0.58	1.09
in $\epsilon_h = 1$	0.10	3.40	0.22	1.22	1.34
	0.20	3.37	0.22	1.87	1.76
Ag particles	0.03	2.27	0.23	1.77	6.14
in $\epsilon_h = 6$	0.10	2.19	0.23	3.26	6.58
	0.20	2.04	0.23	4.56	7.07
Cu particles	0.03	1.90	0.23	1.07	6.49
in $\epsilon_h = 6$	0.10	1.88	0.26	2.20	7.42
	0.20	1.78	0.27	3.32	8.35

Table 2. Values of ${}^L\omega_{max}$ and L_{max} from the MG model and calculated using the Lorentz parameters (table 1) for some composite materials with three values of the filling factor (f).

		MG model		Lorentz model	
Composite material	f	$\hbar\,{}^L\omega_{max}$ (eV)	L_{max}	$\hbar\,{}^L\omega_{max}$ (eV)	L_{max}
Ag particles	0.03	3.52	0.37	3.52	0.38
in $\epsilon_h = 1$	0.10	3.57	0.97	3.56	1.06
	0.20	3.65	1.46	3.65	1.40
Ag particles	0.03	2.39	0.16	2.38	0.15
in $\epsilon_h = 6$	0.10	2.55	0.51	2.53	0.42
	0.20	2.77	0.91	2.66	0.68
Cu particles	0.03	1.97	0.06	1.94	0.06
in $\epsilon_h = 6$	0.10	2.01	0.16	2.04	0.17
	0.20	2.08	0.18	2.11	0.28

4. Discussion

The dielectric functions obtained using the MG theory present an anomalous region in a frequency range that depends on the intensity of the electric field inside the metal particles. This fact can be understood based on equation (1). This equation shows that the electric field inside the particles will tend to infinity when $2\epsilon_h = -\epsilon_m$. In the present case ϵ_h is real but the metal particles present an imaginary part that causes a damping of the electric field in its interior. For those metals satisfying the relation $2\epsilon_h \cong -\epsilon_{m1}$ in a frequency where ϵ_{m2} *is small, the anomalous region will be observed. The symmetry of the real part of this* dielectric function (the occurrence of a maximum and a minimum) around ϵ_0 is related to the existence of interband transitions of the metal in the anomalous region. The first interband transition for Ag occurs at 3.9 eV [9], a frequency that is greater than the frequency where $2\epsilon_h \cong -\epsilon_{m1}$ (table 3); consequently, for Ag particles the symmetry is observed (figures 1 and 2). This does not always happen for Cu particles. The Cu first interband transition occurs at 2.1 eV [9], so when $\epsilon_h = 1$, this value is smaller than the value of the frequency where the anomalous region happens, and this implies a damping on the maximum and in particular on the minimum values of ϵ_1^{MG} (figure 3). On the other hand, when $\epsilon_h = 6.0$ the anomalous region (table 3) is not affected by the interband transition and in figure 4 a dielectric function of the composite material is observed with the same general aspects as those of the composite material containing Ag particles.

Table 3. Real (ϵ_{m1}) and imaginary (ϵ_{m2}) parts of the dielectric function of Ag and Cu particles, at the resonance frequency (ω), such that $\epsilon_{m1}(\omega) = -2\epsilon_h$, for three values of ϵ_h.

	Ag particles			Cu particles		
ϵ_h	ϵ_{m1}	ϵ_{m2}	$\hbar\omega$ (eV)	ϵ_{m1}	ϵ_{m2}	$\hbar\omega$ (eV)
1	−2.00	0.64	3.49	−2.00	5.79	3.37
3	−6.01	0.84	2.88	−5.99	5.96	2.19
6	−12.03	1.64	2.30	−12.03	3.94	1.93

The composite material is like a homogeneous material with a resonance frequency (ω_0) that corresponds to the frequency where $2\epsilon_h \cong -\epsilon_{m1}$. The red shift of the anomalous region, and consequently of ω_0, that occurs when f increases can be understood by considering the different behaviour of insulators and conductors at low frequencies. In a metal the lowest resonance frequency tends to zero, once it has a certain number of free electrons. So, the ω_0 red shift could be caused by an increase of the number of free electrons in the composite material as a whole when the filling factor increases. The observed ω_0 red shift when ϵ_h increases, for a given filling factor, is due to the fact that the real part of the metal dielectric function tends to more negative values as ω tends to zero. Then the relation $2\epsilon_h \cong -\epsilon_{m1}$ is satisfied for smaller values of ω as ϵ_h increases.

When in the Lorentz model only the electronic excitations are taken into account, ϵ_0 has the value of unity. A modification of this model leads to a valid extension for lattice vibrations of a material, once these vibrations occur in lower-energy regions, far away from the electronic excitations, and in this extension ϵ_0 assumes a value different from unity [7]. In the present case the ϵ_0 value is approximately equal to ϵ_h for small values of the filling factor, so it can assume values other than unity. In addition, an increase in ϵ_0 is accompanied by a small red shift of the anomalous region and by an increase of the dielectric function in this region (table 1 and figures 1, 2, and 4). These facts lead to a new and important analogy between the dielectric functions of the composite and of the homogeneous materials. In this sense, the metal particles in the composite material play the same role as the ionic oscillators in a lattice, and it is possible to interpret the plasma frequency (ω_p) calculated through the Lorentz model as the oscillation frequency of the oscillator assembly (in this case, the metal particles). This frequency is proportional to the number of oscillators; consequently, it increases as f increases (table 1).

The damping factor γ, which corresponds to the width of the bell-shaped curve ϵ_2^{MG}, is approximately constant (table 1) because both metal particles are of the free-electron type and the variation of ϵ_h considered is not large enough.

For a free-electron metal the maximum of the loss function occurs at the electronic plasma frequency. In the Lorentz model the loss energy function is maximum for ${}^{L}\omega_{max}^2 = \omega_0^2 + \omega_p^2/\epsilon_0$, which is equal to ω_p only when $\omega_p \gg \omega_0$ and $\epsilon_0 = 1$ (free-electron metals). So for composite materials, in the same way as for the lattice vibrations in homogeneous materials, the Lorentz model predicts a value of ${}^{L}\omega_{max}$ greater than the plasma frequency, and this fact is observed in the loss energy functions calculated using the MG theory.

5. Conclusions

The MG dielectric functions of the composite materials considered present an anomalous region when the interband transitions of the metal particles occur at frequencies above the resonance frequency, ω_0, where $\epsilon_{m1} \cong -2\epsilon_h$. In this case the Lorentz oscillator model can be used to describe and understand the optical properties of the composite material, ω_0 being the proper oscillator frequency, which can be displaced by changing the value of the dielectric function of the host material, and is almost independent of the filling factor.

In the Lorentz model the plasma frequency is the oscillation frequency of the oscillator assembly in the host material. Consequently it increases with the oscillator number, that is, with the filling factor, and with the value of the dielectric function of the host material, but the frequency (${}^{L}\omega_{max}$) at which the loss function is maximum is the frequency that indicates a decrease of the reflectance function, so this frequency is interpreted as the plasma frequency of the composite material.

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Appendix. The dielectric function of small metal particles

The dielectric function of free-electron-type metals can be expressed as a sum of the free-electron part plus the contribution of the electronic interband transitions. The free-electron part in the Drude model is given by [10]

$$\epsilon^{D}(\omega) = (1 + i\omega_p^2\tau)/\omega(1 - i\omega\tau) \tag{A1}$$

where ω_p is the free-electron plasma frequency, and τ is the mean scattering time for conduction electrons.

In the case of small particles the scattering time must be modified in order to include the surface scattering effects. The correction is assumed to be of the form [11]

$$1/\tau_p = 1/\tau_b + V_F/r \tag{A2}$$

Where V_F is the metal Fermi velocity and r is the particle radius, assumed to be equal to 50 Å; τ_b and τ_p are the scattering times for bulk metal and for metal particles respectively. In the present work the values of V_F and τ_b for Cu and Ag are taken from [10] and [11].

The dielectric function ($\epsilon_p(\omega)$) of the metal particles is obtained from the experimental bulk values ($\epsilon_{exp}(\omega)$) in the following way:

$$\epsilon_p(\omega) = \epsilon_{exp}(\omega) - \epsilon_b^{D}(\omega) + \epsilon_p^{D}(\omega) \tag{A3}$$

where ϵ_b^D and ϵ_p^D are given by (A1) with τ equal to τ_b and τ_p respectively.

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