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Absorption of Far-Infrared Electromagnetic Radiation by Disperse Systems with Metallic Inclusions

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Abstracts

The calculation procedure of far-infrared absorption by composites with metallic inclusions is proposed. The calculated absorption spectra of $Pd - KCl$ composite in the far-infrared region are in a good agreement with experimental data.

1. Introduction

The anomalous far-infrared FIR absorption by small metal particles has been a puzzling problem for a long time [1]-[6]. Despite the classical effective medium theories give a correct description of light scattering and absorption by small metal particles in the visible frequency region, they predict too small FIR absorption [1]-[5]. Many theoretical approaches have been proposed to explain this phenomenon, including effects of coating the particle surfaces, clustering of individual particles into needle-shaped structures [4], quantum size effects, direct coupling of external electric fields to phonons through unscreened surface ions in the small particles [5]. Nevertheless, all these approaches could not explain the above phenomenon and the problem of FIR absorption in small metal particles has been remained a "mystery" [4].

In this study we show that the above phenomenon can be explained if we will take into account the fact that the wavelength in metallic inclusions is reduced due to a large dielectric permeability of the metallic inclusions. Therefore, we have modified the classical Maxwell-Garnet approximation (MGT) for a dilute suspension of small metallic particles. Our numerical calculations of the absorption coefficient of random small metal particle composite are in good agreement with the experimental results [3]. Furthermore, we have derived the expression connecting the maximum of the absorption coefficient with the radius of metallic inclusions.

2. Theory

The classical Maxwell-Garnet theory gives for the effective dielectric permeability $\tilde{\varepsilon}$of the metal-dielectric composites with small spherical metallic inclusions the following expression [1]-[4]

$$\frac{\tilde{\varepsilon}-\varepsilon}{\tilde{\varepsilon}+2\varepsilon}=f\frac{\varepsilon_p-\varepsilon}{\varepsilon_p+2\varepsilon} \tag{1}$$

where ε is the dielectric permeability of the matrix, ε_p is the dielectric permeability of the metallic inclusions, f is the inclusions concentration.

Note that direct calculation of effective dielectric permittivity of composites with high conductive metallic inclusions $\sigma_p \sim 10^{17}$-10^{18} s^{-1} using equation (1) is not valid in the FIR $\nu \sim$ (1-100) cm^{-1}. In this case we have

$$\begin{array}{lcl} a/\lambda & \langle\langle & 1 \\ a/\lambda_p & \geq & 1 \end{array} \tag{2}$$

were $a$is the radius of metal particles, $\lambda$is the wavelength of incident radiation, $\lambda_p$is the wavelength in the metallic particles.

To modify MGT approximation in the case of high conductive metallic inclusions it is necessary to analyze more accurately the process of interaction of electromagnetic radiation with spherical particle of radius a using Mie theory. For this purpose let us consider the homogeneous dielectric matrix with real dielectric constant ε and the electrically small metallic spherical inclusions with complex dielectric permittivity ε_p. The scattering cross-section of an isolated sphere is given by the following expression

$$Q_{sca}=\frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2+|b_n|^2) \tag{3}$$

here k is the wave vector of the incident wave. The coefficients a_n and b_n have the form

$$a_n=\frac{m\psi_n'(x)\psi_n(mx)-\psi_n'(mx)\psi_n(x)}{m\xi_n'(x)\psi_n(mx)-\psi_n'(mx)\xi_n(x)} \tag{4}$$

$$b_n=\frac{\psi_n'(x)\psi_n(mx)-m\psi_n'(mx)\psi_n(x)}{\xi_n'(x)\psi_n(mx)-m\psi_n'(mx)\xi_n(x)} \tag{5}$$

$$x=ka=\frac{2piNa}{\lambda} \tag{6}$$

$$m=\frac{N_p}{N} \tag{7}$$

were x is the diffraction parameter, N is the refractive index of the matrix, N_p is the refractive index of the particle, μ_p is the magnetic permeability of the particle, μ is the magnetic permeability of the matrix, $\psi_n, \xi_n$are Riccati -Bessel functions. In case of high conductive metallic particle the coefficient b_1 may have the same order as the coefficient a_1, while the terms a_2, b_2 and all others can be neglected. To find the coefficients a_1 and b_1 it is necessary to expend the expressions (4) in series in x, confining the first terms (precision up to x^5). After a series of manipulations we have the expressions for the coefficients

$$a_1=\frac{2}{3i}x^3\frac{1-\frac{\varepsilon}{\varepsilon_p}g\left(mx\right)}{1+2\frac{\varepsilon}{\varepsilon_p}g\left(mx\right)}+O\left(x^5\right)q \tag{8}$$

$$b_1=\frac{2}{3i}x^3\frac{1-\frac{\mu}{\mu_p}g\left(mx\right)}{1+2\frac{\mu}{\mu_p}g\left(mx\right)}+O\left(x^5\right) \tag{9}$$

were

$$g\left(mx\right)=\frac{mx}{2}\frac{\psi_1'\left(mx\right)}{\psi_1\left(mx\right)}=\frac{1}{2}\frac{\left[\left(mx\right)^2-1\right]sin\left(mx\right)+mxcos\left(mx\right)}{sin\left(mx\right)-mxcos\left(mx\right)}$$

The Eq.(8-9) have an appropriate form

$$a_1=\frac{2}{3i}x^3\frac{\varepsilon_p F(mx)-\varepsilon}{\varepsilon_p F(mx)+2\varepsilon}+O\left(x^5\right) \tag{10}$$

$$b_1=\frac{2}{3i}x^3\frac{\mu_p F(mx)-\mu}{\mu_p F(mx)+2\mu}+O\left(x^5\right) \tag{11}$$

were the function $F(z)$ is

$$F(z)=2\frac{\sin(z)-z\cos(z)}{(z^2-1)\sin(z)+z\cos(z)} \tag{12}$$

herewith $z\to 0, F(z)\to 1$.
The coefficients a_1 and b_1 at $|mx|<<1$ and $|x|<<1$ turn to

$$a_1\to\frac{2}{3i}x^3\frac{\varepsilon_p-\varepsilon}{\varepsilon_p+2\varepsilon}+O\left(x^5\right) \tag{13}$$

$$b_1\to\frac{2}{3i}x^3\frac{\mu_p-\mu}{\mu_p+2\mu}+O\left(x^5\right) \tag{14}$$

In this case the coefficients a_1 and b_1 have the same order. The coefficient a_1 represents the electric dipole interaction with the particle, while the coefficient b_1 is related to the magnetic dipole interaction. For the nonmagnetic media $\mu=\mu_p=1$, and then $b_1\to 0$. Now comparing the equations (6) and (7) we can see, that the behavior of spherical metallic particle in electromagnetic field can be considered as one having the dielectric permittivity $\bar{\varepsilon}_p\left(\omega\right)$ and magnetic $\bar{\mu}_p\left(\omega\right)$ permeability

$$\bar{\varepsilon}_p(\omega)=\varepsilon_p(\omega)F(mx) \tag{15}$$

$$\bar{\mu}_p(\omega)=\mu_p(\omega)F(mx) \tag{16}$$

Thus, substituting the renormalised expressions $\bar{\varepsilon}_p\left(\omega\right)$ and $\bar{\mu}_p\left(\omega\right)$ into Eq. (1) we can correctly calculate the effective permittivity and permeability of the composite medium in the following approximation

$$\frac{\tilde{\varepsilon}-\varepsilon}{\tilde{\varepsilon}+2\varepsilon}=f\frac{\bar{\varepsilon}_p-\varepsilon}{\bar{\varepsilon}_p+2\varepsilon} \tag{17}$$

$$\frac{\tilde{\mu}-\mu}{\tilde{\mu}+2\mu}=f\frac{\bar{\mu}_p-\mu}{\bar{\mu}_p+2\mu} \tag{18}$$

Together with the expression for the absorption coefficient

$$\alpha=\frac{2\omega}{c}Im\sqrt{\tilde{\varepsilon}(\omega)\tilde{\mu}(\omega)} \tag{19}$$

the expressions Eq.(15)-Eq.(19) give the complete solution of the problem of the FIR absorption of electromagnetic waves by the composites with high conductive spherical metallic inclusions.

3. Numerical calculations and discussion

The complex permittivity for metallic inclusions has the following form

$$\varepsilon_p = \varepsilon_p' + i\frac{4\pi\sigma}{\omega} = \varepsilon_p' + i\varepsilon_p'' \tag{20}$$

where $\sigma$is the conductivity of metallic inclusions.

In the FIR $\omega \sim (1 \div 100)cm^{-1}$ the value σ practically does not depend on the frequency and nearly equals to σ_0. Moreover, the imaginary part of the permittivity ε_p'' increases with frequency decreasing, and thus, we can neglect the real part of the permittivity ε_p'

$$\varepsilon_p = i\frac{4\pi\sigma_0}{\omega} = ip \tag{21}$$

Taking into account a skin depth for metallic particles

$$\delta = \frac{c}{\sqrt{2\pi\mu_p\sigma\omega}} \tag{22}$$

we can write for nonmagnetic inclusions

$$mx = \frac{r}{2}(1+i) \tag{23}$$

were $r = 2a/\delta$ is a parameter of the theory. We further assume that we have a nonmagnetic matrix $\mu = 1$. Using equations (17-22) we have

$$\tilde{\varepsilon}(\omega) = \varepsilon(1 + \frac{3f\varepsilon}{\alpha_E^{-1} - f}) \tag{24}$$

$$\tilde{\mu}(\omega) = (1 + \frac{3f}{\alpha_M^{-1} - f}) \tag{25}$$

here

$$\alpha_E = \frac{1 - \frac{\varepsilon}{2\varepsilon_p}[H(mx) - 1]}{1 + \frac{\varepsilon}{\varepsilon_p}[H(mx) - 1]} \tag{26}$$

$$\alpha_M = \frac{1 - \frac{1}{2\mu_p}[H(mx) - 1]}{1 + \frac{1}{\mu_p}[H(mx) - 1]} \tag{27}$$

$$H_z = \frac{z^2}{1 - zctg(z)} \tag{28}$$

were the following function was introduced for a convenience

$$F(z)^{-1} = \frac{1}{2}(H(z) - 1) \tag{29}$$

Dividing here the real and imaginary parts we have in the case of low concentration $f << 0.1$

$$\tilde{\varepsilon} = \varepsilon_m[(1 + 3f - \frac{9fD\varepsilon_p}{2p}) + i\frac{9fC\varepsilon_p}{2p}] \tag{30}$$

$$\tilde{\mu} = [(1 + 3f - \frac{9f(C+1+iD)}{2(C+1)^2 + D^2})] \tag{31}$$

were

$$H^{-1}(r) = A(r) + iB(r) \tag{32}$$

$$D = -\frac{B}{A^2 + B^2} \tag{33}$$

$$C = \frac{A}{A^2 + B^2} - 1 \tag{34}$$

$$B(r) = -\frac{2}{r^2} - \frac{1}{r}(\frac{sh(r) + sin(r)}{ch(r) - cos(r)}) \tag{35}$$

$$A(r) = \frac{1}{r}(\frac{sh(r) - sin(r)}{ch(r) - cos(r)}) \tag{36}$$

In this approximation from Eqs.(19,27) we obtain

$$\alpha = \frac{9\pi f}{\lambda}\sqrt{\varepsilon_p}(\frac{\varepsilon}{\varepsilon_p}[\frac{B}{A^2 + B^2} - 1] + A) \tag{37}$$

The Eq. (**??**) determines the magnitude of absorption as a function of incident wavelength (λ=$2\pi c/\omega$) and the parameters of the system $f, a$and σ. On Figs.[1,2] the numerical calculations of FIR absorption coefficient as a function of the wavelength are shown for Pd particles with a radius $a = 1\mu m$ embedded in KCl matrix. The calculations were performed using Eq.(37). The calculated curves are in good agreement with experimental results taken from [3]. From Eq.(37) a very important condition follows, relating the wavelength λ_0, conductivity of the particles σ_0 and their size a_0 at the point r_0

$$a_0^2\sigma_0 \approx \frac{r_0^2\lambda_0}{4\pi} \approx 5 * 10^{-3}\lambda_0 \tag{38}$$

i.e. the maximum of the absorption coefficient $\alpha(\lambda, \sigma, a)$ at fixed wavelength $\lambda_0$is reached with those values $\sigma_0$and a_0, which satisfy the relation (38). Thus, from (38) we can obtain the radius of the particles which have the maximum absorption coefficient at a given wavelength. On the Fig.[3] the calculated absorption coefficient for the composite with filling coefficient $f = 0.01$ the wavelength $\omega = 70sm^{-1}$ as a function of radii of metallic inclusions and their conductivity is shown. The calculated absorption coefficient α of a composite with metallic inclusions as a function of the particle conductivity σ and the wavelengthω is shown on Fig.[4]. As can be seen from these calculations the maximum of the absorption coefficient is shifted with increasing the radii of the metallic particles.

Thus, we have showed that the anomalous FIR absorption in small metallic particles can be explained by the account of the wavelength dependence of the permittivity of metallic particles. The modified Maxwell-Garnet approximation (MGT) for a dilute suspension of small metallic particles correctly predicts the value of FIR absorption. Finally, we have obtained the expression connecting the maximum of the absorption coefficient with the radius of metallic inclusions.

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