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On a Problem of Anomalous Absorption of Far-Infrared Radiation by Small Metallic Particles

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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 [1-3]. Many theoretical approaches have been proposed to explain this phenomenon, including effects of coating the particle surfaces, clustering the individual particles into needle-shaped structures [4], quantum size effects, direct coupling external electric fields to phonons through unscreened surface ions in small particles [5,6]. 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 calculation of the absorption coefficient of random small metal particle composite are in good agreement with 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 effective dielectric permeability $\tilde{\varepsilon}$ of metal-dielectric composites with small spherical metallic inclusions the following expression [1-3]:

$$\frac{\tilde{\varepsilon}-\varepsilon}{\tilde{\varepsilon}+2\varepsilon}=f\,\frac{\varepsilon_p-\varepsilon}{\varepsilon_p+2\varepsilon}, \qquad (1)$$

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

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

$$a/\lambda << 1, \qquad a/\lambda_p \ge 1, \qquad (2)$$

where a is the radius of metal particles λ is the wavelength of incident radiation, λ_p is the wavelength inside the metallic particle.

To modify MGT approximation in the case of high conductive metallic inclusions it is necessary to analyse 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 permeability ε_p. The complete scattering cross-section of an isolated sphere is given by the following expression [8]:

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

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

$$a_n = \frac{m\mu\psi_n(mx)\psi_n'(x) - \mu_p\psi_n(x)\psi_n'(mx)}{m\mu\psi_n(mx)\xi_n'(x) - \mu_p\xi_n(x)\psi_n'(mx)},$$

$$b_n = \frac{\mu_p\psi_n(mx)\psi_n'(x) - m\mu\psi_n(x)\psi_n'(mx)}{\mu_p\psi_n(mx)\xi_n'(x) - m\mu\xi_n(x)\psi_n'(mx)}, \quad (4)$$

$$x = ka = \frac{2\pi Na}{\lambda}, \quad m = \frac{N_p}{N},$$

were x is the diffraction parameter, N is the refractive index of a matrix, N_p is the refractive index of a particle, μ_p is the magnetic permeability of a particle, μ is the magnetic permeability of a matrix, ψ_n, ξ_n are Riccati-Bessel functions. In case of a 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 expand the expressions (4) in series over x, confining the first terms (with precision up to x^5). After a series of manipulations we have the expressions for the coefficients:

$$a_1 = \frac{2}{3i}x^3 \frac{1 - \frac{\varepsilon}{\varepsilon_p}g(mx)}{1 + 2\frac{\varepsilon}{\varepsilon_p}g(mx)} + O(x^5),$$

$$b_1 = \frac{2}{3i}x^3 \frac{1 - \frac{\mu}{\mu_p}g(mx)}{1 + 2\frac{\mu}{\mu_p}g(mx)} + O(x^5), \quad (5)$$

where

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

The Eq. (5) has an appropriate form:

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

$$b_1 = \frac{2}{3i}x^3 \frac{\mu_p F(mx) - \mu}{\mu_p F(mx) + 2\mu} + O(x^5); \quad (6)$$

here the function $F(z)$ is

$$F(z) = 2\frac{\sin z - z\cos z}{\left(z^2 - 1\right)\sin z + z\cos z},$$

herewith $z \to 0$, $F(z) \to 1$.

The coefficients a_1 and b_1 at $|mx| << 1$ and $|x| << 1$ turn to

$$a_1 \to \frac{2}{3i}x^3 \frac{\varepsilon_P - \varepsilon}{\varepsilon_p + 2\varepsilon} + O(x^5),$$

$$b_1 \to \frac{2}{3i}x^3 \frac{\mu_p - \mu}{\mu_p + 2\mu} + O(x^5). \quad (7)$$

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 Eqs. (6) and (7) we can see that the behaviour of spherical metallic particle in electromagnetic field can be considered as one having the effective dielectric $\overline{\varepsilon}_p(\omega)$ and magnetic $\overline{\mu}_p(\omega)$ permeabilities:

$$\overline{\varepsilon}_p(\omega) = \varepsilon_p(\omega)F(mx),$$
$$\overline{\mu}_p(\omega) = \mu_p(\omega)F(mx). \quad (8)$$

Thus, substituting the renormalized expressions $\overline{\varepsilon}_p(\omega)$ and $\overline{\mu}_p(\omega)$ into Eq. (1) we can correctly calculate the effective dielectric and magnetic permeabilities of the composite system in following approximation:

$$\frac{\tilde{\varepsilon} - \varepsilon}{\tilde{\varepsilon} + 2\varepsilon} = f\frac{\overline{\varepsilon}_p - \varepsilon}{\overline{\varepsilon}_p + 2\varepsilon}, \quad (9)$$

$$\frac{\tilde{\mu} - \mu}{\tilde{\mu} + 2\mu} = f\frac{\overline{\mu}_p - \mu}{\overline{\mu}_p + 2\mu}. \quad (10)$$

Together with the expression for the absorption coefficient [7]

$$\alpha = \frac{2\omega}{c}\mathrm{Im}\left(\sqrt{\tilde{\varepsilon}(\omega)\tilde{\mu}(\omega)}\right) \quad (11)$$

the expressions (8)-(11) 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 dielectric permeability of the metallic inclusions has the following form [9]:

$$\varepsilon_p = \varepsilon'_p + i\frac{4\pi\sigma}{\omega} = \varepsilon'_p + i\varepsilon''_p, \qquad (12)$$

where σ is the conductivity of metallic inclusion.

In FIR $\omega \sim 1 \div 100$ cm^{-1} the value σ practically does not depend on the frequency and nearly equals to dc conductivity σ_0. Moreover, the imaginary part of dielectric permeability ε''_p increases with frequency lowering, and thus, we can neglect the real part of the dielectric permeability ε'_p:

$$\varepsilon_p = i\frac{4\pi\sigma_0}{\omega} = ip. \qquad (13)$$

Taking into account that the skin depth for the metal

$$\delta = \frac{c}{\sqrt{2\pi\mu_p\sigma\omega}}, \qquad (14)$$

we can write the equation for nonmagnetic inclusions:

$$mx = \frac{r}{2}(1+i), \qquad (15)$$

here $r = 2a/\delta$ is the parameter of theory. We further assume that we have a nonmagnetic matrix, $\mu = 1$. Using Eqs. (9-14) we have:

$$\tilde{\varepsilon}(\omega) = \varepsilon\left(1 + \frac{3f\varepsilon}{\alpha_E^{-1} - f}\right), \quad \tilde{\mu}(\omega) = \left(1 + \frac{3f}{\alpha_M^{-1} - f}\right); \qquad (16)$$

here

$$\alpha_E = \frac{1 - \frac{\varepsilon}{2\varepsilon_p}[H(mx) - 1]}{1 + \frac{\varepsilon}{\varepsilon_p}[H(mx) - 1]}, \quad \alpha_M = \frac{1 - \frac{1}{2\mu_p}[H(mx) - 1]}{1 + \frac{1}{\mu_p}[H(mx) - 1]}, \qquad (17)$$

$$H(z) = \frac{z^2}{1 - z\,\mathrm{ctg}\,z}, \qquad (18)$$

where the following function was introduced for a convenience:

$$[F(z)]^{-1} = \frac{1}{2}(H(z) - 1).$$

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

$$\tilde{\varepsilon} = \varepsilon_m\left[\left(1 + 3f - \frac{9fD\varepsilon_p}{2p}\right) + i\frac{9fC\varepsilon_p}{2p}\right], \quad \tilde{\mu} = \left[1 + 3f - \frac{9f(C + 1 + i\cdot D)}{2\left((C+1)^2 + D^2\right)}\right], \qquad (19)$$

where

$$H^{-1}(r) = A(r) + iB(r),$$

$$D = -\frac{B}{A^2 + B^2}, \quad C = \frac{A}{A^2 + B^2} - 1,$$

$$B(r) = -\frac{2}{r^2} - \frac{1}{r}\left(\frac{\mathrm{sh}\,r + \sin r}{\mathrm{ch}\,r - \cos r}\right), \quad A(r) = \frac{1}{r}\left(\frac{\mathrm{sh}\,r - \sin r}{\mathrm{ch}\,r - \cos r}\right).$$

In this approximation, from Eqs. (11) and (17) we obtain:

$$\alpha = \frac{9\pi f}{\lambda}\sqrt{\varepsilon_p}\left[\frac{\varepsilon_m}{\varepsilon_p}\left(\frac{B}{A^2 + B^2} - 1\right) + A\right]. \qquad (20)$$

The Eq. (20) determines the magnitude of absorption coefficient as a function of incident wavelength ($\lambda = 2\pi c/\omega$) and 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

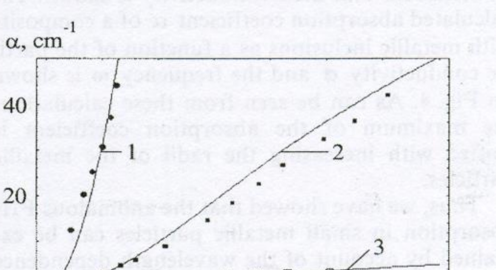

Fig. 1. *The calculated absorption coefficient of Pd small particles $a = 1$ μm embedded in KCl matrix with the volume fractions: 1 – $f = 0.1$, 2 – $f = 0.01$, 3 – $f = 0.001$ (—— – theory; □•■ – experiment)*

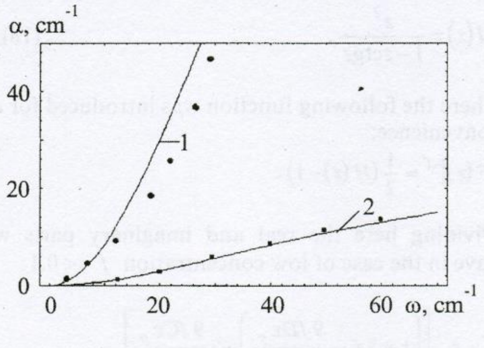

Fig. 2. *The calculated absorption coefficient of Pd small particles $a = 1$ μm embedded in KCl matrix with the volume fractions: 1 – $f = 0.03$, 2 – $f = 0.003$ (—— – theory; ●■ –experiment)*

with a radius $a = 1$ μm, embedded in KCl matrix. The calculations were performed using Eq. (20). The curves are in a good agreement with experimental results taken from the paper [3]. From Eq. (20) the very important conclusion follows, relating the wavelength λ_0, conductivity of the particles σ_0 and their size a_0 at the point r_0:

$$a_0^2\sigma_0 \approx \frac{r_0^2\lambda_0}{4\pi} \approx 5\cdot 10^{-3}\lambda_0\,, \qquad (21)$$

i. e. the maximum of the absorption coefficient $\alpha(\lambda,\sigma,a)$ at fixed wavelength λ_0 is reached with those values σ_0 and a_0, which satisfy the relation (21). Thus, from Eq. (21) we can obtain the radius of the particles which have the maximal absorption coefficient at a given wavelength. On the Fig. 3 the calculated absorption coefficient for the composite with filling factor $f = 0.01$ at wavelength $\omega = 70$ cm^{-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 frequency ω 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 account of the wavelength dependence of dielectric permeability of metallic particles. The modified classical 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 inclusion.

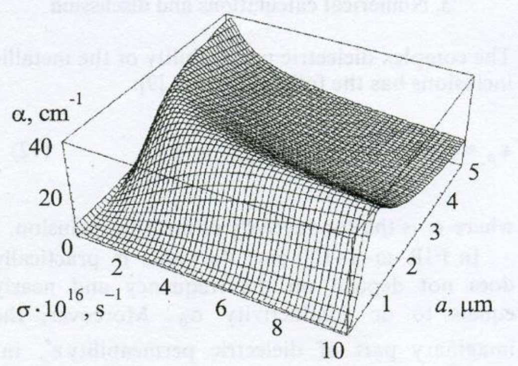

Fig. 3. *The calculated absorption coefficient α of composite with filling factor $f = 0.01$ at the frequency $\omega = 70$ cm^{-1} as a function of the conductivity of particles σ and their radius a*

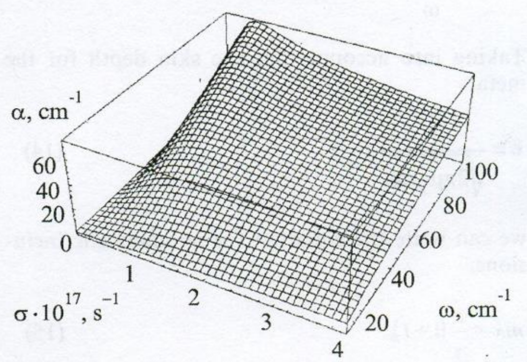

Fig. 4. *The calculated absorption coefficient α of composite with metallic inclusions as a function of the conductivity of particles σ and the frequency ω. The filling factor $f = 0.01$*

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Про проблему аномального поглинання далекого інфрачервоного випромінювання дрібними металевими частинками

Л. Г. Гречко, А. О. Пінчук, Ю. С. Курской, А. Лесьо

Запропоновано процедуру розрахунку коефіцієнта поглинання далекого інфрачервоного випромінювання композитами з дрібними металевими частинками. Розраховані спектри поглинання композиту типу Pd-KCl в далекому інфрачервоному діапазоні добре узгоджуються з експериментом.

О проблеме аномального поглощения инфракрасного излучения малыми металлическими частицами

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Предложена процедура расчета инфракрасного поглощения композитами, содержащими металлические включения. Рассчитанные спектры поглощения композита Pd-KCl в ИК области находятся в хорошем согласии с экспериментальными данными.