DETERMINATION OF THE EFFICIENCY FACTORS OF THE ABSORPTION AND SCATTERING OF NICKEL NANOPARTICLES

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Abstract. In the dipole approximation for the spherical nickel nanoparticle with a diameter $D_0 = 2.5 \div 7$ nm in the spectral range from 0.2 to 1.1 µm at $T = 300$ K, efficiency factors of the absorption K_a and scattering K_s were determined with the help of the experimental values of the complex specific electrical polarizability. Numerical calculations of the K_a and K_s of the nickel nanoparticles were carried out in accordance with the theories of classical and quantum dimensional effects. It was shown that it is impossible to explain the photoabsorption of nickel nanoparticles by the intraband (Drude) type of absorption even taking into account classical or quantum dimensional effects.

Keywords: nickel nanoparticles, optical parameters

WYZNACZANIE WSPÓŁCZYNNIKÓW EFEKTYWNOŚCI ABSORPCJI I ROZPRASZANIA NANOCZĄSTEK NIKLU

Streszczenie Na podstawie wartości eksperymentalnych zespolonej właściwej polaryzacji elektrycznej zostały wyznaczone współczynniki efektywności absorpcji K_a i rozpraszania K_s w przybliżeniu dipolowym dla sferycznej nanocząstki niklu o średnicy $D_0 = 2,5 \div 7$ nm w zakresie spektralnym od 0,2 do 1,1 µm przy $T = 300$ K. Wykonano obliczenia numeryczne K_a i K_s nanocząstek niklu na podstawie teorii efektów klasycznego i kwantowego. Wykazano, że fotoabsorpcji nanocząstek niklu nie można wyjaśnić absorpcją wewnątrzstrefową (Drudowską), nawet biorąc pod uwagę efekty klasyczne lub kwantowe.

Słowa kluczowe: nanocząstki niklu, parametry optyczne

Introduction

Significant interest in the metal nanoparticles, in particular nickel, arise from their use in the nanocomposite systems, which found a wide practical application in the information systems [1], switching devices of the nonlinear optics [2], power engineering [3].

The increasing need for such materials determines the necessity of the investigation of the frequency and size dependences of the electromagnetic parameters of the nanosized particles and nanocomposite systems based on them. Among them, the phenomenon of anomalous photoabsorption of such structures is essential in practical terms. Because of the limited experimental data in the literature on the size dependences of the electromagnetic parameters of the nickel nanoparticles, they are generally identified with values in the macroscopic volumes of metals or theoretical dimensional dependences [1, 4]. At the same time, information on theoretical dimensional dependences is very contradictory and, as follows from [5, 6], most of these theoretical models are not able to describe the dimensional changes in their optical parameters that are observed during the reduction of the spherical metal particles radius. In [6], we determined the complex specific electrical polarizability of nickel nanoparticles with the help of the data of the spectral and electron microscopic investigations of the island nickel films with a statistically homogeneous structure on the glass substrates and on the basis of the exact solution of the inverse problem of the spectrophotometric systems of Rosenberg's equations [7].

The properties of nanostructured materials are determined by their microstructure, processes of the absorption and scattering of the optical radiation by nanoparticles, effects caused by the dimension of the nanoparticles and their interaction with each other, as well as the influence of the external environmental factors on them, etc. [8, 9]. Analysis of the experimental information about the optical characteristics indicates the determining effect of the real distribution function of the nanoparticles by size on their properties. In connection with this, we have improved the experimental and analytical method for determining the values of the complex specific electrical polarizability of the nanoparticles taking into account the statistics of their distribution by size, which made it possible to increase the accuracy of obtaining the experimental values of optical parameters [10].

So, in this connection it is necessary to evaluate the experimental values of the photoabsorption parameters of the nanoparticles and to analyze the nature of their dimensional changes in accordance with the theories of classical and quantum dimensional effects.

The purpose of this paper is to evaluate the absorption and scattering efficiency factors of the nickel nanoparticles in the spectral range of wavelengths of $0.2 \div 1.1$ µm on the basis of the experimental values of their optical parameters.

1. Calculation procedure

According to the Mi theory [1, 11], the efficiency factors of the absorption (K_a) and scattering (K_s) of the nanoparticle are determined by the following expressions:

$$K_a = \frac{8\pi}{3} \cdot \frac{R_0}{\lambda} \cdot \sqrt{\varepsilon_m} \cdot a_2, \qquad (1)$$

$$K_d = \frac{128}{27} \cdot \pi^4 \cdot \frac{R_0}{\lambda^4} \cdot \sqrt{\varepsilon_m} \cdot \left(\alpha_1^2 + \alpha_2^2\right), \qquad (2)$$

where R_0 – particle radius, ε_m – dielectric conductivity of the medium, λ – the light wavelength, α_1, α_2 – the real and virtual parts of the specific complex electrical polarizability of the particle.

The expressions (1) and (2) are valid with the following approximations:
- particle shape is spherical;
- the particle size ($D_0 = 2R_0$) is much smaller than the length of the electromagnetic wave in the given medium ($D_0 << \lambda$) – the dipole approximation;
- metal particles are randomly distributed over the volume of the dielectric matrix;
- volume concentration of the particles is small and the distance between particles is much larger than their dimensions (a system of the non-interacting particles).

According to the classical electromagnetic theory [12], for the specified approximations the complex specific electrical polarizability of the particle can be described by the following relations:

$$\alpha_1 = \frac{3\left[(\varepsilon_1 - \varepsilon_m)(\varepsilon_1 + 2\varepsilon_m) + \varepsilon_2^2\right]}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}, \qquad (3)$$

$$\alpha_1 = \frac{9\varepsilon_m\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}, \qquad (4)$$

where $\varepsilon_1 = n^2 - k^2$ – the real part of the complex dielectric conductivity of the particle; $\varepsilon_2 = 2nk$ – the virtual part of the complex dielectric conductivity of the particle; n, k – respectively, the refractive and absorption indices of the particle.

According to [12], the relations (1) – (4) are valid for the values of ε_1 and ε_2 satisfying the inequality $2\pi n R_0/\lambda \ll 1$. This condition, due to the phenomenological meaning of the dielectric conductivity, allows to apply the indicated expressions for the values of ε_1, ε_2, depending on D_0 for the sizes of the investigated nanoparticles $D_0 < 10$ nm. Analysis of the relations (1) and (4) shows that in the presence of the dispersion peaks ε_2, the corresponding bands should appear also on the spectral curves α_2 and K_a. The resonance peak in the spectra of the α_2 and K_a can also arise at $\lambda = \lambda_R$ and at the monotonic change of the ε_2 with λ, if among the values of the ε_1, the equality $\varepsilon_1(\lambda_R) = -2\varepsilon_m$ is realized for ε and ε_m measured relatively to the air. The resonance in the dispersion α_2 and K_a determined by the criterion $\varepsilon_1(\lambda_R) = -2\varepsilon_m$ is called the dipole [5, 12].

In the theories of classical [13] and quantum [14] dimensional effects in the small spherical metal particle, the dipole resonance (caused, from the phenomenological point of view, by the jump of the values of ε on the surface of the particle) is associated, at the microscopic consideration of the problem, with a surface plasma resonance of the conduction electrons.

The dimensional dependences of the real $\varepsilon_1(\omega, R_0)$ and virtual $\varepsilon_2(\omega, R_0)$ parts of the dielectric conductivity of an ultradisperse particle are approximated by the expressions:

$$\varepsilon_1(\omega, R_0) = \varepsilon_{1v}(\omega) + \varepsilon_{1s}(\omega, R_0), \qquad (5)$$

$$\varepsilon_2(\omega, R_0) = \varepsilon_{2v}(\omega) + \varepsilon_{2s}(\omega, R_0). \qquad (6)$$

where: $\omega = 2\pi c/\lambda$ – the cyclic frequency of the electromagnetic radiation; c – the speed of light; $\varepsilon_{1v}(\omega)$ and $\varepsilon_{2v}(\omega)$ – respectively, the values of the real and virtual parts of the dielectric conductivity of a massive (in the macroscopic volume) metal; $\varepsilon_{1s}(\omega, R_0)$, $\varepsilon_{2s}(\omega, R_0)$ – respectively, the values of the real and virtual parts of the dielectric conductivity of the particle that take into account the dimensional changes caused by the influence of the particle surface on the conduction electrons in it.

The classical dimensional effect [13] is based on the assumption about the diffuse nature of the scattering of electrons by the particle surface and the quasicontinuity of the energy spectrum of the conduction electrons. In this case, the impact of the particle size is manifested in limiting the average value of the length of the free path of conduction electrons by the surface of the particle (its diameter).

In [1] it was shown that in the case of the small particles of a spherical shape, the average length of the free path of conduction electrons is expressed through the effective length of the free path l_{eff}, which is connected to the other parameters of the particle by the relation:

$$l_{eff}^{-1} = l_\infty^{-1} + R_0^{-1}, \qquad (7)$$

where l_∞ – the average length of the free path of conduction electrons in the macroscopic volumes of metals (massive metal).

In this case, it is also legitimate to establish an effective relaxation time of conduction electrons in the particle, depending on its size:

$$\tau_{eff}^{-1} = \tau_\infty^{-1} + \frac{v_F}{R_0}, \qquad (8)$$

where $\tau_\infty = \dfrac{l_\infty}{v_F}$ – the relaxation time of the electrons in a massive metal; v_F – the electron velocity on the Fermi surface.

In the [13], under the assumption about the applicability of the theory of the optical properties of the Drude's metals [1] for describing the intraband absorption of a particle within the framework of the notions about the classical dimensional effect and under the condition that ω significantly exceeds the frequency of concussions of the electrons in a massive metal, the following expressions were obtained:

$$\varepsilon_{1s}(\omega, R_0) = 0, \qquad (9)$$

$$\varepsilon_{2s}(\omega, R_0) = \frac{\omega_p^2}{\omega^3} \cdot \frac{v_F}{R_0}, \qquad (10)$$

where ω_p – the frequency of the volume plasmous resonance for a massive metal.

$$\omega_p = \sqrt{\frac{4\pi n_0 e^2}{m_0}} \qquad (11)$$

where n_0, m_0 – the number, the effective mass of the free electrons; e – the electron charge.

In the theory of the quantum dimensional effect, dimensional changes are manifested in the splitting of the continuous energy spectrum of electrons in the conduction band into the discrete states. The dependence $\varepsilon_{2s}(\omega, R_0)$ takes the form [14]:

$$\varepsilon_{2s}(\omega, R_0) = \frac{32 e^2 f(\nu)}{\pi \eta \omega R_0} \qquad (12)$$

where

$$f(\nu) = \nu^{-3} \int_{\nu_0}^1 \sqrt{x^3(x+\nu)}\, dx, \qquad (13)$$

where $\hbar$ – Planck constant; $\nu = \dfrac{\eta \omega}{E_F}$, $\nu_0 = 1 - \nu$ for $\nu < 1$ and $\nu_0 = 0$, when $\nu > 1$; E_F – Fermi energy.

In the [14] $\varepsilon_{1s}(\omega, R_0)$ is not explicitly represented.

2. Results and discussion

The values of the complex specific electrical polarizability of the nickel nanoparticles were determined by the improved experimental analytical method taking into account the statistics of the nanoparticle distribution by size [11] with the help of the measured transmission and reflection spectra in the wavelength range $\lambda = 0.2 \div 1.1$ μm of the island nickel films on the quartz substrates. The island films represented a morphological microstructure in the form of the monolayers of the isolated from each other spherical nickel nanoislands with a surface concentration $N_0 = (0.8 \div 2.0) \times 10^{12}$ cm^{-2} and a diameter $D_0 = 2.5 \div 7$ nm. The experimental values of α_1, α_2 of the nickel nanoparticles were determined under the condition with $\varepsilon_m = (1 + \varepsilon_0)/2$, where $\varepsilon_0 = 2.38$ (fused quartz).
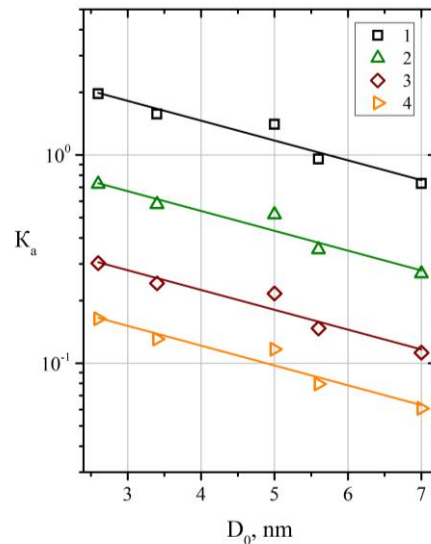

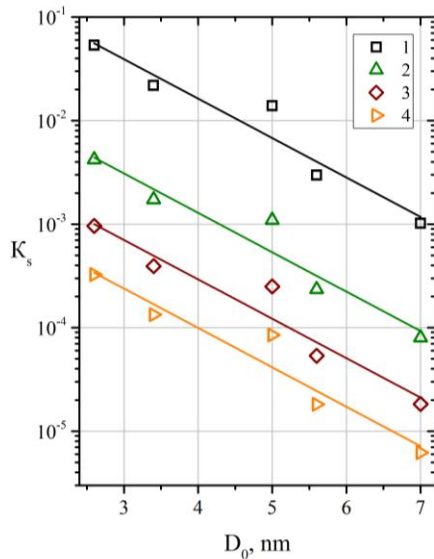Fig. 1. Dimensional dependence of the absorption efficiency factor of the nickel nanoparticles at the different wavelengths λ: 1 – 0.2 μm, 2 – 0.4 μm, 3 – 0.6 μm, 4 – 0.8 μm

A significant increase in the absolute values of α_1 and α_2 was established during the decrease of the size of nickel nanoparticles and, in comparison with the absolute values of α_1 and α_2, also in the model spheres with optical parameters for macroscopic samples of nickel. Dispersion changes of α_2 nanoparticles of the nickel are monotonous. A comparative analysis of the spectral and dimensional dependences α_1, α_2 with the corresponding data for nanoparticles – nickel islands on a glass substrate, obtained in [7],

has shown that they are qualitatively identical. Quantitatively, it was established that taking into account the real distribution function of the nanoparticles by size during the determination of α_1, α_2 with the help of the experimental-analytical method, makes it possible to increase the accuracy up to 40%.

Fig. 2. Dimensional dependence of the scattering efficiency factor of the nickel nanoparticles at the different wavelengths λ: 1 – 0.2 μm, 2 – 0.4 μm, 3 – 0.6 μm, 4 – 0.8 μm

The obtained experimental values of α_1, α_2 were used for estimating K_a, K_s by means of relations (1), (2). The results of the numerical calculations of the dependences of K_a, K_s on the size of the nickel nanoparticles at the different wavelengths of the electromagnetic radiation are presented in Fig. 1 and 2.

It can be seen that when the size of the nickel nanoparticle increases from 2.6 to 7 nm, the increase of the values of K_a, K_s for all λ in the investigated spectral range can be observed. It should be noted, that in the spectral interval $\lambda = 0.2 \div 1.1$ μm, the structure of the dispersion curves K_a, K_s in general repeated the regularity inherent to the spectral dependences α_1, α_2. Analysis of the data in Fig. 1 and 2 and relations (1), (2) ($K_a \sim 1/\lambda$, $K_s \sim 1/\lambda^4$) shows a faster decrease of K_a in comparison with K_s as λ increases.

The specificity of the calculations of the efficiency factors of absorption and scattering of nickel nanoparticles (with dimensions of 2.6, 3.4, 4.0, 5.0, 7.0 nm) according to the theories of classical [13] and quantum [14] dimensional effects was as follows. Firstly, $\varepsilon_1(\omega, R_0)$, $\varepsilon_2(\omega, R_0)$ were calculated with the help of the relations (5) – (13) and experimental values of $\varepsilon_{1v}(\omega)$ and $\varepsilon_{2v}(\omega)$. The last ones were estimated according to the presented in [15] dispersion dependences of the refractive index n and absorption index k of nickel in a macroscopic volume. Then with the obtained $\varepsilon_1(\omega, R_0)$, $\varepsilon_2(\omega, R_0)$ by formulas (3), (4), α_1, α_2 were calculated and, by formulas (1), (2), K_a, K_s were calculated. In order to achieve a correspondence between the calculated and experimental α_1, α_2, K_a, K_s of an individual nickel particle in an island film on a fused quartz substrate with a dielectric conductivity ε_0, according to [6], in the expressions (1) – (3) $\varepsilon_m = (1 + \varepsilon_0)/2$ were used, where $\varepsilon_0 = 2.38$ of the fused quartz. Because of the ambiguity in the nature of the dimensional changes of $\varepsilon_{1s}(\omega, R_0)$, in the theory of the quantum dimensional effect, the calculation of α_1, α_2, K_a, K_s for this theory was carried out, just as in the case of the theory of the classical dimensional effect under the condition $\varepsilon_{1s}(\omega, R_0) = 0$.

The results of numerical calculations of K_a, K_s of the nickel nanoparticles $\lambda = 0.8$ μm that were determined by the theories of classical and quantum dimensional effects are presented in Fig. 3 and 4.

For comparison, the corresponding experimental (estimated with the help of the relations (1), (2) with the experimental values of α_1, α_2) dimensional dependences K_a, K_s are given in the same place. In the Fig. 3 and 4, the significant discrepancies can be observed between the experimental and calculated, with the help of the theories of classical and quantum dimensional effects, dimensional dependences of K_a, K_s of nickel nanoparticles. At the same time, the values of K_a, K_s, calculated from the theories of the dimensional effects, decrease with the decreasing of the nanoparticle size. In contrast, the experimental values of K_a, K_s increase with a reduction of the nanoparticle volume. It should be noted that this trend is preserved for all λ in the entire considered spectral interval.
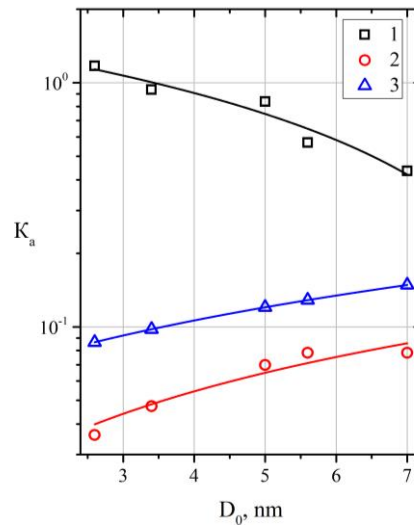

Fig. 3. Dimensional dependence of the absorption efficiency factor of nickel nanoparticles at λ = 0.3 μm. 1 – experimental curve, 2 – the results of the calculations according to the theory of the classical dimensional effect, 3 – results of the calculations according to the theory of the quantum dimensional effect
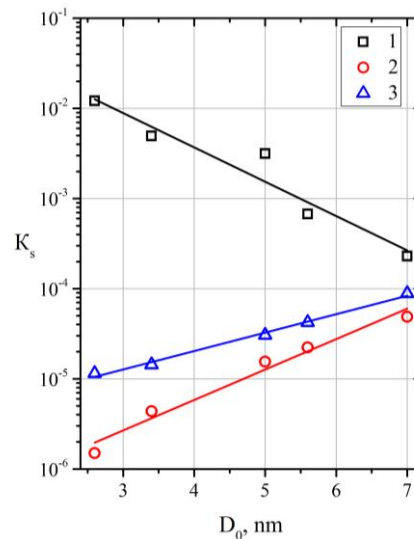

Fig. 4. Dimensional dependence of the scattering efficiency factor of nickel nanoparticles at λ = 0.3 μm. 1 – experimental curve, 2 – the results of the calculations according to the theory of the classical dimensional effect, 3 – results of the calculations according to the theory of the quantum dimensional effect

3. Conclusion

The study of the dimensional dependences of the complex specific electrical polarizability and absorption and scattering efficiency factors of the spherical nickel particles with a size from 2.5 to 7 nm with a radius of 1.5 to 8.0 nm in the spectral range from 0.2 to 1.1 μm was carried out.

The experimental values of the complex specific electrical polarizability of the nickel nanoparticles on the basis of the spectrophotometric and electron-microscopic measurements of the island nickel films on the quartz substrates were determined with the help of the improved experimental analytical method taking into account the statistics of the nanoparticle distribution by size. Such approach for the case of the inhomogeneous nanostructures made it possible to increase the accuracy of the determination of α_1, α_2 and associated with them optical characteristics (the absorption and scattering efficiency factors) up to 40%.

A significant increase (found by us [7]) up to one order of the absolute values of the real and virtual parts of the complex specific electrical polarizability of the nickel nanoparticles, during reduction of their size and as compared to the values that are typical for the macroscopic volumes of nickel was proved.

The growth of the values of the absorption efficiency factor up to one order and the scattering efficiency factor up to two orders of the magnitude of nickel nanoparticles with decreasing their size from 7 to 2.5 nm was established.

In order to clarify the nature of this phenomenon, numerical calculations of the specific dynamic polarizability, dielectric conductivity and also absorption and scattering efficiency factors of the investigated nickel nanoparticles were carried out on the basis of the theories of classical and quantum dimensional effects in the particle. It was shown that calculated in such way values of the absorption and scattering efficiency factors of the nickel particles are in 2 – 3 orders of magnitude lower compared to the experimental ones.

On the basis of these results, it can be concluded that experimental dimensional dependences of K_a, K_s, and also α_1, α_2 in the range $\lambda = 0.2 \div 1.1$ μm can be explained by manifestations of the classical or quantum dimensional effects in the dipole resonance of the nickel nanoparticle.

Thus, the results of the experimental investigations of the optical characteristics and photoabsorption parameters of the nickel nanoparticles can be used during the development of the metal-dielectric nanostructured systems for the use in the light control devices in optoelectronics, selective energy-efficient coatings in the energy-saving technologies and in the information security systems.

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