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OPTICAL RESONANCES OF THE SYSTEMS OF NANOPARTICLES WITH A METALLIC SHELL

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Characteristic features of the formation of the plasma resonance absorption spectra of double-layer nanoparticles with a dielectric core and metal shell were investigated theoretically and experimentally. Two peaks of the surface plasma resonances were observed with the example of an AgI–Ag system. The model of the conductivity electron free path limitation suggested by Kreibig for describing the dimensional dependence of the optical constants of homogeneous spherical metal nanoparticles was extended to the case where metal is concentrated in the shell of the particle. It is established that allowance for the dimensional effect leads to a decrease in plasma resonance absorption and expansion, with the two-peak band structure being preserved. The influence of the metal shell granularity and the degree of the polydispersity of particles on the spectral position, halfwidth, and absolute value of absorption resonances was investigated.

Keywords: *metal-containing nanoparticles, plasma absorption resonances.*

Introduction. At the present time, metal-containing nanostructures are being actively investigated as materials promising for micro- and optoelectronics and laser physics [1–4]. The study of the optical properties of two-layer, metal-containing nanoparticles is of particular interest, since changes in the parameters of the internal structure of the nanoparticles affords additional possibilities of controlling their linear and nonlinear optical characteristics in comparison with the elements based on homogeneous metallic nanoparticles. The most important feature is the two-peak structure of the optical absorption spectra of a system of nanoparticles consisting of a dielectric core and a metallic shell. For the first time this structure was observed in [5]. In [6], the splitting of the peak of the plasmon surface is explained by the existence of plasma fluctuations of electron density in such particles not only on the outer surface of the particle but also on the inner surface of the metallic shell. In the present work, we investigate also the dimensional dependence of the frequencies of both plasmons from quantum-mechanical standpoints. In [7, 8], it is shown theoretically that as the volumetric fraction of the metal in a two-layer particle decreases, the difference in the frequencies of these resonances increases, whereas their relative intensity can be regulated by changing the relationship between the values of the dielectric constant of the nanoparticle core material and of the surrounding medium.

The present work is devoted to the rather unknown problem of the mechanisms underlying the broadening of plasma resonances of two-layer particles, which substantially influences the possibility of resolving the two-peak structure of absorption spectra. These mechanisms are governed by both fundamental reasons (for example, by the further considered dimensional dependence of the optical constants of a metallic shell) and circumstances which can be eliminated due to further improvement of the technological processes of obtaining metal-containing nanoparticles. For the techniques of formation of nanoparticles with silver shells in photolysis and chemical reduction of ultradisperse AgI in colloidal solutions, the most essential of these factors are the polydispersity of two-layer nanoparticles and the granularity of a metallic shell, and we study them in this work.

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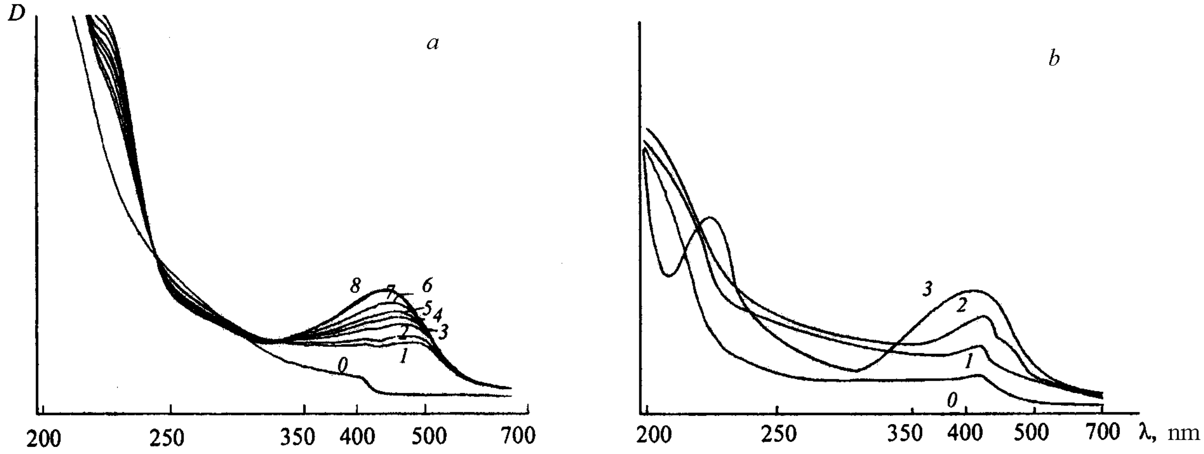

Fig. 1. Attenuation spectra of AgI colloids: a) in the process of reduction of $NaBH_4$, *t* = 1–60 sec (1–8, respectively); b) after irradiation with a dose of 0.2 (1), 1.0 (2), and 5.0 J/cm^2 (3); 0) initial AgI colloid.

Experimental Technique. At the present time, the problem of producing metallic ultradisperse particles is being tackled with the aid of both physical and chemical methods. In applying physical methods (in particular, the most effective method of evaporation in a gaseous atmosphere) uncontaminated particles with a pure surface are formed which require formation of a protective shell around them to prevent coagulation [9, 10]. In many cases, the process of formation of particles using methods of colloidal chemistry is intrinsically heterogeneous, that is, metallic shells are formed on small extraneous nuclei due to aggregation of metallic molecular clusters from a solution onto the surface of a nucleus and are restored in the course of solid-phase reactions from the material of primary nonmetallic particles [11, 12]. There exists the possibility of creating spherical nanoparticles with regulated overall size and thickness of the metallic shell.

In the present work, we used the techniques of the formation of nanoparticles with silver shells in photolysis and chemical reduction of nanodisperse AgI in colloidal solutions. Colloidal solutions of AgI were obtained as a result of interaction of diluted aqueous solutions of $AgNO_3$ and KI at various molar Ag^+/I^- ratios with stabilization by polyvinyl alcohol. Chemical reduction of AgI was made by sodium borohydride ($AgI:NaBH_4$ = 1:10); photolysis was carried out by radiation of a UV lamp with an intensity of 0.01 W/cm^2. Specimens were investigated using the methods of optical spectroscopy, electron microscopy, and x-ray phase analysis.

The process of chemical reduction of AgI colloids, the dimensions of whose particles lie within the limits 5–40 nm, occur virtually without an induction period with formation of a highly disperse silver, which is confirmed by x-ray investigation of deposits separated from colloidal solutions after the reduction of AgI. The absence of the diffraction peaks of AgI on x-ray photographs points to its complete reduction to silver. According to the data of the electron microscopy investigation, the silver nanoparticles formed on reduction of AgI are characterized by smaller (by a factor of 2–3 in comparison with the initial particles of AgI) dimensions and by a narrower size distribution.

The time evolution of the attenuation spectra (caused by absorption and scattering of light) of AgI colloids in the process of reduction is presented in Fig. 1a. In the initial period of reduction of AgI colloids two attenuation bands (two smooth maxima at 420 and 500 nm) appear in their spectra in the visible region. In the course of reduction these maxima get closer and are transformed into one (λ_{max} = 445 nm) with a simultaneous noticeable increase in the band intensity. The broad attenuation band with λ_{max} = 445 nm corresponds to complete reduction of AgI to metallic silver. In the UV region, a decrease in the optical density in the range 230–330 nm is observed with time as well as the presence of two isobestic points (at λ = 242 and 322 nm), the first of which is due to the appearance of I^- ions and the other to those of ultradisperse silver.

Analysis of the character of change in the attenuation spectra of AgI with a mean size of particles of 7 nm in the process of reduction of $NaBH_4$ (transition from a two-peak structure to a single-peak one) with consideration of the electron spectroscopy data allows the assumption that the reduction AgI → Ag follows the solid-phase mechanism through the formation of intermediate core (AgI)–shell (Ag) structures. It is essential that here the shell is not a solid one but consists of silver nanoparticles which can be considered as the product of recrystallization of primarily formed silver clusters stabilized by the AgI surface. The granularity of the Ag shell, while ensuring a constant arrival of the reducer to the surface of AgI, makes the process of reduction of AgI to occur to the end. The additional fact confirming the granularity of the shell is the fact of dispersion (decomposition) of initial particles into finer silver nanoparticles observed at the final stage of reduction.

According to the data of optical spectroscopy, on exposure of colloidal solutions of AgI with >10-nm-size particles to an UV light (in the case of the colloids of still finer particles the efficiency of photolysis decreases sharply) (Fig. 1b) the intensity of absorption typical of AgI increases sharply. Along with the change in the shape of the band, its two-peak structure can be noted at some stages (Fig. 1b, curve 2). This character of the change in the spectrum, just as in the above-described case of reduction of colloids of AgI, points to the formation of a shell of photolytic silver on the surface of AgI particles.

Model of Calculation of Attenuation Spectra. In the approximation of single incoherent scattering, the optical density of a polydisperse sample, which is a mixture of differently sized particles, is proportional to the arranged attenuation section:

$$S = \frac{\sum_j n_j Q_{\text{ext},j} \pi R_j^2}{\sum_j n_j}, \tag{1}$$

where n_j is the concentration of the jth species particles, R_j is the radius of the jth species particle, and $Q_{\text{ext},j}$ is the factor of efficiency of radiation attenuation by the jth species particle.

In the case of two-layer particles, for numerical calculation of Q_{ext} it is possible to use a rigorous solution of the problem of scattering on one sphere in a shell of constant thickness [13, 14]:

$$Q_{\text{ext}} = \frac{2}{\rho_2^2} \sum_{n=1}^{\infty} (2n+1)\,\mathrm{Re}\,(a_n + b_n), \tag{2}$$

where $\rho_2 = 2\pi R/\lambda$ is the parameter of diffraction of the entire particle and a_n and b_n are the coefficients of the series of scattering which depend on the outer radius of the particle R, radius of the core r, and dielectric constants of the core and shell. In carrying out numerical calculations from Eqs. (1) and (2), we considered particles having an Ag shell and a core made of a dielectric material ($n = 2.2$, $k = 0$) which are located in a nonabsorbing matrix ($n = 1.4$). The refractive indices of dielectric materials were selected to be close to the refractive indices of silver iodide used in the experiment (a core of lamellar nanoparticles) and polyvinyl alcohol (matrix).

Since, under the conditions of our experiment, the thicknesses of metallic shells on nanoparticles are comparable with the mean free path of conduction electrons in a massive metal I_0, in the calculations we used dimensionally dependent values of the complex dielectric constant of silver. The dimensional dependence was introduced within the framework of the model of limitation of the mean free path of conduction electrons (LMFPCE) suggested in [15, 16] and allowing for the additional attenuation of conduction electrons in a metallic nanoparticle due to their collisions with the particle surface:

$$\gamma_R = \gamma_0 + \frac{v_F}{L}, \tag{3}$$

where v_F is the electron velocity on the Fermi surface, γ_0 is the mean frequency of collisions (i.e., attenuation constant) in a bulk substance, and L is the effective free path of an electron before collision with the boundary. On the

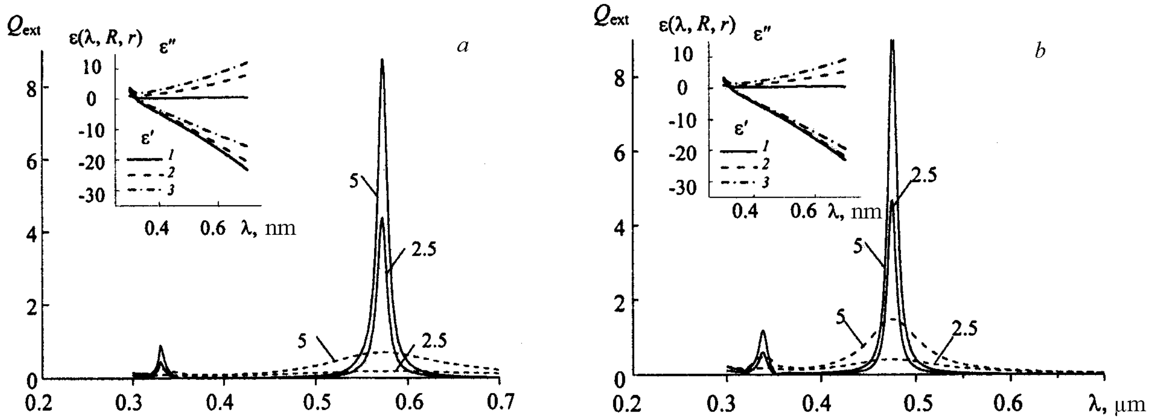

Fig. 2. Factors of the efficiency of attenuation of a particle with a dielectric core and Ag shell calculated without allowance (solid line) and with allowance (dashed line) for the dimensional dependence of the dielectric constant of the shell for differently sized spherical particles at the volumetric fraction of silver in the particle f = 0.6 (a) and 0.8 (b); the figures at the curves correspond to the radius R of the particle; the spectral dependences of ε′ and ε″ of the Ag shell for differently sized particles at f = const (massif (1), R = 5 (2) and 2.5 mm (3)).

assumption of isotropic scattering on the metallic particle–dielectric matrix interface for a spherical particle $L = R$ [15, 16].

In [7], the LMFPCE model was modified for particles with a metallic shell taking into account the fact that for metal-containing particles of arbitrary shape the value of L can be defined by the ratio

$$L = \frac{\int\limits_S \int\limits_\Omega L(r', \theta)\, \rho(\theta)\, d\Omega d^2 r'}{\int\limits_S \int\limits_\Omega \rho(\theta)\, d\Omega d^2 r'}, \tag{4}$$

where $L(r', \theta)$ is the free path of the electron leaving an infinitely small surface element d^2r' at the angle θ, ρ(θ) is the probability density of scattering at the angle θ, Ω is the solid angle, and S is the surface area of the metal.

In [7] it is shown that for a particle of radius R with a dielectric core of radius r and metallic shell of thickness $h = R - r$ on the assumption of diffuse reflection of electrons from both the outer (S_R) and inner (S_r) boundary of the metallic shell the following relation is valid:

$$L_{\text{sh}}(R, a) = R\left[\frac{1}{1+a^2} - \frac{a}{2} - \frac{1}{4}\frac{(1-a^2)}{(1+a^2)}(1-a)\ln\frac{(1-a)}{(1+a)}\right], \tag{5}$$

where $a = r/R$ and $0 < a < 1$. When $r \to 0$ (the particle becomes a homogeneous metallic one), from Eq. (5) we have that $L_{\text{sh}} \to R$, which coincides with the expression obtained in [15, 16] for a metallic sphere.

The spectral dependences of the complex dimensionally dependent dielectric constant of a spherical silver shell ε(λ, R, r) calculated at different values of the volumetric fraction of silver f in a particle of radius R are presented in Fig. 2a and 2b (see the insets). In calculations, just as in [15, 16], we used the division of the dielectric constant taken from the experiment in [17] for a massive metal into two parts corresponding to the contribution of free and bound electrons. It was assumed that the dielectric constant owing its origin to the contribution of bound electrons is independent of the geometric parameters of the particle. The dielectric constant owing its origin to the contribution of free electrons was calculated from the Drude formula with allowance for the dimensional effect in conformity with expression (5). For this purpose, the following values of the parameters were used: $\gamma_0 = 0.25 \cdot 10^{14}$ sec^{-1}; $\omega_p = 1.38 \cdot 10^{16}$ sec^{-1}, where $\omega_p = \sqrt{\frac{\bar{n}e^2}{m^* \varepsilon_0}}$ is the plasma frequency ($\bar{n}$ is the concentration of free electrons and m^* and e are the effective mass and charge of the electron).

It is seen from the insets in Fig. 2 that allowance for the limitation of the free path in the case of shelled particles leads to an increase in both the imaginary (ε'') and real (ε') parts of the dielectric constant of a metallic shell in the entire visible range. Moreover, with the same fraction of metal in a particle, the values of ε' and ε'' are the larger, the smaller the overall size of the particle (and, correspondingly, the thickness of the shell).

It is seen from Fig. 2 that if metal is encased in a shell, then the attenuation spectrum of two-layer nanodimensional particles have two peaks of plasma resonance (resonances correspond to the fluctuations of the electron density on the outer and inner boundaries of the shell). The spectral location of the peaks of the attenuation band depends only on the fraction of the metal in the particle f and is independent of the shell thickness for $R < 15$ nm. As f decreases, the outer plasmon of the metallic shell shifts to the region of low energies and the inner plasmon to the region of high energies.

Mechanisms of Broadening of the Plasma Absorption Resonances. The data given in Fig. 2 make it possible to analyze the influence of dimensional effects on the spectra of plasma attenuation of nanoparticles having a metallic shell. As is seen, the dimensional effects manifest themselves mainly as a decrease in the attenuation maxima which correspond to the electron density fluctuations on both the outer and inner surface of the shell, whereas the attenuation bands themselves are broadened. This adversely affects the possibilities of spectral resolution of the doublet structure in the transmission spectra. Numerical calculations show that the dimensional effect is the stronger, the smaller the outer radius of the two-layer particle irrespective of the fact of which of the parameters — the thickness of the metallic shell or volumetric fraction of metal in the particle — is constant.

Since, as was already mentioned, the spectral location of the attenuation band maxima depends on the fraction of metal in the particle, another reason for the broadening of the plasma resonance band can be the difference in the sizes of particles, i.e., the polydispersity of the medium.

The outer-size distribution of shelled particles can be incorporated in two ways. Let the case where the equally sized cores (r = const) are encased into shells of different thickness h_j be called polydispersity of the 1st kind. Polydispersity of the 2nd kind will refer to the case where a system involves particles with cores of different radii R_j covered with shells of the same thickness (h = const). It should be noted that in both cases the content of metal f_j in the particles of different species is different.

We will consider symmetric size distribution of particles and for definiteness assume the halfwidth of the distribution to be equal to 40% of the most probable radius of the particle $\langle R \rangle$ (see Fig. 3a, inset). We well approximate the size distribution by a three-stage function. This corresponds to the replacement of a real polydisperse system of particles by a set of three monodisperse fractions of particles of definite dimensions. The results of the calculations of the attenuation sections for systems with polydispersity of both kinds and also for a monodisperse phase carried out for the visible region of the spectrum with allowance for dimensional effects in an Ag shell in accordance with Eq. (5) are given in Fig. 3a. The volumetric fraction of a metal in the particles of the monodisperse phase (the radius of the particles $R = 5$ nm) and in the most likely sized particles of the polydisperse system is the same. The resonance response of the particles of each of the fractions is presented for the case of the polydispersity of the 1st kind in Fig. 3b and of the 2nd kind in Fig. 3c. The precise values of the parameters used in the calculations are given in Table 1.

From Fig. 3a it is seen that transition from a monodisperse system of particles to a polydisperse one is accompanied by broadening of the plasma resonance band due to the fluctuations of the electron density at the metallic shell/dielectric matrix interface for the system with polydispersity of both kinds. However, for the case where the polydispersity is associated with the difference in the sizes of dielectric cores, the degree of attenuation of the intensity at the maximum of the plasma band and also the magnitude of its broadening are more substantial. Moreover, in contrast to the polydispersity of the 1st kind, the shortwave displacement of the plasma absorption band maximum is absent.

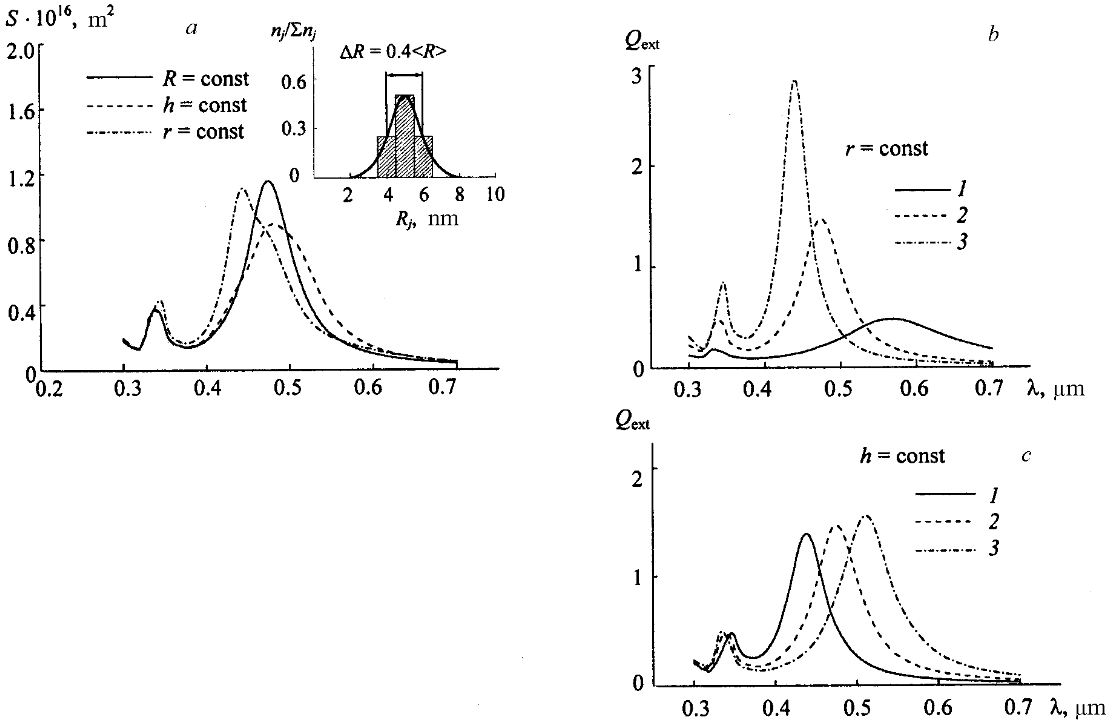

Fig. 3. Spectral dependence of attenuation: a) for a monodisperse suspension (R = 5 nm) and polydisperse system of the 1st and 2nd kinds consisting of spherical particles with an Ag shell and a dielectric core; b and c) for each of the fractions constituting the suspension in the case of polydispersity of the 1st and 2nd kinds, respectively; R = 4 (1), 5 (2), and 6 nm (3) (the calculations were performed with allowance for the dimensional dependence of the dielectric constant of the shell); the size distribution of particles of the polydisperse system is shown in the inset.

In our opinion, the noted differences in the character of the transformation of bands for the polydispersity of the 1st and 2nd kinds can be explained proceeding from the following considerations. As has already been mentioned, in an incoherent single approximation the optical response of a polydisperse system of particles represents a sum of responses of each fraction of particles taken with a corresponding weight function. For each particular fraction the spectral location of the external and internal resonances is determined in the main by the quantity f, whereas the intensity of these resonances depends on the entire set of internal parameters of the particle, increasing with increase in the outer size and/or on increase in the fraction of a metal in the particle (Fig. 2). As is seen from Table 1, the relative fraction f of a metal in the particle for the polydispersity of the 1st kind increases with increase in the outer size of particles of definite fractions. Therefore, the optical response of the fraction of large particles in the case of the polydispersity of the 1st kind is displaced to the shortwave region and greatly exceeds the optical response of the fractions of finer particles. This is manifested as a shortwave displacement of the maximum of the overall attenuation of the entire polydisperse system. Thus, it is evident that the main tendency in the transformation of the plasma bands of a polydisperse system with a constant size of the cores of the particles (except for its broadening) will consist of a shortwave shift of the intensity maximum.

For the case of the polydispersity of the 2nd kind, conversely, the magnitude of the resonance of plasma absorption for all the fractions of particles is approximately the same, since, as is seen from Table 1, an increase in the size of the particles is compensated by a decrease in f_j. Therefore, the broadening of the overall band is more substantial, whereas there is virtually no shift of its maximum.

TABLE 1. Structural Parameters of Spherical Polydisperse Particles with a Three-Stage Distribution Function ($\Delta R = 0.4\langle R\rangle$, $\langle R\rangle = 5$ nm)

R_j, nm	Polydispersity of 1st kind			Polydispersity of 2nd kind		
	r_j, nm	h_j, nm	f_j, nm	r_j, nm	h_j, nm	f_j, nm
4	2.925	1.075	0.609	1.925	2.075	0.889
5	2.925	2.075	0.800	2.925	2.075	0.800
6	2.925	3.075	0.884	3.925	2.075	0.720

The problem of the possible effect of the granularity of the metallic shell on the spectra of plasma absorption is to be specially discussed. The experimental results obtained in the present work point to the fact that the metallic shell formed in the process of the reduction of AgI is not a solid one but rather represents a granular (or island) structure on the surface of the AgI core. The data on the influence of such a structure in the system nonmetallic core–metallic shell on the characteristics of resonance plasma have not been described in the literature. In view of the above-said, the necessity of creating a theoretical model which would make it possible to evaluate this phenomenon arises.

We will consider a granulated shell (with a volumetric fraction of metal c in it and volumetric fraction of dielectric inclusions $p = 1 - c$) as a quasi-homogeneous medium. The effective dielectric constant of such a medium can be calculated in the Maxwell–Garnett approximation (see, e.g., [18]) from the formula

$$\varepsilon_{\text{ef}} = \frac{2\varepsilon_2\,(\varepsilon_1 - \varepsilon_2)\,p + \varepsilon_2\,(\varepsilon_1 + 2\varepsilon_2)}{(\varepsilon_1 + 2\varepsilon_2) - (\varepsilon_1 - \varepsilon_2)\,p}\,, \tag{6}$$

where ε_1 and ε_2 are the complex dielectric constants of the material of the inclusions and of the metallic matrix.

Then the well-known conditions for the Frelich frequencies that determine the spectral location of the internal and external plasma resonances [4] can be written in the form

$$\varepsilon_3\,(\omega_{1,2}) = -\,2\varepsilon_{\text{ef}}\,(\omega_{1,2})\left[\frac{\varepsilon_{\text{ef}}\,(\omega_{1,2})\,f + (3 - f)\,\varepsilon_0\,(\omega_{1,2})}{\varepsilon_{\text{ef}}\,(\omega_{1,2}) + (3 - 2f) + 2f\varepsilon_0\,(\omega_{1,2})}\right]. \tag{7}$$

Here ε_0 and ε_3 are the dielectric constants of the medium surrounding the particle and of the material of its dielectric core; $\omega_{1,2}$ represents the effective Frelich frequencies that determine the spectral location of the internal and external plasma resonances of the metallic granulated shell, respectively. As is seen from comparison of Eqs. (6) and (7), these frequencies depend on the concentration of metallic granules in the shell.

We considered two cases of transformation of the attenuation spectra of such particles on change in the characteristics of a granulated shell with retention of the overall dimensions of the particle. The first case corresponds to deposition of silver granules from a solution on monodisperse dielectric nuclei, as a result of which in an effective shell of constant thickness (h = const) the concentration of silver granules c and also the volumetric fraction of the metal f in the particle increase as a whole. In the second case, a change in the thickness of the shell occurs at a constant concentration of silver granules (c = const) at the expense of the dimensions of the dielectric core. In this case, the fraction of the metal in the particle increases as the core decreases. Such a case is implemented in the process of the formation of the structure of the type nonmetallic core–metallic shell with interaction of the material of the core with the reducer from the solution. In both cases $\varepsilon_1 = \varepsilon_0$. The parameters of the particle corresponding to the investigated concentrations of silver in a composite shell were calculated from the formula $(r/R)^3 = 1 - f/c$ and presented in Table 2.

The attenuation spectra of particles with a composite Ag shell for both cases of its formation are presented in Fig. 4a and 4b. Figure 4a illustrates the change in the structure of the plasma attenuation spectrum with an increase in the concentration of silver in the shell of constant thickness. The attenuation spectra in Fig. 4b demonstrate the

TABLE 2. Structural Parameters of Spherical Particles with a Granulated Metallic Shell

f	h = 2.075 nm	c = 0.9
	c	h, nm
0.64	0.8	1.695
0.72	0.9	2.075
0.80	1.0	2.0595

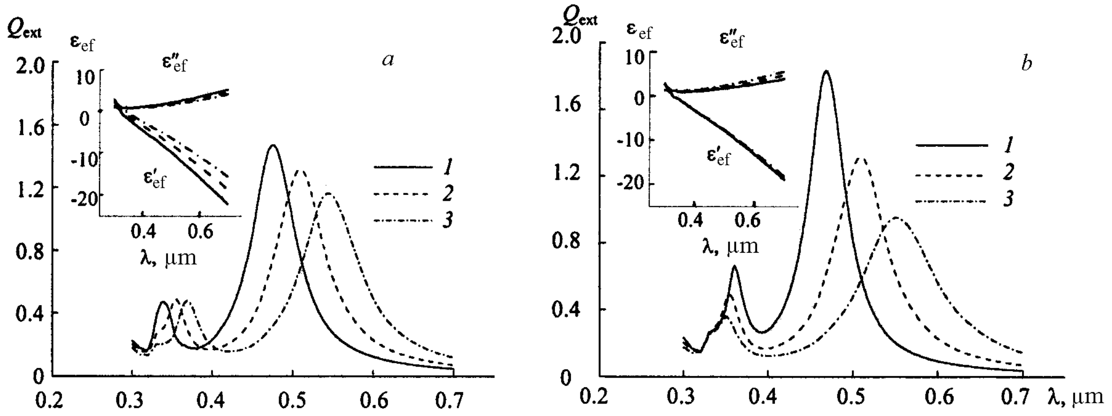

Fig. 4. The attenuation efficiency factors for a particle with a dielectric core and granulated Ag shell (R = 5 nm) calculated for particles with the content of silver f = 0.80 (1), 0.72 (2), and 0.64 (3): a) with the shell thickness h = 2.075 nm; b) at the concentration of the metal in the shell c = 0.9 with allowance for the dimensional dependence of the optical constants of the shell; the insets show the spectral dependences ε' and ε'' of a granulated shell for particles with a different content of silver at h = const (a) and c = const (b).

changes caused by the increase in the thickness of the shell with a constant concentration of silver. The spectral dynamics of the effective dielectric constant for both cases is shown in the inset.

The calculations were performed for the same set of values of the volumetric fraction of metal f in the particle with allowance for the dimensional dependence of the dielectric constant of the metal. It was assumed here that the tunneling of conduction electrons between the granules of the ultradisperse composite shell makes it possible, just as in the case of a solid metallic shell, as the boundaries of their free path to consider the internal and external envelopes of the shell surface as one whole. In other words, it was assumed that the granularity of a highly disperse metal does not influence the parameters that play an important role in determining the dimensionally dependent constants of the metal phase (v_F, γ_0, ω_p), with the key role belonging, as ever, to the shell thickness. Proceeding from these arguments, in Eq. (6) the values of ε_2 were used with correction for the additional attenuation as a result of limitation of the free path length of electrons in a shell.

As is seen from Fig. 4a, in the process of transition from a granular metal shell to a solid one the narrowing of the band of the most intense (external) plasma resonance and its shortwave displacement, both accompanied by an increase in plasma absorption at the maximum of the band, are observed. In our opinion, the shortwave displacement can be explained by the concentrational dependence of the Frelich effective frequency determined for particles with a small core by the conditions Re $[\varepsilon_{ef}(\omega_1] \approx -2\varepsilon_0(\omega_1)$, Im $[\varepsilon_{ef}(\omega_1)] \approx 0$. In fact, as is seen from the inset in Fig. 4a, as the volumetric fraction of the metal decreases (at h = const this corresponds to a decrease in the concentration of the metal c in a shell), the Frelich effective frequency is displaced to the longwave region. Since this corresponds to transition to the region of large values of Im $[\varepsilon_{ef}(\omega)]$, broadening of plasma resonance and a decrease in its intensity are observed simultaneously.

In addition, comparing Fig. 4a and 4b it can also be noted that at high concentrations of a metal in a granulated shell the spectral location of the plasma attenuation peaks with fluctuations of the electron density on its outer boundary is mainly determined by the overall fraction of a metal in a particle of constant radius. However, attenuation of the plasma resonance with decrease in f in particles with a constant concentration of a metal in their shells is more pronounced than in particles of constant thickness (Fig. 4b). This fact can be explained using the data of Table 2. As is seen from the table, a decrease in f at c = const is accompanied by a decrease in the shell thickness and, consequently, by a more marked manifestation of dimensional effects that usually lead to broadening of the plasma absorption band and decrease in its maximum.

Conclusions. The theoretical analysis carried out has shown that two-layer nanospheres with a dielectric core and metallic shell are characterized by the presence of two types of plasma resonances associated with fluctuations of electron density on the inner and outer surface of the shell. In the investigated region of the dimensions of particles ($R < 10$ nm) the spectra of particles with a metallic shell have a two-peak structure. The spectral location of resonances depends in the main on the volumetric fraction of the metal f, with the resonances being approached with increase of f. Allowance for the polydispersity and dimensional effects in the LMFPCE model for a metallic shell leads to a decrease in the intensity of plasma resonances and their broadening; however, the two-peak structure of the spectra is preserved. An additional mechanism of broadening of plasma resonances appears when the metallic shell is not solid but granular.

The dynamics of a change in the experimental optical spectra of nanoparticles with a silver shell formed during photolysis and chemical reduction of ultradisperse silver iodide in colloidal solutions has been qualitatively interpreted.

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