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Optical Metamaterial with Near-Zero Random Refractive Index

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Abstract: **A relation is obtained for the complex refractive index of an optical metamaterial, taking into account the structural factor that determines the discrete distribution of inclusions in the composite. It is shown that a small random change in the structure factor leads to a significant decrease in the refractive index of the metamaterial in a wide range of visible and IR wavelengths. The obtained theoretical results are confirmed by experiment on the example of a synthesized metamaterial from a polymer matrix with silver nanoparticles.**

Keywords: **optical metamaterial, refractive index close to zero, structure factor, silver nanoparticles, polymethyl methacrylate**

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Contents

1. INTRODUCTION

Is it possible to reduce the refractive index of this matrix by ten or more times using a small (about 3 wt.%) content and a random arrangement of metal nanoparticles in a dielectric matrix? This article provides a theoretical justification for the possibility of such a structural transition. Moreover, it will be shown that this structural transition is observed experimentally in the PMMA@Ag metamaterial with silver nanoparticles synthesized according to the technology developed by us [1,2].

As a rule, to simulate the optical properties of composite materials with random inclusions the Garnett formula [3,4] is used on the basis of which it is possible to prove the possibility of achieving a zero refractive index in a narrow wavelength range at certain values of the matrix permittivity. In review [3] various methods of mathematical modeling of the effective permittivity of various composite materials are analyzed in sufficient detail. Without going into the details of these methods we only note that composite materials are considered in them within the framework of the concept of a continuous medium. This article uses the concept of a discrete-continuous medium taking into account the discrete distribution of nanoparticles in the vicinity of any composite nanoparticle. In this case the discrete region has linear dimensions that are much smaller than the wavelength of the external radiation. Therefore, this region is not considered as a light-scattering inhomogeneity. As shown in [5], in a dielectric consisting of atoms or molecules in the framework of the concept of a discrete-continuous dielectric the refractive index of the dielectric is always fluctuating in the vicinity of a certain average value. The magnitude of these fluctuations is about 1-2%. It was also noted in [5] that the role of these fluctuations increases significantly near the boundary of the dielectric where a quasicrystalline transition layer is formed, which made it possible to explain the anomalies in the Fresnel formulas for Brewster reflection of light [6]. This article will show that in a discrete-continuous composite material with a low weight content of silver the refractive index of the composite not only decreases significantly, but also fluctuates around zero in a wide wavelength range, at least from 450 to 1200 nm. Moreover, this wavelength range is the region of transparency of the composite, where the absorption index is much less than the refractive index. The idea of a random refractive index close to zero made it possible to explain the experimental reflection and transmission spectra of a nanocomposite layer on glass.

Previously, in a series of works [7–11], the effects discovered by the authors were described, such as light interference in thick composite layers, the thickness of which is much greater than the wavelength [7], enhanced optical transmission of the composite layer compared to the optical transmission of a layer made of the matrix material of the composite the same thickness [8], non-specular reflection of light at an inhomogeneous interface between two media and in a nanostructured layer with a refractive index close to zero [9], violation of the principle of reversibility of light fluxes in an optical medium with a random refractive index close to zero [10], photon localization in metamaterials with a refractive index close to zero [11]. It was shown in [12] that all these effects can be theoretically described using non-Fresnel formulas for the reflection and transmission coefficients of a layer with a random refractive index close to zero.

Therefore, the purpose of this article is the further development of a mathematical apparatus useful for describing the optical properties of a discrete-continuous medium. Below, we derive a formula for the complex refractive index of a composite metamaterial, taking into account the structure factor, and it will be shown that this formula transforms into the Garnett formula for a continuous effective medium.

2. POLARIZATION VECTOR OF A COMPOSITE MEDIUM WITH SPHERICAL SILVER NANOPARTICLES

For dimensional polarization, we write the polarization vector of the composite medium in the form:

$$\mathbf{P} = \left(N_0 \alpha_p \frac{n_0^{\ 2} + 2\varepsilon_m}{3\varepsilon_m} + N_m \alpha_m \frac{\varepsilon_m + 2}{3} \right) \mathbf{E}, \quad (1)$$

where $\mathbf{E}$ is the strength of the macroscopic electric field, $n_0^2 = \varepsilon_0$ is the complex permittivity of bulk silver, ε_m is the dielectric (real) permittivity of the dielectric matrix (polymethyl methacrylate), N_0 is the concentration of silver spherical silver nanoparticles, N_m the concentration of dipoles in the matrix, α_m and α_p the polarizability of the matrix and silver nanoparticles, respectively. Wherein: $N_m\alpha_m = (3/4\pi)(\varepsilon_m - 1)/(\varepsilon_m + 2)$, $\varepsilon_m = n_m^2$, $n_m = 1.49$. The polarizability of a silver nanoparticle can be represented as:

$$\alpha_p = a^3 \frac{\varepsilon_0 - \varepsilon_m}{\varepsilon_0 + 2\varepsilon_m}, \tag{2}$$

where α is the nanoparticle radius.

Substituting (2) into the Lorentz-Lorentz formula, we obtain the Garnett formula [3]:

$$\varepsilon = \varepsilon_m + \frac{3p\varepsilon_m\left(\varepsilon_0 - \varepsilon_m\right)}{\left(\varepsilon_0 + 2\varepsilon_m\right) - p\left(\varepsilon_0 - \varepsilon_m\right)}, \tag{3}$$

where $p = (4\pi/3)\alpha^3 N_0$ is the volume fraction of nanoparticles in the polymer matrix. This formula is usually used to describe continuous media with inclusions. For nanoparticles of small radius $\alpha = (2\div7)$ nm in the metamaterials considered in this article $p << 1$.

Let us pass in formula (1) from the dimensional polarizability (2) to the dimensionless polarizability α_{eff}, which can be represented as

$$\alpha_{eff} = \mathrm{Re}\left(\alpha_{eff}\right) + i\,\mathrm{Im}\left(\alpha_{eff}\right), \tag{4}$$

where

$$\mathrm{Re}\left(\alpha_{eff}\right) = \frac{N_0 a^3}{3\varepsilon_m}\left(\varepsilon_{10} - \varepsilon_m\right) + \frac{1}{4\pi}\left(\varepsilon_m - 1\right),$$
$$\mathrm{Im}\left(\alpha_{eff}\right) = \frac{N_0 a^3}{3\varepsilon_m}\varepsilon_{20}. \tag{5}$$

Let us consider the dielectric matrix using the real value ε_m, and the silver nanoparticle using the complex permittivity $n_0^2 = \varepsilon_{10} + i\varepsilon_{20}$ of bulk silver. In this case, in accordance with [13]:

$$\varepsilon_{10}\left(\lambda\right) = 1 - \frac{\omega_p{}^2\tau^2}{1 + \left(2\pi\tilde{n}/\lambda\right)^2\tau^2},$$
$$\varepsilon_{20}\left(\lambda\right) = \frac{\omega_p{}^2\tau}{\left(2\pi\tilde{n}/\lambda\right)\left(1 + \left(2\pi\tilde{n}/\lambda\right)^2\tau^2\right)}, \tag{6}$$

where the plasma frequency is $\omega_p = 1.386\cdot10^{16}$ rad/s, $\tau = 31\cdot10^{-15}$ s. In bulk silver at wavelength $\lambda = 0.5893\cdot10^{-4}$ cm $n_0 = 0.2$ is the real part of the refractive index and $k_0 = 3.44$ is the imaginary part of the refractive index [14]. Using these numerical values, we obtain $\varepsilon_{10} = -17.786$ and $\varepsilon_{20} = 0.18$. Then $\mathrm{Re}(\alpha_{eff}) = 0.0948$ and $Im(\alpha_{eff}) = 0.192\cdot10^{-4}$. Similarly, for other wavelengths in the range from 450 to 1200 nm, we obtain the following relationship:

$$\frac{\mathrm{Im}\left(\alpha_{eff}\right)}{\mathrm{Re}\left(\alpha_{eff}\right)} << 1. \tag{7}$$

This ratio means that the considered metamaterial with silver nanoparticles has a high optical transparency.

3. THE REFRACTIVE INDEX OF A METAMATERIAL WITH SILVER NANOPARTICLES, TAKING INTO ACCOUNT THE STRUCTURAL FACTOR

The relative refractive index of the composite medium (n/n_m) is determined using the following relation:

$$\frac{4\pi}{\left(n/n_m\right)^2 - 1}\alpha_{eff} = 1 - \beta\alpha_{eff} - \frac{4\pi}{3}\alpha_{eff}, \tag{8}$$

where the structure factor is defined as

$$\beta = \frac{2}{N_0}\left(\frac{2\pi}{\lambda}\right)^2 n_m{}^2 \sum_a \frac{\exp\left(i\mathbf{k}\mathbf{R}_a\right)}{R_a}. \tag{9}$$

The summation in (9) is performed over the positions of nanoparticles inside the Lorentz sphere, the radius of which is much less than the wavelength λ, where **k** is the wave vector of the polarization wave in the composite, $|\mathbf{k}| = \left(\frac{2\pi}{\lambda}\right)n_m$, $\mathbf{R}_\alpha$ is the radius vector of nanoparticle centers.

We assumed (8) that the polarization vector at points $\mathbf{R}_\alpha$ inside the Lorentz sphere is the same at different points $\mathbf{R}_\alpha$, i.e. $\mathbf{P}_\alpha \approx \mathbf{P}$. The structure factor (9) takes into account only one part of the dipole field inside the Lorentz sphere, proportional to $1/R_\alpha$. Other parts of the dipole field are proportional to $1/R_\alpha{}^3$ and $1/R_\alpha{}^2$

vanish for different types of discrete distribution of nanoparticles.

In the electrodynamics of dielectrics, it is generally accepted that the field of discretely distributed dipoles of atoms (molecules) in the vicinity of any observation point is equal to zero. However, for discrete-continuous media, the retarded part of the dipole field in the vicinity of observation points is nonzero for any type of symmetry in the arrangement of atoms or molecules [5]. This property of dielectrics corresponds to the near field effect. The structural factor in the considered optical metamaterial with silver nanoparticles is a manifestation of the near field effect, but now silver nanoparticles in the vicinity of observation points are considered instead of atoms (molecules). The calculation of the structure factor is related to the calculation of the lattice sums of an ideal cubic lattice, in which the role of the lattice constant is played by the average distance between the centers of spherical nanoparticles. In this case, the random deviation from the ideal lattice is determined using a random order parameter of unity.

The lattice sum for a cubic lattice has the form [15]:

$$S_0 = \sum_a \frac{\exp\left(i\mathbf{k}\mathbf{R}_a\right)}{R_a} = \frac{4\pi N_0 \lambda^2}{\left(2\pi\right)^2 n_m^{\ 2}}. \tag{10}$$

Let us represent the structural factor (9) taking into account (10) as:

$$\beta = 8\pi s_0, \tag{11}$$

where s_0 is a dimensionless random parameter that takes into account the deviation of the discrete distribution of nanoparticles from the cubic one in a composite with a uniform distribution of nanoparticles with concentration N_0. At a 3% weight content of silver in the polymer and nanoparticle radius α = 2.5 nm, the average distance between the centers of nanoparticles is 28 nm, which makes it possible to ignore the interaction between nanoparticles.

From equation (8), we obtain the following formula for the complex refractive index of a metamaterial with inclusions:

$$\frac{\left(n+i\kappa\right)^2}{n_m^{\ 2}} = \frac{1+\dfrac{8\pi}{3}\dfrac{\alpha_{eff}}{1-\beta\alpha_{eff}}}{1-\dfrac{4\pi}{3}\dfrac{\alpha_{eff}}{1-\beta\alpha_{eff}}}. \tag{12}$$

In a continuous medium when β = 0 and $N_0\alpha_p >> N_m\alpha_m$ formula (12) coincides with the Garnett formula [3]. It will be shown below that at $\beta\alpha_{eff} \approx 1$ it is possible to achieve zero and close to zero values of the refractive index.

4. NUMERICAL EXPERIMENT

For a polymer matrix made of poly(methyl methacrylate) with a refractive index of 1.49, the presence of a low concentration of inclusions $N_0\alpha_p$ makes it close in value to $N_m\alpha_m$. Thus, in the numerical example considered above, at a 3% weight content of silver in the composite $N_0 = 0.455\cdot10^{17}$ cm^{-3}, α = 2.5 nm, the negative part of the permittivity of silver nanoparticles is less than the positive part of the permittivity of the polymer matrix. When the refractive and absorption indices of the composite vanish exactly the numerator in formula (12) vanishes, and the denominator is nonzero. As a result, we get two equations:

$$\begin{aligned} &1+\mathrm{Re}\left(\alpha_{eff}\right)\left(\frac{8\pi}{3}-\beta\right)=0, \\ &\left(-\frac{8\pi}{3}+\beta\right)\mathrm{Im}\left(\alpha_{eff}\right)=0. \end{aligned} \tag{13}$$

Let us estimate the values of the structural factor β for which n = k = 0. Taking into account relation (7) the second equation (13) is fulfilled with high accuracy, and from the first equation we obtain the following relation for the parameter s_0:

$$s_0 = \frac{1}{8\pi}\left(\frac{1}{\mathrm{Re}\left(\alpha_{eff}\right)}+\frac{8\pi}{3}\right). \tag{14}$$

This means that when such a value s_0 is reached from the range of acceptable values

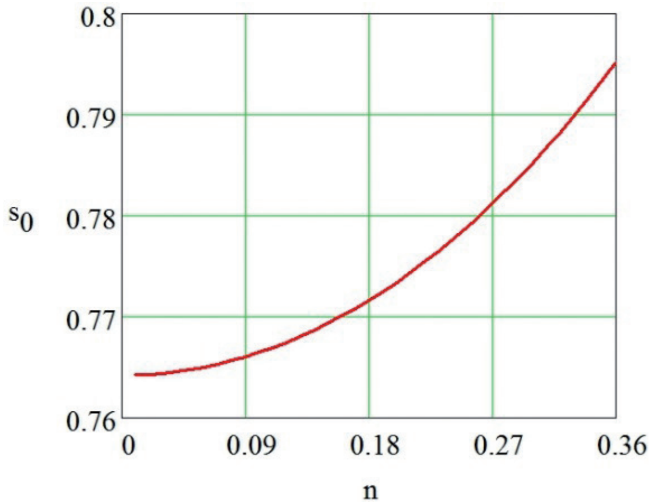


Fig. 1. *Correspondence between the structure factor and the refractive index of a metamaterial Ag@PMMA.*

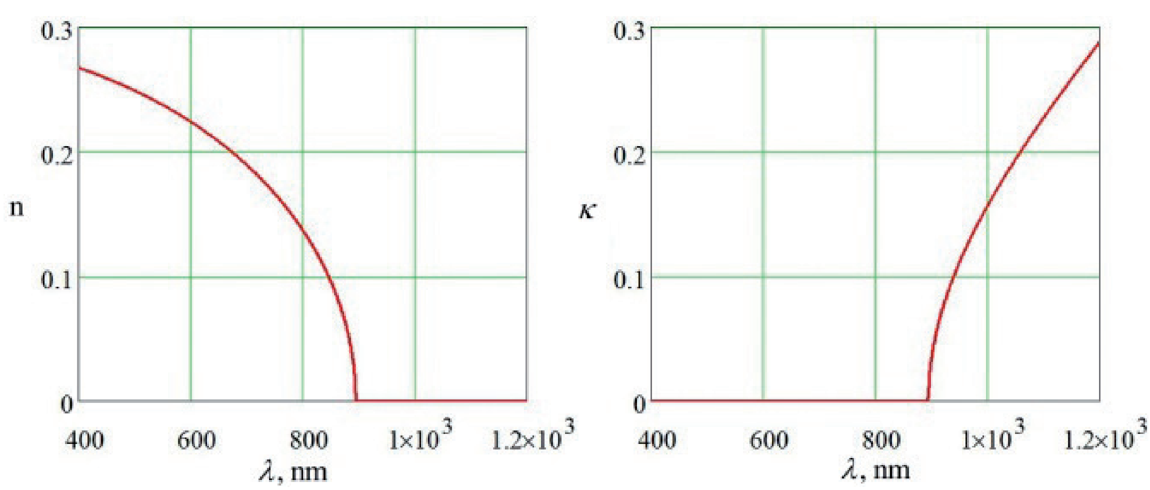
the refractive index of the composite vanishes. For other values s_0, values of n and k can be achieved close to zero, while $n >> k$. Below, we will present the results of numerical simulation of the possible values n and k the composite for random values of s_0.

On **Fig. 1** shows the correspondence between the possible values of the refractive index of the composite from the interval [0, Δn_2] with the possible values of the random parameter s_0. The value $\Delta n_2 = 0.36$ is determined from the location of the interference minima in the reflection and transmission spectra of a layer with a thickness of $d_2 = 3.5$ μm [7].

On **Fig. 2** presents the results of numerical simulation of the refractive and absorption indices of the composite at various values of the structure factor and wavelength. As can be seen from Fig. 2(*a-c*) at corresponding values in the infrared wavelength region the absorption index of the composite reaches large values, that is, in this wavelength region the composite has strong absorption. In this case the refractive index of the composite in this wavelength region is equal to zero. On Fig. 2(*d,e*) shows that in a wide wavelength range from 400 to 1200 nm the absorption coefficient vanishes. In this case, the refractive index of the composite with silver nanoparticles varies in the range from 0.46 to 0.12 depending on the value of the structure factor.

On **Fig.** 3 shows the experimental values of the refractive index n and the optical reflection coefficient R at a wavelength of 628 nm for coatings made of Ag@PMMA metamaterial of various thicknesses from 5 μm to 30 μm on a glass plate. It can be seen that the measured values of the refractive index are in good agreement with the calculated ones.

Taking into account the experimental data obtained from [7] and presented in this paper in Fig. 3 it can be concluded that in the synthesized composite with a 3 wt.% and thickness from 3 μm to 30 μm, the values of the parameter s_0 lie in the range from 0.79 to 0.81.



a

Fig. 2*a*

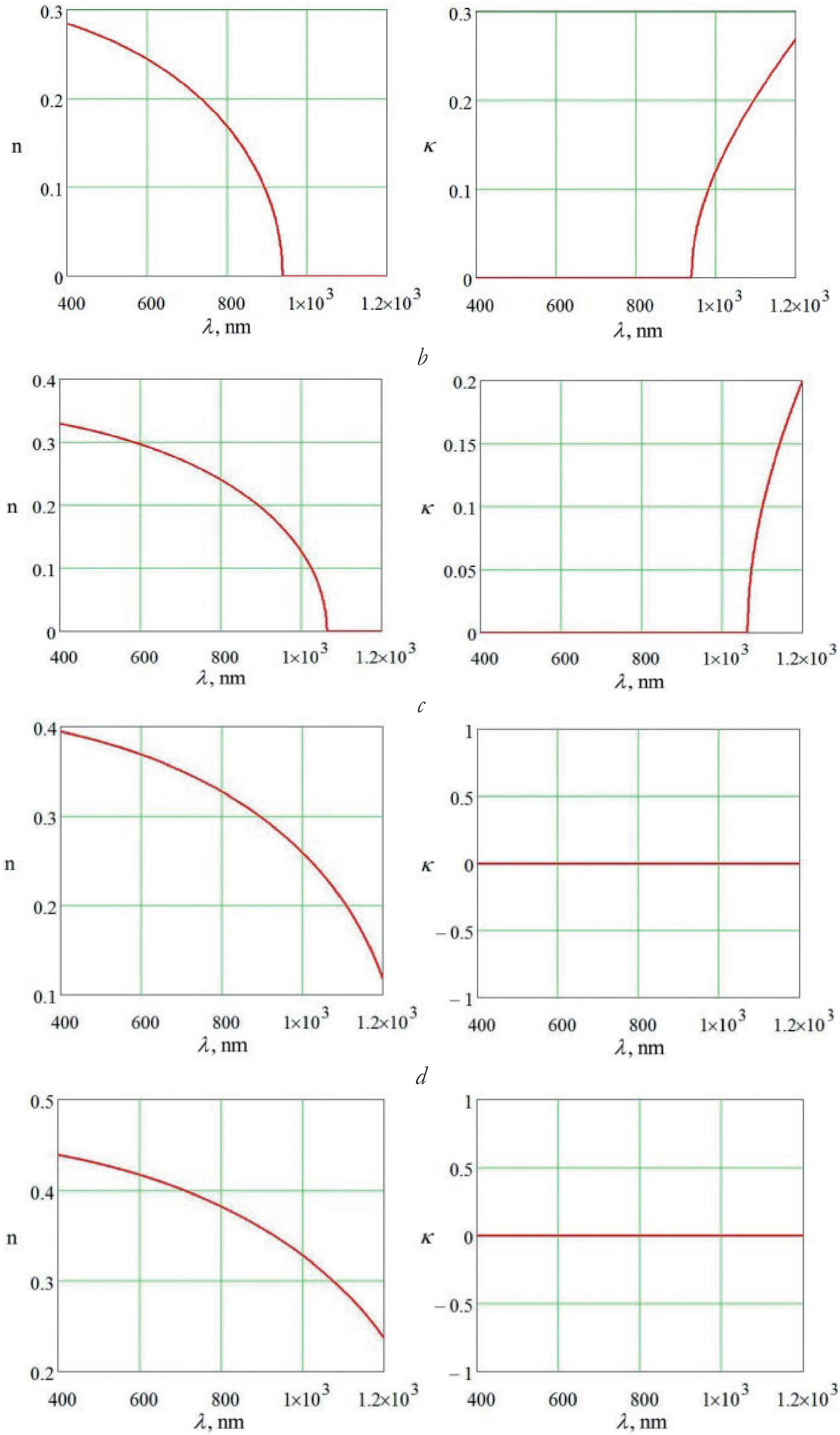


Fig. 2. Va*lues n and k depending on the structure factor and wavelength. The radius of silver nanoparticles is a = 2.5 nm, the mass content of silver in the polymer is 3 wt. %, refractive index of PMMA is* $n_m = 1.49$*;*
a)$s_0 = 0.764$, *b)*$s_0 = 0.766$, *c)*$s_0 = 0.773$, *d)*$s_0 = 0.785$, *e)*$s_0 = 0.795$.

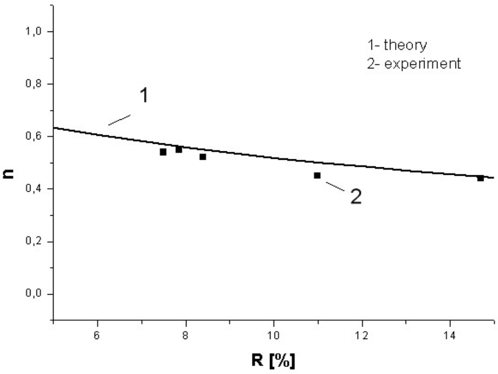


Fig. 3. *Experimental values of the refractive index n and the optical reflectance R at a wavelength of 628 nm of the Ag@PMMA metamaterial 30 μm thick on a glass plate.*

5. CONCLUSION

It is shown that a low weight content of metal inclusions in a composite metamaterial can greatly change the optical properties of the dielectric matrix. The transition to the concept of a discrete-continuous medium made it possible to obtain a formula for the complex refractive index which only in a particular case coincides with the Garnett formula. A model of a discrete-continuous medium is proposed in which the retarded part of the dipole field in the vicinity of observation points is nonzero for any type of symmetry in the arrangement of silver nanoparticles in a dielectric matrix, which is a manifestation of the near-field effect. The calculation of the structure factor is associated with the calculation of the lattice sums of an ideal cubic lattice in which the role of the lattice constant is played by the average distance between the centers of spherical nanoparticles. In this case, the random deviation from the ideal lattice is determined using a random parameter order of unity. It is shown that when the product of the structural factor and the effective polarizability of a metamaterial are equal to unity, it is possible to achieve zero and close to zero values of the refractive index of such a material. Based on experimental data with Ag@PMMA metamaterial coatings of various thicknesses from 5 μm to 30 μm on a glass plate, the measurement results were compared with calculated data, which showed good agreement between experiment and theory.

REFERENCES

1. Gadomsky ON, Ushakov NM. Nanokompozitsionnoye prosvetlyayushcheye pokrytiye v vide tolstoy plenki i sposob yego polucheniya [Nanocomposite antireflection coating in the form of a thick film and method for its production]. *Patent of the Russian Federation No. 2456710* dated 07/20/2012 (in Russ.).
2. Katnov VE, Gadomsky ON, Stepin SN, Katnova RR. Sposob polucheniya prosvetlyayushchego pokrytiya [Method for obtaining an antireflection coating]. *Patent of the Russian Federation No. 2554608* dated 06/27/2015 (in Russ.)
3. Vinogradov AP, Dorofeenko AV, Zouhdi S. On the problem of the effective parameters of metamaterials. *Phys. Usp.*, 2008, 51:485-492; DOI: 10.1070/PU2008v051n05ABEH006533.
4. Moiseev SG. Optical properties of a Maxwell–Garnett composite medium with nonspherical silver inclusions. *Russian Physics Journal*, 2009, 52(11):1121-1127.
5. Gadomskii ON. Two electron problem and the nonlocal equations of electrodynamics. *Phys. Usp.,* 2000, 43:1071-1102; DOI: 10.1070/PU2000v043n11ABEH000795.
6. Gadomsky ON, Kadochkin AS. Mikroskopicheskaya teoriya kvazikristallicheskogo perekhodnogo sloya na poverkhnosti zhidkikh dielektrikov pri bryusterovskom otrazhenii sveta i effekt blizhnego polya [Microscopic theory of quasi-crystalline transition layer on the surface of liquid dielectrics during Brewster reflection of light and the near field effect]. *Optika i Spektroskopiya*, 2003, 94(3):504-512 (in Russ.).

7. Gadomsky ON, Stepin SN, Katnov VE. Nanostrukturnyye kompozitnyye sloi s kvazinulevym pokazatelem prelomleniya [Nanostructured composite layers with a quasi-zero refractive index]. *Zhurnal Prikladnoy Spektroskopii*, 2013, 80(5):738-742 (in Russ.).
8. Gadomsky ON, Stepin SN, Ushakov NM. Enhancement and fokusing of light in nanostructured quasi-zero-refractive index films. *Optics communications*, 2014, 330:99-105.
9. Gadomsky ON, Gadomskaya IV. Nezerkal'noye otrazheniye sveta na neodnorodnoy granitse razdela dvukh sred i v nanostrukturnom sloye s blizkim k nulyu pokazatelem prelomleniya [Non-specular reflection of light at an inhomogeneous interface between two media and in a nanostructured layer with a refractive index close to zero]. *ZhETF*, 2015, 147(2):195-211 (in Russ.)
10. Gadomsky ON, Ushakov NM, Shchukarev IA. Narusheniye printsipa obratimosti svetovykh potokov v opticheskoy srede so sluchaynym blizkim k nulyu pokazatelem prelomleniya [Violation of the principle of reversibility of light fluxes in an optical medium with a random refractive index close to zero]. *ZhETF*, 2017, 125:564-571 (in Russ.)
11. Gadomsky ON, Ushakov NM, Gadomskaya IV. Photon localization in optical metamaterials with a random close to zero refractive index. *RENSIT: Radioelectronics. Nanosystems. Information technologies,* 2019, 11(2):159-170. DOI: 10.17725/rensit.2019.11.177.
12. Gadomsky ON, Shchukarev IA. Non-Fresnel reflection and refraction of light in quasi-zero-refractive index composite film. *Optics communications*, 2015, 348:38-42.
13. Born M, Wolf E. *Principles of Optics*. Oxford ·London Edinburg New York Paris ·Frankfurt, Pergamon Press, 1964.
14. Jonson PB, Christy RW. Optical Constants of the Noble Metals. *Phys.Rev.*, 1972, B6: 4370-4392.
15. Ziman JM. *Principles of the theory of solids*. Cambridge, Univ. Press, 1972.