Linear and nonlinear solid-state optics

Optical properties of nanocomposite materials based on plasmon nanoparticles

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Abstract. In this work, optical properties of nanocomposite materials based on plasmon metallic spherical nanoparticles have been studied. The authors have compared four different effective theories that take into account the size dispersion, interaction between nanoparticles and extrinsic size effect for calculation of the effective refractive index of Au, Ag and Cu nanoparticles in polymer. It has been demonstrated that size distribution induces an inhomogeneous broadening and change in the amplitude of plasmon band. The lowest shift of resonance characteristics has been observed for copper based nanocomposite for all the effective theories. It has been shown that the same nanocomposite material but with other parameters (size and concentration of inclusions) can be described by the different effective theories.

Keywords: nanocomposite, effective refractive index, plasmon nanoparticles.

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1. Introduction

Modern trends in the development of materials and technologies demonstrate the actuality of creating objects which dimensions are commensurate with the electron free path. The study and development of nanostructures not only satisfy the need for creation of materials with unique linear and nonlinear optical properties, but also help to find the answer how the properties of a substance change in the transition from individual atoms and molecules to organized nanostructures, and then to the solid state [1]. Nanocomposite materials based on plasmon metallic nanoparticles acquire new properties due to the growing role of surface atoms and interactions, quantum-dimensional effects as well as the predominance of wave properties over the corpuscular ones, with the decrease in sizes of nanoparticles and their structural parameters to the nanoscale [2]. The interest of physicists, chemists, and materials scientists in nanoscale materials is associated with formulation of fundamentally new scientific problems [3] and with the prospects to find new physical phenomena and develop novae quantum devices and systems with wide functional properties for opto- and nanoelectronics, measuring technology, information technologies of new generation, and communication [4, 5].

Nanocomposite materials can be characterized by an effective refractive index, if the inclusions are smaller or comparable with the wavelength. The amount of theories that allow us to determine the effective refractive index is sufficiently high [6-9]. Each of them has its advantages and disadvantages, and in various cases application of the only theory does not provide good correlation with experimental data.

Thus, in this work, four different approximations were applied to calculate the effective refractive index of a nanocomposite material based on plasmon nanoparticles in order to consider their unique characteristics and possibilities for practical application.

2. Theoretical background

Propagation of electromagnetic waves in nonhomogeneous composite material is often considered in terms of effective dielectric permittivity. The most known approximations for the effective dielectric permittivity are the Maxwell–Garnett and Mie theories. Simple spherical nanoparticle of the homogeneous isotropic material dispersed in the homogeneous isotropic, endless medium, and irradiated by plane waves propagating in a certain direction is considered by the Mie theory based on solving the Maxwell equations. According to the Mie theory, the scattering and extension are determined by the relations [6]:

$$Q_S = \frac{2}{\chi^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2+|b_n|^2\right), \quad (1)$$

$$Q_E = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2n+1) \mathrm{Re}(a_n + b_n). \quad (2)$$

It should be noted that $Q_S = Q_E$, if the particle does not absorb the incident radiation. The absorption efficiency coefficient Q_A is defined as $Q_A = Q_E - Q_S$, if the particle absorbs the incident radiation. The Mie coefficients a_n and b_n are expressed in terms of Riccati–Bessel functions as follows:

$$a_n = \frac{\psi_n(x)[\psi'_n(y)/\psi_n(y)] - m\psi'_n(x)}{\xi_n(x)[\xi'_n(y)/\psi_n(y)] - m\xi'_n(x)}, \quad (3)$$

$$b_n = \frac{\psi_n(x)[\psi'_n(y)/\psi_n(y)] - \psi'_n(x)}{\xi_n(x)[\xi'_n(y)/\psi_n(y)] - \xi'_n(x)}. \quad (4)$$

The Maxwell–Garnett (MG) effective medium theory [10] is available tool to obtain good approximation for the dielectric properties dependence on the filling factor. The effective permittivity of the composite material that includes two media with the dielectric constants ε_i and ε_m and the filling factor of inclusions f can be written as follows:

$$\varepsilon_{eff} = \varepsilon_m \frac{\varepsilon_i(1+2f) + 2\varepsilon_m(1-f)}{\varepsilon_i(1-f) + \varepsilon_m(2+f)}. \quad (5)$$

Thus, the surface plasmon resonance condition can be written as follows:

$$\varepsilon_i(1-f) + \varepsilon_m(2+f) = 0. \quad (6)$$

Taking into acount the size effect, the effective permittivity in accord to extended Maxwell–Garnett (EMG) theory [7] is expressed as follows:

$$\varepsilon_{eff} = \varepsilon_m \frac{\varepsilon_i(1+2f) + 2\varepsilon_m(1-f) + (\varepsilon_m - \varepsilon_i)(1-f)\Delta}{\varepsilon_i(1-f) + \varepsilon_m(2+f) + (\varepsilon_m - \varepsilon_i)(1-f)\Delta}, \quad (7)$$

where $\Delta = x^2 + (2/3)ix^3$, $x = \sqrt{\varepsilon_m}\,2\pi R/\lambda$. The composite consisting of randomly dispersed inclusions in the dielectric matrix is considered by this theory.

In the work [11], it was proposed that the Maxwell–Garnett size-dependent theory can be obtained using the electric dipole polarization from the Mie theory as follows:

$$\alpha_{\mathrm{MGM}} = \frac{3i\lambda^3}{16\pi^3 \varepsilon_m^{3/2}} a_1, \quad (8)$$

where a_1 is the first electric coefficient by Mie obtained from:

$$\alpha_1 = \frac{\left[\begin{array}{l}\sqrt{\varepsilon_i}\,\psi_1\left(2\pi R\sqrt{\varepsilon_i}/\lambda\right)\psi'_1\left(2\pi R\sqrt{\varepsilon_m}/\lambda\right) - \\ -\sqrt{\varepsilon_m}\,\psi_1\left(2\pi R\sqrt{\varepsilon_m}/\lambda\right)\psi'_1\left(2\pi R\sqrt{\varepsilon_i}/\lambda\right)\end{array}\right]}{\left[\begin{array}{l}\sqrt{\varepsilon_i}\,\psi_1\left(2\pi R\sqrt{\varepsilon_i}/\lambda\right)\psi'_1\left(2\pi R\sqrt{\varepsilon_m}/\lambda\right) - \\ -\sqrt{\varepsilon_m}\,\psi_1\left(2\pi R\sqrt{\varepsilon_m}/\lambda\right)\psi'_1\left(2\pi R\sqrt{\varepsilon_i}/\lambda\right)\end{array}\right]}, \quad (9)$$

where ψ_1 and ξ_1 are the first order Riccati–Bessel functions.

The effective dielectric permittivity ε_{eff} of the composite material is related with the polarizability α of the inclusions accordingly to the Maxwell–Garnett–Mie (MGM) theory [12] as follows:

$$\frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + 2\varepsilon_m} = \frac{f}{R^3} \alpha_{\mathrm{MGM}}. \quad (10)$$

Each particle in the actual composite materials exhibits its own polarization. Therefore, the equations (7) and (10) should be reviewed taking into account the average polarization of the nanoparticles. As a result, the modified Maxwell–Garnett–Mie (MGMM) theory [13] can be written as follows:

$$\frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + 2\varepsilon_m} = \frac{3i\lambda^3}{16\pi^3 \varepsilon_m^{3/2}} \frac{f}{R^3} \int_{R_{\min}}^{R_{\max}} P(R)\alpha_1 dR, \quad (11)$$

where $P(R)$ is the distribution of nanoparticles' sizes, $R_{\min}$ and $R_{\max}$ are the lower and upper limits of this size distribution.

3. Results and discussions

In order to compare different effective theories, the polymer with a refractive index of 1.516 was selected as a matrix of nanocomposite. Polymer matrices found wide use in different optical applications [14, 15]. Spherical nanoparticles of noble metals such as gold and silver as well as copper were used as inclusions. The refractive indices of metallic nanoparticles can be expressed as follows [16]:

$$\varepsilon_{NP}(\lambda, R) = \varepsilon_{bulk}(\lambda) - i\eta \frac{\omega_p \lambda^3}{(2\pi c)^3} \frac{V_F}{R}, \quad (12)$$

where ω_p is the plasma frequency, V_F – Fermi velocity of the conduction electrons, c – speed of light, and the factor η changes from 0.6 to 1. These parametrs for gold were taken from [17], for silver – from [18] and for copper – from [19]; $\varepsilon_{bulk}(\lambda)$ was calculated using the analytical expressions presented in the work [20].

Simulations of the optical response of nanocomposites based on Au, Ag and Cu spherical nanoparticles were performed using the Maxwell–Garnett, extended Maxwell–Garnett, Maxwell–Garnett–Mie and modified Maxwell–Garnett–Mie. The radius of nanoparticles was 10 nm and the filling factor was 1%. The modeling was performed using the modified Maxwell–Garnett–Mie approach for a lognormal size distribution with σ = 1.4 that corresponds to the typical distributions often observed in TEM histograms. The obtained results have been adduced in Fig. 1 for gold-based nanocomposites. The curves calculated using the Maxwell–Garnett–Mie and modified Maxwell–Garnett–Mie approaches show the peak position of plasmon resonance close to 495 nm. The curves calculated using the Maxwell–Garnett and extended Maxwell–Garnett approaches show the peak positions of plasmon resonance near 538 and 534 nm, respectively. Moreover, the spectra of real and imaginary parts of the effective refractive index calculated using the Maxwell–Garnett and extended Maxwell–Garnett methods show higher amplitudes of values (see Fig. 1). The similar situation is observed in the spectra of absorption coefficient, since the curve of imaginary parts of the effective refractive index corresponds to absorption spectra. It must be noted that the half-width of this spectrum is practically the

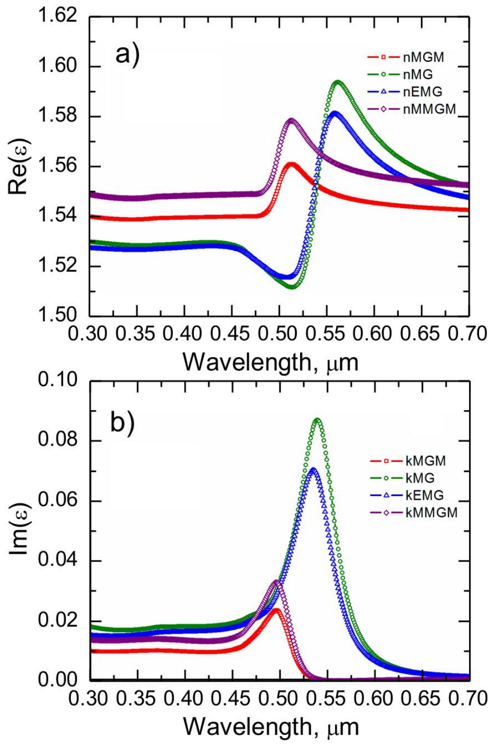

Fig. 1. Spectral dependences of real (a) and imaginary parts (b) of the refractive index of gold-based nanocomposite: squares stand for MGM, circles – MG, triangulars – EMG, rhombi – MGMM.

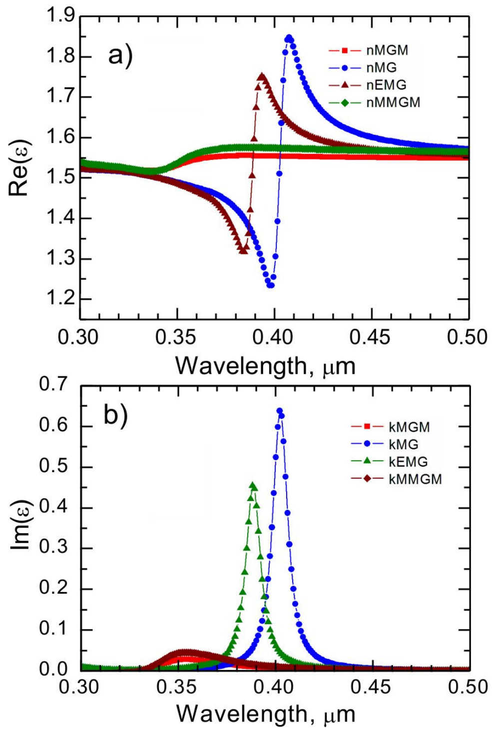

Fig. 2. Spectral dependences of real (a) and imaginary parts (b) of the refractive index of silver-based nanocomposite: red squares stand for MGM, blue circles – MG, green triangulars – EMG, olive rhombi – MGMM.

same for all the considered theories. In addion, the size of nanoinclusions influences on the inhomogeneous broadening and change of the amplitude of the surface plasmon resonance band.

The spectra of real and imaginary parts of the effective refractive index for silver-based nanocomposites are presented in Fig 2. The curves calculated using the Maxwell–Garnett–Mie approach and the modified Maxwell–Garnett–Mie one show the peak position of plasmon resonance close to 353 nm. The curves calculated using the Maxwell–Garnett and extended Maxwell–Garnett methods demonstrate the peak position of plasmon resonance near 402 and 393 nm, respectively. The increment of refractive index amplitudes, when using the Maxwell–Garnett–Mie and modified Maxwell–Garnett–Mie models is much more important for gold-based composites as compared to silver-based composites. Since, the curves calculated using these models are very similar to each other for silver-based nanocomposites. At the same time, the spectra calculated using the Maxwell–Garnett and extended Maxwell–Garnett theories are similar for gold- and silver-based nanocomposites. The difference between refractive indeces calculated with Maxwell–Garnett and Maxwell–Garnett–Mie theories is much clearer pronounced for silver nanoparticles. It is caused by the dynamic depolarization effects, which are hardly visible in gold due to the presence of interband transitions close to the plasmon energy [6].

The surface absorption of Cu nanoparticles is about 560 nm, but in the composite material, due to the influence of matrix, the absorption peak is shifted. In the case of copper nanocomposites based on polymer, the shift of spectra inherent to real and imaginary parts of the effective refractive index calculated with the Maxwell–Garnett–Mie and modified Maxwell–Garnett–Mie theories to the infrared spectrum is not as significant as for gold and silver (see Fig. 3). The same situation is observed in the absorption coefficient spectrum. The difference in the amplitude is the same. Nanocomposites based on copper demonstrate lower absorption as compared to the case of gold or silver.

In order to test in practice how the effective refractive index theory presented above operates, a comparative analysis of experimental curves with the theoretically calculated ones has been carried out. The description of composite based on silver, when using the effective theory, has already been repeatedly presented by the authors in a number of papers [21-23], so here we will consider composite materials based on gold and copper.

The experimentally observed absorbance spectrum of the gold–poly(methyl methacrylate) nanocomposites [24] was compared with the simulated spectra (see Fig. 4). The band position of the simulated spectra about 540 nm shows an excellent agreement with the observed using the effective Maxwell–Garnett approach. The maximum absorbance spectrum calculated with the Maxwell–Garnett–Mie and extended Maxwell–Garnett theories is shifted to the short-wave region.

A completely different situation is observed for the copper nanocomposite. Comparison of theoretical results with the experimental data presented in [25] for the Cu-SiO_2 composite is adduced in Fig. 5. The band position of the measured absorbance spectrum is about 540 nm. As can be seen from Fig. 5, the absorption peak near 540 nm was obtained using the effective Maxwell–

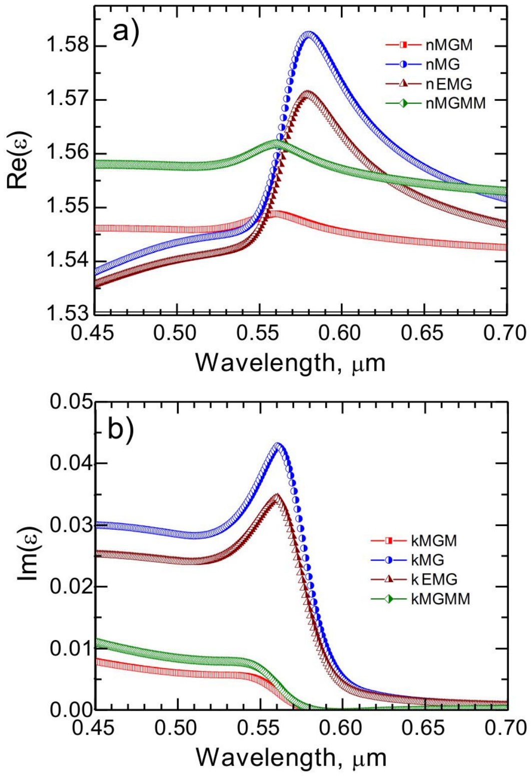

Fig. 3. Spectral dependences of real (a) and imaginary parts (b) of the refractive index of copper based nanocomposite: red squares stand for MGM, blue circles – MG, green triangulars – EMG, olive rhombi – MGMM.

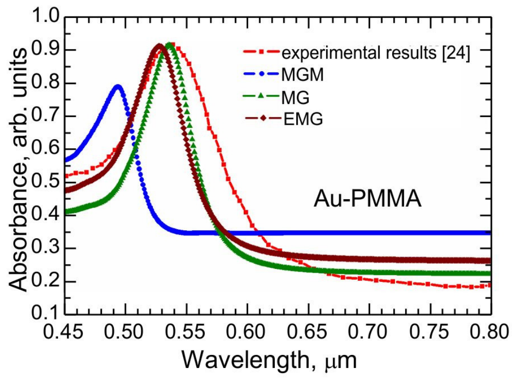

Fig. 4. Comparison of simulated results with the experimental data presented in [24] for the Au-PMMA composite.

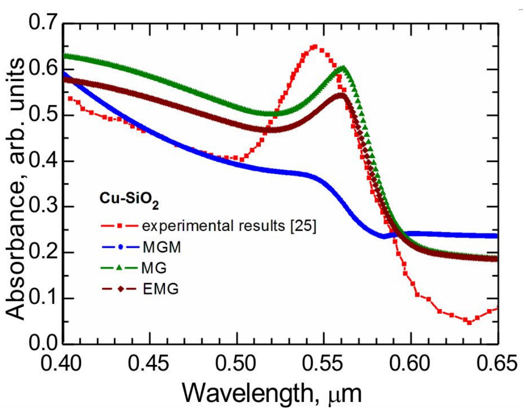

Fig. 5. Comparison of simulated results with the experimental data presented in [25] for the Cu-SiO_2 composite.

Garnet–Mie theory. However, the maximum of absorption simulated using this theory is low.

The theories of Maxwell–Garnet and extended Maxwell–Garnet approaches provide the absorption peak close to 580 nm. It should be noted that in the work [26], Cu-SiO_2 was also investigated, where the absorption peak is at the wavelength of 580 nm. These results confirm once again that the same nanocomposite material, but with other parameters (size and concentration of inclusions) can be described by different theories.

4. Conclusions

The complex refractive index and absorption coefficients of gold, silver and copper nanoparticles dispersed inside polymer matrix have been studied for the cases of different effective theories. The size was found to induce the inhomogeneous broadening and change in the amplitude of the surface plasmon resonance band. It has been demotstrated using the effective theories that include the size effect. The large divergence of the spectral curves modeled by the presented effective theories is observed for silver nanocomposites. The smallest shift of resonance characteristics has been observed for copper-based nanocomposite for all the considered effective theories. It should be noted that nanocomposites with the absorption peak lying in the shorter wavelength region are best described by these theories that take into account Mie scattering coefficients. Thus, if the size of inclusions and interaction between them are taken into account, then the absorption peak in these nanocomposites will be shifted to the region of shorter wavelengths.

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References

1. Maier S.A., Atwater H.A. Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. *J. Appl. Phys.* 2005. **98**, No 1. P. 10.
2. Prasad P.N. *Nanophotonics*. John Wiley & Sons, Inc.: Hoboken NJ., 2004.
3. Su C. Environmental implications and applications of engineered nanoscale magnetite and its hybrid nanocomposites: A review of recent literature. *Journal of hazardous materials*. 2017. **322**. P. 48–84.
4. Huang X., Jiang P. Core–shell structured high polymer nanocomposites for energy storage and dielectric applications. *Adv. Mater.* 2015. **27**, No. 3. P. 546–554.
5. García M.A. Surface plasmons in metallic nanoparticles: Fundamentals and applications. *J. Phys. D: Appl. Phys.* 2011. **44**, No. 28. P. 283001.
6. Bohren C.F., Huffman D.R. *Absorption and Scattering of Light by Small Particles*. John Wiley & Sons, 2008.

7. Ruppin R. Evaluation of extended Maxwell–Garnett theories. *Opt. Commun.* 2000. **182**, No 4. P. 273–279.
8. Jylhä L., Sihvola A. Equation for the effective permittivity of particle-filled composites for material design applications. *J. Phys. D: Appl. Phys.* 2007. **40**, No. 16. P. 4966.
9. Mallet P., Guérin C.A., Sentenac A. Maxwell–Garnett mixing rule in the presence of multiple scattering: Derivation and accuracy. *Phys. Rev. B*. 2005. **72**, No. 1. P. 014205.
10. Levy O., Stroud D. Maxwell–Garnett theory for mixtures of anisotropic inclusions: Application to conducting polymers. *Phys. Rev. B*. 1997. **56**, No. 13. P. 8035.
11. Doyle W.T. Optical properties of a suspension of metal spheres. *Phys. Rev. B*. 1989. **39**, No. 14. P. 9852.
12. Myroshnychenko V., Rodríguez-Fernández J., Pastoriza-Santos I., Funston A.M., Novo C., Mulvaney P., de Abajo F.J.G. Modelling the optical response of gold nanoparticles. *Chem. Soc. Rev.* 2008. **37**, No. 9. P. 1792–1805.
13. Battie Y., Resano-Garcia A., Chaoui N., Zhang Y., En Naciri A. Extended Maxwell–Garnett–Mie formulation applied to size dispersion of metallic nanoparticles embedded in host liquid matrix. *J. Chem. Phys.* 2014. **140**, No 4. P. 044705–044705.
14. Bockstaller M.R., Thomas E.L. Optical properties of polymer-based photonic nanocomposite materials. *J. Phys. Chem. B*. 2003. **107**, No 37. P. 10017–10024.
15. Faupel F., Zaporojtchenko V., Strunskus T., Elbahri M. Metal-polymer nanocomposites for functional applications. *Adv. Eng. Mater.* 2010. **12**, No 12. P. 1177–1190.
16. Yaremchuk I., Tamulevičienė A., Tamulevičius T., Šlapikas K., Balevičius Z., Tamulevičius S. Modeling of the plasmonic properties of DLC-Ag nanocomposite films. *phys. status solidi* (*a*). 2014. **211**, No 2. P. 329–335.
17. Johnson P.B., Christy R.W. Optical constants of the noble metals. *Phys. Rev. B*. 1972. **6**, No 12. P. 4370.
18. Palik E.D. Silver (Ag), in: *Handbook of Optical Constants of Solids*, 1997. P. 429–443.
19. West P.R., Ishii S., Naik G.V., Emani N.K., Shalaev V.M., Boltasseva A. Searching for better plasmonic materials. *Laser & Photonics Rev.* 2010. **4**, No 6. P. 795–808.
20. Fitio V., Vernygor O., Yaremchuk I., Bobitski Y. Analytical Approximations of the Noble Metals Dielectric Permittivity. *TCSET-2018*.
21. Yaremchuk I., Fitio V., Bobitski Y. Shape effect of silver nanoparticles on plasmon properties of DLC:Ag nanocomposites. *TCSET-2016*. P. 392–394 (2016).
22. Meškinis Š., Yaremchuk I., Grigaliūnas V., Vasiliauskas A., Čiegis A. Plasmonic properties of nanostructured diamond like carbon/silver nanocomposite films with nanohole arrays. *Mater. Sci.* 2016. **22**, No 4. P. 467–471.
23. Yaremchuk I., Meškinis Š., Fitio V., Bobitski Y., Šlapikas K., Čiegis A., Tamulevičius S. Spectroellipsometric characterization and modeling of plasmonic diamond-like carbon nanocomposite films with embedded Ag nanoparticles. *Nanoscale Res. Lett.* 2015. **10**, No 1. P. 157.
24. Alsawafta M., Badilescu S., Paneri A., Truong V.V., Packirisamy M. Gold-poly(methyl methacrylate) nanocomposite films for plasmonic biosensing applications. *Polymers*. 2011. **3**, No 4. 1833–1848.
25. Yeshchenko O.A., Dmitruk I. M., Alexeenko A.A., Dmytruk A.M. Size-dependent melting of spherical copper nanoparticles embedded in a silica matrix. *Phys. Rev. B*. 2007. **75**, No 8. P. 085434.
26. Zhang C., Zhang S., Yu L., Zhang Z., Wu Z., Zhang P. Preparation and tribological properties of water-soluble copper/silica nanocomposite as a water-based lubricant additive. *Appl. Surf. Sci.* 2012. **259**. P. 824–830.

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