

Temperature dependence of the surface plasmon resonance in silver nanoparticles

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The temperature dependences of energy and width of the surface plasmon resonance were studied for silver nanoparticles with sizes 24 nm and 60 nm in silica host matrix in the temperature range of 17–700°C. The temperature increase leads to red shift and broadening of the surface plasmon resonance in Ag nanoparticles. The obtained temperature dependences were analyzed within the framework of theoretical model considering the thermal expansion of a nanoparticle, the electron-phonon scattering in the nanoparticle and the temperature dependence of dielectric permittivity of the host matrix. The thermal expansion was shown to be the main mechanism responsible for the temperature induced red shift of the surface plasmon resonance in silver nanoparticles. Meanwhile, the increase of electron-phonon scattering rate with increasing temperature was shown to be the dominant mechanism of the surface plasmon resonance broadening in the silver nanoparticles.

Температурные зависимости энергии и полуширины поверхностного плазмонного резонанса в наночастицах серебра размерами 24 нм и 60 нм, инкорпорированных в кварцевую матрицу, исследованы в диапазоне температур 17–700°C. Увеличение температуры приводит к красному сдвигу и уширению поверхностного плазмонного резонанса в наночастицах Ag. Полученные температурные зависимости проанализированы в рамках теоретической модели, в которой учитываются тепловое расширение наночастицы, электрон-фононное рассеяние в наночастице и температурная зависимость диэлектрической проницаемости матрицы. Показано, что тепловое расширение является основным механизмом вызванного увеличением температуры красного сдвига поверхностного плазмонного резонанса в наночастицах серебра. В то же время показано, что увеличение частоты электрон-фононного рассеяния с увеличением температуры является доминирующим механизмом уширения поверхностного плазмонного резонанса в наночастицах серебра.

Температурна залежність поверхневого плазмонного резонансу в наночастичках срібла. *О.А.Єщенко, І.С.Бондарчук, А.А.Алексєєнко, А.В.Котко.*

Температурні залежності енергії та півширини поверхневого плазмонного резонансу в наночастичках срібла розмірами 24 нм і 60 нм, інкорпорованих в кварцеву матрицю, досліджено в діапазоні температур 17–700°C. Збільшення температури призводить до червоного зсуву і розширення поверхневого плазмонного резонансу у наночастичках Ag. Отримані температурні залежності проаналізовано в рамках теоретичної моделі, в якій враховано теплове розширення наночастички, електрон-фононне розсіяння у наночастиці та температурну залежність діелектричної проникності матриці. Показано, що теплове розширення є основним механізмом викликаного збільшенням температури червоного зсуву поверхневого плазмонного резонансу в наночастичках срібла. У той же час показано, що збільшення частоти електрон-фононного розсіяння зі збільшенням температури є домінуючим механізмом розширення поверхневого плазмонного резонансу в наночастичках срібла.

1. Introduction

Noble metal nanoparticles (NPs) exhibit unique optical properties, such as resonant absorption and scattering of light, not found in bulk counterparts [1, 2]. Collective coherent excitations of free electrons in the conduction band, also known as Surface Plasmon Resonance (SPR), are responsible for the strong absorption and scattering of light by the particles [1]. The energy and width of the SPR depend on the size, morphology, spatial orientation and optical constants of the particles and the embedding medium [1, 2]. An influence of the temperature on the SPR in metal NPs is crucial for pure and applied science of the NPs [1, 3]. The temperature dependence of the SPR is important because of the recent applications of noble metal NPs in thermally assisted magnetic recording [4], thermal cancer treatment [5–7] catalysis and nanostructure growth [8], and computer chips [9]. However, the SP temperature dependence was not studied in detail to date because a broad temperature interval requires a usage of materials with high thermal stability. Colloids, thin films, and glasses, which are major media in optical materials with metal NPs, possess not enough thermal stability (~500–600°C at maximum for glasses). The more advanced material which is highly transparent in the optical range is silica, and the facile sol-gel technique allows produce metal NPs of the different chemical nature and size range within the matrix that is stable in air up to 1300°C. In the present work, we use the silica sol-gel glasses admitting the usage of wider temperature interval without the sample destruction. Also, the full reversibility in variation of optical properties occurred for these samples.

The underlying physics of the temperature dependence of optical properties of metal NPs is a precondition for the development of successful and reliable applications and devices. The temperature effects on the SPR absorption band in metal NPs were studied e.g. by Kreibig [1, 10], Doremus [11, 12], and the origin of the temperature effects upon the SPR was analyzed by Mulvaney [13]. Recently, the influence of temperature on SPR in Au-based plasmonic nanostructures was reported for low temperatures in [14] and for high temperatures in [15], where appreciable red shift and broadening of SPR with increasing temperature were observed. The temperature induced broadening of SP extinction band

led to an appreciable decrease of the light extinction at the frequency of SPR and, correspondingly, to an increase of extinction on the wings of SP extinction band. The interplay of temperature effects and material quality in nanoscale plasmonic waveguiding structures is also discussed in [16]. Let us note that most of the effects related to the temperature dependence of the SPR were observed for low temperatures. Therefore, there is a lack of data on influence of temperature on SPR in metal nanostructures for temperatures higher than the room one. Link and El-Sayed studied the temperature dependence of the SPR energy and bandwidth for gold colloidal NPs [17] for temperatures higher than the room one. Gold colloidal NPs within the size range of 9 nm up to 99 nm were studied at elevated temperatures up to 72°C. No significant influence of the temperature on the SPR energy and bandwidth was found that is due to quite narrow temperature range studied. In our recent work [15] we have studied the temperature dependences of SPR in the gold NPs at high temperatures in the silica matrix similar to that of the present work. We observed the noticeable red shift and the broadening of SPR in Au NPs with increasing of temperature that is in full accordance with effects reported for plasmonic Au-nanostructures at low temperatures [14].

In this paper, we present experimental results on the temperature dependence of the SPR energy and width in 24 nm and 60 nm silver NPs embedded in the silica matrix in the wide temperature range of 17–700°C. We have observed that in Ag NPs an increase of the temperature of the sample leads to the red shift and broadening of the SPR that is similar to our results [15] obtained for Au NPs in silica at high temperatures and to results of Bouillard et al. [14] obtained for Au nanostructures at low temperatures. We analyze the observed temperature dependence of SPR within the framework of theoretical model considering such phenomena as thermal volume expansion of the NP, electron-phonon scattering in the NP and temperature dependence of dielectric permittivity of the host matrix. We show that the main cause of the red shift of the SPR with increasing temperature is the thermal volume expansion of the NP, while the electron-phonon scattering in the NP is the dominant mechanism of the SPR broadening.

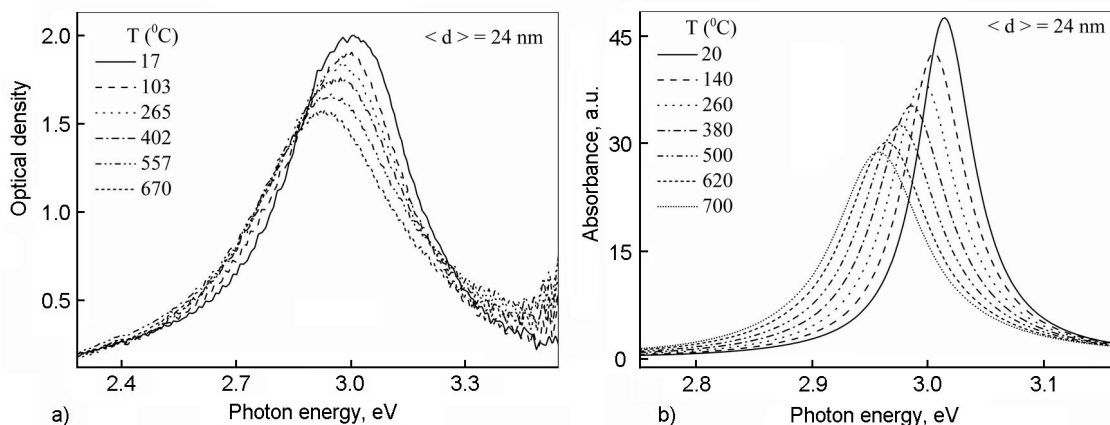


Fig. 1. Measured (a) and calculated (b) evolution of the absorption spectrum of Ag NPs with size of 24 nm in silica with gradual increase of temperature.

2. Synthesis of silver nanoparticles and their characterization

Composite Ag/SiO₂ samples containing silver NPs were produced using the modified sol-gel technique based on hydrolysis of tetraethoxysilane (TEOS) with Ag-doping followed by a chemical transformation of the dopants precursors under annealing in molecular hydrogen. A precursor sol was prepared by mixing of TEOS, water and ethyl alcohol with the acid catalyst HNO₃. Silica powder (named as aerosil A-300) was added to the sol followed by ultrasonication in order to prevent a large volume contraction during drying. The next gelation step resulted in formation of gels from the sols. Porous materials (xerogels) were obtained, after the gels were dried at the room temperature. The porosity of SiO₂ matrices was controlled by annealing the samples in air at 600°C during 1 h. Doping by silver was performed by immersion of xerogels into AgNO₃ alcohol solution during 24 h. We used AgNO₃ solutions with two concentrations (mmol/50 ml): 0.01 and 0.02. Then, the Ag-doped samples were dried in air and annealed in hydrogen with gradual increase of temperature from 20°C to 1200°C. The annealing resulted in the decomposition of AgNO₃ followed by a nucleation and aggregation of Ag clusters resulting in formation of Ag NPs. We fabricated two sets of samples using the two different concentrations of AgNO₃ in the solution mentioned above: H0.01 and H0.02, correspondingly.

The silver NPs formed were characterized with transmission electron microscopy (TEM) to determine their mean size and morphology. TEM characterization was

performed using JEOL JEM-100CX electron microscope operating at 100 kV. TEM indicates that NPs are isolated and have spherical shape. As well, TEM shows a large separation between NPs. Therefore, the electro-dynamical coupling cannot affect their optical spectra, and we use one-particle model for simulations below. TEM gives the mean sizes of Ag NPs in different sets of samples as $\langle d \rangle = 24$ nm with standard deviation $\sigma_d = 6$ nm for H0.01 samples, and $\langle d \rangle = 60$ nm with $\sigma_d = 12$ nm for H0.02 samples. One can see that the increase of the concentration of AgNO₃ in initial xerogel leads to formation of larger silver NPs that is quite expectable.

A tungsten-halogen incandescent lamp was used as a light source at the measurements of absorption spectra. The single grating spectrometer DFS-12 was used for the registration of the spectra. The samples were placed into an open furnace during the spectral measurements. Each spectrum was measured at its own stabilized temperature.

3. Temperature dependence of SPR in Ag nanoparticles: experiment

We measured absorption spectra of silver NPs in silica host matrix. The samples containing Ag NPs with a mean size of 24 nm and 60 nm, respectively, were studied. Absorption spectra were measured in the temperature range of 17–700°C. The aim was to study the effects of temperature influence on the spectral characteristics (energy and bandwidth) of SPR in silver NPs. Evolution of the experimental absorption spectrum of the composite sample containing Ag NPs with a mean size of 24 nm is shown in

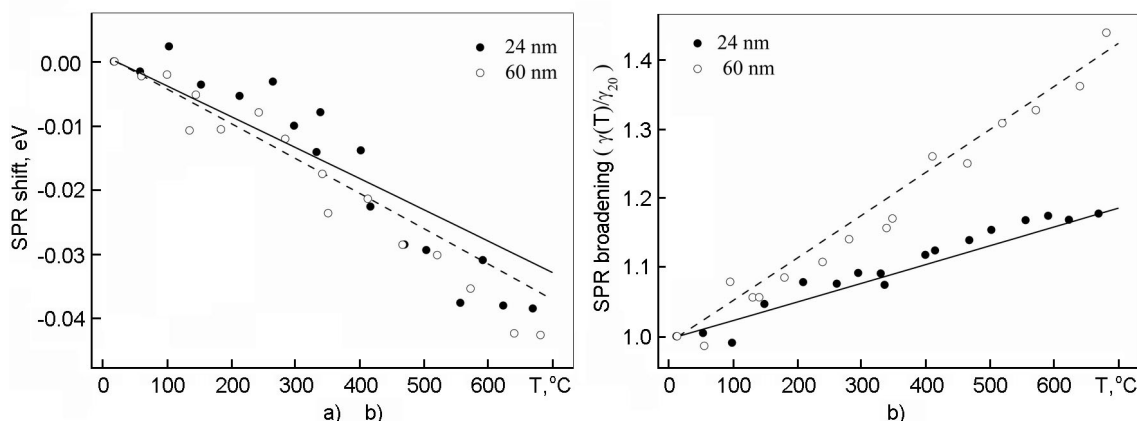


Fig. 2. Dependences of the SPR energy (a) and bandwidth (b) for silver NPs of various sizes in silica. Filled circles and solid line for 24 nm NPs, open circles and dashed line — 60 nm NPs. Points are related to the experiment, lines — to the theory.

Fig. 1a. We determined the energy and width of SPR by fitting of the observed SP absorption band by Lorentzian function. For the samples studied, the SP band is located in the spectral range of 2.93–3.06 eV depending on NP size and temperature. Such spectral position of SP band is typical for silver NPs embedded in silica [1]. The errors of peak fitting were small, specifically the error of determination of the SPR energy was about 0.5–0.8 % and one of determination of the SPR bandwidth was within 5 %. This allowed us to obtain reliable experimental temperature dependences of the SPR energy and bandwidth.

Fig. 2 presents the obtained temperature dependences of the SPR energy and bandwidth for the silver NPs of various sizes. Figs. 1 and 2 show that monotonous increase of the temperature from 17 to 700°C leads to monotonous red shift (shift to lower frequencies) of SPR band and its broadening. One can see that the manifestations of temperature effects on the SPR in silver NPs are quite prominent. It is seen that obtained dependences are not qualitatively different for the silver NPs with different sizes. Note that observed temperature dependences for Ag NPs in silica are quite similar to ones observed for Au NPs in the same host matrix [15], i.e. the red shift and broadening of SPR with increasing temperature.

Let us note that we measured the absorption spectra of Ag/SiO₂ composite samples both at their heating and cooling. We observed the full reversibility of the temperature behaviour of the spectra. This indicates the high thermal stability and high optical

quality of the sol-gel prepared Ag/SiO₂ nanocomposites. It is important for applications of such nanocomposites in the optical devices working at extreme thermal conditions.

4. Temperature dependence of SPR in metal nanoparticles: theory

In this section we give the theoretical analysis of the various mechanisms that can cause the observed temperature effects, namely the red shift and broadening of SPR in silver NPs occurring with the temperature increase. Those effects are: (1) electron-phonon scattering in the NP, (2) thermal expansion of the NP and (3) temperature dependence of the dielectric permittivity of the silica host matrix.

It is well known (see, e.g. [1, 2]) that absorption coefficient of the composite containing the non-interacting spherical metal NPs much smaller than the light wavelength ($d < \lambda$) is

$$\kappa(\omega) = \frac{9f\omega\epsilon_m^{3/2}}{c} \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2}, \quad (1)$$

where ω is a frequency, c is a light velocity, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ is a dielectric permittivity of the NP, f is a filling factor of the composite, ϵ_μ is a dielectric permittivity of the host matrix. It is clear that the temperature dependence of the permittivities of NP and host matrix would affect the energy and width of SPR in the NP and, correspondingly, affect the absorption spectrum

of the composite. The dielectric permittivity of metal can be expressed as

$$\varepsilon(\omega) = \varepsilon_{ib}(\omega) + \varepsilon_D(\omega), \quad (2)$$

where $\varepsilon_{ib}(\omega) = \varepsilon_{ib1}(\omega) + i\varepsilon_{ib2}(\omega)$ is the contribution of interband transitions (bound electrons) in dielectric permittivity of metal, and $\varepsilon_D(\omega)$ is the contribution of free electrons that is given by Drude theory as

$$\varepsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (3)$$

Here

$$\omega_p = \sqrt{\frac{4\pi ne^2}{m^*}} \quad (4)$$

is a bulk plasmon frequency, where n is free electrons concentration, e is an electron charge, m^* is an effective mass of the free electron; γ is the damping constant of plasma oscillations. In approximation of small damping ($\varepsilon_2 < |\varepsilon_1 + 2\varepsilon_m|$), that is quite good for noble metals, the condition of excitation of the SPR in the NPs much smaller than light wavelength is the following [1]

$$\varepsilon_1(\omega) = -2\varepsilon_m. \quad (5)$$

The SPR energy is then obtained by substituting the dielectric permittivity for metal NP from Eqs. (2) and (3) into Eq. (5):

$$\omega_{sp} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m + \varepsilon_{ib1}} - \gamma^2}, \quad (6)$$

where ε_{ib1} is a real part of the contribution of interband transitions to permittivity of NP. The plasmon damping constant can be expressed [1, 2] as

$$\gamma = \gamma_\infty + A \frac{v_F}{R}, \quad (7)$$

where R is a radius of the NP, γ_∞ is the size-independent damping constant caused by scattering of free electrons on electrons, phonons and lattice defects, A is a theory-dependent parameter that includes details of the scattering process (e.g., isotropic or diffuse scattering [1, 18, 19]) and v_F is the Fermi velocity in bulk metal ($v_\infty = 1.39 \cdot 10^8$ cm/sec in bulk silver [20]). Note, that there exists more correct theory on the size dependence of surface plasmon damping

constant $\gamma(R)$ [21]. This theory predicts the oscillating character of the dependence $\gamma(R)$ that is the result of quasidiscrete spectrum of phonons in the NP. Really, electron scattering on long-wave phonons dominates in metal, and for metal NPs long-wave spectrum is limited by the size of the particle that has to lead to oscillations in $\gamma(R)$ dependence. Note, however, that noticeable oscillations in dependence $\gamma(R)$ appear for NPs smaller than about 15 nm. For larger particles the oscillations are small and decrease with the increasing size. As a result, for larger particles the dependence $\gamma(R)$ is nearly monotonically decreasing and, correspondingly, is described well by expression (7). The NPs studied in our work are quite large (24 and 60 nm), so our choice of simplified expression (7) to describe the size dependence of surface plasmon damping constant is quite correct. Moreover, since the NPs in studied samples are not monosize, their size distribution has to lead to blurring of the slight oscillations of damping constant for the large NPs.

Let us analyze an influence of temperature on the energy and width of SPR in metal NP embedded in the host matrix. **First mechanism** of the dependence of SPR on temperature is **electron-phonon scattering** in the metal NP. The size-independent damping constant γ_∞ depends on temperature due to the temperature dependence of electron-phonon scattering rate. Really, at the temperature increase the phonon populations in the metal increase that leads to the increase of electron-phonon scattering probability, which results in the increased scattering rate for the electrons. The $\gamma_\infty(T)$ dependence caused by electron-phonon scattering is given by [22]

$$\gamma_\infty(T) = K'T^5 \int_0^{\theta/T} \frac{z^4 dz}{e^z - 1}, \quad (8)$$

where $\theta = -48^\circ\text{C}$ is the Debye temperature for silver [20] and K' is a constant [22]. Knowing bulk damping constant γ_∞ for certain temperature, e.g. for room one $T_0 = 20^\circ\text{C}$, K' can be calculated as

$$K' = \frac{\gamma_{\infty}(T_0)}{\theta/T_0} \cdot T_0^5 \int_0^{\infty} \frac{z^4 dz}{e^z - 1} \quad (9)$$

For bulk silver at $T_0 = 20^\circ\text{C}$: $\gamma_{\infty} = 0.02 \text{ eV}$ [23]. Thus, the increase of electron-phonon scattering rate with increasing temperature would lead to increase of damping constant γ_{∞} . Apparently, this would lead to the broadening of SPR as well as to its red shift, in accordance with Eqs. (6) and (7).

Second mechanism of the dependence $\varepsilon(T)$ is **thermal expansion** of the NP. Indeed, at the increase of temperature the volume of NP increases as

$$V(T) = V_0(1 + \beta\Delta T), \quad (10)$$

where $\Delta T = T - T_0$ is a change in temperature from the room one $T_0 = 20^\circ\text{C}$, β is the volume thermal expansion coefficient ($5.67 \cdot 10^{-5} \text{ K}^{-1}$ for bulk silver [20]), V_0 is volume of NP at $T_0 = 20^\circ\text{C}$. The free electrons density in a metal particle is given by $n = N/V$, where N is the number of electrons and V is the particle volume. Let us denote the free electron density at the room temperature n_0 , then, since the total number of free electrons in the NP is temperature-independent [24], $N = n_0 V_0 = n(T)V(T)$, and combining Eqs.(4) and (10), we can obtain expression for the frequency of bulk plasmon

$$\omega_p = \sqrt{\frac{4\pi n_0 e^2}{m^*(1 + \beta\Delta T)}}. \quad (11)$$

Substituting Eq.(11) into Eq.(6), we obtain the expression for the SPR frequency in metal NP

$$\omega_{sp} = \sqrt{\frac{\omega_{p0}^2}{(1 + 2\varepsilon_m + \varepsilon_{ib1})(1 + \beta\Delta T)}} - \gamma^2, \quad (12)$$

where $\omega_{p0} = \sqrt{\frac{4\pi n_0 e^2}{m^*}}$ is bulk plasmon frequency at room temperature. Thus, the thermal expansion of NP would lead to decrease of a concentration of free electrons in the NP and, correspondingly, to decrease of energy of SPR, i.e. to its red shift with increasing temperature. It is well known [1] that the damping constant of plasma oscillations depends on the size of NP as $\gamma(R) \propto 1/R$ (see Eq. (7)). That is due to the free electrons

scattering on the NP surface. At the thermal expansion the NP radius increases as

$$R(T) = R_0(1 + \beta\Delta T)^{1/3}, \quad (13)$$

where R_0 is the NP radius at room temperature. Therefore, the NP thermal expansion would affect the SPR frequency not only through the frequency of bulk plasmon but through the size-dependent part of the plasmon damping constant as well. The volume expansion coefficient depends on temperature according to [25] as

$$\beta(T) = \frac{192\rho k_b}{r_0\phi(16\rho - 7Tk_b)^2}, \quad (14)$$

where k_b is the Boltzmann constant, and ρ , ϕ , r_0 are the parameters of Morse potential used in [25] to describe the potential of interatomic interaction in silver, $U(r) = \rho[e^{-2\phi(r-r_0)} - 2e^{-\phi(r-r_0)}]$.

Note, that we consider the NP thermal expansion, assuming that it is free. However, the NP is embedded in the silica matrix. Correspondingly, taking into account that volume thermal expansion coefficient for silica is considerably smaller ($1.65 \cdot 10^{-6} \text{ K}^{-1}$ for fused silica) than one for silver ($5.67 \cdot 10^{-5} \text{ K}^{-1}$), at first glance it seems that the silica host matrix would block the expansion of the NP. However, our procedure of fabrication of Ag/SiO₂ composite samples is that the formation of Ag NPs in silica occurs at temperature 1200°C that is higher than maximum temperature used in our optical measurements (700°C). So, the sizes of the NP and the hosting cavity of silica matrix are equal only at the highest temperature, i.e. at 1200°C . After annealing at 1200°C the samples were cooled down to room temperature. At the cooling both the NP and hosting cavity contracted, but due to considerable difference of the thermal expansion coefficients the silver NP contracted considerably stronger than the hosting cavity. Thus, at any temperature lower than 1200°C , including entire temperature range of $17-700^\circ\text{C}$ used in our experiments, the silver NP size is smaller than one of the hosting cavity of silica matrix. Therefore, we can conclude that in our experiments the silver NPs expanded freely, i.e. the matrix did not affect the thermal expansion of the NPs.

At last, third mechanism of the SPR temperature dependence can be temperature dependence of the dielectric permittivity of

host matrix $\varepsilon_m(T)$. Indeed, the reference data [26] show that the permittivity of silica increases with the temperature increasing. It is seen from Eq.(12) that such temperature induced an increase of ε_m would lead to the red shift of SPR as well. Thus, summarizing the above arguments, we obtain below expressions that explain the temperature dependences of the SPR energy and width in silver NPs in the silica host matrix

$$\omega_{sp}(T) = \sqrt{\frac{\omega_{p0}^2}{(1 + 2\varepsilon_m(T) + \varepsilon_{ib1})(1 + \beta(T)\Delta T)} - \gamma^2(T)}, \quad (15)$$

$$\gamma(T) = \gamma_\infty(T) + A \frac{v_F}{R(T)}, \quad (16)$$

where dependences $\gamma_\infty(T)$, $R(T)$ and $\beta(T)$ are given by Eqs.(8), (13) and (14), correspondingly.

5. Results and discussion

In this section we use the theory outlined in the previous section to rationalize the experimental temperature dependences of the SPR energy and bandwidth for silver NPs in silica. We calculated the absorption spectra of Ag NPs in silica at various temperatures by Eq.(1). The temperature dependence of the silica host matrix was taken from [26]. To take into account the temperature dependence of the NP dielectric permittivity we first calculated the contribution of interband transitions in ε of the NP as

$$\varepsilon_{ib}(\omega) = \varepsilon_\infty(\omega) - \varepsilon_{D,\infty}(\omega), \quad (17)$$

where $\varepsilon_\infty(\omega)$ is a dielectric permittivity of the bulk silver taken from [27], $\varepsilon_{D,\infty}(\omega)$ is the Drude term for the bulk silver (contribution of free electrons) calculated by Eq.(3). At the calculations we used: $\omega_p = 8.97$ eV and $\gamma_\infty = 0.02$ eV [23]. Then we calculated the temperature dependent dielectric permittivity of the NP as following

$$\varepsilon(\omega, T) = \varepsilon_{ib}(\omega) + \varepsilon_D(\omega, T), \quad (18)$$

where $\varepsilon_D(\omega, T)$ was calculated by Eq.(3). At calculations of $\varepsilon_D(\omega, T)$: (1) the temperature dependent bulk plasmon frequency was calculated as $\omega_p(T) = \frac{\omega_{p0}}{\sqrt{1 + \beta(T)\Delta T}}$, where $\omega_{p0} =$

8.97 eV and the volume thermal expansion coefficient was calculated by Eq.(14); (2) the temperature dependent damping constant $\gamma(T)$ was calculated by Eq.(16), where $\gamma_\infty(T)$ was calculated by Eqs.(8)–(9) and $R(T)$ — by Eq.(13). Additionally, in the calculations we used $v_\infty = 1.39 \cdot 10^8$ for Fermi velocity in the bulk silver, $A = 1$, and the parameters of Morse potential $\rho = 0.3257$ eV, $\phi = 13.535$ nm⁻¹, $r_0 = 0.31300$ nm from [28].

The evolution of the calculated absorption spectrum of 24 nm silver NPs in silica with increasing temperature is presented in Fig. 1b. It is seen that an increase of the temperature has to lead to the red shift and broadening of the SPR band. This trend is similar to the one observed experimentally. To check quantitatively our above assumptions of the physical mechanisms of these two phenomena we also calculated the temperature dependences of the SPR shift and broadening in silver NPs. To compare the respective experimental and calculated dependences correctly, we obtained the theoretical values of SP energy and bandwidth by fitting of the calculated spectra by Lorentzian function, since the corresponding experimental values we determined from the fitting of the experimental spectra as well. The obtained calculated temperature dependences of the SPR energy and bandwidth are presented in Fig. 2. The respective experimental dependences are shown on this figure as well. It is seen that quite good agreement of the experimental and calculated dependences takes place. This fact proves the correctness of our theoretical model.

As we note above, the theoretically calculated dependences contain contribution of three mechanisms. Those are electron-phonon scattering in the NP, thermal expansion of the NP and temperature dependence of the dielectric permittivity of the host matrix. It is important to know the relative contribution of each mechanism to the total temperature effect. To do so we performed corresponding calculations for both the temperature dependence of the SPR energy and width. The results for 24 nm Ag NPs in silica are presented in Fig. 3. It is seen from Fig. 3a that the thermal expansion is the dominant mechanism of the temperature induced red shift of SPR in silver NPs. Contributions of the increase of electron-phonon scattering rate and the increase of the permittivity of the host matrix with the

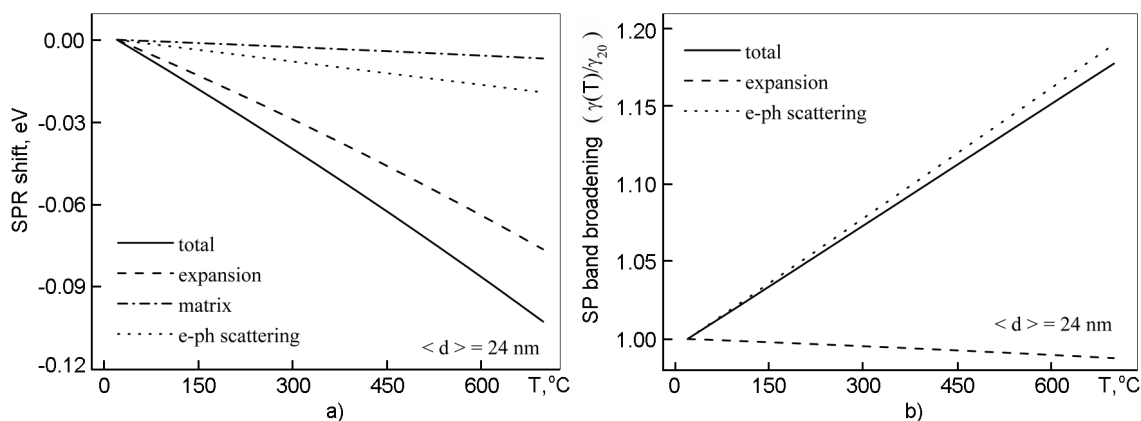


Fig. 3. Calculation of the different mechanisms contributions to the temperature induced shift (a) and broadening (b) of SPR in 24 nm silver NP in silica. Solid lines mark the total shift or broadening, dashed lines — contribution of the thermal expansion of the NP, dotted lines — the electron-phonon scattering in the NP, dash-dotted lines — the temperature dependences of dielectric permittivity of the host matrix.

temperature increasing are close to each other and are quite small comparing to the one of the thermal expansion. Meanwhile, the dominant mechanism of the temperature induced SPR broadening in silver NPs is the electron-phonon scattering that is seen from Fig. 3b. Thermal expansion of the NP leads to a very small decrease of the SPR width. However, this decrease is negligibly small and it can be neglected. The temperature dependence of the host matrix permittivity does not affect the width of SPR. Note that a good agreement of the experiment with outlined above theory takes place as well for the temperature dependences of SPR in gold NPs [15]. This proves the similarity of the physical mechanisms of observed temperature dependences for the SPR in silver and gold NPs, i.e. the thermal expansion of the NP as a cause of the red shift and electron-phonon scattering as a cause of the SPR broadening.

It is seen from Fig. 2a that a rate of the SPR red shift with the temperature increasing is the same for Ag NPs of both studied sizes. This indicates that the volume thermal expansion coefficient is the size-independent in studied range (24–60 nm) of the NP sizes. Concerning the temperature dependences of the SPR width (damping constant) $\gamma(T)$, it is seen from Fig. 2b that both the experimental and theoretical dependences are linear. This observation agrees entirely with the well known fact that the rate of electron-phonon scattering increases linearly with the temperature increasing, when the temperature exceeds considerably the Debye temperature $T > \theta$. This is clear from

Eq.(8). Since the Debye temperature for silver $\theta = -48^\circ\text{C}$ [20], the condition $T > \theta$ is satisfied well for temperatures used in our study.

6. Conclusions

Thus temperature dependences of the SPR energy and width in silver NPs with mean sizes 24 nm and 60 nm embedded in silica glass host matrix were studied in the temperature range of 17–700°C. We observed that as the temperature increases the red shift and broadening of SPR occur. The theoretical model including the phenomena of electron-phonon scattering in the NP, the NP thermal expansion and the temperature dependence of the dielectric permittivity of the host matrix was considered to rationalize the observed temperature behaviour of SPR in silver NPs. As the temperature of the particle increases, the NP volume increases while the density of the free electrons decreases. The lower electron density leads to the lower plasma frequency of the electrons and subsequently to the SPR red shift. The rate of electron-phonon scattering increases with the temperature increasing. This leads to an increase of the damping constant of the plasma oscillations and, as a result, to the red SPR shift. The dielectric permittivity of silica increases with the temperature increasing that leads to the SPR red shift as well. The performed calculations of the temperature dependences of SPR energy and width are in a very good agreement with the respective experimental data that proves the validity of the used theoretical model. It was shown that the

thermal expansion of silver NPs is the dominant mechanism of the temperature induced red shift of SPR in the silver NPs. Meanwhile, the dominant mechanism of the SPR broadening occurring with the increase of temperature is the electron-phonon scattering in the NP.

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