Specifics of d-metals (Au) emission in case of non-equilibrium heating of electrons and lattice with femtosecond laser pulses

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Abstract. The paper refers to the mechanisms of emission of noble metals taking into account the specifics associated with the two-temperature state of matter. The emission is caused by the action of an ultrashort infrared laser pulse. It is shown that the two-temperature state results in two effects contributing to the radiated emission of hot electrons. The first effect is interband radiative recombination of electrons induced by thermal smearing of the Fermi distribution of conduction-band electrons. The second effect is radiation of hot conduction-band electrons in case of inelastic electron–phonon interaction. This effect is due to the fact that thermal smearing of the Fermi distribution of conduction-band electrons, taking into account the electron–phonon interaction, and in the presence of strong near fields, enables intraband radiative transitions for electrons in the sp-band.

1. Introduction
Ultrashort laser pulses make it possible to transfer solids into the non-equilibrium state of warm dense matter (WDM). The investigation of properties of these states is important for a wide range of applications in the field of geophysics, high pressure physics, condensed matter physics, astrophysics and is of fundamental scientific interest. As the laser pulse energy is absorbed by electrons in the conduction band, the system passes to states with various electron and ion temperatures [1]. Thus, in the WDM state, the matter has both high electron and ion temperatures at which the crystal lattice keeps its structure.

Recently, a number of theoretical models of the interaction of intense femtosecond laser pulses with solid targets based on the two-temperature equation of the state of the irradiated substance have been developed that allow to describe the dynamics of formation and scattering of plasmas [2], interactions with targets from aluminum [3] and silver [4, 5].

A numerical hydrodynamic study of femtosecond laser ablation [6], the shock-wave and ablation phenomena in tantalum lms of submicron thicknesses irradiated by femtosecond laser pulses [7], heat conductivity of copper [8], electronic heat capacities and thermal pressures for aluminum and tungsten [9] in two temperature states have been studied. Fundamental physical phenomena in metals irradiated by ultrashort laser pulses and models of electron heat conductivity coefficients and electron-ion coupling parameter are investigated in [10]. In [11], a review of the most important results of the experimental studies of thermonuclear plasma in
conical targets, the generation of shock waves and of spallation phenomena in different materials is presented.

An exact quantitative method using a quantum molecular dynamic approach in combination with density functional theory and the Kubo–Greenwood formula was used in [12, 13] of the static electrical and thermal conductivities of liquid aluminum.

During the period of action of the laser pulse (LP) and after it there are large temperature gradients depthwise the absorbing layer up to the time when the lattice and electron gas temperatures are equalized. This causes the non-equilibrium nature of radiative processes both timewise and depthwise the absorbing layer of the matter. On the other hand, in addition to superfast electron gas heating, the processes related to the interband absorption of exciting radiation occur and intensify, which further leads to the radiative recombination of conduction-band electrons.

The paper refers to noble metals (Au, Ag, Cu) which are classified as d-metals. For this type of metals, the depth of the d-band relative to the Fermi surface is characterized by the interband transition threshold (ITT), the magnitude that determines the minimum quantum energy of the exciting radiation $\hbar \omega_0$ needed for photoluminescence (PL) in case of single-photon absorption (SPA). If the quantum energy of the exciting radiation is lower than the ITT, it is referred to multi-photon and, in particular, two-photon absorption (TPA) which enables the PL. However, in WDM environment, the quantum energy of the exciting LP, which is lower than the metal ITT, causes the SPA due to thermal blurring of the Fermi surface, which leads to the increased LP absorption and enhanced PL.

The paper describes the mechanism of thermal radiation of hot electrons based, firstly, on the thermal enhancement of PL in WDM environment. The enhancement of PL is related to both the increased quantum yield of radiation in case of TPA and the occurrence of the process competing in quantum yield and associated with SPA of quanta of exciting radiation the energy of which is lower than the ITT. Secondly, in addition to thermal enhancement of PL, the thermal radiation of hot electrons in the WDM state are significantly determined by the processes related to inelastic electron–phonon interaction (EPI) of conduction-band electrons, in the presence of strong surface electromagnetic fields caused by the action of LP on the rough metal surface.

2. Interband radiative recombination of hot electrons
The interband radiative recombination of hot electrons fundamentally has the PL mechanism, and since this mechanism is studied in detail we will briefly describe the basic relationships and specify the effect of two-temperature state of matter generating the specifics of radiative recombination of hot electrons (RRHE).

The mechanism of FL arrays of precious metals was first developed in papers of Mooradian [14] and based on the process of excitation of d-band electrons, in the areas closest to the sp-band of conductivity in the energy space of the electron subsystem. Later, the theoretical aspects of this mechanism were investigated in detail in papers of [15–17]. It was noted that the peaks of the broadband PL corresponded to the energies of interband transitions of sp- and d-bands of metals in case of FL induced by single-photon excitation. However, in case of multi-photon excitation, in [16] it was noted that characteristic peaks disappeared. In the latter paper, in addition to the developed theoretical model, a detailed experimental study of PL for smooth and rough arrays of copper, silver and gold were presented.

Experimental results are presented in [18] showing the changing absorption in Ag at a certain level of intensity of LP, which, according to the conclusions made, indicates that hot electrons has an effect on the absorption processes. In the experiment of [19], the changing surface reflectivity of Au array measured with a delay after the action of the main pulse heating up conduction-band electrons shows a rapid increase in the absorption factor at the end of the heating LP action and a later decrease in the absorption factor while the electron subsystem is cooling down. It
should also be noted that in papers of [20] an increase in the LP absorption factor by metals as a result of thermalization of conduction-band electrons can be explained by an increasing rate of electron–electron collisions.

A study using thin Au and Ni films in [21] was carried out in order to analyze spatial and temporal variations in the non-equilibrium distribution of energy characteristics caused by the optical excitation of metals. According to the authors, the main purpose of the study was to highlight the role of interband transitions in obtaining information on the temperature dynamics in noble metals.

A large number of papers address the study of the emission properties of nanoparticles exposed to the exciting LP. For example, in papers of [22, 23] based on the phenomenological model of [16] it is demonstrated that the radiated emission as a result of radiative recombination of sp-band electrons and d-band holes is intensified by the action of local fields related to plasmon oscillations. This model was used, taking into account the two-temperature state of matter, by [24] in order to study the broadband radiation of Au nanorods induced by the ultrashort infrared LP.

The action of femtosecond laser radiation on conduction-band (sp-band) electrons leads to the appearance of surface plasmons [25] the later decay of which ensures that the LP energy is transferred to conduction-band electrons. Different orders of magnitude of electron and ion heat capacity [26] lead to the dual-temperature state in the area of LP action. The model of two-temperature state of matter caused by the action of ultrashort LP was presented in the paper of [1]. The distribution of conduction-band electrons as a result of the action of femtosecond LP with the quantum of ITT was considered to be the Fermi distribution in the study of the non-equilibrium electron heating and temperature dynamics in Au [27]. In case of ultrafast (femtosecond) action of low-intensity infrared LP causing a slight gap in the electron temperature ($\Delta T_e \sim 40–200$ K) in [28–30] it is showed that the nonequilibrium nonthermalized distribution of conduction-band electrons within the time frame of electron gas thermalization significantly contributes to the determination of optical properties of matter.

Levels of intensity of the exciting LP considered in this paper ensure a significant gap in the electron temperature ($\Delta T_e \sim 1.5–10$ kK), and therefore, without going into the nonlinear dynamics of nonequilibrium electron distribution function during the period of LP action and right after it, in this paper it is considered that there is the Fermi distribution of hot conduction-band electrons with a certain effective value of the electron temperature $T_e$. The following mechanism of increasing the absorption of ultrashort infrared laser pulse (UIRLP) in the metal is considered. During the first stage, as a result of the TPA, hole states in d-band are generated. Due to thermal blurring of the Fermi distribution of the conduction-band electrons, the hole states can be located deep enough inside the Brillouin zone, unlike when the excited states are located near the surface of the Brillouin zone as described in [14–17].

During the second stage of the process, there is the thermal scattering of holes in case of electron–phonon interaction of d-band electrons. As noted by Mooradian, near the Fermi surface, due to the relatively flat nature of energy d-surfaces in the area of symmetrical L and X points, excited d-band holes can be scattered in a fairly broad range of states in the k-space, which can lead to the observed broadband radiation spectrum. The estimated time interval of interband radiative recombination is in the order of $10^{-13}–10^{-12}$ s according to [31]. Taking into account the rate of the EPI and the fact that the phonon energy is much lower than the energy on the energy surfaces in the d-band where holes are scattered, the scattering of holes can be considered to be quasi-elastic. Thus, the hole generated at the second stage of the process as a result of the EPI appears to be at an arbitrary point on the surface of the constant d-band energy in both the Stokes and anti-Stokes area of recombination. Possible location of the hole up to the upper boundary of thermal blurring shows the expansion of the anti-Stokes portion of the emission spectrum with increasing electron temperature. The narrow area of
thermal blurring of the Fermi distribution at room temperature $T = 0.3$ kK shows the narrow portion of the anti-Stokes spectrum in experiments of Mooradian [14].

Then, during the third stage of the process, the hole and the conduction-band electron recombine with the quantum energy $h\omega$. The first and third stages of the process represent vertical interband transitions when the law of conservation of momentum is true for the transition condition. The second stage of the process is usually not considered in detail since it is believed that the scattering of d-band holes is not critical and only required for a qualitative description of changes in the location of the electron-hole pair for later vertical interband transition. At low temperatures of the electron gas in the conduction band, it is enough to provide a qualitative description. However, at high temperatures of sp-band electrons, possible scattering of the hole as a result of the EPI plays a significant role in this process and requires a detailed description taking into account matrix elements of the electron–phonon interaction.

The intensity of interband RRHE caused by ultrashort laser pulses, according to [16,17,32], is considered to be a three-step process including photo-excitation of electron–hole pairs, scattering of excited electrons and holes and later radiated emission caused by electron-hole recombination. During the first and third stages of the process only direct transitions are considered. According to [33], radiated emission is determined by the matter volume $V_0 = S_0[\alpha(\omega_0) + \alpha(\omega)]^{-1}$, where $S_0$ is the area of LP action, $\omega_0$, $\omega$ is the rate of LP radiation or emission rate, respectively, and $\alpha(\omega)$ is the linear matter absorption factor at $\omega$.

The intensity of RRHE induced by TPA at the rate interval $\omega$, $\omega + d\omega$, from the volume $V_0$ to the solid angle $\Delta\Omega$ can be expressed as follows:

$$I_2(\omega, T_i, T_e) = \omega\omega_0^{-1}I_0\sigma_2(I_0)[\alpha(\omega_0) + \alpha(\omega)]^{-1}\Delta\Omega w(2\omega_0, \omega, T_i, T_e),$$

(1)

where $I_0$ is the intensity of exciting LP, $\sigma_2(I_0)$ is the effective cross-section of TPA, $w(2\omega_0, \omega, T_i, T_e)$ is two-temperature probability of radiative transitions in case of TPA, $T_i$ and $T_e$ is the lattice and electron temperature, respectively. The effective cross-section of TPA increases linearly as a function of the peak intensity of exciting LP and, according to, for example, [34], it can be expressed as follows:

$$\sigma(I_0) = \frac{\delta I_0\tau f}{\hbar\omega_0} n_l,$$

(2)

where $\delta$ is the cross-section of TPA, $\tau$ is the LP duration, $f$ is the LP repetition rate, $n_l = n_0l$, $n_0$ is the concentration of matter atoms, $V_l = S_l, S_e$ is the unit area, $l$ is the depth of absorbing skin layer. Since Mooradian identified a slight variation in the luminescence spectrum depending on the angle and polarization of exciting LP, we will make it simpler and consider $p$-polarized exciting LP.

The two-temperature probability of emission transition $w(2\omega_0, \omega, T_i, T_e)$ in the third order of perturbation theory, according to [17,32,35,36], can be calculated by integrating the product of matrix elements of transitions between the upper electron and lower hole levels and matrix elements of EPI $M_{k,k'}^{\pm}$ (matrix elements of the phonon creation and annihilation) [26,37], over all possible final states and initial states in the quasi-momentum space.

It is believed that the lattice potential $V(\bf{r})$ is a superposition of atomic potentials: $V(\bf{r}) = \sum_{l} V_a(\bf{r} - \bf{R}_l)$ where $\bf{R}_l$ determines the actual location of $l$-th lattice site. The environmental impact on the potential $V(\bf{r})$ will be considered in view of Lindhard screening theory.

The approximation when matrix elements of electron transitions are considered to be independent of $\bf{k}$ in the vicinity of symmetrical L and X points of the Brillouin zone of the quasi-momentum space is described. This approximation was used in papers of [15,38] when calculating the dielectric constants in noble metals. Likewise [15,39,40], using the expression for the matrix element of emission transition [17], the expressions for matrix elements of EPI, the expression for the two-temperature probability of emission transition $w(2\omega_0, \omega, T_i, T_e)$ can
be obtained, in the context of which the intensity $I_2(\omega)$ can be expressed as follows:

$$ I_2(\omega, T_i, T_e) = I_0^2 \left( \frac{\omega^2}{\omega_0^2} \right) b_2 \frac{\delta f n_1}{\hbar \omega_0} \frac{I_2^2}{n_2^2 + k_2^2} \frac{\alpha(\omega)}{\alpha(\omega) + \alpha(\omega)} \times \left[ 1 - f \left( \frac{E + h\omega - E_f}{k_b T_e} \right) \right] f \left( \frac{E - E_f + E_{\text{ITT}}}{k_b T_i} \right), $$

where $n$ and $k$ are the matter refraction and absorption factor at the rate $\omega_0$; $\delta$, $n_2$ and $k_2$ are matter transmittance, refraction and absorption factors at the rate $\omega$; $f(\xi) = [1 + \exp(\xi)]^{-1}$ is the Fermi–Dirac distribution function of electron levels; $E_f$ and $E_{\text{ITT}}$ are the Fermi energy and the energy of interband transitions in the area of intersection of the Fermi surface and the Brillouin zone boundary, respectively,

$$ \Phi(\omega, \omega, E) = \left( \frac{k_e^2}{4\pi} \right)^2 \int_0^{2\pi} \frac{V_q(q)}{\varepsilon(q)} |q|^2 P(q, T_i) d\theta, $$

$V_q(q) = 4\pi e^2 q^{-2}$ is the Fourier component of the Coulomb potential, $\varepsilon(q)$ is the dielectric constant according to [41], $P(q, T_i)$ is the functions of electron–phonon interaction [37]; $E_z(\omega)$ is the upper boundary of integration determined by the parameters of the band structure in the vicinity of symmetric L and X points of the Brillouin zone of quasi-momentum space; $k_e = \pi(4 a_e)^{-1}$, $a_e$ is the unit cell size; $q$ is the module of the vector $q k_e^{-1}$, $q$ is the unit vector such that $q = k_e q \hat{q}$.

The two-temperature dependence of the integral in the expression (3) for RRHE intensity $I_2(\omega)$ in case of TPA of laser radiation with the quantum energy $\hbar \omega_0 = 1.18$ eV was calculated for gold at the electron temperature variations of 0.3–6 K. The ion temperature variations were 0.3–0.43 K, which corresponded to the ion temperature by the end of the LP action calculated according to the formula of [42]. Figure 1 shows the calculation of two-temperature dependence of the integral in the expression (3) on the radiated emission wavelength for the values $T_e = 0.3$, 2, 4 and 6 K. The maximum peak corresponds to the wavelength $\lambda_1 = 525$ nm ($h \omega_1 = 2.36$ eV).

The calculations show the expansion of the area where the anti-Stokes portion of radiated emission is observed.

### 3. Intensification of radiated emission influenced by SPA

The mechanism of intensification of radiated emission influenced by hot electrons also leads to emission processes related to SPA. Thermal blurring of conduction-band electrons leads to the situation when free states appear in the sp-band at energy levels closer than $E_{\text{ITT}}$ and, starting from certain electron temperature values, transitions of d-electrons become possible as a result of the quantum absorption at the fundamental LP rate $\hbar \omega_0 = 1.18$ eV. D-band “holes” generated by such transition due to EPI can be displaced over the surface of constant energy and then recombine with hot sp-band electrons.

The RRHE intensity induced by SPA at the rate interval $\omega, \omega + d\omega$, from the volume $V_0$ to the solid angle $\Delta \Omega$ can be expressed as follows:

$$ I_1(\omega, T_i, T_e) = \omega \omega_0^{-1} I_0 |L(\omega_0)|^2 \left( \alpha(\omega_0) + \alpha(\omega) \right)^{-1} \Delta \Omega w(\omega_0, \omega, T_i, T_e), $$

where $|L(\omega_0)|^2$ is the Fresnel coefficient for incident radiation at the rate $\omega_0$; $w(\omega_0, \omega, T_i, T_e)$ is the number of radiative transitions at the radiation rate $\omega$ per unit time from the unit volume of matter in the dual-temperature state due to the LP action with a peak intensity $I_0$ and radiation rate $\omega_0$. The function $w(\omega_0, \omega, T_i, T_e)$, according to [17, 32, 35, 36], in the third order of perturbation theory, can be calculated by integrating the product of matrix elements.
Figure 1. Two-temperature dependence of the integral in the expression (3) for RRHE intensity $I_2(\omega)$ for Au at TPA of laser radiation with the quantum energy $\hbar \omega_0 = 1.18$ eV, for the values $T_e = 0.3$ (dotted line), 2 (short-dash), 4 (long-dash) and 6 kK (solid line).

of transitions between the upper electron and lower hole levels and matrix elements of EPI $M_{k,k'}^\pm$, over all possible final states and initial states in the quasi-momentum space. Here, the approximation of [15, 38] is used when matrix elements of electron transitions are considered to be independent of $k$ in the vicinity of symmetrical L and X points of the Brillouin zone of the quasi-momentum space. As a result, using the representation for the Fresnel coefficient $|L(\omega_0)|^2 = 4n(n^2 + k^2)^{-1}$ and considering $t_e = \alpha(\omega)^{-1}$ and $\Delta \Omega = 2\pi$, the expression (5) can be represented as follows:

$$I_1(\omega, T_i, T_e) = I_0 \left(\frac{\omega^2}{\omega_0}\right) \frac{4nb_0}{n^2 + k^2} \frac{|t_2|^2}{n^2 + k^2} \frac{\alpha(\omega)}{\alpha(\omega_0) + \alpha(\omega)}$$

$$\times \int_0^{E_z(\omega)} \Phi(\omega_0, \omega, E)\frac{dE}{(\zeta(E_z(\omega) - E))^{1/2} (\zeta(E_z(\omega_0) - E))^{1/2}}$$

$$\times f \left( E - E_f + E_{ITT} \right) \left[ 1 - f \left( E + \hbar \omega_0 - E_f \right) \frac{k_bT_e}{k_bT_i} \right] f \left( E + \hbar \omega - E_f \right).$$

The integral in the expression (6) for RRHE intensity $I(\omega)$ in case of LP SPA with the quantum energy $\hbar \omega_0 = 1.18$ eV was calculated for the electron temperature in the range of 0.3–6.0 kK for Au. The ion temperature variations were 0.3–0.43 kK, which corresponded to the ion temperature by the end of the LP action calculated according to the formula of [42]. Figure 2 shows the calculation for values $T_e = 3, 4, 5$ and 6 kK.

The dependences on the temperature $T_e$ of the integral component $I(\omega)$ shown in figure 2 indicate that SPA can have an effect on the general nature of radiated emission for Au starting from $T_e > 2.5$ kK. It is known, that during the one-photon and two-photon absorption of the exciting radiation with the intensity $I_0$, the intensity of the PL is characterized by power dependence of the first and second order, respectively. As follows from (6) and (3), the dependence of the PL intensity of $I_0$ is more complicated in the case of hot electrons radiation.
Figure 2. Dependence on the radiated emission wavelength of the integral component in the expression (6) for RRHE intensity $I(\omega)$ for Au in case of LP SPA with the quantum energy $\hbar\omega_0 = 1.18$ eV for the values $T_e = 3$ (dotted line), 4 (short dash), 5 (long dash) and 6 kK (solid line). Ion temperature varies 0.3–0.43 kK.

The dependence of integral components in formulas (6) and (3) on the electron temperature will be evaluated using the power dependence of the type $w(\omega_0, \omega, T_i, T_e) \sim T_{e1}^{a_1(\omega,T_e)}$ and $w(2\omega_0, \omega, T_i, T_e) \sim T_{e2}^{a_2(\omega,T_e)}$ where, generally speaking, $a_1(\omega, T_e)$ and $a_2(\omega, T_e)$ also depend on $T_e$. Calculations show that both exponents behave monotonically when electron temperature $T_e$ change in 0.5–6 kK and vary slightly (about 10%), and subsequently exponents are considered to be averaged over $T_e$ in 0.5–6 kK. The variation range of the exponents in accordance to the temperature $T_e$ is indicated in figure 4 in the form of error limits. In the rate interval corresponding to 525 $\leq \lambda \leq$ 1000 nm, indicators $a_1(\omega)$ and $a_2(\omega)$ averaged over $T_e$ in the range of 0.5–6 kK are as follows: $3.4 \leq a_1(\omega) \leq 3.6$, $0.8 \leq a_2(\omega) \leq 1.1$. According to [42], the dependence of the maximum temperature $T_e$ of the electron gas on the peak LP intensity is considered quadratic. Thus, the relevant exponent $I_{0r}(\omega)$ averaged over $T_e$ for the peak LP intensity $I_0$ indicative dependences $w(\omega_0, \omega, T_i, T_e) \sim I_{0r1}(\omega)$ and $w(2\omega_0, \omega, T_i, T_e) \sim I_{0r2}(\omega)$ range within $1.7 \leq r_1(\omega) \leq 1.8$ and $0.4 \leq r_2(\omega) \leq 0.55$ at $T_e$ in the range of 0.5–6 kK, accordingly. Considering the obtained power dependence on the temperature, the general order of dependence of the radiated emission intensity on $I_0$ is in the range of 2.7–2.8 for SPA and 2.4–2.6 for TPA.

4. Emission of hot conduction-band electrons in case of inelastic electron–phonon interaction

The mechanism of radiative transitions of sp-band electrons occurring in case of inelastic interaction with the lattice is described below. Radiative transitions in the conduction band in metals have traditionally been considered to be unresolved due to the fact that it was impossible to ensure the conservation of momentum and parity of the interacting electron emitting the photon of electric type in the dipole approximation. However, in the presence of strong electromagnetic fields in the vicinity of rough surfaces, radiative transitions of conduction-
band electrons can be considered in the quadrupole approximation [43], which ensures parity of the electron emitting the photon of electric type. The law of conservation of momentum is true as a result of EPI. This approach was used in the paper of [44] when analyzing the infrared portion of the radiation spectrum of Au and Ag nanoparticles influenced by femtosecond LP at a wavelength of 770 nm. The experimental data were explained by recombination transitions of hot electrons in the conduction band. According to [45], the radiation in the infrared portion of the spectrum of nanoparticles influenced by femtosecond LP at a wavelength of 770 nm can be explained by resonant Raman shift in the Stokes and anti-Stokes portions of the spectrum in relation to the fundamental exciting harmonics.

Conduction-band electrons that received the excess thermal energy due to the electromagnetic radiation absorption by the metal can later relax in series, partially giving their energy, interacting with other electrons, ions and lattice defects or they can emit the light quantum with the energy \( \hbar \omega \) as a result of indirect transition caused by EPI. In the latter case, we believe that the conditions of the existence of strong electromagnetic surface fields making it possible for [43] to consider radiative transitions in the quadrupole approximation are met. In this case, the emission of the photon of electric type does not breach the law of conservation of parity. Due to the blurring of electron states for energies, the heated electron gas can potentially emit light quanta in the visible range. For such transitions, a number of conditions shall be met.

First, electrons with the energies much higher than the Fermi level and hole states located below the Fermi level shall be present. This condition is met by thermal blurring of the distribution of conduction-band electrons in the two-temperature state. Second, since indirect sp-band electron transitions are under discussion, to observe the law of conservation of momentum, EPI shall be considered as a constraint imposed on quasi-momenta of electrons and phonons before and after interaction. These constraints are recorded using the phonon creation and annihilation operators when the electron interacts with the lattice. The relevant analytical expressions taking into account the laws of conservation of momentum and energy in case of intraband transitions of hot sp-band electrons are provided below.

We believe that conduction electrons in the metal are exposed to inelastic scattering due to lattice vibrations [46]. According to [35,36], the number of photons emitted (per unit time) with a certain pulse value and at a rate in the range of \( \omega \) varied from \( E \) to \( E + \delta \omega \) when the electron state energy varies from \( E_k \) to \( E_{k+q} \) in the continuous spectrum influenced by small perturbation introduced by EPI in the first order of perturbation theory can be expressed as follows:

\[
d\omega_{k,k+q}(\omega,T,T_e) = \frac{2\pi}{\hbar} \left[ \left|M_{k,k+q}^+\delta(E_k - E_{k+q} - \hbar \omega + \hbar \omega_s(q))\right|^2 \right. \\
\left. + \left|M_{k,k+q}^-\delta(E_k - E_{k+q} - \hbar \omega - \hbar \omega_s(q))\right|^2 \right] d\omega.
\] (7)

In order to calculate the number of radiative transitions of electrons (per unit time) with the photon emission rate \( \omega \), (7) shall be integrated over all final states \( \mathbf{k}' = \mathbf{k} + \mathbf{q} \) and initial states \( \mathbf{k} \), taking into account the distribution function of electron levels in the conduction band. As a result, taking into account the expressions for matrix elements of EPI \( M_{k,k'} \) [37, 46, 47], omitting detailed computations, assuming the surface layer as deep as \( t_s = (\alpha(\omega))^{-1} \) is emitting and using the expression for the Fresnel coefficient [48] at the emission rate \( \omega : |L(\omega)|^2 = 4n(n^2 + k^2)^{-1} \), we find that the intensity of radiated emission of hot electrons (per unit time) as a result of intraband transitions is defined by:

\[
I_{sp}(\omega,T,T_e) = b_{sp} \frac{\omega}{\alpha(\omega)} \frac{|t_2|^2}{n^2 + k^2} \int dE \Phi_{sp}(E,\hbar \omega) \left[ 1 - f \left( \frac{E - \hbar \omega - E_f}{k_b T_e} \right) \right] f \left( \frac{E - E_f}{k_b T_e} \right). \] (8)

The function \( \Phi_{sp}(E,\hbar \omega) \) is introduced herein:

\[
\Phi_{sp}(E,\hbar \omega) = \left( \frac{k^3}{4\pi} \right)^2 \int_{k_1}^{k_{1,max}(E)} dk_1 \int_{-k_1}^{k_{1,max}(E)} dq_1 \int_0^{2\pi} d\theta \frac{V_s(q)}{\varepsilon(r)} q^2 P(q, T_s). \] (9)
The function $P(q, T_i)$ represents electron–phonon interaction [37].

The components of the normalized vector $\mathbf{q} = (q_1, q_2x, q_2y)$ are defined by

$$q_{2x} = (k_2 + q_{2x}) \cos \theta - k_2,$$

$$q_{2y} = (k_2 + q_{2y}) \sin \theta,$$

$$k_2 = (m_{2u} \left[ \varsigma (E - E_f - \Delta_u - \hbar \omega) - (k_1 + q_1)^2 / m_{1u} \right]^{1/2} - k_2,$$

$$\Delta_u, m_{1u}, m_{2u}$$ are the parameters of the sp-band structure.

Expression (8) was numerically calculated for Au. The Coulomb potential $V_a(q) = 4 \pi e^2 q^{-2}$ and the dielectric constant $\varepsilon(q)$ presented by the expression from [41] were used in the calculations.

The type of dependence $w_{sp}(\omega, T_e, T_i)$ at different values $\hbar \omega$ and $T_e$ is shown in figure 3. The dependence $I_{sp}(\omega)$ on the electron temperature in the constrained rate interval corresponding to $600 \leq \lambda \leq 1000$ nm can also be estimated using the power dependence $I_{sp}(\omega, T_i, T_e) \sim T_e^{a_{sp}(\omega, T_e)}$. The indicator $a_{sp}(\omega, T_e)$ averaged over $T_e$ in the range of 4–6 kK is within $3.3 \leq a_{sp}(\omega) \leq 4.8$. Considering the dependence of the maximum temperature $T_e$ of the electron gas on the peak LP intensity $I_0$ to be quadratic [42], the relevant exponent $I_0^{r_{sp}(\omega)}$ averaged over $T_e$ for the peak LP intensity indicative the dependence $I_{sp}(\omega, T_i, T_e) \sim I_0^{r_{sp}(\omega)}$ ranges within $1.6 \leq r_{sp}(\omega) \leq 2.4$ at $T_e$ in the range of 4–6 kK. At lower temperatures of the electron gas in this range of wavelengths, the relevant dependences decrease exponentially depending on $T_e$.

5. Discussion

Models that take into account the effect of hot electrons on emission spectra of luminescence presented in this paper and the calculations allow to identify the following specifics of radiated emission with the participation of hot electrons. At low intensities of exciting LP, the main reason for radiated emission is multi-photon absorption. The calculations carried out for TPA without taking into account the factor in (3), which characterizes EPI, show that the two-temperature
Figure 4. Graphs of functions $r_2(\omega) + 2$ (squares), $r_1(\omega) + 1$ (diamonds), $r_{sp}(\omega)$ (circles) averaged over the temperature of exponents of the peak intensity $I_0$ reflecting the dependence for $I_2(\omega, T_i, T_e) \sim I_0^{r_2(\omega)+2}$, $I_1(\omega, T_i, T_e) \sim I_0^{r_1(\omega)+1}$, $I_{sp}(\omega, T_i, T_e) \sim I_0^{r_{sp}(\omega)}$, respectively. Solid line indicates the trend of relevant indicators obtained in the experiment in papers of [44].

Probability of radiative transitions $w(2\omega_0, \omega, T_i, T_e)$ in case of TPA is almost independent of the temperature in the Stokes (in relation to $2\omega_0$) portion of the spectrum, thus ensuring the expected quadratic order $I_0^2$ of LP intensity. However, when considering EPI, the exponent has an additional component $r_2(\omega)$ reflecting the dependence $w(2\omega_0, \omega, T_i, T_e) \sim I_0^{r_2(\omega)}$ that ranges within $0.4 \leq r_2(\omega) \leq 0.55$ at $T_e$ in the range of 0.5–6 kK. The type of dependence $r_2(\omega) + 2$ averaged over $T_e$ is shown in figure 4. In the anti-Stokes portion, the factor $w(2\omega_0, \omega, T_i, T_e)$ in the expression (1) for $I_2(\omega, T_i, T_e)$, as shown in figure 1, at the increasing electron temperature, first, extends the range of the observed radiation emission and, second, increases the power dependence on $I_0$. Likewise in the Stokes area, EPI taken into account in (3) increases the power dependence by $\sim 0.5$. When the exciting radiation intensity is enough to reach a certain temperature level ($T_e \sim 2.5$ kK for Au and $T_e \sim 4$ kK for Ag), the competing radiated emission caused by SPA occurs. The behavior of the exponent $r_1(\omega)$ averaged over the temperature $T_e$ reflecting the dependence $w(\omega_0, \omega, T_i, T_e) \sim I_0^{r_1(\omega)}$ is shown in figure 4 (diamonds indicate the dependence $r_1(\omega) + 1$).

A similar behavior of power dependences shows that the action of hot electrons leads to the fact that two emission process caused by TPA and SPA are almost indistinguishable by the order of power dependence on $I_0$. Therefore, a low order of power dependence of radiated emission observed in a number of papers [43, 44] in the infrared range cannot be explained by SPA. If radiated emission caused by intraband radiative transitions is taken into account, the order of power dependence $I_{sp}(\omega, T_i, T_e) \sim I_0^{r_{sp}(\omega)}$ in the rate interval corresponding to $600 \leq \lambda \leq 1000$ nm ranges within $1.6 \leq r_{sp}(\omega) \leq 2.4$ in the range of 4–6 kK (full circles in
Figure 5. Modelling of the emission spectra of hot electrons for Au at different values of the electron temperature $T_e = 3$ (dotted line), 4 (short dash), 5 (long dash) and 6 kK (solid line).

A good correlation of estimated exponents and experimental data of [44] presented in this paper is shown by the trend line (solid line) in figure 4 according to [44] where radiated emission of hot spots on thin gold films were experimentally studied. Experiments carried out according to [18, 19] are also well correlated to the described mechanism of SPA occurrence in case of thermalization of conduction-band electrons by exciting radiation with the quantum energies lower than the interband transition threshold.

A summation of the described mechanisms of electron radiative transitions is presented as a model of hot electron emission spectra in figure 5 for the following values of the electron temperature $T_e = 3, 4, 5$ and 6 kK. The emissivity of the substance is calculated according to [49] and to the temperature of the lattice, which ranged 0.32–0.43 kK and corresponded to the values of the ion temperature at the end of the LP calculated by [42]. The quantitative relationship between the intensities of emission radiation in single-photon and two-photon absorption processes requires the calculation of the constants in expressions (3) and (6), and also the evaluation of the two-photon absorption cross section for the metal under consideration.
This problem is of independent interest for a correct interpretation of the experimental spectra, which can be the subject of further research. The use of more precise methods (see, for example, [12, 13]) for the quantitative evaluation of the emission spectra of noble metals is faced with the problem of constructing a density functional and direct application of the KuboGreenwood formula for heavy atoms of noble metals.

Spectra of Au radiation effected by the ultrashort infrared LP, that shown in [50] have a specific maximums in the vicinity of 525 nm. The maximum of joint electronic states of density for Au, characterizing the interband radiative transitions is located in this area.

A similar behavior of the spectra obtained out of the computational model (figure 5) shows qualitative agreement of the presented model and experimental studies. However, the model demonstrates the inflated radiation intensity values in the red frequency region compared with the experiment [50]. We can assume that the reason for non-compliance is determined by the method of calculation of Au emissivity, which is also influenced by hot electrons [51]. Accounting for this effect is the subject of a further research.

6. Conclusion

When exposed to the metal ultrashort infrared pulses with photon energies smaller than the width of the interband transitions, thermal smearing of the conduction band increases the probability of two-photon absorption, and the mechanism of one-photon absorption is started. Hot electrons arising at the LP affect the photoluminescence quantum yield and expand the anti-Stokes area of the spectra. The degree of dependence of the intensity of radiation on the intensity of the exciting radiation has an order higher than the square, which is also due to the effect of hot electrons. The existence of the strong surface electric fields during the LP period, the thermal smearing of the distribution of the conduction electrons and electron–phonon interaction permits intraband radiative transitions of the conduction band electrons.

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References

[1] Anisimov S I, Kapeliovich B L and Perelman T L 1974 Zh. Eksp. Teor. Fiz. 39 375
[2] Agranat M B, Andreev N E, Ashitkov S I, Veisman M E, Levashov P R, Ovchinnikov A V, Sitnikov D S, Fortov V E and Khishchenko K V 2007 JETP Lett. 85 271–6
[3] Komarov P S, Ashitkov S I, Ovchinnikov A V, Sitnikov D S, Veysman M E, Levashov P R, Povarnitsyn M E, Agranat M B, Andreev N E, Khishchenko K V and Fortov V E 2009 J. Phys. A: Math. Theor. 42 214057
[4] Veysman M E, Agranat M B, Andreev N E, Ashitkov S I, Fortov V E, Khishchenko K V, Kostenko O F, Levashov P R, Ovchinnikov A V and Sitnikov D S 2008 J. Phys. B: At. Mol. Opt. Phys. 41 125704
[5] Petrov Yu V, Khokhlov V A, Inogamov N A, Khishchenko K V and Anisimov S I 2016 J. Phys.: Conf. Ser. 774 012099
[6] Povarnitsyn M E, Itina T E, Sentis M, Khishchenko K V and Levashov P R 2007 Phys. Rev. B 75 235414
[7] Ashitkov S I, Komarov P S, Struleva E V, Agranat M B, Kanel G I and Khishchenko K V 2015 J. Phys.: Conf. Ser. 653 012001
[8] Migdal K P, Petrov Yu V, Il’nitsky D K, Zakhovsky V V, Inogamov N A, Khishchenko K V, Knyazev D V and Levashov P R 2016 Appl. Phys. A 122 408
[9] Sin’ko G V, Smirnov N A, Ovechkin A A, Levashov P R and Khishchenko K V 2013 High Energy Density Phys. 9 309–14
[10] Inogamov N A et al 2013 Contrib. Plasma Phys. 53 796–810
[11] Krasyuk I K, Pashinin P P, Semenov A Yu, Khishchenko K V and Fortov V E 2016 Laser Phys. 26 094001
[12] Knyazev D V and Levashov P R 2014 Phys. Plasmas 21 073302
[13] Witte B B L, Fletcher L B, Galtier E, Gamboa E, Lee H J, Zastrau U, Redmer R, Glenzer S H and Sperling P 2017 Phys. Rev. Lett. 118 225001
[14] Mooradian A 1969 Phys. Rev. Lett. 22 185
[15] Rosei R 1974 Phys. Rev. B 10 474
[16] Boyd G T, Yu Z H and Shen Y R 1986 Phys. Rev. B 33 7923
[17] Apell P, Monreal R and Lundqvist S 1988 Phys. Scr. 38 174
[18] Chan W L, Averback R S and Cahill D G 2009 Appl. Phys. A 97 287
[19] Guo C, Rodriguez G and Taylor A J 2001 Phys. Rev. Lett. 86 1638
[20] Isakov V A, Kanavin A P and Uryupin S A 2006 Quantum Electron. 36 928
[21] Hohlfeld J, Wellershoff S, Güdde J, Conrad U, Jähnke V and Matthias E 2000 Chem. Phys. 251 237
[22] Mohamed M B, Volkov V, Link S and El-Sayed M A 2000 Chem. Phys. Lett. 317 517
[23] Varnavski O P, Goodson T, Mohamed M B and El-Sayed M A 2005 Phys. Rev. B 72 235405
[24] Sitnikov D S, Yurkevich A A, Kotelev M S, Ziangirova M, Chefonov O V, Ilina I V, Vinokurov V A, Muradov A V, Itzkan I, Agranat M B and Perelman L T 2014 Laser Phys. Lett. 11 075902
[25] Maier S A 2007 Plasmonics: Fundamentals and Applications (Springer Science)
[26] Ashcroft N W and Mermin N D 1976 Solid State Physics 1st ed (Philadelphia: Saunders Colledge Publishing)
[27] Schoenlein R W, Lin W Z, Fujimoto J G and Eesley G L 1987 Phys. Rev. Lett. 58 1680
[28] Groeneveld R, Sprik R and Lagendijk A 1995 Phys. Rev. B 51 17
[29] Sun C K, Vallee F, Asioli L, Ippen E P and Fujimoto J G 1994 Phys. Rev. B 51 15337
[30] DelFatti N, Voisin C, Achermann M, Tsourtzakis S, Christofilos D and Vallee F 2000 Phys. Rev. B 61 16956
[31] Zhakov V P and Chulkov E V 2009 Phys. Usp. 52 113–46
[32] Mahan G D 1978 Phys. Rev. B 15 4821
[33] Camley R E and Mills D L 1978 Phys. Rev. B 15 4821
[34] Bridinov V I, Galanin M D and Genkin V N 1973 Phys. Usp. 110 3
[35] Landau L D and Lifshitz E M 1989 Course of Theoretical Physics vol 3 (Moscow: Nauka)
[36] Landau L D and Lifshitz E M 1989 Course of Theoretical Physics vol 4 (Moscow: Nauka)
[37] Blatt F J 1971 Physics of Electronic Conduction in Solids (Moscow: Mir)
[38] Lässer R, Smith N V and Benbow R L 1981 Phys. Rev. B 24 1895
[39] Kane E O 1962 Phys. Rev. 127 131
[40] Koyama R Y and Smith N V 1970 Phys. Rev. B 2 3049
[41] Mermin N D 1970 Phys. Rev. B 1 2362
[42] Anisimov S I and Rethfeld B 1997 Proc. SPIE 3093 192
[43] Beversluis M R, Bouhelier A and Novotny L 2003 Phys. Rev. B 68 115433
[44] Haug T, Klemm P, Bange S and Lupton J M 2015 Phys. Rev. Lett. 115 067403
[45] Huang J, Wang W, Murphy C J and Cahill D G 2014 Proc. Natl. Acad. Sci. U. S. A. 111 906–11
[46] Ziman J 1972 Principles of the Theory of Solids (Cambridge: Cambridge University Press)
[47] Abrikosov A A 1976 Fundamentals of the Theory of Metals (Moscow: FIZMATLIT)
[48] Born M and Wolf E 1964 Principles of Optics (Oxford: Pergamon Press)
[49] Watanabe H, Susa M, Fukuyama H and Nagata K 2003 Int. J. Therm. 24 223–37
[50] Ashitkov S I, Komarov P S, Struleva E V, Yurkevich A A and Agranat M B 2015 High Temp. 53 887–90
[51] Ashitkov S I, Komarov P S, Struleva E V, Yurkevich A A and Agranat M B 2016 High Temp. 54 899–901