Ionization of atoms on the surfaces of metals in a laser radiation field

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An expression is derived for the degree of surface ionization resulting from irradiation of the surface with high-intensity hf laser radiation. It is assumed that the evaporation (desorption) of an atom from the metal substrate is of thermal nature. It is shown that deformation of the electron energy distribution function and appearance of radiation-induced channels of electron exchange between an atom and the surface makes the ionization process much more effective than predicted by the Saha–Langmuir relationship. The case of evaporation of copper from a copper substrate is analyzed in detail.

1. INTRODUCTION

The dynamics of electron transitions in the surface layer, particularly the dynamics of electron exchange in the surface–adatom system, is currently one of the most active and interesting topics in the physics of surfaces.[1–3] This topic is particularly important because of the development of laser methods for the analysis and modification of surfaces, such as laser heterogeneous catalysis, laser mass spectroscopy, selective surface photoionization, etc. The main physical feature of the topic is that both the adatom and the surface itself are subject to an electromagnetic radiation field which, for a number of reasons (such as enhancement of the field at surface irregularities and generation of surface electromagnetic waves) cannot be regarded as *a priori* weak even at moderate laser radiation intensities.

One must point out two possible ways the electromagnetic field can influence the nature of electron exchange near the surface. One the one hand, this is a change in the quantum-mechanical structure of an adatom and, on the other, it is a change in the electron energy distribution function in the irradiation zone. Recent investigations show that both these effects are quite important and cannot be ignored on the basis of general considerations. We shall try to analyze the situation using the example of such a familiar effect as the emission of positively charged ions from the surface under the influence of laser radiation.

The emission of positive ions was one of the first effects observed when the laser began to be used as a physical instrument.[4] The possibility of formation of ions is almost self-evident if we bear in mind that very high temperatures can be reached at the focal spot of laser radiation.[5] The subsequent rapid realization of laser capabilities and the associated hope for laser thermonuclear fusion has led to the concentration of interest on problems associated with the generation of ions in a plasma. The established view on the processes of surface ionization is that they can all be described by the Saha–Langmuir model, as apparently confirmed by the experiments of Knecht many years ago.[6] Doubts which have been raised have been put forward as hypotheses[7] and, to the best of our knowledge, have not been analyzed in detail. True, there have been some recent indications that the process of laser-stimulated desorption may be of nonthermal nature,[8] but charge exchange has not been considered.

However, there are many experimental observations demonstrating that the interaction of laser radiation with the surface is basically nonthermal. This applies also to the emission of "hot" electrons which have essentially a nonthermal spectrum; it is also true of the emission of negative ions observed under conditions when deformation is not very likely;[11] finally, it applies to the "hot" luminescence of metals,[12,13] which is impossible to observe under equilibrium conditions. All these reports make it essential to carry out a thorough analysis of the process of laser-stimulated ion emission allowing for the influence of the electromagnetic field on the dynamics of electron transitions.

2. ADIABATIC APPROXIMATION

We derive a relationship governing the surface ionization coefficient which explicitly allows for electron states of the surface and of the desorbed particles. We assume that the emission of positive ions is the result of two independent processes, evaporation of atomic particles and their ionization as a result of charge exchange with the surface. We also assume that the exchange is a purely resonant process, i.e., it occurs without a change in the energy of an electron that undergoes such a transition. We therefore ignore the possible contribution of the Auger processes. It should be pointed out that, because of the strong broadening of an atomic level of a particle located near the surface, the range of resonant transitions may be very wide.

We postulate that the evaporation of particles from the surface is a purely thermal process and can be described by an equation of the form

$$N=B\omega T\exp(-\Lambda/kT), \tag{1}$$

where N is the number of particles evaporated at a temperature T, B is a numerical coefficient; ω is a frequency factor, k is the Boltzmann constant, and Λ is the heat of evaporation.

We assume that in escaping from the surface an atomic particle may, as a result of resonant exchange, lose an electron and go over to an ionic state with a probability W_s and again capture an electron (at a vacant level) with a probability W_c. It is worth noting that in the adiabatic approximation these probabilities are governed by the configuration of the adatom–surface system, i.e., they are a function only of position and are independent of the velocity. Consequently, we find that the population of a selected level of an adatom

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moving away from the surface is related to the probabilities W_s and W_c by the following simple differential equation:

$$\frac{\partial\beta}{\partial t}=W_c(r)(1-\beta)-W_s(r)\beta, \tag{2}$$

the solution of which is

$$\beta(t)=\beta_0\exp\left\{-\int_0^t[W_c(\tau)+W_s(\tau)]d\tau\right\}$$
$$+\int_0^t d\tau W_c(\tau)\exp\left\{-\int_\tau^t dt'\exp[W_c(t')+W_s(t')]\right\}. \tag{3}$$

In view of the indeterminacy of the path $r(t)$, we estimate $\beta(\infty)$ [because we have to determine specifically the quantity $\beta(\infty)=\lim_{t\to\infty}\beta(t)$] using the mean-value theorem:

$$\beta(t)=\frac{W_c(\tau^*)}{W_c(\tau^*)+W_s(\tau^*)}$$
$$\times\left\{1-\exp\left[-\int_0^t dt'(W_c(t')+W_s(t'))\right]\right\}, \tag{4}$$

where $\tau^*\in[0,t]$ is a certain average value.

We can show that $\beta(\infty)$ differs from $\beta(t)$ by an amount smaller than

$$\delta=\frac{W_t}{av}=\Omega A\exp[-ar(t)]/av, \tag{5}$$

where W_t is the probability that an electron tunnels across a rectangular barrier of width $r(t)$, Ω is the classical frequency of electron oscillations in an atom, $A=16I\times(\varphi+\varepsilon_F-I)/(\varphi+\varepsilon_F)^2$; $a=(2mI)^{1/2}/\hbar$, I is the ionization potential of an atom, φ is the work function; ε_F is the Fermi level, m is the mass of an electron, and v is the particle velocity. If we select t to be sufficiently large [$r(t)\to\infty$ in the limit $t\to\infty$], we can make this correction negligibly small. On the other hand, we can show that if the condition

$$\Omega A\gg av \tag{6}$$

is satisfied, we can ignore the exponential function on the right-hand side of Eq. (4).

The inequality (6) means that the rate of exchange of electrons (charge exchange) during the removal of an atomic particle away from the surface should be much greater than the particle removal rate, which is known to be satisfied at velocities corresponding to thermal processes. An atomic particle moving away from the surface and experiencing the process of resonant charge exchange has in general an indeterminate path because of the various forces exerted by the surface on an ion and on a neutral atom. However, if the condition (6) is satisfied, we can assume that, irrespective of the velocity of the departing particle, this particle is in the field of a certain effective potential which determines uniquely the equation of motion, so that

$$r=r(t),$$

where $r(t)$ is a single-valued function of t.

In view of this, we can transform Eq. (4) to

$$\beta(t)=W_c(r_{cr})/[W_c(r_{cr})+W_s(r_{cr})], \tag{7}$$

where $r_{cr}=r(\tau^*)$ is the critical distance for resonant charge transfer and r_{cr} is a parameter of the theory.

It therefore follows that the degree of surface ionization defined as the ratio of the number of ions N^+ to the total number of evaporated neutral atoms N_0, is

$$\alpha=\frac{N^+}{N_0}=\frac{W_s(r_{cr})}{W_c(r_{cr})}\exp\left(\frac{\Lambda_a-\Lambda_i}{kT}\right), \tag{8}$$

where Λ_a and Λ_i are the heats of evaporation of an atom and an ion, respectively.

In the absence of the field the probabilities W_c and W_s are governed by the resonant exchange with the surface and are described by

$$W_c=g_a(\varepsilon')f_0(\varepsilon')W_t(r_{cr}), \tag{9}$$

$$W_s=g_i\nu(\varepsilon')(1-f_0(\varepsilon'))W_t(r_{cr}), \tag{10}$$

where g_a and g_i are, respectively, the statistical weight of an atom or an ion, ε' is the energy of an atomic level which is involved in a resonant transition of an electron from the metal $\nu(\varepsilon')$ is the density of the electron states in the metal, $f_0(\varepsilon)$ is the distribution function of the electron energy in a metal and $W_t(r_{cr})$ is the probability of tunneling of an electron. If we assume that $f_0(\varepsilon)$ is the Fermi function and substitute Eqs. (9) and (10) into Eq. (8), we readily obtain the familiar Saha–Langmuir expression for the surface ionization coefficient:

$$\alpha=\frac{g_i}{g_a}\exp\left(\frac{\varphi-I}{kT}\right). \tag{11}$$

It should be noted that the choice of the probabilities W_c and W_s in the form given by Eqs. (9) and (10) is based on the assumption that broadening of the energy level of an atom which is at a critical distance r_{cr} can be ignored, whereas the Stark shift of the level $\Delta\varepsilon=\varepsilon_a'-\varepsilon_a$ (ε_a' and ε_a are the energies of a resonant level of an atom at a distance r_{cr} from the surface and of an isolated atom, respectively) cannot be regarded as small. These assumptions are usually made in discussing the process of surface ionization[1] and in the subsequent discussion we shall allow for the position of the level ε_a', which reflects the influence of the surface on the electron structure of the evaporated atom.

3. EVAPORATED ATOM IN AN ELECTROMAGNETIC FIELD

Equation (8) is derived without any assumptions restricting the values of W_c, W_s, Λ_a, and W_i, so that we can apply it also in the case of evaporation (desorption) in an electromagnetic field.

We assume that Λ_a and Λ_i are not affected by the field. The changes in W_c and W_s are due to deformation of the distribution function and also due to the multichannel nature of the exchange process associated with the induced absorption and emission of radiation quanta under tunneling conditions.

This multichannel charge exchange can be described as occurring between the surface of a metal heated by the incident radiation with a deformed distribution function and the compound atom–field system. When the energy of a laser radiation photon is considerably less than the difference between the energies of the ground and first excited states of an atom, we can assume that the amplitudes of the probabili-

ties of finding an electron in an excited state are small and the wave function is governed by the process of the interaction of radiation with an electron in the ground state. We regard this approximation as of single-level nature and the corresponding wave function of an electron is then of the form[14]

$$\psi(\mathbf{r},t)=\sum_{n=-\infty}^{\infty}u_n(\mathbf{r})\exp[-i(\varepsilon_0+n\hbar\omega)t], \tag{12}$$

where the different functions u_n are orthogonal to one another and represent the amplitudes of the probabilities of finding an electron in a state of energy $\varepsilon_n=\varepsilon_a+n\hbar\omega$, ε_0 is the quasienergy approximately equal to the energy of an atomic level unperturbed by the field; ω is the radiation frequency, the average energy of an atomic electron in the field is

$$E=\frac{\omega}{2\pi}\int_{-\pi/\omega}^{\pi/\omega}d\tau\langle\psi|H|\psi\rangle=\sum_{n=-\infty}^{\infty}\varepsilon_n p_n, \tag{13}$$

where $p_n=\langle u_n|u_n\rangle$, $H=H_0+V_f$, $H_0=-(\hbar^2/2m)\Delta+V_a(\mathbf{r})+V_s(r)$ is the unperturbed Hamiltonian of an atom near the surface, $V_a(\mathbf{r})$ is the potential of an atom, $V_s(\mathbf{r})$ is the surface potential, and $V_f(\mathbf{r},t)=V_f(\mathbf{r})e^{i\omega t}$ is the perturbing electromagnetic field. Note that in view of the orthogonality of $u_n(\mathbf{r})$ and $u_m(\mathbf{r})$ we have $E=\langle\psi|H|\psi\rangle$. In weak fields ($V_f<V_a$) the functions u_n can be found using perturbation theory. For example, u_0, $u_{\pm1}$, and $u_{\pm2}$ are described by

$$u_0(\mathbf{r})\approx\varphi_0(\mathbf{r}),$$

$$u_{\pm1}(\mathbf{r})\approx\sum_{\mu}V_{\mu\nu}\varphi_\mu(\mathbf{r})/(\varepsilon_\mu-\varepsilon_0\pm\hbar\omega),$$

$$u_{\pm2}(\mathbf{r})\approx\frac{1}{4\hbar\omega}\sum_{\mu}\frac{|V_{\mu0}|^2(\varepsilon_\mu-\varepsilon_0)\varphi_0(\mathbf{r})}{(\varepsilon_\mu-\varepsilon_0)^2-(\hbar\omega)^2}-\sum_{\mu,\nu}\frac{V_{\mu\nu}V_{\nu0}\varphi_\mu(\mathbf{r})}{(\varepsilon_\mu-\varepsilon_0\pm2\hbar\omega)(\varepsilon_\nu-\varepsilon_0\pm\hbar\omega)},$$

where φ_μ and ε_μ are the eigenfunctions and the eigenvalues of the Hamiltonian H_0 and $V_{\mu\nu}=\langle\varphi_\mu|V_f(\mathbf{r})|\varphi_\nu\rangle$ is a matrix element of a transition.

It therefore follows that an atom subjected to an electromagnetic field has an additional system of equidistant levels (Floquet levels) whose wave functions are given by Eq. (14). This circumstance has an important influence on the rates of charge exchange, which should not involve not only to the ground level, but also to the other Floquet levels (naturally, after allowing for their populations p_n). When these points are taken into account, the expressions for the probability of charge exchange given by Eqs. (9) and (10) can be generalized as follows:

$$W_c=g_a\sum_{n=-\infty}^{\infty}\nu(\varepsilon_n)f(\varepsilon_n)p_n W_t^{(n)}(r_{cr}), \tag{15}$$

$$W_s=g_i\sum_{n=-\infty}^{\infty}\nu(\varepsilon_n)[1-f(\varepsilon_n)]p_n W_t^{(n)}(r_{cr}). \tag{16}$$

Here p_n represents the statistical weight of the n-th charge exchange channel, $W_t^{(n)}(r_{cr})$ is the probability of an electron of energy ε_n crossing a barrier, and $f(\varepsilon)$ is the distribution function of electrons in the investigated metal.

4. DISTRIBUTION OF ELECTRONS IN A METAL SUBJECTED TO AN ELECTROMAGNETIC FIELD

The problem of the nature of the electron distribution function of a metal subjected to the field of a high-power electromagnetic radiation is still a matter of discussion. Some authors[15,16] retain the equilibrium form of this function even for interaction times comparable with the electron–electron relaxation time $\tau_{ee}\sim10^{-12}$–10^{-14} s. However, the interaction of an equilibrium subsystem in a metal with a photon flux far from equilibrium when the photon energy is comparable with the average energy of electrons ($\hbar\omega\sim\varepsilon_F$) may give rise to an electron distribution function, the form of which cannot be determined from any general considerations.

The true electron distribution function can be found by solving the kinetic problem describing the behavior of an electron gas in a metal subjected to the field of high-intensity laser radiation and allowing for the quantum nature of the interaction between electrons and photons.[17] This problem is formulated in Ref. 18 and can in fact be reduced to finding the steady-state electron distribution function in the presence of a source and a sink of particles in the energy space which would allow, on the one hand, for the pumping of an electron gas with laser radiation and, on the other hand, for dissipative collisional processes. Since the required probabilities W_c and W_s are governed by the classical distribution function $f(\varepsilon)$, it follows that is sufficient to write down the relevant differential–difference equation for this function, which after linearization in the quasisteady-state approximation becomes[18]

$$f(\varepsilon)-f_0(\varepsilon)+\varkappa\{f(\varepsilon+\hbar\omega)-f(\varepsilon)+u(\varepsilon-\hbar\omega)[f(\varepsilon-\hbar\omega)-f(\varepsilon)]\}=0, \tag{17}$$

where $f_0(\varepsilon)=1/\{1+\exp[(\varepsilon-\varepsilon_F)/kT]\}$ is the Fermi function, $u(\varepsilon)$ is the Heaviside function, and $\varkappa$ is a small dimensionless parameter:

$$\varkappa=(1-R)q\tau_{ee}/(\delta n_1\hbar\omega). \tag{18}$$

Here, q is the laser radiation power density, δ is the effective depth of absorption of laser radiation, and n_1 is the effective density of electrons participating in the absorption process.

We can easily see that $\varkappa$ represents the probability for one photon to be absorbed by one electron in a time equal to τ_{ee} and, as usual, we have $\varkappa\ll1$. Then the solution of Eq. (17) can be found in the form of a series in $\varkappa$:

$$f(\varepsilon)=\sum_{n=0}^{\infty}f_n(\varepsilon)\varkappa^n,$$

$$f_n(\varepsilon)=\sum_{m=0}^{2n}(-1)^m B_{2n}^{\ m}(\varepsilon)f_0[\varepsilon+(n-m)\hbar\omega]. \tag{19}$$

The coefficients $B_{2n}^{\ m}(\varepsilon)$ satisfy the following recurrence relationships:

$$B_{2n}^{\ m}(\varepsilon)=B_{2n-2}(\varepsilon+\hbar\omega)+[1+u(\varepsilon-\hbar\omega)]\times B_{2n-2}^{m-1}(\varepsilon)+u(\varepsilon-\hbar\omega)B_{2n-2}^{m-2}(\varepsilon-\hbar\omega),$$

$$B_{2n}^{m}(\varepsilon)=0, \quad \text{if} \quad m<0 \quad \text{or} \quad m>2n.$$

If the electron gas is degenerate, then the following estimate applies:

$$f(\varepsilon)=f_0(\varepsilon)+\begin{cases}-\varkappa^n, & \varepsilon<\varepsilon_F,\\ \varkappa^n, & \varepsilon>\varepsilon_F,\end{cases} \tag{20}$$

where $n=[|\varepsilon_F-\varepsilon|/\hbar\omega]+1$ and $[b]$ denotes the integral part of b.

Substituting Eqs. (15) and (16) into Eq. (8), we obtain the final expression for the surface ionization coefficient:

$$\alpha=\frac{g_i}{g_a}\exp\left(\frac{\Lambda_a-\Lambda_i}{kT}\right)\frac{\sum_{n=-\infty}^{\infty}[1-f(\varepsilon_n)]p_n\nu(\varepsilon_n)W_i^{(n)}(r_{cr})}{\sum_{n=-\infty}^{\infty}f(\varepsilon_n)p_n\nu(\varepsilon_n)W_i^{(n)}(r_{cr})}. \tag{21}$$

5. SURFACE IONIZATION OF COPPER IN A LASER RADIATION FIELD

We obtain quantitative estimates of the influence of an electromagnetic field on the charge state of evaporated particles by considering the evaporation of a copper atom from a copper substrate. The expression for the degree of ionization of Eq. (21) can then be simplified greatly, because at practically all temperatures we can regard the function $f_0(\varepsilon)$ as degenerate and we then have $(q/V_a)\ll 1$. Equation (21) thus becomes

$$\alpha=\alpha_{S\text{-}L}+\delta\alpha_1+\delta\alpha_2, \tag{22}$$

where $\alpha_{S\text{-}L}$ is the degree of ionization in accordance with the Saha–Langmuir theory, defined from the expression (11), while $\delta\alpha_1$ and $\delta\alpha_2$ are the additional terms:

$$\delta\alpha_1=\frac{g_i}{g_a}\exp\left(\frac{\Lambda_a-\Lambda_i}{kT}\right)\frac{1-f_0(\varepsilon_N)}{f_0(\varepsilon_0)}\frac{p_N\nu(\varepsilon_N)}{p_0\nu(\varepsilon_0)}\frac{W_i^{(N)}(r_{cr})}{W_i^{(0)}(r_{cr})}, \tag{23}$$

$$\delta\alpha_2=\frac{g_i}{g_a}\exp\left(\frac{\Lambda_a-\Lambda_i}{kT}\right)\varkappa^N, \quad N=\left[\frac{|\varepsilon_F-\varepsilon_0|}{\hbar\omega}\right]+1. \tag{24}$$

The first additional term $\delta\alpha_1$ in Eq. (22) is related to the multichannel nature of the exchange process and an electron is captured by the zeroth Floquet level, and the loss of an electron occurs from the N-th level, while the second term $\delta\alpha_2$ appears because the distribution function $f(\varepsilon)$ deviates from the equilibrium form. Figure 1 shows the energy diagram of a copper atom evaporated from a copper substrate. The width of the conduction band of copper is 10.6 eV, the work function is $\varphi=4.5$ eV, and the ionization potential is $I=7.78$ eV. The ground state of copper ε_a is $3s(S^0_{1/2})$ and the first excited state ε_a^* is $4p^2(P^0)$; the latter lies 0.49 eV above the Fermi level. Under the action of an electromagnetic field a valence electron may be transferred to a quasi-Floquet level (dashed curve), and if the latter is above the Fermi level an electron tunnels resonantly into the metal.

It is quite obvious that the competing process is the ionization described by the Saha–Langmuir relationship (11). Therefore, the problem is to find the ranges of values of the power density q in which dominance of one or another ionization channel may be observed. We note first of all that

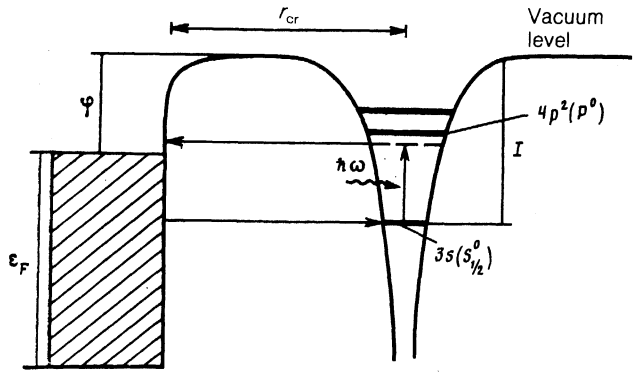

FIG. 1. Diagram of a copper atom evaporated from a copper substrate.

$\alpha_{S\text{-}L}$ is related to the intensity of the laser radiation via the surface temperature T and

$$T(t)=T_0+\frac{1-R}{(\pi\chi c)^{1/2}}\int_0^t\frac{q(t')}{(t-t')^{1/2}}dt', \tag{25}$$

where T_0 is the initial temperature of the surface, R is the reflection coefficient, χ and c are the thermal diffusivity and the thermal conductivity of a metal.[4]

Assuming that the laser radiation pulse has the Gaussian time profile $[q=q_m\exp(-t^2/\tau_i^2)]$, we can obtain simple relationships between the maximum temperature of the surfaces T_m and the quantities q_m and $\varkappa_m$:

$$T_m\approx\frac{(1-R)\tau_i^{1/2}}{2^{1/4}\cdot(\pi\chi c)^{1/2}}q_m=\frac{\delta n_1\hbar\omega\tau_i^{1/2}}{2^{1/4}\cdot(\pi\chi c)^{1/2}\tau_{ee}}\varkappa_m=Aq_m. \tag{26}$$

Hence it is easy to derive the relationship between the parameters of a laser radiation pulse τ_i and q_m ensuring that one particular ionization process will dominate. Comparing Eq. (11) with Eqs. (23) and (24), substituting Eq. (26), and ignoring a factor of order unity, we obtain an expression for τ_i^* which is the critical length of a pulse governing the maximum duration τ_i and the power density q_m of laser radiation, in accordance with the above condition:

$$\tau_i\gtrsim\tau_i^*=\{(I-\varphi)/[kAq_m\ln(p_1+\varkappa_m)]\}^2, \tag{27}$$

$$p_1\approx\frac{8\pi e^6}{c(\varepsilon_a^*-\varepsilon_a)^2(\varepsilon_a^*-\varepsilon_a-\hbar\omega)^2}.$$

The results of calculations of τ_i^* are plotted in Fig. 2. The calculations were carried out for copper atoms and different reflection coefficients R (this coefficient can be varied quite readily if only by altering the angle of incidence of a laser radiation beam on the surface). The shaded region in Fig. 2 indicates where the thermal ionization process dominates, but it is quite clear that this is limited greatly by the processes of damage to the surface and plasma formation.

From the experimental point of view it is interesting to consider the behavior of α as the intensity q_m increases when the length of the laser radiation pulses τ_i is kept constant. Figure 3 shows the relationship between $\ln\alpha$ and the reciprocal of the maximum surface temperature, $1/T_m$, which corresponds to the generally accepted representation of dependences of this type.[1] The corresponding values of q_m are shown on the lower abscissa. Curves *1* and *2* represent values of α calculated allowing for corrections due to different re-

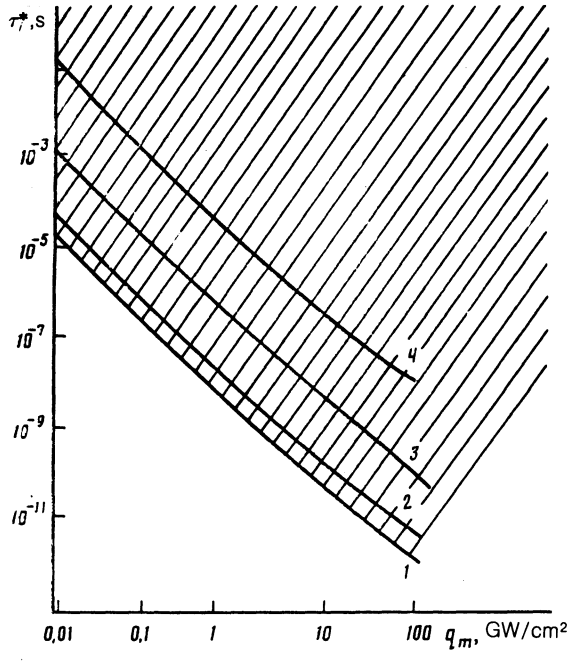

FIG. 2. Dependence of τ_i^* on the maximum amplitude of laser radiation q_m, plotted for different reflection coefficients R: *1*) $R = 0$; *2*) 0.5; *3*) 0.9; *4*) 0.99.

flection coefficients $R = 0.5$ and $R = 0$, and curve *3* represents the Saha–Langmuir surface ionization coefficient $\alpha_{S\text{-}L}$. Up to temperatures $T \lesssim 4000$ K the contribution of "nonthermal" processes dominates. An increase in the temperature of the metal reduces the population of the level with the energy ε_a', the quantity $1 - f_0(\varepsilon_0)$ becomes comparable with $1 - f_0(\varepsilon_n)$ and then larger than the latter, so that it now assumes the role of the main channel of the loss of electrons by an atom, resonant exchange takes place with the ground level ε_a', and the value of α approaches asymptotically $\alpha_{S\text{-}L}$. Note that calculations are carried out for a specific value $\tau_i = 10^{-7}$ s and the nature of the dependence for dif-

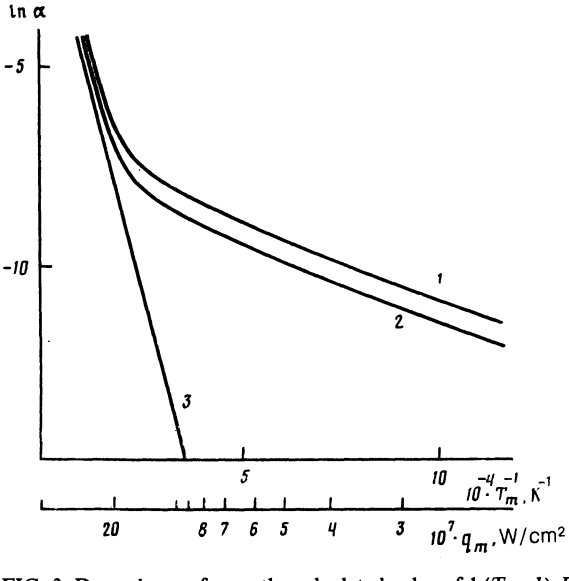

FIG. 3. Dependence of α on the calculated value of $1/T_m$: *1*) $R = 0.5$; *2*) $R = 0$; *3*) $\alpha_{S\text{-}L}$. The lower abscissa gives the corresponding values of q_m.

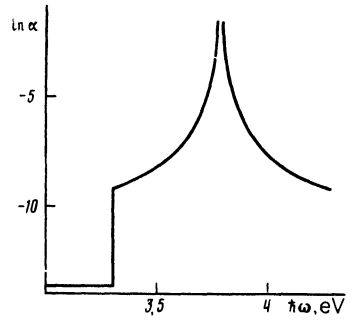

FIG. 4. Dependence of ln α on the energy of laser radiation photon $\hbar\omega$.

ferent values of τ_i will be different; however, their behavior is readily found by analyzing Fig. 2.

The situation described above applies to the case when the additional ionization channel $\delta\alpha_1$ is of the one-photon nature, i.e., when the first Floquet level lies above the Fermi level of the metal: $\hbar\omega > I - \varphi$. It is quite obvious that in the opposite case ($\hbar\omega < I - \varphi$) the contribution of $\delta\alpha_1$ decreases considerably, because the ionization begins to be dominated by the higher-order processes. Similarly, it follows from Eq. (24) that $\delta\alpha_2$ is governed by a higher degree of $\varkappa$. On the other hand, the value of $\alpha_{S\text{-}L}$ is loosely related to ω and the relationship is only via the frequency dependence $R(\omega)$, which as a rule has no sharp singularities. Figure 4 shows the dependence of ln α on the radiation photon energy. This dependence is calculated assuming that $\tau_i = 10^{-7}$ s and $q_m = 10^8$ W/cm². The sharp kink at $\hbar\omega \approx 3.3$ eV is related to activation of a one-photon ionization channel. The value of ln α obtained in the range $\hbar\omega < 3.3$ eV is close to ln $\alpha_{S\text{-}L}$.

At $\hbar\omega = 3.79$ eV the value of ln α diverges, since the radiation frequency is then equal to the frequency of a transition to the first excited state of the Cu atom. The one-level approximation is no longer valid, but allowance for resonance can be made by considering a two-level problem exactly as in Ref. 19. There is no need to apply the Floquet theorem to find the transient wave function, because the transition process is first-order. The expression for the ionization coefficient in the case of our resonance is of the form

$$\alpha = \frac{g_i}{g_a} \exp\left(\frac{\Lambda_a - \Lambda_i}{kT}\right) \times \frac{1 - f(\varepsilon_a' + \hbar\omega + \hbar\Delta\omega/2)}{f(\varepsilon_a' + \hbar\Delta\omega/2)} \frac{|V_{12}|^2}{|V_{12}|^2 + 2(\hbar\Delta\omega/2)^2}, \quad (28)$$

where $\Delta\omega$ is the frequency detuning or offset ($\Delta\omega = \omega_{12} - \omega$), ω_{12} is the transition frequency, V_{12} is the matrix element of the transition, and $f(\varepsilon)$ is the distribution function. The positions of all the singularities in the frequency dependence of α are somewhat arbitrary because calculations are carried out using the data on the energy spectrum of an isolated Cu atom, and because the positions of the levels of which ε_a are generally different from the levels ε_a' of an atom located near the surface. Therefore, an experimental investigation of the $\alpha(\omega)$ dependence makes it possible to find the energy spectrum of an atom disturbed by the influence of the surface, which is of itself an important problem.

These effects can be observed in a limited range of pho-

ton energies $\hbar\omega$ and of the values of τ_i and q_m, which can be found by comparing the curves plotted in Figs. 2 and 4. Under specific calculation conditions assumed in plotting the graphs in Fig. 3 these effects are limited only to temperatures $T < 4000$ K, which is associated with the exponential rise of the contribution of the thermal ionization channel, while the contributions of $\delta\alpha_1$ and $\delta\alpha_2$ increase as functions of the laser radiation intensity in accordance with the power law. However, we should point out that 4000 K is much higher than even the boiling point of copper and that the formation of ions at certain laser radiation intensities is related to the processes of charge exchange in a plasma, which is outside the scope of the present paper.

6. CONCLUSIONS

The mechanism of charge exchange between a departing atom and the surface subjected to an electromagnetic radiation field provides an additional "easier" surface ionization channel, which is much more effective than that predicted by the Saha–Langmuir formula. Moreover, the ionization in this channel has the property of frequency selectivity, and it requires photon energies $\hbar\omega$ which are considerably less than the ionization potential.

The multichannel nature of the exchange and the nonequilibrium nature of the distribution function should have a significant influence on the process of formation not only of positive but also of negative ions and of excited atoms, whose anomalous formation as a result of laser irradiation of a surface was already pointed out in Ref. 11.

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