Theory of ultrashort nonlinear multiphoton photoelectric emission from metals

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A phenomenological theory of the nonlinear multiphoton electron emission at the surface of a metal is proposed. We consider principally the situation of photocathodes illuminated by UV, visible, or near-infrared, picosecond, or femtosecond laser pulses. For ultrashort pulse duration, the temporal profiles of the electron gas and the lattice temperatures have to be considered separately, because of the local nonequilibrium between the electrons and the phonon gas. Both reflectivity and work function depend on the electron state density in the conduction band. To take into account the observed nonlinear enhancement of the photocurrent density consecutive to this nonequilibrium, we propose to replace the classical multiharmonic integer order N appearing in the generalized Fowler-Dubridge expression of the photoelectric current by a noninteger order k which depends on the absorbed laser intensity and can be related to N by a simple expression. This method makes the treatment of experimental data easier, i.e., the determination of the amplitude of the nonlinearity versus the incident and absorbed laser intensities, the state of polarization, and the angle of incidence of the laser beam. The method also gives a way to compare and analyze experimental data in the range of very high laser intensities until the laser damage threshold of metals, i.e., 100–300 GW/cm^2. It also makes possible an estimation of the N-photon photoemission cross sections. The application of this model to our experimental data from Au and W, reported earlier, is given as a justification of our model assumptions.

I. INTRODUCTION

We propose to broaden the field of application of the phenomenological and generalized multiharmonic photoelectron generation theory[1] to take into account the nonlinear behavior of the photocurrent, observed when metals are illuminated by ultrashort laser pulses with very high peak intensities.[2,3] We are also looking for a simple method to analyze the data corresponding to a large range of experimental situations. The main question, then is, does the use of laser pulses with very high intensity and ultrashort length change the photoemission process? A consequence of the shortening of the laser pulse duration τ_p is the spectral broadening of the radiation. The monochromaticity of the radiation is no longer effective, and makes a description of the phenomenon from quantum analysis much more complicated.[4] Another consequence is the absolute necessity of taking into account the coupling of absorbed photons with the surface as well as the behavior of elementary constituents of the metal, i.e., the electrons, principally those in the s- and d-conduction bands, and the lattice. A major result is the net enhancement of the laser-surface-damage threshold, typically from about 1 GW/cm^2 in the picosecond range to a few 100 GW/cm^2 in the subpicosecond range.[5,6] In addition to fundamental interest in the physical process, photoemission with lasers of very high intensity and ultrashort length constitutes a real advantage for the production of very high peak current density up to 10 kA/cm^2 per pulse and of mean current of a few 100 A/cm^2. An additional question, then is, does the enhancement of the photoelectron density correspond to an effective increase of the photoemission cross section? We will show that this enhancement depends on the temporary nonequilibrium between the electrons and the phonon gas. Metals only are convenient for the production of ultrashort electron pulses because of the very short photon-to-electron conversion delay, which is typically of a few femtoseconds, while it is about 0.5–1 ps in semiconductor and dielectric materials, respectively.

All aspects emphasized above have to be understood for the efficient application of ultrashort high electron multiharmonic generation to the realization of modern electron sources. These sources are useful in the development of free-electron lasers, rf-linac high power tubes, and more recently ultrashort x-ray sources.[7] For all these reasons, our attention will be focused at first on an energetic description of the ultrafast photoemission process. The situation of femtosecond thermionic emission, as described by Riffe *et al.*,[8] is not considered here.

A knowledge of photoelectron energy distribution at the output of a photocathode is essential to estimate the strengths of photon-to-electron and electron-to-phonon couplings at the surface of metal. However, when the intensity of photoelectrons is high, the measurement of the electron energy distribution, to a sufficient precision, is not realistic because of the space-charge effects.[9,10]

A discussion of the expression for the multiphoton photoemission current density, proposed by Yen[1] and based on basic works by Fowler[11] and Dubridge[12] (FD), is reported in Sec. II. This formulation, successively applied to nanosecond and subnanosecond pulse ranges, will be used as a basis for the development of a best suited photocurrent expression for picosecond and subpicosecond pulse lengths. Several remarks concerning the founding conditions of the FD current density expression

are reported in Sec. III. These give rise to a discussion of the main representative physical parameters, i.e., the photoemission probability, the coupling of the incident laser radiation with the surface of the photocathode, and the thermodynamic nonequilibrium between the electron gas and the lattice. An expression for the current density is derived in Sec. IV. Application to our recent experimental data for Au and W will be given as a justification for the validity of our assumptions.

II. LINEAR AND NONLINEAR STRONG-FIELD PHOTOEMISSION

Photoelectric emission consecutive to the ionization of atoms in a strong field was first considered by Keldysh.[13] It was extended to the treatment of a strong radiation field interacting with a metal by Bunkin and Federov[14] and Silin.[15] A review was given later by Anisimov, Benderskii, and Farkas,[16] who introduced the dimensionless parameter

$$\Gamma=\Phi/\Lambda \ , \tag{1}$$

where Φ is the work function of the material and

$$\Lambda=\frac{e^2E_z^2}{2m\omega^2} \ , \tag{2}$$

where E_Z is the electric field component of the electromagnetic (EM) wave, normal to the surface with frequency ω; e and m are the charge and the mass of the electron, respectively; and Λ is the oscillation (quivering) energy of a free electron in the EM field. The main conclusions were the following.

(i) In the limit when $\Gamma \ll 1$, the current density is the Fowler-Nordeim equation for the dc field emission current.

(ii) In the opposite limit, when $\Gamma \gg 1$, the expression for the current density can be interpreted as the N-photon surface effect photoemission current.

The above conclusions tell us that, for $\hbar\omega$ radiation, when the EM field is weak enough such that the quivering energy Λ of the electron is much less than the work function, multiphoton photoemission results. When the field strength is increased to $\Lambda > \Phi$, the electron can essentially tunnel through the surface barrier during the half period when the electric field is normal to the surface. That is the so-called optical field emission (OFE). However, the triumph of the above treatment in the unification of the phenomena of multiphoton photoemission and field emission can be observed only in diluted media. Because of the recently observed laser damage threshold, OFE from the surface of a solid is very unlikely. To effectively reach the condition $\Gamma < 1$, the amplitude of electric field would be $E_Z > 10^7$ V/cm. Considering a visible or near-IR incident radiation, one calculates easily that such a field strength is only possible with a laser peak intensity $I_\omega > 300$ GW/cm^2, i.e., for a laser intensity higher than the subpicosecond laser damage threshold of most metals.[5] Recall that laser damage thresholds of metals in nanosecond and picosecond regimes are about 50 MW/cm^2 and 1 GW/cm^2, respectively.[17] Conclusions reported in Ref. 18 for electron emission from a gold sample illuminated by 10.6-μm laser pulses of 5-ns duration are not realistic for the conditions presented by the authors, because of the laser damage limit of gold in the far-IR range.[19] The thermal action of the laser beam in the nanosecond range was probably the origin of the measured current. A calculation made earlier by Shishido[20] leads to the conclusion that an emission current due to tunneling might be observed using a picosecond laser pulse with a wavelength higher than 600 nm, peak power ~ 1 GW, and duration $\sim 10^{-11}$ s, focused into a diameter of 300 μm at a grazing angle of about 10^{-2} rad. This conclusion is wrong because the effective incident laser peak intensity is larger than 1 TW/cm^2, and is consequently much higher than the laser damage threshold of the most resistant metal. For a laser intensity of 1 GW/cm^2 we calculated that the field-emission current from tungsten illuminated by the same laser pulses is about 10^5 times lower than the two-photon photocurrent intensity.

Thus, one can certainly assert that the action of laser pulses with durations above a few tens femtoseconds and peak intensities lower than the damage threshold results only in N-photon photoelectric and thermionic effects.[8]

A distinction should be made at this point between the terms nonlinear and multiphoton to avoid any confusion. A pure multiphoton process has an integer power dependence on the laser intensity, whereas a nonlinear process may have any dependence on the laser intensity. Note that very few works examined effective nonlinear photoemission.

Theories about photoelectric emission can be divided into phenomenological approaches and quantum-mechanical treatments (QMT's). The review by Anisimov, Benderskii, and Farkas[16] has to be considered again. To summarize, recall that the perturbation treatment of multiphoton photoemission from metals has been carried out by many authors: Jones and Reiss,[21] Kantorovich,[22] and more recently Mishra and Gersten[23] and Daniele *et al.*[24] In almost all these quantum-mechanical treatments, a Sommerfeld model of the metal was used, necessarily assuming that only a surface effect mechanism is operative. The specific situations of an incident strong field was not really considered. Finally, expressions for the current density are reminiscent of the result of the generalized FD theory. The only difference is that in the FD theory the free parameter which is proportional to the photoemission cross section now has been determined within the context of a surface potential effect model. In spite of the fact that the photoelectric effect plays a crucial role in the birth and development of quantum mechanics, it is not yet completely understood. For all these reasons, the FD theory is considered here as a valuable basis for additional developments.

III. SUMMARY OF THE GENERALIZED FOWLER-DUBRIDGE THEORY

At few-eV photon energy and high-field intensity, the electron flux observed from a solid surface illuminated by an electromagnetic radiation results, as noted previously,

from the superposition of two different coexisting effects: (i) the standard photoelectric effect in which electrons in the conduction band absorb one or more photons, and (ii) the thermionic emission caused by the heating of the metal surface.

The relative importance of the two effects depends on intensity, radiation frequency, polarization, and duration of the laser pulses. Disentangling the two effects is one of the experimental goals in this area of research.[25–27]

The first theory that successfully explained the temperature dependence of linear photoemission near the work function threshold was given by Fowler,[11] and was improved by Dubridge[12] subsequently. Their starting point is the assumption that electrons in metal obey Fermi-Dirac statistics and are uniformly distributed in momentum space. Then they assume the following successively.

(i) The absorption probability of a photon is independent of the initial state of the electron.

(ii) An electron may escape from the metal if its normal kinetic energy, associated with the component of velocity normal to the surface, is greater than the potential-energy barrier.

(iii) The whole energy of the photon, $\hbar\omega$, when absorbed is used to increase only the normal kinetic energy of the electron; its velocity components parallel to the surface remain unchanged.

(iv) The number of electrons emitted per absorbed photon is proportional to the number of electrons per unit volume of the metal whose normal kinetic energy, when increased by $\hbar\omega$, is sufficient to escape the potential-energy barrier.

The model of Fowler and Dubridge was later extended by Bechtel[27] to include N-photon photoemission (PE). The basic tenet is that the total current density is the superposition of partial current densities, each one having a simple interpretation:

$$J=\sum_{n=0}^{\infty} J_N \ . \tag{3}$$

Considering the classical expression for the N-photon ionization rate,[28] the partial current density is

$$J_N=\sigma_N I_\omega^N \ , \tag{4}$$

where I_ω is the laser intensity and σ_N is the generalized N-photon ionization cross section:

$$\sigma_N=a_N A\left[\left[\frac{e}{\hbar\omega}\right](1-R_\omega)\right]^N T^2 F(X_N) \ , \tag{5}$$

with

$$X_N=(N\hbar\omega-\Phi)/k_B T \tag{6}$$

and

$$F(X_N)=\int_0^\infty dy \ \ln(1+e^{-(y+X_N)})$$

$$=\begin{cases}\displaystyle\sum_{n=1}^{\infty}(-1)^{n+1}\frac{e^{nX_N}}{n^2}, & x_N<0 \quad (7a)\\ \dfrac{\pi^2}{12}, & x_N=0 \quad (7b)\\ \dfrac{\pi^2}{6}+\dfrac{x_N^2}{2}-\displaystyle\sum_{n=1}^{\infty}(-1)^{n+1}\frac{e^{-nX_N}}{n^2}, & x_N>0 \ . \quad (7c)\end{cases}$$

In these equations, $A=120$ A cm^{-2}K^{-2} is Richardson's constant, k_B is Boltzman's constant, R_ω is the surface reflectance, and T is usually identified to the mean temperature of the surface. a_N is proportional to the N-photon ionization constant. In Eq. (5), the optical coupling of the laser beam with the surface is characterized by $[\lambda(1-R_\omega)]$. As illustrated by Fig. 1, this quantity shows a maximum for visible or near-IR radiation, while the absorptance of light by metal surfaces is generally higher for short wavelengths.

For $N=0$, $J_N=J_0$ corresponds to the well-known Richardson's equation for the thermionic emission. The meaning of the Nth partial current simply represents the photocurrent due to the N-photon photoemission process. This interpretation is strictly correct only for the terms where the argument X_N is above the photoemission threshold, i.e., $(N\hbar\omega-\Phi)>0$. For $(N\hbar\omega-\Phi)<0$, and for a finite temperature of the photocathode, these terms represent N-photon photoemission from electrons at the high-energy tail of the Fermi-Dirac distribution, and are sometimes called thermally assisted multiphoton photo-

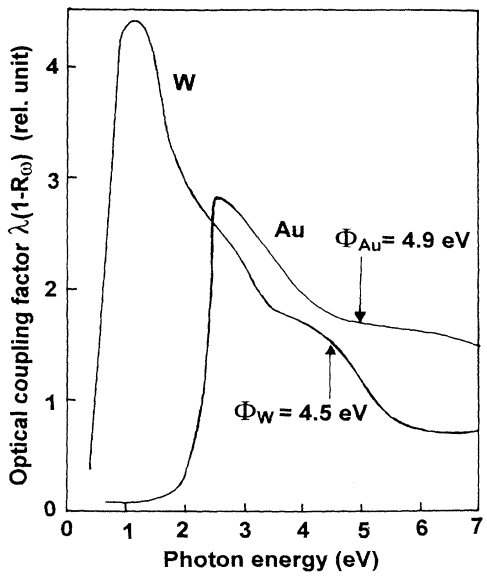

FIG. 1. Variations of $\lambda(1-R_\omega)$ vs λ in visible and near-UV ranges for gold and tungsten.

emission. However their contributions are small, unless the cathode temperature reaches several thousand degrees. This is verified essentially in nanosecond and picosecond regimes.[25,29] In phenomenological theory the exact photoexcitation mechanism is not really taken into account. This theory is applicable to bulk as well as to surface effect photoemission. Adaptations have to be made to represent the effective situation. For example, for the pure surface effect, Yen proposes[1] to replace the absorbed laser intensity $I_\omega(1-R_\omega)$ in Eqs. (4) and (5) by $|E_Z|^2$.

IV. EXTENSION OF THE GENERALIZED FD THEORY TO THE ULTRASHORT NONLINEAR PHOTOEMISSION

Photon energies of typical picosecond and femtosecond lasers are usually 1 eV $\leq\hbar\omega\leq$ 6 eV. They are lower than or equal to both the Fermi energy ε_F of electrons in the conduction band, and the work function of most metals. The interaction takes place mainly with the free electrons of the s band, and sometimes with the bound electrons of the d band.

For a laser-pulse duration longer than a few picoseconds, the electron gas and the lattice are in thermodynamical equilibrium. They are characterized by a common temperature T. For shorter pulse durations, this picture no longer holds. In the femtosecond range, the laser-pulse duration τ_p is of the same order of magnitude as the relaxation time of the conduction electrons $\tau_{ee}\approx 10^{-14}-10^{-13}$ s, while the electron-phonon collision energy relaxation time is $\langle\tau_{e\varphi}\rangle\sim 10^3-10^4 te\varphi$, where $te\varphi\sim 10^{-15}$ s is the electron-phonon-scattering momentum relaxation time. As suggested by Anisimov, Kapeliovich, and Perel'man,[30] the electron gas and lattice are characterized by two different temperatures T_e and T_L, respectively. The equilibrium between these two temperatures ($T_e=T_L=T$), being reached only after a few picoseconds, depends on the coupling constant g. Assuming the local thermal equilibrium of each system, at any time, temporal and spatial evolutions of T_e and T_L are well described by the coupled thermal equations

$$C_e(T_e)\frac{\partial T_e}{\partial t}=\nabla\cdot(K\nabla T_e)-\nabla\varepsilon+G(\mathbf{r},t)\ , \tag{8a}$$

$$C_L(T_L)\frac{\partial T_L}{\partial t}=\nabla\varepsilon\ , \tag{8b}$$

where

$$G(\mathbf{r},t)=\alpha_\omega(1-R_\omega)I_\omega(\mathbf{r},t) \tag{9}$$

is the laser energy density deposited on the surface. α_ω is the optical-absorption coefficient of the metal surface, C_e and C_L are the specific-heat capacities of the electron gas and lattice, respectively, and K is the thermal conductivity. The electron-phonon-coupling energy density is represented by the term

$$\nabla\varepsilon=g(T_e-T_L) \tag{10}$$

Kaganov, Lifshitz, and Tanatarov[31] proposed an expression for g,

$$g=\frac{\pi^2}{6}\frac{mN_e v_s^2}{\langle\tau_{e\varphi}\rangle T_L}\ , \tag{11}$$

where N_e is the free-electron gas density ($\simeq 5\times 10^{22}$ cm^{-3}) and v_s is the sound velocity in the bulk of metal. A more recent expression for g, based on factors related to the superconducting theory, was derived by Allen:[32]

$$g=\frac{3\hbar\gamma\bar{\lambda}\langle\Omega^2\rangle}{\pi k_B^2}\ , \tag{12}$$

where $\gamma=C_e/T_e$, $\bar{\lambda}$ is the electron-phonon-coupling constant used in the Eliashberg generalization of BCS theory,[33] and $\langle\Omega^2\rangle$ is the second moment of the phonon spectrum defined by McMillan.[34] The measurements of $\bar{\lambda}$ reported recently by Brorson *et al.*[35] for thin metallic films confirm the theoretical predictions of Allen. For metals such as Cu, Mo, W, and Au, for example, g is found to be about 10^{17} W m^{-3} K^{-1}. Equations (11) and (12) give similar results. Usually, $\langle\tau_{e\varphi}\rangle$ is supposed to be proportional to T_L^{-1}, so that g is independent of the lattice temperature. For a gold surface, the comparison of experimental time τ_r with this one calculated from Eqs. (8)–(12) suggests a power dependence of g on the electron temperature such as $g\propto T_e^r$, with $0.5<r<1$. For parameters in Eqs. (8) depending on T_e or T_L, only a numerical solution can be found, and the incertitude of g introduces a significant incertitude of the calculated value of τ_r. In Fig. 2 we report the calculated temporal profiles of T_e and T_L at the surface of a gold photocathode, irradiated by a 30-fs, 620-nm Gaussian laser pulse with 1-mJ energy

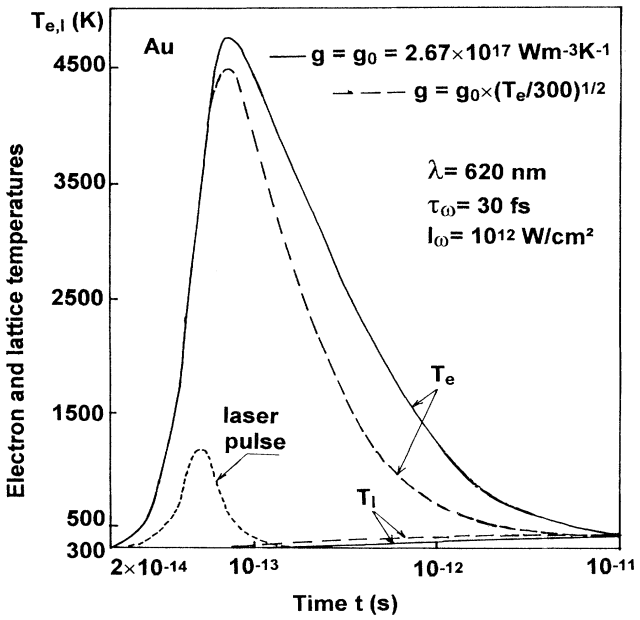

FIG. 2. Time variations of electron-gas temperature T_e and lattice temperature T_L of a gold surface irradiated by a 30-fs, 620-nm TEM_{00} laser pulse with 1-mJ energy and a 2-mm spot diameter, calculated from Eqs. (9)–(13).

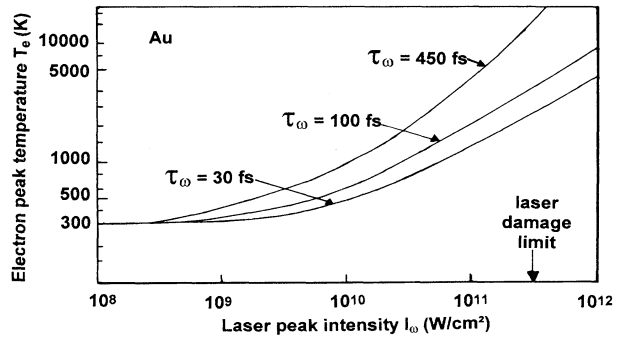

FIG. 3. Calculated variation of the peak electron-gas temperature vs the incident laser peak intensity.

and a 2-mm spot diameter. These laser beam characteristics are very close to the damage threshold of gold. With $g \simeq 2.7\times10^{17}$ W m^{-3} K^{-1}, deduced from Eqs. (11) and (12), we find that T_e is increased up to 4800 K, before meeting with T_L at 410 K, after 10 ps. Such a duration is about 2.5 times higher than the observed value. The calculated value of τ_r could be reduced by a factor of 2.5 only if g depends on the electron temperature, i.e., $g \propto T_e^r$, where $r=0.5$. The temperature of the surface is then increased up to $T_L=420$ K, while the peak electron temperature T_{em} is reduced by a small amount. Taking into account this power dependence of g on T_e, T_{em} was calculated for various incident intensities and three pulse durations, $\tau_p=30$, 100, and 450 fs. The variations of T_{em} vs I_ω are reported in Fig. 3. Note that the maximum electron gas energy $k_B T_{em}$ is always <1 eV for $I_\omega \leq 1$ TW/cm^2. That means that the enhancement of the electron gas energy up to few eV is possible only by using a much higher laser intensity, a situation which corresponds always to the production of a plasma at the surface. From Fig. 3, one observes that T_{em} is proportional to I_ω^Δ with $\Delta=0$ for $I_\omega<0.1$ GW/cm^2, $\Delta\simeq1$ for 0.1 GW/cm$^2 \leq I_\omega \leq 10$ GW/cm^2, and $\Delta>1$ for $I_\omega>10$ GW/cm^2 typically. Assuming that the time of electron thermalization at the surface is much shorter than the duration of electron-to-lattice conversion, the two-temperature model was used to deduce the values of g from optical data for different materials.[35] The electrons were supposed to be instantaneously thermalized into the FD distribution, but no direct experimental measurement of the electron energy distribution was reported to justify this assumption. Using a 270-fs resolved photoemission, Fann *et al.*[36] observed a nascent distribution of the thermalized FD distribution in a thin film of Au. The relaxation of nonequilibrium electrons was found to be inadequately described by the standard electron-phonon-coupling model. Our opinion is that the effective electron temperature is probably higher than the value calculated from Eqs. (8). However, nonequilibrium thermodynamic solutions being not available, we have to assume, with the majority of authors, that electron and phonon gases are always in local equilibrium. On the other hand the resolution of Eqs. (8) needs the assignment of correct values to the main physical quantities. For example, in the expression of the deposited laser energy at the surface [(Eq. (9)], R_ω, and α_ω are dependent on T_e and T_L, i.e., on I_ω. The reflectance R_ω can be represented as a sum of three terms:

$$R_\omega = R_{\omega0} + a(T_e - T_0) + b(T_L - T_0) , \tag{13}$$

where $R_{\omega0}$ is the surface reflectance at the room temperature T_0, and a and b are constant coefficients describing how electron and lattice heating affect R_ω. The variation $\Delta R_\omega = R_\omega - R_{\omega0}$ arising from the change in T_L will typically decay on a very slow time scale (≥ 10 ps), while any relaxation signal occurring on a fast time scale (≤ 1 ps) is due to electronic relaxation only. A similar description can be used for α_ω. Concerning the thermal quantities C_e, C_L, and K, we note that C_e/T_e is approximately constant as long as T_e is lower than 5000 K, C_L is accurately described by the law of Dulong and Petit,[37] and the thermal conductivity K corresponds to the extreme surface of the metal. Because the K values reported in the literature generally correspond to the bulk conductivity K_B, we consider the approach of Harrington[38] as more convenient. From this model, K varies from 0 to K_B with the distance Z normal to the surface, as long as Z is lower than ten times the mean free path of the electrons.

Consequently, the temperature T in Eqs. (5)–(8) represents the electron gas temperature T_e at any time. As with T_e, the optical coupling parameters R_ω and α_ω and the work function Φ depend on I_ω. To take into account the general dependence on T_e of the main physical quantities, we propose to derive each one by using a first-order limited perturbative development:

$$f = f_0 \left[1 + \frac{\Delta f}{f_0} \right] , \tag{14}$$

where f_0 is the amplitude of the quantity f at room temperature, and Δf represents the absolute variation of f. The total photocurrent density can be expressed as

$$J = \sum_{N=0}^{\infty} J_{k(N)} , \tag{15}$$

with

$$J_{k(N)} = J_N \Gamma_{\beta(N)} . \tag{16}$$

J_N is given by Eqs. (5)–(7), in which all the quantities are calculated for the initial temperature $T_e = T_L = T_0$, and

$$\Gamma_{\beta(N)} = \left[1 - \frac{\Delta R_\omega}{I - R_{\omega0}} \right]^N \left[1 + \frac{\Delta T_e}{T_0} \right]^2 \left[1 + \frac{\Delta F}{F_0} \right] \tag{17}$$

is a dimensionless power function of I_ω. Far from the singular points,[39] the absolute reflectance variation ΔR_ω is negative when I_ω is increased. The first term in the right-hand side of Eq. (17) is then equal to $\approx 1 - N\Delta R_\omega/(1-R_{\omega0}) \geq 1$. One verifies easily that the two other terms are positive and ≥ 1. Consequently $\Gamma_{\beta(N)}$ is always positive and ≥ 1. We propose to identify it as the ratio of two laser intensities:

$$\Gamma_{\beta(N)}=\left[\frac{I_\omega}{I_c}\right]^{\beta(N)}, \tag{18}$$

in which I_c is the intensity threshold of the nonlinear multiphoton photoelectric emission process, i.e.,

$$\lim_{I_\omega \to I_c}\beta(N)=0 . \tag{19}$$

$J_{k(0)}=J_0\Gamma_{\beta(0)}$ is the classical thermionic term, enhanced by laser heating, while, with $N\geq 1$, $J_{k(N)}$ are the nonlinear N-photon photoelectric terms.

The total current density is given by Eq. (15), but all terms do not have a similar strength. In reality, one term outclasses all the others, as can be shown from the following example.

Consider the situation of photoelectric emission from a metal illuminated by an ultrashort laser pulse with radiative energy $\hbar\omega$ such as $\Phi/\hbar\omega\approx 2$. When the laser intensity is not too high, the main photoelectric contribution corresponds classically to the two-photon process, while from Eq. (15) the total current is theoretically equal to

$$J\approx J_0\Gamma_{\beta(0)}+J_1\Gamma_{\beta(1)}+J_2\Gamma_{\beta(2)}+J_3\Gamma_{\beta(3)}+\cdots . \tag{20}$$

When I_ω increases typically up to 1 GW/cm^2, the electron-gas temperature is clearly increased so that the thermionic term $J_0\Gamma_{\beta(0)}$ presents a net enhancement. Now, supposing that $I_\omega\approx 10$ GW/cm^2, $T_e\approx 1000$ K, the ratio of $J_{k(0)}/J_{k(2)}$ is found to be $\ll 1$ (lower than 10^{-100}), and for $I_\omega\approx 100$ GW/cm^2, while T_e is much higher ($T_e\approx 5000$ K), the ratio $J_{k(0)}/J_{k(2)}<1\%$. Consequently, the contribution of the thermionic component to the total current is certainly lower than a few percent in any case. Now consider the second term in Eq. (20), $J_{k(1)}=J_1\Gamma_{k(1)}$ corresponding to single-photon photoemission. Because the two-photon process is dominant for $\hbar\omega\approx\Phi/2$, the measurement of the single-photon photoelectric probability a_1 is not possible for the same radiation energy $\hbar\omega$. The relative variation of $J_{k(1)}$ and $J_{k(2)}$ can only be estimated from a consideration of electron population density above the Fermi level in the conduction band. It is well known that these levels are filled up as the electron-gas temperature is increased, and $J_{k(1)}$ is then enhanced as T_e grows. However, simultaneously, the levels which are just above the Fermi level, and which constitute the main electron reservoir for the two-photon process, are filled much more than the upper levels constituting the usual electron reservoir for the single-photon process. Our conclusion is that $J_{k(2)}/J_{k(1)}$ is probably always $\gg 1$.

Concerning the terms with $N>2$, the N-photon processes are effective only from levels below the Fermi level. These levels are depopulated when T_e is increased, and it is slightly probable that the situation observed at room temperature and low laser intensity $J_{k(N>2)}\ll J_{k(2)}$ would change significantly.

Consequently, the dominant photoelectric term is $J_{k(2)}$, and more generally it will be the term corresponding to the dominant N-photon process, with $N\approx\Phi/\hbar\omega$. Because the thermionic term is always small and very difficult to estimate with a good precision, we propose to identify, in a first approximation, the total current with the N-order term, i.e.,

$$J\approx J_{k(N)} . \tag{21}$$

Then $J_{k(N)}$ can be expressed in a way similar to Eq. (4):

$$J_{k(N)}=\sigma_k I_\omega^{k[N]} , \tag{22}$$

where

$$\sigma_k=\frac{\sigma_N}{I_c^\beta} \tag{23}$$

is the nonlinear multiphoton photoemission cross section, and the nonlinear order $k(N)$ is

$$k(N)=N+\beta(I_\omega^{[a]}). \tag{24}$$

β is a continuous function of the absorbed laser intensity $I_\omega^{[a]}=(1-R_\omega)I_\omega$. For example, we observed such a typical dependence from W irradiated by 450-fs 248-nm laser pulses with 10–60-GW/cm^2 peak intensities (Fig. 4). When I_ω tends to I_c, evaluated in this case to few 10 MW/cm^2, β tends toward zero, so that $J_k=J_N$.

The illumination of the metal surface by an ultrashort laser pulse with a very high peak intensity leads to a net enhancement of the photoelectric efficiency.[2] From relative variations of the nonlinear photoemission sensitivity $S_k=J_k/I_\omega$,

$$\frac{\Delta S_k}{S_k}=\frac{\Delta F}{F}+2\frac{\Delta T_e}{T_e}+(N-1)\frac{\Delta I_\omega}{I_\omega} , \tag{25}$$

two situations have to be considered.

(i) The incident intensity $I_\omega\leq I_c$. From previous considerations, we know that $T_e\approx T_0$, and that the relative electron temperature variation is very small compared to the relative variation of the laser intensity.

The same conclusion holds for $\Delta F/F$, and consequently

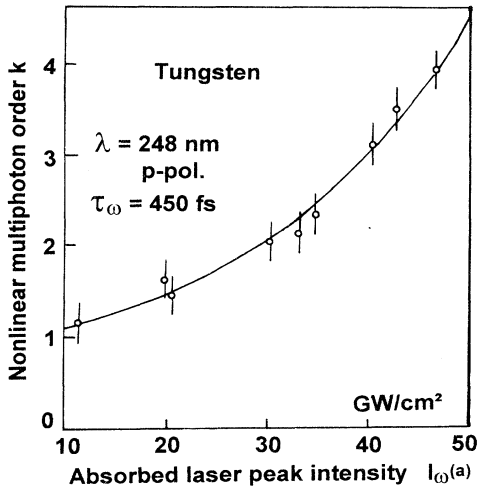

FIG. 4. Dependence of the nonlinear multiphoton photoemission order k of tungsten vs the absorbed laser peak intensity $I_w^{(a)}$ in the subpicosecond regime.

$$\frac{\Delta S_k}{S_k} \ll 1 \quad \text{for } N=1 \ , \tag{26}$$

$$\frac{\Delta S_k}{S_k} \approx (N-1)\frac{\Delta I_\omega}{I_\omega} \quad \text{for } N \geq 2 \ . \tag{27}$$

For a single-photon process, the sensitivity S_k can be considered as constant, in good agreement with most observations. For multiphoton processes, the slope of the representative graph of S_k vs I_ω is constant and equal to $N-1$, as forecasted by the classical theory of linear multiphonon photoemission.

(ii) The laser intensity $I_\omega > I_c$. The relative variation of the electron temperature is now higher than or equal to the relative variation of I_ω:

$$\frac{\Delta T_e}{T_e} \geq \frac{\Delta I_\omega}{I_\omega} \ , \tag{28}$$

and, as

$$\frac{\Delta F}{F} \geq 0 \ , \tag{29}$$

consequently, for any N,

$$\frac{\Delta S_k}{S_k} \geq N\frac{\Delta I_\omega}{I_\omega} \ . \tag{30}$$

The slope of S_k vs I_ω is no longer constant and becomes higher than $N-1$. Such a result is in good agreement with recent experimental data,[2,3,5] and is typical of a nonlinear response of the photocathode. Similar results are derived from the time derivative of the photoemitted charge q_k:

$$\frac{\partial qk}{\partial_{\tau_p}} = q_k \left\{ \frac{1}{\Gamma_\beta}\frac{\partial F}{\partial_{\tau_p}} + \frac{2}{T_e}\frac{\partial Te}{\partial \tau_p} - \frac{N-1}{\tau_p} \right] \ . \tag{31}$$

Supposing that the incident laser energy ε_ω is high enough and constant, and the laser pulse duration τ_p is shortened, T_e is increased and its time derivative $\partial T_e/\partial \tau_p$ is <0. A similar result is observed with $\partial \Gamma_\beta/\partial \tau_p$, so that $\partial q_k/\partial \tau_p$ is negative and q_k grows when τ_p is lowered. The photoemission sensitivity S_k, also equal to the ratio q_k/ε_ω, is therefore enhanced. The expression of the photocurrent density given by Eq. (22) is also representative of both linear and nonlinear behaviors. Using such a phenomenological expression, it is now possible to estimate, with a valuable precision from the experimental data, the main representative parameters, i.e., the nonlinear multiphoton order k and its enhancement relatively to N, the photoelectric probability a_N, and the linear and nonlinear photoelectric cross sections σ_N and σ_k, respectively. This model offers also a simple way to estimate the laser intensity I_g corresponding to the crossing of multiphonon sensitivities with different N orders. The crossing condition, deduced from Eqs. (5), (22), and (23) for N- and N' - photon processes such that $N\hbar\omega = N'\hbar\omega'$, is

$$I_g^{k'-k} = \frac{a_N}{a_{N'}} \left[\frac{N}{N'} \right]^{N'} \left[\frac{e}{\hbar\omega} \right]^{N-N'} \frac{(1-R_\omega)^N}{(1-R'_{\omega'})^{N'}} \frac{I_{c'}^{\beta'}}{I_c^{\beta}} \ . \tag{32}$$

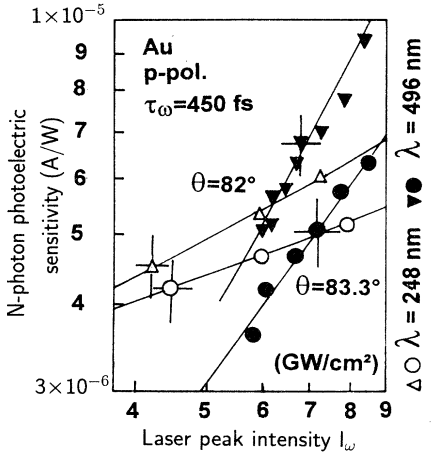

FIG. 5. Crossing of nonlinear single- and two-photon photoelectric emission sensitivities of gold vs the peak intensity of p—pol. 248 nm and 496-nm, 450-fs laser pulses for an incidence angle beyond 80°.

A test of validity of Eq. (32) was made from the recent measurements of single- and two-photon photoemission sensitivities of polycrystalline Au,[40] in the subpicosecond range (Fig. 5). The gold surface was irradiated by p-polarized 248- and 496-nm laser pulses of 450-fs duration, under an angle of incidence of 82°. The values of the main parameters, estimated from these experimental data, are $a_1 = 2\times10^{-14}$ cm^2/A, $a_2 = 4\times10^{-23}$ cm^4/A^2, $I_c \simeq 10$ MW/cm^2, and $I_{c'} \simeq 90$ MW/cm^2, respectively. We found $\beta \simeq 1.5$ and $\beta' \simeq 2.0$. Using the data reported by Weaver *et al.*[41] for the reflectance of the gold surface ($R_\omega = 0.483$ and $R'_\omega = 0.617$), Eq. (28) gives $I_g \simeq 6.83$ GW/cm^2, while the measured crossing laser intensity was found to be about 6.5 GW/cm^2. This difference can certainly be explained by the difference between the effective reflectance of the surface and the values used.

V. CONCLUSION

This theory unfortunately does not justify a link between processes at the microscopic scale and the macroscopic photoelectric response of the material. A general theory could be founded on a metal description as detailed as possible, but we know that this is extremely difficult to do because of the complexity of the solid material and of the incident laser beam representations. As we tried to show here, the nonequilibrium of the electron gas and lattice at the surface of metals, effective principally in the subpicosecond range, again make such a description more complicated. However, the phenomenological model described here offers the main advantage of making an analysis and comparison of experimental data observed from various metals more easy, as well as providing different experimental conditions focused on the radiation frequency, polarization, and angle of in-

cidence of the radiation, as well as the laser intensity and the order of the multiphoton process. Finally, this model provides a general expression which can be used both to analyze linear and nonlinear multiphoton photoelectric emissions produced from metal with laser intensity until the laser damage threshold.

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[1]R. T. Yen, Ph.D. thesis, Harvard University, 1981.

[2]J. P. Girardeau-Montaut, C. Girardeau-Montaut, S. Moustaizis, and C. Fotakis, Appl. Phys. Lett. **62**, 426 (1993).

[3]J. P. Girardeau-Montaut, C. Girardeau-Montaut, and S. Moustaizis, J. Phys. D **27**, 848 (1994).

[4]N. B. Delone and V. P. Krainov, *Atoms in Strong Light Fields* (Springer-Verlag, Berlin, 1985).

[5]J. G. Fujimoto, E. P. Ippen, J. M. Liu, and N. Bloembergen, Phys. Rev. Lett. **53**, 1837 (1984).

[6]N. K. Sherman, F. Brunel, P. B. Corkum, and F. A. Hegmann, Opt. Eng. **28**, 1114 (1989).

[7]J. P. Girardeau-Montaut, C. Girardeau-Montaut, M. Afif, G. Haouat, C. Couillaud, F. Sabary, and S. Joly (unpublished).

[8]D. M. Riffe, X. Y. Wang, M. C. Downer, D. L. Fischer, T. Tajima, J. L. Erskine, and P. M. More, J. Opt. Soc. Am. B **10**, 1424 (1993).

[9]C. Girardeau-Montaut and J. P. Girardeau-Montaut, Phys. Rev. A **44**, 1409 (1991).

[10]T. L. Gilton, J. P. Cowin, G. D. Kubiak, and A. V. Hamza, J. Appl. Phys. **68**, 4802 (1990).

[11]R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[12]L. A. DuBridge, Phys. Rev. **43**, 727 (1932).

[13]L. V. Keldysh, Zh. Eskp. Teor. Fiz. **34**, 1138 (1958) [Sov. Phys. JETP **34**, 788 (1958)].

[14]F. V. Bunkin and M. Fedorov, Zh. Eskp. Teor. Fiz. **48**, 1341 (1965) [Sov. Phys. JETP **21**, 896 (1965)].

[15]A. P. Silin, Fiz. Tverd. Tela (Leningrad) **12**, 3553 (1970) [Sov. Phys. Solid State **12**, 2886 (1971)].

[16]S. I. Anisimov, V. A. Benderskii, and G. Farkas, Usp. Fiz. Nauk **122**, 185 (1977) [Sov. Phys. Usp. **20**, 467 (1977)].

[17]R. M. Wood, in *Laser Damage in Optical Materials* (Adam Hilger, Bristol, 1986), p. 77.

[18]Gy. Farkas and S. L. Chin, Appl. Phys. B **37**, 141 (1985).

[19]J. P. Girardeau-Montaut, C. Bonetti, C. Couillaud, R. Dei-Cas, J. Dicrescenzo, G. Haouat, J. P. Laget, M. Renaud, and S. Striby, in *Proceedings of the 2nd EPAC, Nice, 1990,* edited by P. Martin and P. Mandrillon (CERN, Geneva, 1991), Vol. 1, p. 700.

[20]S. Shishido, Jpn. J. Appl. Phys. **12**, 1001 (1973).

[21]H. D. Jones and H. R. Reiss, Phys. Rev. B **16**, 2466 (1977).

[22]I. I. Kantorovich, Zh. Tekh. Fiz. **47**, 660 (1977) [Sov. Phys. Tech Phys. **22**, 397 (1977)].

[23]A. Mishra and J. I. Gersten, Phys. Rev. B **43**, 1883 (1991).

[24]R. Daniele, G. Ferrante, E. Fiordilino, and S. Varro, J. Opt. Soc. Am. B **9**, 1916 (1992).

[25]R. Yen, J. Liu, and N. Bloembergen, Opt. Commun. **35**, 277 (1980).

[26]R. Yen, J. M. Liu, N. Bloembergen, T. K. Yee, J. G. Fujimoto, and M. M. Salour, Appl. Phys. Lett. **40**, 185 (1982).

[27]J. H. Bechtel, Ph.D. thesis, University of Michigan, 1973.

[28]G. Mainfray and C. Manus, in *Normal Multiphoton Ionization of Atoms (Experimental) in Multiphonon Ionization of Atoms,* edited by S. L. Chin and P. Lambropoulos (Academic, New York, 1984), p. 7.

[29]M. Von Allmen, *Laser-beam Interactions with Materials* (Springer-Verlag, Berlin, 1987), p. 49.

[30]S. I. Anisimov, B. L. K. Apeliovich, and T. L. Perel'man, Zh. Eksp. Teor. Fiz. **66**, 776 (1974) [Sov. Phys. JETP **39**, 375 (1974)].

[31]M. I. Kaganov, I. M. Lifshitz, and L. V. Tanatarov, Zh. Eksp. Teor. Fiz. **31**, 232 (1956) [Sov. Phys. JETP **4**, 173 (1957)].

[32]P. B Allen, Phys. Rev. Lett. **59**, 1460 (1987).

[33]P. B. Allen, in *Dynamical Processes in Solids,* edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1980), Vol. 3, p. 85.

[34]W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[35]S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. Lett. **64**, 2172 (1990).

[36]W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Phys. Rev. Lett. **68**, 2834 (1992).

[37]N. W. Ascroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1985), p. 426.

[38]R. E. Harrington, J. Appl. Phys. **37**, 2028 (1966); **38**, 3266 (1967); **39**, 3699 (1968).

[39]G. L. Eesley, Phys. Rev. B **33**, 2144 (1986).

[40]J. P. Girardeau-Montaut, C. Girardeau-Montaut, S. Moustaizis, and C. Fotakis, in *Ultrafast Phenomena VIII,* edited by J. L. Martin (Springer-Verlag, Berlin, 1993), p. 340; Appl. Phys. Lett. **64**, 3664 (1994).

[41]J. H. Weaver, C. Krafka, D. N. Lunch, and E. E. Koch, *Optical Properties of Metals* (Fach-Inform-Zentrum, Karlsruhe, 1981), p. 49.