Theory of hot electrons in island metal films

E. D. Belotskiĭ, S. N. Luk'yanets, and P. M. Tomchuk

Institute of Physics, Academy of Sciences of the Ukrainian SSR

The rate of electron-phonon surface energy exchange in small metal particles is derived by a quantum-mechanical approach. This rate is found to be sharply lower (by about two orders of magnitude) in such particles than in bulk samples. An expression is derived for the local electric field which arises in an ensemble of metal ions to which the electromagnetic wave of a CO_2 laser is applied. The local fields and the electron-phonon energy exchange in small particles are studied and discussed in connection with the problem of laser heating of electrons in island metal films.

INTRODUCTION

Recent experiments have demonstrated convincingly that the application of power to island metal films gives rise to hot electrons in these films.[1-3] An emission of electrons and photons from island films of gold and copper on insulating substrates was observed in these experiments when the pulsed laser beam from a CO_2 laser was applied to the films (at power densities of $5 \cdot 10^4$–$5 \cdot 10^6$ W/cm^2 and at pulse lengths of 10^{-6} s).

Remarkably, when continuous films of the same materials were subjected to the same laser pulses, these effects were not observed.

The observed electron emission from these island films could not be explained in terms of either a single-photon photoelectric effect (the work function was more than an order of magnitude larger than the energy of the absorbed photon) or a multiphoton effect (a nonlinearity of such a high order would not be expected at these power levels). It was pointed out in Refs. 1–3 that the electron emission pulse has the same shape as the laser pulse; i.e., the emission occurs under essentially steady-state conditions. The reason is that the pulse length is orders of magnitude longer than all the relaxation times involved. The laser power densities used in those experiments were below the levels at which damage would be caused to the film structure.

It was shown in Refs. 4–6 that the effects observed in Refs. 1–3 stemmed from a heating of the electron gas by the absorbed power. The idea of hot electrons had been used previously[7,8] to explain some similar effects which arise during current flow through a tunneling-coupled system of metal islands of this sort. Hot electrons thus arise in island metal films under steady-state conditions regardless of the mechanism by which the power is introduced (by light or an electric current). On the other hand, it is known that hot electrons cannot be produced in the steady state in bulk metals or continuous metal films. During the application of laser beams to continuous metal films, hot electrons can be observed only for ultrashort times[9] ($t < 10^{-10}$ s).

The reasons why a highly nonequilibrium electron gas (with an electron temperature an order of magnitude or more above the lattice temperature) can be produced under steady-state conditions in island magnetic films, in contrast with continuous films, were found in Refs. 4–6 to be the following:

1) Electron-phonon energy exchange is greatly suppressed in small metal islands. 2) High power densities can be introduced into island metal films. 3) Small metal islands with good thermal contact can transport high energy fluxes without being destroyed.

Let us briefly examine the reason for the strong suppression of the electron-phonon energy exchange in small metal islands.[10,11] The primary mechanism by which hot electrons lose energy in a bulk metal is known to be the excitation of longitudinal acoustic waves in the lattice by the moving electrons, via a Cherenkov mechanism (Ref. 12, for example). The equation for these waves induced by the moving electron is[12]

$$\frac{\partial^2 \mathbf{U}}{\partial t^2} - s^2 \Delta \mathbf{U} = -\frac{W}{\rho} \nabla \delta(\mathbf{r} - \mathbf{v}t). \tag{1}$$

Here $\mathbf{U}$ is the longitudinal component of the displacement vector, ρ is the mass density, W is the interaction constant, $\mathbf{v}$ is the electron velocity, and s is the sound velocity.

The energy lost by a moving electron per unit time can be expressed in terms of the vector $\mathbf{U}$ in the following way:[12]

$$\frac{d\mathscr{E}_e}{dt} = W \int \frac{\partial \mathbf{U}}{\partial t} \nabla \delta(\mathbf{r} - \mathbf{v}t) d^3 r. \tag{2}$$

A summation of (2) over all the nonequilibrium electrons (with energies above the Fermi energy) gives us the power which the electrons transfer to the lattice.

From (1) we find the following expression for a Fourier component of the vector $\mathbf{U}$:

$$\mathbf{U}(\omega, \mathbf{k}) = \frac{1}{(2\pi)^3} \frac{W}{\rho} \frac{i\mathbf{k}\delta(\omega - \mathbf{k}\mathbf{v})}{\omega^2 - k^2 s^2}. \tag{3}$$

We see from this expression that the driving force due to the moving electron has a nonzero Fourier component at the resonant frequency of the lattice vibrations ($\omega = ks$). This is the essence of the Cherenkov mechanism for the excitation of acoustic vibrations (resonant pumping). This is the situation as it prevails in a bulk metal.

We turn now to a small metal island, with a length scale R_0 smaller than the mean free path l_f. The electron then oscillates in a potential well with a frequency v/R_0. In this case the argument of the δ function in (1) is no longer $\mathbf{r} - \mathbf{v}t$ but $\mathbf{r} - \mathbf{r}(t)$, where $\mathbf{r}(t)$ is the trajectory of the vibrational motion of the electron [e.g., $r_\perp = $ const, $r_\parallel \equiv z = R_0 \sin(vt/R_0)$]. The Fourier transform of the driving force now contains only harmonics which are multiples of the oscillation frequency v/R_0. If this frequency is above the maximum frequency of lattice vibrations, ω_D (the Debye

frequency), a resonant excitation is not possible.[10,11] It can thus be asserted that in metal islands with a length scale R_0 which satisfies the conditions

$$R_0 < l_f, \quad R_0 < v/\omega_D,$$

the energy-loss mechanism which is the primary mechanism in a bulk metal drops out of the picture.

In this situation, the electron-phonon energy exchange which stems from collisions of electrons with the vibrating surface of the island emerges as the predominant factor. Accordingly, our primary task in this paper is to derive a theory for surface electron-phonon energy exchange in small metal particles. In addition, we will analyze (in Sec. 3) the local electric fields in an island metal film, which are determined by the level of the power absorption during the application of laser beams to island films. We will thus be examining two of the reasons listed above for the appearance of hot electrons in island metal films. The third reason—the possibility that a small metal island can transport large energy fluxes without being damaged—is discussed in Ref. 13.

1. SURFACE VIBRATIONS OF SMALL PARTICLES

Since we will be discussing metal films with dimensions on the order of or less than the mean free path, we can use the following model to calculate the surface energy exchange.

The electron gas is in a spherical potential well of radius R_0 (if thermal vibrations are ignored) and height V_0. This model was used in Ref. 14 to study optical absorption in island metal films.

As we have already mentioned, the reason for the energy exchange is an interaction of the electron with thermal vibrations of the surface. These vibrations can be classified somewhat crudely as either shape vibrations (so-called capillary vibrations), in the course of which the volume does not change, or surface vibrations, which are accompanied by a change in density (acoustic vibrations). A theory for the surface vibrations of a spherical particle is set forth in detail (for the case of vibrations of the surface of an atomic nucleus) in Ref. 15.

We begin our analysis with the capillary vibrations. We expand the radius of the vibrating surface in spherical harmonics $Y_{\lambda\mu}(\theta, \varphi)$:

$$R(\theta, \varphi) = R_0 \left\{ 1 + \sum_{\lambda,\mu} \alpha_{\lambda\mu} Y_{\lambda\mu}^*(\theta, \varphi) \right\}. \quad (4)$$

The Hamiltonian of the capillary vibrations can then be written in the following form, in accordance with Ref. 15:

$$H = \frac{1}{2} \sum_{\lambda,\mu} \{ D_\lambda | \dot{\alpha}_{\lambda\mu} |^2 + C_\lambda | \alpha_{\lambda\mu} |^2 \}$$

$$= \frac{1}{2} \sum_{\lambda,\mu} \left\{ \frac{| \pi_{\lambda\mu} |^2}{D_\lambda} + D_\lambda \omega_\lambda^2 | \alpha_{\lambda\mu} |^2 \right\}. \quad (5)$$

Here $\pi_{\lambda\mu} = D_\lambda \dot{\alpha}_{\lambda\mu}^*$ is a generalized momentum, and $\omega_\lambda = (C_\lambda / D_\lambda)^{1/2}$ is the frequency of the capillary vibrations. The constants D_λ and C_λ depend on the island dimensions in different ways. According to Ref. 15, they are given by

$$D_\lambda = MnR_0^5/\lambda, \quad C_\lambda = \sigma_s R_0^2 (\lambda - 1)(\lambda + 2). \quad (6)$$

Here M is the mass of the atom, n is the density, and σ_s is the surface energy.

It can be seen from (6) that the frequency of the shape vibrations depends strongly on the radius of the metal island, R_0:

$$\omega_\lambda = \left(\frac{C_\lambda}{D_\lambda} \right)^{1/2} = \left\{ \sigma_s \frac{(\lambda - 1)\lambda(\lambda + 2)}{MnR_0^3} \right\}^{1/2}. \quad (7)$$

For the discussion below we will take a quantum-mechanical approach in which $\pi_{\lambda\mu}$ and $\alpha_{\lambda\mu}$ are replaced by corresponding operators, which are related to the operators which create ($b_{\lambda\mu}^+$) and annihilate ($b_{\lambda\mu}$) vibrations by

$$\hat{\pi}_{\lambda\mu} = i(D_\lambda \hbar \omega_\lambda / 2)^{1/2} (b_{\lambda\mu} - b_{\lambda\mu}^+), \quad (8)$$

$$\hat{\alpha}_{\lambda\mu} = \left(\frac{\hbar}{2D_\lambda \omega_\lambda} \right)^{1/2} (b_{\lambda\mu} + b_{\lambda\mu}^+). \quad (9)$$

After this replacement, the Hamiltonian of the capillary vibrations takes the standard form:

$$\hat{H} = \sum_{\lambda,\mu} \hbar \omega_\lambda \left(b_{\lambda\mu}^+ b_{\lambda\mu} + \frac{1}{2} \right). \quad (10)$$

To find the electron-phonon energy exchange, we need an explicit expression for the corresponding Hamiltonian. According to the model adopted above, the potential energy of an electron in a metal island is

$$W(r) = V_0 \Delta(r - R(\theta, \varphi)), \quad (11)$$

where

$$\Delta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}. \quad (12)$$

Using expansion (4) for $R(\theta, \varphi)$, we find from (11)

$$W(r) \approx V_0 \Delta(r - R_0) + \delta(r - R_0) V_0 R_0 \sum_{\lambda,\mu} \alpha_{\lambda\mu} Y_{\lambda\mu}^*(\theta, \varphi). \quad (13)$$

The second term in (13) describes the energy of the electron-phonon interaction associated with the surface vibrations. Writing this term in the second-quantization representation [using (9)], we find

$$\hat{H}_{int} = V_0 R_0 \sum \left(\frac{\hbar}{2D_\lambda \omega_\lambda} \right)^{1/2} \langle \Psi_{lnm}^* | \delta(r - R_0) Y_{\lambda\mu}^*(\theta, \varphi) | \Psi_{l'n'm'} \rangle$$

$$\times (b_{\lambda\mu} + b_{\lambda\mu}^+) a_{lnm}^+ a_{l'n'm'}. \quad (14)$$

The operators a_{lnm}^+ and a_{lnm} in (14) create and annihilate an electron in the corresponding state. The meaning of the subscripts on these operators becomes clear when we recall that the electron wave function in a "spherical potential square well" is

$$\Psi_{lnm}(r) = \frac{1}{C_{ln}} R_l(r) Y_{lm}(\theta, \varphi). \quad (15)$$

Here C_{ln} is a normalization factor, and the radial wave function is

$$R_l(r) = \begin{cases} j_l(k_{ln}'r), & \text{for} \quad r < R_0 \\ h_l^{(1)}(iK_{ln}r), & \text{for} \quad r > R_0 \end{cases}. \quad (16)$$

The quantity $j_l(x)$ in (16) is the spherical Bessel function, and $h_l^{(1)}(x)$ is the spherical Hankel function. In addition,

$$k_{ln}' = \left(\frac{2m_e}{\hbar^2}\varepsilon_{ln}\right)^{1/2}, \qquad K_{ln} = \left[\frac{2m_e}{\hbar^2}(V_0-\varepsilon_{ln})\right]^{1/2}. \quad (17)$$

Here m_e is the mass of an electron, and ε_{ln} is the energy of the electronic levels in a spherical square potential well. These conditions are found from the condition for the joining of the electron wave function and its derivative at the point $r = R_0$. In view of the rapid decay of the electron wave function inside the barrier, we write k'_{ln} in the following form, as in Ref. 14:

$$k_{ln}' = k_{ln} + \Delta k_{ln}, \quad (18)$$

where k_{ln} are the roots of the equation

$$j_l(k_{ln}R_0) = 0. \quad (19)$$

Equation (19) corresponds to the case of an infinitely deep potential well. Assuming that Δk_{ln} is small in comparison with k_{ln} (this point is easily checked), we find the following result from (again) the condition for the joining of the wave function and its derivative at the point R_0:

$$\Delta k_{ln} = -k_{ln}/R_0 K_{ln}. \quad (20)$$

Here we have used the asymptotic expression

$$R_{ln}(r) \approx \frac{1}{iK_{ln}r}\exp\left\{-K_{ln}r - \frac{i\pi}{2}(l+1)\right\}, \quad r > R_0. \quad (21)$$

Since we will be interested below in the electron levels near (and above) the Fermi energy, we can use the method of Ref. 14, finding approximate solutions of (19) through the use of the asymptotic representation of the spherical Bessel function:

$$k_{ln} = \frac{\pi}{2R_0}(2n+l). \quad (22)$$

Now, in accordance with (18), (20), and (22), we have an explicit expression for k'_{ln}. Consequently, the electron wave functions in (15) and (16) have been determined completely. Using them, we can put the Hamiltonian for the electron-phonon interaction, (14), in the form

$$\hat{H}_{int} = V_0\sum\left\{\frac{2\hbar}{D_\lambda\omega_\lambda}\cdot\frac{\varepsilon_{ln}\varepsilon_{l'n'}}{(V_0-\varepsilon_{ln})(V_0-\varepsilon_{l'n'})}\right\}^{1/2}$$

$$\times \int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\sin\theta Y_{ln}^*(\theta,\varphi)$$

$$\times Y_{l'n'}(\theta,\varphi)Y_{\lambda\mu}^*(\theta,\varphi)(b_{\lambda\mu}+b_{\lambda\mu}^+)a_{lnm}^+a_{l'n'm'}. \quad (23)$$

2. SURFACE ELECTRON-PHONON ENERGY EXCHANGE

Now that we have explicit expressions for the electron and phonon spectra and also for the Hamiltonian of the electron-phonon interaction, we can move on to the problem of determining the electron-phonon energy exchange. This exchange can be taken into account systematically by a kinetic-equation approach. For brevity we will be using the notation

$$\nu = \{l, n, m\}, \qquad q = \{\lambda, \mu\}. \quad (24)$$

The change caused per unit time in the distribution of elec-

trons among states by the scattering of electrons by phonons is then given by

$$\frac{\partial f_{\nu\nu}}{\partial t} \equiv \hat{I}f_{\nu\nu} = \sum_{\nu',q}W_{\nu\nu'q}\{[(N_q+1)f_{\nu\nu}(1-f_{\nu'\nu'})-N_qf_{\nu'\nu'}(1-f_{\nu\nu})]$$

$$\times \delta[\varepsilon_{\nu'}-\varepsilon_\nu+\hbar\omega_q]$$

$$+[N_qf_{\nu\nu}(1-f_{\nu'\nu'})-(N_q+1)f_{\nu'\nu'}(1-f_{\nu\nu})]\delta[\varepsilon_{\nu'}-\varepsilon_\nu-\hbar\omega_q]\}. \quad (25)$$

Here $f_{\nu\nu} = \langle a_\nu^+ a_\nu\rangle$ is the electron distribution function, and $N_q = \langle b_q^+ b_q\rangle$ the phonon distribution function. As usual, the angle brackets mean an average over the statistical operator. Furthermore, in our case we have $\varepsilon_\nu = \varepsilon_{ln}$, $\omega_q = \omega_\lambda$; i.e., the spectrum is degenerate. It is a simple matter to derive an explicit expression for the transition probabilities, by first writing interaction Hamiltonian (23) in the compact form

$$\hat{H}_{int} = \sum_{\nu,\nu',q}C_{\nu\nu'q}[b_q+b_q^+]a_\nu^+a_{\nu'}. \quad (26)$$

Then

$$W_{\nu\nu'q} = \frac{2\pi}{\hbar}|C_{\nu\nu'q}|^2. \quad (27)$$

The energy transferred from the electrons to the phonons per unit time is

$$\frac{\partial\mathscr{E}}{\partial t} = \frac{\partial}{\partial t}\sum_\nu\varepsilon_\nu f_{\nu\nu} = \sum_\nu\varepsilon_\nu\hat{I}f_{\nu\nu}. \quad (28)$$

We note that the electron distribution in a metal island, $f_{\nu\nu}$, depends on only the electron energy: $f_{\nu\nu} = f(\varepsilon_\nu)$.

Treating the phonon system as a heat reservoir (with respect to the electron subsystem), we take the phonon distribution function N_q to be Planckian with a temperature T. Expanding collision integral (25) in a series in the small quantity $\hbar\omega_q$ (i.e., actually expanding in the ratio of the phonon energy to the Fermi energy), we find the following result for expression (28):

$$\frac{\partial\mathscr{E}}{\partial t} \approx \sum_{\nu,\nu',q}W_{\nu\nu'q}N_q(\hbar\omega_q)^2$$

$$\times\left\{\frac{f(\varepsilon_\nu)[1-f(\varepsilon_{\nu'})]}{k_BT}+\frac{df(\varepsilon_\nu)}{d\varepsilon_\nu}\right\}\delta(\varepsilon_{\nu'}-\varepsilon_\nu). \quad (29)$$

We can now write an explicit expression for the electron distribution function. Because of the intense electron-electron interaction, the power acquired by the electron subsystem from the external source becomes distributed among many electrons rapidly. As a result, a Fermi distribution with some effective electron temperature T_e is established:

$$f(\varepsilon_\nu) = \left\{\exp\left[\frac{\varepsilon_\nu-\varepsilon_F}{k_BT_e}\right]+1\right\}^{-1}, \quad (30)$$

where ε_F is the Fermi energy. Substituting (30) into (29), we find

$$\frac{\partial\mathscr{E}}{\partial t} = \left(\frac{T_e}{T}-1\right)\sum_{\nu,\nu',q}W_{\nu\nu'q}N_q(\hbar\omega_q)^2\delta(\varepsilon_{\nu'}-\varepsilon_\nu)\delta(\varepsilon_\nu-\varepsilon_F). \quad (31)$$

To pursue the calculations we need to use the explicit expression for $W_{\nu\nu'q}$ which follows from (27) and from a

comparison of (23) and (26):

$$W_{vv'q} = \frac{4\pi}{D_\lambda \omega_\lambda} \cdot \frac{V_0^2 \varepsilon_{ln}\varepsilon_{l'n'}}{(V_0-\varepsilon_{ln})(V_0-\varepsilon_{l'n'})}$$

$$\times \left\{ \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, Y_{ln}^*(\theta,\varphi) Y_{l'n'}(\theta,\varphi) Y_{\lambda\mu}^*(\theta,\varphi) \right\}^2. \quad (32)$$

Substituting (32) into (31) we find that an explicit dependence of the integrand on the indices characterizing the electron states remains in only the spherical harmonic, because of the presence of the function $\delta(\varepsilon_v - \varepsilon_F)$ $\equiv \delta(\varepsilon_{ln} - \varepsilon_F)$ in the integral. We can thus sum over the electron indices in (31). In doing so, we make use of the orthogonality of the spherical harmonics:

$$\sum_{l=0}^{\lambda} \sum_{m=-l}^{l} Y_{lm}^*(\theta,\varphi) Y_{lm}(\theta',\varphi') = \frac{\delta(\varphi-\varphi')\delta(\theta-\theta')}{\sin\theta}. \quad (33)$$

In our case the summation over l is bounded by the condition $\varepsilon_{ln} \leqslant \varepsilon_F$. This circumstance does not introduce any significant error, however, since the maximum value of l is large, $l_{max} \sim 10^2$. This estimate of l_{max} follows from the relation

$$\varepsilon_F = \left(\frac{\hbar\pi l_{max}}{2R_0}\right)^2 \frac{1}{2m_e}. \quad (34)$$

As a result of these calculations, we find from (31)

$$\frac{\partial \mathscr{E}}{\partial t} \approx \left(\frac{T_e}{T} - 1\right) \frac{R_0^4}{2\pi^2} \left(\frac{m_e \varepsilon_F}{\hbar}\right)^2 \left(\frac{V_0}{\varphi_0}\right)^2 \sum_{\lambda,\mu} \frac{\omega_\lambda N_\lambda}{D_\lambda}. \quad (35)$$

Here $\varphi_0 = V_0 - \varepsilon_F$ is the work function of the metal, and $N_\lambda = N(\omega_\lambda)$ is the Planckian distribution function of the capillary vibrations.

We are left with the task of evaluating the phonon sum in (35):

$$\sum_{\lambda=2}^{\lambda_{max}} \sum_{\mu=-\lambda}^{\lambda} \frac{\omega_\lambda N(\omega_\lambda)}{D_\lambda} \approx \frac{k_B T}{\hbar} \sum_{\lambda=2}^{\lambda_{max}} \frac{2\lambda+1}{D_\lambda}. \quad (36)$$

In (36) we have recognized that the energy corresponding to the Debye frequency of the capillary vibrations is considerably smaller than $k_B T$ (at room temperature). It follows from (7) in this case that

$$\omega_D = \omega_{\lambda_{max}} \approx \left(\frac{\sigma_s}{MnR_0^3}\right)^{1/2} \lambda_{max}^{3/2}. \quad (37)$$

As a result of these calculations we find

$$\frac{\partial \mathscr{E}}{\partial t} \approx \left(\frac{4\pi R_0^3}{3}\right) k_B(T_e-T) \frac{3}{16\pi} \frac{v_F}{R_0} n \frac{m_e \omega_D^2}{\sigma_s} \left(\frac{V_0}{\varphi_0}\right)^2. \quad (38)$$

In the literature, the power transferred from the electrons to the phonons is customarily written in the form

$$\frac{\partial \mathscr{E}}{\partial t} \equiv \left(\frac{4\pi R_0^3}{3}\right) \alpha (T_e-T). \quad (38')$$

Here we have assumed that the particle is a sphere in our case. The constant α, which is a measure of the rate of the electron-phonon energy exchange, is given in our case by

$$\alpha = \frac{3}{16\pi} k_B \frac{v_F}{R_0} n \frac{m_e \omega_D^2}{\sigma_s} \left(\frac{V_0}{\varphi_0}\right)^2. \quad (39)$$

Let us evaluate this quantity for a gold particle (a sphere) with the following parameter values: $n = 6 \cdot 10^{22}$ cm^{-3}, $v_F = 10^8$ cm/s, $R_0 = 10^{-6}$ cm, $\sigma_s = 10^3$ erg/cm^2, $\omega_D = 3 \cdot 10^{12}$ s^{-1} (Ref. 16), and $(V_0/\varphi_0)^2 = 5$. We find $\alpha = 2 \cdot 10^{15}$ erg/(cm$^3 \cdot$s$\cdot$deg).

The value found for α is two orders of magnitude lower than the corresponding value in bulk metals. A recent experiment carried out to determine α in small particles[17] has indeed shown that this value is two orders of magnitude smaller than in the case of the bulk metal.

As we mentioned earlier, the shape vibrations (the capillary vibrations) of the particles are accompanied by some surface vibrations which do involve a change in density (acoustic vibrations). The dispersion relation for these phonons is[15]

$$\omega_{n\lambda} = k_{n\lambda} s, \quad (40)$$

where s is the sound velocity, and the wave vector $k_{n\lambda}$ is determined by the roots of the equation

$$j_\lambda(k_{n\lambda} R_0) = 0. \quad (41)$$

The interaction of the electrons with these vibrations can be dealt with by an approach like that taken above. As a result we find the following expression for the value of α determined by the surface acoustic vibrations:

$$\alpha \approx \frac{1}{16\pi} k_B \frac{nv_F}{R_0^2} \frac{m_e}{\rho} \left(\frac{\omega_D'}{s}\right)^2 \left(\frac{V_0}{\varphi_0}\right)^2. \quad (42)$$

Here ω_D' is the Debye frequency of the acoustic vibrations, and ρ is the density of the material.

An estimate of α from (42) for the same gold particles as discussed above yields a value an order of magnitude smaller than the result in (39). Consequently, the interaction with capillary waves is predominant for these particles.[1)] We would simply like to point out that the idea of classifying the vibrations as either capillary or acoustic is valid only if ω_D and ω_D' are quite different. This condition is satisfied in the case under consideration here.

3. LOCAL FIELD IN SMALL METAL PARTICLES

As we mentioned back in the Introduction, in the laser method of introducing power into islands, an important role in the appearance of hot electrons is played by the strength of the local electric fields induced by the external wave (this factor acts in addition to the pronounced weakening of the electron-phonon energy exchange).

What is the difference between the absorption of the incident light by an individual metal island and that by an island metal film? The power absorbed by a metal island is

$$\mathscr{P} = V \operatorname{Re}[J(\omega)E_L(\omega)] = V\sigma(\omega)|E_L|^2. \quad (43)$$

Here V is the volume of the island, $J(\omega)$ is the density of the high-frequency current, $\sigma(\omega)$ is the high-frequency conductivity, and E_L is the local electric field in an island. (The notation used in this section of the paper is independent of the notation used previously.)

Writing the dielectric constant as

$$\epsilon = \epsilon' + i\epsilon'' \approx 1 - \frac{\omega^2}{\omega_p^2} + i\frac{4\pi}{\omega}\sigma(\omega), \quad (44)$$

we find that the local field E_L associated with the external wave field E is given by the following expression for a spherical island:

$$E_L = E - {}^4\!/_3 \pi P = E - {}^1\!/_3 (\epsilon - 1) E_L. \qquad (45)$$

Here P is the dipole moment per unit volume, and ω_p is the plasma frequency. From (45) we can find an expression for the local field within an island in terms of the external field E:

$$E_L = \frac{E}{1 + {}^1\!/_3 (\epsilon - 1)}. \qquad (46)$$

If the island is not a sphere, the relationship between the local field and the polarization is instead

$$E_L = E - \mathscr{L} 4\pi P. \qquad (47)$$

Here $\mathscr{L}$ is a depolarization factor. In this case, the factor of $1/3$ in the denominator in (46) should be replaced by $\mathscr{L}$.

Substituting (46) into (43) [and using $V = (4/3)\pi R_0^3$], we find

$$\mathscr{P} = \frac{12\pi\omega}{c} \frac{\epsilon'' R_0^3}{(2+\epsilon')^2 + \epsilon''^2} \frac{c|E|^2}{4\pi}, \qquad (48)$$

where c is the velocity of light.

Dividing the power in (48), i.e., the power absorbed by the island, by the incident power density, we find a known expression for the absorption cross section of a small spherical island:[18]

$$\varkappa = \frac{12\pi\omega}{c} \frac{\epsilon'' R_0^3}{(2+\epsilon')^2 + \epsilon''^2}. \qquad (49)$$

Note that the relation $\omega \ll \omega_p$ holds at the output frequencies of a CO_2 laser, so we have $|\epsilon'| \gg 1$ (or, more precisely, $|\epsilon'| \approx 10^2$). In this frequency range the external field thus penetrates only very slightly into an individual spherical ·metal island. The absorbed power is accordingly also small. The situation changes radically when we deal with an ensemble of islands of various shapes. In this case the field inside a given island is formed not only by the field of the incident wave but also by the fields of the dipoles induced by this external wave in the other islands. The ensemble will contain islands with small values of the depolarization factor $\mathscr{L}$. If we assume that all the islands are identical, then the local field in a given island is[19]

$$E_L(\omega) = \frac{E}{1 + (\epsilon - 1)(\mathscr{L} + B)}, \qquad (50)$$

$$B = \frac{V}{4\pi} \sum_i \frac{1 - \cos^2 \theta_i}{r_i^3}. \qquad (51)$$

Here r_i is the distance between the given island and island i, and θ_i is the angle between the vector $\mathbf{r}_i$ and the direction of the incident-wave field (which induces the dipoles). The sums over the dipoles are calculated by placing the identical islands on a regular lattice. We find

$$E_L(\omega) = \frac{E}{1 + (\epsilon - 1)(\mathscr{L} - \beta V/a^3)}, \qquad (52)$$

where β is a numerical factor which depends on the lattice geometry, and a is the distance between islands.

It can be seen from this expression that under the condition $|\mathscr{L} - \beta V/a^3| \ll 1$ the local field may be close in value to the external field, regardless of the value of ϵ. However, there is the question of just how applicable expression (52) is at small distances, since this expression was derived in the dipole approximation, i.e., for distances on the order of the size of the islands themselves. As we know, the dipole approximation arises when we expand the exact expressions in powers of the ratio of the size of the system to the distance at which the potential is determined. For our purposes here, that approach is not valid.

We accordingly consider a very simple model which makes it possible to incorporate the distribution of the charge induced by the wave field at the surface of a metal island and the mutual effects of the charges of different islands. Specifically, we assume a uniform, periodic arrangement of identical metal islands along a certain axis. We assume that the electric field of the wave is parallel to the same axis. Since the dimensions of the islands and the distances between islands are much smaller than the wavelength of the incident wave in our case, the problem of determining the resultant field reduces to one of solving a Laplace equation under corresponding boundary conditions:

$$\Delta\varphi(\mathbf{r}) = 0, \qquad (53)$$

$$\varphi_+(\mathbf{r})|_s = \varphi_-(\mathbf{r})|_s,$$

$$\left(\frac{\partial\varphi}{\partial\mathbf{n}}\right)_- \bigg|_s = \epsilon\left(\frac{\partial\varphi}{\partial\mathbf{n}}\right)_+ \bigg|_s,$$

where the $+$ and $-$ correspond to the limiting values of the functions inside and outside the surface S, and $\mathbf{n}$ is the outward normal to the surface.

A solution of (53) can be written in the form

$$\varphi(\mathbf{r}) = -\mathbf{E}\mathbf{r} + \sum_{k=-\infty}^{\infty} \int_s \frac{\tilde{\sigma}(\mathbf{r}')dS_\mathbf{r}}{|\mathbf{r} - \mathbf{r}' - \mathbf{a}k|}, \qquad (54)$$

where the surface charge density $\tilde{\sigma}(r)$ (we are taking the assumed periodicity into account) satisfies the following integral equation (Ref. 20, for example):

$$\tilde{\sigma}(\mathbf{r}) + \frac{1-\epsilon}{1+\epsilon} \int \tilde{\sigma}(\mathbf{r}') \sum_{k=-\infty}^{\infty} \frac{\cos\vartheta}{2\pi|\mathbf{r} - \mathbf{r}' - \mathbf{a}k|^2} dS_{\mathbf{r}'} = -\frac{1}{2\pi} \frac{1-\epsilon}{1+\epsilon} \mathbf{E}\mathbf{n}_\mathbf{r}. \qquad (55)$$

Here ϑ is the angle between the vectors $\mathbf{r} - \mathbf{r}' - \mathbf{a}k$ and $\mathbf{n}_{\mathbf{r}'}$, $\mathbf{n}_\mathbf{r}$ is the outward normal to the surface of the island at the point $\mathbf{r}$, and $\mathbf{a}$ is the on-center distance between islands.

In the case of an isolated island, i.e., with $k = 0$, Eq. (55) has the exact solution

$$\tilde{\sigma} = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} \mathbf{E}\mathbf{n}_\mathbf{r}. \qquad (56)$$

Substituting (56) into (54), and retaining only the term with $k = 0$, we find the known result for a dielectric sphere in a uniform external field. (At frequencies $\omega \ll \omega_p$, a conducting metal island behaves as if it were a dielectric.)

When there is a chain of spherical islands, $\tilde{\sigma}(\mathbf{r})$ depends on only θ, i.e., the angle between the field $\mathbf{E}$ and the radius $\mathbf{r}$ to the point on the surface of the sphere. In general, we can thus expand $\tilde{\sigma}$ in a series:

$$\tilde{\sigma} = \sum_{m=1}^{\infty} C_m P_m(\cos\theta). \qquad (57)$$

It is clear from the symmetry of the problem that (57) contains only odd terms in terms of the Legendre polynomials $P_m(\cos\theta)$. Substituting (57) into (55), multiplying by $P_n(\cos\theta)\sin\theta$, and integrating over θ, we find a system of algebraic equations for the coefficients C_n:

$$\sum_{m=1}^{\infty}\left\{\frac{4}{(2m+1)(2n+1)}\frac{(n+m)!}{n!m!}\left(\frac{R_0}{a}\right)^{n+m+1}\sum_{k=1}^{\infty}\frac{1}{k^{n+m+1}}\right\}C_m$$
$$+\frac{1}{n(2n+1)}\left(\frac{1+\epsilon}{1-\epsilon}+\frac{1}{2n+1}\right)C_n = -\frac{E}{6\pi}\delta_{1,n}. \quad (58)$$

The indices m and n in (58) take on only odd values. The sums over k rapidly converge on one. For example,

$$\sum_{k=1}^{\infty}\frac{1}{k^3} \approx 1.2, \qquad \sum_{k=1}^{\infty}\frac{1}{k^5} \approx 1.04. \qquad (59)$$

It is easy to see from (58) that even at $a \approx 3R_0$, i.e., even when the gap between the islands is equal to the radius, the coefficient C_3 and the following coefficients are much lower than C_1. When the islands are nearly touching, in contrast, C_3 is comparable in magnitude to C_1.

Knowing the charge distribution, we can find the electrostatic potential with the help of (54). However, our problem is simplified substantially by the circumstance that the power absorbed by an island is determined by the component of the local field inside the island which is normal to the surface. This component can be calculated easily from the boundary conditions (with known $\tilde{\sigma}$):

$$(\mathbf{E}_i - \mathbf{E}_L)\mathbf{n}_r = 4\pi\tilde{\sigma}, \qquad (60)$$

$$\mathbf{E}_i\mathbf{n}_r = \epsilon \mathbf{E}_L\mathbf{n}_r.$$

Here $\mathbf{E}_i$ is the field on the outer side of the metal island. From (60) we find

$$\mathbf{E}_L\mathbf{n}_r = \frac{4\pi\tilde{\sigma}}{\epsilon-1}. \qquad (61)$$

The normal component of the local field has its maximum value (which is the same as the total local field) when it is directed along the external field $\mathbf{E}$, i.e., at the value $\theta = 0$ in expansion (57).

If we retain only the coefficient C_1 in (57) and (58), and substitute it into (61), we find the following expression for the total local field inside a spherical metal island in a periodic chain of such islands:

$$\mathbf{E}_L(\omega) = \mathbf{E}\left\{1+(\epsilon-1)\left[\frac{1}{3}-\frac{4}{3}\left(\frac{R_0}{a}\right)^3\sum_{k=1}^{\infty}\frac{1}{k^3}\right]\right\}^{-1}. \qquad (62)$$

Actually, we have derived expression (52), but now the meaning of the parameters involved has been made concrete. Since the maximum value of the local field [according to (61)] is expressed in terms of $\tilde{\sigma}|_{\theta=0} = \Sigma C_m$, this value can be found easily, at any desired accuracy, with the help of (58).

Correspondingly, we could consider a periodic chain of metal islands of ellipsoidal shape (an ellipsoid of revolution whose long axis is directed along the chain). Making use of the explicit form of the right side of (55), we then specify the charge distribution to be

$$\tilde{\sigma} = \left(\frac{R_\perp R_\parallel}{R_\perp^2\cos^2\theta + R_\parallel^2\sin^2\theta}\right)^{1/2}\sum C_n P_n(\cos\theta). \qquad (63)$$

Here θ is the angle between the radius vector to the point on the surface of the ellipsoid and the long axis of the ellipsoid (this axis is directed along the external field), and $R_\parallel$ and $R_\perp$ are the major and minor semiaxes of the ellipsoid, respectively. To determine the coefficients C_n in (63), we can again derive a system of algebraic equations like (58). In the same approximation which we used in deriving (62), we find the following expression for a chain of ellipsoids:

$$E_L(\omega) \approx E\left\{1+(\epsilon-1)\left[\mathscr{L}-\frac{4}{3}(1-e_p^2)\left(\frac{R_\parallel}{a}\right)^3\sum_{k=1}^{\infty}\frac{1}{k^3}\right]\right\}^{-1}. \qquad (64)$$

Here

$$\mathscr{L} = \frac{1-e_p^2}{2e_p^3}\left[\ln\left(\frac{1+e_p}{1-e_p}\right)-2e_p\right]$$

is the depolarization factor of the ellipsoid, and $e_p = [1-(R_\perp/R_\parallel)^2]^{1/2}$. Expression (64) naturally becomes (62) in the limit $e_p \to 0$. We also see that as $e_p \to 1$ the local field E_L tends toward the external field E (despite the comparatively large value of ε at these frequencies). The role played by the neighbors in determining the local field is also clear. In particular, in the case described by (62), incorporating these neighbors may double the local field in a given island.

We thus see that the local field in a specific island is determined by the depolarization factor (which depends on the shape of the island) and by the effect of the neighbors. In an inhomogeneous island metal film, the local fields in the different islands will of course be quite different, so such films will produce a nonuniform emission.

The problem of determining local electric field presents serious difficulties even in the case of two identical spheres (Refs. 21 and 22, for example), and in the case of an ensemble of such particles are the difficulties of course much more formidable.[23]

It seems to us that the method proposed here for calculating local fields is the simplest one.

CONCLUSION

We have derived an analytic expression for a coefficient which characterizes the energy exchange of hot electrons with surface vibrations of small metal islands. For certain island dimensions (specified in the Introduction), this energy-exchange mechanism becomes the predominant one. Previous attempts have been made to evaluate the surface energy-exchange constant in small metal films.[8,24] In Ref. 8, the fraction of the energy transferred by an electron in a collision with a surface atom was assumed to be proportional to the ratio of the masses of the electron and the atom. In Ref. 24, the fraction of the electron energy which was given up in a single collision with a surface was assumed to be proportional to the ratio of the mass of the electron to the mass of all surface atoms within a circle of diameter λ_e, where λ_e is the

electron wavelength. The number of such atoms is $(1/4)\pi\lambda_e^2 n_{surf}$. Using $n_{surf} = n^{2/3}$ and $\lambda_e = 2\pi\hbar/p_F \approx 2n^{-1/3}$, we find that this result reduces to the result of Ref. 8, within a factor on the order of unity.

Note, however, that an estimate of the fraction of its energy which an electron gives up in a collision with the surface on the basis of a mass ratio can be justified only at electron energies well above the Fermi energy.

We have derived here a constant which characterizes the electron-phonon energy exchange in small metal particles. We have shown that this constant is smaller than the corresponding constant in a bulk sample by two orders of magnitude. This circumstance is one of fundamental importance for the existence of hot electrons in island metal films.

It has also been shown here that the local field in the individual islands can be arbitrarily close to the external field of the CO_2 laser wave, depending on the shape of the islands and their relative arrangement. It can thus be said that the hypothesis, first offered in Refs. 7 and 8, that hot electrons exist in island metal films has now acquired a definitive theoretical foundation as well as direct experimental proof.

[1] We have been discussing the vibrations of a smooth surface. A real surface may be rough. (On the other hand, as the size of the particles decreases, their surfaces become smoother, and their shape becomes more nearly symmetric.) A surface roughness has a substantial effect on elastic scattering of electrons, but it appears to have no significant effect on inelastic scattering. In particular, it can be seen from (36) that the inelastic contribution is determined integrally, by the entire spectrum of surface vibrations, although frequencies near the Debye frequency are predominant. Such frequencies could be sensitive to only very small roughnesses.

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