SOVIET PHYSICS JETP VOLUME 36, NUMBER 5 MAY, 1973

EFFECT OF ADSORPTION ON ELECTRON EMISSION FROM METALS

A. M. BRODSKIĬ, Yu. Ya. GUREVICH, and S. V. SHERBERSTOV

Institute of Electrochemistry, USSR Academy of Sciences

Submitted April 29, 1972

Zh. Eksp. Teor. Fiz. 63, 1793–1808 (November, 1972)

Some effects of the surface lattice, produced by adsorbed particles, on auto- and photo-electron emission which cannot be ascribed simply to a change of the work function are considered. Effects due to the potential created by the adsorbed particles not being one-dimensional are manifest already in the first harmonic of the Fourier expansion of the corresponding solution; at low energies, precisely this harmonic yields the major contribution. A number of experimental facts can successfully be described by means of these expressions and by employing only independent microscopic characteristics of the adsorbed particles.

1. INTRODUCTION

THE effect of adsorption and the ensuing phenomena on the laws governing electron emission from metal surfaces have recently attracted considerable attention[1-7]. In the earlier studies, the influence of adsorption was taken into account simply by introducing an additional dipole jump, i.e., by replacing in the corresponding formulas the work function of the pure metal by the work function of a surface with the produced structure[8]. Recent experimental[2,3] and theoretical[1,5,6] researches have shown that adsorption can alter significantly the form of the functional dependence of the corresponding electron-emission currents I and the energy distributions of the emitted electrons P on the external fields. It is natural to connect qualitative changes of this kind with effects of direct elastic and inelastic interaction of the emitted electrons with the adsorbed particles[9,10] and with the change in the character of the collective interaction as a result of the adsorption[11,12]. At the same time, even under conditions when the processes of inelastic and incoherent scattering directly on the metal boundary are negligible (for example, at electron energies close to threshold), the presence of adsorbed particles can lead to a sharp change in the laws governing the photoelectronic emission, particularly electron field emission.

In the case of field emission, the effects due to adsorption and not reducible to a simple change in the work function were first discussed qualitatively by Dobretsov[13]. Attempts at a quantitative treatment within the framework of a very simple model were first made by Duke and Alferieff[1]. A similar one-dimensional picture was used somewhat later to describe field emission from metals coated by one or several layers of inert gas[4], and also to calculate the oscillations of the photoemission current[5]. The metal is described in the cited papers in the form of s Sommerfeld model of a "box," occupying a half-space $z < 0$, and the action of the adsorbed atoms in the region $z > 0$ on the emitted electron is described with the aid of additional one-dimensional potentials in the form of a deep and narrow potential well, a δ-function, or their superpositions. The energy distribution of the electrons emitted under field-emission conditions, calculated in such models, can have sharp maxima, owing to resonant tunneling effects. The energies corresponding to these maxima are close to the energies of the bound states in an attraction potential that stimulates the influence of the adsorbed atoms.

The indicated theoretical concepts have made it possible to describe the experimentally established main qualitative effects[2]. This circumstance has stimulated further research, and it was even proposed to use field emission under adsorption conditions as a method for investigating the energy spectrum of the adsorbed particles (surface spectroscopy[3,6]). At the same time, attempts to go beyond the framework of the one-dimensional model[1,6,14,15] cannot be regarded as satisfactory. In particular, it was proposed[1,15] to take into account the presence of an occupied part of the surface in purely classical fashion, by simply representing the total current in the form of a sum of currents from the "unoccupied" and "occupied" parts of the surface. Nor were the following questions answered: first, how to take the limit on going from the case when individual adsorbed particles are present on the surface to the case of a relatively dense adsorption layer, when the one-dimensional description may turn out to be correct. Second, how the phenomenologically introduced one-dimensional potential is connected with the independently measurable individual characteristics of the adsorbed particles, the degree of filling of the surface, the geometry of the adsorption lattice, etc. The last question is closely related with the problem of the control of the properties of metallic emitters by deposition of adsorption layers. These questions are considered in the present article using a previously developed[16,17] generalization of the threshold description of emission. The results obtained in this case are only weakly connected with model representations concerning the structure of the metal.

As shown by calculation, the deviations from one-dimensionality become manifest already in the first harmonic of the Fourier expansion of the corresponding solution. This harmonic makes the main contribution at low energies and can be observed before the interference phenomena on the periodic structure become noticeable. The expressions obtained in this paper for the emission currents have made it possible to describe successfully the experimental data, using only independent microscopic characteristics of the adsorbed particles.

2. INITIAL RELATIONS

We assume that adsorption on the metal surface has produced a structure that can be represented approximately as a regular two-dimensional lattice. The coordinates of the lattice points are then expressed in the form $\mathbf{r}_l = \mathbf{l} + \mathbf{d}$. Here $\mathbf{l} = \mathbf{l}_1 n_1 + \mathbf{l}_2 m$, where $\mathbf{l}_1$ and $\mathbf{l}_2$ are the basis vectors of the two-dimensional lattice, n and m are integers, and $\mathbf{d} = \{0, 0, d\}$ is a vector normal to the metal surface, which is by assumption the plane $z = 0$. The three-dimensional potential $V_a(\mathbf{r})$, which takes account of the effective interaction of the electrons with the adsorbed particles in this model, is given by

$$V_a(\mathbf{r}) = \sum_{\mathbf{l}} U_a(\mathbf{r} - \mathbf{r}_l),$$

where U_a corresponds to interaction with an individual adsorbed particle.

The main theoretical problem in the description of electron emission is the calculation of the emission current I and (or) the energy distribution P of the emitted electrons. These quantities can be obtained by summing the quantum-mechanical current j over the corresponding initial states[16,17]. Under quasistationary conditions, the quantum-mechanical current j is made up of the wave functions (orbitals) of the final state ψ_f, which describe the electrons produced outside the metal (more accurately, outside the region of the electron source) after the external action is applied. In the case of photoemission, such an external action is the electric field of the electromagnetic wave, and in the case of field emission it is an external field of constant intensity F.

If each initial state characterized by definite energy E_i and a two-dimensional vector $p_{\parallel}$ of the quasimomentum projection on the (x, y) plane (we assume for simplicity that the quantum numbers of the initial state reduce to E_i and $p_{\parallel}$) is set in correspondence with a definite final-state function ψ_f, then outside the metal ψ_f satisfies the Schrödinger equation

$$\left\{\frac{\hbar^2}{2m}\Delta + E_f - V(\mathbf{r})\right\}\psi_f = 0, \qquad z > 0, \tag{1}$$

where m is the electron mass and E_f is the final-state energy and is uniquely connected with E_i. For example, in the single-photon photo effect, in the field of a monochromatic wave with frequency ω we have $E_f = E_i + \hbar\omega$, and in the case of field emission we have $E_f = E_i$.

The potential $V(\mathbf{r})$ in (1) depends, generally speaking, on all three coordinates $\mathbf{r} = \{x, y, z\}$. In accordance with the physical formulation of the problem, as $z \to \infty$ the function ψ_f is a superposition of wave traveling out of the metal. The boundary conditions at $z = 0$ call for some additional discussion. When deviations from one-dimensional behavior, due to the adsorption lattice, are considered, it is necessary to take into account in general also the fact that the metallic surface itself is not one-dimensional. If, however, the periods of the crystal lattice of the metal are smaller than the distance l_a between the nearest adsorbed particles ($l_a \approx |\mathbf{l}_1| \approx |\mathbf{l}_2|$), and if at the same time the interaction of these particles with the emitted electrons is sufficiently strong, then the adsorbed lattice will make the decisive contribution to the effects connected with deviation from the one-dimensional behavior.

Under the indicated conditions, the metal can be described without appreciable error in the model of the one-dimensional potential. Accordingly, the boundary condition on ψ_f at $z = 0$ can be written in the threshold energy interval in the form[17]

$$\psi_f|_{z=0} = \Lambda \exp(i\mathbf{p}_{\parallel}\mathbf{r}/\hbar), \tag{2}$$

where Λ is a constant independent of E_f or $p_{\parallel}$ and is determined by the properties of the metal. The independence of the constant Λ of the characteristics of the final state of the emitted electrons is due to the fact that the considered energy interval, in which the final energies of the electrons are contained, turns out to be much smaller than the characteristic energy parameters in the metal, which are of the order of the kinetic energy E_F, of the electrons on the Fermi surface[17]. If d exceeds the period of the crystal lattice of the metal, then the use of the boundary condition (2) can be valid also without the model assumption made above concerning the structure of the metal.

Taking the foregoing into account, we represent the potential $V(\mathbf{r})$ in (1) in the form of a sum

$$V(\mathbf{r}) = V(z) + V_a(\mathbf{r}) = V(z) + \sum_{\mathbf{l}} U_a(\mathbf{r} - \mathbf{r}_l), \tag{3}$$

where the summation is over all the lattice points. In this case we can assume, even several interatomic distances away from the surface, that $V(\mathbf{r}) = V(z)$, where $V(z)$ coincides with the one-dimensional potential is usually considered in the theory of electron emission. For example, in the case of photoemission from a metal into a vacuum we have $V(z) = -e^2/4z$ (the image-force potential), and in the case of field emission $V(z) = -eFz$, where F is the intensity of the con stant external field, the energy being reckoned here and henceforth relative to the energy of the electron at rest outside the metal in the absence of external fields.

Introducing now the vectors $\mathbf{g}$ of a lattice that is reciprocal to the adsorption lattice ($\mathbf{g}_i \cdot \mathbf{l}_j = \delta_{ij}$; i, j = 1, 2) and using the translational invariance of V_a following a displacement $\mathbf{l}$, we obtain

$$\psi_f = \sum_{\mathbf{g}} C_{\mathbf{g}} f_{\mathbf{g}}(z) \exp\{i(\mathbf{k}_{\parallel} + 2\pi\mathbf{g})\mathbf{r}\}, \tag{4}$$

where C_g are certain constant and $\mathbf{k}_{\parallel} = \mathbf{p}_{\parallel}/\hbar$ is a two-dimensional wave vector, which can be regarded as conserved by virtue of the assumed translational invariance and equal to the corresponding vector of the electrons in the metal.

The functions $f_g(z)$ in (4) satisfy the system of coupled equations obtained by substituting (4) in (2), and go over asymptotically as $z \to \infty$ into solutions of the one-dimensional Schrödinger equation which move away from the metal or are damped at infinity:

$$f_{\mathbf{g}}'' + \left(k_{\mathbf{g}}^2 - \frac{2mV(z)}{\hbar}\right) f_{\mathbf{g}} = 0. \tag{5}$$

Here $k_{\mathbf{g}}^2 \equiv k^2 - (\mathbf{k}_{\parallel} + 2\pi\mathbf{g})^2$ and $k^2 \equiv 2mE_f/\hbar^2$. By using (4) to construct a current j averaged in the plane (x, y), we get

$$j=\sum_{\mathbf{g}}|C_{\mathbf{g}}|^2 j[f_{\mathbf{g}}], \tag{6}$$

where $j[f_g]$ denotes the usual quantum-mechanical current constructed from the function f_g.

If the final energy of the emitted electrons is not too large, then it is sufficient to retain in the sum (6) a single term corresponding to g = 0. Indeed, in the case of photoemission, when the condition $E_f < (2\pi\hbar)^2/2ml_a^2$ is satisfied, the contribution made to the emission current by terms with $g \neq 0$ is exactly equal to zero, since, as follows from (5), in this case $f_g(z) \to 0$ as $z \to \infty$. In the case of field emission, as can be readily seen from estimates perfectly similar to those made in[18], this contribution is exponentially small relative to the contribution of the term containing C_0. The smallness parameter in this case is the expression

$$\exp\left\{-\frac{\hbar}{2eF}\left(\frac{2\pi}{l_a}\right)^2\left(\frac{w}{2m}\right)^{1/2}\right\},$$

where w is the work function. In similar cases, to which we shall henceforth confine ourselves, the problem of finding j reduces effectively to calculating the single quantity C_0. We emphasize at the same time that C_0 is a functional of $V_a(\mathbf{r})$ and its calculation calls for the solution of the non-one-dimensional problem.

To describe the interaction of the electrons with the adsorbed particles, we shall use the method of small-radius potentials[19-22]. It is applicable because the de Broglie length of the emitted electrons exceeds in the considered energy interval the dimensions $\mathcal{R}$ of the region of the effective interaction U_a of the electrons with the individual adsorbed particles: $\mathcal{R}^{-1} > \hbar^{-1}(2m|E_f|)^{1/2}$. It should be borne in mind here that even for rather complicated particles, for example molecules, the region of the strongest interaction with the electron is usually localized and its dimensions are much smaller than the geometrical dimensions of the particle[1].

In the small-radius potential method, the action of the potential

$$V_a=\sum_{\mathbf{l}} U_a(\mathbf{r}-\mathbf{r}_{\mathbf{l}})$$

is taken into account with the aid of an effective boundary condition imposed on the function ψ_f as $\mathbf{r} \to \mathbf{r}_l$ for all $\mathbf{r}_l$:

$$\psi_f(\mathbf{r}) \to \mathrm{const}\left(\frac{1}{|\mathbf{r}-\mathbf{r}_{\mathbf{l}}|}-\frac{1}{a}\right)\Big|_{|\mathbf{r}-\mathbf{r}_{\mathbf{l}}|\to 0}. \tag{7}$$

The quantity a, called the scattering length and measurable independently, characterizes the action exerted on the electron by an individual adsorbed particle. In our problem, a can be treated as an empirical characteristic of the adsorbed particles. We emphasize that the approach based on the use of the scattering-length concept is actually more general in the low-energy limit than the potential model, since the scattering length can be introduced in cases when the potential description is impossible.

3. DERIVATION OF GENERAL FORMULA FOR THE EMISSION CURRENT

Within the framework of our approximations, the problem reduces to a solution of Eq. (1) with potential (3), where, in accordance with the model of the zero-radius potential, the action of the potentials U_a is replaced by the boundary condition (7). The solution ψ of the Schrödinger equation with potential V_a, satisfying the Bloch condition

$$\psi(k, \mathbf{k}_\parallel, \mathbf{r}) = \exp(i\mathbf{k}_\parallel \mathbf{l})\psi(k, \mathbf{k}_\parallel, \mathbf{r}-\mathbf{l}) \tag{8}$$

and behaving like $|\mathbf{r}-\mathbf{r}_l|^{-1}$ as $|\mathbf{r}-\mathbf{r}_l| \to 0$, takes the form

$$\psi(k, \mathbf{k}_\parallel, \mathbf{r})=\sum_{\mathbf{r}_{\mathbf{l}}}\frac{1}{|\mathbf{r}-\mathbf{r}_{\mathbf{l}}|}\exp\{i\mathbf{k}_\parallel\mathbf{l}+ik|\mathbf{r}-\mathbf{r}_{\mathbf{l}}|\}. \tag{9}$$

Expanding (9) in a Fourier series in g, we obtain

$$\psi(k, \mathbf{k}_\parallel, \mathbf{r})=\sum_{\mathbf{g}}\frac{2\pi i}{k_{\mathbf{g}}S}\exp[ik_{\mathbf{g}}|z-d|+i(\mathbf{k}_\parallel+2\pi\mathbf{g})\mathbf{r}_\parallel], \tag{10}$$

where S is the area of the unit cell of the adsorbed-particle lattice.

To calculate the function $\psi_f(\mathbf{r})$, we break up the region $0 < z < \infty$ into three parts: $0 < z < d-\epsilon$, $d-\epsilon < z < d+\epsilon$ and $z > d+\epsilon$, our subsequent intention being to take the limit as $\epsilon \to 0$. In the region $d-\epsilon < z < d+\epsilon$ we put $V(z) = \mathrm{const} = V_d$. Finally, we introduce for Eq. (5) two linearly-independent solutions $\varphi_g^{(1)}$ and $\varphi_g^{(2)}$ that satisfy the following boundary conditions at z = 0:

$$\varphi_{\mathbf{g}}^{(1)}\Big|_{z=0}=\frac{d\varphi_{\mathbf{g}}^{(2)}}{dz}\Big|_{z=0}=0,\quad \varphi_{\mathbf{g}}^{(2)}\Big|_{z=0}=\frac{d\varphi_{\mathbf{g}}^{(1)}}{dz}\Big|_{z=0}=1. \tag{11}$$

With the aid of the function $\psi(\mathbf{k}, \mathbf{k}_\parallel, \mathbf{r})$ and of the solutions $\varphi_g^{(1)}$ and $\varphi_g^{(2)}$, the sought solution ψ_f, satisfying the boundary condition (2), can be expressed in the form

$$\psi_f(\mathbf{r})=\begin{cases}\sum_{\mathbf{g}}\exp\{i(\mathbf{k}_\parallel+2\pi\mathbf{g})\mathbf{r}_\parallel\}[\Lambda\delta_{\mathbf{g},0}\varphi_{\mathbf{g}}^{(2)}+\alpha_{\mathbf{g}}\varphi_{\mathbf{g}}^{(1)}], & 0\leqslant z\leqslant d-\varepsilon,\\ \sum_{\mathbf{g}}\exp\{i(\mathbf{k}_\parallel+2\pi\mathbf{g})\mathbf{r}_\parallel\}[\beta_{\mathbf{g}}\cos\tilde{k}_{\mathbf{g}}(z-d)+\gamma_{\mathbf{g}}\sin\tilde{k}_{\mathbf{g}}(z-d)] & \\ \qquad +\Omega\psi(\tilde{k}, \mathbf{k}_\parallel, \mathbf{r}), & d-\varepsilon\leqslant z\leqslant d+\varepsilon,\\ \sum_{\mathbf{g}}C_{\mathbf{g}}f_{\mathbf{g}}(z)\exp\{i(\mathbf{k}_\parallel+2\pi\mathbf{g})\mathbf{r}_\parallel\}, & z\geqslant d+\varepsilon.\end{cases} \tag{12}$$

Here $\tilde{k}_g^2 \equiv k_g^2 - 2mV_d/\hbar^2$, $\tilde{k}^2 \equiv k^2 - 2mV_d/\hbar^2$, α_g, β_g, γ_g, C_g and Ω are constants to be determined.

The quantity Ω is determined from the condition (7), while α_g, β_g, γ_g, and C_g are determined from the condition that the solution (12) be continuous together with its derivatives at $z = d-\epsilon$ and $z = d+\epsilon$. Namely, taking the limit as $\mathbf{r} \to \mathbf{r}_1$, we obtain from (12) at fixed l

$$\psi_f(\mathbf{r})=\sum_{\mathbf{g}}\beta_{\mathbf{g}}+\Omega\left\{\frac{1}{|\mathbf{r}-\mathbf{r}_{\mathbf{l}}|}+i\tilde{k}+\sum_{\mathbf{l}}{}'\frac{1}{|\mathbf{l}|}\exp(i\mathbf{k}_\parallel\mathbf{l}+i\tilde{k}|\mathbf{l}|)\right\},$$

from which we get, by comparing with (7),

$$\Omega=-\sum_{\mathbf{g}}\beta_{\mathbf{g}}\left\{\sum_{\mathbf{l}}{}'\frac{1}{|\mathbf{l}|}\exp(i\mathbf{k}_\parallel\mathbf{l}+i\tilde{k}|\mathbf{l}|)+i\tilde{k}+a^{-1}\right\}^{-1}$$

---

[1] If charged particles are present on the surface, it is possible to describe within the framework of the considered approximation, as before, a number of qualitative laws which, as will be shown later on, are quite general in character.

(the prime at the summation sign denotes that the term corresponding to $\mathbf{l} = 0$ has been left out of the sum).

After substituting the last expression in (12) and subsequently joining the solutions (12) in the planes $d - \epsilon$ and $d + \epsilon$ with allowance for the expansion (10), we obtain the following system of equations for the unknown constants

$$\begin{gathered}\delta_{g,0}\Lambda\varphi_g^{(2)}(d)+\alpha_g\varphi_g^{(1)}(d)=\beta_g+\Omega 2\pi i/\tilde{k}_g S,\\ \delta_{g,0}\Lambda\varphi_g^{(2)\prime}(d)+\alpha_g\varphi_g^{(1)\prime}(d)=\tilde{k}_g\gamma_g+\Omega 2\pi/S,\\ \beta_g+\Omega\frac{2\pi i}{\tilde{k}_g S}=C_g f_g(d),\qquad \tilde{k}_g\gamma_g-\Omega\frac{2\pi}{S}=C_g f_g'(d),\end{gathered}\tag{13}$$

from which we obtain after simple operations, using the condition $W[\varphi_g^{(2)}, \varphi_g^{(1)}] = 1$, where w is the Wronskian,

$$C_g=\frac{\Lambda}{f_g^{(0)}}\left\{\delta_{g,0}-\frac{4\pi\varphi_g^{(1)}(d)f_0(d)}{Sf_0(0)\,(i\tilde{k}+a^{-1}+\mathscr{Z})}\right\},\tag{14}$$

$$\mathscr{Z}=\sum_{\mathbf{l}}{}'\frac{1}{|\mathbf{l}|}\exp(i\mathbf{k}_{\parallel}\mathbf{l}+i\tilde{k}|\mathbf{l}|)+\frac{4\pi}{S}\sum_{g}\left\{\frac{\varphi_g^{(1)}(d)f_g(d)}{f_g(0)}-\frac{i}{2\tilde{k}_g}\right\}$$

$f_g(d)$ and $f_g(0)$ are the functions $f_g(z)$ from (5) at $z = d$ and $z = 0$.

Using (6), we now obtain for the quantum-mechanical emission current the final basic formula

$$j=R\,(\mathbf{k},\mathbf{k}_{\parallel})\frac{|\Lambda|^2}{|f_0(0)|^2}j[f_0],\tag{15}$$

where

$$R=\left|1-\frac{4\pi}{Sf_0(0)}\frac{\varphi_0^{(1)}(d)f_0(d)}{i\tilde{k}+a^{-1}+\mathscr{Z}}\right|^2.\tag{16}$$

The quantity $\mathscr{Z}$ in (15) and (16) is a functional of the one-dimensional potential $V(z)$ (via $\varphi_g^{(1)}$ and f_g) and of the geometrical characteristics of the adsorption structure (l_1, l_2, d); at the same time, $\mathscr{Z}$ does not depend explicitly on the individual properties of the adsorbed particles located at the lattice points.

The presented formulas yield a general mathematical solution of our problem and we shall use them in the succeeding sections to analyze the laws governing the photoelectronic and field emissions under adsorption conditions. We shall stop first, however, to discuss several general limiting cases that follow from (14)–(16).

First, taking the limits as $a \to 0$ (no interaction between the particles and the electron) and $S \to \infty$ (no particles) we get $R = 1$ and (15) goes over into the well-known expression for the quantum-mechanical emission current in the absence of adsorption[17]. In connection with the use in the cited papers[1,4,5] of one-dimensional models to describe the adsorption, let us examine furthermore how the limiting transition to the one-dimensional picture is made in formulas (14)–(16). A transition to a one-dimensional potential model is possible in the limit when the kinetic energy of the emitted electrons tends to zero. Under adsorption conditions, this limit corresponds to satisfaction of the rather stringent inequality

$$|2mE_fS/\hbar^2|\ll 1.\tag{17}$$

Only in this limit can the one-dimensional description of the influence of adsorption on field emission and photoemission be justified[1,4,5].

Taking (17) into account, we can approximately express the first sum in (14), in the limit as $\tilde{k} \to 0$, in the form

$$\sum_{\mathbf{l}}{}'\frac{1}{|\mathbf{l}|}\exp(i\mathbf{k}_{\parallel}\mathbf{l}+i\tilde{k}|\mathbf{l}|)\approx\frac{2\pi i}{S(\tilde{k}^2-\mathbf{k}_{\parallel}^2)^{1/2}}-\frac{\gamma_0}{S^{1/2}}+O(\tilde{k}),$$

where γ_0 is a dimensionless parameter that depends on the geometrical structure of the lattice[2)]. Separating furthermore in the second sum of (14) the term with $g = 0$, equal to $2\pi i/S(\tilde{k}^2 - k_{\parallel}^2)^{1/2}$, and introducing the notation

$$\frac{1}{b}=\frac{1}{a}+\frac{\gamma_0}{S^{1/2}}+\frac{4\pi}{S}\sum_{g\neq 0}\left\{\frac{\varphi_g(d)f_g(d)}{f_g(0)}-\frac{i}{2\tilde{k}_g}\right\},$$

we obtain in accordance with (15)

$$j=j[f_0]\frac{|\Lambda|^2}{|f_0(0)|^2}\left|f_0(0)+\frac{4\pi b}{S}f_0(d)\varphi_0^{(1)}(d)\right|^2.\tag{18}$$

When the condition (17) and the definition of $\tilde{k}_g$ are taken into account, the quantity b in (18) is real and independent of k or $k_{\parallel}$.

It is easy to verify that the current j in the form (18) coincides formally with the current calculated when $V_a(r)$ is calculated by a one-dimensional potential $V_a(z)$ in the form

$$\frac{2m}{\hbar^2}V_a(z)=-\frac{4\pi b}{S}\delta(z-d)$$

Such a potential (apart from the substitution $\lambda \equiv 4\pi b/S$) was used, in particular, for the model one-dimensional description of the influence of adsorption on field emission and photoemission[1,4,5]. It is seen from (18), at the same time, that the quantity λ, formally introduced in[1,4,5] as a certain adjustment parameter, actually depends not only on the individual properties of the adsorbed particles, but also on the geometry of the lattice. Since the region of applicability of the one-dimensional model is limited by the condition (17), which corresponds to rather small $|E_f|$, it turns out, the statements in[1,5] notwithstanding, to be unsuitable in most cases for the description of resonant tunneling under conditions of electron field emission and for the description of the behavior of electrons at relatively high energies under photoemission conditions.

4. INFLUENCE OF PERIODIC STRUCTURE ON PHOTOEMISSION

We use the obtained general relations to describe photoemission at low energies of the emitted electrons. We start with the simplest case, when the potential $V(z)$ decreases so rapidly (for example, exponentially or faster), that we can put $V(z) = 0$ in the calculation of $\varphi_g^{(1,2)}(z)$ and $f_g(z)$ in the energy interval adjacent to the threshold. Using the corresponding boundary conditions, we obtain

$$\varphi_g^{(1)}=\frac{1}{k_g}\sin k_g z,\qquad \varphi_g^{(2)}=\cos k_g z,\qquad f_g(z)=\exp(ik_g z).$$

The sum over g in (14) can be expressed in this case in the form

---

[2)] In particular, as shown by direct calculations, $\gamma_0 = 3.9$ for a quadratic lattice and $\gamma_0 = 4.0$ for a hexagonal one.

$$\frac{4\pi}{S}\sum_{\mathbf{g}}\left(\frac{\sin k_{\mathbf{g}}d}{k_{\mathbf{g}}}e^{ik_{\mathbf{g}}d}-\frac{1}{2k_{\mathbf{g}}}\right)=-\frac{2\pi i}{S}\sum_{\mathbf{g}}\frac{\exp(2ik_{\mathbf{g}}d)}{k_{\mathbf{g}}}$$
$$=-\sum_{\mathbf{l}}\frac{\exp[i\mathbf{k}_{\parallel}\mathbf{l}+ik|\mathbf{l}-2\mathbf{d}|]}{|\mathbf{l}-2\mathbf{d}|}. \qquad (19)$$

A comparison of (19) with the sum contained in the solution describing the motion of an electron in the field of a two-dimensional lattice made up of point centers[19] (see also (9)) shows that the last term in (14) can be interpreted as the action of an "image" potential, as it were, on the emitted electron. The primary adsorption lattice is located at a distance d from the surface of the metal, and the image is located, as it were, at a distance –d in the interior of the metal. Substituting (19) in (16) and using the explicit form of the functions f_g and $\varphi_g^{(1,2)}$, we obtain

$$j=\frac{k_0\hbar}{m}|\Lambda|^2\left|1-\frac{4\pi e^{ik_0d}\sin(k_0d)}{Sk_0(ik-a^{-1}+\mathscr{Z})}\right|^2, \qquad (20)$$

where $k_0 \equiv (k^2 - k_{\parallel}^2)^{1/2}$ is the z component of the wave vector of the emitted electron and

$$\mathscr{Z}=\sum_{\mathbf{l}}{}'\frac{1}{|\mathbf{l}|}\exp\{i\mathbf{k}_{\parallel}\mathbf{l}+ik|\mathbf{l}|\}-\sum_{\mathbf{l}}\frac{1}{|\mathbf{l}-2\mathbf{d}|}\exp\{i\mathbf{k}_{\parallel}\mathbf{l}+ik|\mathbf{l}-2\mathbf{d}|\}.$$

We note that when (17) is satisfied the function $\mathscr{Z}$ can be expanded in powers of ik_0 and $i\mathbf{k}_{\parallel}$, so that

$$\mathscr{Z}=\mathscr{Z}_0+ik_0\mathscr{Z}_{1,0}-k_0^2\mathscr{Z}_{1,1}-\mathbf{k}_{\parallel}^2\mathscr{Z}_{2,2}+\ldots \qquad (21)$$

(there are no terms linear in the components $\mathbf{k}_{\parallel}$, because the function $\mathscr{Z}(\mathbf{k}_{\parallel})$ is even) Then

$$\mathscr{Z}_0=\frac{1}{2d}+\sum_{\mathbf{l}}{}'\left(\frac{1}{|\mathbf{l}|}-\frac{1}{|\mathbf{l}-2\mathbf{d}|}\right), \qquad \mathscr{Z}_{1,0}=\frac{4\pi d^2}{S},$$
$$\mathscr{Z}_{1,1}=-8\pi d^3/3S+\mathscr{F}(0)-\mathscr{F}(2d)+2d\mathscr{F}'(2d),$$
$$\mathscr{Z}_{2,2}={}^3/_2[\mathscr{F}(0)-\mathscr{F}(2d)+2d\mathscr{F}'(2d)]-2d^2\mathscr{F}''(2d),$$
$$\mathscr{F}(x)\equiv\frac{\pi}{S}\sum_{\mathbf{g}}{}'\frac{1}{|\mathbf{g}|^3}e^{(-|\mathbf{g}|x)}.$$

At low values of the parameter $d/S^{1/2}$, the last two expressions are respectively

$$\mathscr{Z}_{1,1}\approx-d(1+\gamma_0d/2S^{1/2}+\ldots),\ \mathscr{Z}_{2,2}=-d(1+\gamma_0d/S^{1/2}+\ldots)$$

The obtained relations make it possible to establish an explicit dependence of the photoemission current on the characteristics of the absorption lattice, and also to analyze a problem of fundamental interest, that of describing an essentially three-dimensional structure by a one-dimensional effective potential. To this end we consider first the limiting case $V_a = 0$. If we normalize the solution $f_0(z)$, as was done at the beginning of the section, by the condition

$$f_0(z)\underset{z\to\infty}{=}e^{ik_0z},$$

then $f_0(0)$ coincides with the known Jost function of scattering theory $f_0(0) \equiv f(p)$[23]. In the case of a sufficiently rapid decrease of the one-dimensional potential V(z) with increasing z, the function f(p) can be expanded in a series

$$f=\xi+\zeta p^2+\cdots, \qquad (22)$$

where $p = \hbar k_0 = (2mE_f - p_{\parallel}^2)^{1/2}$, and ξ and ζ are constants independent of p. Further, with the aid of (22) and the expression (15) for j with R = 1, we can calculate the total photoemission current I, which is obtained, as already mentioned, by integrating j over the corresponding initial state characterized by the quantum numbers E_i and $p_{\parallel}$.

Assuming the metal temperature to be equal to zero, we have for I in the threshold energy interval, in the absence of adsorption[17],

$$I=\frac{e\pi\rho_0}{2m}\int_0^{p_0}p[2m(\hbar\omega-\hbar\omega_0)-p^2]j(p)\,dp, \qquad (23)$$
$$p_0=[2m(\hbar\omega-\hbar\omega_0)]^{1/2},$$

where $\rho_0 \equiv \rho(E_i, p_{\parallel})$ is the density of states on the Fermi surface of the metal $(E_i = E_F, p_{\parallel} = 0)$[3)]. Substitution of (22) in (23) with allowance for the condition $\xi \gg \zeta p^2$, corresponding to the limit of small final energies, yields

$$I=\xi^{-1}I^{(0)}[1-{}^6/_7\zeta m(\hbar\omega-\hbar\omega_0)+\ldots]. \qquad (24)$$

Here $I^{(0)}$ is the value of the photoemission current I in the absence of the potential V(z). (The dependence of $I^{(0)}$ on the difference $\hbar\omega - \hbar\omega_0$ is determined, as follows from (23), by the "five-halves law"[16,17]: $I^{(0)} \backsim (\hbar\omega - \hbar\omega_0)^{5/2}$).

In the presence of an adsorption lattice, the current j depends, in accord with (20), on all the components of the wave vector (or momentum), and not only on its z-component as in the one-dimensional case. At the same time, by integrating (20) over the initial state with allowance for (21), we obtain for the photoemission current I, as before, in full analogy with (24), the expression

$$I=I^{(0)}[\nu+\nu_1(\hbar\omega-\hbar\omega_0)+\ldots], \qquad (25)$$

where ν and ν_1 are constants independent of $\hbar\omega - \hbar\omega_0$. Here

$$\nu=[1-4\pi dS^{-1}/(a^{-1}-\mathscr{Z}_0)]^2,$$

and the coefficient ν_1 can also be expressed in terms of the coefficients of the expansion (21). At small values of the parameter $d/S^{1/2}$ we have

$$\nu_1={}^8/_7\pi md^4\hbar^{-2}S^{-1}(20\tau^{-2}+8\tau^{-1}),\ \tau\equiv2d/a-1.$$

A comparison of (24) with (25) shows that the non-one-dimensional picture produced upon adsorption can be described within the framework of assumptions made by using a one-dimensional effective potential $V_{eff}(z)$. This potential must be chosen such that the expansion coefficients ξ and ζ of the quantity f corresponding to it satisfy the conditions $\xi = \nu^{-1}$ and $\zeta = 7\nu_1/6m\nu^2$. Since the values of the Jost function do not define the corresponding potential uniquely, we can obviously indicate an entire family of one-dimensional effective potentials V_{eff}, the action of which at low energies is equivalent to the action of the considered two-dimensional lattice. We emphasize that the quantity $V_{eff}(z)$ introduced in this manner is by far not equal to $\overline{V(r)}$, i.e., to the true-three-dimensional potential averaged in the (x, y) plane. Moreover, the quantities V_{eff} and $\overline{V}$ can even have opposite signs.

Let us analyze furthermore certain characteristic features of the photoemission current, determined by the adsorbed particles. In the immediate vicinity of the threshold, the second term in (25) can be discarded

---

[3)] It is assumed here that the Fermi surface contains the point $p_{\parallel} = 0$ and is sufficiently smooth in its vicinity.

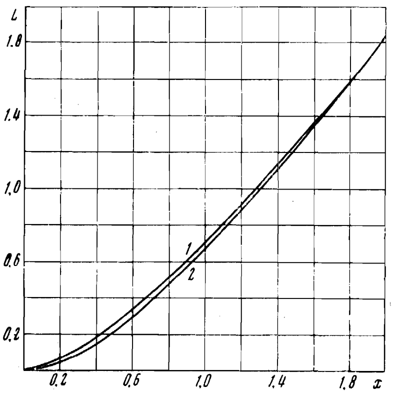

FIG. 1. Plot of the structure function L(x). 1—Quadratic lattice, 2—hexagonal lattice.

and the quantity I turns out to be proportional to $I^{(0)}$. We denote by θ the relative surface concentration of the adsorbed particles. θ is connected with the area of the unit cell of the adsorption lattice by the relation $s\theta = S_0$, where S_0 is the area per particle at the maximum density of the monolayer. Defining furthermore the structure function L by the equality

$$L \equiv 1 + 2d\mathscr{Z}_0 = 2d \sum_{\mathbf{l}}{}' \left\{ \frac{1}{|\mathbf{l}|} - \frac{1}{|\mathbf{l} - 2\mathbf{d}|} \right\}$$

and putting $\theta = S_0/4\pi d^2$, we obtain from (25)

$$I = \nu I^{(0)} = \left\{ 1 - \frac{2\theta/\theta_0}{2d/a - 1 + L(\theta/\theta_0)} \right\}^2 I^{(0)}. \tag{26}$$

A plot of the function L(x) is shown in Fig. 1. The limiting forms of L(x) are

$$L(x) = \begin{cases} \gamma_1 x^{3/2}, & x \ll 1, \\ 2x - \gamma_0 (x/\pi)^{1/2} + 1 + O(x^{1/2} e^{-1}), & x \gg 1. \end{cases}$$

Here $\gamma_{0,1}$ are constants that depend on the geometry of the surface structure[4)]. We note that the dependence of I on θ is not linear. Physically this nonlinearity is connected with the wave properties of the emitted electron, which, being smeared out, interacts simultaneously with several particles, and is not connected with the mutual influence of the adsorbed particles on one another (which can lead, in principle, to a dependence of a on θ).

If the relative surface concentration of the adsorbed particles is such that $(\theta/\theta_0)^{3/2}\gamma_1/\tau \ll 1$, we obtain from (26)[5)]

$$I = I^{(0)} \left[1 - \frac{4}{\tau}\left(\frac{\theta}{\theta_0}\right) + \frac{4}{\tau^2}\left(\frac{\theta}{\theta_0}\right)^2 + \frac{4\gamma_1}{\tau^2}\left(\frac{\theta}{\theta_0}\right)^{5/2} + \ldots \right]. \tag{27}$$

A comparison of the measured $I(\theta)$ dependence with (26) and (27) makes it possible, in principle, to determine experimentally the parameters characterizing the surface structure.

If each individual particle acts as a repulsion center, then[22] $0 \leq a \leq \mathscr{R}$. Since usually $2d > \mathscr{R}$, we get $2d > a$, and according to (27), $I < I^{(0)}$, i.e., an effective repulsion takes place. On the other hand, if the individual adsorbed particles are attraction centers, different cases are possible[22]. If this attraction is relatively weak, then $a < 0$ and, as seen from (27), at small relative surface concentrations we have effective attraction, so that $I > I^{(0)}$, In the region of large θ/θ_0, according to (26) we can have $I < I^{(0)}$, i.e., the effective attraction gives way to an effective repulsion, in spite of the fact that each individual particle acts on the electron as an attraction center. If the attraction of one center is large enough, so that a bound electronic state can be produced on it, then $0 < a < \infty$, and either $I < I^{(0)}$ or $I > I^{(0)}$ is possible, depending on the values of the parameters 2d/a and θ/θ_0.

As follows from (26) and (27), the photoemission current can increase anomalously at definite values of the parameters, corresponding to vanishing of the constant ξ. This effect is analogous in its physical nature to an increase in the cross section of the elastic scattering of slow particles by a potential well having a virtual level, the virtual bound states being realized in this case on an aggregate of centers producing the adsorption lattice[6)].

5. RESONANT TUNNELING IN FIELD EMISSION

To describe the laws governing electron field emission it is necessary to substitute in (14)—(16) the corresponding solutions of the one-dimensional equation with $V(z) = -eFz$. The solutions $\varphi_g^{(1,2)}$ and f_g can be expressed in this case in terms of the Airy functions Ai and Bi. In fields that are not too strong, so that $eFd/w \ll 1$, it can be easily shown with the aid of the asymptotic formulas for the function Ai and Bi that $\varphi_g(d)$ and $f_g(d)$ can be calculated in the interval from $0 < z < d$ by using the solutions of the free equation $V(z) = 0$. The sum over g in (14) can then be transformed in analogy with the procedure used in the preceding section. As a result, in accordance with (15), we obtain for the field-emission current with allowance for the substitution $k = i\kappa$

$$j = j^{(0)} \left| 1 + \frac{M}{\varkappa - H - iQ} \right|^2 \equiv R(\varkappa, \mathbf{k}_\parallel) j^{(0)}, \tag{28}$$

where $j^{(0)}$ is the known[8, 17] expression for the field-emission current with allowance for the influence of adsorption:

$$M(\varkappa, \mathbf{k}_\parallel) = \frac{4\pi}{S} \exp[-d(\varkappa^2 + \mathbf{k}_\parallel^2)^{1/2}] \frac{\operatorname{sh}[d(\varkappa^2 + \mathbf{k}_\parallel^2)^{1/2}]}{(\varkappa^2 + \mathbf{k}_\parallel^2)^{1/2}}, \tag{29}$$

$$H(\varkappa, \mathbf{k}_\parallel) = \frac{1}{a} + \sum_{\mathbf{l}}{}' \frac{1}{|\mathbf{l}|} \exp(i\mathbf{k}_\parallel \mathbf{l} - \varkappa|\mathbf{l}|) - \sum_{\mathbf{l}} \frac{1}{|\mathbf{l} - 2\mathbf{d}|} \exp(i\mathbf{k}_\parallel \mathbf{l} - \varkappa|\mathbf{l} - 2\mathbf{d}|),$$

The quantity Q depends essentially on the structure of the metal and cannot be obtained in general form. In the simplest model of a square well of depth V_0, we obtain

$$Q = \frac{2\pi\hbar^2}{SV_0 m} \sum_{g} \left(\frac{2mV_0}{\hbar^2} + \varkappa_g^2 \right)^{1/2} \exp(-2\varkappa_g d). \tag{30}$$

Here $\kappa_g^2 \equiv \kappa^2 + (\mathbf{k}_\parallel + 2\pi \mathbf{g})^2$. Formula (28) is analogous in its structure to the Breit-Wigner formula for the resonant-scattering cross section[23]. Accordingly, the field emission current can have under certain condi-

---

[4)] The numerical values of γ_0 were cited in footnote 2. The numerical values of γ_1 are 0.82 and 0.93 for a quadratic and hexagonal lattice, respectively.

[5)] Simple estimates show that this inequality holds at d = 1–2Å and $|\tau| = 1$, starting with values $l_a \approx$ 10–20Å.

[6)] These expressions are prevented from going formally to infinity when $\xi = \nu^{-1} = 0$ by taking into account the next terms of the expansion in the parameter of the threshold approximation. Physically, of course this means only a sharp increase of I (see, in particular, [5]).

tions a maximum in the vicinity of the values of κ and $k_{\parallel}$ corresponding to the vanishing of the difference $H - \kappa$.

Before we proceed to a more detailed analysis of formula (28), we note the following. As already indicated in Sec. 2, to be able to neglect the contribution made to the current by the terms of the series (6) with $q \neq 0$, it is necessary to satisfy a condition that, when account is taken of the relation $|E_f| \approx w$, can be expressed in the form

$$\frac{\hbar^2\pi^2}{eFl_a^2}\left(\frac{2|E_f|}{m}\right)^{1/2} > 1. \qquad (31)$$

Furthermore, the inequality $\pi^2\hbar^2/eFml_a^3 \gg 1$ holds for all the field intensities F and that l_a that are realized in experiments. From a comparison of this inequality with (31) it follows that even where (31) is satisfied there are two limiting cases:

$$l_a(2m|E_f|)^{1/2} \ll \hbar \text{ and } l_a(2m|E_f|)^{1/2} > \hbar.$$

Satisfaction of the first inequality is equivalent to satisfaction (17), and is possible under field-emission conditions only when the surface is very densely covered. In addition, since obviously $d^2 < S$, the inequality $(d\kappa)^2 < 1$ holds simultaneously with (17), so that the possible strong dependence of R on κ does not occur in the indicated limit.

Let us turn to the case $l_a(2m|E_f|)^{1/2} > \hbar$. Bearing in mind that we can simultaneously put here $\kappa d \gtrsim 1$, we confine ourselves in the expression for H only to one term in the second sum and to several terms corresponding to the nearest neighbors in the first sum. In the simplest case of a quadratic lattice, when $|\mathbf{l}_2| = |\mathbf{l}_1| = l_a$ and $|\mathbf{l}_1 \times \mathbf{l}_2| = l_a^2 = S$, we obtain from (29)

$$H(\varkappa, \mathbf{k}_{\parallel}) = \frac{1}{a} - \frac{e^{-\varkappa d}}{2d} - \frac{2}{l_a}\exp(-2\varkappa l_a)\left[\cos(\mathbf{k}_{\parallel}\mathbf{l}_1) + \cos(\mathbf{k}_{\parallel}\mathbf{l}_2)\right], \qquad (32)$$

$$M = 2\pi / (\varkappa^2 + \mathbf{k}_{\parallel}^2) l_a^2.$$

As follows from (32), the function R has a maximum when κ and $k_{\parallel}$ are in the vicinity of values corresponding to the satisfaction of the equation $H = \kappa$. Physically, this maximum corresponds to resonant tunneling through a bound state on a lattice of adsorbed particles. As $l_a \to \infty$ and $d \to \infty$, the condition $H = \kappa$ corresponds to $\kappa = a^{-1}$, i.e., the resonant energy is equal to the energy of the bound state on one adsorbed center. The second term in the right-hand side of (32) describes the shift of the energy of the bound state on the potential of one particle, due to the presence of metal at a distance d from its surface[7)]. Finally, the third term is due to the influence of the periodic surface structure and takes into account the interaction of the particles with one another. Owing to the dependence of this term on $k_{\parallel}$, the resonant values $\kappa = \kappa_*$ also turn out to depend on $k_{\parallel}$. Physically this reflects the existence of an entire band of bound states in the considered system, as also on an isolated lattice[19].

As follows from (32), within the framework of the one-dimensional picture[1] only certain qualitative features of the phenomenon are correctly reflected: since it is possible to form quasistationary surface states, the tunneling probability for definite groups of electrons is not small. At the same time, the relations obtained with the aid of the one-dimensional analysis have at least three essential differences. First, the resonant values are those of the total energy of the emitted electrons, and not of $E_z = E_f - p_{\parallel}^2/2m$ as in the one-dimensional model. Second, in the general case there exists not one value of the resonant total energy, but a certain band. Finally, the position and form of the resonance depend, generally speaking, on the geometrical characteristics of the surface structure.

In the limiting case $S \gg a^2$ corresponding to individual isolated atoms, Eq. (27) with allowance for (31) can be recast in a form similar to the main formula of[3,6]. Namely, near the resonance, assuming $|k - a^{-1}| \ll a^{-1}$ and putting $E_* = -\hbar^2/2ma^2$, we obtain

$$R = \left|1 + \frac{2\pi\hbar^2/mS}{E_f - E_* + i\Gamma}\right|^2. \qquad (33)$$

In the simplest model of a metal (square "box" of depth $V_0 > 0$), putting $2\pi d/l_a \ll 1$ and replacing approximately the summation by integration in (30), we obtain

$$\Gamma = \frac{|E_*|\hbar}{d(2mV_0)^{1/2}}\exp(-2d\varkappa_*).$$

The energy distribution P of the emitted electrons is obtained by integrating j over all the permissible values of P. Since R does not depend on $k_{\parallel}$, the connection between the values of P in the presence and in the absence of adsorption is also described by (33). Figure 2 shows the result of the reduction, with the aid of (33), of the experimental data[2] on the energy distribution of electrons, obtained under conditions of field-emission from a pure tungsten surface and from the same surface but covered with individual zirconium atoms. The value of Γ was calculated by starting from the formula presented above, under the assumption that $d = 0.87$ Å (the approximate ionic radius of Zr) and $V_0 = 12$ eV (Γ depends little on V_0 and there is no need to make the model value of V_0 more precise). The values of S were chosen approximately by starting from the data of[3], according to which one Zr atom is located on an area occupied by 20–30 W atoms (corresponding to $S = 100$–120 Å^2), and also from allowance

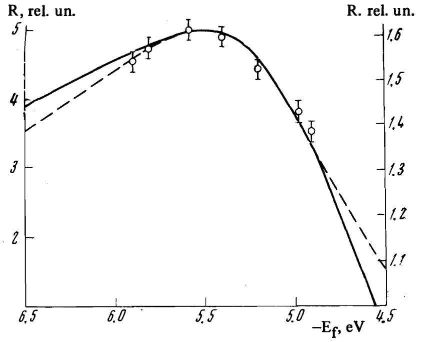

FIG. 2. Comparison of the dependence of R on $-E_f$, given by formula (33) (curves), with experiment [3] (points). The solid and dashed curves correspond to S = 100Å^2 (left-hand scale) and S = 30Å^2 (right-hand scale).

[7)] It follows from (32) that when a particle capable of forming a bound state with an electron approaches a metal surface from the outside, the absolute value of the energy of the bound state decreases. This agrees with the results of model calculations of the behavior of an atom near a metal surface [24].

for the possibility that the emission comes from only part of the surface. As seen from Fig. 2, there is good agreement between theory and experiment.

We note in conclusion that if the energy level corresponding to the quasistationary state of the system is outside the energy interval of the emitted electrons, we can obtain from (28)

$$j \approx j^{(0)}[1 + 4\pi S^{-1}\chi(\varkappa, \mathbf{k}_{\parallel})], \tag{34}$$

where

$$\chi(\varkappa, \mathbf{k}_{\parallel}) = \frac{1}{(\varkappa^2 + \mathbf{k}_{\parallel}^2)^{1/2}} \frac{\varkappa - a^{-1}}{(\varkappa - a^{-1})^2 + Q^2}.$$

Taking $S \backsim \theta^{-1}$ into account, we see that the correction term in (34) tends to zero in proportion to θ.

6. CONCLUSION

The general scheme of the performed calculations can be summarized in the following manner: The wave function of the emitted electrons outside the metal is expanded in a two-dimensional Fourier series. In the low-energy limit, the main contribution to the emission current is made by the zeroth harmonic of the Fourier expansion. This harmonic can subsequently be obtained by solving a system of linear equations that take into account the inhomogeneity of the micropotential near the surface, and in the limit of infinitesimally small electron energy it is possible to construct for this harmonic an equation with an effective one-dimensional potential. The usual threshold reasoning is used to match the corresponding solutions on the boundary with the source. The most significant influence of the microscopic inhomogeneity of the metal surface is caused at low energies by the lattice with the largest period if, of course, the interaction of the emitted electrons with the corresponding centers is large enough. An influence of this kind is exerted by particles adsorbed on the surface. The influence of the adsorbed particles was calculated using the model of small-radius potentials. Such an approach not only explains the qualitative effects, but makes it possible also to express the observed influence of the adsorption on the photoemission and field emission in terms of independent characteristics of the adsorbed particles. The approach developed in the paper can be generalized also to include other cases, particularly thermionic emission. We take particular note in this connection of the possibility, mentioned at the end of Sec. 4, that the photoemission current can increase sharply as a result of adsorption in comparison with the current from a pure surface. Under thermionic emission conditions this effect can lead to an appreciable change in the energy distribution of the emitted thermoelectrons, and also to a change in the temperature dependence in the pre-exponential factor.

It is possible to take into account in similar fashion the microscopic inhomogeneity of the metal surface itself. This inhomogeneity becomes essential at higher energies of the emitted electrons (on the order of several times 10 eV). It has been shown in a number of papers, especially in connection with investigations of electron reflection from metal surfaces[25], that the metal itself can be described quite effectively by taking into account the discrete nature of the structure of only the monatomic layer closest to the surface, by regarding the "internal" region of the metal as a continuous "substrate." Within the framework of such an approach, it is natural to use methods similar to those developed in the present paper. In particular, we can estimate with the aid of the results of Sec. 4 that part of the difference in the photoemission properties of different faces of a single crystal which is due to the difference between the geometry of the surface plane lattice on the faces. The influence exerted on the emission by the adsorption lattice can also be directly generalized in the case when the potential V(z) has a more complicated form.

It was assumed in this paper that the adsorbed particles form a regular two-dimensional lattice on the surface of the metal. At the same time, at relatively low energies, an important role is played only by the first Fourier harmonic of the sought solution, and the role of the lattice geometry is determined the main only by the area of the corresponding unit cell, and not by its shape. We can conclude from the foregoing that the results at sufficiently low energies, do not change significantly when S is replaced by its mean value $\overline{S}$, even if the surface structure cannot be regarded as strictly ordered.

---

[1] C. B. Duke and M. E. Alferieff, J. Chem. Phys., **46**, 923 (1967).

[2] H. E. Clark and R. D. Young, Surf. Sci., **12**, 385 (1968).

[3] E. W. Plammer, J. W. Gadzuk, and R. D. Young, Sol. Stat. Com., **7**, 487 (1969).

[4] A. Modinus, Surf. Sci., **20**, 55 (1970); **22**, 473 (1970).

[5] J. W. Gadzuk, Surf. Sci., **18**, 193 (1969).

[6] J. W. Gadzuk, Phys. Rev., **B1**, 2110 (1970).

[7] B. Halpern and R. Gomer, J. Chem. Phys., **51**, 3043 (1969).

[8] L. N. Dobretsov and M. V. Gomoyunova, Emissionnaya élektronika (Emission Electronics), Nauka, 1966.

[9] D. J. Flood, J. Chem. Phys., **52**, 1355 (1970).

[10] A. D. Brailsford and L. C. Davis, Phys. Rev., **B2**, 1708 (1970).

[11] J. G. Endriz and W. E. Spiser, Phys. Rev. Lett., **27**, 570 (1971); **24**, 64 (1970).

[12] J. M. Elson and R. H. Ritchie, Phys. Rev., **B4**, 4129 (1971).

[13] L. N. Dobretsov, Fiz. Tverd. Tela **7**, 3200 (1965) [Sov. Phys.-Solid State **7**, 2589 (1966)].

[14] M. L. Glasser, Phys. Rev., **B3**, 1772 (1971).

[15] E. W. Plammer and R. D. Young, Phys. Rev., **B1**, 2088 (1970).

[16] A. M. Brodskiĭ and Yu. Ya. Gurevich, Zh. Eksp. Teor. Fiz. **54**, 213 (1968) [Sov. Phys.-JETP **27**, 114 (1968)].

[17] A. M. Brodskiĭ and Yu. Ya. Gurevich, Izv. AN SSSR ser. fiz. **33**, 388 (1969).

[18] F. I. Itskovich, Zh. Eksp. Teor. Fiz. **50**, 1425 (1966) [Sov. Phys.-JETP **23**, 945 (1966)].

[19] G. Subramannan, Vestnik MGU, ser. fiz.-khim. **10**, 10 (1970).

[20] R. G. Arkhipov, Zh. Eksp. Teor. Fiz. **59**, 1711 (1970) [Sov. Phys.-JETP **32**, 931 (1971)].

[21] Yu. N. Demkov and V. N. Ostrovskiĭ, ibid. 59, 1765 (1970) [32, 959 (1971)].

[22] F. Cologero, Phase Function Method in the Theory of Potential Scattering (Russian Transl.), Mir, 1972.

[23] R. Newton, Scattering Theory of Waves and Particles, McGraw, 1964.

[24] A. J. Bennet and L. M. Falicov, Phys. Rev., 151, 512 (1966).

[25] C. W. Tucker and C. B. Duke, Surf. Sci., 24, 31 (1971).

Translated by J. G. Adashko
199