

The effect of the microscopic structure of metal surfaces on their optical properties

A. M. Brodskii and M. I. Urbakh

Institute of Electrochemistry of the Academy of Sciences of the USSR
Usp. Fiz. Nauk 138, 413-453 (November 1982)

This review treats the current state of studies on the optical properties of metal surfaces. We discuss the use of the theory developed in recent years for describing the results of concrete experiments in modulation spectroscopy of surfaces. We especially examine the dependence of the surface-plasmon spectrum on the microscopic structure of the surface. We describe how one can obtain information from the data of optical measurements on the electronic structure of the surface, and in particular, we discuss the effect of adsorption on this structure. The review of the literature covers the period to the end of 1980.

PACS numbers: 78.20.Dj, 68.45.Da, 73.20. - r, 68.20. + t

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1. INTRODUCTION

In recent years the optics of metal surfaces has again occupied the focus of attention of researchers concerned with surface phenomena. This has primarily involved the fact that the experimental technique of the studies has taken a true revolutionary leap in the past decade. This involves the development of ellipsometry,^{1,2} modulation spectroscopy,^{3,4} attenuated-total-reflection spectroscopy (ATRS),^{5,6} studies of external photoemission at the boundary of a metal with a vacuum or other media,^{7,8} and also studies of surface Raman scattering by molecules adsorbed on a surface, which have led to the discovery of the so-called¹⁾ anomalously intense Raman scattering*.^{9,10} These studies have enabled us to obtain considerably more accurate quantitative data than previously on the light reflection coefficients and on the characteristics of surface excitations. In order to characterize the potentialities of optical studies of metal surfaces, it suffices to mention the extreme accuracy of the results obtained in the experiments listed above. For example, in using the modulation methodology, the accuracy of measuring the phase shift of the reflected light caused by a change in the properties of the surface reaches $\gamma = 10^{-6}$ radians, or if we transform to lengths, then we have $\gamma c/\omega \approx 10^{-12}$ cm,

¹⁾In the English-language literature this phenomenon is called surface enhanced Raman scattering (SERS).

where ω and c are the frequency and velocity of the light.²⁾

In a number of cases, the observable relative effects of the electronic structure of the surface of metals have proved to be considerably larger than the natural parameter $\delta\omega/c$, where δ is a quantity of the order of atomic dimensions. This development of the experimentation was substantially stimulated by the demands of theory and applications in microelectronics, metal physics, catalysis, adsorption, etc. It was found that one can determine from the results of optical measurements the most important characteristics of the electronic structure of metal surfaces, and the effect on it of adsorption and external fields. In interpreting the new experimental data, it has proved necessary to develop the electrodynamics of metal surfaces with the microscopic structure of the surface taken into account. Here we should stress that experiment considerably outstripped theory until recently. A number of experimental results, in particular, anomalously intense Ra-

²⁾Whereas the results of the studies employing ellipsometry, photoemission, and ATRS are relatively well known,^{1, 2, 5-8} the very recent development of the modulation methods such as electroreflection (ER) and electromodulation of the phase of reflection [= modulation interferometry (MI)] have not yet been duly reflected in the physics review literature. In line with this, we shall give a special description in Sec. 3 of the various possible applications of ER and MI.

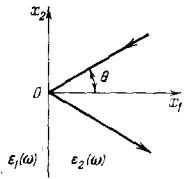


FIG. 1. Schematic diagram of light reflection from a metal-external medium boundary. The x_1 axis lies along the normal to the surface of the metal, which occupies the half-space $x_1 < 0$. The plane of incidence of the light coincides with the plane (x_1, x_2) , and θ is the angle of incidence of the light.

man scattering, had not yet found even an unambiguous, generally accepted explanation, not to speak of a quantitative one. In view of the complexity of the phenomena that we are describing, one has often employed phenomenological models with unclear limits of applicability in interpreting the experiments.

In recent years the theory of the optics of metal surfaces has begun to develop especially intensively. Substantial results have been obtained that have made it possible not only to provide a quantitative or semiquantitative description of various phenomena, but also to predict a number of new effects. The description and analysis of the fundamental results of the development of the theory in the given field in the past decade constitute the main content of this review. Here we have restricted the treatment to discussing problems in which the dimensions of the transition region from the metal to the external medium are much smaller than the wavelength of light. For example, we do not treat the influence on reflection of rather thick films on the surface of a metal. Since we are discussing the optical range of frequencies, we shall pay especial attention to the electron response to an external electromagnetic field.

We recall the scheme of derivation of the well-known¹¹ Fresnel formulas for the coefficients of light reflection, which we shall employ later in the theoretical description as a zero-order approximation. We consider the reflection of light in the geometry presented in Fig. 1. Reflection is described by the macroscopic Maxwell equations with the dielectric function $\epsilon(x_1, \omega)$, which has a discontinuity at the surface:

$$\epsilon(x_1, \omega) = \epsilon_1 \theta(-x_1) + \epsilon_2 \theta(x_1), \quad (1.1)$$

Here $\epsilon_1 \equiv \epsilon_1(\omega)$ and ϵ_2 are respectively the permittivities of the metal and of the external medium, and $\theta_1(x_1)$ is a step function. Upon employing the continuity of the tangential components of the electric field $\mathcal{E}_\parallel = \{\mathcal{E}_2, \mathcal{E}_3\}$ and the component of the displacement D_1 normal to the surface, one can derive¹¹ without difficulty the following expressions for the reflection coefficients R_s and R_p for s - and p -polarized light, respectively:

$$R_s^F = |r_s^F|^2, \quad r_s^F = \frac{\left(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2\right)^{1/2} - \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2\right)^{1/2}}{\left(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2\right)^{1/2} + \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2\right)^{1/2}},$$

$$R_p^F = |r_p^F|^2, \quad r_p^F = \frac{\epsilon_2 \left(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2\right)^{1/2} - \epsilon_1 \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2\right)^{1/2}}{\epsilon_2 \left(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2\right)^{1/2} + \epsilon_1 \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2\right)^{1/2}}; \quad (1.2)$$

Here $\mathbf{k}_\parallel = \{k_2, k_3\}$ are the tangential components of the

wave vector in the incident monochromatic wave. Let us state immediately the features that will be essential below in the derivation and structure of the formulas (1.2). First, in deriving (1.2), we have treated only the components of the field continuous at the surface. This can be interpreted as a rearrangement of Maxwell equations by choosing the continuous quantities \mathcal{E}_\parallel and \mathcal{D}_1 as the sought functions. The need to pass in a similar manner to treating only quantities continuous in the zero order in $\delta\omega/c$ subsequently arises in taking into account the microscopic structure of the transition layer at the surface.

Second, the magnitude of the amplitude of the reflection coefficient for p -polarized light $r_p^F(k_\parallel)$ becomes infinite when

$$k_\parallel^2 = \frac{\omega^2}{c^2} \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}, \quad (1.3)$$

That is, this happens when the frequency ω and the wave vector \mathbf{k}_\parallel are related by the dispersion law for surface plasmons.¹² As we shall elucidate below, the fulfillment of the relationship (1.3) is equivalent to the appearance of a pole in the Fourier components with respect to \mathbf{x}_\parallel of the Green's function for the Maxwell equation. The appearance of this pole in the Green's function proves to be the most general condition for appearance of surface excitations. Third, the formulas of (1.2) imply a substantial dependence on the frequency ω of the tangential component $\mathcal{E}_\parallel(0)$ and the normal component $\mathcal{E}_1(+0) = \mathcal{D}_1(0)/\epsilon_2$ of the fields near the surface. This is caused by interference of the wave incident on the metal with the reflected wave. For example, for p -polarized light we have

$$|\mathcal{E}_1(+0)|^2 = |1 - r_p^F(k_\parallel)|^2 \sin^2 \theta \cdot \mathcal{E}_p^2,$$

$$|\mathcal{E}_\parallel(0)|^2 = |1 + r_p^F(k_\parallel)|^2 \cos^2 \theta \cdot \mathcal{E}_p^2, \quad k_\parallel = \frac{\omega}{c} \sqrt{\epsilon_2} \sin \theta, \quad (1.4)$$

Here \mathcal{E}_p is the amplitude of the field in the incident wave, and θ is the angle of incidence of the light. How essential is a relationship of the form of (1.4) for effects determined by the value of the field near the surface can be seen from Fig. 2, which is drawn from the

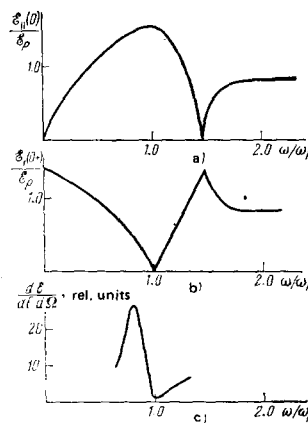


FIG. 2. Frequency-dependences of the tangential component $|\mathcal{E}_\parallel(0)|$ and the normal component $|\mathcal{E}_1(0+)|$ of the fields near the surface, as given by the relationships (1.4). Diagram (c) shows the experimentally measured¹⁴ frequency-dependence of the photoemission cross-section from surface states localized in the (100) surface of Al. The angle of incidence is $\theta = 45^\circ$, and the plasma frequency is $\hbar\omega = 15$ eV.

data of Refs. 13 and 14, which dealt with photoemission from surface levels. In order to emphasize the non-triviality of the explicit correlation between the vanishing of the normal component of the field and the suppression of photoemission (Fig. 2), we note that until very recently the frequency-dependence of photoemission had been associated only with the features of behavior of the electron densities of states in metals. The general laws of the effect of the structure of the surface layer on the spatial distribution of the electromagnetic field and the light reflection coefficients have been treated in greatest detail within the framework of the microscopic theory in Refs. 15-22. Just like the authors of the cited studies, we shall start with the following mode of writing the Maxwell equations in the medium for the monochromatic field $\vec{\mathcal{E}}(\mathbf{x}, \omega)$ having the frequency ω :

$$\Delta \vec{\mathcal{E}}(\mathbf{x}, \omega) - \text{grad div } \vec{\mathcal{E}}(\mathbf{x}, \omega) = -\frac{\omega^2}{c^2} \int d^3x' \vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega) \vec{\mathcal{E}}(\mathbf{x}', \omega). \quad (1.5)$$

Equation (1.5) is derived in first-order perturbation theory with respect to the interaction of the electromagnetic field with matter. Henceforth the main role will be played by the Green's function corresponding to Eq. (1.5), in terms of which the observable macroscopic quantities are expressed, rather than by Eq. (1.5) itself. The tensor for the nonlocal dielectric permittivity $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$ that enters into (1.5) describes the response of the system being studied to the external electromagnetic field. According to the scheme of Kubo,²³ the quantity $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$ is expressed in terms of the values of the commutators of the electron currents averaged over the Gibbs ensemble. The possibility arises similarly of taking microscopic effects²³ into account within the framework of various models. In the general case Eq. (1.5) must be supplemented with the dynamic equation for the material (for the electrons), including its own response function. The latter equation can describe independent electron excitations, which are dynamically coupled with the field $\vec{\mathcal{E}}(\mathbf{x}, \omega)$ only in the higher orders of perturbation theory. The problems that arise here are still far from solution. We shall touch upon them in Sec. 6, which is concerned with the spectrum of surface excitations.

It proves convenient to represent the quantity $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$ that enters into (1.5) in the form

$$\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega) = \epsilon_{ij}^0(\mathbf{x}, \mathbf{x}', \omega) + \delta\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega), \quad (1.6)$$

Here we have

$$\epsilon_{ij}^0(\mathbf{x}, \mathbf{x}', \omega) = \epsilon_{ij}^m(\mathbf{x} - \mathbf{x}', \omega) \theta(-x_1) + \epsilon_2 \delta_{ij} \delta(\mathbf{x} - \mathbf{x}') \theta(x_1) \quad (1.7)$$

The coordinate x_1 lies along the normal to the surface of the metal, whose bulk properties are characterized by the nonlocal dielectric-permittivity tensor $\epsilon_{ij}^m(\mathbf{x} - \mathbf{x}', \omega)$. We shall assume that the dielectric permittivity ϵ_2 of the external medium is a real quantity in the frequency interval under study. The term $\delta\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega)$ that takes into account the effect of the surface region rapidly declines at atomic distances from the surface $|x_1|, |x'_1| < \delta$. The quantity δ denotes the distance at which an external perturbation becomes screened by the electrons of the metal. Correspondingly, δ is much less than both the wavelength of light in the external medium $\lambda_2 = (\epsilon_2)^{-1/2} \cdot 2\pi c/\omega$ and the wavelength in the

metal $\lambda_1 = (|\epsilon|)^{-1/2} \cdot 2\pi c/\omega$. In the frequency interval under study, we can also rule out features of light reflection involving the anomalous skin effect.

At a fixed point \mathbf{x} , the tensor $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$ usually differs substantially from zero only in a certain region with dimensions of the order of δ near the point $\mathbf{x}' = \mathbf{x}$. The influence of nonlocality, or what is the same thing, of spatial dispersion of the dielectric permittivity $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$ is determined by the parameter δ/λ_1 . Usually δ is of the order of the lattice constant: $\delta \sim 10^{-7} - 10^{-8}$ cm. Therefore in the optical region the parameter δ/λ_1 is very small. Nevertheless it proves necessary to take into account spatial dispersion in treating cases in which several types of waves can propagate simultaneously in the metal, e.g., transverse and longitudinal.²⁴ Moreover, the role of spatial dispersion increases near absorption lines (resonances), since here the refractive index $\epsilon_1^{1/2}$ of the metal increases, and this means that the parameter δ/λ_1 does likewise. The stated effects must affect the optical characteristics of the separation boundaries. Consequently one must construct a theory that would allow one to take into account simultaneously both the dispersion of the dielectric permittivity in the metal and the microscopic effects at its surfaces. A number of serious problems arise here. These problems have been discussed in Refs. 17, 24, and 25. The general solution of the corresponding problem using the method of the Riemann boundary problem has been given in Ref. 17. As the results of Refs. 17, 24, and 25 imply, as a rule one can neglect spatial dispersion in the bulk of the metal far from its boundaries when the frequency lies outside the interval of bulk plasmons and far from absorption lines. Correspondingly, we assume for simplicity everywhere below, except for Sec. 6, that the bulk properties of the metal are described by a diagonal dielectric-permittivity tensor without spatial dispersion $\epsilon_i(\omega) \delta_{ij}$. In this case in (1.7) we can set

$$\begin{aligned} \epsilon_{ij}^m(\mathbf{x} - \mathbf{x}', \omega) &= \epsilon_i(\omega) \delta_{ij} \delta(\mathbf{x} - \mathbf{x}'), \\ \epsilon_{ij}^0(\mathbf{x}, \mathbf{x}', \omega) &= \epsilon_0(x_1, \omega) \delta_{ij} \delta(\mathbf{x} - \mathbf{x}'). \end{aligned} \quad (1.8)$$

The general expressions for the observable quantities that are obtained upon substituting (1.8) into the Maxwell equations are treated in Sec. 2. The formulas derived in Sec. 2 are employed in Sec. 3 in analyzing the results of modulation-spectroscopic studies. Here it proves necessary to introduce a concrete expression for $\vec{\epsilon}(\mathbf{x}, \mathbf{x}', \omega)$. Usually one employs the simplest expression for the nonlocal dielectric-permittivity tensor, which is derived in the so-called random-phase approximation (RPA)^{25, 26} without allowance for relativistic effects. This approximation allows one to obtain a reasonable relationship between the features of the spectrum of the system of electrons in the inhomogeneous medium and the behavior of the light reflection coefficient with relatively simple intermediate formulas.³⁾

³⁾ If we restrict the study to the behavior of various quantities near the features of the electron spectrum, then the results obtained upon using the RPA are to a certain degree model-free. Here the RPA serves only as a convenient language for presenting the accumulated information on the electron spectrum. Thus far in examining experiments on light reflection from metal surfaces no account has actually been taken of correlation effects beyond the framework of the RPA.

Section 4 discusses the effect of adsorption on the electrodynamics of metal surfaces. It turns out that one can effectively determine from the experimentally measurable optical quantities the most important electron characteristics of adsorption. This section also points out the relation between the effect of adsorption at the surface of metals on the reflection of light and anomalously intense Raman scattering by adsorbed molecules.

Real separation boundaries of media always have a certain roughness, whose dimensions depend on the concrete material, the method of preparing the surface, and the presence on the surface of adsorbed particles. A large number of experimental and theoretical studies has been devoted to studying the effect of roughness on the optical properties of metal surfaces. In Sec. 5 we shall discuss the effect of microroughness of the surface whose mean dimension $(\xi^2)^{1/2}$ is much smaller than the wavelength of light: $(\xi^2)^{1/2} \ll \lambda_1$. In Sec. 6 we analyze the dependence of the surface-plasmon spectrum on the microscopic characteristics of the surface. In the Conclusion we list the as yet unsolved problems which in our opinion merit the greatest attention at present.

2. BASIC RELATIONSHIPS

Starting with Eqs. (1.5), we shall discuss the reflection of light from a metal whose bulk characteristics are described by the local dielectric permittivity of (1.8). In the absence of roughness, we can assume that averaging over the two-dimensional crystal lattice takes place in the directions along the surface. Correspondingly we have $\delta\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega) = \delta\epsilon_{ij}(x_1, x'_1, \mathbf{x}_\parallel - \mathbf{x}'_\parallel, \omega)$. For simplicity, we shall assume below that $\delta\epsilon_{ij}(x_1, x'_1, \mathbf{x}_\parallel - \mathbf{x}'_\parallel, \omega) = \delta\epsilon_{ij}(x_1, x'_1, \mathbf{x}_\parallel - \mathbf{x}'_\parallel, \omega) \delta_{ij}$. The general case has been treated in Ref. 17. Under the assumptions that we have made, the Eqs. (1.5) are equivalent to the integral equations:

$$\xi_i(x_1, \mathbf{k}_\parallel) = \mathcal{E}_i^0(x_1, \mathbf{k}_\parallel) - \frac{\omega^2}{c^2} \sum_{j=1}^3 \int dx'_1 dx'_2 \mathcal{D}_{ij}^0(x_1, x'_1, \mathbf{k}_\parallel) \delta\epsilon_j(x'_1, x'_2, \mathbf{k}_\parallel) \xi_j(x'_1, \mathbf{k}_\parallel), \quad (2.1)$$

Here we have

$$(2\pi)^2 \delta^2(\mathbf{k}_\parallel - \mathbf{k}'_\parallel) \xi_i(x_1, \mathbf{k}_\parallel) = \int d^2x_\parallel e^{i\mathbf{k}_\parallel \cdot \mathbf{x}_\parallel} \xi_i(\mathbf{x}),$$

$$\delta\epsilon_i(x'_1, x'_2, \mathbf{k}_\parallel) = \int d^2x_\parallel e^{i\mathbf{k}_\parallel \cdot \mathbf{x}_\parallel} \delta\epsilon_i(x_1, x'_1, \mathbf{x}_\parallel).$$

In (2.1), $\mathcal{E}_i^0(x_1, \mathbf{k}_\parallel)$ and $\mathcal{D}_{ij}^0(x_1, x'_1, \mathbf{k}_\parallel)$ respectively denote the solution and the Green's function of the Maxwell equations with a sharp boundary, i.e., with $\delta\epsilon = 0$, which corresponds to the assigned value of the projection of the wave vector $\mathbf{k}_\parallel = \mathbf{k}_\parallel^0$ on the plane of the surface. We shall often below omit the value of \mathbf{k}_\parallel in the arguments of functions. The form of $\mathcal{E}_i^0(x_1, \mathbf{k}_\parallel)$ is determined by the choice of boundary conditions for the electromagnetic field. The expression for the Green's function is given in the Appendix.

In solving the problem it proves necessary to rearrange Eqs. (2.1) so that they contain only functions that vary slowly at atomic distances near the surface. For these functions we can choose

$$\xi_2(x_1, \mathbf{k}_\parallel), \xi_3(x_1, \mathbf{k}_\parallel) \text{ и } \mathcal{D}_1(x_1, \mathbf{k}_\parallel) = \int dx'_1 e_i(x_1, x'_1, \mathbf{k}_\parallel) \xi_1(x'_1, \mathbf{k}_\parallel). \quad (2.3)$$

Here we can derive from (2.1) (see the Appendix) the following system of integral equations^{15, 21}:

$$\mathcal{D}_1(x_1) = \mathcal{D}_1^0(x_1) - \frac{\omega^2}{c^2} \int dx'_1 dx'_2 \tilde{\mathcal{D}}_{11}^0(x_1, x'_1) \delta\epsilon_1^{-1}(x'_1, x'_2) \mathcal{D}_1(x'_1) - \frac{\omega^2}{c^2} \sum_{i=2,3} \int dx'_1 dx'_2 \tilde{\mathcal{D}}_{1i}^0(x_1, x'_1) \delta\epsilon_i(x'_1, x'_2) \xi_i(x'_1), \quad (2.4)$$

$$\xi_j(x_1) = \mathcal{E}_j^0(x_1) - \frac{\omega^2}{c^2} \int dx'_1 dx'_2 \tilde{\mathcal{D}}_{j1}^0(x_1, x'_1) \delta\epsilon_1^{-1}(x'_1, x'_2) \mathcal{D}_1(x'_1) - \frac{\omega^2}{c^2} \sum_{i=2,3} \int dx'_1 dx'_2 \tilde{\mathcal{D}}_{ji}^0(x_1, x'_1) \delta\epsilon_i(x'_1, x'_2) \xi_i(x'_1), \quad j=2, 3;$$

Here \mathcal{D}_{ij}^0 denotes the elements of the rearranged Green's function, whose explicit form is given in the Appendix. An essential point is that all the matrix elements of $\tilde{\mathcal{D}}_{ij}^0$ are continuous functions of x_1 and x'_1 for $x_1 \neq x'_1$. In addition to $\delta\epsilon_i(x_1, x'_1)$, the equations of (2.4) also contain the function

$$\delta\epsilon_1^{-1}(x_1, x'_1) = \epsilon_1^{-1}(x_1, x'_1) - \frac{\delta(x_1 - x'_1)}{\epsilon_0(x_1)}, \quad (2.5)$$

Here $\epsilon_1^{-1}(x_1, x'_1)$ is determined by the equality

$$\int \epsilon_1^{-1}(x_1, x'_1) \epsilon_1(x'_1, x'_1) dx'_1 = \delta(x_1 - x'_1). \quad (2.6)$$

Just like $\delta\epsilon_i(x_1, x'_1)$, the function $\delta\epsilon_1^{-1}(x_1, x'_1)$, which depends on the microscopic structure of the surface, differs from zero only for x_1 and x'_1 lying at atomic distances from the surface.

We can seek the solutions of the Eqs. (2.4) in the form of an iterative series. Here the parameter of the expansion proves to be the quantity $\delta\omega/c \ll 1$, as is shown by a simple estimate of the integrals. In order to obtain the observable quantities (coefficient of light reflection, ellipsometric parameters, etc.), it suffices to treat the asymptotic behavior of the fields far from the metal as $x_1 \rightarrow \infty$. In particular, in the case of incidence of p-polarized light, we find from (2.4):

$$\xi_2(x_1)_{x_1 \rightarrow \infty} \approx \xi_p [e^{-i(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2)^{1/2} x_1} + r_p(k_\parallel) e^{i(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2)^{1/2} x_1}] \cos \theta, \quad (2.7)$$

Here r_p is the amplitude of the reflection coefficient for p-polarized light. To the accuracy of first-order terms in the parameter $\delta\omega/c$, the latter is equal to

$$r_p(k_\parallel) = r_p^0(k_\parallel) \left\{ 1 - i \frac{2\epsilon_2 \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2 \right)^{1/2}}{(\epsilon_2 - \epsilon_1) [(\epsilon_1 + \epsilon_2) k_\parallel^2 - (\omega^2/c^2) \epsilon_1 \epsilon_2]} \times \left[\left(\frac{\omega^2}{c^2} \epsilon_1 - k_\parallel^2 \right) \Delta\epsilon_2(\omega) + \epsilon_1^2 k_\parallel^2 \Delta\epsilon_1^{-1}(\omega) \right] \right\}; \quad (2.8)$$

Here we have introduced the quantities $\Delta\epsilon_i$ and $\Delta\epsilon_1^{-1}$, which have the dimensions of distance, and which are equal to

$$\Delta\epsilon_i(\omega) = \int dx_1 dx'_1 \delta\epsilon_i(x_1, x'_1, \omega), \quad (2.9)$$

$$\Delta\epsilon_1^{-1}(\omega) = \int dx_1 dx'_1 \delta\epsilon_1^{-1}(x_1, x'_1, \omega). \quad (2.9')$$

Analogously we can write the amplitude of the reflection coefficient for s-polarized light in the form

$$r_s(k_\parallel) = r_s^0(k_\parallel) \left[1 + i \frac{2 \left(\frac{\omega^2}{c^2} \epsilon_2 - k_\parallel^2 \right)^{1/2}}{\epsilon_2 - \epsilon_1} \Delta\epsilon_3(\omega) \right]. \quad (2.10)$$

We note that, in deriving the formulas (2.8) and

(2.10), we have essentially employed the circumstance that the relative increments of all the fields that enter into (2.4) as x_1 varies over atomic distances near the surface are of the order of $\delta\omega/c$. At the accuracy at which we are working, this allows us to consider them constant within the limits of the surface layer and to remove them from the integrals containing $\delta\epsilon_i(x_1, x'_1, \omega)$ and $\delta\epsilon_i^{-1}(x_1, x'_1, \omega)$.

In the case of a surface layer having strictly defined boundaries, expressions of the form of (2.8) and (2.10) can be derived somewhat more simply by integrating the differential Maxwell equations over the layer and introducing corrections into the boundary conditions for the fields \mathcal{E}_2 , \mathcal{E}_3 , and \mathcal{D}_1 according to the scheme of Refs. 20, 24, and 34. However, the described method of integral equations has a number of advantages, since it enables one to treat surface layers having diffuse boundaries and it can be directly generalized to the case of media having spatial dispersion in the bulk¹⁷ and to the case of rough surfaces (see Sec. 4). Moreover, the use of this method allows one to calculate the terms of higher order in $\delta\omega/c$ and to find the behavior of the fields in the surface region. The latter is necessary, for example, in analyzing photoemission from surface states.^{13,14}

One can carry out a formal analysis of the iterative solution for $r_s(k_{||}, \omega)$ and $r_p(k_{||}, \omega)$, just as is done in the quantum-mechanical theory of potential scattering in treating the properties of the S-matrix using an equation of the Lippmann-Schwinger type.²⁷ Such an analysis implies that the quantities $r_{s,p}(k_{||}, \omega)$ as functions of the frequency in the complex plane can have only the same branch points as $r_{s,p}^F(k_{||}, \omega)$. Moreover, $r_p(k_{||}, \omega)$ can have poles corresponding to surface polaritons, as treated below. The stated properties of $r_{s,p}$ enable one (while taking account of the fact that they are response functions and vanish as $\omega \rightarrow \infty$) to construct the obvious dispersion relationships for them.

The reflection coefficients for s- and p-polarized light $R_s = |r_s|^2$ and $R_p = |r_p|^2$ are expressed in terms of the quantities r_s and r_p , as are the ellipsometric parameters Δ and ψ , which are defined by the equality

$$\text{tag } \psi e^{i\Delta} = \frac{r_p}{r_s}. \quad (2.11)$$

In particular, the following expressions are obtained from (2.8) and (2.10) for the relative changes in the light reflection coefficients $\Delta R_s/R_s$ and $\Delta R_p/R_p$, as compared with the Fresnel formulas:

$$\frac{\Delta R_s}{R_s} \equiv \frac{R_s - R_s^F}{R_s} = -\frac{4\omega \sqrt{\epsilon_2}}{c} \cos \theta \cdot \text{Im} \left(\frac{\Delta \epsilon_2(\omega)}{\epsilon_2 - \epsilon_1} \right), \quad (2.12)$$

$$\frac{\Delta R_p}{R_p} \equiv \frac{R_p - R_p^F}{R_p} = -\frac{4\omega \sqrt{\epsilon_2}}{c} \cos \theta \cdot \text{Im} \{ [(\epsilon_1 - \epsilon_2 \sin^2 \theta) \Delta \epsilon_2(\omega) + \epsilon_2 \epsilon_1^{-1} \Delta \epsilon_1^{-1}(\omega) \sin^2 \theta] [(\epsilon_1 - \epsilon_2)(\epsilon_2 \sin^2 \theta - \epsilon_1 \cos^2 \theta)]^{-1} \}. \quad (2.13)$$

The formulas that we have derived imply that the variation of the characteristics of light reflection and of the behavior of the field near a homogeneous surface of a metal on the structure of this surface is given by the complex quantities $\Delta \epsilon_i(\omega)$ and $\epsilon_i^{-1}(\omega)$, into which the microscopic characteristics of the surface enter in an averaged, integral form. Here the quantity $\Delta \epsilon_i^{-1}(\omega)$ has a considerably more complicated structure than $\Delta \epsilon_i(\omega)$,

with possible sharp maxima at certain $\omega = \omega_1$ that correspond to the eigenfrequencies of the system.

Dispersion law for surface plasmons

In certain cases special surface waves (surface polaritons) can arise at the surface of solids. In the case of metals the best known are the so-called surface plasmons. Surface polaritons are localized near the separation boundary of the media, and propagate along it with the wave vector $k_{||} = k_s(\omega)$, which is related to the frequency ω by the dispersion law $\omega = \omega_s(k_{||})$. Whenever the thickness of the layer where the surface wave is localized considerably exceeds the lattice constant of the metal, the conditions for the existence of such waves can be found from equations of the form of (1.5). It was first noted in Ref. 12 that the wave vectors of the surface polaritons correspond to a pole of the amplitude of the reflection coefficient of p-polarized light treated as a function of the frequency. Actually, as we see from (2.7), a solution of the Maxwell equations exists in this case that does not contain the incident wave, and which is proportional to $\exp[i((\omega^2/c^2)\epsilon_2 - k_{||}^2)^{1/2}x_1]$ as $x_1 \rightarrow \infty$, and to $\exp[-i((\omega^2/c^2)\epsilon_1 - k_{||}^2)^{1/2}x_1]$ as $x_1 \rightarrow -\infty$. For this to be so, it suffices to take one coefficient \mathcal{E}_p in (2.7) proportional to r_p^{-1} . The sections of the functions $((\omega^2/c^2)\epsilon_1 - k_{||}^2)^{1/2}$ and $((\omega^2/c^2)\epsilon_2 - k_{||}^2)^{1/2}$ that enter into the arguments of the exponentials given above were chosen such that we have $\text{Im}\{((\omega^2/c^2)\epsilon_1 - k_{||}^2)^{1/2}, ((\omega^2/c^2)\epsilon_2 - k_{||}^2)^{1/2}\} \geq 0$ in the physical plane. The condition of conservation of energy flux implies that the solution not containing the incident wave must necessarily decay on moving away from the surface (as $|x_1| \rightarrow \infty$). In order to satisfy the decay condition, the wave vector of the surface wave must satisfy the inequality $k_{||}^2 > (\omega^2/c^2)\epsilon_2$. Taking this circumstance into account yields the result that surface polaritons cannot be excited on the smooth surface of a metal by the field of an incident electromagnetic wave.²⁸

As we can easily test by employing (A.2), the poles of the amplitude of the reflection coefficient $r_p(k_{||})$ are at the same time poles of the Green's function of the Maxwell equations. As we know, the latter fix the spectrum of eigenexcitations of the system. The amplitude of the reflection coefficient r_p treated as a function of the complex variable $q = ((\omega^2/c^2)\epsilon_2 - k_{||}^2)^{1/2}$ has the following property:

$$r_p(q) = \frac{1}{r_p(-q)}. \quad (2.14)$$

This relationship does not depend on the model of the boundary, and is derived in exactly the same way as the corresponding condition for the matrix elements of the T-matrix in the theory of potential scattering.²⁷ In the case of a sharp metal-outer medium boundary, the condition $r_p(q) \rightarrow \infty$ (or $r_p(-q) = 0$) leads to the well-known relationship (1.3). In the presence of a surface layer the spectrum of surface polaritons becomes more complicated. A general expression for the dispersion law, which holds for an arbitrary structure of the surface layer, has been derived in Refs. 17 and 29. Here the scheme for calculating the amplitudes of the reflection coefficients that we have presented above was used. In agreement with the results of the cited studies, substi-

tution of the expression (2.8) into the equality⁴⁾ $r_p(-q) = 0$ yields the following equation for finding the dispersion law for surface polaritons:

$$\frac{1}{\varepsilon_1} \left(\frac{\omega^2}{c^2} \varepsilon_1 - k_{\parallel}^2 \right)^{1/2} + \frac{1}{\varepsilon_2} \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} = i \left[\frac{1}{\varepsilon_1 \varepsilon_2} \left(\frac{\omega^2}{c^2} \varepsilon_1 - k_{\parallel}^2 \right)^{1/2} \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} \Delta \varepsilon_2(\omega) - k_{\parallel}^2 \Delta \varepsilon_1^{-1}(\omega) \right]. \quad (2.15)$$

In the so-called three-layer model of the surface, which is characterized by introduction of the dielectric permittivity ε_1 , which is independent of the coordinates x_1 and x_1' , of an intermediate layer having the finite transverse dimension d , Eq. (2.15) transforms into the equation derived in Refs. 25 and 30. We can employ the smallness of the right-hand side of (2.15) with respect to the parameter $\delta\omega/c^5$ to write the dispersion law for the frequency of the surface plasmons as follows:

$$\omega_s(k_{\parallel}) = \omega_s^0(k_{\parallel}) - B(\omega_s^0) |k_{\parallel}| [\Delta \varepsilon_2(\omega) + \varepsilon_1 \varepsilon_2 \Delta \varepsilon_1^{-1}(\omega)]_{\omega=\omega_s^0}, \quad (2.16)$$

$$B(\omega) = \frac{2e^{1/2} (-\varepsilon_1)^{1/2}}{(\varepsilon_1 - \varepsilon_2) \{ \varepsilon_2 d \ln \varepsilon_1(\omega) / d\omega + [2(\varepsilon_1 - \varepsilon_2) \omega] \}};$$

Here $\omega_s^0(k_{\parallel})$ is the frequency of a surface plasmon propagating along the boundary of the two-phase system $\varepsilon_1/\varepsilon_2$, which is a solution of Eq. (1.3). We see from (2.16) that the presence of the surface layer gives rise to a term linear in $|k_{\parallel}|$ in the dispersion law. Correspondingly, the effect of the structure of the surface layer on the dispersion law should be especially substantial at large $|k_{\parallel}|$, for which the quantity $\text{Re } \varepsilon_1(\omega_s)$ approaches $-\varepsilon_2$. We note the nonanalyticity with respect to k_{\parallel} at the zero in the dispersion law, which is characteristic of surface waves. This nonanalyticity has been specially discussed in Refs. 32-34.

3. OPTICAL MODULATION METHODS

An effect of changes occurring at atomic distances from the surface on the parameters of light reflection was discovered in the pioneer study of Feinleib,³⁵ who first studied the reflection of light from metals in electrochemical systems. He did not measure directly the light reflection coefficients, but their increments upon changing the potential jump φ in the double layer at the metal-electrolyte surface. This potential jump is concentrated at atomic distances and can reach several volts.³⁶ Feinleib applied a technique based on modulating this potential jump. This enabled him to improve the accuracy of the measurements by more than two orders of magnitude and to increase their resolution. A similar method in which one measures $(1/R)dR/d\varphi$ has been named electroreflection (ER). Somewhat earlier³⁷

an analogous technique began to develop for studying semiconductor-electrolyte boundaries, which subsequently has enabled one to obtain considerable information on the electron structure of the surface layers of a semiconductor. In addition to the potential jump, the following can serve as the parameters to be modulated: the magnetic field, the hydrostatic compression or uniaxial strain, extra illumination, temperature variation, or the parameters of the beam-wavelength, polarization state, angle of incidence, and also the orientation of the surface. The fundamental principles of modulation spectroscopy are presented in Refs. 3 and 38.

A large number of experimental studies on ER has been performed in the years that have passed since Feinleib's study. The results of these studies have been summarized in a series of reviews.³⁹⁻⁴⁵ In employing the ER method, one experimentally determines the derivatives of the reflection coefficients for s- and p-polarized light $(1/R_s)dR_s/d\varphi$ and $(1/R_p)dR_p/d\varphi$ as functions of the frequency and the potential. The information on four other functions is lost in these experiments: the dependences of the phases of the reflection coefficients on the frequency and the potential. In principle the phases can be connected with the reflection coefficients by the dispersion relations.^{3,45} However, the application of the dispersion relations requires one to make further assumptions whose rigor is hard to estimate. In very recent years the method of modulation interferometry (MI) has begun to be developed. It enables one directly to measure the derivatives of the potential from the phase shifts for the x- and p-components separately. (The derivatives of the differences of the phase shifts for the s- and p-components of a light wave are measured by using the rather well known method of modulation ellipsometry.) This very promising experimental method was first realized in an experimental study⁵⁶ employing the Michelson interferometer. Figures 3 and 4 show typical examples of ER curves from metals.

Until recently, the experimental data on the effect of the microscopic structure of the surface on light reflection were usually processed within the framework of the so-called three-layer model, which McIntyre and Aspnes have used, in particular, to describe ER.^{46,47} In this model exact expressions are obtained⁴⁸ for the light reflection coefficients R_s and R_p in the three-layer

⁴⁾ The expression (2.8) amounts to the sum of the first two terms of the expansion of the exact expression for $r_p(q)$ in terms of the parameter $\delta\omega/c$. Consequently the condition $[r_p(q)]^{-1} = 0$ proves unsuitable for use in finding the dispersion law.

⁵⁾ If the eigenfrequencies of the vibrations in the surface layer ω_s [poles of $\Delta \varepsilon_2(\omega)$ and $\Delta \varepsilon_1^{-1}(\omega)$] fall in the surface polariton band $\omega_s(k_{\parallel})$, the right-hand side of Eq. (2.15) ceases to be small, and correspondingly, Eq. (2.6) loses force. In this case, in solving (2.15) we must explicitly allow for the form of the dependence of $\Delta \varepsilon_2$ and $\Delta \varepsilon_1^{-1}$ on $\omega - \omega_s$, and in this case splitting can arise in the surface-plasmon spectrum.³¹

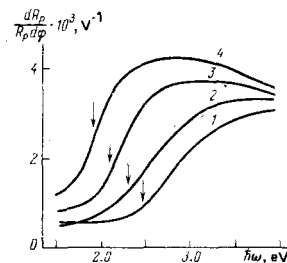


FIG. 3. ER spectra of an indium electrode in 0.1 N solution of Na_2SO_4 for p-polarized light. The potentials of the electrode (V) are: -0.1 (1), -1.2 (2), -1.4 (3), and -1.6 (4). The arrows indicate the position of the photoemission threshold. Here we have $\theta = 70^\circ$.

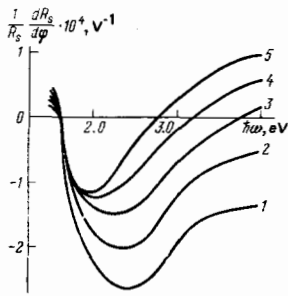


FIG. 4. ER spectra of a lead electrode in a 0.1 N solution of Na_2SO_4 for s-polarized light for the potentials (V): -0.8 (1), -1.0 (2), -1.2 (3), -1.4 (4), and -1.6 (5). Here we have $\theta = 70^\circ$.

system (Drude formula). Usually one restricts the treatment to an approximation linear in the parameter $d\omega/c$, which is derived from the Drude formula under the condition

$$\frac{d\omega}{c} \ll 1. \quad (3.1)$$

When (3.1) is satisfied, the following expressions are obtained for the relative changes in the reflection coefficients for s- and p-polarized light as compared with the Fresnel formulas:

$$\frac{\Delta R_s}{R_s} \equiv \frac{R_s - R_s^F}{R_s} = -\frac{4d\omega}{c} \sqrt{\epsilon_2} \cos \theta \operatorname{Im} \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_2 - \epsilon_1} \right), \quad (3.2)$$

$$\frac{\Delta R_p}{R_p} \equiv \frac{R_p - R_p^F}{R_p} = -\frac{4d\omega}{c} \sqrt{\epsilon_2} \cos \theta \operatorname{Im} \left\{ \left(\frac{\epsilon_1 - \epsilon_1}{\epsilon_2 - \epsilon_1} \right) \times \left[\frac{1 - (\epsilon_2/\epsilon_1)\epsilon_1(\epsilon_1 + \epsilon_1) \sin^2 \theta}{1 - (1/\epsilon_1)(\epsilon_2 + \epsilon_1) \sin^2 \theta} \right] \right\}. \quad (3.3)$$

One can also formally derive Eqs. (3.2) and (3.3) from the general expressions (2.12) and (2.13) with the substitution

$$\begin{aligned} \Delta \epsilon_i(\omega) &= d(\epsilon_i - \epsilon_2), \quad i = 2, 3, \\ \Delta \epsilon_1^{-1}(\omega) &= d \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right). \end{aligned} \quad (3.4)$$

While the expressions (2.12) and (3.2) for the reflection of s-polarized light are similar in structure, the expression (2.13) for p-polarized light sharply differs from the expression (3.3) derived in the three-layer model. This difference involves the fact that in real systems the quantity $\Delta \epsilon_1^{-1}(\omega)$ that enters into (2.13) is not expressed using (3.4) in terms of the mean over the layer of the dielectric permittivity ϵ_i . The defects that we have noted of the three-layer model lead to a set of contradictions in processing optical experimental data by Eqs. (3.2) and (3.3). First, for a particular system the values of ϵ_i found from experiments in which only s-polarized light has been used (the reflection and transmission coefficients were measured) prove to differ from the values of ϵ_i obtained in experiments employing simultaneously s- and p-polarized light.⁴⁹ Second, the values of ϵ_i prove to depend on the angle of incidence of the light.⁵⁰

The relation of reflection to the microscopic characteristics of the surface

In order to gain information on the microscopic properties of the phase boundary from light-reflection experiments, one must relate the quantities $\Delta \epsilon_i(\omega)$ and

$\Delta \epsilon_1^{-1}(\omega)$ to the concrete characteristics of the system under study and analyze the different mechanisms of modulation of the optical properties of the surface region. We shall pay most attention to ER experiments, for which the most extensive experimental information exists.

1) *Plasma mechanism of electroreflection.* The most physically grounded mechanisms of ER are based on concepts of the modulation of the behavior of the conduction electrons near the surface of the metal. We can write the electronic component of the dielectric permittivity $\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega)$ as the sum of two terms⁵¹:

$$\epsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega) = \epsilon_p(x_1, \omega) \delta_{ij} \delta(\mathbf{x} - \mathbf{x}') + \epsilon_{ij}^{\text{tr}}(\mathbf{x}, \mathbf{x}', \omega), \quad (3.5)$$

Here the first term amounts to the plasma component, while the second corresponds to the optical transitions. McIntyre and Aspnes⁴⁷ and a number of authors following them have proposed that $\epsilon_{ij}^{\text{tr}}$ is not modulated by the electric field of the double layer, and hence the ER effect involves modulation of $\epsilon_p(x_1, \omega)$ owing to changes in electron density near the boundary as the external electric field is applied. This hypothesis can be valid only in a restricted interval of the parameters ω and φ lying far from the threshold for external photoemission and from frequencies corresponding to optical transitions in the surface layer. The authors of Ref. 47 employed an expression for the plasma component $\epsilon_p(x_1, \omega)$ of the dielectric permittivity derived from the electron theory of Drude⁵²:

$$\begin{aligned} \epsilon_p(x, \omega) &= 1 - \frac{\omega_p^2}{\omega[\omega + (i/\tau)]}, \\ \omega_p^2 &= \frac{4\pi\rho(x_1)e^2}{m^*}, \quad \omega\tau \gg 1, \end{aligned} \quad (3.6)$$

Here τ is the relaxation time, m^* and e are the effective mass and charge of the electrons of the metal, and $\rho(x_1)$ is the electron density as a function of the distance from the surface. Under the assumptions that we have adopted, the change in the dielectric permittivity of the surface layer averaged over the surface can be written in the form

$$\Delta \epsilon_p(x_1, \omega) = (\epsilon_p(\omega) - 1) \frac{\Delta \rho(x_1)}{N}. \quad (3.7)$$

In Eq. (3.7), $\epsilon_p(\omega)$ and N are respectively the plasma component of the dielectric permittivity and the electron concentration in the bulk of the metal, and $\Delta \rho(x_1)$ is the change in the electron concentration at the point x_1 near the surface produced by a change in the potential jump by the amount $\Delta \varphi$. For the case of normal incidence of the light on the metal, the described model yields the following expression for the relative change in the light reflection coefficient:

$$\frac{\Delta R}{R} = -\frac{4\omega\sqrt{\epsilon_2}}{c} \frac{\Delta Q}{eN} \operatorname{Im} \left(\frac{\epsilon_p - 1}{\epsilon_1 - \epsilon_2} \right) = -\frac{4\omega\sqrt{\epsilon_2}}{c} \frac{C_{dl} \Delta \varphi}{eN} \operatorname{Im} \left(\frac{\epsilon_p - 1}{\epsilon_2 - \epsilon_1} \right); \quad (3.8)$$

Here we have

$$\Delta Q = -e \int_{-\infty}^{\infty} dx_1 \Delta \rho(x_1), \quad C_{dl} = \frac{dQ}{d\varphi}, \quad (3.9)$$

Also, ΔQ is the change in the surface charge upon changing the potential jump by $\Delta \varphi$, and C_{dl} is the so-called differential capacitance of the double layer.³⁶

According to (3.8), the integral ER signal depends linearly on the surface-charge density. Correspondingly, the differential ER signal is proportional to the differential capacitance. These predictions have been qualitatively confirmed for a number of systems.⁵³⁻⁵⁵ In particular, it has been shown^{54,55} that a linear dependence of $\Delta R/R$ on the charge ΔQ is observed for a lead electrode placed in 0.1 and 0.25 M NaF solutions in the region of negative potentials where there is no specific adsorption.

It was shown in Ref. 56 that, although the results of measuring $(1/R_s) dR_s/d\varphi$ for indium are not described by the formulas of (3.8), the derivative of the phase r_s , $d\delta_s/d\varphi$, proves to be proportional to the differential capacitance C_{dl} . We can understand this fact by taking into account the following circumstance: Equations (2.10) and (2.12) imply that, when $\text{Im } \varepsilon_1 \ll |\text{Re } \varepsilon_1|$ (this condition is satisfied for In when $1.5 \text{ eV} < \hbar\omega < 3 \text{ eV}$), the ER signal $(1/R_s) dR_s/d\varphi$ is proportional to $\text{Im } \Delta\varepsilon(\omega)$, while $d\delta_s/d\varphi \sim \text{Re } \Delta\varepsilon(\omega)$. Correspondingly, we find upon taking (3.7) into account that modulation of the plasma component $\varepsilon_p(x_1, \omega)$ gives a considerably greater contribution to $d\delta_s/d\varphi$ than to $(1/R_s) dR_s/d\varphi$. Consequently the change in the phase is described well by the plasma model, although the quantity $(1/R_s) dR_s/d\varphi$ may be governed by the optical transitions.

In contrast to $\Delta\varepsilon(\omega)$, the quantity $\Delta\varepsilon^{-1}(\omega)$ that enters into the expression for the ER signal in p-polarized light depends substantially not only on the surface charge Q , but also on the form of the electron-density distribution $\rho(x_1)$ near the surface. Let us restrict the treatment here to a simple model for $\rho(x_1)$ in which we have^{57,58}

$$\rho(x_1) = \begin{cases} N - \left(\frac{\beta Q}{2e} + \frac{N}{2} \right) \exp(\beta x_1), & x_1 < 0, \\ \left(\frac{N}{2} - \frac{\beta Q}{2e} \right) \exp(-\beta x_1), & x_1 > 0; \end{cases} \quad (3.10)$$

Here β is a variation parameter defined by the condition of minimum energy of the ground state of the electron gas when situated in the external field.⁵⁸ For metals such as In, Ag, . . . , whose bulk properties are described well by the plasma component of the dielectric constant ε_p , we have

$$\frac{d}{dq} \Delta\varepsilon^{-1}(\omega) \approx \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 \varepsilon_2} \frac{C_{dl}}{eN} + \frac{1}{\beta^2} \frac{d\beta}{d\varphi} \left[\frac{\varepsilon_1 + \varepsilon_2}{\varepsilon_1 \varepsilon_2} \ln \left(-\frac{\varepsilon_1 + \varepsilon_2}{2} \right) - \frac{1}{\varepsilon_1} \ln(-\varepsilon_1) - \frac{1}{\varepsilon_2} \ln \varepsilon_2 + \frac{i\pi}{\varepsilon_2} \right] \quad \text{at } |\beta Q| < eN. \quad (3.11)$$

We see from (3.11) that the main contribution to $\text{Im}(d\Delta\varepsilon^{-1}(\omega)/d\varphi)$ when $\text{Re } \varepsilon_1 < 0$ and the bulk attenuation is small comes from a region near the point $x_1 = x_1^0$ defined as the solution of the equation $\text{Re } \varepsilon_p(x_1, \omega) = 0$. The vanishing of $\text{Re } \varepsilon_p(x_1, \omega)$ leads to the appearance in $(1/R_p) dR_p/d\varphi$ of a positive term proportional to $(1/\beta^2) d\beta/d\varphi$, which does not vanish even for purely real values of ε_1 .⁶⁾ A calculation of $(1/R_p) dR_p/d\varphi$ was performed in Ref. 60 for In using $\rho(x_1)$ in the form (3.10). It turned out that $(1/R_p) dR_p/d\varphi$ is negative when $d\beta/d\varphi$

$= 0$. In accord with the results of the experiments of Refs. 61 and 62, it becomes positive when $d\beta^{-1}/d\varphi < -0.02 \text{ \AA}/\text{V}$. In the frequency region lying below the external-photoemission threshold (near the threshold the ER signal is governed by another effect; see below), the values of $(1/R_p) dR_p/d\varphi$ calculated⁶⁰ for $d\beta^{-1}/d\varphi = -0.06 \text{ \AA}/\text{V}$ agree with the experimentally determined values,^{61,62} which are presented in Fig. 3.

As the experimental studies show, far from all the effects observed in reflection of light from metals can be explained by simple modulation of the surface charge. It has been shown^{63,64} in measuring electroreflection and electrotransmission spectra for s-polarized light for a silver electrode in a 1 N solution of Na_2SO_4 that $\text{Re } \Delta\varepsilon_3(\omega)$ and $\text{Im } \Delta\varepsilon_3(\omega)$ are of the same order of magnitude and have the same signs over a broad frequency range. The latter result qualitatively contradicts the conclusions drawn from the plasma model, in which these quantities must have opposite signs. A positive value of the signal $(1/R_s) dR_s/d\varphi$ has been obtained^{61,62} in ER in indium, in contradiction with the plasma model. In order to explain the lack of agreement with the plasma model that they had noted, the authors of Ref. 64 proposed that not only the electron concentration near the surface can change as the potential jump is altered, but also their relaxation time.⁷⁾

In order to describe the effect of the properties of the surface on the relaxation time τ , and thereby on the conductivity of the surface layer, Refs. 64 and 65 have applied the Fuchs-Boltzmann method.^{67,68} This consists in using the classical kinetic Boltzmann equation with the boundary condition of Fuchs to seek the distribution function of the electrons. Varying the potential jump alters the concentration of adsorbed ions, atoms, and defects at the surface, which serve as additional scattering centers for electrons. According to Refs. 64 and 65, this leads to modulation of the scattering, and correspondingly, of the relaxation time of the electrons near the surface.

We note that the use of the classical Fuchs-Boltzmann method to describe the scattering of electrons at the surface cannot be strictly justified on the quantum level. As has been shown in Ref. 68, one cannot take into account the modulation of the scattering at the surface simply by introducing a relaxation time that depends on the external conditions, even within the framework of the model of almost free electrons.

Other, as yet unexamined possibilities exist for explaining the positive sign of the ER signal in s-polarized light in the frequency interval in which the contribution from optical transitions is insignificant and the plasma model must hold. They involve taking into account correlation effects in the response function and/or taking into account the dependence of the effective mass of an electron on x_1 in the surface region of the metal. Elucidation of the problems stated above is of considerable general interest for metal physics.

⁶⁾ This effect, which has been discussed previously in Refs. 15 and 59, and which involves the sharp increase in the normal component of the field at the point $x_1 = x_1^0$, cannot in principle be described by the three-layer model.

⁷⁾ Apparently a possible effect of modulation of the relaxation time in ER was first pointed out in Ref. 65.

2) *The effect of electron transitions.* In the models described above, which take into account the modulation of the surface charge and the relaxation time, the optical characteristics of the surface layer are smooth functions of the frequency ω . Thus, as we know, these models do not allow one to explain the presence of maxima and minima in the functions $\Delta\varepsilon(\omega)$ and $\Delta\varepsilon_1^{-1}(\omega)$ obtained from the experimental data. To describe these effects, we must take into account the dependence of the component of the dielectric permittivity ε^{tr} associated with optical transitions on the potential jump φ .

Hansen and Prostek⁶⁵ proposed one of the first theoretical models for describing the modulation of interband transitions. Upon analyzing the electroreflection spectra of a gold film,³⁵ Hansen and Prostek concluded⁶⁹ that the observed effects can be explained by a frequency shift of the optical constants of the thin surface layer of the metal caused by a change in the charge of this layer, so that $\Delta\varepsilon(\omega)$ goes over into $\Delta\varepsilon(\omega + \Delta\omega)$.

It was assumed⁶⁵ in order to justify such a frequency shift that the Fermi level of the surface layer is displaced upon changing the surface electron concentration, but the boundaries of the bands remain fixed. Here the threshold energies of transitions from the filled bands into the free part of the conduction band are also altered. The model described here arouses objections, since the introduction of a dependence of the Fermi level on the distance from the surface is not physically justified. Attempts to apply the theory of Hansen and Prostek to explain the ER spectra of other metals besides gold also have been unsuccessful.^{4,70}

Recently the problem of the modulation of electron transitions has begun to be analyzed more thoroughly. It has been shown^{61,62,71-74} that in a number of cases the main contribution to $d\varepsilon^{\text{tr}}/d\varphi$ comes from direct intraband transitions. These transitions are made possible by the breakdown of translational invariance in a semi-bounded metal. Correspondingly they are very sensitive to the state of the surface, which can be altered by an external field localized near the surface. Here, although the first term in (3.5) for metals in the frequency range of visible light and the near ultraviolet is larger than the second, the screening effect causes the first term to depend weakly on the potential jump φ . Consequently the derivative of the second term in (3.5) with respect to φ can prove larger than the derivative of the first term, especially near the threshold for external photoemission. It is precisely the derivative of the second term that must govern the features of the ER curves near the photoemission threshold.

It proved possible in Refs. 62, 71-74 to obtain the relationship between the expressions for the photoemission current and the ER signal. The parameters entering into this relationship contain information on the microscopic mechanism of photoemission and the structure of the metal surface. It turned out that it is most convenient for comparison with experiment to deal with the second derivatives $(1/R)d^2R/d\varphi^2$, which also can be measured directly.⁶² A smaller number of parameters enters into the second derivatives, and the threshold

feature is revealed most sharply in them. Formulas of the following form are obtained for $(1/R)d^2R/d\varphi^2$ near the external photoemission threshold:

$$\frac{1}{R} \frac{d^2R}{d\varphi^2} = A + B (\hbar\omega - \hbar\omega_0 - e\varphi)^{1/2} \theta(\hbar\omega - \hbar\omega_0 - e\varphi) + C (\hbar\omega_0 + e\varphi - \hbar\omega)^{1/2} \theta(\hbar\omega_0 + e\varphi - \hbar\omega); \quad (3.12)$$

Here ω_0 denotes the threshold photoemission frequency at the potential $\varphi = 0$ [the potential is referred to the so-called zero-surface-charge potential,³⁶ at which $Q(\varphi) = 0$]. The functions of the frequency and angle of incidence (A , B , and C) introduced into (3.12) do not depend on φ , and are expressed in terms of the bulk dielectric permittivities of the metal and electrolyte and in terms of the matrix elements of the optical transitions, which also enter into the expression for the photocurrent. The explicit form of these functions has been given in Ref. 72. The formulas that we have written out hold in the neighborhood of the photoemission threshold to the accuracy of terms of the order of

$$\left(\frac{\hbar\omega - \hbar\omega_0 - e\varphi}{\hbar\omega_0} \right)^2.$$

The appearance of a feature at $\hbar\omega = \hbar\omega_0 + e\varphi$ in $(1/R)d^2R/d\varphi^2$ is qualitative in nature, and does not involve the details of the calculation. The experimental discovery of such a feature, both in the ER spectra and in the dependence of the ER on φ confirms the validity of the chosen physical mechanism of ER. Figures 5 and 6 compare the theoretical curves for $(-1/R_p)d^2R_p(\omega, \varphi)/d\varphi^2$ with the experimental ER data for indium.⁶² Here the values of the matrix elements were taken from independent photoemission experiments.⁷⁵ The adjustable parameter was the phase of the matrix element of the optical transition excited by the field δ_1 normal to the surface. It turned out that $\tan \delta_1/2 = -0.7$. This value agrees qualitatively with the model of photoemission developed in Refs. 76 and 77, which corresponds to optical transitions in the ionic cores, and it contradicts the results corresponding to the surface mechanism of photoemission. As we see from Figs. 5 and 6, the behaviors of the experimental and the theoretical curves agree. We stress that analysis of the dependence of δ_1 on the state of the surface

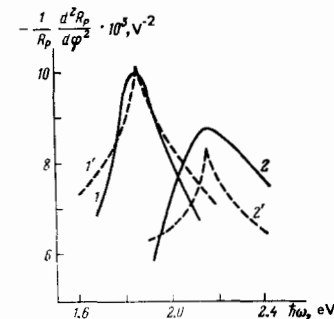


FIG. 5. Comparison of the experimental and theoretical frequency-dependences of $(1/R_p)d^2R_p/d\varphi^2$. The solid curves correspond to the experimental data on ER of indium in a 0.01 N solution of Na_2SO_4 .⁶² The dotted curves have been obtained theoretically.⁷² Curves 1 and 1' correspond to the potential $\varphi = -1.6$ V, while curves 2 and 2' correspond to $\varphi = -1.3$ V. The position of the maximum corresponds to the photoemission threshold frequency $\hbar\omega = \hbar\omega_0 + e\varphi$.

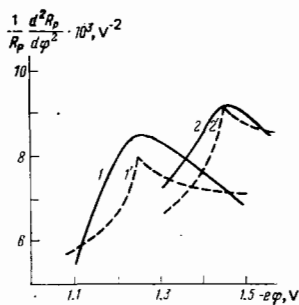


FIG. 6. Comparison of the experimental and theoretical potential-dependences of $(1/R_p)d^2R_p/d\varphi^2$. The solid curves correspond to the experimental data on ER of indium in a 0.01 N solution of Na_2SO_4 .⁶² The dotted curves have been obtained theoretically.⁷² Curves 1 and 1' correspond to the frequency $\hbar\omega = 2.2$ eV. Curves 2 and 2' correspond to the frequency $\hbar\omega = 2$ eV. The position of the maximum corresponds to the threshold potential $e\varphi = \hbar\omega - \hbar\omega_0$.

can yield information on its electron structure. It was shown in Ref. 74 that a threshold feature should also be manifested in modulation ellipsometry and interferometry.

Let us proceed to examine certain generalizations of Eq. (3.12), which are necessary for explaining a number of the observed experimental facts. We have assumed in writing (3.12) that the spectrum of the metal possesses no features either near the photoemission threshold at an energy $E = E_F + \hbar\omega_0 + e\varphi$, or near the Fermi surface $E = E_F$. In particular, surface electron levels are absent. In this situation the only special point to be taken into account remains the photoemission threshold. However, in some cases the ER spectra contain additional features in the potential-dependence of the ER, which can be associated with features of the electron spectrum of the metal-electrolyte boundary. In particular, an additional special point (a minimum) has been observed in the ER spectrum of lead.^{62,78} The qualitative hypothesis was advanced⁶² that this minimum involves the existence of a surface electron level having an energy lying near the photoemission threshold. Another possible candidate for such a level is a localized electron state in water—an electron in a solvated or presolvated state.⁷⁹

An important qualitative feature of the experimental curves visible in Figs. 5 and 6 is the smoother decline as compared with the developed theory in the quantity $(1/R_p)d^2R_p/d\varphi^2$ as a function of ω or φ in moving away from the maximum corresponding to the photoemission threshold. As the special analysis⁶² showed, this contradiction is not fully eliminated by taking into account the finite temperature of the electrons. We can naturally assume that the phenomenon under study at least partially involves collective effects whose influence is especially important immediately near the threshold. The most substantial effect of this type must be the influence of fluctuations in the polarization (longitudinal optical phonons) in the polar medium into which emission occurs, and also the influence of various surface vibrations. Thus, in principle it proves possible to determine directly the correlation function

for the polarization fluctuations near the surface of the metal.⁸⁰ In line with what we have said, it is highly essential to single out and diminish the contribution to the width of the peaks of $(1/R)d^2R(\omega, \varphi)/d\varphi^2$ involving instrumental effects.

3) *Electroreflection from single crystals.* Until very recently, ER spectra had been measured on polycrystalline materials. This led to loss of a part of the information (owing to averaging over the different faces) and to a certain extent hindered the interpretation of the experiments. Experimental studies have now begun on ER of single crystals.^{43,81-84} It has been shown that, in metals such as Ag, Au, and Cu, the magnitude and form of the ER signal depend on the orientation of the surface of the single crystal. The effect that we have noted can arise from the known fact that the differential capacitance, the work function, photoemission matrix elements, and the two-dimensional cross-sections of the Brillouin zones differ for different faces. With a fixed orientation of the surface, an anisotropy of the ER spectra of pure Ag, Au, and Cu has also been found,^{43,81-84} i.e., a dependence of the ER on the direction of the electromagnetic field intensity vector in the incident wave with respect to the crystallographic axes of the metal. Moreover, it has been shown that anisotropy of ER can arise from adsorption.⁸⁵

4. MICROSCOPIC DESCRIPTION OF THE EFFECT OF ADSORPTION

When one measures the relative changes in the light reflection coefficients caused by the appearance on the surface of the metal of adsorbed atoms or ions (adatoms), one observes a nonmonotonic behavior of the light reflection coefficient as a function of the frequency, with characteristic maxima that are absent in reflection from pure metals.⁸⁶⁻⁹³ Whenever the measurements are performed at a metal-electrolyte boundary, the stated maxima are shifted and deformed upon changing the potential jump in the double layer.

In describing these phenomena, it is known that one must use microscopic models. The first to reject the application of the macroscopic three-layer model in studying light reflection from submonolayer films were Strachan⁹⁴ and Sivukhin.⁹⁵ They described the surface layer using the model of a two-dimensional lattice of dipoles interacting with the light. We shall not discuss here the results obtained in the models proposed by Strachan and Sivukhin, which were developed further in Refs. 96-98. This has been done in the reviews of Refs. 4, 42, 99. We note only that, as the recent theoretical and experimental studies show,¹⁰⁰⁻¹⁰³ the electron properties of adatoms that are manifested in the optical range cannot be described in the dipole model.

A number of studies⁸⁶⁻⁹³ have associated the effects of adsorption with the appearance of extra electron transitions from the resonance levels of the adatoms into which the levels of the isolated atoms are transformed upon adsorption. If this assumption is justified, then an analysis of the experiments should allow one to ob-

tain important information on the microscopic properties of the adatoms. In order to do this, one must associate the quantities $\Delta\varepsilon(\omega)$ and $\Delta\varepsilon^{-1}(\omega)$ that enter into the expressions (2.12) and (2.13) for the relative changes of the light reflection coefficients with the electron characteristics of the metal + adatom system. For this purpose, Refs. 104 and 105 have used the random-phase approximation for calculating the nonlocal dielectric-permittivity tensor $\varepsilon_{ij}(\mathbf{x}, \mathbf{x}', \omega)$. Here we can write the quantity $\text{Im} \Delta\varepsilon(\omega)$, which characterizes the change in the optical absorption upon introducing the adatoms, in the form

$$\begin{aligned} \text{Im} \Delta\varepsilon_{33}(\omega) = \Delta\varepsilon_{33}''(\omega) = & \frac{8e^2 N_a}{m^2 \omega^4} \int dE \theta(-E) [1 - \theta(-E - \hbar\omega)] \\ & \times \left\{ \int d^3x d^3x' \frac{\partial V_a(|\mathbf{x} - \mathbf{x}_0|)}{\partial x_3} \text{Im} \langle \mathbf{x} | G_a(E) | \mathbf{x}' \rangle \frac{\partial V_a(|\mathbf{x}' - \mathbf{x}_0|)}{\partial x_3'} \right. \\ & \left. \times \text{Im} \langle \mathbf{x}' | G_a(E + \hbar\omega) | \mathbf{x} \rangle \right\}; \end{aligned} \quad (4.1)$$

Here $G_a(E)$ is the one-particle Green's function of the metal + adatom system, $V_a(|\mathbf{x} - \mathbf{x}_0|)$ is the self-consistent potential of an adatom, and N_a is the surface concentration of adatoms. In writing (4.1) we have assumed that the concentration of adatoms at the surface is small enough that we can neglect their interaction. The energy E is measured from the Fermi level, so that at a temperature of absolute zero, the distribution function has the form $2\theta(-E)$. We should note that formulas analogous to (4.1) have been employed also¹⁰⁷ to describe the optical properties of adatoms. However, a number of objectionable approximations have been made¹⁰⁷ in calculating $\Delta\varepsilon''(\omega)$, and the final results have not been reduced to a form admitting comparison with experiment.

In order to calculate the Green's function $G_a(E)$ that enters into (4.1), the authors of Refs. 104 and 105 developed a quantum-mechanical method of describing the crystal + adatom system based on a pole approximation⁹⁾ for the scattering amplitudes at the adatom.^{108,109} Here the fact has been taken into account that the electron levels of the atoms are not only shifted by the amount Λ owing to adsorption, but are also split and spread out into resonance states with the width Γ , owing to the possibility of tunneling of the electrons between an adatom and a metal atom. The quantities Λ and Γ are the fundamental microscopic characteristics of an adatom. They depend on the electron state of the isolated atom, on the band structure of the metal, and on the potential jump φ . The determination of the shift in the level and its width are highly essential in solving many of the problems of the thermodynamics and kinetics of surface phenomena.

The change in the optical properties of the surface owing to adsorption, as described by Eq. (4.1), also can be related to the quantities Λ and Γ . In the simplest case of an adatom having one s-level lying below the Fermi level of the metal and far from the band boundaries, the imaginary component of $\Delta\varepsilon(\omega)$ can be

⁹⁾ The pole approximation is a development and refinement of the well-known Anderson model,^{106,101,110} which has recently been widely applied in adsorption problems.

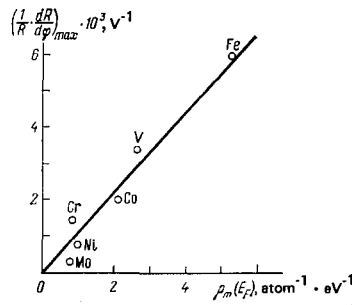


FIG. 7. Dependence of the maximum value of $((1/R)(dR/d\varphi))_{\text{max}}$ on the density of electron states at the Fermi level of the metal as obtained in Ref. 111 in studying adsorption of water on different transition metals.

written in the form^{104,105}

$$\begin{aligned} \Delta\varepsilon_{33}''(\omega) = \Delta\varepsilon_{33}''(\omega) = & \frac{\pi e^2 N_a}{3\hbar^2 m \omega^4} \frac{|E_0 + \Lambda + \hbar\omega - \hbar\omega_0|^2}{|E_0 + \Lambda - \hbar\omega_0|^{1/2}} \Gamma_{l=1} \\ & \times \left(\tan^{-1} \frac{E_0 + \Lambda + \hbar\omega}{\Gamma} - \tan^{-1} \frac{E_0 + \Lambda}{\Gamma} \right), \end{aligned} \quad (4.2)$$

Here E_0 is the position of the level of the isolated atom with respect to the Fermi level in the metal, and $\Gamma_{l=1}$ is the width that the level of the adatom with the orbital angular momentum $l=1$ and $E=0$ would have. In the case being discussed, the quantity $\Delta\varepsilon''(\omega)$ corresponds to an optical transition from a filled (or partially filled) level of the adatom into the conduction band of the metal.⁹⁾ Analogous formulas have been derived in Refs. 104 and 105 for transitions from occupied states of the metal to free levels of adatoms. We see from (4.2) that the function $\Delta\varepsilon''(\omega)$ has a maximum in the neighborhood of the frequency $\hbar\omega_m = |E_0 + \Lambda|$ and is nonsymmetrical with respect to this frequency. The physical meaning of Eq. (4.2) is rather simple: the imaginary part of the dielectric permittivity is proportional to the number of filled initial states (the factor in parentheses) and to the number of final states ($\Gamma_{l=1}$) to which a transition can occur. According to Refs. 104 and 105, the width function $\Gamma_{l=1}$ is proportional to the density of electron states of the metal at the Fermi level $\rho_m(0)$. We can easily derive from the fact that $\Delta\varepsilon'(\omega)$ is connected to $\Delta\varepsilon''(\omega)$ by the Kramers-Kronig transformation the inequality $|\Delta\varepsilon'(\omega_m)| \ll |\Delta\varepsilon''(\omega_m)|$ that holds near the maximum. Taking what we have said into account Eq. (4.2) implies that $\Delta R_s/R_s$ has an extremum at $\omega \approx \omega_m$. In the case of adsorption of identical atoms on different metals, the value of $\Delta R_s/R_s(\omega_m)$ is proportional to $\rho_m(0)$. This behavior of $\Delta R_s/R_s(\omega_m)$ has been experimentally observed¹¹¹ in studying the adsorption of water on various transition metals (Fig. 7). Moreover, measurements of the ER spectra of iron in alkali solutions¹¹² have shown that the position of the extremum of $\Delta R_s/R_s(\omega_m)$ involving transfer of an electron from water to iron depends on the electrode potential φ . This result also agrees with the views developed in Refs. 100, 104, and 105. In a number of studies^{86,87,89,90} of the effect of adsorption on light reflection from metals, the change

⁹⁾ It was assumed in deriving (4.2) that the frequency of the incident light satisfies the inequality $\hbar\omega < |E_0 + \Lambda - \hbar\omega_0|$. That is, we have not considered transitions from a level of the adatom to the external medium.

in the dielectric permittivity $\Delta\epsilon(\omega)$ in the surface region was represented in the form of a sum of Lorentz oscillator functions, while the parameters of these functions were associated with the electron characteristics of the adatoms. We see from (4.2) that $\Delta\epsilon(\omega)$ does not have a Lorentz form. Hence the method of data reduction used in the cited studies can yield incorrect positions, and especially, widths of the levels of the adatoms.

In order to test the theory that had been developed, the results of the experiments⁸⁶ on reflection of s-polarized light from the (100) surface of tungsten covered with CO molecules and placed in a vacuum were processed^{104,105} by using the derived formulas (2.12) and (4.2). For this system the parameters Λ and Γ are known from independent photoemission measurements¹¹³: $|E_0 + \Lambda| = 3$ eV, $\Gamma = 0.6$ eV. As we see from Fig. 8, the values of $\Delta\epsilon''(\omega)$ calculated with (4.2) for the given values of the parameters Λ and Γ agree well with the values of $\Delta\epsilon''(\omega)$ obtained experimentally.⁸⁶ Another group of experiments that have been treated within the framework of the theory under discussion involves studies of adsorption of atomic oxygen on platinum.¹¹⁴

The theory developed in Refs. 104 and 105 is easily generalized to the case in which several transitions can occur in the frequency region being considered. Here several maxima appear in the $\Delta R/R$ spectrum, possibly not always resolved from one another. This effect has been observed experimentally in Ref. 93 in studying optical reflection from a platinum electrode covered with copper atoms (the degree of covering was less than a monolayer). Apparently one observes here transitions from the 3d levels of Cu to the 4p level of Cu and to the free part of the conduction band of platinum, and also a transition from the 4s levels of Cu to the 4p levels of Cu. In the frequency region corresponding to each of the stated transitions, the form of the function $\Delta\epsilon''(\omega)$ qualitatively agrees with that predicted in Refs. 104 and 105. Unfortunately, the experimental data were processed⁹³ by using the three-layer model, which is inapplicable in this region. Therefore, in extracting quantitative information on the parameters of the Cu adatoms, one must not use the values of $\Delta\epsilon'(\omega)$ and $\Delta\epsilon''(\omega)$ determined in Ref. 93. The value of $\Delta\epsilon(\omega)$ has been calculated¹¹⁵ for the case in which an ordered, two-dimensional lattice of adatoms is formed on the surface of the metal. By starting with the RPA for the dielec-

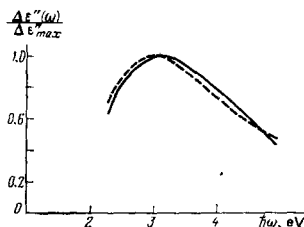


FIG. 8. Spectral dependence of $\Delta\epsilon''(\omega)/\Delta\epsilon''_{\max}$ in the case of adsorption of CO molecules on the (100) surface of tungsten. The solid curve shows the values of $\Delta\epsilon''(\omega)/\Delta\epsilon''_{\max}$ obtained⁸⁶ from experimental data at a degree of filling of the surface of ~ 0.4 . The dotted curve shows the values of $\Delta\epsilon''(\omega)/\Delta\epsilon''_{\max}$ calculated in Ref. 104.

tric-permittivity tensor, the qualitative features in the reflection coefficients were shown that can arise from van Hove singularities in the two-dimensional band structure of the surface layer of adatoms.

It is of considerable interest that the optical transitions in adatoms discussed in this section can be manifested in surface Raman scattering by adsorbed molecules. According to the views of Refs. 116–118, the sharp increase in the Raman cross-section that arises here is of a resonance type, and is due to an electron transition between the level of a certain adatom and the bulk of the metal. Simultaneously with this transition, a change occurs in the state of the vibrational degrees of freedom of adsorbed molecules associated with the given adatom, and this shifts the frequency of the reflected light. By using in the matrix elements the representation of wave functions in the form of a product of the electron wave functions and the wave functions of the motion of the nuclei it can be shown¹¹⁹ that the Raman cross-section will be proportional to the absorption cross-section $\text{Im} \Delta\epsilon(\omega)$ for the electron transition. Thus one can quantitatively explain the phenomenon of anomalously intense Raman scattering by adsorbed molecules by using formulas of the type of (4.2) taking the considerations of Refs. 116 and 117 into account. Here one must also take into account the amplification of the field near the surface owing to creation of surface plasmons caused either by roughness or by the presence of surface vibrations,^{120–122} as is discussed in Sec. 5. Only when one takes this amplification into account can one explain the absolute magnitude of the effect in the resonance region, and also the increase in the background in the nonresonance region.

5. THE EFFECT OF MICROROUGHNESS ON THE OPTICAL PROPERTIES

a) Different methods of taking roughness into account

Microroughness of metal surfaces gives rise to a number of qualitative effects. First, not only a specularly reflected wave arises on reflection of light, as in the case of an ideally smooth surface, but also diffusely reflected waves appear. Measurement of the flux of diffusely scattered light allows one to estimate the degree of roughness of the surface.^{123,124} Second, the presence of roughness leads to the possible creation of surface plasmons by the electromagnetic wave incident on the metal, and also to scattering of plasmons, whereby they transform into bulk excitations or into other states of a surface plasmon. These effects lead to experimentally observable considerable changes in the form of the coefficients for specular reflection of light^{125–127} and of the dispersion law for surface plasmons.^{128–130} Owing to the sharp amplification of the field at the surface, the creation of surface plasmons can lead to an increase by several orders of magnitude in such observable surface effects as photoemission^{131–133} and the cross-section for Raman scattering by adsorbed molecules.^{121,122}

In addition to metal optics, the problem of scattering of waves from a rough surface arises in a number of

other fields of physics: in the theory of diffraction by gratings,¹³⁴ in acoustics,^{135,136} in interpreting radar signals,¹³⁷ in the theory of scattering of atoms by a surface,¹³⁸ and in treating electron scattering from a metal surface.^{68,139} The mathematical problems that arise here are analogous in many ways. In particular, two limiting cases arise. In the first case the roughness has a scale much larger than the wavelength of the incident light. In this case one applied the quasiclassical approximation or the ray-optic approximation using the Huygens-Fresnel principle (usually retaining the first Fresnel zone^{140,141}). Such an approach has been developed by a number of authors (see Ref. 142, and also the literature cited in Refs. 143-145). In the second limiting case, the characteristic dimension of the roughness is much smaller than the wavelength. Here one can naturally use some variant of perturbation theory with respect to the ratio of the mean dimension of the roughness to the wavelength. We shall pay our major attention to this case, the theory of which has developed intensively in recent years as applied to light scattering from metals.^{120,146-163}

A rather large number of studies has been devoted also to a model treatment of roughness.¹⁶⁴⁻¹⁶⁷ These studies take into account the roughness of the surface within the framework of models with small particles of spherical¹⁶⁴ or any other simple shape¹⁶⁵⁻¹⁶⁷ arranged in a certain way on the smooth surface of a metal. Within the framework of some particular approximations, one calculates the cross-sections for scattering by the given particles, and then expresses the change in the reflection coefficients in terms of them. As a rule, one does not take into account here the substantial effects of multiple scattering. Another model approach¹⁶⁸⁻¹⁷⁰ consists of replacing the roughness with an equivalent surface layer of small particles whose effective dielectric permittivity is calculated within the framework of an effective-medium theory of the Maxwell-Garnett type.^{10,171} Thereupon one finds the reflection coefficients by the standard formulas derived in the three-layer model. One can find a detailed discussion of these studies in the review of Ref. 145. Here we note only that in the stated approach one can attain agreement with experiment only after introducing number of adjustable parameters having no direct physical meaning.

b) Perturbation theory

In employing perturbation theory with respect to the ratio of the mean dimension $(\bar{\xi}^2)^{1/2}$ of the roughness to c/ω , one usually describes the surface of the metal by introducing a local dielectric function of the following form:

$$\varepsilon(\mathbf{x}, \omega) = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) f(x_1 + \xi(\mathbf{x}_{||})). \quad (5.1)$$

Here the coordinate x_1 lies along the normal to the smoothed surface of the metal. The function $f(x_1)$, which determines the law of variation of the dielectric properties at microscopic distances on going from the

¹⁰Originally¹⁷¹ the Maxwell-Garnett theory was proposed for describing the properties of thin, inhomogeneous films.

metal to the outside medium, vanishes when $x_1 \rightarrow -\infty$ and becomes unity when $x_1 \rightarrow \infty$. In the limiting case of Fresnel reflection we have $f(x_1) = \theta(-x_1)$. The function $\xi(\mathbf{x}_{||})$ that we have introduced into (5.1) describes the roughness—the deviation of the coordinate of the position of the surface $x_1 = -\xi(\mathbf{x}_{||})$ from the mean value, which we take as the origin, so that we have

$$\int d^2\mathbf{x}_{||} \xi(\mathbf{x}_{||}) = 0. \quad (5.2)$$

The expansion of the electromagnetic field in terms of a small roughness parameter has been carried out in the literature by one of the following methods: (1) By using a method proposed by Rayleigh¹³⁵ and developed by Fano.¹³⁴ This method is based on employing the boundary conditions for the tangential component of the electric and magnetic fields at the surface $x_1 = -\xi(\mathbf{x}_{||})$.^{150,151,158-160} It has been applied only to the Fresnel case, in which $f(x_1) = \theta(-x_1)$. (2) By using the extinction theory of Ewald and Oseen.¹⁶⁰⁻¹⁶² (3) By using integral equations analogous to those treated in Sec. 2.^{120,148,149,152-155}

If one employs in the calculations only functions ξ_2 , ξ_3 , and \mathcal{D}_1 continuous at the surface, all three methods yield identical results. For unity of presentation, just as in the case of smooth surfaces in considering roughness, we shall adopt the third of the approaches cited above. Let us introduce the functions $\delta\varepsilon$ and $\delta\varepsilon^{-1}$, where

$$\begin{aligned} \delta\varepsilon(x_1, \xi(\mathbf{x}_{||})) &= \varepsilon(x) - \varepsilon_0(x_1) \approx \xi(\mathbf{x}_{||}) \frac{d}{dx_1} \varepsilon_0(x_1), \\ \delta\varepsilon^{-1}(x_1, \xi(\mathbf{x}_{||})) &= \frac{1}{\varepsilon(x)} - \frac{1}{\varepsilon_0(x_1)} \approx \xi(\mathbf{x}_{||}) \frac{d}{dx_1} \frac{1}{\varepsilon_0(x_1)}, \\ \varepsilon_0(x_1) &= \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) f(x_1). \end{aligned} \quad (5.3)$$

In the final result after averaging, and taking into account the effect of roughness in the first nonvanishing approximation, the observable quantities will contain terms proportional to $\bar{\xi}^2$. The retention of terms of only the first order in $\xi(\mathbf{x}_{||})$ on the right-hand side of (5.3) is motivated by the idea that the addition of second-order terms in $\xi(\mathbf{x}_{||})$ to $\delta\varepsilon$ and $\delta\varepsilon^{-1}$ can be reduced to introducing certain special surface currents and charges. The additional effects that arise here prove insubstantial in the most interesting frequency region corresponding to the creation of surface plasmons.

The terms in the Maxwell equations including $\delta\varepsilon$ and $\delta\varepsilon^{-1}$ can be treated as perturbations. We can write the equations (1.5) in integral form, and in such a way that only the functions \mathcal{E}_2 , \mathcal{E}_3 , \mathcal{D}_1 that vary slowly near the surface enter into the derived equations. Here the zero-order approximation corresponds to a smooth surface, and the kernel of the equations contains $\xi(\mathbf{x}_{||})$ to the first power. We note that in Refs. 152-155, 163 the corresponding integral equations were written not for \mathcal{E}_2 , \mathcal{E}_3 , \mathcal{E}_3 , and \mathcal{D}_1 , but for the fields \mathcal{E}_2 , \mathcal{E}_3 , and \mathcal{E}_1 . Owing to the discontinuity of the normal component of the field \mathcal{E}_1 , indeterminacies arise in the integrals of the form

$$\int \mathcal{E}_1(x) \delta\varepsilon(x_1, \xi(\mathbf{x}_{||})) \mathcal{E}_1(x) d^3\mathbf{x} \sim \int \mathcal{E}_1(x) \delta(x_1) \xi(\mathbf{x}_{||}) \mathcal{E}_1(x) d^3\mathbf{x}. \quad (5.4)$$

This situation has compelled the authors of Refs. 152-

155, 163 to offer formally a special definition of the corresponding integrals. Here it turned out that the final expressions for the observable quantities depend on the way of making this special definition.^{155, 160}

We must average over the surface in order to construct the observable quantities. In the case of a Gaussian roughness distribution corresponding to a stationary stochastic process, all the means are expressed in terms of a pairwise correlation function:

$$\langle \xi(\mathbf{k}_{||}) \xi(\mathbf{k}') \rangle = (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}') \bar{\xi}^2 a^2 \pi e^{-a^2 k_{||}^2 / 4},$$

$$\xi(\mathbf{k}_{||}) = \int d^2 x_{||} e^{i \mathbf{k}_{||} x_{||}} \xi(x_{||}). \quad (5.5)$$

In Eq. (5.5), the angle brackets denote averaging, $\bar{\xi}^2$ is the rms value of the roughness, and a is the correlation length. Similarly to what was done in Refs. 144 and 145, we can represent the equations for the averaged Green's functions and other quantities by a graphic technique analogous in many respects to that used in quantum field theory.¹⁷² Upon writing the solution of the equation for the Green's function $\mathcal{D}_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||})$ in the form of an iterative series, and then averaging over the surface, we obtain an equation that can be represented graphically in the following form¹¹⁾:

$$\langle \mathcal{D}_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||}) \rangle = \text{diagram with shaded loop} = \text{diagram with shaded loop} + \text{diagram with shaded loop and shaded propagator} + \text{diagram with shaded loop and two shaded propagators} + \dots \quad (5.6)$$

The meaning of the diagrams that enter into (5.6) arises from the following equalities:

$$\text{diagram with shaded loop} = (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) \tilde{\mathcal{D}}_{ij}(x_1, x'_1, \mathbf{k}_{||}),$$

$$\text{diagram with shaded loop and shaded propagator} = \left(\frac{\omega}{c}\right)^4 \sum_{l, m=1}^3 \int \frac{d^2 q}{(2\pi)^2} \frac{d^2 \mathbf{k}_{||}^{(l)}}{(2\pi)^2} d x_1^* d x'' \left\{ (2\pi)^2 \times \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) - q \right\} (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) - q \tilde{\mathcal{D}}_{il}(x_1, x'_1, \mathbf{k}_{||}) d_1(x_1^*) \times \tilde{\mathcal{D}}_{lm}(x_1^*, x''_1, \mathbf{k}_{||}^{(l)}) d_m(x''_1) \tilde{\mathcal{D}}_{mj}(x''_1, x'_1, \mathbf{k}'_{||}) \cdot \pi \bar{\xi}^2 a^2 e^{-a^2 q^2 / 4} \left. \right\}$$

$$= (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) \left(\frac{\omega}{c}\right)^4 \bar{\xi}^2 a^2 \pi \sum_{l, m=1}^3 \int \frac{d^2 \mathbf{k}_{||}^{(l)}}{(2\pi)^2} d x_1^* d x''_1 \times \left\{ \tilde{\mathcal{D}}_{il}(x_1, x'_1, \mathbf{k}_{||}) d_1(x_1^*) \tilde{\mathcal{D}}_{lm}(x_1^*, x''_1, \mathbf{k}_{||}^{(l)}) \times d_m(x''_1) \tilde{\mathcal{D}}_{mj}(x''_1, x'_1, \mathbf{k}'_{||}) \exp\left[-\frac{a^2}{4}(\mathbf{k}_{||} - \mathbf{k}'_{||})^2\right] \right\}, \quad (5.7)$$

Here we have

$$d_1(x_1) = \frac{d}{dx_1} \frac{1}{\epsilon_0(x_1)}, \quad d_2(x_1) = d_3(x_1) = \frac{d}{dx_1} \epsilon_0(x_1). \quad (5.8)$$

Also, $\tilde{\mathcal{D}}_{ij}$ is the Green's function for the case of a smooth surface. Upon convoluting the series in (5.6), we obtain the equation

$$\text{diagram with shaded loop} = \text{diagram with shaded loop} + \text{diagram with shaded loop and shaded propagator} \quad (5.9)$$

¹¹⁾ The obtained analogy with the Feynman diagrams of field theory arises because, in the Gaussian averaging, e. g., of polynomials in $\xi(\mathbf{x}_{||})$, $\xi(\mathbf{x}'_{||})$, etc., the means of all possible pair combinations of $\xi(\mathbf{x}_{||})$, $\xi(\mathbf{x}'_{||})$ enter on an equal footing, just in the same way as is required in satisfying Wick's theorem in field theory.¹⁷² Here the pair correlation function $\xi^2 \exp[-(\mathbf{x}_{||} - \mathbf{x}'_{||})^2 / a^2]$ plays the role of the free propagator for the "field" $\xi(\mathbf{x}_{||})$.

The polarization operator δP that we have introduced in (5.9) is represented in the form of an infinite series in terms of only the irreducible diagrams, i. e., the diagrams that have no internal sections containing only one line. The operator $\delta P_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||})$ is proportional to $\delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||})$:

$$\delta P_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||}) = (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) \delta P_{ij}(x_1, x'_1, \mathbf{k}_{||}). \quad (5.10)$$

That is, translational invariance with respect to motions in the directions $\mathbf{x}_{||}$ is restored after averaging. Moreover, δP has no pole singularities for $k_{||} = k'_s$. Allowing for the fact that $\delta P_{ij}(x_1, x'_1, \mathbf{k}_{||})$ differs from zero only at microscopic distances $|x_1|, |x'_1| < \delta$ from the surface, in (5.9) we can take the slowly varying functions of x_1 and x'_1 , $\tilde{\mathcal{D}}_{ij}(x_1, x'_1, \mathbf{k}_{||})$ and $\langle \mathcal{D}_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||}) \rangle$ outside the integrals with respect to x_1 and x'_1 . As a result we obtain the algebraic equation

$$\langle \mathcal{D}_{ij}(x_1, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||}) \rangle = (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) \tilde{\mathcal{D}}_{ij}(x_1, x'_1, \mathbf{k}_{||}) + \sum_{l, m=1}^3 \tilde{\mathcal{D}}_{lm}(x_1, 0, \mathbf{k}_{||}) \delta P_{lm}(\mathbf{k}_{||}) \langle \mathcal{D}_{mj}(0, x'_1; \mathbf{k}_{||}, \mathbf{k}'_{||}) \rangle. \quad (5.11)$$

Here we have

$$\delta P_{lm}(\mathbf{k}_{||}) = \int d x_1 d x'_1 \delta P_{lm}(x_1, x'_1, \mathbf{k}_{||}). \quad (5.12)$$

Equation (5.11), when considered for $x_1 = 0$, gives rise to the equality

$$\langle \mathcal{D}_{ij}(0, x'_1, \mathbf{k}_{||}, \mathbf{k}'_{||}) \rangle = (2\pi)^2 \delta^2(\mathbf{k}_{||} - \mathbf{k}'_{||}) \left\{ \tilde{\mathcal{D}}^{-1}(0, 0, \mathbf{k}_{||}) - \delta \vec{P}(\mathbf{k}_{||})^{-1} \tilde{\mathcal{D}}^{-1}(0, 0, \mathbf{k}_{||}) \tilde{\mathcal{D}}(0, x'_1, \mathbf{k}_{||})_{ij} \right\}. \quad (5.13)$$

c) Finding the observable quantities

1) *Reflection coefficients.* The formulas given above enable one to derive expressions for the observable quantities in the presence of roughness—for the light reflection coefficients, the dispersion law of surface plasmons, and photoemission. When the bulk absorption in the metal is small ($\text{Im } \epsilon_1 \ll 1$), the relative changes in the specular reflection coefficients associated with the existence of roughness can be written in the form

$$\frac{\Delta R_\alpha}{R_\alpha} = -\frac{1}{R_\alpha} \int \frac{d R_{\alpha-\alpha}}{d \Omega} d \Omega - \frac{1}{R_\alpha} \int \frac{d R_{\alpha-\beta}}{d \Omega} d \Omega - \frac{\Delta R_\alpha^{s-p}}{R_\alpha}; \quad \alpha, \beta = s, p. \quad (5.14)$$

The terms $(1/R_\alpha) d R_{\alpha-\beta} / d \Omega$ ($\alpha, \beta = s, p$) in (5.14) show what part of the energy of the incident α -polarized light is converted into β -polarized light diffusely scattered into the solid angle $d \Omega = \sin^2 \theta_s d \theta_s d \varphi$. We consider that the correct expressions for them are those given in Refs. 159, 160, 162. In the neighborhood of the intrinsic frequency of surface plasmons $\omega_s = \omega_s(k_{||})|_{k_{||} \rightarrow \infty}$, the main contribution to (5.14) comes from the terms $\Delta R_s^s / R_s$ and $\Delta R_s^p / R_p$, which show what fraction of the incident light, respectively s- or p-polarized, is converted into surface plasmons. The corresponding quantities have the form

$$\Delta R_s^{s-p} = \frac{\omega^4}{c^4} \bar{\xi}^2 a^2 \cos \theta \frac{|\epsilon_1|^2 \epsilon_2^{5/2}}{(1 - \epsilon_1 - \epsilon_2)^{5/2}} \int_0^{2\pi} \sin^2 \varphi \times \exp\left[-\frac{a^2}{4}(k_s^2 k_{||} - k_{||}^2)\right] d \varphi \theta(-\epsilon_1 - \epsilon_2), \quad (5.15)$$

$$\Delta R_p^{s,p} = \frac{\omega^4}{c^4} \bar{\xi}^2 a^2 \cos \theta \frac{|e_1|^2 e_2^{5/2}}{(|e_1| - e_2)^{5/2} e_2 \sin^2 \theta + |e_1| \cos^2 \theta} \times \int_0^{2\pi} [(e_2 \sin^2 \theta - e_1)^{1/2} \cos \varphi - |e_1|^{1/2} e_2^{1/2} \sin \theta]^2 \times \exp \left[-\frac{a^2}{4} (k_s^2 k_{||} - k_{||}^2) \right] d\varphi \theta (-e_1 - e_2). \quad (5.16)$$

Here k_s^0 is the wave vector of a surface plasmon in the smooth surface as defined by Eq. (1.3), $k_{||}^0$ is the projection of the wave vector in the incident wave on the plane of the surface, and $\hat{k}_{||} = (\cos \varphi, \sin \varphi)$ is a unit vector in the plane of the surface.

We note that, although the formula (5.15) for $\Delta R_p^{s,p}$ and the expressions for $(1/R_s) dR_{s-s}/d\Omega$, $(1/R_s) dR_{s-p}/d\Omega$, and $(1/R_p) dR_{p-s}/d\Omega$ given in Refs. 159, 160, and 162 coincide with the corresponding results in Ref. 152, the expressions (5.16) for $\Delta R_p^{s,p}$ and those for $(1/R_p) dR_{p-p}/d\Omega$ from Refs. 159, 160, and 162 differ from those derived in Ref. 152. This discrepancy involves the existence in Ref. 152 of the indeterminacies of the type of (5.4) that we have already noted above. For the case of normal incidence of light, results coinciding with those given in Refs. 159, 160, and 162 have also been obtained in Refs. 148, 149, 158, and 161.

In order to explain the role of the individual terms in (5.14), let us give the results of numerical calculations¹²⁴ of the quantities

$$\Delta R_{s-\alpha} = \int \frac{dR_{s-\alpha}}{d\Omega} d\Omega$$

and $\Delta R_p^{s,p}$ for the case of normal incidence of light from a vacuum onto silver. These results are shown in Fig. 9. The calculations employed the known¹⁷³ optical constants of silver, while the mean dimension of the irregu-

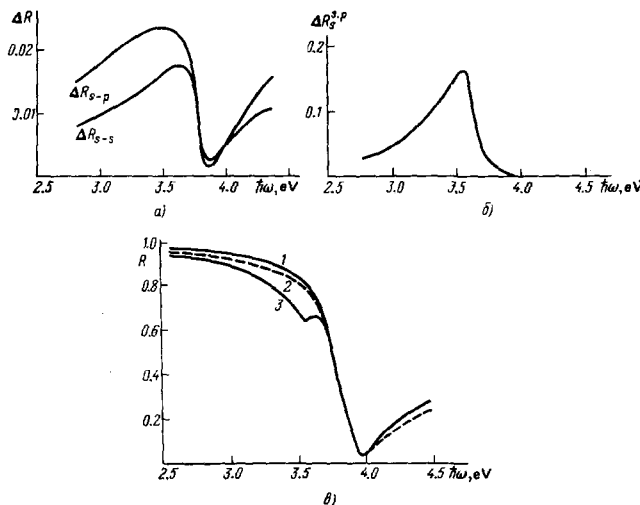


FIG. 9. Illustration of the calculation of the reflection of light from a rough silver surface. a) Form of the functions ΔR_{s-s} and ΔR_{s-p} describing the conversion of normally incident light into s- and p-polarized light diffusely scattered from the metal; b) form of the function $\Delta R_p^{s,p}$, which gives the fraction of the energy of the incident light absorbed by surface plasmons; c) specular reflection coefficients for a smooth silver surface (curve 1), with only the terms ΔR_{s-s} and ΔR_{s-p} taken into account (2), and with only the term $\Delta R_p^{s,p}$ taken into account (3), taken from Ref. 124.

ularities $(\bar{\xi}^2)^{1/2}$ and the correlation length a were taken respectively as 85 Å and 1000 Å. We see from Fig. 9 that the term $\Delta S_p^{s,p}$ describing the absorption of light by surface plasmons has a sharp maximum and makes the main contribution to $\Delta R_s/R_s$ near the frequency ω_s^0 for which $\epsilon_1 \approx -1$. It was shown in Ref. 124 that, with a reasonable choice of the parameters $\bar{\xi}^2$ and a , one can gain good agreement between the experimentally measured and calculated values of the light reflection coefficients. Moreover, the differential intensities of scattered light $(1/R_\alpha) dR_{\alpha-\beta}/d\Omega$ ($\alpha, \beta = s, p$) were directly measured¹²⁴ for silver as a function of the scattering angle θ_s at five different frequencies. It was possible to reconstruct from these relationships, using the formulas derived in Ref. 159 for $(1/R_\alpha) dR_{\alpha-\beta}/d\Omega$, the values of the parameters $\bar{\xi}^2$ and a . Here they proved to be practically the same in all cases [$(\bar{\xi}^2)^{1/2} = 39$ Å, $a = 200$ Å]. This confirms the validity of the theory. We should also note that, according to the results of Refs. 159 and 160, the quantities $(1/R_s) dR_{s-s}/d\Omega$ and $(1/R_p) dR_{p-s}/d\Omega$ are monotonic functions of the scattering angle θ_s , whereas $(1/R_s) dR_{s-p}/d\Omega$ and $(1/R_p) dR_{p-p}/d\Omega$ have a maximum at the angle θ_s that satisfies the equation $\tan \theta_s = \epsilon_1$. When $\text{Im} \epsilon_1 \neq 0$, this maximum is somewhat shifted and smoothed out. The noted behavior of the differential intensities $(1/R_\alpha) dR_{\alpha-\beta}/d\Omega$ has been found experimentally in Ref. 124.

2) *Dispersion law of surface plasmons.* Let us take up in greater detail the effect of microscopic roughness of metal surfaces on the dispersion law of surface plasmons $\omega = \omega_s(k_{||})$. This law is determined by the position of the poles of the Green's function of (5.13), which are fixed by the condition

$$\text{Det} \{ \vec{\mathcal{D}}^{-1}(0, 0, \mathbf{k}_{||}) - \vec{\delta} \bar{P}(\mathbf{k}_{||}) \} = 0. \quad (5.17)$$

We can rewrite the condition (5.17) as an equation defining $\omega_s(k_{||})$ in the form

$$e_1 \left(\frac{\omega^2}{c^2} e_2 - k_{||}^2 \right)^{1/2} + e_2 \left(\frac{\omega^2}{c^2} e_1 - k_{||}^2 \right)^{1/2} = \pi (e_1 - e_2)^2 \bar{\xi}^2 a^2 \int \frac{d^2 k_{||}}{(2\pi)^2} \left\{ \exp \left[-\frac{a^2}{4} (k_{||} - k_{||}')^2 \right] \times \left[e_1 \left(\frac{\omega^2}{c^2} e_2 - k_{||}'^2 \right)^{1/2} + e_2 \left(\frac{\omega^2}{c^2} e_1 - k_{||}'^2 \right)^{1/2} \right]^{-1} \times (k_{||} k_{||}' - \left(\frac{\omega^2}{c^2} e_1 - k_{||}^2 \right)^{1/2} \left(\frac{\omega^2}{c^2} e_2 - k_{||}'^2 \right)^{1/2}) \right\}. \quad (5.18)$$

If we assume the change in the dispersion law caused by the existence of roughness to be small, we obtain the following expression from (5.18) when $|ak_s^0| < 1$ outside the frequency region for which $\epsilon_1 + \epsilon_2 \sim 0$:

$$\omega_s(k_{||}) \approx \omega_s^0(k_{||}) + \frac{3}{4} \bar{\xi}^2 a^2 \left(\frac{\omega_s^0}{c} \right)^4 \omega_s^0 \left(\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^3 \times \frac{\epsilon_1 [2 \ln(k_s^0 a/2) + i\pi]}{(\omega_s^0/2) \epsilon_2 (d\epsilon_1/d\omega) + \epsilon_1 (\epsilon_1 + \epsilon_2)} \Big|_{\omega = \omega_s^0(k_{||})} \quad (5.19)$$

Here $\omega_s^0(k_{||})$ is the solution of Eq. (5.10) at $\bar{\xi}^2 = 0$, which gives the dispersion law for a smooth surface. Equations of the type of (5.18) for the dispersion law $\omega_s(k_{||})$ have been derived in Refs. 120, 151, 155, 160, and 163. Unfortunately, no measurements have been made of the dispersion law for a surface with random irregu-

larities with independent measurement¹²⁾ of the autocorrelation functions $\langle \xi(\mathbf{x}_1) \xi(\mathbf{x}_1') \rangle$. This hinders comparison of theory and experiment. For a surface with a known sinusoidal profile, the theoretically calculated¹⁵¹ $\omega_s(k_{||})$ relationship of the type of (5.18) has been compared¹⁷⁶ with the experimentally measured dispersion law of surface plasmons. In this case good agreement was obtained between theory and experiment.

In the frequency region of special interest where $\varepsilon_1 + \varepsilon_2 \sim 0$, the solution of (5.18) demands especial caution as $|\varepsilon_1 + \varepsilon_2| \rightarrow 0$, owing to the singularity of the functions on the right-hand side of (5.18). At these frequencies we find that the wave vector of a surface plasmon satisfies $k_s \gg (\omega/c)|\varepsilon_1|, (\omega/c)|\varepsilon_2|$. However, owing to the presence of a term having a pole in the integrand in (5.18), one cannot take the limit as $c \rightarrow \infty$ [with $\varepsilon_1(\omega) + \varepsilon_2 \sim 0$ and finite $[(k_s^0)^2 = (\omega^2/c^2)\varepsilon_1\varepsilon_2/(\varepsilon_1 + \varepsilon_2)]$ in calculating the right-hand side of (5.18) prior to integration, as was actually done in Ref. 156. We also note that, if we take the limit as $c \rightarrow \infty$ in the integrals in Eq. (5.18) and drop the terms having poles, then the dispersion law that we obtain will exactly coincide with that found in Ref. 157, where the nonrelativistic equations were used from the outset. However, as we have already said, this dropping of terms cannot be justified when $\varepsilon_1 + \varepsilon_2 \sim 0$.

In order to elucidate the problems that arise here, to which, we think, due attention has not been paid heretofore, let us rewrite Eq. (5.18) in the simplest case in which the inequality $|k_{||}| > |\varepsilon_1| \omega/c$ is satisfied, but $k_{||}$ still remains smaller than a^{-1} . Representing $\omega_s(k_{||})$ in the form $\omega_s = \omega_s^0 + \Delta$, where ω_s^0 is the solution of the equation $\varepsilon_1 + \varepsilon_2 = 0$, we obtain the following expression from (5.18):

$$\left[\Delta \frac{d\varepsilon_1(\omega_s^0)}{d\omega} \right]^{7/2} = -\frac{3}{2} i \bar{\xi}^2 a^2 \varepsilon_2 k_{||} \left(\frac{\omega}{c} \right)^3 \times \left[\ln \left(\frac{a^2 \omega^2}{4 c^2} \varepsilon_1 \varepsilon_2 \right) - \frac{2}{7} \ln \left(\Delta \frac{d\varepsilon_1(\omega)}{d\omega} \right)^{7/2} + i\pi \right]_{\omega=\omega_s^0}. \quad (5.20)$$

The right-hand side of Eq. (5.20) has a branch point at $\Delta = 0$. Correspondingly, we shall seek the solution in a form nonanalytic in $\bar{\xi}^2 a^2 k_{||} (\omega/c)^3$:

$$\left[\Delta \frac{d\varepsilon_1}{d\omega} \right] = \alpha \bar{\xi}^2 a^2 k_{||} \left(\frac{\omega}{c} \right)^3 \ln \left[\bar{\xi}^2 a^2 k_{||} \left(\frac{\omega}{c} \right)^3 \right] \left[1 + O \left(\bar{\xi}^2 a^2 k_{||} \frac{\omega^2}{c^3} \right) \right]. \quad (5.21)$$

Here α is a coefficient to be determined. Substitution of (5.21) into (5.20) yields the value $\alpha = (3/7)i\varepsilon_2^5$. Among the seven roots of Eq. (5.21), which have different phases, only two can correspond to surface plasmons with decay, their imaginary component being negative and small. The appearance of nonphysical solutions having a positive imaginary component of ω_s , which corresponds to unlimited growth of the field with time, indicates the unsuitability of keeping a finite number of terms in the perturbation-theory series with respect to δP_{ij} . The contribution of the earlier terms of the series must become essential near $\omega = \omega_s^0$ owing to the presence in term of additional singular factors $(\varepsilon_1 + \varepsilon_2)^{-n}$. This complicated problem has not been discussed in the literature. We note that the splitting of

the surface-plasmon spectrum in the presence of roughness was first treated in Refs. 156 and 157. In the cited studies the splitting of the surface-plasmon spectrum was twofold. As it seems to us, this is physically justified in a not very clear fashion as a consequence of the removal by the roughness of degeneracy among plasmons having different directions of the vector $\mathbf{k}_{||}$. According to (5.21), the magnitude of the splitting is

$$\begin{aligned} \text{Re}(\Delta_1 - \Delta_2) &= \left(\frac{3}{7} \varepsilon_2^5 \right)^{2/7} \left[\bar{\xi}^2 a^2 k_{||} \frac{\omega^3}{c^3} \ln \left(\bar{\xi}^2 a^2 k_{||} \frac{\omega^3}{c^3} \right) \right]_{\omega=\omega_s^0}^{2/7} \\ &\quad \times \left[\frac{d\varepsilon_1(\omega_s^0)}{d\omega} \right]^{-1} \left(1 + \cos \frac{\pi}{7} \right), \\ \text{Im} \Delta_1 &\approx 0, \\ \text{Im} \Delta_2 &= - \left(\frac{3}{7} \varepsilon_2^5 \right)^{2/7} \left[\bar{\xi}^2 a^2 k_{||} \frac{\omega^3}{c^3} \ln \left(\bar{\xi}^2 a^2 k_{||} \frac{\omega^3}{c^3} \right) \right]_{\omega=\omega_s^0}^{2/7} \\ &\quad \times \left[\frac{d\varepsilon_1(\omega_s^0)}{d\omega} \right]^{-1} \sin \frac{\pi}{7}. \quad (5.22) \end{aligned}$$

We note the deviation of (5.22) from the results of Ref. 156, in which the splitting was found to be proportional to $(\bar{\xi}^2)^{1/2} \omega/c$. We should also note that, according to (5.22), the quantity $\text{Im} \Delta_2$ proves to be comparable with the magnitude of the splitting $\text{Re}(\Delta_1 - \Delta_2)$, which should impede its experimental observation. Experimental observations of the splitting of the spectrum of surface plasmons has been indicated in Refs. 129, 130, and 177. We should stress here that the entire problem of splitting of the plasmon spectrum in the presence of roughness is yet far from being explained, and it requires further experimental and theoretical study.

Equation (5.18) can also be used to determine the dependence of the wave vector $k_{||} = k_s(\omega)$ of surface plasmons on the frequency ω . In Ref. 124 $\text{Re} k_s(\omega)$ has been calculated numerically, starting with an equation of the type of (5.18), for a rough silver surface with various values of the parameters $\bar{\xi}^2$ and a . It turned out that the existence of roughness increases the wave vector $\text{Re} k_s$ (at fixed ω) as compared with a smooth surface. This prediction of the theory agrees with the results of experiments.^{178,179} One can also determine from (5.18) the decay length of surface plasmons l

$$= [2 \text{Im} k_s(\omega)]^{-1}. \quad 154, 155$$

3) *Frequency-dependence of photoemission.* In discussing the angular, polarization, and frequency dependences of photoemission by solid metals, in many cases one must take into account the effect of microscopic roughness of the surface. One can expect substantial effects in the frequency-dependence of photoemission from a rough surface in the frequency interval of generation of surface plasmons. Endriz and Spicer¹³¹ have established that excitation of surface plasmons gives rise to a maximum in the quantum yield of photoemission in the frequency region of ω_s^0 , at which $\text{Re}(\varepsilon_1 + \varepsilon_2) = 0$. They have observed this effect experimentally for aluminum.¹³¹ Sass *et al.*^{132,133} have observed a considerable enhancement of the photocurrent in the formation of surface plasmons at a silver-electrolyte boundary. A theoretical description of this phenomenon has been proposed.¹²⁰ As the calculation¹²⁰ shows, the creation of surface plasmons can increase the quantum yields of photoemission by two orders of magnitude, owing to the sharp enhancement of the field at the surface. We can

¹²⁾ The autocorrelation functions of roughness have been determined for a number of surfaces by using the interference method.^{172,175}

interpret physically this result, which agrees with experiment, as arising from the addition of the amplitudes of the surface waves generated by the incident light wave at different points of the metal surface. The comparison¹²⁰ of the results of calculation with experiment¹³² on photoemission from silver in an 0.5 M solution of K_2SO_4 showed that not only does one obtain a correct overall course of the frequency-dependence of the photocurrent at values of the parameters $(\xi^2)^{1/2} = 30 \text{ \AA}$ and $a = 200 \text{ \AA}$, but also quantitative agreement.

This effect of enhancement of the field near the surface in the presence of surface polaritons is also of interest in treating other phenomena that occur upon illuminating an electrode. In particular, it must be taken into account in analyzing the data on anomalously intense Raman scattering.

6. SURFACE PLASMA WAVES

Up to now, the theory of surface plasma waves in metals has been developed in detail predominantly on the basis of simplified models of the electron-density distribution near the boundary. The reviews of Refs. 32, 33, 180, 181 have been devoted to presenting the results of these studies. In most cases the model expressions for the response function are constructed by using the wave functions of electrons treated as not interacting with one another and existing in the field of a rectangular well having an infinite potential barrier. This model has been employed within the framework of the random-phase approximation in Refs. 182 and 183. In the simple limiting case of high density, the results of these studies coincide with those of the theory of surface waves in a plasma with a sharp boundary.^{184, 185} The further development of these models has been associated with taking into account the finite height of the boundary barrier and its actual form. In particular, Refs. 186 and 187 have been carried out along these lines.

In addition to the calculations pointed out above, we should also mention the calculations of the spectrum of surface excitations associated with the intrinsic density oscillations given by the equations of motion for matter interacting with an electromagnetic field. Such calculations of the dispersion laws have been mainly performed with models having a smooth boundary. In these models the electron density in the region near the surface is assumed to be a slowly varying function of the coordinates, and its oscillation is described by equations of the hydrodynamic type^{34, 188-192} having the form

$$\left. \begin{aligned} \nabla^2 \varphi(x_i) &= -4\pi e \rho(x_i) & (\vec{E} &= -\nabla \varphi), \\ -i\omega \rho(x_i) + \nabla j(x_i) &= 0 & (j &= \rho v), \\ i\omega m j_i(x_i) &= e \rho(x_i) \nabla_i \varphi(x_i) + \sum_{j=1}^3 \nabla_j G_{ij} \{\rho(x_i)\}. \end{aligned} \right\} \quad (6.1)$$

In (6.1) the functional $G_{ij}\{\rho\}$, which has a different form in different studies, takes concentration effects into account. In principle it includes the influence of correlation and exchange effects. Additional types of surface excitations (as compared with ordinary surface plasmons) have been obtained within the framework of the hydrodynamic model. They amount to the intrinsic os-

cillations of the electron density of the surface layer that have been modified by the electromagnetic interactions.^{189, 191, 192} In principle the frequencies ω_s of the surface plasmons can be close to the frequencies of the additional surface excitations that we have pointed out above. Here specific resonance effects can arise, even with weak coupling between the plasmons and these excitations. Such effects have not been treated in the literature up to now. However, we should emphasize that in metals the scale of the changes of electron density in the surface layer is close in order of magnitude to the characteristic wavelength of an electron. Under these conditions the smooth-boundary model cannot be justified at all rigorously. Therefore the conclusions of Refs. 34, 188-192, which are based on (6.1), are only qualitative in nature. With each complication of the model, all the cited studies have treated anew the microscopic Maxwell equations (or the equations for the surface charge) that were used to study the dispersion of the surface waves. Here it proved necessary to make additional approximations and to resort to numerical calculations. The equations of the type of (2.15) for the dispersion law of surface plasmons (but not for the extra excitations) that were formulated in Refs. 17, 193, and which do not depend on the structure of the surface layer, enable one to avoid the unwieldy stage of calculations, and to find directly the coefficients $\Delta\epsilon(\omega)$ and $\Delta\epsilon^{-1}(\omega)$ by the formulas (1.6), (2.5), and (2.9) using the adopted approximation for the dielectric-permittivity tensor. As has been shown in Refs. 17, 24, 25, and 28, the presence of spatial dispersion leads to an additional damping of the surface waves that depends on $|k_{||}|$. This effect is due to the interaction of the surface bands with the bulk bands, which is made possible by the overlap of their spectra upon taking account of spatial dispersion. Moreover, this interaction gives rise to a dependence of the position of the surface-plasmon level on $|k_{||}|$. Depending on the models used to describe the bulk optical properties of the crystals, the coefficient of the term linear in $|k_{||}|$ in $\omega_s(k_{||})$ proves to be either of the order of the Debye length, or of the mean free path, or of the lattice constant, or of v_F/ω_p , where v_F is the Fermi velocity.

As we have shown in Sec. 2, the presence of a transition layer also gives rise to terms linear in $|k_{||}|$ in the dispersion law $\omega_s(k_{||})$. Whenever the effective thickness of the transition layer is large in comparison with the lengths listed above, which characterize the effects of spatial dispersion in bulk, the term linear in $|k_{||}|$ that appears in (2.16) must apparently be the major term, and must exceed in absolute magnitude all the other corrections to the dispersion law.

The simplest model that enables one to write explicitly the dependence of the dispersion law of surface plasmons on the electron density is the plasma model that has already been discussed above in Sec. 3. Here the dependence of the dielectric permittivity on the coordinates is determined by the electron-density profile and is represented by Eq. (3.6). If we assume the damping τ^{-1} to be infinitesimal we obtain from (2.5), (2.15), and (3.6) in the nonrelativistic limit ($c \rightarrow \infty$) the following relationship¹⁷ between the coefficient λ of the

term linear in $|k_{||}$ in the dispersion law $\omega_s(k_{||})$ and the electron-density profile:

$$\lambda = \frac{\omega_p}{\sqrt{2}} \left\{ P \int_{-\infty}^{\infty} \left[\frac{\rho(x_1)}{N} + \frac{\rho(x_1)}{N-2\rho(x_1)} \right] dx_1 - i \frac{\pi}{2} \left[\frac{d \ln \rho(x_1)}{dx_1} \right]_{x_1=x_1^0}^{-1} \right\}. \quad (6.2)$$

Here P denotes the integral in the sense of its principal value, and the point x_1^0 is defined as the solution of the equation $\text{Re}\{\epsilon(x_1^0, \omega)_{\omega=\omega_p/\sqrt{2}}\} = 0$. The imaginary component of λ arises from the possibility of transforming surface waves into bulk waves. An expression of the form of (6.2) can be derived by using the corresponding approximations of the equation for the nonequilibrium charge density in the random-phase approximation¹⁸⁰ and from equations of the form of (6.1), as has been done in Ref. 34. As a rule, the scale of the change in electron density in the surface layer $[d \ln \rho(x_1)/dx_1]^{-1}$ is close to the parameter v_F/ω_p that characterizes the effects of spatial dispersion. Therefore, in studying the effect of the electron-density distribution on the surface-plasmon spectrum, one must take into account the presence of spatial dispersion in the bulk of the metal.

The coefficient λ , which determines the dependence of the frequency of a surface plasmon on the wave vector $k_{||}$, can be measured experimentally, e.g., by using the ATRS method. The problem of the sign of λ has aroused discussion, both in analyzing the experimental data,^{194,195} and in the theory of this phenomenon.^{24,196} The results of Refs. 17, 24, and 25 and the formulas given above imply that the sign of the coefficient λ depends on the properties of the bulk dielectric permittivity $\epsilon(\omega, \mathbf{k})$ of the metal and on the details of the electron-density distribution in the surface layer, and it can be either positive or negative. In this regard it becomes especially important to measure λ sufficiently accurately under strictly controlled conditions.

Considerably more unequivocal and informative results are obtained from experimental and theoretical studies of the changes in the dispersion laws that arise from changing certain properties of the surface, rather than studying the dispersion laws themselves. Studies along this line have begun in recent years. The dependence of the dispersion law of surface plasmons $\omega_s(k_{||})$ localized at the (111) boundary of an Ag single crystal with an 0.5 M solution of NaClO₄ solution on the potential jump φ has been studied in Refs. 197. The measurements were made by the ATRS method at fixed $k_{||}$. It was shown¹⁹⁷ that the form of the dependence of ω_s on φ varies sharply in the vicinity of the point of zero charge. In the region of potentials more positive than the point of zero charge, we have $-d\hbar\omega_s/d\varphi \approx 2 \times 10^{-2}$ eV/V, while $|d\hbar\omega_s/d\varphi|$ is much smaller than this quantity for potentials more negative than the point of zero charge. This effect has been explained¹⁷ within the framework of the plasma model of the dielectric permittivity of (3.6). It has been shown^{197,198,199} that the dispersion law of surface plasmons is highly sensitive to the state of the surface, and depends both on the concentration and on the type of atoms and ions adsorbed on it. The interpretation of the experiments in Refs. 198 and 199 was carried out using the three-layer model, which, as we have already noted, is valid only for

thick adsorbed layers. What we have said above implies that a detailed analysis of the data on the dependence of the characteristics of the surface plasmons on the microscopic structure of the metal surface still remains a matter for the future. Evidently, such an analysis can serve as an important source of information on this structure.

7. CONCLUSION

We note in concluding the review that a number of interesting problems involving the manifestation of microscopic characteristics of the surface in optical experiments has remained untreated owing to restricted space. In particular, the numerous studies on external photoemission at the boundary of a metal with vacuum or with other media have been merely mentioned. The experimental and theoretical studies performed in recent years^{7,8,13,14,200} have shown that the study of the dependence of photoemission on the frequency, polarization, and angle of incidence of light, and also on the orientation of the plane of incidence with respect to the symmetry elements of the crystal enables one to get substantial information on the mechanism of photoexcitation of electrons and on the state of the surface. Such studies also enable one to extract the values of the matrix elements proper of the optical transitions from the overall expressions for the photocurrent, which also contain substantially the optical parameters that determine the behavior of the field intensity near the surface of the metal.

Experiments on the spectroscopy of surface plasmons,^{6,24} which have not been discussed in the review, are also of considerable interest. In particular, it is highly interesting to observe photons formed in the decay of surface plasmons that are being excited by any independent method, e.g., by interaction with an electron beam. It has been shown in these experiments^{201,202} that the probability of creation of photons formed in the decay of surface plasmons shows strong angular and polarization dependences. In particular, the photons were preferentially p-polarized. The prospects of studying the structure of the surface using data on the decay of surface plasmons pointed out in Ref. 203 are highly interesting.

Despite the well-known incompleteness that we have pointed out above, we hope that the content of this review makes it possible to support to a sufficient extent the assertion made in the Introduction concerning the dramatic development in recent years of theory and experiment in the field of optics of metal surfaces. The detailed information on the structure of surfaces and on the processes that occur near them that can be obtained in optical experiments will undoubtedly play a very important role in the near future in the development of the physics and physical chemistry of metal surfaces.

In closing the review, we list some unsolved problems in the field under discussion that seem central to us. We must point out as the first of these the fundamental problem of going beyond the framework of the approximation based on writing the equations for the Green's functions of the electromagnetic field in the

medium with linear response functions calculated in the random-phase approximation. This approximation does not take into account correlation effects, the dynamics of surface short-wavelength electron excitations, nor the dynamics of interaction of such excitations or of light directly with other surface and bulk collective modes. Up to now, no complete analysis has even been performed of the type of experiment in which one should expect the effects mentioned above to be manifested in a way amenable to quantitative description. Apparently most of the experimental schemes that have been developed up to now are individually inadequate to attain such a goal, and one must design special experiments with additional independent methods of monitoring the state of the surface excitations. Definite prospects are also offered by analysis of results of optical measurements of the surface properties of metals (in particular the line shapes in ER and modulation interferometry) performed at different temperatures in a range in which the equilibrium concentration of collective excitations depends strongly on the temperature.

A second important group of problems involves further experimental and theoretical study of the effect of microroughness on the characteristics of surface plasmons. Under conditions in which the correlation length of the roughness is of stomic dimensions and/or the damping in the metal is very small (as in ultrapure silver), the perturbation-theory series with respect to the ratio of the characteristics length of the roughness to the decay length of surface excitations begin to converge poorly in the frequency region of the surface plasmons. Here one should expect new effects that can apparently be described only by using a more complex field technique that is not based on perturbation theory. The essential point is that the latter effects can be not only of theoretical, but also applied importance, e.g., in connection with sharply increasing the quantum yield of photoemission at rough surfaces, and also in connection with problems of catalysis on metals. Further, there is as yet no final clarification, neither experimentally nor theoretically, concerning the suggested splitting of the spectrum of surface plasmons due to roughness.

As a third problem we deem it necessary to cite the problem of the analysis and systematics of the curves obtained in optical measurements such as electroreflection and ellipsometry. In contrast to semiconductors, in metals the ER and ellipsometry spectra have no sharp extrema as a rule, which hinders the interpretation of experiments. In order to reveal the mechanism of the processes that occur, one must redesign the experiment (e.g., measure the second derivatives of the reflection coefficients) or bring in extra information on the properties of the surface, including capacitive and photoemission measurements. This review has cited several successful examples (for indium and lead) in which such an analysis facilitated important conclusions to be made on the electron structure of surfaces, and in particular, on the shift and broadening of the electron levels of atoms when adsorbed on metals, and on the values of the emission thresholds. However, these examples are as yet solitary, and many observ-

able features of the curves and their shape have not yet found even a firm qualitative explanation. It has not yet been elucidated how substantially the band structure of a metal is manifested in the optical characteristics of surfaces. In this field we need further extensive work which will undoubtedly lead to the development of an entire new field of metal-surface spectroscopy. As we see it, the most promising developments in the theory, at least in the near future, will not be attempts at total (ab initio) calculation, but semiphenomenological analysis based on treating the interaction of light and the collective modes for fixed characteristic levels and resonances. This approach is analogous to the method of model Hamiltonians, which has been successfully employed in solid-state physics, and especially, in the theory of adsorption.²⁰⁴

Of course, we should mention the problem of interpreting experiments on anomalously intense Raman scattering by adsorbed molecules.^{205,206} The preliminary arguments presented in Sec. 4, c3 and Sec. 5 show that these experiments allow one to obtain important information on the electron and vibrational levels of molecules and on inhomogeneities of the surface. However, as yet only the first steps have been taken in this direction.

APPENDIX

Let us transform to the space of the wave vectors \mathbf{k} and select in it three orthogonal, unnormalized basis vectors $e^\alpha(\mathbf{k})$ ($\alpha = \text{TE}, \text{TM}, \text{L}$):

$$e_i^{(\text{TE})}(\mathbf{k}) = \sum_{j=1}^3 e_{ij} \frac{k_j}{k_{\parallel}}, \quad e_i^{(\text{TM})}(\mathbf{k}) = \frac{1}{k_{\parallel}} (k_i k_{\parallel} - \delta_{i\parallel} k^2), \quad e_i^{(\text{L})}(\mathbf{k}) = k_i. \quad (\text{A1})$$

Here e_{ij} is a fully antisymmetric tensor and \mathbf{k}_{\parallel} is the wave vector of motion in a plane parallel to the surface that is conserved in the absence of roughness. We shall take the direction of the latter as that of the x_2 axis, i.e., $\mathbf{k}_{\parallel} = \{0, k_2, 0\}$. In this case the plane of incidence of the light wave coincides with the plane $\{x_1, x_2\}$. The directions of the vectors $e_i^{(\text{TE})}(\mathbf{k})$ and $e_i^{(\text{TM})}(\mathbf{k})$ outside the metal coincide respectively with the directions of the field in s-polarized and p-polarized waves. The longitudinal wave in the metal lies along $e_i^{(\text{L})}(\mathbf{k})$.

In the case being discussed, we can write the Green's function $\mathcal{D}_{ij}^0(k_1, k_1')$ that enters into (2.1) as follows:

$$\begin{aligned} \mathcal{D}_{ij}^0(k_1, k_1') &= e_i^{(\text{TE})}(k_1) \mathcal{Z}^{(\text{TE})}(k_1, k_1') e_j^{(\text{TE})}(k_1') \\ &+ \frac{c^2}{\omega^2} \int \frac{dk_1''}{2\pi} \frac{dk_1'''}{2\pi} \varepsilon_0^{-1}(k_1 - k_1'') e_i^{(\text{TM})}(k_1'') \mathcal{D}^{(\text{TM})}(k_1'', k_1''') e_j^{(\text{TM})}(k_1''') \varepsilon_0^{-1}(k_1'' - k_1''') \\ &+ \frac{c^2}{\omega^2} \varepsilon_0^{-1}(k_1 - k_1') [\delta_{ij} - e_i^{(\text{TE})}(k_1) e_j^{(\text{TE})}(k_1')]. \end{aligned} \quad (\text{A2})$$

In (A.2) $\varepsilon_0^{-1}(k_1)$ denotes the Fourier transform of the function $1/\varepsilon_0(x_1)$, and we have introduced the scalar retarded Green's functions $\mathcal{D}^{(\text{TE})}$ and $\mathcal{D}^{(\text{TM})}$, which respectively obey the equations

$$\left(\frac{d^2}{dx_1^2} + \frac{\omega}{c^2} \varepsilon_0(x_1) - k_{\parallel}^2 \right) \mathcal{D}^{(\text{TE})}(x_1, x_1') = \delta(x_1 - x_1'), \quad (\text{A3})$$

$$\left(\frac{d}{dx_1} \frac{1}{\varepsilon_0(x_1)} \frac{d}{dx_1} + \frac{\omega^2}{c^2} \frac{k_{\parallel}^2}{\varepsilon_0(x_1)} \right) \mathcal{D}^{(\text{TM})}(x_1, x_1') = \delta(x_1 - x_1'). \quad (\text{A3}')$$

Here we have

$$\mathcal{D}^{(\text{TE}, \text{TM})}(x_1, x_1') = \int \frac{dk_1}{2\pi} \frac{dk_1'}{2\pi} e^{i k_1 x_1} \mathcal{D}^{(\text{TE}, \text{TM})}(k_1, k_1') e^{-i k_1' x_1'}. \quad (\text{A4})$$

An important advantage of this way of writing (A2) is that one can use the relatively simple apparatus of the theory of ordinary differential equations in analyzing the functions $\mathcal{D}^{(TE)}$ and $\mathcal{D}^{(TM)}$ that enter into \mathcal{D}_{ij}^0 . In particular, according to this theory the scalar Green's functions $\mathcal{D}^{(TE, TM)}(x_1, x_1')$ can be represented in the form

$$\begin{aligned} \mathcal{D}^{(TE)}(x_1, x_1', k_{\parallel}) &= \frac{1}{2i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2}} \left[\mathcal{E}^>(x_1, k_{\parallel}) \mathcal{E}^<(x_1', k_{\parallel}) \right. \\ &\quad \left. \times \theta(x_1 - x_1') + \mathcal{E}^>(x_1', k_{\parallel}) \mathcal{E}^<(x_1, k_{\parallel}) \theta(x_1' - x_1) \right], \\ \mathcal{D}^{(TM)}(x_1, x_1', k_{\parallel}) &= \frac{\varepsilon_2}{2i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2}} \left[H^>(x_1, k_{\parallel}) H^<(x_1', k_{\parallel}) \theta(x_1 - x_1') \right. \\ &\quad \left. + H^>(x_1', k_{\parallel}) H^<(x_1, k_{\parallel}) \theta(x_1' - x_1) \right]. \end{aligned} \quad (A5)$$

The symbols $\mathcal{E}^<(x_1, k_{\parallel})$ in (A.5) denote the solutions of one-dimensional equation of the form of (A.3) with the right-hand side set to zero, which corresponds to the boundary conditions of the outgoing or the damped waves, respectively, as $x_1 \rightarrow \infty$ and $x_1 \rightarrow -\infty$. The symbols $H^<(x_1, k_{\parallel})$ denote the analogous solutions of (A3') without the right-hand side. The normalization of the solutions entering into (A.5) has been chosen such that the following equalities hold outside the metal for $x_1 > 0$ "

$$\left. \begin{aligned} \mathcal{E}^>(x_1, k_{\parallel}) &\underset{x_1 > 0}{\approx} \exp \left[i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right], \\ H^>(x_1, k_{\parallel}) &\underset{x_1 > 0}{\approx} \exp \left[i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right], \\ \mathcal{E}^<(x_1, k_{\parallel}) &\underset{x_1 > 0}{\approx} \exp \left[-i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right] \\ &\quad - r_s^F(k_{\parallel}) \exp \left[i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right], \\ H^<(x_1, k_{\parallel}) &\underset{x_1 > 0}{\approx} \exp \left[-i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right] \\ &\quad - r_p^F(k_{\parallel}) \exp \left[i \left(\frac{\omega^2}{c^2} \varepsilon_2 - k_{\parallel}^2 \right)^{1/2} x_1 \right]. \end{aligned} \right\} \quad (A6)$$

In (A.6) we have introduced the quantities $r_s^F(k_{\parallel})$ and $r_p^F(k_{\parallel})$. When $k_{\parallel}^2 < (\omega^2/c^2)\varepsilon_2$, they have the meaning of the amplitudes of the reflection coefficients, respectively, of s- and p-polarized light from the surface of the metal. Their values are given by the Fresnel formulas (1.2).

Upon substituting the expression (A.2) for the Green's function into the integral equation (2.1) and simultaneously rewriting it so that it contains only the functions in (2.3) that vary slowly near the surface, we obtain the system of integral equations (2.4) in the text. The symbol \mathcal{D}_{ij}^0 in (2.4) denotes the quantities that are the elements of the 3×3 matrix

$$\begin{aligned} \mathcal{D}_{ij}^0(x_1, x_1') &= \frac{c^2}{\omega^2} \\ &\times \begin{pmatrix} k_{\parallel}^2 \mathcal{D}^{(TM)}(x_1, x_1') & -ik_{\parallel} \left[\frac{1}{\varepsilon_0(x_1)} \mathcal{D}^{(TM)}(x_1, x_1') \right] & 0 \\ ik \left[\frac{1}{\varepsilon_0(x_1)} \frac{d}{dx_1} \mathcal{D}^{(TM)}(x_1, x_1') \right] & \frac{1}{\varepsilon_0(x_1)} \left[\frac{1}{\varepsilon_0(x_1)} \frac{d}{dx_1} \frac{d}{dx_1'} \right. \\ &\quad \left. \times \mathcal{D}^{(TM)}(x_1, x_1') + \delta(x_1 - x_1') \right] & 0 \\ 0 & 0 & \frac{\omega^2}{c^2} \mathcal{D}^{(TE)}(x_1, x_1') \end{pmatrix} \end{aligned} \quad (A7)$$

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Translated by M. V. King