Crystal optics of suface polaritons and the properties of surfaces

V. M. Agranovich

Institute of Spectroscopy, USSR Academy of Sciences, Krasnaya Pakhra (Moscow District)
Usp. Fiz. Nauk **115**, 199–237 (February 1975)

Analysis of the physical properties of surfaces should be based on the maximum possible amount of information deduced from studies of the propagation of surface rather than volume electromagnetic waves, in which the energy is transported only along surfaces or separation boundaries between media. The present review, therefore, discusses a broad range of problems in the crystal optics of surface electromagnetic waves (surface polaritons), a subject developed in the course of the last few years. Various theoretical and experimental methods of investigating surface waves in crystals are discussed and compared, including a detailed review of Raman scattering of light. Other topics discussed include different effects in the spectra of surface waves due to the transition layer, the role of damping and spatial dispersion, the transformation of surface into volume waves, and so on. Possible fields of future research are suggested.

CONTENTS

1. GENERAL REMARKS. CRYSTAL OPTICS OF SURFACES

It is well-known that the development of any particular topic in solid state physics is determined, above all, by the internal logic of the studies themselves and by possible practical applications. Whenever both stimuli are acting simultaneously, in any particular field, the subject attracts wide interest and develops very rapidly.

One such rapidly developing field of study is the physics of the surfaces of condensed media and, in particular, the physics of the surfaces of solids. Duke and Park [1] have rightly pointed out that "the scientific interest in surfaces, however, arises from their unique properties, which frequently have no counterpart in bulk solid-state physics. The renewed sense of excitement that currently pervades the surface-science community stems from the construction of new techniques for observing these surface properties and of theoretical models that convert observations into quantitative measures of the condition of the outermost layers of a solid. The confluence of these two developments is transforming the study of surfaces from a qualitative art into a quantitative science."

The latter fact is particularly important for practical purposes since the properties of various thin films, layered structures, and, generally, separation boundaries between media play a determining role in the function of many physical instruments (see, for example, [2]).

The usual question that arises when the properties of a surface are investigated is: what is its structure? There is also the associated question as to what is the spectrum of the surface excited states. Many very effective methods of investigating the structure of surfaces have been developed in recent years (they are reviewed in [1]). The spectrum of surface excited states, i.e., states due to the very presence of the surface or of a separation boundary, is an old problem (it will be sufficient to recall Rayleigh waves in the theory of elasticity or the Tamm states of electrons), but it continues to remain very topical. There are many examples of specific physical situations for which it is important to know the excited states of the surface, and this occurs not only in physics but also in physical chemistry (for example, in the analysis of the mechanisms responsible for the catalytic action of the surfaces of solids), biology, and elsewhere. We shall confine ourselves to recalling only some of them. Thus, for example, in searches for high-temperature superconductors with the exciton mechanism of Cooper pairing in planar geometry (the sandwich model, see [3]), there is particular interest in excited states and, generally, in the electron structure of the metal-dielectric or metal-semiconductor contact. The electronic changes in the spectrum of surface excitations of dielectrics and semiconductors (their analysis is only just beginning; see [4]) must be taken into account in any theory of the effect of nonmetal coatings on the temperature of the superconducting transition in thin

(~10–20 Å) metal films. The role of small-radius surface excitons is interesting in connection with the structure of the spectrum of low-temperature luminescence of molecular crystals and the surface quenching of excitons.[5] There is a whole series of problems involving excited states of surfaces (surface phonons, excitons, magnons, electrons, and so on) that arises in connection with the very interesting possibility of observing surface, i.e., two-dimensional or quasi-two-dimensional analogs of ferromagnets, ferroelectrics, piezoelectrics,[1)] superconductors, superfluids, and so on (see[6]), and also the many other problems connected with the properties of the spectrum of surface excitations.

In our review below, we shall discuss the spectra of excited states of surfaces or separation boundaries that can be studied within the framework of crystal optics.

We note that crystal optics is usually employed to investigate the propagation of plane monochromatic light waves through the body of a crystal, with definite values of frequency ω and wave vector $\mathbf{k}$. Experimental determination of the dispersion relation for these waves [i.e., of the function $\omega = \omega(\mathbf{k})$, or the equivalent dependence of the complex refractive index $\tilde{n}$ or ω], followed by comparison of this relation with the phenomenological Maxwell equations (using the permittivity tensor), yields information on, mainly, the spectrum of bulk excitations of the medium or, for example, its conductivity (metal optics). It is clear that the maximum information about the surface properties of a medium is likely to be obtained by studying the propagation not of body but of surface electromagnetic waves in which energy is transported only along surfaces or separation boundaries. Studies of the attenuation of such surface waves, and of their reflection and refraction at separation boundaries (lines), which can be referred to as the crystal optics of surfaces, will probably play a fundamental role in the physics of surfaces in the same way as ordinary (bulk) crystal optics has in spectral studies of the bulk properties of crystals. The main problem which arises in this connection is that it is essential to have sources and receivers of surface waves which are sufficiently convenient in practice. We shall touch on the question of possible devices of this kind in our account below, when we consider methods of transformation of body waves into surface waves. Since the properties of surface waves themselves are very important for the analysis of these problems, we shall start by discussing possible dispersion relations for them, their polarization and attenuation, and the influence of these parameters on the properties of the surface layers of a crystal.

2. VOLUME AND SURFACE POLARITONS. ATTENUATION OF SURFACE POLARITONS AND THEIR REFLECTION AND REFRACTION ALONG SEPARATION LINES

The dispersion of long-wave ($\lambda \gg a$; a is the lattice constant) electromagnetic waves in an isotropic medium is completely determined by the frequency dependence of the permittivity $\epsilon = \epsilon(\omega)$ (when spatial dispersion is ignored). In particular, the function $\omega = \omega(\mathbf{k})$ for transverse waves [electric field $\mathbf{E} \perp \mathbf{k}$, $\mathbf{k} = (\omega/c)n(\omega)\mathbf{s}$, $\mathbf{s} = \mathbf{k}/k$, and $n(\omega)$ is the refractive index] is determined by the formula

$$\varepsilon(\omega) = k^2c^2/\omega^2. \tag{1}$$

Near the resonance $\omega = \Omega_\perp$, the permittivity can be written in the form

$$\varepsilon(\omega) = \varepsilon_\infty + \{(\varepsilon_0 - \varepsilon_\infty)\,\Omega_\perp^2/[\Omega_\perp^2 - \omega^2]\}, \tag{2}$$

where ϵ_∞ is the asymptotic value of $\epsilon(\omega)$ for $\omega \gg \Omega_\perp$, whereas ϵ_0 is the permittivity for $\omega \ll \Omega_\perp$. Hence, if we use (1) and (2) to determine the function $\omega = \omega(k)$, we obtain two frequencies for each $\mathbf{k}$, namely, $\omega^\perp_{1,2}$ (Fig. 1). Elementary excitations with energy $\hbar\omega(k)$, the dispersion of which is determined by the function $\omega^\perp_{1,2}$, are usually called polaritons. For isotropic media, polaritons with the dispersion relation $\omega^\perp_{1,2}(\mathbf{k})$ are strictly transverse.

The frequencies of longitudinal electromagnetic waves, on the other hand, satisfy the condition $\epsilon(\omega) = 0$. Using (2), we find that $\omega_\parallel = \Omega_\parallel = \sqrt{\epsilon_0/\epsilon_\infty}\,\Omega_\perp$, in accordance with the Lyddane-Sachs-Teller relation. The essential point is that the frequency of the longitudinal electromagnetic wave (longitudinal polariton) is independent of $\mathbf{k}$ in this approximation, i.e., when spatial dispersion is ignored (see Fig. 1). Moreover, it follows from (1) that, when retarded effects are ignored (i.e., when $c \to \infty$), the transverse-wave frequencies satisfy the condition $\epsilon(\omega) = \infty$ which, in the model defined by (2), corresponds to the resonance at $\omega = \Omega_\perp$. Therefore, it is clear from Fig. 1 that retarded effects are important only for transverse waves in the region where $k \lesssim (\Omega_\perp/c)\sqrt{\epsilon_\infty}(\Omega_\perp/c)\sqrt{\epsilon_0}$. If, on the other hand, $k \gg (\Omega_\perp/c)\sqrt{\epsilon_0}$, then $\omega^\perp_1(k) \approx \Omega_\perp$, so that, in this case, the polariton belonging to the lower branch is not very different from the optical Born phonon. Since, however, even when spatial dispersion is taken into account the macroscopic analysis used above is valid only for wavelengths λ that are large in comparison with the lattice constant a, the above solutions do not describe the actual oscillations of the crystal for wave vectors $\mathbf{k}$ satisfying the inequality $ka \lesssim 1$. The microscopic theory is necessary in this part of the spectrum.

We note that, although the dispersion relation for polaritons reflects the well-known relation $n^2 = \epsilon(\omega)$ for transverse and $\epsilon(\omega) = 0$ for longitudinal waves in isotropic media, its representation in the form $\omega = \omega(k)$, shown in Fig. 1, has appeared only relatively recently in the papers of Tolpygo and Huang (see[7]), who used specific models of oscillations in ionic crystals. It is, of course, clear that the dispersion relation for polaritons illustrated in Fig. 1 is, in general, independent of the model and is valid for arbitrary nongyrotropic and nonmetallic isotropic media near permittivity resonances, including resonances in the electronic part of the spectrum. Moreover, this analysis can be generalized in a natural fashion to the case of anisotropic media (see, for example,[9]). The dispersion relation for polaritons belonging to the l-th branch of $\omega_l = \omega_l(\mathbf{k})$ in such media is then found from the equation $k^2c^2/\omega^2 = n_l^2(\omega, \mathbf{s})$, $\mathbf{s} = \mathbf{k}/k$, where $n(\omega, \mathbf{s})$ is the refractive index for the l-th normal electromagnetic wave. At present, the dispersion of polaritons in the region of lattice-vibration frequencies is being extensively investigated through studies of Raman scattering of light by polar-

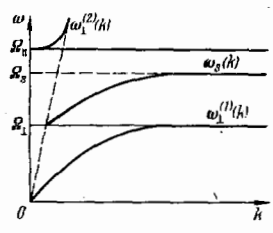

FIG. 1. Dispersion of polaritons with allowance for a plane separation boundary between the media.

itons in both cubic and anisotropic crystals. A review of the resulting extensive information on the properties of elementary excitations in crystals is, however, beyond the scope of the present work, and would take us outside the main theme of the present paper.

We must now return to the crystal optics of surfaces, and continue our analysis of the spectrum of electromagnetic waves in isotropic media, taking into account the presence of a plane surface or a separation boundary (see below), which leads to the appearance of surface electromagnetic waves (Zenneck-Sommerfeld waves, 1907–1909).[2)]

We shall suppose that a sharp separation boundary between two media with permittivities ϵ_1 ($z > 0$) and ϵ_2 ($z < 0$) is located in the (x, y) plane, and that the y component of the wave vector of the required surface waves is zero ($k_y = 0$). The Maxwell equations for a nonmagnetic medium are then of the form (for surface waves in magnetic media—see[14,59,72])

$$\operatorname{rot}\mathbf{E}=\frac{i\omega}{c}\mathbf{H},\qquad \operatorname{rot}\mathbf{H}=-i\varepsilon\frac{\omega}{c}\mathbf{E}, \tag{3}$$

and their solution (see, for example,[10] Sec. 68) can be sought in the form:[3)]

$$\mathbf{H}=\mathbf{H}_{+0}e^{ikx-\varkappa_1 z}\ (z>0),\quad \mathbf{H}=\mathbf{H}_{-0}e^{ikx+\varkappa_2 z}\qquad (z<0),$$

and similarly for the field $\mathbf{E}$, where $\kappa_1 = [k^2 - (\omega^2/c^2)\epsilon_1]^{1/2}$, and $\kappa_2 = [k^2 - (\omega^2/c^2)\epsilon_2]^{1/2}$. The vector $\mathbf{H}$ may be assumed to be parallel to the y axis, and the continuity of H_y across the boundary is ensured by the condition $H_{+0} = H_{-0} = H$. The second Maxwell equation in (3) then yields

$$i\frac{\omega}{c}E_x=\frac{1}{\varepsilon}\frac{\partial H_y}{\partial z},$$

so that the continuity condition for E_x is also satisfied if $-\kappa_1/\epsilon_1 = \kappa_2/\epsilon_2$ which, for positive κ_1 and κ_2, is possible only when ϵ_1 and ϵ_2 have opposite signs. To be specific, let us suppose that $\epsilon_1 > 0$ and $\epsilon_2 = -|\epsilon_2| < 0$. If we then use the explicit expressions for κ_1 and κ_2, we find that the dispersion relation for the surface wave is

$$k^2=\frac{\omega^2}{c^2}\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}. \tag{4}$$

It follows from this result that $k^2 > 0$ if $|\epsilon_2| > \epsilon_1$, which is to be expected for real k, ω and ϵ_1, ϵ_2. Thus, when $\epsilon_1 = 1$, i.e., when the crystal has a vacuum on one side, the dependence of the frequency ω_S of the surface polariton on k is as shown in Fig. 1. It follows from this figure that the surface-wave spectrum lies between $\omega = \Omega_\perp$ and $\omega = \Omega_S$, where Ω_S is the solution of (4) when $c \to \infty$ (i.e., when retardation is ignored). It also follows from (4) that the frequency Ω_S satisfies the equation

$$\varepsilon_1+\varepsilon_2=0, \tag{5}$$

and, when $\epsilon_1 = \text{const}$, $\epsilon_2 = \epsilon(\omega)$ [see (2)], we find that

$$\Omega_s=\Omega_\perp\sqrt{\frac{\varepsilon_1+\varepsilon_0}{\varepsilon_1+\varepsilon_\infty}}. \tag{6}$$

Therefore, the position of the frequency Ω_S is essentially dependent on the permittivity ϵ_1 of the substrate. Thus, when $\epsilon_1 \ll \epsilon_0$, ϵ_∞, the frequency Ω_S approaches the frequency $\Omega_\parallel$ of the longitudinal oscillations and may be difficult to observe (for more detailed discussion of the role of the substrate, see Chaps. 4 and 5)[4)].

So far, as in[10], we have neglected the attenuation of the waves. When attenuation is taken into account, this leads to a number of interesting effects, many of which can probably be found experimentally. However, we shall precede our discussion of these effects with a few remarks concerned with the formulation of the problem. The point is that attenuation can manifest itself in different ways, depending on the experimental situation. Thus, when a source of surface waves of given frequency ω is present on the separation boundary between media then, for complex permittivities, i.e., when dissipative processes are taken into account, the surface waves excited by the source will be attenuated during their propagation along the separation boundary. As in body crystal optics, we can then introduce a complex refractive index $\tilde{n}$ for the surface wave, defined by $\mathbf{k} = (\omega/c)\tilde{n}\mathbf{s}$, $\mathbf{s} = \mathbf{k}/k$, $\mathbf{k} \equiv (k_1, k_2)$. According to (4),

$$\tilde{n}^2=(n-i\varkappa)^2=\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}. \tag{7}$$

Let us consider the functions $n = n(\omega)$ and $\kappa = \kappa(\omega)$ in the case of sufficiently weak attenuation ($\kappa \ll n$), assuming that $\epsilon_1 = \text{const}$ and $\epsilon_2(\omega)$ is represented by the following natural generalization of (2):

$$\varepsilon_2(\omega)=\varepsilon(\omega)=\varepsilon_\infty+\frac{(\varepsilon_0-\varepsilon_\infty)\Omega_\perp^2}{\Omega_\perp^2-\omega^2+i\omega\Gamma(\omega)}. \tag{2'}$$

Substituting (2′) in (7), we obtain

$$(n-i\varkappa)^2=\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\omega^2-\Omega_\parallel^2-i\omega\Gamma}{\omega^2-\Omega_s^2-i\omega\Gamma},$$

and hence (see also Fig. 2)

$$n^2(\omega)=\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{(\Omega_\parallel^2-\omega^2)(\Omega_s^2-\omega^2)+\omega^2\Gamma^2}{(\omega^2-\Omega_s^2)^2+\omega^2\Gamma^2},\qquad 2n\varkappa=\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\omega\Gamma(\Omega_\parallel^2-\Omega_s^2)}{(\omega^2-\Omega_s^2)^2+\omega^2\Gamma^2}. \tag{8}$$

Therefore, the frequency $\omega = \Omega_S$ is a resonance frequency for surface polaritons. When $\omega \to \Omega_S$ and the attenuation is weak enough (i.e., Γ is small enough), the quantity n^2 increases rapidly, so that spatial dispersion effects may also become important near resonance. We shall discuss them below (see Chap. 7). Here, we shall confine our attention to estimating κ and comparing it with the corresponding values for body waves. Outside an absorption band, i.e., for $\Omega_S^2 - \omega^2 \gg \omega\Gamma$,

$$n^2\approx\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\Omega_\parallel^2-\omega^2}{\Omega_s^2-\omega^2},$$
$$2n\varkappa\approx\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\omega\Gamma(\Omega_\parallel^2-\Omega_s^2)}{(\omega^2-\Omega_s^2)^2}.$$

Assuming, for example, that $\Omega_\perp \approx 500\ \text{cm}^{-1}$, $\epsilon_1 = 1$, $\epsilon_0 = 5$, $\epsilon_\infty = 2$, and $\Omega_S - \omega \approx 100\ \text{cm}^{-1}$ [in which case $\Omega_S^2 - \omega^2 = \frac{1}{2}(\Omega_\parallel^2 - \omega^2)$] we obtain

$$n^2\approx\frac{4}{3},\qquad \varkappa\approx\frac{1}{12}\frac{\Gamma}{\Omega_s-\omega},$$

and, therefore, when $\Gamma \sim 10\ \text{cm}^{-1}$, we have $\kappa \approx 10^{-2}/3$. The path length L over which the intensity of the surface wave decreases by a factor of e, i.e., $L = c/2\omega\kappa$ is, in this case, of the order of a millimeter. For another choice of the band parameters, it can be several times greater, or smaller. One way or another, this length is much greater than the penetration depth for all body waves. All this follows quite simply from an analysis of the resonance situation. In fact, when $\omega = \Omega_S$, $n^2 = \epsilon_1\epsilon_\infty/(\epsilon_1 + \epsilon_\infty)$ [see (8)] and

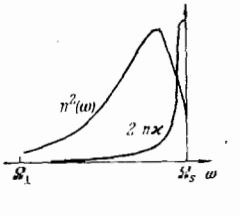

FIG. 2. Complex refractive index $\tilde{n} = n - i\kappa$ of dielectrics as a function of frequency ω.

$\omega = \Omega_s$, $n^2 = \frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}$ (см. (8)), а

$$\varkappa_{surf} = \frac{1}{2}\sqrt{\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\Omega_\parallel^2-\Omega_s^2}{\Omega_s\Gamma}} \approx \sqrt{\frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1+\varepsilon_\infty}\frac{\Omega_\parallel-\Omega_s}{\Gamma}}.$$

At the same time, for body waves with $\omega = \Omega_\perp$, we have $n^2 = \epsilon_\infty$, $\varkappa_b \approx (\epsilon_0 - \epsilon_\infty)\Omega_1/2\Gamma\sqrt{\epsilon_\infty}$. Therefore,

$$\frac{\varkappa_b}{\varkappa_{surf}} = \frac{(\varepsilon_0-\varepsilon_\infty)\,\Omega_\perp\,\Gamma(\Omega_s)\sqrt{\varepsilon_1+\varepsilon_\infty}}{2\Gamma(\Omega_\perp)\sqrt{\varepsilon_\infty}(\Omega_\parallel-\Omega_s)\sqrt{\varepsilon_1\varepsilon_\infty}}.$$

Assuming that $\Gamma(\Omega_s) \approx \Gamma(\Omega_\perp)$, and using the Lyddane-Sachs-Teller relation for $\Omega_\parallel$ and (6), we obtain

$$\frac{\varkappa_b}{\varkappa_{surf}} = \frac{(\varepsilon_0-\varepsilon_\infty)\sqrt{\varepsilon_1+\varepsilon_\infty}}{2\varepsilon_\infty\sqrt{\varepsilon_1}}\left(\sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}}-\sqrt{\frac{\varepsilon_1+\varepsilon_0}{\varepsilon_1+\varepsilon_\infty}}\right)^{-1}. \qquad (9)$$

Subject to the above assumptions with regard to the quantities ϵ_1, ϵ_0, and ϵ_∞, we have $\varkappa_b/\varkappa_{surf} \approx 6.5$, and this ratio has a comparable value in the nonresonant situation. This is very important because it facilitates the design of experiments on the attenuation of surface polaritons (see Chap. 4, Sec. d).

Let us now consider the reflection and refraction of surface waves at separation boundaries. In particular, let us suppose that medium I in which $\epsilon_1(\omega) > 0$ (ω is the surface-wave frequency) has a plane separation boundary (x, y plane) with medium II in which $\epsilon_2(\omega) < 0$ for $x < 0$ and with medium III in which $\epsilon_3(\omega) < 0$ for $x > 0$ (Fig. 3a). In this case, the separation line, i.e., the Oy axis, divides the surface into two. The dispersion relation for the surface polaritons is different in each of these regions, and we therefore have the natural question as to what are the laws of reflection and refraction which the surface wave must obey on the separation line. Since, in this situation, translational symmetry obtains only for displacements along the Oy axis, reflection and refraction should conserve the y component of the wave vector. Hence, it follows immediately that the angle of incidence must be equal to the angle of reflection (Fig. 3b). However, the angle of refraction θ must be determined from the condition[5)]

$$n_{I,II}\sin\varphi = n_{I,III}\sin\theta, \quad \text{or} \quad \frac{\sin\theta}{\sin\varphi} = \frac{n_{I,II}}{n_{I,III}}, \qquad (10)$$

where n_{ik} is the refractive index for the surface wave at the boundary between the media i and k. In this case, the incidence of a surface wave on the separation line is not accompanied by a surface wave propagating along the separation boundary between media II and III, since we have assumed that ϵ_2 and ϵ_3 are negative. However, in anisotropic media, the appearance of two refractive waves is possible, in principle. It is interesting that if $n_{I,II}/n_{I,III} > 1$ then for a certain value of the angle of incidence, $\varphi = \varphi_0$, we have $\theta = \frac{1}{2}\pi$ ($\sin\varphi_0 = n_{I,III}/n_{I,II}$).

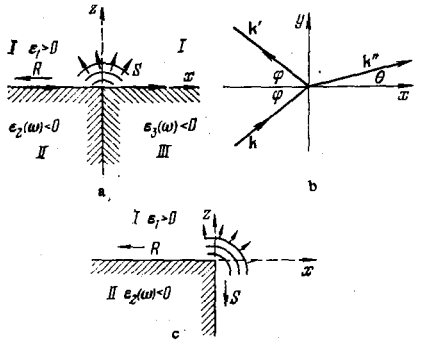

FIG. 3. Reflection and refraction of surface waves at separation boundaries (lines).

This means that total internal reflection of the surface wave occurs for $\varphi > \varphi_0$. This does not, however, mean that the energy of the reflected wave is equal to the energy of the incident wave. The point is that we have been concerned only with the refracted surface waves. On the other hand, in the case we have considered, reflection from the separation line may be accompanied by the appearance of a body wave in medium I. This is connected with the violation of translational invariance along the Ox axis, and can readily be seen from the following simple considerations. Let us suppose, for the sake of simplicity, that the angle of incidence is $\varphi = 0$. We then have $k_y = 0$ and, therefore, with the corresponding choice of the values of q_x and q_z for the body wave in medium I (q is the wave vector of the body wave and $q_y = 0$), we can always satisfy the resonance condition

$$\frac{1}{\sqrt{\varepsilon_1}}\,c\sqrt{q_z^2+q_x^2} = \omega_s(k_x).$$

An analogous situation occurs for $\varphi \neq 0$, provided only that for such angles there exist q_z and q_x for which there is a real k_y satisfying the equation

$$\frac{c}{\sqrt{\varepsilon_1}}\sqrt{q_z^2+q_x^2+k_y^2} = \omega_s\left(\frac{k_y}{\sin\varphi}\right).$$

Thus, it follows from the foregoing that the transformation of a surface wave into a body wave is possible on the separation line. Analogous phenomena occur when a medium with $\epsilon(\omega) < 0$ forms a wedge of the form illustrated in Fig. 3c. If a surface wave arrives from infinity in the z = 0 plane on the Oy axis, then, in addition to the reflected wave R, we have the refracted wave S propagating in the x = 0 plane. As in the preceding case, we then have the transformation of surface into body waves along the Oy axis.

Calculations of the intensity and angular distribution of the induced body wave, and of the amplitude of the reflected wave, for the situation shown in Fig. 3, require solution of the diffraction problem for a wedge (see Fig. 3c) or two contacting wedges (Fig. 3a). It is well-known that these problems have been encountered in connection with radiowave propagation, and are among the fundamental problems of the mathematical theory of diffraction (see, for example, [8a] for a review of these problems). They have been solved only in the impedance approximation.[8b] In this approximation, the analysis of the electromagnetic problem in the region external to the wedge (or wedges) ignores the fields inside the wedge and uses the Leontovich boundary condition

$$\mathbf{E}_t = Z[\mathbf{H}_t \times \mathbf{n}],$$

where $\mathbf{E}_t$ and $\mathbf{H}_t$ are the tangential components of the electric and magnetic fields, n is the normal to the wedge surface, and Z is the surface impedance. The use of impedance boundary conditions is justified only for $|\epsilon| \gg 1$. For surface waves, this inequality is always satisfied for frequencies $\omega \gtrsim \Omega_\perp$ (Fig. 1), and is also satisfied for the entire branch of surface-wave frequencies provided only that the wedge [$\epsilon_2(\omega) < 0$] does not lie in a vacuum but in a medium in which $\epsilon_1 \gg 1$ (see Fig. 3). Assuming that $|\epsilon(\omega)| \gg 1$, we can estimate the intensity of body waves which appear as a result of diffraction of the surface wave by the impedance wedge (Fig. 3c). In accordance with [8], the modulus of the amplitude of the reflected surface wave (the incident amplitude is assumed equal to unity) is

$$R = \operatorname{sh}\frac{\pi\xi}{\alpha}\sqrt{\frac{1+\cos(\pi^2/\alpha)}{\operatorname{ch}(2\pi\xi^2/\alpha)-\cos^2(\pi^2/\alpha)}},$$

whilst the modulus of the amplitude of the reflected wave (cf. Fig. 3) is

$$S = \operatorname{sh}\frac{\pi\xi}{\alpha}\sqrt{\frac{1-\cos(\pi^2/\alpha)}{\operatorname{ch}(2\pi\xi/\alpha)+\cos(\pi^2/\alpha)}},$$

where α is the external angle of the wedge ($\alpha = 3\pi/2$ in Fig. 3c) and the quantity ξ is determined from the formula $z = -i \sinh \xi$. If the wedge is in a vacuum, then $\sinh \xi = 1/\sqrt{|\epsilon|}$, and for $|\epsilon| \gg 1$ we have $\xi \approx 1/\sqrt{|\epsilon|}$. It follows from the above expression for R and S that, when $|\epsilon| \gg 1$, we have $R \ll 1$ and $S \ll 1$, so that practically the entire energy of the incident surface wave is transformed into the energy of the generated body waves.[6)]

This fact is very important in the light of the foregoing remarks about the necessity of having surface-wave receivers in crystal optics, since it means that, when separation lines are present or can be produced, detectors of body radiation can be employed to determine the surface-wave intensity.[7)] As the frequency of the surface wave deviates from $\omega = \Omega_\perp$ (cf. Fig. 1; this is accompanied by an increase in the wave vector and the wave itself becomes increasingly mechanical), the rate at which the wave is transformed into electromagnetic body waves should fall. However, this fall occurs when the impedance boundary conditions are not suitable, and this complicates the numerical estimates.

We have considered some of the most characteristic questions in the crystal optics of surface waves. In the ensuing account, we shall emphasize more specifically the new possibilities for investigating the physical properties of surfaces with the aid of these waves. Here, however, we shall merely note that, as already indicated, the crystal optics of surfaces is concerned with the study of the propagation of waves along a surface with frequency ω determined by the source. However, the dispersion relation (4) also gives information about waves for which the given quantity is not the frequency but the wave vector k (for example, in experiments on ATIR and in Raman scattering of light by surface polaritons). In this case (see Chap. 4), the intensity of the process is

$$I(k, \omega) \sim \left| k^2 - \frac{\omega^2}{c^2}\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right|^{-2},$$

and hence the use of (2′) with fixed k leads to a Lorentz dependence on $\omega - \omega_p(k)$ for $I(k, \omega)$ (ω_p is the polariton frequency when the damping is neglected), with the linewidth a function of k (cf. Chap. 4 for further details).

3. SPECTRA OF SURFACE POLARITONS IN ANISOTROPIC CRYSTALS

The spectra of surface polaritons in anisotropic crystals have a number of specific features.[11, 12] These include, above all, the fact that surface electromagnetic waves in anisotropic crystals may not exist in a given frequency band for all orientations of the crystal surface relative to the crystallographic axes, and there is also a strong dependence of the dispersion of the surface polariton on the direction of its two-dimensional wave vector (nonanalyticity in k).[8)]

These properties of the spectrum of surface polaritons have now been investigated experimentally as well (see Chap. 4 below). Calculations of the spectra of surface polaritons in anisotropic crystals, on the other hand, for a series of simple orientations have also been reported in[13-18, 72]. In particular, the properties of surface waves in uniaxial crystals were investigated in[14, 15] and in[11, 12], whereas the properties of surface polaritons in biaxial crystals were investigated in[16-18]. The main, although purely formal, difficulty which makes calculations of the dispersion of surface polaritons rather laborious arises when the normal to the surface or to the separation boundary between media is not parallel to one of the principal axes of the tensor $\epsilon_{ij}(\omega)$. In all other respects, however, these calculations are very elementary although they are given in the above papers only for a number of special situations. Because of this, we shall start by deriving the basic relationships for the dispersion and polarization of surface H-waves in arbitrary anisotropic crystals, using the reciprocal tensor $\epsilon^{-1}_{ij}(\omega) = A_{ij}$ instead of the tensor $\epsilon_{ij}(\omega)$, which will be found to simplify substantially the derivation of many of the results. We shall then consider the derivation of surface waves of a more general form and, without taking delay into account, we shall discuss surface waves in anisotropic crystals of arbitrary symmetry for arbitrary directions of propagation.

As in the analysis of the properties of surface polaritons in isotropic media (Chap. 2), we shall suppose that the separation boundary lies in the xy plane and that the medium is isotropic for $z > 0$ (permittivity tensor $\epsilon_{ij} = \epsilon_1\delta_{ij}$, $\epsilon_1 > 0$), whereas for $z < 0$ it is anisotropic [permittivity tensor $\epsilon_{ij} = \epsilon_{ij}(\omega)$, $A_{ij}(\omega) = \epsilon^{-1}_{ij}(\omega)$].

It follows from Maxwell's equations that the amplitudes of the required fields satisfy the following set of equations for $z > 0$ (subscript I) and $z < 0$ (subscript II):

$$\begin{aligned}
&\mathbf{H} = \frac{c}{\omega}[\mathbf{K}^{\mathrm{I}}\times\mathbf{E}^{\mathrm{I}}], \quad \mathbf{D}^{\mathrm{I}} = -\frac{c}{\omega}[\mathbf{K}^{\mathrm{I}}\times\mathbf{H}], \quad E^{\mathrm{I}}_i = \varepsilon_1^{-1}D^{\mathrm{I}}_i \qquad (z>0),\\
&\mathbf{H} = \frac{c}{\omega}[\mathbf{K}^{\mathrm{II}}\times\mathbf{E}^{\mathrm{II}}], \quad \mathbf{D}^{\mathrm{II}} = -\frac{c}{\omega}[\mathbf{K}^{\mathrm{II}}\times\mathbf{H}], \quad E^{\mathrm{II}}_i = A_{ij}D^{\mathrm{II}}_j \qquad (z<0),
\end{aligned} \tag{11}$$

where $\mathbf{K}$ is a vector with components $(k_1, k_2, i\kappa_1)$ (Re $\kappa_1 > 0$) for fields corresponding to $z > 0$ ($\mathbf{K} = \mathbf{K}^{\mathrm{I}}$), and components $(k_1, k_2, -i\kappa_2)$ (Re $\kappa_2 > 0$) for $z < 0$ ($\mathbf{K} = \mathbf{K}^{\mathrm{II}}$). Equation (11) takes into account the fact that all three components of $\mathbf{H}$ are continuous across the separation boundary ($\mathbf{H}^{\mathrm{I}} = \mathbf{H}^{\mathrm{II}} = \mathbf{H}^{\mathrm{III}}$). It then follows from the orthogonality conditions $\mathbf{K}^{\mathrm{I}} \cdot \mathbf{H} = 0$ and $\mathbf{K}^{\mathrm{II}} \cdot \mathbf{H} = 0$ that in waves with $\mathbf{H} \neq 0$ we must have $H_3 = 0$. Further simplification can be achieved by choosing the set of coordinates so that the x axis lies along $\mathbf{k}(k_1, k_2)$ (in which case $k_2 = 0$). We then have from (11) $E^{\mathrm{I}}_1 = E^{\mathrm{II}}_2 = 0$, $H^{\mathrm{I}}_1 = H^{\mathrm{II}}_1 = 0$, whereas $H^{\mathrm{I}}_2 = H^{\mathrm{II}}_2 = H \neq 0$. Thus, the waves which we are considering are H-waves as in the case of isotropic media (see above and[10]). Hence, substituting the expression $E_j = -(c/\omega)A_{ij}[\mathbf{K}\times\mathbf{H}]_j$ into the first equation in (11), we obtain

$$A_{11}K_3^2 + A_{33}k^2 - 2A_{13}kK_3 = \frac{\omega^2}{c^2}, \tag{12}$$

which gives κ_1 and κ_2 in terms of k and ω for both $z > 0$ and $z < 0$. In particular, for $z > 0$ we have $A_{11} = A_{33} = 1/\epsilon_1$, $A_{13} = 0$, $K_3 = i\kappa_1$, so that

$$\varkappa_1 = \sqrt{k^2 - \frac{\omega^2}{c^2}\varepsilon_1}. \tag{13}$$

For $z < 0$, we have $K_3 = -i\kappa_2$ and when Re $\kappa_2 > 0$ we find that[9)]

$$\varkappa_2 = ikA_{13}A_{11}^{-1} + \sqrt{(A_{33}A_{11}^{-1} - A_{13}^2A_{11}^{-2})k^2 - \frac{\omega^2}{c^2}A_{11}^{-1}}. \tag{14}$$

It follows from (13) and (14) that the conditions Re $\kappa_1 > 0$ and Re $\kappa_2 > 0$ can only be satisfied for frequencies ω such that

$$k^2 > \frac{\omega^2}{c^2}\varepsilon_1 \tag{13′}$$

and

$$\frac{A_{33}}{A_{11}}-\left(\frac{A_{13}}{A_{11}}\right)^2>0, \tag{14'}$$

$$k^2>\frac{\omega^2}{c^2}A_{11}^{-1}\left[\frac{A_{33}}{A_{11}}-\left(\frac{A_{13}}{A_{11}}\right)^2\right]^{-1}. \tag{14''}$$

It follows from (14′) that A_{33} and A_{11} should have the same sign. From the condition $E_2 = 0$ we also have

$$A_{21}D_1 + A_{23}D_3 = 0,$$

so that the frequencies of the surface waves which we are considering must be such that

$$iA_{21}\varkappa_2 + A_{23}k = 0. \tag{14'''}$$

This is a very stringent condition and restricts the region of existence of the H-waves.

The last boundary condition which must still be satisfied is the continuity of E_1 across the separation boundary. We find from (11) that the condition $E_1^{I} = E_1^{II}$ is satisfied if

$$E_1^{II} = -\frac{Hc}{\omega}(A_{13}k + i\varkappa_2 A_{11}) = E_1^{I} = i\frac{Hc}{\omega\varepsilon_1}\varkappa_1,$$

i.e., if

$$A_{13}k + iA_{11}\varkappa_2 = -i\frac{\varkappa_1}{\varepsilon_1}. \tag{15}$$

In view of (14), we can rewrite (15) in the form

$$\frac{\varkappa_1}{\varepsilon_1} = -A_{11}\sqrt{\left(\frac{A_{33}}{A_{11}}-\frac{A_{13}^2}{A_{11}^2}\right)k^2-\frac{\omega^2}{c^2}A_{11}^{-1}}, \tag{16}$$

and hence it follows that, in the frequency band of the surface polaritons, $A_{11}(\omega) < 0$ [and hence $A_{33}(\omega) < 0$; see (14′) and below]. The quantity ϵ_1 is assumed positive, as already noted.

Substituting the explicit expression for κ_1 in (16) and determining k^2 from the result, we finally obtain the following dispersion relation for the surface wave:

$$k^2 = \frac{\omega^2}{c^2}\frac{A_{11}-\varepsilon_1^{-1}}{A_{11}A_{33}-A_{13}^2-\varepsilon_1^{-2}}. \tag{17}$$

To illustrate (17), let us consider some of the most interesting examples. In particular, when the x and z axes lie along the principal axes of the tensor A_{ij}, i.e., if $A_{ij} = \delta_{ij}/\epsilon_{ij}$, then (14) is satisfied and (17) can be written in the form

$$k^2 = \frac{\omega^2}{c^2}\varepsilon_1\varepsilon_{33}\frac{\varepsilon_{11}-\varepsilon_1}{\varepsilon_{11}\varepsilon_{33}-\varepsilon_1^2}, \tag{18}$$

which was previously derived in [10] and becomes identical with (4) when $\epsilon_{11} = \epsilon_{33} = \epsilon$. In the case of uniaxial crystals, the condition given by (14‴) can also be satisfied when the optic axis lies in the xz plane at an arbitrary angle θ to the z axis (with this orientation $A_{21} = A_{23} = 0$). Since, under these conditions,

$$A_{11} = \frac{\cos^2\theta}{\varepsilon^{\perp}}+\frac{\sin^2\theta}{\varepsilon^{\parallel}}, \quad A_{33} = \frac{\cos^2\theta}{\varepsilon^{\parallel}}+\frac{\sin^2\theta}{\varepsilon^{\perp}}, \quad A_{13} = \sin\theta\cos\theta\left(\frac{1}{\varepsilon^{\parallel}}-\frac{1}{\varepsilon^{\perp}}\right),$$

it follows that

$$A_{11}A_{33}-A_{13}^2 = \frac{1}{\varepsilon^{\parallel}\varepsilon^{\perp}},$$

and hence

$$k^2 = \frac{\omega^2}{c^2}\frac{(\varepsilon^{\parallel}\cos^2\theta+\varepsilon^{\perp}\sin^2\theta)}{\varepsilon_1^2-\varepsilon^{\perp}\varepsilon^{\parallel}}\varepsilon_1^2. \tag{19}$$

It follows from this relation that resonances in the refractive index $n^2 = k^2c^2/\omega^2$ occur for frequencies ω which satisfy the condition $\epsilon^{\perp}\epsilon^{\parallel} = \epsilon_1^2$ in such a way that their position is independent of the angle θ (only the intensity of the resonance depends on θ).

We have already emphasized that (17) describes dispersion only in the case of the simplest surface H waves. However, in anisotropic crystals, the structure of the surface waves may be substantially more complicated. The point is that the Fresnel equation for an anisotropic crystal with given ω and $\mathbf{k}(k_1, k_2)$ can be used to obtain two, in general different, values of κ_2, Re $\kappa_2 > 0$. This means that, when general surface solutions are found, a superposition of two solutions must be matched to the field in medium I on the separation boundary, which is the usual situation in the case of body waves in the presence of birefringence. This more general approach turns out to be very laborious even for uniaxial crystals (see [15]), and has not as yet led to any useful results which could not be obtained within the framework of H-waves.[10] At the same time, as already shown, the H waves are realized only for special directions of propagation of the surface waves, and therefore provide a very incomplete picture of their spectrum. In view of the foregoing, let us consider the spectrum of surface polaritons, using the same geometry as before, for sufficiently large $k \gg \omega/c$, where delays can be ignored (see [11,12] for an analogous analysis in the case of uniaxial crystals). In this case, as $c \to \infty$, the Maxwell equations reduce to the form

$$\text{rot } \mathbf{E} = 0, \quad \text{div } \mathbf{D} = 0, \quad D_i = \varepsilon_{ij}E_j, \quad \text{rot } \mathbf{H} = 0, \quad \text{div } \mathbf{H} = 0.$$

Let us consider fields with $\mathbf{H} = 0$, since for fields with $\mathbf{E} = 0$ but $\mathbf{H} \neq 0$ it is readily seen that surface waves will not appear in nonmagnetic media.

For a plane wave with wave vector $\mathbf{K}(k, 0, K_3)$, we have $\mathbf{D} \cdot \mathbf{K} = 0$, $\mathbf{E} = C\mathbf{K}$, where C is a scalar and, therefore,

$$\varepsilon_{ij}(\omega)K_iK_j = 0. \tag{20}$$

This enables us to express K_3 in terms of ω and k. In particular, in medium I, $K_3 = i\kappa_1$, where $\kappa_1 = k$. In medium II, $K_3 = -i\kappa_2$, where

$$\varkappa_2 = -ik\frac{\varepsilon_{13}}{\varepsilon_{33}}+k\sqrt{\frac{\varepsilon_{11}}{\varepsilon_{13}}-\left(\frac{\varepsilon_{13}}{\varepsilon_{33}}\right)^2}. \tag{21}$$

It follows from the condition Re $\kappa_2 > 0$ that, at the surface-wave frequencies, the quantities ϵ_{11} and ϵ_{33} should have the same sign. The continuity of E_t across the separation boundary is ensured by setting $c^{I} = c^{II}$. The quantity D_3 is continuous, i.e., $D_3^{I} = D_3^{II}$, if $\epsilon_1 K_3^{I} = \epsilon_{31}k + \epsilon_{33}K_3^{II}$, i.e.,

$$\varepsilon_1 = -\varepsilon_{33}\sqrt{\frac{\varepsilon_{11}}{\varepsilon_{33}}-\left(\frac{\varepsilon_{13}}{\varepsilon_{33}}\right)^2}. \tag{22}$$

For real $\epsilon_{ij}(\omega)$ and $\epsilon_1 > 0$, the expression given by (22) is valid only when $\epsilon_{33} < 0$ [and, consequently, $\epsilon_{11}(\omega) < 0$; see above]. Under these conditions, (22) assumes the form

$$\varepsilon_1 = \sqrt{\varepsilon_{11}(\omega)\,\varepsilon_{33}(\omega)-\varepsilon_{13}^2(\omega)}. \tag{23}$$

This completely determines the limiting frequencies of surface polaritons in arbitrary crystals for $k \gg \omega/c$ (with spatial dispersion ignored), and it is precisely these frequencies, i.e., $\omega = \Omega_S$, which satisfy (23) and determine the resonances in the refractive indices $n^2(\omega)$ for the possible surface wave. For the H wave found above, this follows directly from (17) and, provided only we allow for the fact that when (14‴) is satisfied, i.e., $A_{12} = 0$, $A_{23} = 0$ (and hence $\epsilon_{12} = \epsilon_{23} = 0$),

$$A_{11}A_{33}-A_{13}^2 = (\varepsilon_{11}\varepsilon_{33}-\varepsilon_{13}^2)^{-1}.$$

However, this is also valid for the dispersion of surface

waves which are not H waves, and the dispersion relation for which has not yet been found in explicit form.

For the set of coordinates used here (z axis parallel to the normal, wave vector parallel to the x axis), the components of the tensor ϵ_{ij} in (23) turn out to depend on the orientation of the principal axes of the tensor ϵ_{ij}. This leads to a strong dependence of the frequencies Ω_s which satisfy (23) on the direction of propagation of the surface wave (i.e., the nonanalyticity of the dependence of Ω_s on $\mathbf{k}$ when $\mathbf{k} \to 0$), as already mentioned.

We note in conclusion that, in addition to these branches of the spectrum of surface waves $\omega = \omega(\mathbf{k})$ which propagate into the region of larger k, there may also, in general, be surface polaritons which are realized for values of k bounded not only from below but also from above.[13] It is clear that states of this kind can correspond only to $k \sim \omega/c$ but when delay is ignored they cannot be investigated. Observations of such states are discussed in[25,27].

4. EXPERIMENTAL METHODS FOR STUDYING SURFACE POLARITONS. REVIEW AND COMPARISON OF RESULTS

There has been clear progress in recent years in the development of experimental studies of surface polaritons in semiconductors and dielectrics. These elementary excitations are being successfully investigated by the method of attenuated total internal reflection (ATIR). In addition, experiments using low-energy electron diffraction (LEED) and Raman scattering of light (RSL) have been initiated. These methods are based on different physical processes and have different precision, as is clear from their designations. Nevertheless, they are all important since they augment one another and enable us to investigate surface wave spectra in a broader range of wave vectors. We shall illustrate the foregoing by considering the different methods of investigating surface polaritons and the results obtained thereby. Here, we only emphasize that ATIR, LEED, and RSL can also be used to excite surface polaritons and this must be remembered in connection with the possible types of sources and detectors of surface waves (see also Chaps. 1 and 2) which are necessary for the development of the crystal optics of surfaces.

a) The ATIR method and possibilities of ATR. ATIR has long been known (see, for example,[19]) and was used by Otto in 1968 as a method of investigating surface plasmons in metals.[20] It was subsequently noted in[21] that this method could also be used to investigate surface phonons. The first experimental studies of the spectra of surface polaritons using ATIR were carried out for the cubic crystals NaCl, HBr, NaF, LiF, CdF_2, GaP, and many others.[22-25] On the other hand, the spectra of surface polaritons in uniaxial crystals MgF_2, TiO_2,[15,26] quartz, sapphire, and lithium niobate[27,28] were investigated only recently for certain orientations of the crystal surface and directions of propagation of polaritons, and the results are in reasonable agreement with theory.

In the ATIR method, measurements are made of the spectrum of reflected electromagnetic radiation, where the incident radiation arrives from the denser medium on the plane separation boundary which acts as the plane of total internal reflection (Fig. 4). The presence of an absorbing medium (medium III in Fig. 4) leads to a reduction in the scattered intensity. Penetration beyond the plane of total internal reflection, and possible dissipation of the electromagnetic field in the optically less dense medium was investigated experimentally as far back as the beginning of this century (see, for example,[29]). On the other hand, the significance of the remarks in[20,21] is not at all trivial since the basic possibility of absorption does not in itself signify that this absorption may be due to the excitation of a surface polariton. To elucidate the situation, let us return to the polariton spectra (see Fig. 1). It follows from the form of these spectra that for surface-polariton frequency $\omega_p(\mathbf{k})$ we have the condition $\omega_p(\mathbf{k}) < ck/\sqrt{\epsilon_\infty} < ck$, where $\mathbf{k}(k_x, k_y)$ is the wave vector of the surface polariton. Since in processes involving the interaction of a photon incident, for example, from vacuum on the surface of the crystal, the component of the wave vector along the surface of the crystal must be conserved, the inequality $\omega = c\sqrt{k^2 + k_z^2} > \omega_p(k)$ (ω is the photon frequency in vacuo, and phonons and other similar factors are ignored) means that the excitation of surface polaritons by the usual volume photons is impossible. If, however, we consider plane waves with imaginary k_z, i.e., fields which decrease exponentially with distance from the z = 0 plane, then the conservation of energy $\hbar\omega = \hbar\omega_p(k)$ can be satisfied. It is this fact that lies at the basis of the application of ATIR to the study of surface polaritons. At the same time, one must always remember the following. It would seem, at first sight, that the excitation of surface polaritons will be particularly intensive for $d \to 0$ (Fig. 4). In reality, these waves are not excited at all for d = 0 because there is then no spatial region in which the excited waves have imaginary k_z (there is, at the same time, a slight deformation of the spectrum of the surface waves; see below for the role of the substrate). The gap length d is therefore chosen to have the optimum value, i.e., large enough for the presence of the prism to have practically no effect on the spectrum of surface polaritons, but such that the reduction in the reflection coefficient is still detectable. Calculations of the reflection coefficient in the ATIR method have frequently been carried out (see, for example,[23]) and we shall therefore simplify and reproduce the formula for this coefficient in the case of the situation illustrated in Fig. 4 and sufficiently large d.[11] If ϵ_1 and ϵ_2 are the permittivities of the prism and of the material in the gap, respectively, and $\epsilon_3(\omega)$ is the permittivity of the crystal which is less than zero (ϵ_1, ϵ_2, and ϵ_3 are assumed real), then the reflection coefficient is given by

$$R(\omega) \approx 1 - 16\pi \frac{\varepsilon_3^2 \varkappa_1}{\varepsilon_1 \varkappa_3^2} \delta \left[\frac{\varepsilon_3(\omega)}{\varkappa_3} + \frac{\varepsilon_2}{\varkappa_2} \right] e^{-\varkappa_2 d}, \qquad (24)$$

where $\kappa_i = [k^2 - (\omega^2 \epsilon_i / c^2)]^{1/2}$. It follows from this that the reflection coefficient becomes less than unity only for frequencies ω and angles of incidence φ for which ω and $k \equiv (\omega/c)\sqrt{\epsilon_1} \sin\varphi$ are such that

$$\frac{\varepsilon_3(\omega)}{\varkappa_3} + \frac{\varepsilon_2}{\varkappa_2} = 0,$$

which, in fact, determines the dispersion of a surface

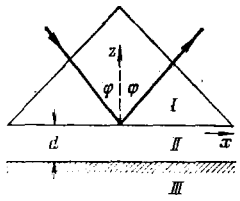

FIG. 4. Ray paths in the ATIR method.

polariton on the boundary between media II and III when $d \to \infty$ (see Chap. 2). The presence of the δ function in (24) is due to the fact that dissipation processes were ignored. On the other hand, the integrated reduction in the reflection coefficient, which is independent within certain limits of this dissipation, and is proportional to the total probability of excitation of a surface polariton with wave vector **k** in the ATIR method, is given by

$$W(k) = 16\pi \frac{\varepsilon_3^2 \varkappa_1}{\varepsilon_1 \varkappa_3^2} C(k) e^{-\varkappa_2 d}, \qquad (25)$$

where the frequency ω must be looked upon as equal to the frequency $\omega_S(k)$ of the surface polariton with wave vector k, and C(k) is given by

$$\frac{d}{d\omega}\left(\frac{\varepsilon_3}{\varkappa_3} + \frac{\varepsilon_2}{\varkappa_2}\right)\Big|_{\omega=\omega_s(k)} \equiv \frac{1}{C(k)}. \qquad (26)$$

If $\Gamma(k)$ is the linewidth for the surface polariton, then the reduction in $R(\omega)$ within this width is roughly $W(k)/\Gamma(k)$. Let us estimate W(k) approximately, neglecting the relativistic terms in $\varkappa_i$. In this approximation, $\varkappa_i = k$ so that, using (2) for ϵ_3, we have

$$C(k) = \frac{k(\varepsilon_0 - \varepsilon_\infty)\Omega_\perp^2}{2\omega_s(k)(\varepsilon_2 + \varepsilon_\infty)}. \qquad (27)$$

Consequently, we have the order of magnitude result $C(k) \sim k\Omega_\perp/10$. Therefore, $W/\Gamma \sim 20(\Omega_\perp/\Gamma)\exp(-kd)$, and when $W/\Gamma \sim 10$ and $d = \lambda$, we have $W/\Gamma \sim 0.5$. It is precisely the large values of W/Γ that have ensured the success of this method. Figure 5 gives typical experimental curves showing the frequency ω at which $R(\omega)$ is a minimum for given k as a function of the angle φ. This figure also shows the function $\omega_S = \omega_S(k)$ (all the data are taken from [28]).

We note that the ATIR method can be used to investigate the spectrum of a surface polariton only up to wave-vector values $k \lesssim (\omega/c)\sqrt{\epsilon_1}$, so that this method will not yield the surface-wave dispersion in the nonrelativistic region of k. Raman scattering and LEED may be particularly useful in this region. Before we proceed to discuss these methods, we must make one further point in connection with light reflection as a means of investigating surface-polariton spectra. It was noted in Chap. 2 that, when lines of separation are present on the surface of a crystal with $\epsilon(\omega) < 0$, and they are of the form shown in Fig. 3, surface waves can transform into volume waves and vice versa. This means that, as in ATIR, the surface light-reflection coefficient should fall in the case of resonance with the surface wave (i.e., the presence of the separation lines also leads to attenuated total reflection of light—ATR). The question is: can this effect be used to determine the dispersion relation for the surface polariton? We shall show that, at least in principle, the answer is yes. Thus, let the separation line lie along the y axis, so that only the component of the wave vector along this axis is conserved. The reflection coefficient should then fall when the following condition is satisfied:

$$\omega = c\sqrt{q_x^2 + q_y^2 + q_z^2} = \omega_s(k), \qquad k = \frac{q_y}{\sin\varphi}, \qquad (28)$$

where ω is the frequency of the volume photon in vacuum ($\epsilon_1 = 1$), $\mathbf{q} = (q_x, q_y, q_z)$ is its wave vector, and φ is the angle between the surface-polariton wave vector and the x axis. Since the frequency ω and wave vector **q** are known for the incident photon, once we determine the reflection minimum (for example, by varying the direction of **q**), we can use (28) to calculate the frequency ω_S of the polariton and the corresponding vector **k**. Therefore, all that remains is the absolute magnitude of the effect. Quantitative estimates of the transformation of

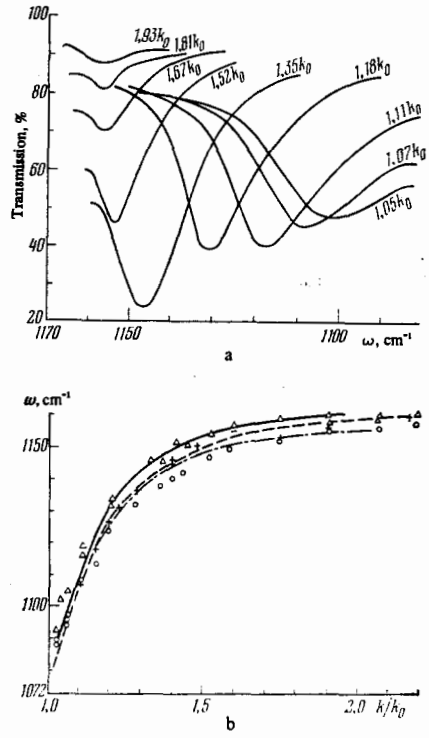

FIG. 5. Experimental results obtained in [28]: (a) position of minimum transmission 1 − R as a function of Q_x (the projection on the plane of total internal reflection of the wave vector of the volume photon; $Q_x = k_0 n_0 \sin\varphi$, φ is the angle of incidence, n_0 is the refractive index of the prism material, and $k_0 = \omega/c$); (b) frequency of the surface phonon (different curves correspond to different surface orientations; see [28] for details).

volume waves into surface polaritons in the presence of surface separation lines can only be made in the impedance approximation at the present time. According to [8b], the incidence of a plane wave on a wedge results both in a reflected wave, an edge wave (the bright line at the edge of the wedge is due to this wave), and surface waves. We shall not reproduce here the expressions for the amplitudes of these waves and will merely note that they are of the order of the surface impedance Z. They are therefore small in the region in which the impedance approximation is valid. This means that ATR is not very effective as a means of studying the dispersion of surface waves. At the same time, when lasers are used, ATR can effectively be employed for pumping surface polaritons.

b) Periodic set of lines on a surface. Suppose that parallel lines are drawn on the surface of the crystal (z = 0) at constant distance d from one another, all of them being parallel to the Oy axis. When light waves interact with the surface polariton, the wave-vector component k_x is then conserved only to within $2\pi/d$. Despite the fact that the inequality

$$\frac{c}{\sqrt{\varepsilon_\infty}}\sqrt{k_x^2 + k_z^2} > \omega_s(k_x),$$

is satisfied for certain values $k_x = k_x^m$, we can satisfy the condition

$$\frac{c}{\sqrt{\varepsilon_\infty}}\sqrt{\left(k_x^m - m\frac{2\pi}{d}\right)^2 + k_z^2} = \omega_s(k_x^m),$$

by suitably choosing one of the values $m = \pm 1, \pm 2, \ldots$. This condition expresses the conservation of energy and of the wave vector k_x, and the transformation of volume photons with frequency $\omega = \omega_S(k_x^m)$ into polaritons [with

a simultaneous reduction in the reflection coefficient $R(\omega)$] becomes possible. It is clear that this reduction in $R(\omega)$ can occur for angles of incidence φ given by the formula $(\omega/c)\sin\varphi = k_x - (m2\pi/d)$, and this has been observed experimentally.[34-38] In most experiments, the surface periodicity was produced mechanically which, of course, led to changes in the structure of the surface layer that were difficult to control, and to the additional attenuation of the waves. Surface acoustic waves (Rayleigh waves) were therefore employed in[39] to produce the surface periodicity. On the whole, however, this method has turned out to be less convenient than ATIR because calculations of the reflecting power of a set of lines are very approximate in the case of photons, or require detailed knowledge of the line profile (see[41] and[59]; a similar problem for waveguides is discussed in[60]).

At the same time, when the separation between the prism and the surface of the crystal is large enough in ATIR, the minima of $R(\omega)$ are very accurately equal to the frequencies of the surface polaritons, as already shown.

c) Raman scattering by surface polaritons. The possibilities of RSL as a means of studying surface polaritons has frequently been discussed in the literature (see[30,31]),[12] but the first successful experiments which resulted in the surface-polariton spectrum were published quite recently in[32]. The RSL spectra were measured in these experiments at room temperature for a thin (~ 2500 Å) film of GaAs grown epitaxially on sapphire. The radiation source was a continuously operated argon laser (4880 Å) with an output power of 400 mWcw. The exciting radiation was polarized at right-angles to the plane of scattering and was incident normally on the plate (Fig. 6). Although gallium arsenide is a strong absorber of the laser radiation (penetration depth ≈900 Å), the use of a thin film meant that transmission experiments could be carried out. If ω_s is the measured photon frequency at angle φ to the direction of incidence of the laser photons ($\omega = \omega_i$) on the film, the surface-polariton frequency $\omega = \omega_i - \omega_s$ corresponds to the wave vector $k = Q\sin\varphi$ where $Q = (\omega_i/cn_i)$ is the wave vector of the laser radiation and n_i is the refractive index of GaAs at ω_i. The experimental results reported in[32] are shown in Fig. 7. The figure also shows the solid line based on results obtained in[33] as a result of calculations of the surface-polariton dispersion in the vacuum-GaAs-sapphire system. As can be seen, the agreement is good but only for large enough k. It is possible that the inferior agreement between theory and experiment for small k is due to the fact that the attenuation of the laser beam in the GaAs film, which leads to an uncertainty in the wave vector of the surface polariton, was not taken into account (this question was not considered quantitatively). It is shown in[33] that the dispersion of surface polaritons in the structure illustrated in Fig. 6 is described by

$$\left[1+\frac{\varkappa_0}{\varkappa_1}\varepsilon(\omega)\right]\left[1+\frac{\varkappa_2}{\varkappa_1}\frac{\varepsilon(\omega)}{\varepsilon_\perp}\right] - \exp(-2\varkappa_1 d)\left[1-\frac{\varkappa_0}{\varkappa_1}\varepsilon(\omega)\right]\left[1-\frac{\varkappa_2}{\varkappa_1}\frac{\varepsilon(\omega)}{\varepsilon_\perp}\right]=0, \tag{29}$$

where d is the thickness of the film

$$\varkappa_0 = \sqrt{k^2-(\omega^2/c^2)},$$
$$\varkappa_1 = \sqrt{k^2-(\varepsilon(\omega)\omega^2/c^2)}, \quad \varkappa_2 = \sqrt{(\varepsilon_\perp/\varepsilon_\parallel)[k^2-(\varepsilon_\parallel\omega^2/c^2)]},$$

$\epsilon(\omega)$ is the permittivity of gallium arsenide, $\Omega_\perp \approx 270\ \text{cm}^{-1}$, $\epsilon_0 = 13.1$, $\epsilon(\omega) < 0$, and $\epsilon_\parallel$, $\epsilon_\perp$ are the permittivities of sapphire (uniaxial crystal; its optic axis lies at right-angles to the separation boundary between media in the experiments described in[32]). As expected, (29) defines two branches of surface polaritons.[13] As $d \to \infty$, these branches are transformed into a surface polariton on the vacuum-GaAs boundary and a surface polariton on the GaAs boundary. However, the branch of the first of these polaritons is found to lie in the immediate neighborhood of the longitudinal-wave frequency in GaAs because the ratio $(\epsilon_0 - \epsilon_\infty)/(\epsilon_0 + \epsilon_\infty)$ is small for GaAs, and the broadening of the RSL lines for longitudinal volume waves was not noted in[32]. The second branch, on the other hand, which as $d \to \infty$ becomes transformed into polaritons on the GaAs-sapphire boundary, turns out to be substantially shifted away from the frequencies of transverse and longitudinal volume waves because of the high values of $\epsilon_\parallel$ and $\epsilon_\perp$ for sapphire ($\epsilon_\parallel = 11.6$, $\epsilon_\perp = 9.35$), which ensured the success of the experiment. To understand the "mechanisms" whereby the substrate makes its presence felt, we note, first of all, that for sufficiently large k, such that $k^2 \gg (\omega^2/c^2)|\epsilon_i|$ and $k \gg 1/d$, the polariton dispersion law is independent of d [which is clear from (29)] and is the same as the dispersion law in the nonrelativistic region for $d = \infty$. Hence, in layered structures of the kind considered in[33], limiting values of the surface frequency Ω_s can be found from the simpler formulas given by (6). Since the frequency of the longitudinal volume wave is $\Omega_\parallel = \Omega_\perp(\epsilon_0/\epsilon_\infty)^{1/2}$ (see Chap. 2), we have, in this case,

$$\Delta\Omega = \Omega_\parallel - \Omega_s = \Omega_\perp\left(-\sqrt{\frac{\varepsilon_0+\varepsilon_1}{\varepsilon_\infty+\varepsilon_1}}+\sqrt{\frac{\varepsilon_0}{\varepsilon_\infty}}\right),$$

so that on the vacuum-GaAs boundary ($\epsilon_1 = 1$, ϵ_0, $\epsilon_\infty \gg \epsilon_1$) $\Delta\Omega \approx \Omega_\parallel(\epsilon_\infty^{-1} - \epsilon_0^{-1})/2 \approx 10^{-2}\Omega_\parallel < \delta$ where $\delta \sim \Omega_\parallel/30$ is the RSL linewidth in GaAs. On the GaAs-sapphire boundary, we have $\Delta\Omega > \delta$ and, moreover, the approach of the $\omega_s(k)$ curve for d = 2500 Å to the asymptotic value is slower than on the vacuum-GaAs boundary (Fig. 8).

It is evidently not accidental that the first experiments on RSL by surface polaritons were carried out for GaAs, since these crystals have very high nonlinear polarizability χ_{ijl} which is determined by the intensity of the process. However, the high nonlinear polarizability is not the only factor which dictates the choice of materials for RSL by surface polaritons. The point is that the rate of RSL by volume phonons and polaritons increases with increasing crystal thickness, whereas the rate of RSL

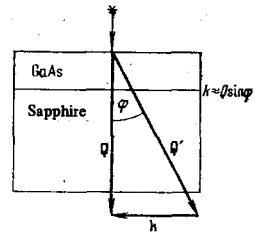

FIG. 6. Experimental arrangement used in [32] to investigate RSL by a surface polariton in gallium arsenide.

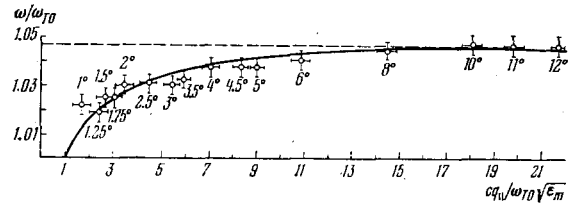

FIG. 7. Experimental data on the dispersion of surface polaritons on the boundary between gallium arsenide and sapphire. [32] Solid curve—theoretical. [33]

by surface polaritons depends on the crystal thickness only for $d \lesssim \kappa = [k^2 - (\omega^2/c^2)\epsilon(\omega)]^{1/2}$. Therefore, for large d, RSL by surface waves is drowned by the background of RSL by volume polaritons. The use of thin films, on the other hand, leads to technologic problems associated with their preparation, and this has probably impeded the development of studies of RSL by surface polaritons.[14)]

d) **Propagation of surface polaritons along separation boundaries.** The first successful observation of the propagation of surface polaritons over macroscopic distances was reported in [42]. This paper was concerned with the propagation of a surface wave along the copper-air boundary in which coupling between volume light waves and surface waves was achieved with the aid of two NaCl prisms (Fig. 9). The surface waves were pumped by a ~250 mW cw laser ($\lambda_0 = 10.6\ \mu$). The length L in which the intensity of the surface wave fell by a factor of e turned out to be 1.6 cm. At the CO_2 laser frequency, the field penetration depth in copper is about 250 Å. Copper films, 3000 Å thick, deposited by evaporation on glass, were therefore used. The gap g between the prism and the metal was 15 μ.

In the case of the normal skin effect (see [43] for nonlocal corrections), the permittivity of the metal is $\epsilon(\omega) = 1 - [\omega_p^3/(\omega^2 + i\omega\Gamma)]$ where ω_p is the prism frequency and Γ is the reciprocal of the relaxation time for a conduction electron. Substituting this expression into (7) with $\epsilon_1 = 1$ and $\epsilon_2 \equiv \epsilon$, we find that when $\omega \ll \omega_p$ we have $(n + i\kappa)^2 \approx 1 + [(\omega^2 + i\omega\Gamma)/\omega_p^2]$, so that $n \approx 1$ and $\kappa \approx \omega\Gamma/2\omega_p^2$. Consequently, the attenuation length is $L = c/2\omega\kappa \approx c\tau(\omega_p/\omega)^2$, $\tau = 1/\Gamma$, so that for $\omega_p/\omega \approx 20$ and $\tau \approx 5 \times 10^{-14}$ sec, the final result is $L \approx 1$ cm. This was, in fact, observed in [42]. Further experiments on the propagation of surface polaritons along a plane surface will undoubtedly result in much valuable information on the structure and properties of excited states of contacting media, and their value to the development of the physics of surfaces cannot be overestimated.

e) **Low-energy electron diffraction (LEED).** Recent progress in producing slow monochromatic electrons has led to a realization of the method of characteristic losses as a means of analyzing surface oscillations in crystals. Since the depth of penetration of slow electrons (electrons of 1–100 eV are usually employed) is very small in crystals (a few lattice constants), an analysis is made of the spectra of electrons which have been reflected from the surface. This, of course, requires ultrahigh vacuum (~ 10^{-10} Torr) and atomically pure surfaces. Modern spectrometers used for this purpose are described in [45]. Here, we shall merely note that the energy resolution achieved so far for slow electrons is no better than 10^{-2} eV and this means that the structure of the surface-oscillation band cannot be investigated by LEED. On the other hand, the frequencies of surface oscillations of atoms determined from the loss spectra, for example, in the case of mirror reflection of electrons, are comparable with the limiting values of the optical lattice vibration frequencies.

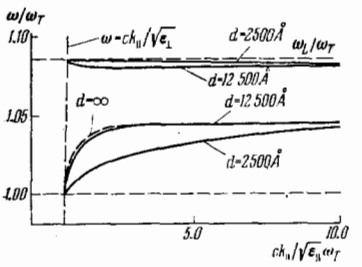

FIG. 8. Results of calculations [33] of the dispersion of surface polaritons in a GaAs film on a sapphire substrate.

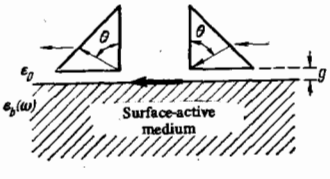

FIG. 9. Experimental arrangement [42] used in the study of the propagation of surface polaritons to macroscopic distances.

The first successful experiments of this kind are described in [46,47]. In particular, the frequencies found for different crystal faces by studying surface oscillations [46] in a ZnO crystal turned out to be in very good agreement with the frequency of surface oscillations found from the condition $\epsilon(\omega) = -1$ ($\omega_S \approx 0.068 \pm 0.005$ eV).

The probability of excitation of a surface oscillation found from the phenomenological theory [48] is given by

$$W(\hbar\omega)\, d(\hbar\omega) = \frac{4}{a_0 k_0} \operatorname{Im}\left(-\frac{1}{\varepsilon+1}\right) \frac{d(\hbar\omega)}{\hbar\omega},$$

where a_0 is the Bohr radius and k_0 is the wave vector of the excited electrons. This, too, is in agreement with experimental data. [46] The use of the phenomenological theory is justified if sufficiently long-wave photons are excited ($k \ll \pi/a$, where a is the lattice constant). This occurs when $v \gg \omega a$, where v is the velocity of the excited electrons. When $\omega \sim 10^{13}$, this inequality is satisfied even for 1 eV electrons, so that the region in which the phenomenological description can be used turns out to be very broad. We also note that estimates of the wavelengths of excited phonons, based on an analysis of the angular distributions of electrons reported in [46], yield $\lambda \sim 20$ Å. LEED can therefore be used to obtain the frequencies of surface phonons for wave vectors greater by roughly two orders than those which can be reached with RSL.

We note in conclusion that LEED can be used as shown in [47] to investigate not only the surface oscillations of atomically pure surfaces, but also to judge the appearance of local oscillations on the crystal surface, due to the presence of adsorbed impurities. We note also the theory of Cerenkov emission of surface waves developed in [65].

5. THEORY OF RAMAN SCATTERING OF LIGHT BY SURFACE POLARITONS, INCLUDING MEDIA WITH A CENTER OF INVERSION (METHOD OF MODIFIED SYMMETRY)

a) **General theory and compensation effect.** Among the methods of studying surface polaritons which were reviewed in the preceding section, RSL is distinguished by the fact that this phenomenon is based on the nonlinear interaction between electromagnetic waves. The general features of this method are therefore connected not only with the "linear" susceptibility of the contacting media (these quantities determine the dispersion relation for a surface polariton; see Chaps. 2 and 3), but also with the corresponding nonlinear properties. This leads to a number of features when surface polaritons are studied

by RSL which, in some cases, can be used to great advantage.

In particular, we have already noted that RSL is one of the main techniques used to investigate volume polaritons. However, this method cannot be used in media with a center of inversion because the nonlinear susceptibility tensor χ_{ijl} which governs the rate of the process is then identically zero. The situation is, however, modified if we consider RSL by surface polaritons when the medium under investigation is in contact along its entire surface with a medium which does not have a center of inversion. Since the electromagnetic field in a surface polariton is nonzero at distances of the order of its wavelength ($\lambda \approx 10\ \mu$) on either side of the separation boundary and, consequently, in the region where $\chi_{ijl} \neq 0$, the rate of RSL by surface polaritons is nonzero and sufficient for observation, as shown above (see also [44]). However, the fact that the surface-polariton field differs from zero on either side of the separation boundary, and the rate of RSL depends on the tensor χ_{ijl} in both media may, in some cases, lead to the reverse effect, namely, to a reduction in the rate of RSL by surface polaritons (the compensation effect).[57]

To explain the foregoing, we must start by calculating the cross section for RSL by a surface polariton, assuming, for the sake of generality, that the tensor χ_{ijl} is nonzero in both bounding media.

We shall suppose that the separation boundary between media I and II lies in the z = 0 plane and that in medium I ($z > 0$) $\chi_{ijl} = \chi^{I}_{ijl}$ and in medium II ($z < 0$) $\chi_{ijl} = \chi^{II}_{ijl}$. Neglecting possible anisotropy in the media, we shall suppose that the permittivity for $z > 0$ is $\epsilon_1 > 0$ and the permittivity for $z < 0$ is $\epsilon_2 = \epsilon(\omega) < 0$. The dispersion of the surface polariton in this case is given by (4). The perturbation operator which leads to RSL is

$$\hat{\mathscr{H}} = -\frac{1}{2}\int \chi_{ijl}(z)\,\hat{E}_i\hat{E}_j\hat{E}^P_l\,d\mathbf{r}. \qquad (30)$$

where $\hat{\mathbf{E}}$ and $\hat{\mathbf{E}}^P$ are operators representing, respectively, the high-frequency electric field (for example, the laser field or scattered-wave field) and the field in the surface polariton. Neglecting the difference between the refractive indices for the laser radiation in media I and II, we shall ignore the possible reflection of the hf field from the separation boundary, which is unimportant in approximate calculations of the cross section for the process.[15] Moreover, we shall suppose that the laser beam travels along the x axis (wave vector $\mathbf{k}^a$) and is polarized along the x axis, whereas the scattered light (wave vector $\mathbf{k}^b \equiv k^b_z, 0, k^b_x$) is polarized along the y axis (Fig. 10). In view of the account given in Chap. 2, the relation between the nonzero amplitudes of the electromagnetic field in a surface polariton with wave vector $k = k^b_x - k^a_x$ lying along the x axis is

$$E^P_1 = i\frac{\varkappa_1}{k}E^P_3 = i\frac{c\varkappa_1}{\omega\epsilon_1}H^P_2, \qquad \varkappa_1 = \sqrt{k^2 - \frac{\omega^2}{c^2}\epsilon_1} \quad \text{at} \quad z>0,$$
$$E^P_1 = -i\frac{\varkappa}{k}E^P_3 = -i\frac{c\varkappa}{\omega\epsilon}H^P_2, \qquad \varkappa = \sqrt{k^2 - \frac{\omega^2}{c^2}\epsilon} \quad \text{at} \quad z<0. \qquad (31)$$

The absolute values of these amplitudes, on the other hand, are determined from the normalization conditions, i.e., the fact that $\hbar\omega$ is the energy of the electromagnetic-wave field in the polariton. In a dispersive nonmagnetic medium, the electromagnetic energy density is given by [10]

$$W = \frac{1}{4\pi}\left[\frac{d}{d\omega}(\omega\epsilon_{ij})E^P_iE^{*P}_j + H^P_iH^{*P}_j\right], \qquad (32)$$

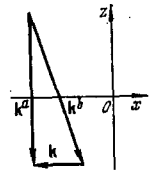

FIG. 10. Wave vectors of surface ($\mathbf{k}^a$) and volume ($\mathbf{k}^b$) waves in RSL transmission experiments.

where we have ignored spatial dispersion, $\mathbf{E}^P$ and $\mathbf{H}^P$ are space varying amplitudes which determine the real fields $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}^P(\mathbf{r})e^{-i\omega t} + \mathbf{E}^{*P}(\mathbf{r})e^{i\omega t}$ and so on. Recalling the dependence of these amplitudes on x, y, z (Chap. 2), and the equations given by (31), we find that, in the above case of contacting isotropic media

$$W(\mathbf{r}) = \frac{|E^P_1|^2}{4\pi}\left[\hat{\epsilon}_1\left(1+\frac{k^2}{\varkappa_1^2}\right) + \frac{\epsilon_1^2\omega^2}{c^2\varkappa_1^2}\right]e^{-2\varkappa_1 z}, \qquad z>0;$$
$$W(\mathbf{r}) = \frac{|E^P_1|^2}{4\pi}\left[\hat{\epsilon}\left(1+\frac{k^2}{\varkappa^2}\right) + \frac{\epsilon^2\omega^2}{c^2\varkappa^2}\right]e^{2\varkappa z}, \qquad z<0, \qquad (33)$$

where $\hat{\epsilon} = \epsilon + \omega(d\epsilon/d\omega)$. Consequently, from the condition $\hbar\omega = \int W d\mathbf{r}$ and (31), we find that

$$|E^P_1|^2 = \frac{4\pi\hbar\omega}{S}\Phi(k), \qquad (34)$$

where S is the area of the separation boundary and

$$\Phi(k) = \left[k^2\left(\frac{\epsilon_1}{\varkappa_1^3} + \frac{\epsilon}{\varkappa^3}\right) + \frac{\omega}{2\varkappa_1}\left(1+\frac{k^2}{\varkappa_1^2}\right)\frac{d\epsilon_1}{d\omega} + \frac{\omega}{2\varkappa}\left(1+\frac{k^2}{\varkappa^2}\right)\frac{d\epsilon}{d\omega}\right]^{-1}. \qquad (35)$$

We shall choose the initial phase so that E^P_1 is real and positive. We then have

$$E^P_3 = -i\frac{k}{\varkappa_1}\sqrt{\frac{4\pi\hbar\omega}{S}}\sqrt{\Phi} \quad \text{at} \quad z>0,$$
$$E^P_3 = i\frac{k}{\varkappa}\sqrt{\frac{4\pi\hbar\omega}{S}}\sqrt{\Phi} \quad \text{at} \quad z<0.$$

The fact that E^P_3 is the only quantity in (30) (for the chosen polarizations of incident and scattered light) that is different in both absolute magnitude and sign in media I and II leads, in some cases, to the suppression of RSL by surface polaritons through the compensation of the contributions, as shown above. Since in isotropic media $\chi_{ijl} = \chi|e_{ijl}|$, where e_{ijl} is the fully antisymmetric unit tensor of rank three, the matrix element of the operator (30) corresponding to RSL with the creation of a polariton turns out to be

$$\mathscr{H}^{if} = ik\sqrt{4\pi\hbar\omega S\Phi}\sqrt{1+n(\omega)}\left[\frac{\chi^{(1)}}{\varkappa_1(\varkappa_1 - i\Delta)} - \frac{\chi}{\varkappa(\varkappa+i\Delta)}\right]E^0_1E^{*0}_2, \qquad (36)$$

where we have taken into account only the chosen polarizations of incident and scattered radiation. In this expression, E^0_1 and E^0_2 are the amplitudes of the electric field in the exciting and scattered laser radiation, $\chi^{(1)}$ and χ are the nonlinear polarizabilities for $z > 0$ and $z < 0$, respectively, $\Delta = k^a_3 - k^b_3$, and $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$. The probability of the process, on the other hand, is

$$P^{if} = \frac{2\pi}{\hbar^2}\sum_f |\mathscr{H}^{if}|^2 \cdot V\frac{k_b^2\,d\Omega\,d\omega_b}{(2\pi)^3 v_b}\Delta(k^a_1 - k^b_1 - k)[1+n(\omega)]\delta(\omega_a - \omega_b - \omega),$$

where $\Delta(k)$ is the Kronecker symbol and $v_b = d\omega_b/dk_b$ is the group velocity of the scattered photon. Hence, the second-order differential efficiency is

$$\frac{\partial^2 I}{\partial\Omega\,\partial\omega_b} = \frac{2\pi}{\hbar^2}|\mathscr{H}^{if}|^2\frac{V^2k_b^2}{S(2\pi)^3 v_a v_b}\delta(\omega_a - \omega_b - \omega). \qquad (37)$$

If we now use (36), we can rewrite this in the form

$$\frac{\partial^2 I}{\partial\Omega\,\partial\omega_b} = \frac{4\pi\hbar\omega_a^2k_b^2\omega\Phi\{1+n(\omega)\}}{v_a v_b\hat{\epsilon}^2(\omega_a)}\left|\frac{\chi^{(1)}}{\varkappa_1(\varkappa_1 - i\Delta)} - \frac{\chi}{\varkappa(\varkappa+i\Delta)}\right|^2\delta(\omega_a - \omega_b - \omega). \qquad (38)$$

Before we consider numerical estimates, we note certain

properties of (38). Thus, for small angles of scattering, $\Delta \sim k_a\theta^2/2$, whereas $\kappa \sim k_a\theta$. Consequently, we have the approximate result[16)]

$$\left|\frac{\chi^{(1)}}{\varkappa_1(\varkappa_1-i\Delta)}-\frac{\chi}{\varkappa(\varkappa+i\Delta)}\right|^2 \approx \left(\frac{\chi^{(1)}}{\varkappa_1^2}-\frac{\chi}{\varkappa^2}\right)^2,$$

so that when $\kappa^2/\kappa_1^2 = \chi/\chi^{(1)}$, the efficiency of RSL by surface polaritons is zero. It is clear that this compensation of contributions to the RSL cross section is not always possible and occurs only for media for which χ and $\chi^{(1)}$ are both positive or both negative. It is not, however, a unique condition. In fact, the ratio κ^2/κ_1^2 becomes infinite for $\omega = \omega_1$, and for large k it is equal to unity [see (31); $\epsilon(\omega) < 0$]. The compensation effect is therefore possible when $\chi/\chi^{(1)} > 1$. When this inequality is satisfied, the compensation effect enables us to compare the values of χ for the contacting media, and when the value of χ for one of the media is known, we can determine the value of χ for the other. We must now consider some special cases and estimate the RSL cross sections. Let us suppose that medium I is a vacuum, so that $\chi^{(1)} = 0$, $\epsilon_1 = 1$ and

$$\Phi(k)=\left[k^2\left(\frac{1}{\varkappa_1^3}+\frac{\varepsilon}{\varkappa^3}\right)+\frac{\omega}{2\varkappa}\left(1+\frac{k^2}{\varkappa^2}\right)\frac{d\varepsilon}{d\omega}\right]^{-1}.$$

In the relativistic limit, where $k \gg (\omega/c)|\epsilon(\omega)|$ we have $\Phi(k) \approx k(\Omega_\perp^2/\omega^2)(\epsilon_0-\epsilon_\infty)/(\epsilon_\infty+1)$. Under these conditions, the intensity integrated over the polariton linewidth is

$$\frac{dI}{d\Omega} \approx \frac{4\pi\hbar\omega_a^4\Omega_\perp^2\chi^2(\varepsilon_0-\varepsilon_\infty)^2}{c^4k\omega(\varepsilon_\infty+1)}$$

and decreases with increasing k. When $\omega_a/c = 10^5$, $k = 1000$, $\Omega_\perp = 10^{13}$, $1 + \epsilon_\infty = 10$, $\epsilon_0 - \epsilon_\infty = 3$, and $\chi = 10^{-6}$ (to be specific, we are using the data for GaP and the helium-neon laser radiation—all in cgs units), we obtain $dI/d\Omega \approx 4 \times 10^{11}$ which is sufficient for the observation of RSL by a surface polariton (this is, of course, indicated by the observations described in Chap. 4c). It must be remembered that RSL processes result in the excitation of both surface and volume polaritons under these conditions, so that, when thick crystals are employed, processes with the excitation of surface waves will sink into the background of volume processes. This means that RSL by surface polaritons is difficult to observe, and sufficiently thin media must be used. This was taken into account in[32].

b) Method of modified symmetry. Surface pyro- and piezoelectricity in ionic crystals. It follows from (38) that when medium II has a center of inversion (i.e., $\chi = 0$), the cross section for RSL by a surface polariton with $\epsilon(\omega) < 0$ is nonzero provided only that in the medium (i.e., the substrate) $I\chi^{(1)} \neq 0$. This enables us to use RSL to investigate the spectra of surface polaritons in the case of centrally symmetric media, and then use these spectra to deduce, for example, the permittivity [according to (4), the effect of a nonlinear substrate on the spectrum of surface polaritons, in this case, can readily be taken into account].

The above method is, in fact, the method of modified symmetry and has a number of features which deserve attention. In particular, in the above situation, volume polaritons are not excited. It is therefore important that overtones or component tones of the nonlinear substrate, which are active in the RSL spectra, should not enter the surface wave spectrum region. If this is unavoidable, their role can be reduced, other things being equal, by using a sufficiently nonlinear substrate. Estimates of RSL obtained by the method of modified symmetry (see[44]) show that this cross section is roughly the same as for a nonlinear medium bounded by vacuum for the values of the parameters chosen in Chap. 5a.

In conclusion, we must consider the further basic possibility of exciting polaritons in crystals with a center of inversion, which does not involve the artificial choice of a nonlinear substrate (i.e., a substrate with $\chi_{ijl} \neq 0$). Thus, in ionic crystals, the concentrations of cation and anion vacancies in thermodynamic equilibrium are, generally speaking, equal only well away from the separation boundaries. In the surface region, local neutrality is violated because of the different effect of the crystal surface on the energy of formation of vacancies of different sign and, as shown by Frenkel,[70] a double electric layer with a thickness of a few hundred angstrom is produced. The equilibrium distribution of vacancies inside this layer was found in[71]. It is clear that the region of this layer is pyroelectric, with the spontaneous polarization perpendicular to the surface of the crystal, and varies with layer thickness. For our purposes, the important point is that the region of this layer is also piezoelectric, since the deformed layers should exhibit additional polarization proportional to the deformation. This type of surface piezoelectricity can lead to a whole series of effects, for example, it can affect the spectra of surface Rayleigh waves and their damping. Moreover, nonlinear optical processes such as RSL by polaritons and frequency doubling are allowed in the region of the piezoelectric surface layer (these effects are forbidden well away from the crystal boundary because of the presence of the center of inertia). The associated series of problems, and the possibility of their experimental investigation, require separate analysis.

c) Linewidth of RSL by surface polaritons. The broadening of the RSL line due to the attenuation of light can be found from the condition giving the pole of the Green function for the electromagnetic field in the presence of a separation boundary (the corresponding analysis for volume polaritons is given in[31,49]). It is quite clear that this condition has the form given by (4), or

$$A(\omega) \equiv \varepsilon(\omega) + \frac{\varepsilon_1 k^2}{k^2-(\varepsilon_1\omega^2/c^2)} = 0, \qquad (4')$$

where, when damping is taken into account,

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Omega_\perp^2(\varepsilon_0-\varepsilon_\infty)}{\Omega_\perp^2-\omega^2+2i\omega\Gamma_0}. \qquad (39)$$

Since the frequency of the polariton is several hundred times lower than the laser light frequency, we can neglect the difference between the moduli of the vectors $\mathbf{k}^a$ and $\mathbf{k}^b$ when the polariton wave vector $\mathbf{k} = \mathbf{k}^b - \mathbf{k}^a$ is determined. This means that, in RSL processes in which the wave vectors $\mathbf{k}^a$ and $\mathbf{k}^b$ are at an angle θ, the polaritons created in the crystals have the same wave vectors (in fact, predetermined by the experimental conditions). However, because of dissipation processes, this value of k corresponds to a whole set of polariton frequencies. It is clear that, to determine the width of this set, we must separate the real and imaginary parts in the expressions for $A(\omega)$ [see (4')] and, apart from an unimportant common factor, write the result in the form

$$\omega - \omega_s(k) + i\Gamma(k),$$

where $\omega_s(k)$ is the dispersion of the surface polariton [$\mathrm{Re}\, A(\omega_s) = 0$] and $\Gamma(k)$ is the required width. Since, as a rule, $\omega_s \gg \Gamma(k)$ for these waves, it is clear that

$$\Gamma(k) = \mathrm{Im}\, A(\omega_s)\left(\frac{d}{d\omega}\,\mathrm{Re}\, A\right)^{-1}_{\omega=\omega_s}.$$

To within terms which are quadratic in Γ_0 (they can be

neglected when $\omega - \Omega_\perp > \Gamma_0$), the formula given by (4′) takes the approximate form

$$A(\omega) = \varepsilon_\infty + \frac{\Omega_\perp^2(\varepsilon_0 - \varepsilon_\infty)}{\Omega_\perp^2 - \omega^2} + \frac{\varepsilon_1 k^2}{k^2 - (\varepsilon_1\omega^2/c^2)} - \frac{2i\omega\Gamma_0\Omega_\perp^2(\varepsilon_0 - \varepsilon_\infty)}{(\Omega_\perp^2 - \omega^2)^2}.$$

Since, for arbitrary k, the expression for $\Gamma(k)$ is somewhat unwieldy, we shall consider the two special cases $k^2 \gg \epsilon_1\omega^2/c^2$ and $k^2 \approx \epsilon_1\Omega_\perp^2/c^2$. It is readily verified that, in the former case, $\Gamma(k) \approx \Gamma_0$ and, in the second case,

$$\Gamma(k) = \Gamma_0 k^2\left[k^2 + (\varepsilon_0 - \varepsilon_\infty)\frac{\Omega_\perp^2}{c^2}\right]^{-1}.$$

Since, for large k, this tends to the correct limit $[\Gamma(k) \to \Gamma_0]$, it can be used as the interpolation expression for the entire region of allowed values of k $[k \geq (\omega_\perp/c)\epsilon_1^{1/2}]$. In particular, when $k^2 = \epsilon_1\Omega_\perp^2/c^2$, $\Gamma(k) = \Gamma_0\epsilon_1(\epsilon_1 + \epsilon_0 - \epsilon_\infty)^{-1}$, so that for $\epsilon_0 - \epsilon_\infty > \epsilon_1$ the RSL line is substantially narrowed as the angle of scattering is reduced. If, on the other hand, $\epsilon_0 - \epsilon_\infty \ll \epsilon_1$, Γ is practically independent of k. We note in conclusion that, in the approximation which is linear in Γ, the quantity $\omega_s(k)$ is equal to the surface-polariton frequency when damping processes are ignored (when $\Gamma_0 = 0$; these results can be readily generalized). The function $\Gamma(k)$ for multilayered media can be discussed by analogy.

6. TRANSITION-LAYER EFFECTS IN SURFACE-POLARITON SPECTRA

The phenomenologic Maxwell equations were used in Chaps. 2 and 3 to discuss the properties of surface polaritons with boundary conditions specified on a sharp separation boundary in the absence of surface currents and charges. In this simplified situation, the properties of surface waves are completely determined by the permittivity tensors of the contacting media, so that the information on polariton dispersion, obtained by their experimental investigation, can be used and is being used to determine these tensors.

When surface currents and charges are present on the surfaces or separation boundaries or, more generally, there is a certain surface transition layer, the characteristics of the surface polaritons are found to depend on the properties of this layer, and we have the possibility of studying the properties of such layers. There appear to be only two nontrivial situations where allowance for the surface layer may lead to qualitative effects insofar as surface polaritons are concerned. The first of these corresponds to the presence of a thin metal film on the surface of a dielectric, which leads to the "metal quenching" of the surface polariton.[17] This quenching is accompanied by a substantial broadening of the surface-polariton lines, and it is shown below (see [49]) that measurements of this broadening can be used to determine the electrical conductivity of thin-metal films in the polariton frequency band.

The second nontrivial case corresponds to the presence of a dielectric transition layer, when one of the proper frequencies of its dipole oscillations lies in the surface–polariton frequency band. The resonance situation which appears in this case results in a gap in the surface-polariton spectrum.[50] It is usually considered that the presence of the transition layer leads to optical effects of the order of l/λ, where l is the thickness of the layer and λ is the wavelength of light. This is, in fact, valid in the absence of resonance with the surface polariton. On the other hand, when resonance occurs, the resulting gap in the surface-polariton spectrum is of the order of $\sqrt{l/\lambda}$. These two situations are discussed in detail below.

a) Transition layers with high electrical conductivity. We shall illustrate the foregoing by considering the example of a semi-infinite isotropic crystal, the surface of which is coated with a thin metal film with conductivity σ. If the thickness d of the film is much less than the skin-layer depth, its presence can be taken into account by introducing surface currents. It is then readily verified by taking into account the discontinuity in the tangential component of the magnetic field $H_y^{(1)} - H_y^{(2)} = (4\pi/c)\sigma dE_1$ which is due to the surface current $\sigma d\mathbf{E}_t$ (the second boundary condition is still $E_1^{(1)} = E_1^{(2)}$), that the frequency of the surface polariton satisfies the equation

$$\frac{\varepsilon}{\varkappa_2} + \frac{1}{\varkappa_1} = \frac{4\pi\sigma d}{\omega} i, \tag{40}$$

where $\epsilon(\omega)$ is the permittivity of the crystal given by (39), $\kappa_1 = (k^2 - \omega^2/c^2)^{1/2}$, $\kappa_2 = (k^2 - \epsilon\omega^2/c^2)^2$, k is the wave vector of the surface polariton, and ω is its frequency. In particular, in the nonrelativistic region $[k \gg \omega/c,\ k \gg (\omega/c)|\epsilon|]$ it follows from (40)

$$\Gamma = \Gamma_0 + \frac{2\pi\sigma(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 + 1)(\varepsilon_\infty + 1)} kd. \tag{41}$$

The appearance of the additional term in (41) is obviously due to Joule losses of polariton energy in the metal film.[18]

A particular feature of (41) is the appearance of a linear increase in Γ with increasing k. Since Γ and Γ_0 for the system under discussion can, in principle, be determined experimentally, we have here the possibility of determining the electrical conductivity σ of thin films, including its dependence on various factors (magnetic field, temperature, etc.) at the frequencies of the surface polaritons, i.e., for $\omega = 10^{11}$–10^{14} sec^{-1}).[19] This does not at all require that the film be continuous, since the method does not involve the use of contacts. The only essential limitation is that Γ must be small in comparison with the width of the gap between the frequencies of the longitudinal and transverse volume phonons, which ensures the existence of the surface polariton, other things being equal. However, even for very thin films of good metals, this condition may not be satisfied. For example, when the surface of quartz is coated with a gold film of thickness d = 10 Å we have $\Delta\Gamma \equiv \Gamma - \Gamma_0 \gg 4 \times 10^{13}$ sec^{-1} for a polariton with frequency $\omega \approx \omega_1 = 1072$ cm^{-1} ($\epsilon_0 = 3.03$, $\epsilon_\infty = 2.36$), while the gap width is approximately 10^{13} sec^{-1}. If, instead of this situation, we consider a layer of dielectric of finite thickness D with the metal film deposited on one side only, the quenching of the surface polariton localized on the other surface may be substantially weakened. However, if we suppose that the layer of the dielectric with $\epsilon(\omega) < 0$ along the metal film "lies" on a substrate with permittivity $\epsilon_1 > 0$, we obtain the system which differs from that discussed in [33] (see also Sec. c in Chap. 4) only by the presence of the metal film. Assuming that the substrate occupies a half-space, we can show that the equations for the surface-polariton frequencies have the form

$$\left(1 + \frac{\varepsilon\varkappa_0}{\varkappa_1} + i\frac{4\pi\sigma d\varkappa_0}{\omega}\right)\left(1 + \frac{\varepsilon\varkappa_2}{\varepsilon_1\varkappa_1}\right) - e^{-2\varkappa_1 D}\left(1 - \frac{\varepsilon\varkappa_2}{\varepsilon_1\varkappa_1}\right)\left(1 - \frac{\varepsilon\varkappa_0}{\varkappa_1} + i\frac{4\pi\sigma d\varkappa_0}{\omega}\right) = 0, \tag{42}$$

where $\kappa_0 = (k^2 - \omega^2/c^2)^{1/2}$, $\kappa_1 = (k^2 - \epsilon\omega^2/c^2)^{1/2}$, $\kappa_3 = (k^2 - \epsilon_1\omega^2/c^2)^{1/2}$. This defines two branches of surface polaritons in each of which the polaritons experience

metal quenching. However, the rate of quenching is different for polaritons belonging to different branches. In view of the foregoing, this result is clear even from purely qualitative considerations, especially when $Dk > 1$. In view of our discussion of the determination of $\sigma(\omega)$ from the broadening of the surface-polariton lines, the importance of these lines is that they can be used to find σ even for very good metals. For example, the broadening for a polariton localized on the boundary with the substrate is large in the nonrelativistic limit and is given by

$$\Gamma - \Gamma_0 = 2\pi\sigma\, dk \frac{(\varepsilon_0-\varepsilon_\infty)[(\varepsilon_1-1)-e^{-2kD}(3\varepsilon_1+1)]}{(\varepsilon_1-1)[(\varepsilon_\infty+\varepsilon_1)(\varepsilon_0+\varepsilon_1)+e^{-2kD}(3\varepsilon_1^2+\varepsilon_0\varepsilon_1+\varepsilon_\infty\varepsilon_1-\varepsilon_0\varepsilon_\infty)]} \tag{43}$$

which is identical with (41) for $Dk \gg 1$ and $\epsilon_1 = 1$. On the other hand, for a polariton localized on the boundary with vacuum, the metal broadening is exponentially small:

$$\Gamma - \Gamma_0 = \frac{8\pi\sigma kd\,(\varepsilon_0-\varepsilon_\infty)\,e^{-2kD}}{(\varepsilon_\infty+\varepsilon_1)(\varepsilon_0+\varepsilon_1)+e^{-2kD}(3\varepsilon_1^2+\varepsilon_0\varepsilon_1+\varepsilon_\infty\varepsilon_1-\varepsilon_0\varepsilon_\infty)} \tag{44}$$

so that by choosing the film thickness D to be sufficiently large, this difference can be made as small as desired. According to (44), the dependence of Γ on k will then be nonmonotonic.

In conclusion, we must consider the quenching of polaritons when the dielectric layer $[\epsilon(\omega) > 0]$ of thickness D is in contact with a metal along the $z = -D$ plane, the thickness of which is large in comparison with the skin-layer depth. In this case, we can use the Leontovich boundary condition for polaritons on the $z = -D$ plane:

$$\mathbf{E}_t = Z[\mathbf{H}_t \times \mathbf{n}], \tag{45}$$

where Z is the surface impedance and $\mathbf{n}$ the normal to the surface. When the region $z > 0$ is filled with a medium for which $\epsilon_1 > 0$, and the polariton wave vector $\mathbf{k}(k_x, k_y)$ lies along the x axis, the only nonzero component of the magnetic field H_2 has the form

$$H_y = ae^{ikx-\varkappa_1 z}, \quad \varkappa_1 = \sqrt{k^2 - \varepsilon_1\frac{\omega^2}{c^2}} \qquad (z>0); \tag{46}$$

$$H_y = (b_1 e^{-\varkappa z} + b_2 e^{\varkappa z})\, e^{ikx}, \quad \varkappa = \sqrt{k^2 - \varepsilon\frac{\omega^2}{c^2}} \qquad (-D<z<0).$$

Using Maxwell's equations (3) and (46), we find that the x component of the electric field in the above regions of space is given by

$$E_1 = i\frac{c\varkappa_1}{\omega\varepsilon_1} ae^{ikx-\varkappa_1 z} \qquad (z>0),$$

$$E_1 = i\frac{c\varkappa}{\omega\varepsilon} e^{ikx}(b_1 e^{-\varkappa z} - b_2 e^{\varkappa z}) \quad (-D<z<0),$$

so that from the continuity of H_2 and H_1 on $z = 0$, and the boundary condition (45), we obtain the following set of three equations for a, b_1, b_2:

$$a = b_1 + b_2, \quad \mu a = b_1 - b_2, \quad b_1 e^{\varkappa D}(\rho - 1) + b_2 e^{-\varkappa D}(\rho + 1) = 0, \tag{47}$$

where $\mu = \epsilon\kappa_1/\epsilon_1\kappa$ and $\rho = ic\kappa/\omega\epsilon z$. Since the determinant of (47) must be zero, we obtain the following equation for the spectrum of polaritons:

$$\frac{(\mu+1)(\rho-1)}{(\mu-1)(\rho+1)} = e^{-2\varkappa D}.$$

In general, this defines two branches of surface polaritons, but for sufficiently large D, when $\exp(-2kD) \ll 1$, the polaritons localized along the separation boundaries $z = 0$ and $z = -D$ are found to "split" and, in the first approximation, can be studied independently. In particular, in the above system of layers, the polariton localized along the $z = -D$ plane is strongly damped and, probably, difficult to investigate experimentally. We shall therefore consider in detail the properties of the polariton localized on the $z = 0$ plane, for which the dispersion relation is

$$\frac{\varepsilon\varkappa_1}{\varepsilon_1\varkappa} + 1 + 2e^{-2\varkappa D}\frac{\rho+1}{\rho-1} = 0.$$

It follows from this that the surface-polariton linewidth in the nonrelativistic region ($k \gg \omega/c$), which is relevant for the RSL spectra, is given by [in deriving (48), we are assuming, in addition, that $(\omega\epsilon_1/ck)|Z| \ll 1$)]:

$$\Gamma(k) = \Gamma_0 + \frac{2\Omega_1^2\varepsilon_1(\varepsilon_0-\varepsilon_\infty)e^{-2kD}}{ck(\varepsilon_\infty+\varepsilon_1)^2}\operatorname{Re} Z. \tag{48}$$

At frequencies corresponding to the normal skin effect $\operatorname{Re} Z = \sqrt{\omega/8\pi\sigma}$ and, therefore, in contrast to the case where the quenching of the surface polariton is due to the presence of thin metal films [see (41), (43), and (44)], the contact with thick metal leads to quenching which decreases with increasing σ, which was previously connected with the reduction in the penetration of the field into the metal as σ increased.

b) Dielectric transition layers in the presence of resonance with a surface polariton. The boundary conditions used in the preceding section are, in general, inadequate when we investigate the properties of a dielectric transition layer. This is so because we have ignored the polarizability of the transition layer in the direction perpendicular to the separation boundary between the media although, of course, it is possible to have situations where resonance with the surface polariton is due to the presence in a transition layer of oscillations which are at least partially polarized at right-angles to the layer. More general boundary conditions must be used when tyis type of oscillation in a transition layer is to be taken into account. To do this, we note, to begin with, that the effect of macroscopic transition layers (thickness $l \gg a$, $l \ll \lambda$, where a is the lattice constant or the size of the molecule and λ the wavelength of light) on the properties of condensed media (although, it is true, not in connection with their effect on the properties of surface waves) has a very long history and has been considered in great detail (see, for example, [53-55]). The well-known simplicity of this case is due to the fact that, in the presence of a macroscopic transition layer, the derivation of the boundary conditions for fields outside the layer can be carried out directly within the framework of the phenomenologic Maxwell equations. Assuming, for example, that the permittivity inside the layer $(0 < z < l)$ is constant $(\tilde{\epsilon}_{ij} = \tilde{\epsilon}_1\delta_{ij}, \tilde{\epsilon}_1 = \tilde{\epsilon}_2)$, we shall integrate the equation div D = 0 for z between 0 and l.

For fields of the form $\mathbf{D} = \mathbf{D}(z)\exp(ik_1x + ik_2y)$, this integration leads to the condition

$$D_3(l) - D_3(0) = -i\gamma\mathbf{k}_t\mathbf{E}_t(0),$$

where $\mathbf{k}_t \equiv (k_1, k_2)$, $\gamma = l\tilde{\epsilon}_1$. Since $D_3(l) = D_2(1)$ and $D_3(0) = D_3(2)$, where the subscripts 1 and 2 correspond to media for $z > l$ and $z < 0$, respectively, the following is one of the boundary conditions:

$$D_3(2) - D_3(1) = i\gamma\mathbf{k}_t\mathbf{E}_t(1), \tag{49a}$$

where the presence of the transition layer is taken into account to within small quantities of the first order in $kl \ll 1$. The other boundary conditions can be obtained in a similar way (see, for example, [52]):

$$\mathbf{E}_t(2) - \mathbf{E}_t(1) = -i\mu E_n(1)\,\mathbf{k}_t + ik_0 l\,[\mathbf{nH}(1)], \tag{49b}$$

$$\mathbf{H}_t(2) - \mathbf{H}_t(1) = -ilH_n(1)\,\mathbf{k}_t - ik_0\gamma\,[\mathbf{n}\mathbf{E}_t(1)], \quad (49c)$$

$$H_n(2) - H_n(1) = il\mathbf{k}_t\mathbf{H}_t, \quad (49d)$$

where $k_0 = \omega/c$, $\mu = l\sqrt{\epsilon_3}$. If in these boundary conditions[20] we execute the transition to the metal transition layer ($|\tilde{\epsilon}_1| \gg 1$), retaining only terms of the order of σl, where σ is the electrical conductivity of the metal, we obtain the boundary conditions which we have already used [we must then use the formula $\tilde{\epsilon}_1 = 1 + (4\pi\sigma/i\omega)$ for the metal].

In a series of papers,[56] Sivukhin showed that the general form of the boundary conditions given by (49) remains the same even for microscopic transition layers. There is merely a change in the relationships giving μ and γ in terms of the polarizability of the molecules in the transition layer. We shall not consider these relationships in detail because they are very dependent on the model of the transition layer. We shall merely use the fact that, since γ and μ depend on the polarizabilities of the molecules along and at right-angles to the layer, their resonant frequencies will, in general, be different. Bearing this in mind, let us consider, for example, the frequency region $\omega \approx \omega_0$, where ω_0 is the resonance frequency for $\gamma(\omega)$ [$\gamma(\omega_0) = \infty$; the role of the damping of the excitations will be discussed below]. We then need to retain only terms proportional to γ on the right-hand side of (49), so that (49b) and (49c) assume the form

$$\mathbf{E}_t(2) - \mathbf{E}_t(1) = 0, \quad \mathbf{H}_t(2) - \mathbf{H}_t(1) = -ik_0\gamma\,[\mathbf{n}\mathbf{E}_t(1)]. \quad (50)$$

We shall suppose that the wave vector $\mathbf{k}_t$ of the surface field lies along the x axis, and we will denote the permittivities of media I and II by $\epsilon_1 > 0$ and $\epsilon(\omega) < 0$. Using (31), we find that $H_y(1)$ and $H_y(2)$ satisfy the following equations:

$$\frac{\varkappa}{\epsilon}H_y(2) + \frac{\varkappa_1}{\epsilon_1}H_y(1) = 0, \quad H_y(2) - H_y(1) = \gamma\frac{\varkappa_1}{\epsilon_1}H_y(1),$$

which have a nontrivial solution only when

$$\frac{\epsilon_1}{\varkappa_1} + \frac{\epsilon}{\varkappa} = -\gamma. \quad (51)$$

In the resonance region $\gamma(\omega) \approx A\omega_0/(\omega_0 - \omega)$, $A > 0$. If $\omega_S(k)$ is the dispersion relation of the surface polariton corresponding to the solution of (51) for $\gamma = 0$, then when $\omega \approx \omega_S(k)$

$$\frac{\epsilon_1}{\varkappa_1} + \frac{\epsilon}{\varkappa} = \frac{\omega - \omega_s(k)}{C(k)}, \quad (52)$$

where $C^{-1}(k) = \partial/\partial\omega(\epsilon_1/\varkappa_1 + \epsilon/\varkappa)_{\omega=\omega_S(k)} = 0$. Substituting (52) into (51), using the explicit expression for $\gamma(\omega)$, and solving (51) for ω, we obtain the following dispersion relation for the surface polariton:

$$\omega_{1,2}(k) = \frac{\omega_0 + \omega_s(k)}{2} \pm \frac{1}{2}\sqrt{[\omega_s(k) - \omega_0]^2 + 4A\omega_0 C(k)}. \quad (53)$$

If ω_0 falls into the band of the surface polariton $\omega_S(k)$, i.e., if for a certain $k = k_0$ we have $\omega_S(k_0) = \omega_0$, then in the presence of the transition layer the spectrum of polaritons contains the gap $\Delta = 2\sqrt{A\omega_0 C(k_0)}$ at $k = k_0$ (Fig. 11). If the quantity Δ exceeds the surface polariton linewidth due to damping, the gap in the polariton spectrum can be appreciable and measurable. For a rough estimate, we may suppose that $A \approx l$ and $C(k_0) \approx (\epsilon_0 - \epsilon_\infty)\omega_0 k_0$, so that $\Delta \approx 2\omega_0\sqrt{lk_0(\epsilon_0 - \epsilon_\infty)}$ for $l \approx 10$ Å, $k_0 \approx 5 \times 10^3$ cm^{-1}, $\epsilon_0 - \epsilon_\infty = 4$, and $\Delta/\omega_0 \approx 8 \times 10^{-2}$. This gap size may exceed the polariton linewidth ($\Gamma \sim 2 \times 10^{-2}$) and, consequently, the gap may be detectable. For example, when the ATIR method is used, two reflection maxima with similar positions and intensities

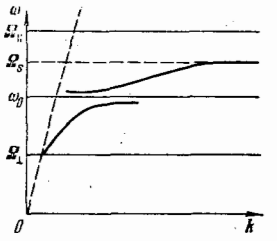

FIG. 11. Dispersion of surface polaritons in the case of resonance with oscillations in the transition layer.

should appear in the region of the gap. If, on the other hand, we consider experiments in which the propagation of surface waves of given frequency is investigated, the presence of the transition layer leads to the appearance of a resonance in the refractive index at surface-polariton frequency $\omega = \omega_0$. Of course, this conclusion follows immediately from Fig. 11. Moreover,

$$\frac{\epsilon_1}{\varkappa_1} + \frac{\epsilon}{\varkappa} \equiv B(\omega)(n^2 - n_0^2(\omega)), \quad (54)$$

where $n_0^2(\omega)$ is the refractive index for the surface polariton when $\gamma = 0$ and $B(\omega) > 0$, so that, using (51) and (54) with $\gamma \neq 0$, we have

$$n^2(\omega) = n_0^2(\omega) + \frac{\gamma(\omega)}{B(\omega)}.$$

We must now consider the case of a macroscopic transition layer. Neglecting anisotropy ($\tilde{\epsilon}_1 = \tilde{\epsilon}_2 = \tilde{\epsilon}_3 = \tilde{\epsilon}$), it is readily verified that the equation for the surface-polariton frequencies is then of the form

$$\frac{\epsilon}{\varkappa} + \frac{\epsilon_1}{\varkappa_1} = \frac{l(\epsilon_1 - \tilde{\epsilon})}{\tilde{\epsilon}\varkappa_1^2}\left[k^2(\epsilon_1 + \tilde{\epsilon}) - \frac{\omega^2}{c^2}\tilde{\epsilon}\right]. \quad (55)$$

The right-hand side of this vanishes when $l = 0$ either for $\epsilon_1 = \tilde{\epsilon}$ or $\tilde{\epsilon} = \epsilon$. In the latter two cases, the transition layer also vanishes, and the separation boundary is shifted by an amount equal to l. Assuming that

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}_\infty\frac{\omega^2 - \tilde{\Omega}_\parallel^2}{\omega^2 - \tilde{\Omega}_\perp^2},$$

we find that the resonances of the right-hand side of (55) occur for $\omega = \tilde{\Omega}_\perp$ and $\omega = \tilde{\Omega}_\parallel$. If, in each of these cases, we retain only the resonant terms, we obtain an expression of the form given by (51), where

$$A^\perp = l\tilde{\epsilon}_\infty\frac{\tilde{\Omega}_\parallel^2 - \tilde{\Omega}_\perp^2}{2\tilde{\Omega}_\perp^2}, \quad A^\parallel = \frac{l}{\tilde{\epsilon}_\infty}\frac{\tilde{\Omega}_\parallel^2 - \tilde{\Omega}_\perp^2}{2\tilde{\Omega}_\parallel^2}\frac{k_0^2}{\varkappa_0^2}, \quad \varkappa_0^2 \equiv k_0^2 - \frac{\tilde{\Omega}_\parallel^2}{c^2}.$$

(we have assumed that $\epsilon_1 = 1$). Thus, in the case which we are considering, and with a suitable choice of $\tilde{\epsilon}(\omega)$, the surface polariton will resonate with both longitudinal and transverse oscillations of the transition layer, leading, in some cases, to the simultaneous appearance of two gaps (which may overlap) in the surface-polariton spectrum.

We note, in conclusion, that the transition layer need not necessarily be connected with the presence of foreign molecules on the surface of the crystal. In those cases where the surface of the crystal (with retarded interaction ignored) leads to the appearance of microscopic surface excitons, i.e., excitons with a penetration depth l of the order of the lattice constant, the boundary conditions given by (49a)—(49d) will retain their form although the quantities μ and γ may be very different for different exciton models. The foregoing results will therefore remain qualitatively valid even in this case and, therefore, enable us to understand how the presence of microscopic surface (Coulomb) excitons affects the surface polariton spectrum. The most interesting case is probably that where the frequency of the microscopic surface

exciton falls into the surface-polariton band. Experimental studies of the gap which appears under these conditions should, in principle, yield information about the characteristics of the surface exciton as well.

7. EFFECT OF SPATIAL DISPERSION ON THE SPECTRA OF SURFACE POLARITONS AND ADDITIONAL SURFACE WAVES

It follows from (8) that, in the case of weak damping, i.e., for sufficiently small Γ, the refractive index of a surface polariton, $n(\omega)$, may become anomalously large as $\omega \to \Omega_S$. We must then, of course, consider the dependence of the frequency of the surface Coulomb exciton, Ω_S, on the two-dimensional wave vector $\mathbf{k}(k_x, k_y)$. When spatial dispersion is ignored, this frequency is determined by the equation $\epsilon(\omega) = -\epsilon_1$. If, on the other hand, we take spatial dispersion into account, then $\epsilon = \epsilon(\omega, \mathbf{K})$, $\mathbf{K} = (\mathbf{k}, -i\kappa)$, where, in the nonrelativistic limit, $\kappa = k$. However, in an isotropic medium and in the case of weak spatial dispersion, $\epsilon(\omega, \mathbf{K}) = \epsilon(\omega) + \alpha K^2 = \epsilon(\omega)$, since for surface waves $\mathbf{K}^2 = \mathbf{K}\cdot\mathbf{K} = k^2 - k^2 = 0$. This means that, for the model of the medium which we are considering, the usual elementary continuum approach will not yield even the first term in the expansion of Ω_S in terms of k. This was emphasized in [69] in connection with the dispersion of surface oscillations for a model of ionic crystals (the results of this were also reflected in [25]). In particular, an analysis was given of the interaction between surface and volume bands, [69] which became possible because of their overlap when spatial dispersion was taken into account. This interaction ensures that surface waves are damped even when anharmonism is ignored and, moreover, leads to the appearance of terms which are linear in k in the dispersion relation (with the exception of special cases of crossing through the van Hove point)[21].

The present author is unaware of any information on the dispersion of surface waves of a more general character and, in particular, for crystals of other nature. In view of this, we shall show below that the transition layer, which is always present in bounded media, will also lead to a linear dependence of Ω_S on k. In fact, in the relativistic limit $k_0 \to 0$, and the boundary conditions for E and D assume the form

$$D_n(2) - D_n(1) = i\gamma \mathbf{k}_t \mathbf{E}_t(1), \quad \mathbf{E}_t(2) - \mathbf{E}_t(1) = -i\mu\varepsilon_1 E_n(1)\,\mathbf{k}_t\varepsilon_1. \quad (56)$$

When retardation is ignored, $\mathbf{E} = A\mathbf{K}$, where A is a scalar, so that in media (1) and (2) we have $\mathbf{E}(1) = A_1\mathbf{K}_1$, $\mathbf{E}(2) = A_2\mathbf{K}_2$, $\mathbf{K}_1 \equiv (k, 0, ik)$, and $\mathbf{K}_2 = (k, -ik)$. Substituting all this in (56), we obtain two linear and homogeneous equations for A_1 and A_2. If we now equate to zero the determinant of this set of equations, we obtain the required dispersion relation

$$\varepsilon(\omega) + \varepsilon_1 = -(\gamma - \varepsilon_1\mu)\,k.$$

We now use (2) to show that, when the transition layer is taken into account, the surface-polariton frequency is

$$\Omega_s(k) = \Omega_s(0) - \frac{\alpha'}{2\Omega_s(0)}k,$$

where

$$\alpha' = \frac{(\gamma - \varepsilon_1^2\mu)(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_\infty + \varepsilon_1)^2}\Omega_\perp^2$$

and, like ϵ_1, the quantities μ and γ are assumed independent of ω near $\omega \approx \Omega_S$.[22] For microscopic transitions layers, the coefficient α' can, of course, be either positive or negative, and it is important that the sign of α' is difficult to control. The situation is quite different for macroscopic layers for which $\gamma - \epsilon_1^2\mu = l[\tilde{\epsilon} - \epsilon_1^2/\tilde{\epsilon}]$ when the transition layer is macroscopic and homogeneous, where l is the layer thickness and $\tilde{\epsilon}$ its permittivity. Therefore, when $\tilde{\epsilon} > \epsilon_1$, we have $\alpha' > 0$.

An additional surface wave appears when $\alpha' > 0$. In fact, $\Omega_S^2 = \Omega_S^2(0) - \alpha' k$ in this case. Substituting this in (8), and ignoring damping, we obtain the following expression for $n(\omega)$:

$$n^2 = \frac{A}{\xi - \alpha n}, \quad (57)$$

where

$$\alpha = \frac{\alpha'}{2\omega_s(0)}, \quad A = \frac{\varepsilon_1\varepsilon_\infty}{\varepsilon_1 + \varepsilon_\infty}\frac{\Omega_\parallel^2 - \Omega_s^2(0)}{2\Omega_s^2(0)}, \quad \xi = \frac{\Omega_s(0) - \omega}{\Omega_s(0)}.$$

Let us estimate the parameters in (57) using, for example, the data for NaCl ($\Omega_\perp = 3.1 \times 10^{13}$ sec^{-1}, $\epsilon_0 = 5.6$, $\epsilon_\infty = 2.25$) and assuming that $\epsilon_1 = 1$. In this case, $A \sim 0.2$, $\alpha \approx l(\tilde{\epsilon} - 1/\tilde{\epsilon}) \times 10^2$ cm^{-1} and, when $\tilde{\epsilon} = 5$ and $l = 500$ Å, we have $\alpha \sim 0.002$. The function $n(\xi)$ is shown in Fig. 12, from which it follows that, when $\xi < \xi_0$, for each value of the frequency there are the two values $n_{1,2}$. The quantity $\xi = \xi_0$, where $n_1 = n_2$, is given by $\xi_0 = (3/\sqrt[3]{4})\alpha^{2/3}A^{1/3}$. Using the parameters for NaCl, we find that $\xi_0 \approx 0.01$. On the other hand, the surface-polariton linewidth is also $\Gamma \approx 0.01\,\Omega_\perp$. This means that damping must be taken into account when $\xi = \xi_0$. However, when $\xi < \xi_0$, the effect of damping on the dispersion relation is reduced. For $\xi \ll \xi_0$, the additional wave ($n = n_2$) is described by the dispersion law (56), whereas for n_1 one can use (8). The dispersion relation (56) can probably be detected by studying RSL by surface polaritons at large scattering angles. On the other hand, when waves of given frequency propagate along a surface (see Chap. 4d), the additional wave may give rise to interference effects of the type discussed for volume waves with spatial dispersion (see [9]).

Let us discuss this by considering waves on the surface formed by two adjacent wedges (Fig. 3a). We suppose that, in the plane of the separation boundary between media I and II, a surface wave has been excited and is propagating, say, at right-angles to the line of separation of the media, i.e., at right-angles to the y axis. Let us further suppose that this wave has a frequency ω which corresponds not to one but two surface waves in the plane of the separation boundary between I and II. Since, in this case, the wave-vector component perpendicular to the separation line, i.e., k_x, is not conserved, two surface waves with the same frequency ω will, in general, be excited under the influence of the primary surface wave in the separation boundary between media I and III, and these will also propagate at right-angles to the y axis but with different values of k_x.

To find the amplitudes of these waves, we must take

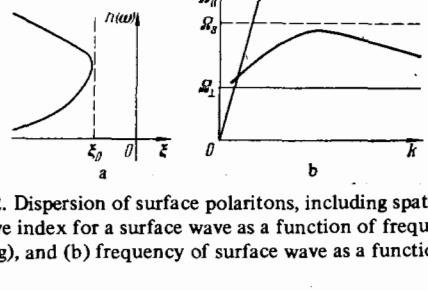

FIG. 12. Dispersion of surface polaritons, including spatial dispersion: (a) refractive index for a surface wave as a function of frequency (ignoring damping), and (b) frequency of surface wave as a function of wave vector.

into account spatial dispersion within the framework cf the theory of surface waves on a wedge, and determine the relationships for the wave amplitudes which will be the additional boundary conditions (ABC). This problem has not as yet been investigated in this formulation. We shall, therefore, only touch upon possible experimental observations of the interference effects.

Let us introduce rulings on the separation boundary between the media, drawn at right-angles to the direction of propagation of the "ordinary" and "additional" surface waves, so that these waves will be transformed into volume electromagnetic waves of the same frequency ω (see Chap. 4b in connection with the role of these rulings). The total volume-wave intensity should then oscillate, depending on the path length traversed by the waves up to the rulings, and these oscillations should be an indication of the role of the particular spatial dispersion effect. It is clear, of course, that one can, in principle, use other surface imperfections instead of the rulings.

8. POSSIBLE FURTHER STUDIES AND CONCLUDING REMARKS

In dielectrics and semiconductors, the spectral bands within which surface waves may exist are relatively narrow and form a discrete set of frequency regions. Nevertheless, the use of surface polaritons in surface physics and, in particular, in the study of chemiadsorption, surface electrical conductivity, surface phonons, excitons, and so on, may turn out to be very useful. This is so not only because, by suitable choice of materials, one can cover a very broad range of frequencies, but mainly because of the strong effect of the properties of near-surface layers of crystals on the surface-wave spectra. As noted in Chap. 6, it is precisely this property of surface waves which reveals new possibilities for the study of excited states of the transition layer.

However, the development of extensive studies in the optics and spectroscopy of surface waves is closely connected with the development of effective sources and detectors of such waves, i.e., the development of a very specialized branch of the optical instrument industry. It is, therefore, very desirable to perform further theoretical analyses (outside the framework of the impedance approximation) of the reflection and refraction of surface waves along separation lines, diffraction by a dielectric wedge with $\epsilon(\omega) < 0$ (when surface waves become possible), and transformation of surface waves into volume waves and vice versa, all of which should provide the foundation for the development of the necessary devices and instruments. Moreover, there is considerable interest in the above topics in connection with anisotropic media and magnetic materials. Surface waves in magnetic materials have not as yet been observed experimentally. The experimental difficulties are connected with the relatively small contribution of magnons to the magnetic susceptibility, as compared with the contribution of photons, excitons or plasmons to the dielectric susceptibility (see [58] for further details).

The development of linear surface-wave optics will stimulate the development of the nonlinear theory and, in particular, the crystal optics of a broader range of effects that are the surface analogs of nonlinear "volume" optical phenomena (for example, Raman scattering of surface light waves by surface lattice oscillations, nonlinear optics of surface waves, and so on). It should also lead to experimental studies of the collective properties of surface excitons.[23] The various possibilities which will ensue from this as a result of the particular properties of surface excitons are difficult to foresee, but the topically of these problems is undoubted.

The author is indebted to V. L. Ginzburg for useful advice and to A. V. Popov, V. I. Yudson, and E. P. Fetisov for discussions of some of the topics reviewed in this paper.

---

[1] For one of the possible models of surface piezo-electricity see Chap. V, Sec. b below).

[2] The importance of the Zenneck-Sommerfeld theory of the propagation of radio waves around the earth surface was discussed in detail more than fifty years ago (see [40]).

[3] Another method of finding surface waves was developed in [72], using the extinction theorem of Ewald and Oseen).

[4] For metals and plasmas, $\epsilon(\omega) = 1-(\omega_p^2/\omega^2)$, where ω_p is the plasma frequency. Therefore, on the boundary with vacuum, for example, surfaces waves exist at frequencies $\omega \lesssim \omega_p/\sqrt{2}$. They have been extensively investigated (see [62] and the references therein).

[5] We are assuming that the frequency ω lies in the surface-wave band of the separation boundary between media II and III.

[6] This lies at the basis of the idea put forward by Naĭman, [73] who suggested the development of radio antennas for surface waves, using the radiation from a bend on a slowing-down surface (see [8b] for further details, where the angular distribution of the body radiation is also discussed).

[7] The fraction of energy carried by the resulting body (edge) wave is

$$\eta = 1 - R^2 - S^2 = \sin^2 \frac{\pi^2}{\alpha} \operatorname{ch} \frac{2\pi\xi}{\alpha} \left(\operatorname{ch}^2 \frac{2\pi\xi}{\alpha} - \cos^2 \frac{\pi^2}{\alpha} \right)^{-1}.$$

[8] Similar properties are encountered in the case of surface waves on a plane boundary of magnetoactive plasma (see, for example, [63] and references therein).

[9] The fact that $\operatorname{Im} \kappa_2 \neq 0$ leads to oscillatory damping of the fields for $z \to -\infty$.

[10] See, however, the recent paper [67], where this discussion is used for the analysis of surface plasmons in semiconductors in the presence of a magnetic field.

[11] In the experiment, for each k one chooses the minimum value of d for which the frequency at the minimum of $R(\omega)$ is independent of d.

[12] This problem was considered for plasma by Alanakyan. [64].

[13] See [25] for a review of the phenomenological theory of surface waves in plates. The spectra of crystals with small linear dimensions are also discussed in [25].

[14] We note the paper [68], where surface phonons were observed in the radiative recombination spectrum on the GaAs surface.

[15] This effect is taken into account in [51].

[16] A more rigorous discussion is given in [51].

[17] An analogous phenomenon occurs in the presence of a sufficiently high surface conductivity.

[18] The first observations of the metal quenching of surface polaritons were published in [74] (Au on SiO_2) and in [75] (Ag and Bi on SiO_2).

[19] The phenomenon we are discussing may also possibly be used to investigate the surface conductivity of semiconductors, which depends on many factors (effect of the field, etc., see [2]). Equation (41) will then still retain its form except that the product σd must be replaced by σ_{eff}—the surface electrical conductivity of the semiconductor.

[20] Of the four conditions, only two are independent. We shall use (49b) and (49c).

[21] Similar questions are also discussed in [61] within the framework of the phenomenologic description. Since the interaction of surface-wave bands with volume-wave bands always occurs for large $k \lesssim \pi/a$, i.e., outside the range of validity of the phenomenologic description, the results established in [61] have only qualitative validity.

[22] The dependence of μ or γ on ω becomes important if the resonance frequency for μ or γ is close to $\Omega_s(0)$. In particular, when these two frequencies are equal, the dependence of Ω_s on k for small k is not linear, but is of the form $\sqrt{k}$.

[23] See [62] and the references therein for nonlinear effects involving the participation of surface waves on plasmas. The interaction of two surface waves is discussed in [66].

[1] C. B. Duke and R. L. Park, Phys. Today 25, 23 (1972).
[2] S. M. Sze, Physics of Semiconductor Devices, Wiley, 1969 (Russian Transl., Energiya, M., 1973).
[3] V. L. Ginzburg, Usp. Fiz. Nauk 101, 185 (1970) [Sov. Phys.-Usp. 13, 335 (1970)].
[4] A. M. Agranovich, A. G. Mal'shukov, and M. A. Mekhtiev, Zh. Eksp. Teor. Fiz. 63, 2274 (1972) [Sov. Phys.-JETP 36, 1203 (1973)]. V. M. Agranovich, Fiz. Tverd. Tela 14, 3684 (1972) [Sov. Phys.-Solid State 14, 3085 (1973)]. V. M. Agranovich and Yu. E. Lozovik, ZhETF Pis'ma Red. 17, 209 (1973) [JETP Lett. 17, 148 (1973)].
[5] V. M. Agranovich, Yu. V. Konobeev, and M. A. Mekhtiev, Fiz. Tverd. Tela 10, 1754 (1968) [Sov. Phys.-Solid State 10, 1383 (1968)]. H. Kuhn, J. Chem. Phys. 53, 101 (1970); H. Kallman, G. Vaubel, and H. Bäsaler, Phys. Status Solidi b 44, 813 (1971).
[6] V. L. Ginzburg, Usp. Fiz. Nauk 108, 749 (1972) [Sov. Phys.-Usp. 15, 839 (1973)].
[7] K. B. Tolpygo, Zh. Eksp. Teor. Fiz. 20, 497 (1950). K. Huang, ERA Report L/T-239 (1950); Proc. R. Soc. Lond. A208, 352 (1951); M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, 1954 (Russ. Transl., IL, M., 1958).
[8] a) E. L. Feĭnberg, Rasprostranenie radiovoln vdol' zemnoĭ poverkhnosti (Propagation of Radio Waves Along the Earth Surface), Izd. AN SSSR, M., 1961); L. A. Vaĭnshteĭn, Teoriya difraktsii i metod faktorizatsii (Theory of Diffraction and the Factorization Method), Sovetskoe Radio, M., 1966; V. Yu. Zavadskiĭ, Vychislenie volnovykh poleĭ v otkrytykh oblastyakh i volnovodakh (Calculation of Wave Fields in Open Regions and Waveguides), Nauka, M., 1972; b) G. D. Malyuzhinets, Dokl. Akad. Nauk SSSR 121, 436 (1959) [Sov. Phys.-Dokl. 3, 752 (1959)]. W. E. Williams, Proc. R. Soc. Lond. A252, 1270, 1376 (1959); N. N. Lebedev, M. S. Bobrovnikov, and V. N. Kislitsyna, Radiotekh. Elektron. 7, 250 (1962).
[9] V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoĭ dispersii i teoriya éksitonov (Crystal Optics Including Spatial Dispersion and the Theory of Excitons), Nauka, M., 1965.
[10] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, M., 1957.
[11] V. M. Agranovich and O. A. Dubovskii, Fiz. Tverd. Tela 7, 2885 (1965) [Sov. Phys.-Solid State 7, 2343 (1966)].
[12] V. M. Agranovich, Teoriya éksitonov (Theory of Excitons), Nauka, M., 1968.
[13] O. A. Dubovskiĭ, Fiz. Tverd. Tela 12, 3054 (1970) [Sov. Phys.-Solid State 12, 2471 (1971)].
[14] V. N. Lyubimov and D. G. Sannikov, Fiz. Tverd. Tela 14, 675 (1972) [Sov. Phys.-Solid State 14, 575 (1972)].
[15] V. V. Bryksin, D. N. Mirlin, and I. I. Reshina, Fiz. Tverd. Tela 15, 1118 (1973) [Sov. Phys.-Solid State 15, 760 (1973)].
[16] Yu. A. Romanov, Izv. Vyssh. Uchebn. Zaved. Radiofiz. 8, 1203 (1965); A. Hartstein, E. Burstein, J. J. Brion, and R. F. Wallis, Surf. Sci. 34, 81 (1973).
[17] A. Harstein, E. Burstein, J. J. Brion, and R. F. Wallis, Solid State Commun. 12, 1083 (1973).
[18] C. Borstel, Phys. Status Solidi b60, 427 (1973).
[19] H. Wolter, Handb. Phys. 24, 46 (1956); N. I. Harrick, Internal Reflection Spectroscopy, New York—London—Sydney, Intersci. Publ., 1967.
[20] A. Otto, Z. Phys. 216, 398 (1968).
[21] R. Ruppin, Solid State Commun. 8, 1129 (1970).
[22] V. V. Bryksin, Yu. M. Gerbshteĭn, and D. N. Mirlin, Fiz. Tverd. Tela 13, 2125 (1971) [Sov. Phys.-Solid State 13, 1779 (1972)]; 14, 543 (1972) [Sov. Phys.-Solid State 14, 453 (1972)].
[23] V. V. Bryksin, Yu. M. Gerbshtein, and D. N. Mirlin, Phys. Status Solidi b51, 901 (1972).
[24] N. Marschall and B. Fischer, Phys. Rev. Lett. 28, 811 (1972).
[25] V. V. Bryksin, D. N. Mirlin, and Yu. A. Firsov, Usp. Fiz. Nauk 113, 29 (1974) [Sov. Phys.-Usp. 17, 305 (1974)].
[26] V. V. Bryksin, Yu. M. Gerbshteĭn, and D. N. Mirlin, ZhETF Pis'ma Red. 15, 445 (1972) [JETP Lett. 15, 315 (1972)].
[27] H. J. Falge and A. Otto, Phys. Status Solidi b56, 523 (1973).
[28] V. A. Yakovlev and G. N. Zhizhin, ZhETF Pis'ma Red. 19, 333 (1974) [JETP Lett. 19, 189 (1974)].
[29] L. I. Mandelstam, Z. Phys. 15, 220 (1914).
[30] R. Ruppin and R. Englman, in: Proc. Intern. Conf. on Light Scattering Spectra of Solids, ed. G. B. Wright, Springer-Verlag, N.Y., 1969, p. 157.
[31] V. M. Agranovich and V. L. Ginzburg, Proc. Second Intern. Conf. on Light Scattering in Solids, ed. M. Balkanski, Flammarion Sci., 1971, p. 226; Zh. Eksp. Teor. Fiz. 61, 1243 (1971) [Sov. Phys.-JETP 34, 662 (1972)].
[32] D. I. Evans, S. Ushioda, and J. D. McMullen, Phys. Rev. Lett. 31, 369 (1973).
[33] D. L. Mills and A. A. Maradudin, Phys. Rev. Lett. 31, 372 (1973).
[34] Y. Y. Teng and E. A. Stern, Phys. Rev. Lett. 19, 511 (1967).
[35] R. H. Titchie, E. T. Arakawa, J. J. Cowan, and R. N. Hamm, Phys. Rev. Lett. 21, 1530 (1968).
[36] D. Beaglehole, Phys. Rev. Lett. 22, 708 (1969).
[37] N. Marschall, B. Fischer, and H. J. Quicisser, Phys. Rev. Lett. 27, 95 (1971).
[38] B. Fischer, N. Marschall, and H. J. Quicisser, Surf. Sci. 34, 50 (1973).
[39] J. Schoenwald, E. Burstein, and R. F. Wallis, Bull. Am. Phys. Soc. 16, 1409 (1971).
[40] L. I. Mandel'shtam, Polnoe sobranie trudov (Complete Collected Works), Vol. 3, Izd. AN SSSR, M., 1950, p. 336.
[41] J. Högglung and F. Sellberg, J. Opt. Soc. Am. 56, 1031 (1966).
[42] J. Schoenwald, E. Burstein, and J. M. Elson, Solid State Commun. 12, 185 (1973).
[43] R. C. Alig, Solid State Commun. 13, 1603.
[44] V. M. Agranovich, ZhETF Pis'ma Red. 19, 28 (1974) [JETP Lett. 19, 16 (1974)].
[45] H. Ekrhardt, L. Langhans, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).
[46] H. Ibach, Phys. Rev. Lett. 24, 1416 (1970).
[47] H. Ibach, Phys. Rev. Lett. 27, 253 (1970).
[48] P. H. Ritchik, Phys. Rev. 106, 874 (1957); H. Boersch, J. Geiger, and W. Stickel, Z. Phys. 222, 130 (1968).
[49] V. M. Agranovich and T. A. Leskova, Fiz. Tverd. Tela 16, 1796 (1974) [Sov. Phys.-Solid State 16, 1168 (1974)].
[50] V. M. Agranovich and A. G. Mal'shukov, Opt. Commun. 11, 169 (1974).
[51] V. M. Agranovich and T. A. Leskova, Fiz. Tverd. Tela 17 (1975) [Sov. Phys.-Solid State 17, in press].
[52] V. M. Agranovich and V. I. Yudson, Opt. Commun. 5, 422 (1972).
[53] P. Drude, Theory of Optics (Russ. Transl., ONTI, L.-M., 1935).

[54] M. Born, Optics (Russ. Transl., GNTIU, Kharkov-Kiev, 1937).
[55] V. A. Kizel', Otrazhenie sveta (Reflection of Light), Nauka, M., 1973.
[56] D. V. Sivukhin, Zh. Eksp. Teor. Fiz. **18**, 976 (1948).
[57] Zh. Eksp. Teor. Fiz. **21**, 94, 367 (1952); Zh. Eksp. Teor. Fiz. **30**, 374 (1956) [Sov. Phys.-JETP **3**, 269 (1956)].
V. M. Agranovich, Opt. Commun. **11**, 389 (1974).
[58] R. Alexander and R. Bell, Opt. Commun. **10**, 59.
[59] U. Fano, Ann. Phys. (N.Y.) **32**, 393 (1938); A. Hessel and A. A. Oliner, Appl. Opt. **4**, 1275 (1965).
[60] R. Kazarinov and A. Suris, Fiz. Tekh. Poluprovodn. 6, 1359 (1972) [Sov. Phys.-Semicond. **6**, 1184 (1972)].
[61] A. A. Maradudin and D. I. Mills, Phys. Rev. **B7**, 2787 (1973).
[62] V. L. Ginzburg, Rasprostranenie élektromagnitnykh voln v plazme (Propagation of Electromagnetic Waves in Plasma), Nauka, M., 1967.
[63] R. N. Kaufman, Zh. Tekh. Fiz. **42**, 746 (1972) [Sov. Phys.-Tech. Phys. 17, 939 (1972)].
[64] Yu. R. Alanakyan, Zh. Tekh. Fiz. **36**, 258 (1966) [Sov. Phys.-Tekh. Phys. **11**, 188 (1966)].
[65] K. A. Barsukov and L. G. Paryshkina, Zh. Tekh. Fiz. **36**, 800 (1966) [Sov. Phys.-Tech. Phys. **11**, 596 (1966)].
[66] Yu. R. Alanakyan, Zh. Tekh. Fiz. **36**, 806 (1966) [Sov. Phys.-Tech. Phys. 11, 600 (1966)].
[67] R. F. Wallis, J. J. Brion, E. Burstein, and A. Hartstein, Phys. Rev. **B9**, 3424 (1974).
[68] V. A. Zuev, D. V. Korbutyan, and V. G. Litovchenko, ZhETF Pis'ma Red. **20**, 3 (1974) [JETP Lett. **20**, 1 (1974)].
[69] V. V. Bryksin and Yu. A. Firsov, Fiz. Tverd. Tela **11**, 2167 (1969) [Sov. Phys.-Solid State **11**, 1751 (1970)]; Fiz. Tverd. Tela **14**, 1148 (1972) [Sov. Phys.-Solid State 00, 0000 (1970)].
[70] Ya. I. Frenkel', Kineticheskaya teoriya zhidkostei (Kinetic Theory of Liquids), Chap. 2, Izd. AN SSSR, M.-L., 1945.
[71] I. M. Lifshitz and Ya. B. Geguzin, Fiz. Tverd. Tela **7**, 62 (1965) [Sov. Phys.-Solid State **7**, 44 (1965)].
[72] G. S. Agarval, Phys. Rev. **B8**, 4768 (1973).
[73] M. S. Naĭman, Izv. Vyssh. Uchebn. Zaved. Radiotekh. **1**, 7 (1958); **3**, 281 (1960); K. I. Grineva, Izv. Vyssh. Uchebn. Zaved. Radiotekh. **2**, 109 (1959).
[74] G. N. Zhizhin, M. A. Moskaleva, V. T. Nazin, and V. A. Yakovlev, Fiz. Tverd. Tela **16**, 1402 (1974) [Sov. Phys.-Solid State **16**, 902 (1974)].
[75] D. N. Mirlin and I. I. Reshina, Fiz. Tverd. Tela **16**, 1141 (1974) [Sov. Phys.-Solid State **16**, 733 (1974)].

Translated by S. Chomet