V. M. Agranovich. *Surface electromagnetic waves and Raman scattering on surface polaritons.* In connection with the development of radio, there was interest in surface waves as early as the beginning of the present century, and the earliest publications known at present that discuss them were E. Cohn's course of lectures "The Electromagnetic Field"[1] (1900) and K. Uller's dissertation[2] (1903). However, the best-known work of that period was done by Zenneck[3] (1907) and Sommerfeld[4] (1909). They discussed the structure of the electromagnetic field created by a radiator situated above the interface between two media.

The first of these studies, namely that of Zenneck, turned out to be erroneous. Zenneck assumed that the electromagnetic field at distances far from the radiator could be described as a surface wave (Zenneck wave). However, Sommerfeld's fundamental study contains the complete analytic solution of the problem, although it is expressed in a form unsuitable for direct comparison with radio-propagation experiments. W. A. Fock and E. Nöther made important contributions to discussion of this solution.

An intriguing and profound discussion of the problems that arise here will be found in the paper by L. I. Mandel'shtam and I. D. Papaleksi.[5] It appears that Mandel'shtam had become interested in surface electromagnetic waves during the years in which the papers of Refs. 1–4 were being published. At that time, Mandel'shtam was working at the University of Strasbourg, and such scientists as C. F. Braun (the 1909 winner of the Nobel Prize in Physics), E. Cohn, and Prof. I. Zenneck, to whom, Papeleksi writes,[6] Mandel'shtam was bound not only by common scientific interest, but also by mutual sympathy, were his university colleagues.

In his well-known 1914 study,[7] Mandel'shtam built an optical analog of Sommerfeld's radiotelegraph experiment, in which he placed a light source near the boundary separating two media. Here Mandel'shtam used a total internal reflection prism, so that the entire setup was closely similar to what now comprises the method of disturbed total internal reflection (DTIR) for pumping surface waves. Mandel'shtam himself makes direct mention of the possibility of exciting surface electromagnetic waves and the interesting problems that would then open up. On the whole, however, the problem of surface waves in the optical range was not actively pursued in those years. Problems of radiotelegraphy were more important for practical needs. Accordingly, wave-propagation research was carried out in the Soviet Union under Mandel'shtam and Papaleksi's direction. A number of decisive experiments were made possible by extensive use of the radiointerference methods that they developed for measuring distances.[5] Their results, which were collected in V. V. Migulin's doctorate dissertation and published in 1947 in this journal,[8] demonstrated contrary to Zenneck[3] that the field at the interface far from the source cannot be described as a surface wave and requires the use of Sommerfeld's more general solution.[4]

Nevertheless, it is stressed in the book of Ref. 5 with respect to Zenneck's approach that "there is no doubt that his work played a role in the sense that its appearance aroused stronger interest in the problem and stimulated publication of further studies."

At any rate, interest in surface electromagnetic waves appeared to have died thirty years ago. Today, these waves, but now in the optical range of frequencies (where they are usually called surface polaritons), are being studied by various methods in the world's leading laboratories, and their properties are being discussed widely in the scientific periodical literature, at conferences and symposia, etc.

The new interest in surface waves has grown out of the rapid development of research on the physical properties of the surfaces of solids, which lend urgency to the search for new optical methods for their study.

Crystal optics is used in studying the propagation of body waves in crystals. Experimental study of the propagation and damping of these waves yields information on the spectrum of elementary "body" excitations. But for analysis of the surface properties of the medium, we may expect the largest amount of information from a study of the propagation in crystals not of body waves, but of surface electromagnetic waves in which energy is propagated only along the surfaces or boundaries separating the media. Study of the damping of these waves and of their reflection and refraction at the boundaries (lines) of separation, i.e., "surface crystal optics," is now playing an important role in study of the spectral properties of crystal surfaces. We have surface-wave metal optics,[18] the thermal stimulation of emission of surface waves,[36] and their selective absorption in ultrathin layers on the surfaces of metals[37] are under study, nonlinear-optics methods involving surface waves are being developed,[35] and so forth. The results that have already been obtained open prospects for the development of new methods for investigating the spectral properties of the transitional layers that are always present at interfaces, and, in particular, new ways of studying phase transitions[33] and chemical (catalytic) and possibly biophysical effects of the surfaces of condensed media. Realization of these possibilities might, for example, promote the use of intracavity laser spectroscopy to design new methods for generation of surface waves and study of their properties.

We stress that in the work of both Zenneck[3] and Sommerfeld,[4] the appearance of normal solutions of the electromagnetic-field equations with the nature of surface waves resulted from the presence of the imaginary part of permittivity (or real conductance) in one of the media. In this context, the discovery of Wood's anomalies (1902)[9] and the interpretation given for them by Fano[10] were fundamental for development of the theory of surface waves.

Wood observed that on reflection of light from a metallic diffraction grating, sharp narrow gaps in reflected intensity appeared for certain wavelengths if the incident light was polarized in the plane of incidence. U. Fano[10] was the first to recognize that the reflection decrease under these conditions was due to generation of surface waves. It was also shown[10] that surface waves may also appear when the imaginary part of the permittivity of one of the media is negligibly small but its real part is negative (for a plasma this corresponds to the case $\omega < \omega_p$ and $\omega\tau \gg 1$, where τ is the relaxation time and ω_p is the plasma frequency). The surface waves that appear in these cases are sometimes called Fano waves. It is important that today, when study of surface waves is developing so broadly, it is Fano waves rather than Zenneck waves that are usually the objects of investigation. This situation should come as no surprise in view of the fact that in the optical range it is the Fano waves that are usually normal surface solutions corresponding to the surfaces of the crystals or the boundaries separating them. This is easily understood when it is recognized that $\varepsilon(\omega)$ $\varepsilon_\infty(\omega^2 - \omega''^2)/(\omega^2 - \omega_\parallel^2)$, for dielectrics in the neighborhood of resonances of the permittivity $\varepsilon(\omega)$, which correspond to rather large oscillator strengths, and damping is quite weak: $\varepsilon = \varepsilon' + i\varepsilon'' \approx \varepsilon'$; $\varepsilon'(\omega) < 0$ for $\omega'' > \omega > \omega_\perp$. In metals, for example, under the conditions of the normal skin effect $\varepsilon(\omega) = 1 - \omega_p^2/\omega[\omega + (i/\tau)] = \varepsilon' + i\varepsilon''$ and for $\omega \gg 1/\tau$ the value of $\varepsilon''(\omega)$ satisfies $\varepsilon''(\omega) \ll |\varepsilon'(\omega)|$, with $\varepsilon'(\omega) = 1 - (\omega_p^2/\omega^2)$ and, if $\omega < \omega_p$, we have $\varepsilon'(\omega) < 0$. For a boundary with a vacuum, the dispersion law of surface waves takes the form

$$k^2 = \frac{\omega^2}{c^2}\frac{\varepsilon'(\omega)}{\varepsilon'(\omega)+1} \tag{1}$$

where k is the two-dimensional wave vector corresponding to wavelike propagation along the interface between the media (more general situations, and, in particular, situations for anisotropic media, are discussed in Ref. 11). The derivation of the dispersion law (1) was given in the 1957 edition of the book by L. D. Landau and E. M. Lifshitz.[12] We know of no earlier publication of this relation[1)].

Relation (1) corresponds to a sharp boundary between the two media. However, allowance for even a micro-

[1)]The 1958 paper by Ferrell[13] states that this relation was also derived in an unpublished paper by E. A. Stern.

scopic transitional layer sometimes results in significant changes in the surface-wave dispersion law. For example, resonance of vibrations in a transitional layer with a surface wave (see Ref. 11) results in the appearance of a gap in its spectrum (for observation of such a gap see Ref. 14). This and similar effects indicate that it may be possible to use surface waves to develop a surface spectroscopy. We also note in this context the possibility (see Ref. 34) that surface electromagnetic waves may appear on a boundary separating the "right-hand" and "left-hand" modifications of a gyrotropic crystal. Such waves could be used to study spatial dispersion effects (gyrotropy, etc.).

We considered it appropriate above to discuss certain stages in the development of surface-wave concepts (see also Ref. 15) because contemporary physical thinking in this area has been extremely closely related to the legacy of one of the first discoverers of Raman scattering—the legacy of L. I. Mandel'shtam, and his penetrating insights into what is common to and is different for optics and radiophysics and the ideas set forth in his 1914 paper are widely used. As we have already noted, one of the methods for pumping surface waves is based on use of the DTIR prism[16,17]; the interaction of optical radiators with metallic surfaces a short distance away is studied in analysis of "metallic" quenching of the luminescence of organic molecules, and so forth.

Although the question of Raman scattering of light by surface waves (by surface polaritons) has arisen more than once (see, for example, Refs. 19 and 20), observation of the process has encountered difficulties of a technical nature owing to the small size of the scattering volume. The first successful results (for CaAs) were obtained only in 1973 by Ushioda's group in the United States.[21] The scheme of the experiment and the results were described in Ref. 11 (see also Ref. 22). As of this writing, Ushioda's work is the only one in which spontaneous Raman light scattering by surface polaritons has been observed. However, surface polaritons have recently been observed for GaP by active Raman spectroscopy and spectroscopy in k-space.[23]

In these studies, Raman scattering methods showed the dispersion law for surface waves to be in full agreement with the theoretical formula (1). The theory of Raman light scattering by surface waves was developed in Refs. 25–32.

Usioda *et al.*[24] also observed Raman scattering of light in extremely thin crystal waveguides (a theory of this scattering is given in Ref. 32).

The results obtained in recent years open up broad prospects for the development of surface crystal optics.

[1]E. Cohn, Das electromagnetishe Feld., Leipzig, 1900.
[2]K. Uller, Beiträge zur Theorie der electromagnetische Strahling, Dissertation, Rostock, 1903.
[3]I. Zenneck, Ann. d. Phys. 23, 846 (1907).
[4]A. Sommerfeld, *ibid.*, 28, 664 (1909).
[5]L. I. Mandel'shtam and N. D. Papaleksi, Noveǐshie issledovaniya rasprostraneniya radiovoln vdol' zemnoǐ poverkhnosti [Recent Studies of Radio Propagation along the Surface of the Earth], Gostekhizdat, Moscow, 1945, p. 7.
[6]N. D. Papaleksi, Leonid Isaakovich Mandel'shtam (A brief sketch of his life and scientific career. In: Polnoe sobranie trudov L. I. Mandel'shtama [Complete Collected Works of L. I. Mandel'shtam], USSR Academy of Sciences Press, Moscow-Leningrad, 1, 1948, p. 7.
[7]L. I. Mandel'shtam, Phys. Zs. 15, 220 (1914).
[8]V. V. Migulin, Usp. Fiz. Nauk 33, 351 (1947).
[9]R. W. Wood, Phil. Mag. 4 (1902), p. 393; 23, (1912), p. 310.
[10]U. Fano, J. Opt. Soc. Amer. 31 (1941), p. 213.
[11]V. M. Agranovich, Usp. Fiz. Nauk 115, 199 (1975) [Sov. Phys. Usp. 18, 99 (1975)].
[12]L. D. Landau and E. M. Lifshits, Élektrodinamika sploshnykh sred [Electrodynamics of Continuous Media], Gostekhizdat, Moscow, 1957.
[13]R. A. Ferrell, Phys. Rev. 111 (1958), p. 1214; E. A. Stern, R. A. Ferrell, *ibid.* 120 (1960), p. 130.
[14]G. N. Zhizhin, M. A. Moskaleva *et al.*, Zh. Eksp. Teor. Fiz. 72, 687 (1977) [Sov. Phys. JETP 45, 360 (1977)].
[15]E. Burstein, in Polaritons, Ed. by E. Burstein and F. De Martini (Pergamon Press, N. Y., 1974).
[16]A. Otto, Phys. Status Solidi, 26, 99 (1968); 216, 398 (1968).
[17](a) V. V. Bryksin, D. N. Mirlin, and Yu. A. Firsov, Usp. Fiz. Nauk 113, 29 (1974) [Sov. Phys. Usp. 17, 305 (1975)]. (b) G. Borstel and H. J. Falge, Phys. Status Solidi B12, 185 (1977).
[18]J. Schoenwald, E. Burstein, and J. M. Elson, Sol. State Commun. 12 (1973), p. 185.
[19]R. Ruppin and R. Engelman in Proc. of 1968 Intern. Conference on Light Scattering Spectra of Solids, Ed. by G. B. Wright (Springer-Verlag, N. Y., 1969), p. 157.
[20]V. M. Agranovich and V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 61, 1243 (1971) [Sov. Phys. JETP 34, 662 (1972)].
[21]D. I. Evans, S. Ushioda, and J. D. McMullen, Phys. Rev. Lett. 31 (1973), p. 369; J. Y. Prieur and S. Ushioda, *ibid.* 34 (1975), p. 1012.
[22]J. Valdez and S. Ushioda, *ibid.* 38 (1977), p. 1098.
[23]F. De Martini and Y. R. Shen, *ibid.* 36 (1976), p. 216. F. De Martini, G. Ginliani., *et al.*, *ibid.*, 37 (1976), p. 440.
[24]J. B. Valdez, G. Mattei, and S. Ushioda, *ibid.*, 1978 (in press).
[25]V. M. Agranovich, Pis'ma Zh. Eksp. Teor. Fiz. 19, 28 (1974) [JETP Lett. 19, 16 (1974)].
[26]V. M. Agranovich, Opt. Comm. 11 (1974), p. 389.
[27]Y. J. Chen, E. Burstein, and D. L. Mills, Phys. Rev. Lett 34 (1975), p. 1516.
[28]J. S. Nkoma and R. Loudon, J. Phys. Ser. C8 (1975), p. 1950.
[29]V. L. Strizhevskii and Yu. N. Yashkir, Phys. Status Solidi B 69, 175, (1975).
[30]D. L. Mills, Y. J. Chen, and E. Burstein, Phys. Rev. B 13 (1976), p. 4419.
[31]V. M. Agranovich and T. A. Leskova, Fiz. Tverd. Tela (Leningrad) 17, 1367 (1975) and 19, 804 (1977) [Sov. Phys. Solid State 17, 880 (1975) and 19, 465 (1977)].
[32]K. R. Subbaswamy and D. L. Mills, Phys. Rev. Lett., 1978 (in press).
[33]V. M. Agranovich, Pis'ma Zh. Eksp. Teor. Fiz. 24, 602 (1976) [JETP Lett. 24, 558 (1976)]; V. M. Agranovich and T. A. Leskova, Sol. State Commun. 21 (1977), p.1065.
[34]V. M. Agranovich and O. A. Dubovskii, Pis'ma Zh. Eksp. Teor. Fiz. 26, 641 (1977) [JETP Lett. 26, 488 (1977)].
[35]Y. J. Chen and E. Burstein, Nuovo Cimento, B 39 (1977), p. 807.
[36]E. A. Vinogradov, G. N. Zhizhin, and A. G. Mal'shukov, Zh. Eksp. Teor. Fiz. 73, 1481 (1977) [Sov. Phys. JETP 46, 778 (1977)].
[37]G. N. Zhizhin, M. A. Moskaleva, E. V. Shomina, and V. A. Yakovlev, Pis'ma Zh. Eksp. Teor. Fiz. 25, 221 (1976) [JETP Lett. 25, 201 (1977)].