Excitation of Nonradiative Surface Plasma Waves in Silver by the Method of Frustrated Total Reflection

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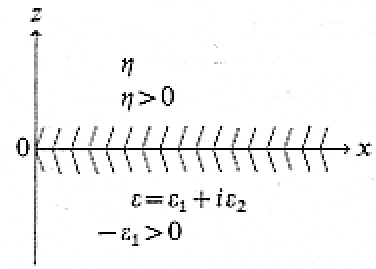
A new method of exciting nonradiative surface plasma waves (SPW) on smooth surfaces, causing also a new phenomena in total reflexion, is described. Since the phase velocity of the SPW at a metal-vacuum surface is smaller than the velocity of light in vacuum, these waves cannot be excited by light striking the surface, provided that this is perfectly smooth.
However, if a prism is brought near to the metal vacuum-interface, the SPW can be excited optically by the evanescent wave present in total reflection. The excitation is seen as a strong decrease in reflection for the transverse magnetic light and for a special angle of incidence. The method allows of an accurate evaluation of the dispersion of these waves. The experimental results on a silver-vacuum surface are compared with the theory of metal optics and are found to agree within the errors of the optical constants.

1. Introduction

Surface plasma waves (SPW) are transverse magnetic (TH) electromagnetic waves, travelling along interfaces of two different media. There are radiative and nonradiative SPW. Radiative SPW can be coupled with plane electromagnetic waves and are involved in phenomena like transition radiation [1] and plasma-resonance absorption [2,3]. ROMANOV [4] and FUCHS and KLIEWER [5] were, as far as the author knows, the first to label these as an intrinsic wave mode.

Nonradiative SPW are known as solutions of Maxwell's equations since SOMMERFELD [6,7]; their theory in terms of the complex dielectric constant has been given mainly by STERN [8] and RITCHIE and ELDRIDGE [9].

In the following part, a short review of theory and experiments is given. The fields of a nonradiative SPW at the interface of a metal with a dielectric constant $\varepsilon(\omega)=\varepsilon_1+i\varepsilon_2$ (or more generally, a medium with negative ε_1) and a dielectric with dielectric constant $\eta(\omega)>0$ are given by



$$E=E_0\, e^{i(kx-\omega t)}\begin{cases}\left(1,0,\dfrac{ik}{\sqrt{k^2-\eta\,\omega^2/c^2}}\right)e^{-\sqrt{k^2-\eta\,\omega^2/c^2}\,z}\\[2ex] \left(1,0,\dfrac{-ik}{\sqrt{k^2-\varepsilon\,\omega^2/c^2}}\right)e^{+\sqrt{k^2-\varepsilon\,\omega^2/c^2}\,z}\end{cases}\quad\text{for}\ \begin{cases}z>0\\ z<0\end{cases}$$

$$H=\frac{i\omega}{c}E_0\, e^{i(kx-\omega t)}\begin{cases}\left(0,\dfrac{-\eta}{\sqrt{k^2-\eta\,\omega^2/c^2}},0\right)e^{-\sqrt{k^2-\eta\,\omega^2/c^2}\,z}\\[2ex] \left(0,\dfrac{\varepsilon}{\sqrt{k^2-\varepsilon\,\omega^2/c^2}},0\right)e^{+\sqrt{k^2-\varepsilon\,\omega^2/c^2}\,z}\end{cases}\quad\text{for}\ \begin{cases}z>0\\ z<0.\end{cases}\tag{1}$$

In x-direction, the solution is a harmonic wave with frequency ω and wave number k. For this solution to make physical sense, it is necessary for the fields on both sides of the interface to be evanescent. That means, that $k^2-\eta\dfrac{\omega^2}{c^2}>0$, which is identical with the condition, that the phase velocity of the SPW should be less than the phase velocity of plane waves in the dielectric.

$$v_{\mathrm{ph}}=\frac{\omega}{k}<\frac{c}{\sqrt{\eta}}\tag{2}$$

$\left(\text{Real part}\sqrt{k^2-\varepsilon\dfrac{\omega^2}{c^2}}>0 \text{ because of } \varepsilon_1<0\right)$.

The dispersion $\omega(k)$ is given implicitly by

$$\frac{\varepsilon(\omega)}{\sqrt{k^2-\varepsilon\dfrac{\omega^2}{c^2}}}=-\frac{\eta(\omega)}{\sqrt{k^2-\eta\dfrac{\omega^2}{c^2}}}.\tag{3}$$

(This relation is deduced from the boundary condition for the z-components of E or the y-components of H in Eq. (1).)

1 FRANK, I.M.: Soviet Physics Uspekhi 8, 729 (1966).
2 YAMAGUCHI, S.: J. Phys. Soc. Japan 18, 266 (1963).
3 MCALISTER, A.J., and E.A. STERN: Phys. Rev. 132, 1599 (1963).
4 ROMANOV, YU.A.: Radiofisika 7, 828 (1964).
5 KLIEVER, K.L., and R. FUCHS: Phys. Rev. 153, 498 (1967).
6 SOMMERFELD, A.: Ann. Physik 28, 665 (1909).
7 SOMMERFELD, A.: Vorlesungen über theoretische Physik, Bd. IV, §32. Wiesbaden: Dieterich 1947.
8 STERN, E.A.: Rand Report 2270, unpublished.
9 RITCHIE, R.H., and H.B. ELDRIDGE: Phys. Rev. 126, 1935 (1962).

As example, Fig. 1 shows the dispersion of a SPW on the border between vacuum and a free electron gas $\left(\varepsilon = 1 - \frac{\omega_p^2}{\omega^2}\right)$ with $\hbar\omega_p = 15$ eV. Because the SPW consists only of evanescent waves, it does not emit light – hence the name non-radiative SPW. It cannot be excited by incident TH-light (which is equivalent to parallel polarized light), because this excites a surface polarization wave, travelling along the interface with a phase velocity $c/(\sqrt{\eta}\sin\alpha) > c/\sqrt{\eta}$ (see Fig. 2a). Therefore, there is no simple spectroscopic way of investigating non-radiative SPW.

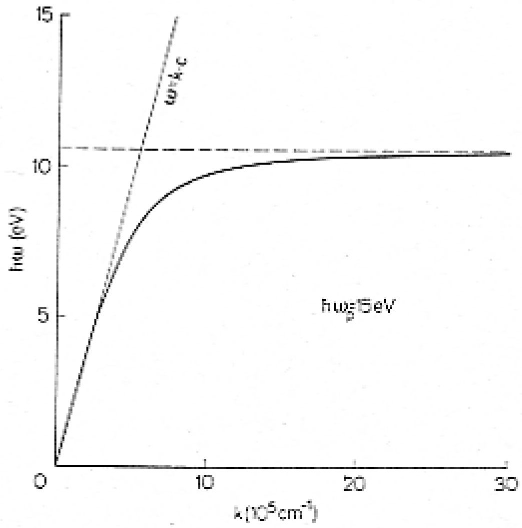


Fig. 1. Dispersion $\omega(k)$ (frequency ω, wavenumber k) of the nonradiative SPW at the surface of a free electron gas ($\varepsilon = 1 - \omega_p^2/\omega^2, \hbar\omega_p = 15$ eV) with vacuum. The straight line is the dispersion of plane electromagnetic waves in vacuum

The quanta of the SPW, the socalled surface-plasmons are excited by electrons in characteristic energy-loss experiments[10]. The dispersion of the SPW is obtained by measuring the energy loss of the electrons in transmission of thin films for different angles of deflection, which are given by the momentum transfer $\hbar k$ of the electrons to the surface plasmons. Because of the finite angular resolution, an accurate check on the dispersion relation is not possible by means of this method. However, SWAN, OTTO and FELLENZER[11] and KLOOS[12] observed a decrease of the energy loss $\hbar\omega$ for small momentum transfers $\hbar k$ in forward scattering direction on Al-foils.

Another way of investigating SPW is the coupling of the nonradiative SPW to incident or emitted light using surfaces, which are not smooth. Experiments of this type have been carried out both on rough evaporated metal films and on metal-coated gratings, by investigating either the emission due to electron bombardment at grazing incidence, or by reflectivity and absorption measurements, or by the investigation of the degree of polarization by metal gratings.

In the last 2 years, there has been a considerable amount of work done in this field; the references will be given in a review article to be published by STEINMANN[13] and in the abstracts of papers given on the Second International Conference on Vacuum Ultraviolet Radiation Physics[14].

II. The Principle of the Frustrated Total Reflection Method[15]

In Fig. 2a, a plane TH-wave of frequency ω is incident upon a completely smooth interface between a dielectric with index of refraction $n_s(\omega)$ $(\eta = n_s^2)$ and a metal with dielectric constant $\varepsilon(\omega)$. The angle of incidence is α. The wavefronts of the incident wave are given as broken lines. The reflected wave and the evanescent wave in the metal are not drawn. A wave of surface charges is induced, the phase velocity of which is $c/(n_s \sin\alpha)$ which is for all α greater than c/n_s, whereas the SPW has a phase velocity smaller than c/n_s. Because of the discrepancy of phase velocities, the SPW cannot be excited.

In Fig. 2b, a spacer layer S with an index of refraction n_s is put between the metal M and a medium P, whose index of refraction n_p is greater than n_s. The velocity of points of fixed phase along the interface between the media P and S is now

$$v_{ph} = \frac{c}{n_p \sin\alpha}. \tag{4}$$

If $c/(n_p \sin\alpha) < c/n_s$ which is equivalent to $n_p \sin\alpha > n_s$, the electromagnetic field penetrates into the spacerlayer only as an evanescent wave whose z-dependence is

$$e^{-\frac{\omega}{c}\sqrt{n_p^2 \sin^2\alpha - n_s^2}\, z}. \tag{5}$$

If the thickness d of medium S were infinite, there would be total reflection. This evanescent wave will be resonant with the surface plasma wave at the metal-spacerlayer-interface, if the phase velocities for both waves are equal.

[10] RAETHER, H.: Springer Tracts of Modern Physics 38, 103 (1965).
[11] SWAN, J.B., A. OTTO, and H. FELLENZER: phys. stat. sol. 23, 171 (1967).
[12] KLOOS, T.: Z. Physik 208, 77 (1968).

[13] STEINMANN, W.: phys. stat. sol. 28, 437 (1968).
[14] To be published in the Bull. Am. Phys. Soc.
[15] OTTO, A.: Phys. stat. sol. 26, K 99 (1968).

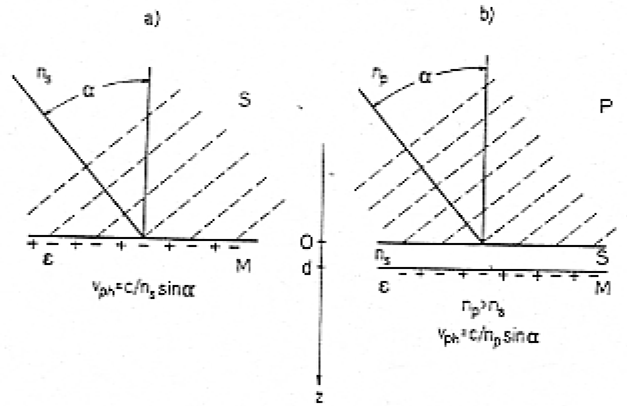


Fig. 2. a) Plane TH-wave incident with angle α upon an interface $z=0$ between a dielectric S (index of refraction n_s) and a metal M (dielectric constant ε). Broken lines are the planes of equal phase of the incident wave. + - signs symbolize the surface chargewave, v_{ph} is its phase velocity. b) Like a, but the dielectric S as a spacerlayer of thickness d between the medium of the prism P (whose index of refraction n_p is greater then n_s) and the metal

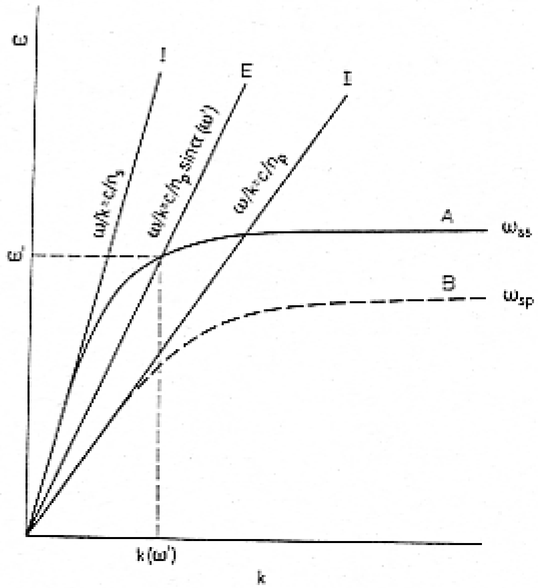


Fig. 3. Qualitative dispersion $\omega(k)$ of the nonradiative SPW, A at the interface $M-S$ (see Fig. 2a, b), B at the interface $M-P$. $\omega(k)$ is given for $k\to\infty$ by $\varepsilon(\omega_{ss})=-n_s^2$, $\varepsilon(\omega_{sp})=-n_p^2$ Lines I and II give the dispersion of plane waves in the media S and P, E the dispersion of the evanescent wave in medium S, if the angle of incidence upon the $P-S$ interface is $\alpha(\omega')$. The crosspoint between E and A means resonance between the evanescent wave and the SPW of frequency ω' and wavenumber $k(\omega')$

For $90°\geq\alpha\geq\arcsin(n_s/n_p)$ v_{ph} varies as $c/n_p\leq v_{ph}\leq c/n_s$.

This range for the phase velocities is given in Fig. 3 by the area between the straight lines I and II. (For simplicity, it is assumed in Fig. 3, that n_s, n_p are constant.) The full curve A gives the dispersion of the SPW at the interface between the metal and the medium S. The part of A, which lies above line II, can be excited. For instance, for a given frequency ω', $\alpha(\omega')$ is the angle of resonance. Because of the absorption of energy by the SPW, the total reflection will be frustrated for this angle of incidence, but only for TH-polarization.

The wave-vector $k(\omega')$ of the SPW is

$$k(\omega')=\frac{\omega'}{c}n_p\sin\alpha(\omega'). \tag{6}$$

The spacerlayer is essential. Without it, the SPW at the interface metal-medium P, whose dispersion is given in Fig. 3 as curve B, cannot be excited for reasons already discussed in context with Fig. 2a.

In the following section, a semiquantitative discussion of the surface plasma resonance, its strength and halfbreadth, depending on the thickness of the spacerlayer, will be given.

III. Semiquantitative Theory

The halfwidth of the resonance can be easily described by introducing a complex wave-number

$$k(\omega')=k_r(\omega')+i\,k_i(\omega').$$

k_r is related to $\alpha(\omega')$, the angle of minimum reflectivity similar to Eq. (6) by

$$k_r(\omega')=\frac{\omega'}{c}n_p\sin\alpha(\omega'). \tag{7}$$

k_i is related to the halfwidth $\Delta\alpha(\omega')$ by

$$k_i(\omega')=\frac{\omega'}{c}n_p\cos\alpha(\omega')\cdot\Delta\alpha(\omega'). \tag{8}$$

On the other hand, k_i is a measure of the damping rate of the SPW. There are two additive damping mechanisms:

First, the internal damping, described by k_{ii}, due to the energy-absorption in the metal, which is proportional to the imaginary part ε_2 of the dielectric constant.

Second, radiation damping, described by k_{ir}, due to the emission of a lightwave into the medium P by the SPW. This coupling to the lightwave is strongly dependent on the thickness d of the spacerlayer and disappears only for $d \to \infty$. As shown in the appendix (for $n_s = 1$)

$$k_{i\,r} = k'_{i\,r}\, e^{-2k_0 d} \quad \text{with} \quad k_0 = \sqrt{k_r^2 - \frac{\omega^2}{c^2}}. \tag{9}$$

The resonance halfbreadth will therefore depend on d as

$$k_i = k_{i\,i} + k'_{i\,r}\, e^{-2k_0 d}. \tag{10}$$

Now the dependence of the resonance absorption A on d can be calculated. The resonance excitation of the SPW will be proportional to the quotient of the exciting field strength and the total damping rate – which is a well known result of the general resonance theory. The exciting field strength of the evanescent wave (5) will be, using Eqs. (7) and (9), proportional to $e^{-k_0 d}$. The fraction of resonance energy, which is absorbed, is given by the ratio of the internal to total damping rate. Therefore

$$A \sim \frac{k_{i\,i}\, e^{-k_0 d}}{(k_{i\,i} + k'_{i\,r}\, e^{-2k_0 d})^2}. \tag{11}$$

A will have its maximum for $d = d_{max}$

$$d_{max} = -\frac{1}{2k_0} \ln \frac{k_{i\,i}}{3k'_{i\,r}}. \tag{12}$$

Using the values, given in the appendix, d_{max} is calculated for a wavelength of 578 nm and silver to be about 12000 Å, and the halfbreadth in this case about 7 minutes. (The results of the exact theory, mentioned in section V are $d_{max} \approx 7250$ Å $\Delta\alpha \approx 18'$.)

As the logarithmic factor in (12) changes only slowly with the frequency of the incident light, the dependence of d_{max} upon frequency is mainly given by k_0. With Eqs. (12) and (9) and the dispersion curve (Figs. 1 and 3) it can easily be seen, that d_{max} decreases for increasing frequency.

IV. Experiment and Results

The experiment was performed with silver, the spacerlayer being air. The schematical arrangement is shown in Fig. 4. An area of about 7 × 15 mm in the middle of a quartz-glass-plate II with an area 95 × 50 mm was evaporated with silver in a high vacuum of about 1×10^{-5} torr, the

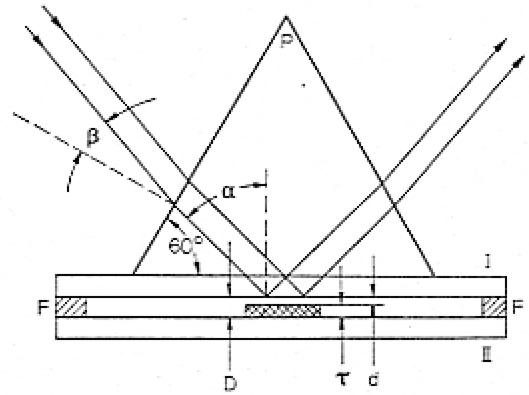


Fig. 4

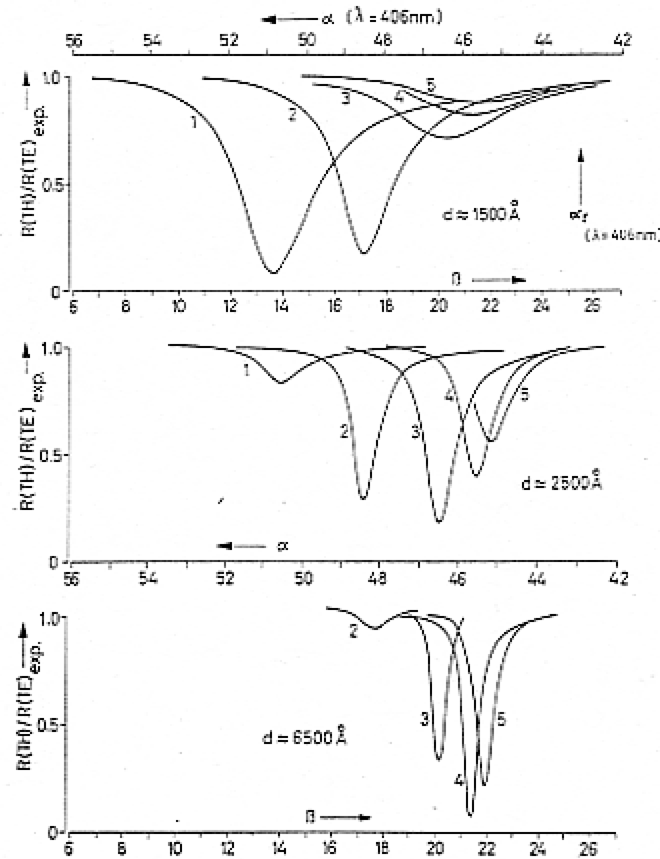


Fig. 5

Fig. 4. Schematical experimental arrangment of the silver surface and the quartz-glass-prism P. I and II are quartz-glass-plates, F spacerfoils

Fig. 5. Ordinate: Experimental ratio of reflectivities R for TH and TE waves, for the experimental arrangment given in Fig. 4. Abscissa: Angles β and α (for $\lambda = 406$ nm) in degrees. $\alpha > \alpha_t$ is the range of total internal reflection in the prism P. Wavelengths: 1 $\lambda = 406$ nm, 2 $\lambda = 436$ nm, 3 $\lambda = 495$ nm, 4 $\lambda = 546$ nm, 5 $\lambda = 578$ nm. d is the thickness of the air layer

thickness τ of this silver layer was greater than 1000 Å.* A second quartz-glass-plate I was held by metallic foils F at some distance to plate II. The distance D between the plates near the silverlayer was controlled by elastic deformation of the plates, it could be measured unambiguously with the help of interference-fringes of white light with an estimated error of ± 1000 Å. The irradiated area of the silverlayer was about 3×3 mm. d is estimated to be constant in this area within 300 Å. Plate I was brought into optical contact with a 60° quartz-glass-prism by means of a liquid. The ratio of reflectivities for transverse magnetic to transverse electric light was measured as function of β, the angle of incidence upon the prism, for 5 different wavelengths in the visible region and for 3 different thicknesses d of the air layer (see Fig. 5).

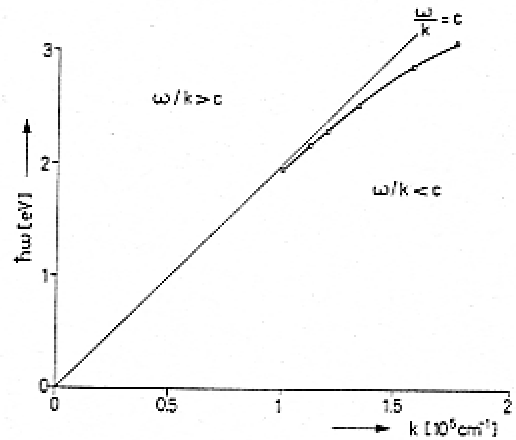


Fig. 6. Experimental dispersion $\omega(k)$ of the nonradiative SPW at the silver air-interface and $\omega = kc$ for plane waves in air

The angle of incidence upon the probe α is also plotted in Fig. 5 for $\lambda = 406$ nm – for the other wavelengths there are small deviations of about 0,5% for the α-scale due to the wavelength dispersion of n.

The results show a shift of the resonance to higher α for shorter wavelength because of the dispersion of the SPW. The dependence of the halfwidth and the strength of the resonance on d is in agreement with the discussion in Section III.

Fig. 6 shows the experimental dispersion of the SPW, the k_r-values are taken from the angle of minimum reflectivity ratio with the help of Eq. (7). The experimental errors are too small to be given in Fig. 6, they are given in Fig. 8.

* This thickness is large compared to the penetration depth of the fields of less than 300 Å. The silver layer can therefore be regarded as bulk material, the splitting of the SPW into the ω^+ and ω^- branches[11] must not be taken into account.

V. Exact Theory and Comparison with Experimental Results

The appropriate theory for this method of exciting nonradiative SPW on smooth surfaces is the Fresnel equations including the complex index of refraction and complex values for the angles of refraction to describe total reflection, extended to a set of different layers, as given by WOLTER[16]*.

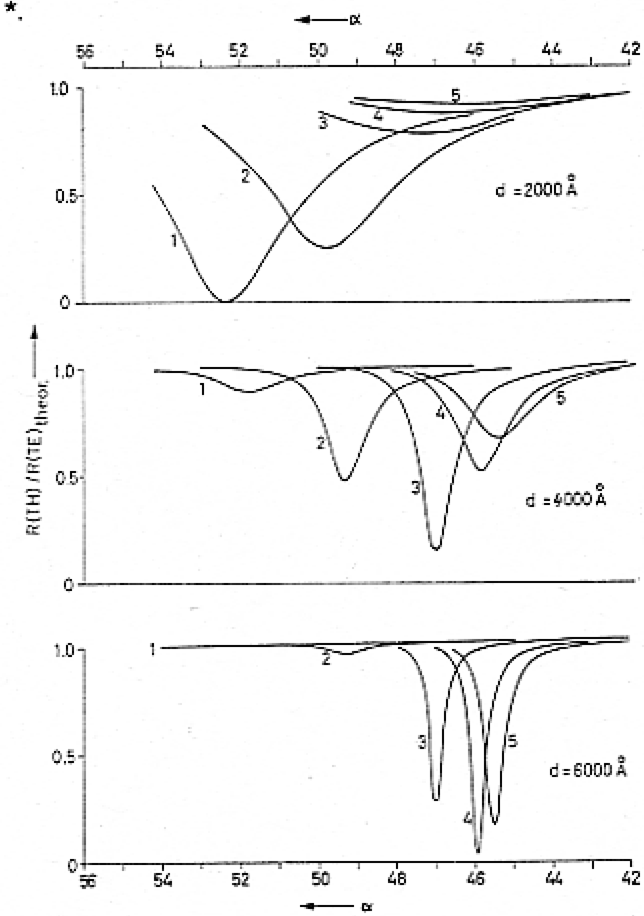


Fig. 7. Ordinate: Theoretical ratio of reflectivities R for TH and TE-waves. Abscissa: Angles α and β (for $\lambda = 406$ nm). Wavelengths as in Fig. 5

* In a series of interesting papers, SAUTER[18], FORSTMANN[19] and STURM[20] have shown, that the use of Fresnel's equations in metal optics is not accurate, because TH-light, striking a metal surface, excites also a longitudinal plasma wave, which is not taken into account in Fresnel's equations.
Calculations with a free electron gas model have shown, that this plasma wave has only a very small effect on the nonradiative plasma wave resonance[21]. It seems

For the calculation of the reflectivities, the reflection on the outer prism planes was also taken into account. The values for the index of refraction and for the angles of the prism are the experimental ones, the optical constants of Ag were taken from EHRENREICH and PHILIPP[17].

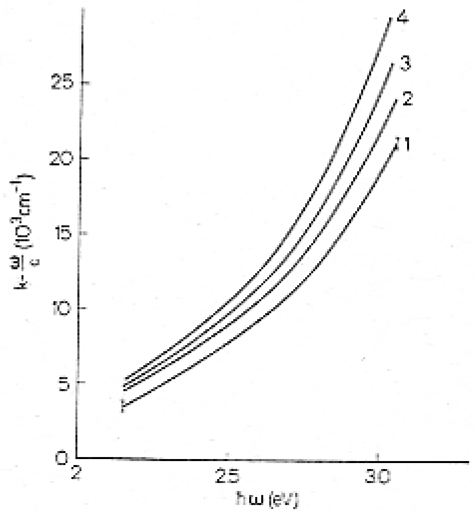


Fig. 8. Ordinate: Difference between wavenumber of the nonradiative SPW at the silver-air-interface and the plane waves in air at the same frequency. Abscissa: Frequency in units of $\hbar\omega$. *1* Experiment, error-bars correspond to errors in α of 10 minutes. *2* Theory, clean silver surface, optical constants (17). *3*, *4* Theory, silver surface contaminated with 10 and 20 Å of AgS

Fig. 7 shows the theoretical ratios of reflectivity for transverse magnetic to transverse electric light for the same wavelengths as in the experiment. No surface-contamination layer of AgS was included. The results are in qualitative agreement with the experimental ones. For $d = 2000$ Å and $\lambda = 406$ nm, the theory predicts that more than 99% of the incident TH-light is absorbed in the metal. For certain values of d, this will occur for the other wavelengths too. This should be compared with the maximal absorption of incident plane TH-waves, which is for $\lambda = 406$ nm and the same optical constants only 8.22%.

To have a comparison between experimental and theoretical k_r-values, the difference $k_r - \frac{\omega}{c}$ between the k_r-values of the SPW and the wavenumber ω/c of a plane light wave in vacuum of the same frequency (that is the horizontal distance between the dispersion curve and the line $k = \omega/c$ in Fig. 6) is plotted as function of ω in Fig. 8. The experimental curve lies underneath the theoretical ones. The discrepancy cannot be due to surface contamination because AgS-layers of 10 and 20 Å thickness increase this discrepancy, but could be explained by the difference of the optical data of evaporated Ag-films[22,23] and bulk material, as given by PHILIPP and EHRENREICH[17].

The comparison of the experimental results with optical data[22-24] other than those of PHILIPP and EHRENREICH has not yet been done.

VI. Conclusion

Nonradiative SPW can be coupled to light waves, without making use of surface roughness, by the method of frustrated total reflection. The appropriate theory is the extended Fresnel equations – no information about surface roughness is needed for a comparison between theory and experiment.

VII. Appendix

The easiest way of calculating internal and radiative damping is from the dispersion relation of the SPW for the geometry as given in Fig. 2b. (For the sake of simplicity, it is assumed $n_s = 1$, $n_p = n$.)

The dispersion relation is obtained in the same way as for the geometry of Fig. 2a, described in Section I.

$$(\varepsilon k_v + k_m) + \frac{i k_v n^2 - k_t}{-i k_v n^2 - k_t} e^{-2 k_v d} (\varepsilon k_v - k_m) = 0 \qquad (13)$$

with

$$k_v = \sqrt{k^2 - \frac{\omega^2}{c^2}}, \quad k_m = \sqrt{k^2 - \varepsilon \frac{\omega^2}{c^2}}, \quad k_t = \sqrt{n^2 \frac{\omega^2}{c^2} - k^2}.$$

The second term describes the influence of the radiation coupling. For $d \to \infty$, this dispersion relation is reduced to Eq. (3) (for $\eta = 1$).

impossible to differentiate between Fresnel's equations and Sauters theory by the type of experiment described here, as Fresnel's equations are a very close approximation of Sauter's theory.

16 WOLTER, H.: Handbuch der Physik, Bd. XXIV. Berlin-Göttingen-Heidelberg: Springer 1956.
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The dispersion relation has only a complex solution, but one is still free to chose as real either ω or k. As the SPW is excited by monochromatic light, ω is taken as real and k as complex, as already mentioned in Section III.

$$k = k_r + i\,k_i. \tag{14}$$

The radiation term has influence both on k_r and k_i, but only its influence on k_i will be discussed here. k_i is calculated from the imaginary part of Eq. (13). Using only first order terms of imaginary expressions, one gets

$$k_i = k_{ii} + k'_{ir}\,e^{-2k_0 d} \tag{15}$$

with

$$k_0 = \sqrt{k_r^2 - \frac{\omega^2}{c^2}}$$

$$k_{ii} = \varepsilon_2 \frac{-\varepsilon_1 k_0^2 - \dfrac{1}{2}\dfrac{\omega^2}{c^2}}{(\varepsilon_1^2 - 1)\,k_r}, \tag{16}$$

$$k'_{ir} = \frac{4\varepsilon_1^2 k_0^2 k_r n^2}{(k_0^2 n^4 + k_r^2)(\varepsilon_1^2 - 1)\,k_r}. \tag{17}$$

The first term describes internal damping and is proportional to ε_2, the second radiation damping.

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Variational Methods for the Ground State of Liquid Helium[4]

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Assuming a Bijl-Jastrow-type wave function for the ground state of liquid He^4, one can express the energy as a functional of the pair distribution function $g(r)$ when use is made of one of several "cluster approximations" known from the theory of classical fluids. The applicability of these approximations, and especially an integrodifferential equation for $g(r)$ derived by Abe and Hiroike, are discussed. It is shown that both the HNC and the PY approximations, when used consistently, yield the phonon behaviour of the liquid-structure factor $S(k)$ for small k. In the HNC approximation the energy as a function of density is calculated by a variational procedure. The velocity of sound following from $\lim_{k\to 0} S(k)$ is in good agreement with experiments and, at the equilibrium density, also with that calculated from the energy-versus-density curve. In the PY approximation a minimum of the energy expectation value does not exist without further restrictions on the trial wave function.

1. Introduction

The hamiltonian of a system of N helium^4 atoms of mass m is given by

$$H(r_1 \ldots r_N) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla_i^2 + \sum_{j>i=1}^{N} v(r_{ij}) \tag{1}$$

where the distance between two particles is abbreviated by $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. One has not yet succeeded in calculating the exact pair potential $v(r)$ from first principles. The most commonly used potential is the empirically determined Lennard-Jones potential[1]

$$v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

with $\sigma = 2.556$ Å and $\varepsilon = 10.22$ °K, which will be used here too to make comparisons with other calculations possible. The influence of many-

* Based an a doctoral dissertation accepted by the Fakultät für Allgemeine Wissenschaften der Technischen Hochschule München.

1 Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird: Molecular theory of gases and liquids, 2nd printing, p. 1110. New York: J. Wiley & Sons, Inc., 1965.