thought to be amenable only to tight-binding or atomic-like treatments, in contrast with previously held notions.[7,8] The success of the Wannier exciton model in interpreting Baldini's krypton results[11] suggests that other electronic properties of the solid rare gases are capable of being understood in the framework of effective-mass theory.

ACKNOWLEDGMENTS

The author is grateful to Professor Robert S. Knox, his principal thesis advisor, for suggesting this problem, and for his indispensable help and assistance. He thanks Dr. Franco Bassani of Argonne National Laboratory, who took an early interest in this problem and assisted the author in several phases of the work. Helpful conversations were held with Professor Giancarlo Baldini and Professor Albert Gold, and Dr. Maria Miasek. The author thanks Dr. O. C. Simpson of Argonne National Laboratory for his hospitality during the summer of 1962, when this work was initiated. He is grateful to M. Yoshimine and the staff of the computing center at Argonne National Laboratory, and thanks the staff of the University of Rochester computing center for their assistance.

PHYSICAL REVIEW VOLUME 132, NUMBER 4 15 NOVEMBER 1963

Plasma Resonance Absorption in Thin Metal Films*

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(Received 15 July 1963)

The transmission of p- and s-polarized light through thin silver films as a function of wavelength and angle of incidence has been measured. As predicted, a dip in transmission occurs in the vicinity of the plasma frequency only for the p-polarized light. This dip is associated with the excitation of a collective-type surface plasma mode in the thin film by the electromagnetic wave. The plasma frequency of the film can be accurately determined from this dip to occur at 3.80 eV.

I. INTRODUCTION

WHEN a charged particle passes from one dielectric medium to another, electromagnetic radiation is is emitted because of the rearrangement of the induced surface charges. This "transition radiation" was first calculated by Ginzburg and Frank[1] and then extended by other authors.[2,3] Ferrell[4] has shown that, for the case of a thin metal film, a simple physical picture can be used to predict a peak in the transition radiation around the plasma frequency. Subsequently, other authors[5–8] have shown that this peak is also predicted by the usual theory of the transition radiation from a metal slab in the limit of small thickness. More recently, a quantum-mechanical calculation of this peak has also been made.[9] This predicted peak in the transition radiation has been seen experimentally.[10]

On the basis of Ferrell's physical picture for the peak, it was predicted that electromagnetic radiation of the correct polarization and non-normal incidence would show anomalous behavior around the plasma frequency in interacting with thin metal films.[11] In the next section we describe in more detail the physical ideas involved and present the theoretical expressions which describe the interaction of electromagnetic waves with thin metal films. The last section describes the experimental results which show the expected behavior and gives a discussion of the results.

II. PHYSICAL CONSIDERATIONS

Consider a metal film of an ideal electron gas of thickness d. If the film is thin enough, then the type of oscillation in the film illustrated in Fig. 1 should occur. This

* This work was reported at the Washington meeting of the American Physical Society [A. J. McAlister and E. A. Stern, Bull. Am. Phys. Soc., 8, 392 (1963)]. This research has been supported in part by the Advanced Research Projects Agency.

[1] V. L. Ginzburg and I. M. Frank, Zh. Eksperim. i Teor. Fiz. **16**, 15 (1946).

[2] V. E. Pafomov, Zh. Eksperim. i Teor. Fiz. **33**, 1074 (1957) [translation: Soviet Phys.—JETP **6**, 829 (1958)].

[3] G. M. Garibian and G. A. Chalikian, Zh. Eksperim. i Teor. Fiz. **35**, 1285 (1958) [translation: Soviet Phys.—JETP **8**, 894 (1959)]. See also R. H. Ritchie and H. B. Eldridge, Bull. Am. Phys. Soc. **4**, 384 (1959).

[4] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).

[5] E. A. Stern, Bull. Am. Phys. Soc. **6**, 11 (1961).

[6] E. A. Stern, Phys. Rev. Letters, **8**, 7 (1962).

[7] V. P. Silin and E. P. Fetisov, Phys. Rev. Letters **7**, 374 (1961).

[8] R. H. Ritchie and H. B. Eldridge, Phys. Rev. **126**, 1935 (1962).

[9] N. Matsudaira, J. Phys. Soc. Japan **18**, 380 (1963).

[10] R. W. Brown, P. Wessel, and E. P. Trounson, Phys. Rev. Letters **5**, 472 (1960); W. Steinmann, Phys. Rev. Letters **5**, 470 (1960); A. L. Frank, E. T. Arakawa, and R. D. Birkhoff, Phys. Rev. **126**, 1947 (1962).

[11] R. A. Ferrell and E. A. Stern, Am. J. Phys. **31**, 810 (1962).

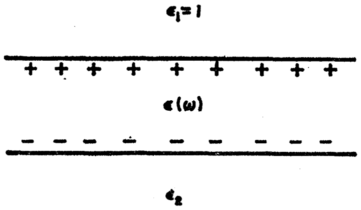

FIG. 1. Illustration of the type of plasma oscillation excited. Charges appear at the surfaces only, with zero volume charge density.

oscillation can be initiated by a rigid displacement of the electrons in the film which produces a negative-surface charge on one face and a positive surface charge on the other face with no volume charge present. The magnitude of the surface charge/cm^2 is nex, where n is the number of electrons per cm^3, e is the electronic charge, and x is the magnitude of the rigid displacement. For a thin enough film the electric fields can penetrate the film and produce a force of $4\pi ne^2x$ on each electron. The subsequent surge of electrons governed by $md^2x/dt^2 = -4\pi ne^2x$, where m is the mass of an electron, overcompensates the charge, reversing its sign. This process then repeats itself oscillating at the plasma frequency $\omega_p = (4\pi ne^2/m)^{1/2}$ of the film. If the charge distribution is allowed to have some sinusoidal dependence in the direction tangent to the surface, then some electric fields would extend outside the film and, as shown by Ferrell,[4] couple to the electromagnetic field and radiate. Ferrell reasoned that electrons passing through thin metal films would excite the described surface charge oscillation which would then radiate at the plasma frequency.

This suggests that the inverse process should occur. An electromagnetic wave which has a component of electric field normal to the surface of the film should be able to excite this surface plasma mode. Thus, at the plasma frequency of the metal, one expects a strong interaction between an electromagnetic wave incident at non-normal incidence and p-polarized with its electric field in the plane of incidence, and the surface plasma mode. This strong interaction manifests itself as a dip in the transmission or a peak in the reflection around the plasma frequency. Also, one would expect no interaction for the s-polarized wave which has no normal electric field. The calculation of this effect is straightforward. The metal film is represented as a frequency-dependent dielectric medium $\epsilon(\omega)$. To agree with the experimental conditions described later, the film is assumed to be in contact on one side with a dielectric medium ϵ_2 and on the other side with vacuum, $\epsilon_1 = 1$. The transmission and reflection from this film are calculated by the standard methods for an incident p-polarized electromagnetic wave. The result of this calculation is

$$T = \frac{4\epsilon_2^{3/2}}{|(\epsilon_2 + k_2/\cos\theta)\cos\beta kd - i(k_2\epsilon/k + k\epsilon_2/\epsilon\cos\theta)\sin\beta kd|^2}, \tag{1}$$

$$R = \left|\frac{(\epsilon_2 - k_2/\cos\theta)\cos\beta kd - i(k_2\epsilon/k - k\epsilon_2/\epsilon\cos\theta)\sin\beta kd}{(\epsilon_2 + k_2/\cos\theta)\cos\beta kd - i(k_2\epsilon/k + k\epsilon_2/\epsilon\cos\theta)\sin\beta kd}\right|^2, \tag{2}$$

where

$$k_2 = (\epsilon_2 - \sin^2\theta)^{1/2}$$
$$k = (\epsilon - \sin^2\theta)^{1/2}, \quad \mathrm{Re}k > 0, \quad \mathrm{Im}k > 0,$$
$$\beta = 2\pi/\lambda.$$

λ is the wavelength of the incident light, d is the thickness of the film, and θ is the angle of incidence measured from the film normal. For very thin films and for $\epsilon_2 = 1$ these expressions reduce to

$$T = [4(\omega - \omega_p)^2 + \tau_d^{-2}]/[4(\omega - \omega_p)^2 + (\tau_d^{-1} + \tau_r^{-1})^2], \tag{3}$$

$$R = \tau_r^{-2}/[4(\omega - \omega_p)^2 + (\tau_d^{-1} + \tau_r^{-1})^2], \tag{4}$$

showing the expected peak in reflection and the dip in transmission. Here,

$$\tau_d^{-1} = \frac{2\epsilon_i}{\epsilon'}; \quad \tau_r^{-1} = \frac{2}{\epsilon'}\frac{\pi d}{\lambda}\frac{\sin^2\theta}{\cos\theta},$$

$\epsilon = \epsilon_r + i\epsilon_i$, and the approximation $\epsilon_r = \epsilon'(\omega - \omega_p)$ is made, where ϵ' is $(d\epsilon_r/d\omega)$ evaluated at the plasma frequency ω_p. The plasma frequency ω_p is defined as that frequency where $\epsilon_r = 0$. Numerical computations of Eqs. (1) and (2) have been made for various cases.[12] The calculation for s-polarized light shows no structure at the plasma frequency.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Measurements were made on the transmission of light through thin silver films as a function of angle of incidence and wavelength. The measurements were made with a Perkin–Elmer model No. 350 spectrophotometer modified somewhat. The two senses of polarization were obtained by passing the light beam through a Wollaston prism. The prism split the beam into two perpendicularly polarized ones and the undesired beam was masked out. The equipment was adjusted so that with no sample present but with the Wollaston prism, a flat response of intensity versus wavelength was obtained for both senses of polarization separately. Next, the quartz substrates without any

[12] Extensive work has been done on Eq. (2) by R. Guertin and F. Stern (private communication). M. Hattori, K. Yamada, and H. Suzuki, J. Phys. Soc. Japan **18**, 203 (1963).

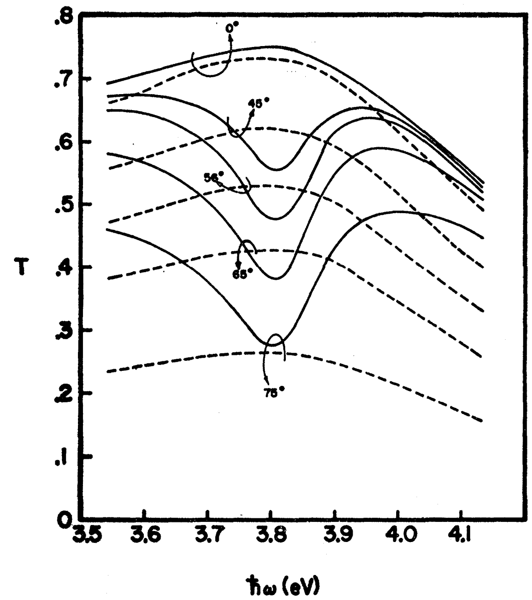

FIG. 2. Experimental values of the transmittance on an arbitrary scale of the 150-Å film as a function of photon energy, for various angles of incidence. The solid curves are for p polarization, the dashed curves for s polarization. The pairs of curves corresponding to a given angle of incidence are encircled with the same arrow.

silver films were placed in the path of the beam and the expected transmission versus wavelength curves were obtained without any unusual structure. Finally, silver films were evaporated on the quartz substrates and the measurements repeated. The experimental results are shown in Figs. 2–4 for film thickness of 150, 190, and 220 Å. The film thicknesses were measured with a Tolansky interferometer. As can be seen, the predicted dip around the plasma frequency of silver is very apparent. Only the light with an electric-field component normal to the film shows this dip. These results are in complete qualitative agreement with the excitation of the surface plasma mode.

An interesting fact is that this effect is not very sensitive to the state of the silver film. The 220-Å film had been stored for $2\frac{1}{2}$ months under vacuum and had been exposed to atmosphere for a time equivalent to several days. The other two films had been evaporated, stored 5 days under vacuum, and exposed to the atmosphere for less than 2 h before all measurements were completed. All films show the expected structure. Measurements by Yamaguchi[13] on extremely thin heat treated silver films of less than 60-Å thicknesses also have some indication of the excitation of the surface plasma mode. He purposely heat-treated the films to produce a two-dimensional aggregate of small silver particles and obtained an absorption spectrum more complicated than for a homogeneous film. The absorptions near the plasma frequency for his films occur at energies a few tenths of electron volt less than the plasma frequency of bulk silver of 3.75 eV as obtained from optical constants measurements.[14] The homogeneous films used in this experiment give a more reliable confirmation of the excitation of the surface plasma mode since the theory assumes a homogeneous film. The effects found in the measurements reported here peak about 0.05 eV higher than the plasma frequency of bulk silver as determined by optical constants measurements.

In Fig. 3, results of Eq. (1) for the 190-Å film at 56° have been plotted. The transmission scale is arbitrary, with the curves fitted to the experimental value at 3.55 eV. The dotted curve has been calculated with the dielectric constants measured optically by Taft and Phillips.[14] As can be seen, the calculated curve shows sharper structure and has a plasma frequency about 0.05 eV lower in energy than the measured value. This indicates that the films used had a larger τ^{-1} and a higher plasma frequency than the published optical data. The dash-dot curve shows the calculated result for ϵ_i about 1.5 times the optical values and ϵ_r the same as the optical values but shifted 0.05 eV higher in energy to give $\hbar\omega_p = 3.80$ eV. As can be seen, this gives a better fit to the measured values.

The values of energy corresponding to the plasma frequency for silver of 3.75 and 3.70 eV were obtained by Steinmann,[10] and Brown *et al.*[10] from unsupported silver films. They measured the peak in the transition

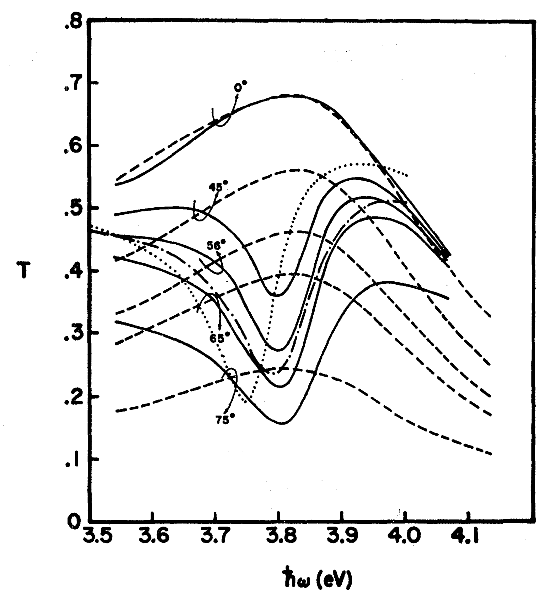

FIG. 3. Experimental values of the transmittance on an arbitrary scale of the 190-Å film as a function of photon energy, for various angles of incidence. The solid curves are for p polarization, the dashed curves for s polarization. The pairs of curves corresponding to a given angle of incidence are encircled with the same arrow. The dotted curve for 56° is a calculated one using Eq. (1) and optical data for the dielectric constants. The dash-dot curve for 56° is a calculated one using Eq. (1) and assumed values of the dielectric constants to give a better fit to the experimental curve.

[13] S. Yamaguchi, J. Phys. Soc. Japan **17**, 1172 (1962).

[14] E. A. Taft and H. R. Philipp, Phys. Rev. **121**, 1100 (1961).

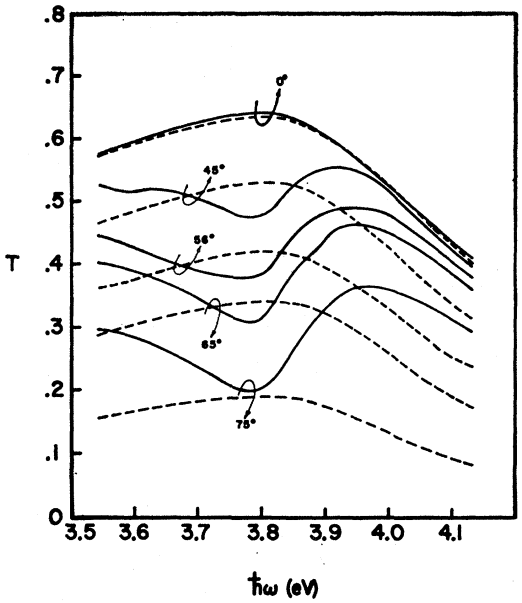

FIG. 4. Experimental values of the transmittance on an arbitrary scale of the 220-Å film as a function of photon energy, for various angles of incidence. The solid curves are for p polarization, the dashed curves for s polarization. The pairs of curves corresponding to a given angle of incidence are encircled with the same arrow.

radiation emitted as electrons of about 20-keV energy passed through the film. As Yamaguchi[13] has pointed out, in these types of experiments, the electron beam heats the film. To study the effect of this heating, Yamaguchi purposely heat-treated thin silver films and found the plasma frequency to be lowered by this process, the thinner films being lowered by the greatest amount. Although the films Yamaguchi studied were much thinner than the ones used by Steinmann and Brown *et al.* it still is indicative that the plasma frequency found in their measurements may be less than the value in the experiment reported here where the silver films are not heat treated. Thus, the plasma frequency of 3.80 eV measured in the experiment here appears to be a reasonable result for the evaporated silver films with no subsequent heat treatment used in this experiment. It should also be mentioned that no particular care was taken in preparing the silver films used in this experiment because its purpose was to detect the coupling between light and the surface plasma mode and not to determine the properties of silver. The evaporation was performed in a vacuum of around 5×10^{-6} mm Hg with a Mo boat. The films were exposed to air from about an hour to several days and the film that had the longest exposure to the air also showed the greatest value for ϵ_i. However, all films showed the dip at the plasma frequency, and all at the same value of 3.80 eV.

The excitation of the surface plasma mode has also manifested itself by producing a peak of photoelectron emission from thin alkali metal films at the plasma frequency.[15] In this case, the large electric fields produced in the thin film at the plasma frequency due to the excitation of the surface plasma mode, enhances the photoelectric emission. The same method of the coupling of the transverse electromagnetic wave in thin films with a plasma oscillation, which in an infinite medium can only be longitudinal, can also be used to couple the electromagnetic field with phonons that would be only longitudinal in an infinite medium.[16,17] Such an experiment has recently been performed[17] and is the complete analog of the experiment reported here with a longitudinal phonon mode replacing the surface plasma mode discussed here.[18]

In conclusion, it is important to emphasize that the dip in transmission found in this experiment can only be explained as the excitation of a collective mode and cannot be explained as an interband-absorption effect. Such an interband absorption would give dips for both s and p polarization and for all angles of incidence. This experiment conclusively proves that silver has a plasma resonance around 3.80 eV and confirms Ferrell's model of the coupling between electromagnetic radiation and a surface plasma mode in thin films. The nature of this plasma resonance in silver has been discussed by various authors.[19] The results presented here also indicate that the plasma frequency and the dielectric constants in the vicinity of the plasma frequency can be obtained quite accurately by the measurement described here. The width of the transmission dip and its magnitude determine the slope of the real part of the dielectric constant and the value of the imaginary part.

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[15] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **28**, 330(1938).
[16] E. Burstein (private communication).
[17] D. W. Berreman, Phys. Rev. **130**, 2193 (1963).
[18] We would like to thank Dr. F. Stern for informing us of the existence of Refs. 15 and 17.
[19] The most recent reference is H. Ehrenreich and H. Philipp, Phys. Rev. **128**, 1622 (1962).