



HAL
open science

The anomalous infra-red absorption of alkali metals and collective oscillations in small metal particles

A. Meessen

► **To cite this version:**

A. Meessen. The anomalous infra-red absorption of alkali metals and collective oscillations in small metal particles. *Journal de Physique*, 1972, 33 (4), pp.371-381. 10.1051/jphys:01972003304037100 . jpa-00207260

HAL Id: jpa-00207260

<https://hal.science/jpa-00207260>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification :
Physics Abstracts
 17.10, 18.10

THE ANOMALOUS INFRA-RED ABSORPTION OF ALKALI METALS AND COLLECTIVE OSCILLATIONS IN SMALL METAL PARTICLES

A. MEESSEN

Département de Physique de l'Etat Solide, Institut de Physique Théorique,
 Parc d'Arenberg, Université Catholique de Louvain, Belgique

(Reçu le 11 août 1971)

Résumé. — Les maxima qui ont été découverts par Mayer dans le spectre d'absorption d'échantillons massifs de Na et de K, et qui n'ont pas pu être expliqués par les propriétés de volume de ces métaux, résultent en réalité d'un effet de rugosité de surface. La méthode ellipsométrique conduit, en effet, à une erreur systématique quand le métal est recouvert d'une distribution assez dense de petits grains métalliques. Les constantes optiques apparentes dépendent des constantes optiques du métal massif et des constantes effectives de la couche granulaire. De tels films minces peuvent être préparés également par évaporation du métal sur un support transparent, et leurs propriétés optiques peuvent être décrites en fonction de deux types d'oscillations collectives dans ces grains. Les résultats de Payan pour des couches granulaires de Na et de K, ainsi que les résultats de Mayer, correspondent à l'excitation d'oscillations collectives, parallèlement à la surface du support. L'absorption de résonance est particulièrement intense, quand elle se situe dans le domaine spectral où l'absorption du métal massif est très faible, comme cela se présentait pour ces métaux alcalins.

Abstract. — It is shown that the resonance like absorption peaks, which were discovered by Mayer for bulk samples of Na and K, and which could not be explained in terms of the bulk properties of the metal, are actually due to a surface roughness effect. The ellipsometric method leads, indeed, to a systematic error when the metal surface is covered by a dense distribution of small metal particles. The apparent optical constants depend on the optical constants of the bulk metal and on the effective optical constants of the thin granular film. Such films can also be prepared by evaporating the metal on a transparent substrate, and their optical properties can be described in terms of two types of collective oscillations within the metal particles. Payan's results for thin granular films of Na and K, as well as Mayer's results, correspond to an excitation of collective oscillations parallel to the plane of the substrate. This resonance absorption is particularly strong, when it occurs in the spectral region where the absorption of the bulk metal is very small, as it happened to be for these alkali metals.

Introduction. — Mayer and co-workers [1], [2] discovered that the optical properties of alkali metals do not follow the predictions of the nearly-free-electron model [3]-[5]. For Na and K they found actually a strong absorption peak, just below the threshold for interband transitions, where the Drude absorption should be quite small. Since they measured the optical constants of bulk samples, of high purity, by observing the polarimetric properties of the light which is reflected at a mirror-like metal-vacuum interface, it was assumed that they determined the true optical properties of the *bulk* metal. The optical constants of a metal are commonly measured, indeed, by the ellipsometric method.

The discovery of this unexpected resonance-like absorption [6] caused considerable interest, and stimulated many theoretical investigations [7]-[20]. Various processes which could lead to an optical absorption, within the bulk of these metals, were considered in great detail. But no satisfactory expla-

nation of Mayer's anomalous absorption peaks seems to have emerged, so far. The situation became even more confusing, when it turned out that Mayer's results could not be reproduced by Smith [21], who applied the ellipsometric method to multiple reflections on metal-quartz interfaces.

We were struck, however, by the correlation which exists between Mayer's results and those of Payan [22], [23], who measured the optical absorption of *thin granular* alkali metal films. These films which are prepared by evaporating the metal in vacuum on a transparent substrate, exhibit « anomalous » absorption peaks, like other metals [24]-[28]. But the anomalous absorption peaks of thin Na and K films occur nearly at the same frequencies as Mayer's anomalous absorption peaks.

The optical properties of thin granular films of alkali metals, on a glass substrate, have been analysed already by Wood [29], in 1902. With remarkable perspicacity he recognized all the essential features,

as well as the true origin of the observed « colours ». Maxwell-Garnett [30] developed then, in 1904, a very satisfactory theory for the optical properties of « metal glasses » which are formed by a uniform colloidal suspension of very small *spherical* metal particles in a glass matrix. The basic idea, was that the electric field of the incident light wave induces a dipole moment in each metal particle, and that one has to consider the average polarization of a small volume, containing many metal particles. The metal particles behave thus like the atoms or molecules of a gas. Gans [31], David [32] and Schopper [33] extended this model to the case of *ellipsoidal* metal particles, that are distributed uniformly within a *plane*, but without taking into account the effect of the lateral interactions among the polarized metal grains. This has been done by Yamagushi [34] and Bousquet [35]. The resulting theory provides a good understanding of the basic mechanism of the « anomalous » absorption in granular metal films, which is actually associated with the excitation of electronic *collective oscillations* in small metal particles. The theory implies some idealizations, of course, since the metal « islands » do rather tend to have a hemispherical form, than an ellipsoidal one. But these idealizations are justified by the simplicity of the corresponding formulas, and by the fact that more complex situations can still be reduced to the same model [36].

To relate the results of Payan and Mayer, we will *postulate* the existence of a dense distribution of small metal particles on the surface of Mayer's bulk metal samples. This could be due to a polycrystalline structure of the surface, or to a delayed condensation of residual alkali metal atoms, which are liberated, for instance, from the walls of the vessel where the metal was distilled. The fact that the metal surface appeared to be « mirror like » [2] does not preclude the possible existence of a surface roughness layer, since a dense ensemble of small metal particles would act like a *continuous* film.

We have then to show that the existence of such a surface layer would lead to a systematic error, when one tries to determine the optical constants of a metal by means of the ellipsometric method. This method corresponds actually [37] to a measurement of the amplitude ρ and the phase Δ of the complex quantity

$$\frac{r_p}{r_s} = \rho e^{i\Delta} \quad (1)$$

where r_p and r_s represent the reflection amplitudes for plane polarized light, whose electric field vector is, respectively, parallel and perpendicular to the plane of incidence. The quantities ρ and Δ can be measured with high accuracy, while the quantities r_p and r_s can be easily related to the optical constants of the reflecting material, by means of Fresnel's

formulas. But what happens when there is a transition layer between the metal and the outside transparent medium ? And what happens, in particular, when this transition layer has the same structure as a thin, granular metal film ?

We will show, in section I, that the results of the ellipsometric method are, indeed, modified in such a way that one determines some « apparent » optical constants instead of the « true » optical constants of the bulk metal, when the metal surface is covered by a thin transition layer. This is suggested already by the experimental results of different authors for Na and K, and is confirmed by the general theoretical expressions. In section II, we recall and analyse the simple analytic formulas which can be obtained for the « effective » optical constants of a thin, granular metal film, using the model of ellipsoidal metal particles. We will stress the resonance character of the corresponding « anomalous » absorption, and its physical origin. We will also derive a simple law for the displacements of the absorption peaks for films of various mass-thickness showing that these displacements are due to the lateral interactions among the metal particles. By combining the results of the two previous sections, we conclude, in section III, that Mayer's anomalous absorption peaks can be explained in a natural way, by the effect of collective oscillations in small, metal particles on the surface of the bulk metal. This conclusion joins actually those of Berreman [38], Beaglehole and Hunderi [39] for other aspects of the optical properties of solids with a granular surface roughness. Fenstermaker and Mc Crackin [40], noted also that large errors can arise in the determination of the refractive index, by the ellipsometric method, in the presence of certain types of surface roughness.

I. The apparent optical constants of a metal with a surface layer. — 1.1 EXPERIMENTAL RESULTS FOR BULK SAMPLES OF Na AND K. — The index of refraction (n) and the index of absorption (k) of a metal are defined by the relations

$$\varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2nk, \quad (2)$$

where ε_1 and ε_2 are the real and imaginary parts of the dielectric constant ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of the metal. The absorption spectrum of the metal can thus be characterized by the spectral distribution of ε_2 or by the spectral distribution of the « optical conductivity »

$$\sigma = \frac{\omega\varepsilon_2}{4\pi} = \frac{c}{2\lambda} \varepsilon_2, \quad (3)$$

where $\omega = 2\pi c/\lambda$ represents the (angular) frequency of the incident light. The expression of σ is reduced, indeed, to the d. c. conductivity when $\omega \rightarrow 0$. Since the alkali metals should be well described by the nearly-free-electron model, we expect that their

absorption spectrum can be considered as a simple superposition of two contributions,

$$\sigma(\omega) = \sigma_D(\omega) + \sigma_I(\omega),$$

where

$$\sigma_D = \frac{A}{\omega^2} \quad (4)$$

and

$$\sigma_I = B(\omega_0 - \omega) \frac{\omega - \omega_1}{\omega^3} \quad (4')$$

A and B being constants.

The separability of the terms σ_D and σ_I follows from the fact that a conduction *electron* can only absorb a *photon*, when the electron is simultaneously scattered by a *third body*, in order to insure the conservation of energy and momentum. Considering separately the effect of electron-phonon and electron-lattice interactions, one finds, respectively the « Drude term » (σ_D) and the « interband term » (σ_I). σ_I is zero below the threshold frequency ω_0 and raises then to a maximum at about $(\frac{3}{2})\omega_0$, to drop slowly off at higher frequencies. This expression of σ_I was obtained by Wilson [4] and Butcher [5], with the assumption that the band structure of the metal corresponds to a parabola in the extended zone scheme. The values of the constants A and B in (4) and (4') depend on the strength of the electron-phonon and electron-lattice interactions in the metal.

The experimental results of different authors concerning the spectral distribution of σ for bulk samples of Na and K, are represented in figures 1a and 2a. There is a striking lack of general agreement among these results, as well as an astonishing variability with respect to the theoretical spectral distributions (4) and (4') for the nearly-free-electron model. It should be noted that all these measurements were performed by means of polarimetric methods. Although some measurements are already quite old [41], [42], they may be trustworthy since they were performed by protecting the alkali metal against contaminations, by observing the light reflection at a metal-glass interface. Ives and Briggs [43] used a metal-quartz interface for K and Rb, while he prepared metallic mirrors in vacuum for Na and Cs, as Mayer [1], [2] did for all his alkali metal samples. Ives and Briggs reported, however, that Cs mirrors have a tendency to become mat, as a consequence of an additional condensation of residual alkali metal atoms. This matness should be regarded as an indication for the formation of large, widely separated, *incoherently* scattering metal islands [29], since a dense distribution of small metal islands would act like a continuous film. The existence of such a fine granular surface soughness is therefore quite probable when the metallic mirror has been formed by condensation,

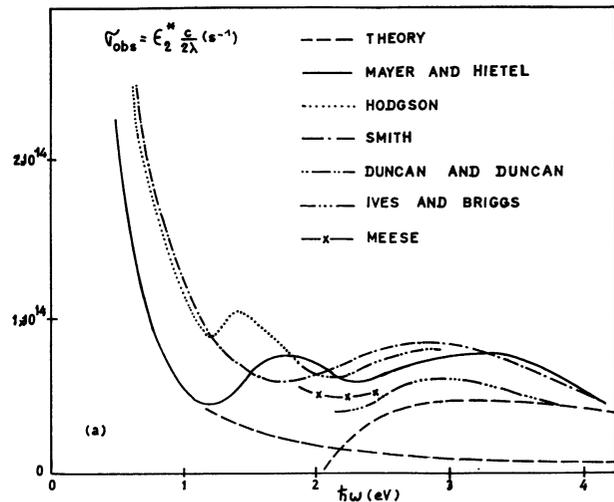


FIG. 1a. — The observed optical conductivity for bulk samples of Na, according to different authors, and the corresponding theoretical curves σ_D and σ_I , according to the nearly-free-electron model.

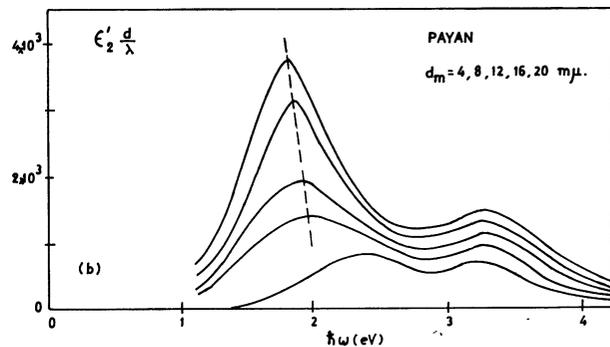


FIG. 1b. — The observed absorption spectrum for thin granular Na films of different mass thickness (redrawn).

after repeated distillations of the metal, as in Mayer's experiments. The fact that the results of the polarimetric methods can be distorted by a « transition layer » was mentioned already by Meese [42], who recalled the observations of Drude [44] for metallic mirrors with different kinds of surface polishing. Smith [21] and Hodgson [45] used multiple reflections at a metal-quartz interface. In this case, one has to expect a relatively flat, but very irregular surface roughness. This leads to an increased Drude absorption, because of diffuse electron-surface scattering, as stated by Smith. Hodgson, on the other hand, noted that σ varied for different Na-quartz interfaces by as much as 20 %. This seems to indicate that the ellipsometric method is, indeed, sensitive to the surface structure. He reported actually a spectral distribution curve for Na, where σ displays an anomalous absorption peak, which reminds us of Mayer's anomalous absorption peaks (see Fig. 1a).

1.2 EXPERIMENTAL RESULTS FOR THIN GRANULAR FILMS OF Na AND K. — The experimental results of Payan [22] for the optical absorption spectrum of

thin granular films of Na and K are represented, respectively, in figure 1*b* and 2*b*. He measured actually the spectral distribution of $2nk d/\lambda = \epsilon_2^* d/\lambda$, where λ is the wavelength of the incident light, while d and ϵ_2^* represent the thickness and the imaginary part of the dielectric constant of a *continuous* film, that is optically equivalent to the granular metal film. The mentioned quantity can be determined directly, by observing the reflection and transmission of very thin films, under nearly normal incidence. By evaporating the metal on a quartz substrate in ultra-high vacuum, he prepared granular films of various mass thickness (d_m), in order to measure their absorption spectrum.

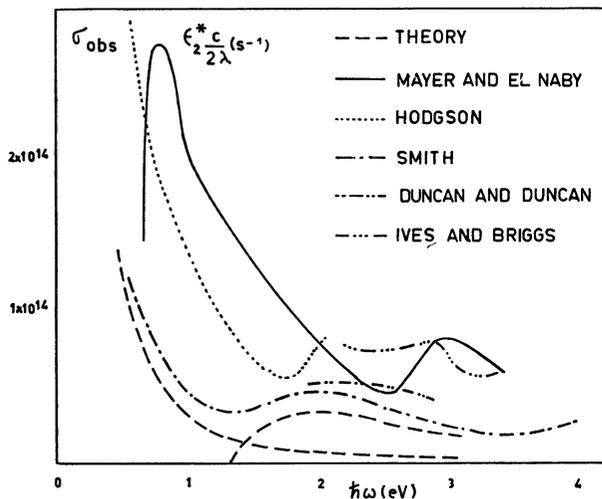


FIG. 2*a* — The observed optical conductivity for bulk samples of K, according to different authors, and the corresponding theoretical curves σ_D and σ_I , according to the nearly free-electron model.

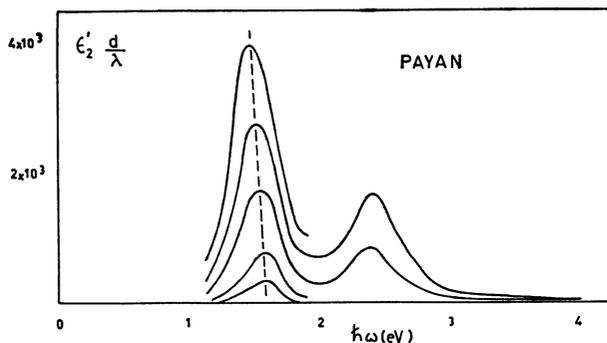


FIG. 2*b*. — The observed absorption spectrum for thin granular K films of different mass thickness (redrawn).

Payan found *two* peaks in the absorption spectrum of thin granular films of Na and K. Although the low frequency peak exhibits the characteristic displacement, which is generally observed for the « anomalous » absorption peak of granular metal films of increasing mass thickness, he suggested that this absorption could eventually be attributed to surface state transitions, while the higher frequency peak

could eventually be attributed to interband transitions. It appears, however (see Fig. 1 and 2), that the position and the form of the higher frequency peak does not correspond to the theoretically predicted distribution for interband transitions (4'). In section II, we will present evidence for attributing both peaks to collective oscillations in the metal islands. For the moment, we want only to call attention to the fact that Mayer's result for Na seems to correspond to the theoretically predicted curve, to which one has added a contribution that is proportional to Payan's results for thin granular films of Na. If this is true, we have to admit that the ellipsometric method did not yield the « true » value of the imaginary part of the dielectric constant of the bulk alkali metal (ϵ_2), but an « apparent » value

$$\epsilon_2^* = \epsilon_2 + \beta \epsilon_2', \quad (5)$$

where β is a constant and ϵ_2' the imaginary part of the effective dielectric constant of a thin granular film of the same metal. The validity of the suggested eq. (5) will be justified at the end of this paper. As a first step towards its proof, we have now to consider how the results of the ellipsometric method can be affected, in general, by the presence of a thin transition layer.

1.3 THE EFFECT OF A TRANSITION LAYER ON THE ELLIPSOMETRIC METHOD. — Since the ellipsometric method is based on eq. (1), we have only to investigate how the ratio p_p/r_s is modified by the presence of a *thin film* between the metal and the transparent medium, where light reflection is observed. The angle of incidence θ is fixed at some rather large value like 75° , for instance, as it is customary to insure optimal sensitivity for the ellipsometric method. The thickness d of the transition layer is assumed to be sufficiently small compared to the wavelength λ of the incident light, so that the parameter

$$\eta = \frac{2\pi d}{\lambda} = \frac{\omega d}{c} \ll 1. \quad (6)$$

ϵ , ϵ' and ϵ_0 represent, respectively, the dielectric constants of the bulk metal, the transition layer and the outside, transparent medium. The general expression [46] of the reflection amplitude reduces then, because of (6), to the following form

$$r = \frac{A^- - i\eta q' B^-}{A^+ - i\eta q' B^+},$$

where

$$A^\pm = g_0 \pm g$$

and

$$B^\pm = \frac{g_0 g}{g'} \pm g'.$$

The parameters g , g' and g_0 are functions of ε , ε' and ε_0 , as well as θ . But these functions are different for s and p polarization. When we define

$$q = (\varepsilon - n_0^2 \sin^2 \theta)^{1/2}, \quad q' = (\varepsilon' - n_0^2 \sin^2 \theta)^{1/2}$$

and

$$q_0 = n_0 \cos \theta$$

we have to set

$$g = q, \quad g' = q' \quad \text{and} \quad g_0 = q_0,$$

for s polarization and

$$g = \frac{q}{\varepsilon}, \quad g' = \frac{q'}{\varepsilon'} \quad \text{and} \quad g_0 = \frac{q_0}{\varepsilon_0},$$

for p polarization.

Since the surface layer is expected to be highly anisotropic, it may be necessary to introduce a *different* value ε'_s and ε'_p for the dielectric constant of the surface layer under the action of s and p polarized light, respectively. Under these circumstances, and retaining only first order corrections in η , we find that (1) takes the form

$$\begin{aligned} \rho e^{i\Delta} &= \frac{A_p^- A_s^+ - i\eta(q_p' B_p^- A_s^+ + q_s' B_s^+ A_p^-)}{A_p^+ A_s^- - i\eta(q_p' B_p^+ A_s^- + q_s' B_s^- A_p^+)} = \\ &= \frac{(a + b) - i\eta(a' + b')}{(a - b) - i\eta(a' - b')} \end{aligned}$$

where

$$\begin{aligned} a &= \varepsilon \cos^2 \theta - q^2, \quad b = \left(\frac{\varepsilon}{n_0} - n_0\right) q \cos \theta \\ a' &= q \left[(\varepsilon + \varepsilon'_p) \cos^2 \theta - q_p'^2 \frac{\varepsilon}{\varepsilon'_p} - q_s'^2 \right] \end{aligned} \quad (7)$$

and

$$b' = \cos \theta \left[q^2 \left(\frac{\varepsilon'_p}{n_0} - n_0 \right) - q_p'^2 \frac{n_0 \varepsilon}{\varepsilon'_p} + q_s'^2 \frac{\varepsilon}{n_0} \right]. \quad (8)$$

The parameters q'_s and q'_p correspond to q' where ε' has been replaced respectively by ε'_s and ε'_p . In the ideal case, where no surface roughness is present we have $\eta = 0$ and

$$\rho e^{i\Delta} = \frac{a + b}{a - b}. \quad (9)$$

This expression is modified in the following way, through the introduction of a thin surface layer ($\eta \ll 1$):

$$\rho e^{i\Delta} = \frac{a^* + b^*}{a^* - b^*} \quad (10)$$

where

$$a^* = a - i\eta a' \quad \text{and} \quad b^* = b - i\eta b'. \quad (11)$$

The expressions (10) and (9) have the same form, and it is only necessary to replace ε , q and θ by corresponding « *apparent* » values ε^* , q^* and θ^* , according to the relations (11). When we don't know that a surface layer exists, we will assume that the measurement of the quantities ρ and Δ , which are defined by eq. (1), have to yield the true optical constants of the bulk metal, while in fact they actually yield a modified value.

The relations (11) can be written explicitly with the aid of (8), when we assume that $q^2 = \varepsilon$ and $q'^2 = \varepsilon^*$. This *assumption* is valid in the spectral region where

$$\varepsilon \gg \varepsilon_0 \quad \text{and} \quad \varepsilon^* \gg \varepsilon_0. \quad (12)$$

The effective dielectric constant ε^* and the effective angle of incidence θ^* which allow us to pass from (9) to (10) are then given by the two equations

$$\begin{aligned} \varepsilon^*(\cos^2 \theta^* - 1) &= \varepsilon(\cos^2 \theta - 1) - i\eta \sqrt{\varepsilon} \times \\ &\times \left[(\varepsilon + \varepsilon'_p) \cos^2 \theta - q_p'^2 \frac{\varepsilon}{\varepsilon'_p} - q_s'^2 \right] \end{aligned} \quad (13)$$

$$\begin{aligned} (\varepsilon^* - \varepsilon_0) \sqrt{\varepsilon^*} \cos \theta^* &= \\ &= \left[(\varepsilon - \varepsilon_0) \sqrt{\varepsilon} - i\eta \varepsilon \left(\varepsilon'_p - \varepsilon_0 + q_s'^2 - \frac{\varepsilon_0 q_p'^2}{\varepsilon'_p} \right) \right] \cos \theta. \end{aligned} \quad (14)$$

In the limiting case where $\cos \theta \rightarrow 0$, we get from (14) that $\cos \theta^* \rightarrow 0$, and from (13) that the effective (complex) dielectric constant

$$\varepsilon^* = \varepsilon + \beta \left[\left(1 - \frac{\varepsilon_0}{\varepsilon'_p} \right) \varepsilon + (\varepsilon'_s - \varepsilon_0) \right] \quad (15)$$

where

$$\beta = -i\eta \sqrt{\varepsilon}. \quad (16)$$

Expression (15) can be corrected, for *small* values of $\cos \theta$ (knowing that $\cos^2 \theta \cong 0.06$ when $\theta \cong 75^\circ$). We have only to take the square of eq. (14), retaining only the first order terms in η , so that we can eliminate $\varepsilon^* \cos^2 \theta^*$ from eq. (13). The effective dielectric constant then becomes

$$\begin{aligned} \varepsilon^* &= \left[1 + \beta \left(1 - \frac{\varepsilon_0}{\varepsilon'_p} \right) + \beta F \cos^2 \theta \right] \varepsilon + \\ &+ \beta [(\varepsilon'_s - \varepsilon_0) - (\varepsilon'_p - \varepsilon_0) \cos^2 \theta] \end{aligned} \quad (17)$$

where

$$F = 1 + \frac{\varepsilon_0}{\varepsilon'_p} + \frac{2(\varepsilon'_p - 3\varepsilon_0)}{\varepsilon - \varepsilon_0} + \frac{2\varepsilon_0(\varepsilon + \varepsilon_0)}{\varepsilon'_p(\varepsilon - \varepsilon_0)}. \quad (18)$$

1.4 THE SPECTRAL REGION OF THE DRUDE ABSORPTION. — In the infra-red, below the threshold for interband transitions, we can express the dielectric

constant $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of the bulk metal, according to the Drude theory :

$$\varepsilon_1 = \varepsilon_c - \frac{\omega_p^2}{\omega^2} \quad \text{and} \quad \varepsilon_2 = \frac{\omega_p^2 \gamma}{\omega^3}. \quad (19)$$

These expressions imply that $\omega \gg \gamma = 1/\tau$, where τ is the Drude relaxation time. The (free-electron) plasma frequency ω_p depends on the density (n) and the effective mass (m^*) of the conduction electrons :

$$\omega_p^2 = \frac{4 \pi n e^2}{m^*} \quad (20)$$

ε_c has been introduced to take into account the polarizability of the ion cores in the crystal lattice. Below the threshold for interband transitions, where $\omega \ll \omega_p$, we get simply

$$\varepsilon \cong \varepsilon_1 \cong - \frac{\omega_p^2}{\omega^2}$$

and (21)

$$\beta \cong \frac{\eta \omega_p}{\omega} = \frac{\omega_p d}{c} = \frac{2 \pi d}{\lambda_p},$$

The parameter β is thus real and small, as long as $d \ll \lambda_p \ll \lambda$. Since (17) differs only from (15) by terms of the order $\beta \cos^2 \theta$, which corresponds to the product of two small quantities, it is usually sufficient to consider the simpler relation (15). The apparent dielectric constant ε^* is, of course, equal to the true dielectric constant ε , when the film thickness parameter $\beta \rightarrow 0$. The first eq. (21) provides a *justification* of the first condition (12), since $\varepsilon_0 \cong 1$. The second condition (12) is justified (for the moment) by the experimentally observed fact that $\varepsilon_1^* \cong \varepsilon_1$.

We conclude therefore that the presence of a surface layer (which could be due to adsorbed atoms as well as to a surface roughness), can induce us into making an error. Instead of the « true » optical constants of the reflecting metal, we will only get the « apparent » optical constants, which are determined by (15) or (17). It should be noted that these expressions depend in a different way on the effective dielectric constants ε'_p and ε'_s of the surface layer for p and s polarized light. This fact will turn out to be very important. But we have first to show that the effective dielectric constant of a thin *granular* metal film has not only a peculiar polarization dependance, but also a resonance like structure that is associated with the excitation of collective oscillations.

II. The optical properties of thin granular metal films.

— 2.1 COLLECTIVE OSCILLATIONS IN SMALL METAL PARTICLES. — Let us consider a metal particle, whose dimensions are very small compared to the wavelength of the incident light, so that it is possible to assume that the particle is bathing in a uniform electric field

E , that changes with time, according to the frequency of the incident light wave. The applied field polarizes the material of the metal particle, and induces a *surface charge* of opposite sign on the two surfaces which delimitate the metal particle in the direction of the applied field. Assuming that the metal particle is surrounded by vacuum, we can say that the surface charge depends only on the polarization density P within the metal grain, and the particular shape of this grain. The induced surface charges create, however, a secondary electric field E' that tends to be oriented in the opposite direction of the applied field E , and since the effective polarization density P is given by

$$P = \alpha(E + E') \quad (22)$$

where α is the polarizability of the material, one usually calls E' the « *depolarizing field* ». When the shape of the metal particle is relatively symmetrical along the direction of the applied field, we can assume that

$$E' = - 4 \pi f P, \quad (23)$$

where f is a « form factor », whose value increases for decreasing dimensions of the metal particle along the direction of the applied field. Combining (22) and (23), we get

$$P = \alpha' E$$

with

$$\alpha' = \frac{1}{4 \pi} \frac{(\varepsilon - 1)}{1 + (\varepsilon - 1)f}, \quad (24)$$

where $\varepsilon = 1 + 4 \pi \alpha$ is the dielectric constant of the material that constitutes the metal particle. The overall result is that the applied electric field E induces in the metal grain a dipole moment, whose value $p = \alpha' V E$ — where V represents the volume of the metal particle — is a frequency dependant function. Although ε is a complex quantity, it is easily deduced from (24) that the induced dipole moment will oscillate with the greatest amplitude, when the frequency of the incident light is such that $1 + (\varepsilon_1 - 1)f = 0$. From (19) it follows that this resonance frequency is given in the spectral region of the Drude absorption by $\omega_r = \omega_p \sqrt{f}$. The same result can be obtained more directly, when we consider the forced oscillations of the conduction electrons, under the action of the applied field E and the depolarizing field E' . Since the polarization density $P = - e n x$, where n represents the density of the conduction electrons and x their average displacement, we find that the equation of motion of each conduction electron becomes

$$m^* \ddot{x} = - e(E + E')$$

or

$$m^*(\ddot{x} + \omega^2 x) = - eE,$$

when we make use of (23), (20) and the previous definition of the frequency ω_r , while m^* represents the effective mass of the conduction electrons. We would obtain a similar equation for all the conduction electrons within the metal particle, by considering the total mass and the total charge of all these electrons. Thus it clearly appears that the conduction electrons in a metal particle behave like *forced harmonic oscillators*, with a resonance frequency ω_r .

The basic relation (23) is only an approximation, in general. But this relation is absolutely correct when the field is applied along the principal axes of *ellipsoidal* metal particles. It is also possible, in that case, to take into account the effect of an ambient medium of dielectric constant ϵ_a . By solving the equations of the electrostatic potential, with the adequate boundary conditions, one finds, indeed, that (24) can be replaced by

$$P_i = \alpha'_i E_i = P_i/V$$

with

$$\alpha'_i = \frac{1}{4\pi} \frac{(\epsilon - \epsilon_a)}{1 + \left(\frac{\epsilon}{\epsilon_a} - 1\right) f_i} \quad (25)$$

where the index $i = x, y, z$, specifies the directions of the principal axes of the ellipsoidal particle. We have thus to distinguish three form factors f_i , whose values depend on the *ratios* of the principal axes of the ellipsoid. The actual size of the metal particle is irrelevant as long as the metal particle is sufficiently small compared to the wavelength of the incident light. Larger metal particles would give rise to quadrupole effects besides the usually predominant dipole behaviour, as it is known already for metal spheres [47]. A very important property of the form factors f_i for *ellipsoidal* particles is that their sum must always equal one. We can thus distinguish three different resonance frequencies for such a particle, corresponding to collective oscillations along the three principal axes, but the values of these frequencies are related by the sum rule for the corresponding form factors f_i .

2.2 THE EFFECTIVE DIELECTRIC CONSTANT OF A THIN GRANULAR METAL FILM. — A thin film, that is prepared by evaporating a metal on a transparent substrate at normal temperature, is generally composed of « islands », which resemble liquid drops, although they are of crystalline structure. The optical properties of such a granular film can be characterized by simple analytic formulas, when one assumes that the metal particles have *ellipsoidal* shapes and that they are surrounded everywhere by an ambient medium of given dielectric constant ϵ_a . It will generally be possible to assume, moreover, that the ellipsoidal particles are *axially symmetric*, so that they have circular cross sections in the plane of the film. We have then to consider only two form factors f_{\parallel} and f_{\perp} , with the sum rule

$$2f_{\parallel} + f_{\perp} = 1. \quad (26)$$

The indices i refer now to directions that are respectively parallel and perpendicular to the plane of the film. A thin film, which is formed by a medium, of dielectric constant ϵ_a , that contains N *identical* metal particles per unit volume, will be characterized by an anisotropic dielectric constant

$$\epsilon'_i = \epsilon_a + 4\pi N V \alpha'_i = \epsilon_a + \frac{q(\epsilon - \epsilon_a)}{1 + \left(\frac{\epsilon}{\epsilon_a} - 1\right) f_i}. \quad (27)$$

The « filling factor » $q = NV$ defines the relative volume that is occupied by metal particles within the film. Assuming that there are N' metal particles per unit surface of the film, and that each metal particle occupies a surface S , we can also define the filling factor by $q = N'S$, i. e. by the relative coverage of the substrate, since $V = Sd$ and $N = N'/d$, where d is the effective film thickness. The mass thickness of the film is, of course, given by $d_m = N'V$.

The simple expression (27) is only valid, when we can assume that the *lateral interactions* among the metal particles are negligible. To get a more general expression, we have to consider also the effect of the secondary electric field, which is created within a given metal particle by the dipoles that are induced in the surrounding metal particles. Considering, separately, the two cases where the dipoles are oriented in a direction that is parallel or perpendicular to the plane of the film, one finds that the total secondary electric field will be parallel or antiparallel to the dipoles, and that its magnitude depends on the average dipole density ($N' p_i$) and on the average separation (a) between the metal particles :

$$E''_i = \beta_i \frac{4\pi N' p_i}{a\epsilon_a}$$

with

$$\beta_{\parallel} = +\frac{1}{2} \quad \text{and} \quad \beta_{\perp} = -1. \quad (28)$$

It is normally not necessary to take into account the modulation of the induced dipole moments in the film, according to the wavelength of the incident light and the angle of incidence [34], since the dipole field decreases very rapidly (like $1/r^3$) and since the distribution of the metal particles has to be sufficiently dense ($a \ll \lambda$), to allow for the definition of an effective dielectric constant. The first relation (25) has thus to be generalized by

$$P_i = \alpha'_i(E_i + E''_i) = \alpha'_i \left(E_i + \beta_i \frac{4\pi N' V}{a\epsilon_a} P_i \right).$$

Solving this equation, we find that $P_i = \alpha''_i E_i$ and that the effective dielectric constant of the film becomes now

$$\epsilon'_i = \epsilon_a + 4\pi N V \alpha''_i = \epsilon_a + \frac{q(\epsilon - \epsilon_a)}{1 + \left(\frac{\epsilon}{\epsilon_a} - 1\right) f_i^*}. \quad (29)$$

This expression has exactly the same form as (27), so that the lateral interactions among the metal grains have no other effect than to *change the form factor*. The « effective form factors » given by

$$f_i^* = f_i - \beta_i \rho,$$

where

$$\rho = \frac{N' V}{a} = \frac{d_m}{a} = \frac{qd}{a} \quad (30)$$

characterizes the « density » of the particle distribution. Using the values (28) for β_i , we see moreover, that the effective form factors still verify the sum rule (26).

It is obvious that a *real* metal film is not necessarily formed of particles of identical shape (their actual size being irrelevant, as long as the particles are sufficiently small) and that there can occur local variations in the particle density ρ . This means that expression (29) should still be generalized by including a statistical distribution for f_i^* [32], [48]-[50]. For our purpose it will be sufficient, however, to assume a *delta function* for the distribution of possible values of f_i^* so that we can keep the simple expression (29).

2.3 THE ω_{\parallel} AND ω_{\perp} RESONANCE ABSORPTION. — The spectral distribution of the real and imaginary parts of the effective dielectric constant of a (somewhat idealized) thin, granular metal film can be deduced directly from the basic relation (29), assuming that we know the spectral distribution of the complex dielectric constant of the metal ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and of the real dielectric constant of the ambient medium (ε_a):

$$\varepsilon'_{i1} = \varepsilon_a + \frac{q[(\varepsilon_1 - \varepsilon_a) + (\varepsilon_1 - \varepsilon_a)^2 f_i^*/\varepsilon_a + \varepsilon_2^2 f_i^*/\varepsilon_a]}{[1 + (\varepsilon_1 - \varepsilon_a) f_i^*/\varepsilon_a]^2 + [\varepsilon_2 f_i^*/\varepsilon_a]^2} \quad (31)$$

$$\varepsilon'_{i2} = \frac{q\varepsilon_2}{[1 + (\varepsilon_1 - \varepsilon_a) f_i^*/\varepsilon_a]^2 + [\varepsilon_2 f_i^*/\varepsilon_a]^2}. \quad (32)$$

The film is an *anisotropic* medium, whose optical properties are different when the electric field is applied in the directions $i = \parallel$ and \perp , with respect to the plane of the film. But in both cases, it appears that the spectral distribution of ε'_{i2} , which defines the absorption spectrum, has a peak when the frequency is such that

$$1 + \left(\frac{\varepsilon_1}{\varepsilon_a} - 1\right) f_i^* = 0. \quad (33)$$

We will call this resonance frequency $\omega_i = \omega_{\parallel}$ or ω_{\perp} . By developing (31) and (32) around the resonance frequency ω_i , we find that

$$\varepsilon'_{i1} = \varepsilon_a + \frac{A_i(\omega_i - \omega) \gamma_i/2}{(\omega - \omega_i)^2 + (\gamma_i/2)^2} \quad (34)$$

and

$$\varepsilon'_{i2} = \frac{A_i(\gamma_i/2)^2}{(\omega - \omega_i)^2 + (\gamma_i/2)^2}, \quad (35)$$

for $\omega \cong \omega_i$. The amplitude and the width of the absorption peak (35) is given by

$$A_i = \frac{q\varepsilon_a^2(\omega_i)}{(f_i^*)^2 \varepsilon_2(\omega_i)} \quad \text{and} \quad \gamma_i = \frac{2\varepsilon_2(\omega_i)}{(d\varepsilon_1/d\omega)_{\omega_i}} \quad (36)$$

which shows that the peak is particularly strong when the resonance occurs in a spectral region where the bulk metal has a low absorbing power ($\varepsilon_2 = \text{small}$). In the low frequency limit ($\omega \ll \omega_i$), it follows from (31) and (32) that

$$\varepsilon'_{i1} = \varepsilon_a + \frac{q}{f_i^*} \quad \text{and} \quad \varepsilon'_{i2} = 0. \quad (37)$$

The granular metal film becomes completely non-absorbing in the far infra-red part of the spectrum, although the metal from which the film is made exhibits a very strong Drude absorption in this spectral region (see Fig. 1b and 2b).

The resonance frequencies ω_{\parallel} and ω_{\perp} depend on the effective form factors and the dielectric constant of the ambient medium. For very flat, or very densely distributed metal particles, we have $f_{\parallel}^* \ll f_{\perp}^*$, so that ω_{\parallel} can be *much smaller* than the plasma frequency ω_p . It follows actually from (33) and (19) that

$$\omega_{\parallel} = \omega_p \sqrt{\frac{f_{\parallel}^*}{\varepsilon_a}}, \quad (38)$$

when f_{\parallel}^* is sufficiently small, to situate the ω_{\parallel} resonance below the threshold for interband transitions in the bulk metal. (36) reduces under the same conditions to

$$A_{\parallel} = \frac{q\omega_p^2}{\gamma\omega_{\parallel}} \quad \text{and} \quad \gamma_{\parallel} = \gamma \quad (39)$$

where γ is the inverse of the Drude relaxation time, defined by (19). It should be noted, however, that γ can be larger in the metal particle than in the bulk metal, since the electron mean free path is generally limited by the small *size* of the metal particle [51], [52]. The electron-surface collisions lead, indeed, to an additional absorption, which can be treated like the Drude absorption, although it has actually some very special features [53].

The ω_{\perp} resonance is characterized, on the other hand, by the fact that the value of ω_{\perp} tends towards the value of the plasma frequency in the bulk material, when the metal film is *nearly continuous*. We know, indeed, that $f_{\parallel}^* \rightarrow 0$ and $f_{\perp}^* \rightarrow 1$ for a single, infinitely flat ellipsoidal particle, or for a very dense distribution of small metal particles. This means, according to (33), that there remains only a single resonance frequency, whose value is determined by the condition $\varepsilon_1(\omega) = 0$,

which defines also the value of the plasma frequency in the bulk material. This can easily be related to what is known for « surface plasmons », at *plane* metal surfaces [54]. The surface plasmon frequency is actually determined by the condition $\varepsilon_1 + \varepsilon_0 = 0$, when we have a semi-infinite metal that is in contact with a semi-infinite medium of dielectric constant ε_0 . In a metal film of finite thickness, with plane parallel surfaces, there is a coupling between the collective oscillations at both surfaces, so that one gets *two* surface plasmon frequencies. One of these frequencies tends towards zero, for very thin continuous films ($d \ll \lambda$), while the other one tends towards the value of the plasma frequency in the bulk material, like ω_\perp .

2.4 THE EFFECT OF S OR P POLARIZED LIGHT. — The ω_\parallel and ω_\perp resonances can only be excited, respectively by the E_\parallel and E_\perp components of the electric field of the incident light wave. It is clear, however, that $E_\perp = 0$ for s polarized light, or for arbitrarily polarized light at *normal* incidence. We can thus only excite the ω_\parallel resonance under these conditions. For p polarized light, at oblique incidence we get however two components E_\perp and E_\parallel , whose ratio increases with the angle of incidence. It becomes thus possible, under these conditions, to excite at once the ω_\parallel and ω_\perp resonance, the ω_\perp resonance becoming stronger when the angle of incidence is increased. This features are neatly demonstrated by the experimental results of Emeric and Emeric [55] for thin granular silver films.

The ω_\perp resonance accounts also for the so called « *vectorial, selective photoelectric effect* », which was extensively studied before the war, especially for alkali metals [56]. This effect was erroneously attributed, for a long time, to the so called « *surface effect* » where the light absorption is associated with electron surface-collisions [57], [53]. The close parallelism between the ω_\perp optical absorption resonance and the selective photoelectric emission of very thin K films was demonstrated by Mayer and Thomas [58]. The ω_\perp resonance can also be detected by observing the « *transition radiation* » [54], which corresponds to the emission of a photon instead of an electron, with a corresponding desexcitation of the collective oscillation.

The fact that ω_\perp has to shift from the value of the plasma frequency in the bulk metal to lower values, when the film passes from a continuous structure to a discontinuous one, has been demonstrated by Bösenberg [59], as well as Deichsel [60] for thin K films. We note also that the observations of Fleischer and Dember [61] for the photoelectric emission of aging K films, in vacuum, could be interpreted by an increased granularity of the films, resulting from coalescence.

The ω_\parallel resonance can be excited alone, under conditions of normal incidence. This corresponds then to the « *anomalous absorption* » which was extensively studied by Rouard and co-workers [25]-[27]. Payan [22] found actually *two* absorption peaks for Na and K films, under these conditions (see Fig. 1b and 2b). This

has to be correlated with the experimental results of Bösenberg [59], who found also two ω_\parallel resonances in granular K films. We may think of *two types* of metal islands : large ones at relatively large separations, and small ones between them. But a quadrupole effect in non-ellipsoidal metal islands cannot yet be excluded.

2.5 THE DISPLACEMENT LAW FOR THE ω_\parallel RESONANCE.

— The quantity $\varepsilon'_2 d/\lambda$, where d represents the effective optical thickness of the film and λ the wavelength of the incident light, is directly accessible to measurements, under conditions of normal incidence. Representing $\varepsilon'_2 d/\lambda$ as a function of λ , one finds that the « *anomalous* » absorption peak is displaced towards the red, for films of different mass-thickness. The peak is practically displaced along a *straight line*, at least when the mass-thickness d_m is not too large [22], [23], [62]. This behaviour can be expressed by the law

$$\left(\frac{\varepsilon'_2 d}{\lambda}\right)_{\max} \cong C(\lambda_{\max} - \lambda_{\max}^0), \quad (40)$$

where C is a constant. It is easily possible to justify this law, by means of the relations (38) and (39) for the ω_\parallel resonance. The whole effect is actually due to the *lateral interactions* among the metal particles. The resonance frequency has, indeed, to be displaced according to (38), (30) and (28) in such a way that

$$\omega_\parallel = \omega_p \sqrt{\frac{(f_\parallel - \rho/2)}{\varepsilon_a}} = \omega_\parallel^0 \left(1 - \frac{\rho \varepsilon_a}{4 f_\parallel} + \dots\right) \quad (41)$$

where $\omega_\parallel^0 = \omega_p \sqrt{f_\parallel/\varepsilon_a}$ is the resonance frequency, when it is possible to neglect the lateral interactions among the metal particles (i. e. for $\rho \ll f_\parallel$). For the wavelength at which the absorption maximum occurs, we get in the same way

$$\lambda_\parallel = \lambda_\parallel^0 \left(1 + \frac{\rho \varepsilon_a}{4 f_\parallel} - \dots\right). \quad (42)$$

On the other hand, it follows from (35), (38) and (39) that

$$\left(\frac{\varepsilon'_2 d}{\lambda}\right)_{\max} = \frac{A_\parallel d}{\lambda_{\max}} = d_m \frac{\omega_p^3}{2nc}, \quad (43)$$

since $q = d_m/d$. Replacing now the mass-thickness d_m in this expression by the expression that results from (42), where $\rho = d_m/a$, we get immediately the suggested law (40) for sufficiently small values of ρ , with

$$C = \frac{8\pi c a}{\gamma(\lambda_{\max}^0)^3}.$$

The constancy of C and λ_{\max}^0 implies that further condensation of the metal on a substrate of given temperature leads essentially to an increase of the particle size, without modifying the shape and the average distance between the particles. It is found, however, that C increases, while λ_{\max}^0 remains practi-

cally constant [22], [23], [62], when the temperature of the substrate is increased. This implies that the average distance between the metal particles has been increased, as a consequence of an increased surface mobility of the atoms. By means of (43) and (41) we could also get the relation

$$\left(\frac{\epsilon'_2 d}{\lambda}\right)_{\max} = C'(\omega_{\max}^0 - \omega_{\max})$$

which corresponds to the results of Payan (Fig. 1*b* and 2*b*).

For completeness, we should mention that the Maxwell-Garnett theory [30] has been found quite adequate for an isotropic distribution of small spherical particles [63]. This theory is *not* adequate, however, for a thin granular metal film, although it does reproduce qualitatively some of their features [64]-[66]. The Maxwell-Garnett theory predicts actually a single resonance frequency, whose value is determined by the form factor ($f = 1/3$) of a sphere, and by the Lorentz field ($E'' = 4\pi P/3a$), which takes into account the lateral interaction among the isotropically distributed metal particles. It is easily shown that this leads to an effective form factor $f^* = (1 - q)/3$.

III. A bulk metal with a granular surface roughness.

— 3.1 THE PREDOMINANT EFFECT OF THE ω_{\parallel} RESONANCE. — We come now to the proposed interpretation of Mayer's experimental results for Na and K, assuming that his bulk samples had a flat surface, with a dense distribution of small metal particles on top of this surface. The E_{\parallel} component of the electric field will then induce positive and negative charges on the lateral surfaces of these metal islands. These surface charges produce a depolarizing field, which is equivalent to an elastic restoring force, allowing for collective oscillations of the electrons in these metal particles. The corresponding resonance frequency is given by (38), at least when the effective form factor f_{\parallel}^* is sufficiently small, so that ω_{\parallel} falls below the threshold for interband transitions, as this happens for the low-frequency resonance in K and Na (see Fig. 1 and 2). The small value of f_{\parallel}^* as well as the small value of ϵ_2 will then be responsible for a particularly large strength of the resonance absorption according to (36). We see also that it is the smallness of f_{\parallel}^* , i. e. the flatness of the metal particles and their relatively high density which shifts the ω_{\parallel} resonance far below the value of the plasma frequency ω_p , although we actually have a kind of surface-plasma oscillation. To interpret Mayer's result and to come to a justification of the suggested relation (5), we have to use the expressions (15) or (17) for the « apparent » dielectric constant ϵ^* . In the previous chapter, we derived expressions for ϵ'_{\parallel} and ϵ'_{\perp} and it is evident that

$$\epsilon'_s = \epsilon'_{\parallel} \quad \text{and} \quad \epsilon'_p \cong \epsilon'_{\perp} \quad (44)$$

where the latter expression is only valid for sufficiently large angles of incidence. A p polarized light wave induces actually a dipole moment

$$p = (p_{\perp}^2 + p_{\parallel}^2)^{1/2},$$

where the components p_{\parallel} and p_{\perp} are respectively proportional to $\cos \theta$ and $\sin \theta$ so that $p \cong p_{\perp}$ when the angle of incidence θ is sufficiently large.

In the spectral region under consideration, where $\omega \ll \omega_{\perp}$, we can adopt the approximation (37), with

$$\epsilon'_p \cong \epsilon'_{\perp} \cong \epsilon_a + (q/f_{\perp}^*) \cong \epsilon_a \cong \epsilon_0 \cong 1.$$

It follows then from (17) that the apparent dielectric constant

$$\begin{aligned} \epsilon^* &\cong (1 + 4\beta \cos^2 \theta) \epsilon + \beta(\epsilon'_{\parallel} - \epsilon_a) \cong \\ &\cong \epsilon + \beta(\epsilon'_{\parallel} - \epsilon_a), \end{aligned}$$

in the spectral region where (21) is valid. This leads to

$$\epsilon_1^* \cong \epsilon_1 \quad \text{and} \quad \epsilon_2^* = \epsilon_2 + \beta\epsilon'_{\parallel 2}. \quad (45)$$

The first relation follows from the fact that ϵ_1 is so large that we can neglect $\epsilon'_{\parallel 1} - \epsilon_a$ which is equal to q/f_{\parallel}^* for $\omega \ll \omega_{\parallel}$, and which varies by the amount A_{\parallel} for $\omega \cong \omega_{\parallel}$, because of (34) and (37). The second relation (45) corresponds exactly to our initial hint (5). The corresponding correlation of Mayer's and Payan's results (see Fig. 1 and 2) suggest again that both « anomalous » absorption peaks have to be attributed to ω_{\parallel} resonances.

We can also deduce from (15) and (17) that the ω_{\perp} resonance will have a negligible effect on the apparent optical constants, since ϵ'_p appears generally, in the denominators, while terms of the order $\epsilon'_p \beta \cos^2 \theta$ remain small.

3.2 NUMERICAL ESTIMATES AND CONCLUSIONS. —

Using (45) and (35), we can derive the value of βA_{\parallel} from the experimental results of Mayer for Na (Fig. 1*a*). To do that, we deduce the extrapolated value for the Drude absorption ϵ_2 at the resonance frequency ω_{\parallel} from the corresponding peak value of ϵ_2^* . The value of ω_{\parallel} allows us, on the other hand, to find the value of f_{\parallel}^* , according to (38), assuming that $\epsilon_a = 1$. Combining these results, we can find the value of βq or $d_m = dq$, by making use of (36) and (21). By this method we come to the conclusion that $f_{\parallel}^* = 0.1$ and that $d_m = 7 \times 10^{-10}$ cm, or that $q \leq 0.07$ since $d \geq 1 \text{ \AA}$. The actual value of q could be larger, however, because of the size effect, which could increase the value of γ in (19) and (36). But the value of d could also be much larger than 1 \AA , so that the value of q may still remain within reasonable limits, $q > 1$ being unacceptable.

It would be highly desirable to prove the presence of

a granular structure on the surfaces of bulk samples of alkali metals, that are prepared according to Mayer's method, by further experiments. But we believe that the proposed interpretation has such a high degree of internal consistency, that it has to point as least to the essential mechanism, even though the ellipsoidal metal particle model is only an idealization.

Note added in proof. — The theory provides also a natural explanation for the anomalous infrared absorption peaks in Au [67] and Ag [68]. A similar, but less detailed theory has been proposed by Marton [69]. The effect of surface roughness on optical reflection and ellipsometry was investigated by Berremann [70]

References

- [1] MAYER (H.) and EL NABY (M. H.), *Z. Phys.*, 1963, **174**, 280, 289.
- [2] MAYER (H.) and HIETEL (B.), Proceedings of the Intern. Coll. on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965, ed. F. Abeles, North-Holland Publ. Co Amsterdam, 1966, 47.
- [3] COHEN (M. H.), *Phil. Mag.*, 1958, **3**, 762.
- [4] WILSON (A. H.), The theory of metals, Cambridge Univ. Press, New York, 1936.
- [5] BUTCHER (P. N.), *Proc. Phys. Soc. (London)*, 1951, **A 64**, 50.
- [6] COHEN (M. H.) and PHILLIPS (J. C.), *Phys. Rev. Letters*, 1964, **12**, 662.
- [7] COHEN (M. H.), *Phys. Rev. Letters*, 1964, **12**, 664.
- [8] OVERHAUSER (A. W.), *Phys. Rev. Letters*, 1965, **13**, 196.
- [9] COHEN (M. H.), ref. 2, 66.
- [10] FERREL (R. A.), ref. 2, 78.
- [11] NETTEL (S.), *Phys. Rev.*, 1966, **150**, 421.
- [12] SMITH (N. V.), *Phys. Rev.*, 1967, **163**, 552.
- [13] ANIMALU (S. O. E.), *Phys. Rev.*, 1967, **163**, 557.
- [14] KLIOWER (K. L.) and FUCHS (R.), *Phys. Rev.*, 1968, **172**, 607.
- [15] NIFOO (E.) and HOPFIELD (J. J.), *Phys. Rev.*, 1968, **173**, 635.
- [16] MISKOVSKY (N. M.) and CUTLER (P. H.), *Solid State Comm.*, 1969, **7**, 253; *Phys. Letters*, 1970, **A 13**, 519.
- [17] CHIAN-YUAN YOUNG, *Phys. Rev.*, 1969, **183**, 627.
- [18] KARAKASHIAN (A.), *Phys. Letters*, 1970, **A 32**, 17.
- [19] STOLZ (H.), *Phys. Stat. Solidi*, 1970, **41**, 57.
- [20] LIPPENS (M.), *Ann. Soc. Scient. de Bruxelles*, 1971, **85**, 265.
- [21] SMITH (N. V.), *Phys. Rev.*, 1969, **183**, 634; 1970, **2**, 2840.
- [22] PAYAN (R.), Thèse, Marseille, 1969; *Ann. Phys.*, 1969, **4**, 543.
- [23] PAYAN (R.) and ROUX (D.), *Opt. Comm.*, 1969, **1**, 37.
- [24] MAYER (H.), Physik dünner Schichten, I, Physik und Technik, Bd. 4. Wissensch. Vlg. Stuttgart.
CHOPRA (K. L.), Thin Film Phenomena, Mc Graw Hill, 1969.
- [25] Colloque sur les propr. opt. des lames minces, Marseille, 1949; *J. Physique rad.*, 1950, **11**, 307-479; Colloque sur l'opt. des couches minces solides, Marseille, 1963; *J. Physique*, 1964, **25**, 1-296.
- [26] ROUARD (P.), Proceedings of the intern. Symp. on Basic Problems in Thin Film Physics, Clausthal-Göttingen 1965 (ed. Niedermayer R. and Mayer H.) Vandenboeck & Ruprecht, Göttingen, 1966, 263.
- [27] ROUARD (P.) and BOUSQUET (P.), *Progress in Optics*, 1965, **4**, 145; *Optical Acta*, 1969, **16**, 675.
- [28] WOLTER (H.), Hdb. Phys. XXIV, Springer, 1956.
- [29] WOOD (R. W.), *Phil. Mag.*, 1902, **3**, 396.
- [30] MAXWELL-GARNETT (J. C.), *Phil. Trans. Roy. Soc.*, 1904, **A 203**, 385.
- [31] GANS (R.), *Ann. d. Phys.*, 1912, **37**, 881.
- [32] DAVID (E.), *Z. Phys.*, 1939, **114**, 389.
- [33] SCHOPPER (H.), *Z. Phys.*, 1951, **130**, 565; 1952, **131**, 146, 215; *Fortschr. Phys.*, 1954, **2**, 6.
- [34] YAMAGUCHI (S.), *J. Phys. Soc. Japan*, 1960, **15**, 1577; 1962, **17**, 184.
- [35] BOUSQUET (P.), *C. R. Acad. Soc. Paris*, 1968, **266**, 505.
- [36] VAN PARIJS (C.) and MEESSEN (A.), to be published.
- [37] BEATTIE (J. R.) and CONN (G. K. T.), *Phil. Mag.*, 1955, **46**, 223, 235.
- [38] BERREMAN (D. W.), *Phys. Rev.*, 1967, **163**, 855; 1970, **B 1**, 381.
- [39] BEAGLEHOLE (O.) and HUNDERI (O.), *Phys. Rev.*, 1970, **B 2**, 1309, 1321; *Opt. Comm.*, 1969, **1**, 101.
- [40] FENSTERMAKER (C. A.) and MCCRACKIN (F. L.), *Surf. Sc.*, 1969, **16**, 85.
- [41] DUNCAN (R. W.) and DUNCAN (R. C.), *Phys. Rev.*, 1913, **1**, 294.
- [42] MEESE (B.), *Nachr. Ges. Wiss. Gött., Math. Phys. Kl.*, 1913, 530.
- [43] IVES (H. E.) and BRIGGS (H. B.), *J. Opt. Soc. Amer.*, 1936, **26**, 238; 1937, **27**, 181, 395.
- [44] DRUDE (P.), *Ann. Phys. Chem.*, 1889, **36**, 886; 1890, **39**, 481.
- [45] HODGSON (J. H.), *J. Phys. Chem. Solids*, 1963, **24**, 1213; *Phys. Letters*, 1963, **7**, 300.
- [46] BORN (M.) and WOLF (E.), Principles of Optics, Pergamon Press, 4th Ed., 1970.
- [47] MIE (G.), *Ann. d. Phys.*, 1908, **25**, 377; DEBYE (P.), *Ann. d. Phys.*, 1909, **30**, 57.
- [48] HAMPE (W.), *Z. Phys.*, 1958, **152**, 470, 476.
- [49] PERROT (M.), DAVID (J. P.) et al., *J. Physique*, 1964, **25**, 104.
- [50] YOSHIDA (S.), YAMAGUCHI (T.) and KINBARA (A.), *J. Opt. Soc. Amer.*, 1971, **61**, 62.
- [51] EULER (J.), *Z. Phys.*, 1954, **137**, 318.
- [52] CARLAN (A.), *Ann. Phys.*, 1969, **4**, 5.
- [53] MEESSEN (A.), *Phys. Stat. Sol.*, 1968, **26**, 125; *Ann. Soc. Scient. Bruxelles*, 1968, **82**, 315.
- [54] STEINMANN (W.), réf. 26, p. 363; *Phys. Stat. Solidi*, 1968, **28**, 437.
- [55] EMERIC (N.) and EMERIC (A.), *Thin Solid Films*, 1967, **1**, 13.
- [56] HUGHES (A. L.) and DUBRIDGE (L. A.), Photoelectric Phenomena, McGraw-Hill, New York, 1932.
- [57] MEESSEN (A.), *J. Physique Rad.*, 1961, **22**, 308.
- [58] MAYER (H.) and THOMAS (H.), *Z. Phys.*, 1957, **147**, 419.
- [59] BÖSENBERG (J.), *Z. Phys.*, 1969, **218**, 282.
- [60] DEICHEL (H.), *Z. Phys.*, 1963, **174**, 136; see also FLEISCHMANN (R.), *ibid.*, 102.
- [61] FLEISCHER (R.) and DEMBER (H.), *Z. f. Tech. Phys.*, 1926, **7**, 133.
- [62] PAYAN (R.) and RASIGNI (G.), *C. R. Acad. Sci. Paris*, 1966, **262**, 1145.
- [63] DOREMUS (R. H.), *J. Chem. Phys.*, 1964, **40**, 2389; DUTHLER (C. J.), JOHNSON (S. E.) and BROIDA (H. P.), *Phys. Rev. Letters*, 1971, **26**, 1236.
- [64] DOREMUS (R. H.), *J. Colloid and Interf. Sc.* 1968, **27**, 412; *J. Appl. Phys.*, 1966, **37**, 2775.
- [65] PETROV (Yu. I.), *Opt. and Spectr.*, 1969, **27**, 359.
- [66] MARTON (J. P.), *J. Appl. Phys.*, 1969, **40**, 5383.
- [67] SHKLYAREVSKII (I. N.) and YAROVAYA (R. G.), *Optics, spectros.* 1966, **21**, 115.
DEVANT (G.) and THEYE (M. L.), *Proc Coll. on Thin Films*, Budapest 1967.
- [68] HODGSON (J. N.), *J. Phys. Chem. Solids*, 1968, **29**, 2175.
- [69] DUJARDIN (M. M.) and THEYE (M. L.), *J. Phys. Chem. Solids*, 1971, **32**, 2033.
- [70] MARTON (J. P.) *Appl. Phys. Lett.* 1971, **18**, 140.
- [70] BERREMAN (D. W.) *J. Opt. Soc. Am.* 1970, **60**, 499.