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# **OPTICAL PROPERTIES OF THIN METAL FILMS**

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# § 1. Anomalous Optical Absorption of Thin Metal Films and Bulk Alkali Metals

#### **1.1. INTRODUCTION**

An established convention characterizes the optical properties of a metal in terms of a refractive index n and an extinction coefficient k, usually combined in the expression of a complex refractive index n = n + ik.

When the metal is in the form of a thin film, n and k must be regarded as the optical parameters, not of the real film, but of an idealized film, homogeneous and isotropic in composition and having plane parallel surfaces. With the addition of an equivalent thickness d the idealized film will be the approximate optical equivalent of the real film (though d is sometimes an ill-defined quantity, especially for very thin films, which are porous or formed of discrete metal granules).

If the magnetic permeability (relative to vacuum) of a metal film is taken as unity (a valid approximation at optical frequencies), Maxwell's equations show that the optical characteristics of the film can be related to the complex relative dielectric constant  $\varepsilon_r$ . The equations are:

$$\mathbf{n}^{2} = \boldsymbol{\varepsilon}_{r}(\omega) = \boldsymbol{\varepsilon}_{1}(\omega) + i\boldsymbol{\varepsilon}_{2}(\omega) = (n + ik)^{2}$$
$$\Rightarrow \boldsymbol{\varepsilon}_{1} = n^{2} + k^{2}; \ \boldsymbol{\varepsilon}_{2} = 2nk = \frac{4\pi\sigma}{\omega} \Rightarrow \sigma = \frac{c}{2\lambda} \boldsymbol{\varepsilon}_{2}$$

where  $\sigma$  is the optical conductivity and  $\omega$  is the angular frequency of the incident radiation.

It can also be shown that within a narrow range of optical wavelengths the imaginary part of the dielectric constant (or, more accurately, the quantity  $nk/\lambda$ ) is proportional to the absorbed energy for films of thickness less than  $\lambda/25$ : it is consequently often termed the "absorption" of the film. Hence, the absorption spectrum of a metal in thin-film form can be characterized by the spectral distribution of  $\varepsilon_2$ , that is, of the product nk or the ratio  $\sigma/\omega$ . It is hardly necessary to emphasize the importance of determining the optical constants n and k of a metal, together with its conductivity  $\sigma$ , its absorption  $\varepsilon_2$ , and the real part  $\varepsilon_1$  of its dielectric constant. Unfortunately, it has to be accepted that the values of these parameters obtained by various workers for a metal in the massive state can differ by as much as 100%. This lack of agreement is explained by the nature of the metal surface at which the measurements are made: penetration into the body of the metal by radiation of visible and near-visible wavelengths is very slight indeed, so that it is in fact not the properties of the pure bulk metal that are measured but those of a superficial layer, of which the purity, exact structure, profile, and other characteristics are usually unknown or, at best, doubtful quantities.

It was hoped that more reliable results would be obtained by replacing polished bulk metals by thin films of sufficient thickness deposited by thermal evaporation on a highly polished transparent support in a vacuum as nearly perfect as possible. Nevertheless, in 1953 ROUARD's and MALÉ research already showed that care was needed in the interpretation of the results so obtained; this was confirmed by MAYER and BÖHME [1964] who, in particular, convincingly demonstrated the important influence of diffusion of light by films and indicated the method of eliminating it by calculation.

Many studies have been carried out on the optical properties of thin solid films in general and of thin metallic films in particular, with the object of solving the problems encountered in determining the optical constants of these films and hence of the metals themselves. These studies, especially those concerned with film thicknesses of less than 10 nanometers, have brought to light some peculiar properties which account for the spread of results from different sources.

Among the films investigated, those of the alkali metals are of very special interest. These metals all crystallize in the simple body-centred cubic system (apart from sodium, which is polymorphic). Their electronic structure is now known and consequently a certain number of theories have been put forward to account for their optical properties. These theories must be tested by experiment, again a reason for ensuring that the experimental results shall be beyond reasonable criticism; a collection of consistent and reproducible results may still be subject to errors arising from some undetected or underestimated extraneous phenomenon.

From this point of view the introduction in the early sixties of ultra-high vacuum pumps and of techniques for the examination of films *in* 

situ completely altered the conditions under which specimens were prepared and examined. Most of the measurements up to that time had been made on surfaces that were, to a greater or lesser degree, contaminated or had been exposed to the atmosphere after deposition; in consequence, they were certain to be subject to error.

In addition to advanced vacuum techniques, the new methods of microscopy (phase contrast, interferometry, Auger electrons) are now currently employed to investigate in depth the structural imperfections of their films and to differentiate between surface effects and volume effects. The former disappear rapidly as the surface is left behind; they are mainly associated with surface irregularities. It seems now to be accepted that surface absorption and diffusion by metallic films result from the optical excitation of surface plasmons, a phenomenon arising from the presence of surface microroughness with peak heights of a few tens of ångstroms. Surface absorption may also be due to an anomalous skin effect or to other phenomena induced by the microroughness (not to be confused with scratches) or by larger-scale surface structures, which can obviously play an important part as far as diffusion is concerned. Volume effects are associated with holes, imperfections in the crystal lattice, and atomic impurities. They can be represented by a volume parameter, such as diffusion or absorption per unit volume.

In the following discussion we shall first survey very briefly the essential results relating to the optical properties peculiar to metals in the form of a two-dimensional distribution of granules on the flat surface of a transparent substrate (glass, quartz, fused silica, etc.) or in the form of a thin porous film (mass thickness less than 10 nanometers). We shall then concentrate on the case of alkali metals and the problem of interpreting values of optical constants derived from the conductivities of both massive and thin-film specimens of these metals.

## 1.2. ANOMALIES IN THE OPTICAL PROPERTIES OF THIN METALLIC FILMS AND BULK METAL

According to elementary solid-state theories, the characteristic shape of the curve giving the optical absorption nk (or the optical conductivity  $\sigma$ ) of a metal as a function of wavelength or photon energy should include structures corresponding to interband electron transitions, superimposed on the intraband absorption arising from collisions of conduction electrons, accelerated by the electric field of the incident radiation, with phonons and lattice defects. Here we meet our first anomaly: granular or porous films of certain metals (e.g. silver, gold, copper, indium) show very strong absorption bands which must be classed as "anomalous" since they do not exist in the absorption spectrum of the corresponding massive metal.

Again, the alkali metals, and, in particular, sodium and potassium, are accepted as good examples of metals to which the theory of the quasi-free electron is applicable. But a study of their optical conductivity when they are in the granular or porous film state reveals the presence of absorption bands entirely analogous to those observed in copper, silver and gold, and of which the origin is inexplicable within the framework of elementary solid-state theory.

Even more surprising is the fact that, under certain conditions, these same anomalous bands can be observed in the absorption spectrum of very thick films of alkali metals, and for the bulk metals themselves.

Here, then, is a phenomenon so significant that the amount of research devoted to it in recent years is amply justified. Its influence bears on, among other things, the determination of optical constants and hence on the real and imaginary parts of the dielectric constant of bulk metals, partially accounting for the misleading results hitherto recorded in this field despite considerable research effort extending over nearly a century.

# 1.3. ANOMALOUS OPTICAL ABSORPTION IN DISCONTINUOUS METALS (VERY THIN GRANULAR OR POROUS FILMS)

## 1.3.1. General

The outcome of numerous studies, particularly with the electron microscope, of thin metal films deposited on a transparent substrate by thermal evaporation is a knowledge of their mode of growth from initial nuclei. The deposit at first consists of distinct micro-crystallites, spherical or, rather, hemispherical in shape. The size and shape of these granules, and their separation, change as the mass thickness increases.

Thicker films generally exhibit transition zones at the vacuum/metal and metal/substrate interfaces. In particular, the surface exposed to the vacuum is usually rather uneven. The same is true, though perhaps to a lesser degree, of the surface in contact with the substrate. Moreover, under certain conditions of deposition some films may even display a п, §1]

slight anisotropy. Metal films are therefore far from being ideal subjects for measurements that are intended to yield the optical constants of bulk metals.

In these circumstances it may be asked why so much refined research is devoted to the optical properties, and particularly the absorption, of metal films that are granular or porous, of which the surface is not perfectly plane, and in which the metal has in all probability been contaminated even though deposition and measurement have been carried out *in vacuo* under the best experimental conditions available today. The reasons are that, firstly, granular films can exhibit effects not encountered in the bulk metal and, secondly, a knowledge of their properties is of extremely useful value in the understanding of certain remarkable results obtained with these metals in the massive state.

The granular model is thus seen as a means of accentuating surface effects and thus of throwing a new light on the very inconsistent and misleading results published during nearly a century's work on the optical constants of metals.

## 1.3.2. Principal results

Since WOOD's first experiments [1902], abnormal optical absorption has been the subject of many investigations. The earliest results have been summarized in several survey articles: ROUARD and BOUSQUET [1965]; ROUARD [1966]; ROUARD and BOUSQUET [1969], and in some other publications: CHOPRA [1969]; ABELÈS [1971]. In addition there is MAYER'S remarkable bibliography [1972], which gives an exhaustive coverage of the whole period from its inception up to 1 January 1969.

It will be useful to review very briefly the most important conclusions, which will offer an explanation of the results obtained for the optical properties of alkali metals measured in the massive state.

a) An "anomalous" absorption band occurs in the absorption spectrum of various metals when they are in a highly discontinuous state (as granular or porous films).

The band is termed "anomalous" because it is not found in the spectrum of the bulk metal, nor is its existence predicted by basic solid-state theory (Drude absorption and interband absorption). This anomalous band moves towards the lower photon energies (longer



Fig. 1. Dependence of 2nkd on wavelength for five silver films of thicknesses ranging from 2 to 10 nm (R. PAYAN and RASIGNI [1964]).

wavelengths) as the mass of deposited metal increases, that is, as the size, shape, and mean distance of separation of the small metal aggregates change.

Figure 1 shows the variation of 2nkd (where d is the film thickness) with wavelength  $\lambda$  for some very thin silver films deposited under strictly identical conditions; the mass thicknesses range from 2 to 10 nm.

For bulk silver only one absorption band is observed within the spectral region under consideration, starting at 120 nm and ending at about 326 nm. Figure 1, however, reveals the existence of two absorption maxima. One is in the region of 250 nm and its position varies only very slightly with film thickness; it seems to correspond to a volume effect. The position of the other peak, beyond 480 nm, depends strongly on mass thickness. Elementary classical theory does not make it possible to predict the existence of this additional band, which is considerably more prominent than the normal band.

## b) This anomalous band is due to an optical resonance phenomenon.

The significance of the anomalous band is revealed by considering the variation of two quantities,  $\varepsilon_2 = 2nk$  and  $n^2 - k^2 - \varepsilon_a = \varepsilon_1 - \varepsilon_a$  (where  $\varepsilon_a = \frac{1}{2}(n_o^2 + n_2^2)$  is a constant equal to the mean dielectric constant of the environment that surrounds the sub-microscopic aggregates composing the film;  $n_o$  is the refractive index of the outer medium,  $n_2$  that of the substrate). To give an example, Fig. 2, after RASIGNI and ROUARD [1962, 1963], plots 2nkd and  $(n^2 - k^2 - \varepsilon_a)d$  as a function of wavelength in the



Fig. 2. Dependence of 2nkd and of  $(n^2 - k^2 - \varepsilon_a)d$  on wavelength for silver film of thickness 2 nm (RASIGNI and ROUARD [1962, 1963]).

anomalous band region for a granular silver film of mass thickness 2.4 nm: it is immediately apparent that these curves are exactly analogous to those representing the variation of the real and imaginary parts of the dielectric constant of a substance in an absorption band. In particular it is seen that the curve of 2nkd passes through a maximum in a region where the  $(n^2 - k^2 - \varepsilon_a)d$  curve shows a point of inflexion. This, then, is indisputably a manifestation of an optical resonance associated with the discontinuous structure of the deposits and is the origin of the brilliant colours observed in transmission by WOOD [1902] and in reflection on the substrate side by ROUARD [1932, 1934, 1936, 1937], who in fact utilized the effect to produce the first antireflection films, the phenomenon is not one of interference or diffraction.

c) This resonance is linked with collective oscillations in the granules constituting very thin films.

From his first experiments WOOD [1902] formed the hypothesis that the colours he observed were due to a granular structure of the metal. Several authors, and in particular SENNETT and SCOTT [1950], have proved the validity of this hypothesis by measuring the optical properties of films and simultaneously observing their structure by electron microscopy; in this way they have been able to establish a qualitative relationship between the two. In more recent times this relationship has been confirmed and more closely defined by S. YAMAGUCHI [1960] and by RASIGNI [1962]. As we have already seen, the position of the anomalous absorption band and its displacement as the film grows are functions of a progressive change in the granular film structure. Thus, they vary as the mass of deposited metal per unit area of surface increases. If, on the contrary, a *continuous* layer

of silver is deposited on a molybdenum substrate (FLECHSIG [1962]), no coloration develops, even in the thinnest films.

The explanation of these phenomena should be capable of development from what is known of film structure. Since the thinnest films are composed of a two-dimensional distribution of granules on the surface of a dielectric, it seemed appropriate to apply the theories that were put forward by MAXWELL-GARNETT [1904], MIE [1908], and GANS [1912– 1915] to explain the optical properties of metal spheres in colloidal suspension.

DAVID [1939] modified Gans' calculations by introducing the concept of a resonance frequency varying with the shape of the granules. In its turn, David's theory was improved and developed by Möglich and ROMPE [1949], and by HAMPE [1958], who introduced the idea of collective oscillations of electrons in the granules, TROMPETTE [1960], RASIGNI [1962], S. YAMAGUCHI [1962], BOUSQUET [1968], CARLAN [1969], T. YAMAGUCHI, YOSCHIDA and KINBARA [1971, 1972] and others. So treated, David's theory correctly explains the experimental results for normal incidence so far reported in this review. We shall return to this point later.

The extension of David's theory to oblique incidence has been carried out, in particular, by S. YAMAGUCHI [1960, 1962, 1963] and by N. and A. EMERIC [1966, 1967, 1969]. These authors investigated the absorption by very thin granular silver films of an incident beam plane-polarized with its electric field vector parallel to the plane of incidence (p-polarization). They predicted and found two absorption bands corresponding respectively to plasma oscillations taking place in directions parallel and perpendicular to the plane of the film. Figures 3a and 3b show the results obtained by N. and A. Emeric for a granular silver film of about 1 nm mass thickness.

It will be seen that the transmission minimum observed in natural light at normal incidence in the region of 4500 Å (Fig. 3a) coincides, in the limits of experimental error, with that found at oblique incidences when the incident light is polarized with the electric vector perpendicular to the plane of incidence (s-polarization). This corresponds to collective oscillations taking place in a direction parallel to the plane of the film. When the incident light is p-polarized (Fig. 3b), the transmission minimum is again present at about 4500 Å, whatever the angle of incidence. In addition, a second minimum appears at about 3450 Å, corresponding to collective oscillations perpendicular to the film plane. It is present but inconspicuous in the curve for  $45^{\circ}$  incidence, whereas at  $70^{\circ}$  incidence the band is



Fig. 3. Transmittance for granular silver films. (a) T, normal incidence; T<sub>⊥</sub>, s-polarization;
(b) T, normal incidence; T<sub>||</sub>, p-polarization (N. and A. EMERIC [1966, 1967, 1969]).

sharply defined, as would be expected since the component of the electric vector perpendicular to the plane of the film is significantly greater for an incident angle of 70°. A secondary effect of this minimum is to displace Wood's "hole" from its normal position at 3200 Å down to about 3100 Å.

When the film thickness is increased and, as a consequence, the granules get a more flattened shape, the transmission minimum due to oscillations perpendicular to the film plane moves from 3450 Å towards shorter wavelengths while the longer-wavelength maximum at 4500 Å is raised in wavelength. These displacements are in accord with theory for flattened ellipsoids.

From the preceding results it is easy to calculate  $\varepsilon_2 = 2nk$  for angles of incidence 0°, 45°, and 70°. The calculated curves confirm the results given above.

The theory of collective oscillations in the granules constituting a film thus appears to explain the anomalous absorption effect, at least in the case of granular silver films. The spectral region in which these oscillations occur seems to be a function of the shape and separation of the component granules (N. and A. Emeric) or of interactions between the particles themselves (DOREMUS [1968]). Oscillations parallel to the plane surface of the substrate are induced at wavelengths above 4000 Å, while those that are perpenducular to the surface occur at wavelengths between approximately 3300 Å and 4000 Å.

#### 1.4. ANOMALOUS OPTICAL ABSORPTION IN ALKALI METALS

## 1.4.1. Introduction

At normal temperatures the alkali metals have the particularly simple body-centred cube structure and the partially filled conduction band, associated with atomic s levels. According to the shape of this band, the conduction electrons can be considered as if they were free.

Sodium and potassium in particular are regarded as good examples of metals to which the quasi-free electron theory is applicable. Now, it is these quasi-free electrons that in theory determine their optical properties, especially in the visible and near infrared regions. In consequence, it becomes extremely important to measure these optical properties as accurately as possible. Unfortunately, the metals are highly reactive: preparation of the perfectly flat, chemically pure, surfaces essential for valid measurements, presents some difficult problems in technique.

It is therefore not surprising that until the early 1960's brought in the routine use of ultra-high vacuum techniques, the alkali metals received very little attention, nor that some of the meagre results had to be viewed with caution. Thus by 1962 practically the only useful data were those of IVES and BRIGGS [1937] and of R. W. and R. C. DUNCAN [1913], the latter analyzed by BUTCHER [1951] on the basis of free-electron theory. Furthermore, these studies were confined to measurements at room temperature in the 2500–6000 Å spectral region, whereas a coherent theoretical interpretation of results requires that measurements be made at very low temperature and at wavelengths extending as far as possible into the infrared and the vacuum ultraviolet.

Against that background, it is not difficult to appreciate the interest accorded to the results of research carried out by HODGSON [1963], by MAYER and EL NABY [1963] and MAYER and HIETEL [1966]. The outstanding feature of these new measurements of optical absorption 2nk or of optical conductivity  $\sigma$ , in both Hodgson's and Mayer's work, was the existence of a strong absorption band for photons with energy below the interband absorption threshold, in a region where the Drude absorption is very weak.

The existence of this extraordinary band, which is found in all the alkali metals under the right experimental conditions, is not predicted by elementary solid state theories based on the quasi-free electron concept; its discovery aroused considerable interest and stimulated many new lines of research. It was, indeed, the first time that an anomalous band had been observed in a bulk metal.

Some very ingenious mechanisms, capable of accounting for an optical absorption corresponding to a bulk metal resonance in alkali metals, were devised by several theoreticians (COHEN [1964, 1966]; OVERHAUSER [1965]; FERREL [1966]; NETTEL [1966]; SMITH [1967]; ctc.), while PIP-PARD [1966] advised a cautious attitude, even going so far as to question the existence of Mayer's anomalous band and particularly its variations with temperature: "The whole thing is so strange, that at the very least we ought to be extremely thankful to him for providing us with so many facts to quarrel over".

Later measurements were extended to the lower photon energy region (ALTHOFF and HERTZ [1967]) and to the very high energies of the vacuum ultraviolet (SUTHERLAND, ARAKAWA and HAMM [1967]; SUTHERLAND and ARAKAWA [1968]; SUTHERLAND, HAMM and ARAKAWA [1969]; WHANG, ARAKAWA and CALLCOTT [1972]), but the results of Mayer et al. held their place as the most complete and the most astonishing.

After having presented the experimental data gained from alkali metals in the massive state and in granular-film form, we shall show how the two sets of data are related. The various explanations which have been put forward will then be examined and finally we shall discuss the theory that today seems to us to offer the most likely interpretation of the facts.

## 1.4.2. Experimental data

a) Alkali metals in massive and very thick film forms.

Sodium and potassium have already been cited as good subjects for application of the quasi-free electron gas theory, in which the optical conductivity is given by

$$\sigma = \sigma_{\rm D} + \sigma_{\rm I}.$$

In the optical frequency region  $\sigma_{\rm D}$  is given by

$$\sigma_{\rm D} = \frac{Ne^2}{m^* \tau \omega^2} = \frac{A}{\omega^2}$$

where N is the number of conduction electrons per unit volume,  $m^*$  the effective mass of electrons in the lattice,  $\tau$  the electron relaxation time and  $A = Ne^2/m^*\tau$  a constant.

The conductivity  $\sigma_I$  due to interband transitions (the "internal photoelectric effect") is given by a relationship due to WILSON [1936] and BUTCHER [1951] (assuming that the band structure of the metal corresponds to a parabola in the zone diagram):

$$\sigma_1 = \frac{B(\omega_0 - \omega)(\omega - \omega_1)}{\omega^3}$$

where B is a constant,  $\omega_1$  and  $\omega_0$  the threshold angular frequencies.

According to theory, only those photons of energy  $\hbar\omega$  such that  $\hbar\omega_1 > \hbar\omega > \hbar\omega_0$  give rise to interband transitions. It follows that  $\sigma_1$  is zero for  $\omega < \omega_0$ , increases to a maximum at a value of  $\omega$  in the neighbourhood of  $\frac{3}{2}\omega_0$ , then slowly decreases as  $\omega$  increases, to become zero again for  $\omega > \omega_1$ .

For the alkali metals the  $\hbar\omega_0$  thresholds are in the visible or nearinfrared while the  $\hbar\omega_1$  thresholds are in the far ultraviolet. The values of







Fig. 5. (a) Optical conductivity of potassium, massive or as thick film, as a function of incident photon energy. Theoretical curves for  $\sigma_1$ , and  $\sigma_1$  (----). Experimental results: DUNCAN and DUNCAN [1913] (-··-); IVES and BRIGGS [1937, 1938] (-··-); HODGSON [1963, 1968] (····-); MAYER and EL NABY [1963] (----); SMITH [1967, 1969, 1970] (-·--); PALMER and SCHNATTERLY [1971] (\*-\*-\*); MONIN [1972, 1973] (--·-). (b) Optical absorption of potassium as granular film. Experimental results: R. PAYAN [1969] (----). Film thickness increases from lower to upper curves.

constants A and B depend on the strengths of the electron-phonon and electron-lattice interactions, respectively.

As already noted, the experimental results obtained by different authors for the same metal show a considerable spread – a statement that is only too clearly confirmed in the case of bulk sodium by Fig. 4. Moreover, it can be seen how these results differ from those predicted by classical theory, the latter being shown in the figure by the broken line. The same is true for bulk potassium, the subject of much study (Fig. 5), rubidium (Fig. 6), and cesium.

Such wide discrepancies demand a meticulous analysis of the experimental conditions under which the results in question were obtained.

The first point to note is that as far as sodium is concerned the earliest



Fig. 6. Optical conductivity of rubidium, massive or as thick film, as a function of incident photon energy. Theoretical curves for  $\sigma_{12}$  and  $\sigma_{1}$  (---). Experimental results: MONIN [1972, 1973] (----); MAYER and VON AUESCHNATTER [1972] (+-+ and -----); SMITH [1967, 1969, 1970] (---). Optical absorption of rubidium as granular film: R. PAYAN [1969] (....). Film thickness increases from lower to upper curves.

measurements, those of R. W. and R. C. DUNCAN [1913], were made under very poor vacuum conditions and within a very restricted photon energy region. Nevertheless, the spectral distribution of their values agrees quite well with those of other authors. The reason apparently lies in the fact that these workers made their measurements on the glass metal interface, which is without question flatter and better protected than the vacuum/metal interface. Ives and BRIGGS [1937] used the vacuum/metal interface for sodium and cesium, and the guartz/metal interface for potassium (1936) and rubidium (1937); their spectral region of measurement extended from 2.1 to 5 eV. Although their specimens were prepared under vacuum the measurements were only made at ambient temperature. Modern theory, however, shows that these measurements should also be made at low temperature and at wavelengths extending into the infrared. Furthermore, Ives and Briggs noticed that their cesium mirrors sometimes had a matt surface as the result of a delayed condensation of residual alkali metal. As MEESSEN [1972] has pointed out, this matt appearance might be due to the formation of relatively large discrete granules of metal on the surface (similar to those studied by WOOD), which would give rise to diffuse scattering. MEESSEN [1972] has also shown that the ellipsometric method utilized by most authors can lead to an erroneous interpretation of measurements since it assumes that light is being reflected by a perfectly plane surface whereas in reality there can exist a superficial layer composed of a dense distribution of very small granules.

We come now to more recent research, with measurements carried out in ultra-high vacuum and within broad spectral regions.

MAYER and EL NABY [1963] and MAYER and HIETEL [1966] took great pains to prepare, without using any polishing process, metal surfaces that retained as nearly as possible their natural structure and purity and that were as flat as possible, "to within atomic dimensions". They abandoned the use of thin films, or even thick films, produced by thermal evaporation: ROUARD and MALÉ [1953] had already drawn attention to the dangers of utilizing such films, which moreover would not have permitted a study of the liquid metal, regarded by the Mayer school as a very important part of the investigation.

In addition to these precautions, Mayer et al. had used a standard polarimetric method to analyze the elliptically polarized light reflected at the metal-vacuum interface in a very high vacuum  $(10^{-10} \text{ torr})$ . There was, therefore, no reason to suppose that they had not determined the true optical constants of the bulk metal, especially as *their results were confirmed when the metal was molten*: in the latter state a metal surface prepared under suitable conditions was thought to be practically perfect as a subject for optical measurements, from the point of view of both purity and flatness. As we shall find later, this opinion is contested by certain authors, who attribute the anomalous band to a possible roughness in the surfaces utilized by Mayer et al.. The maximum of the band in question lies at about 1.8 eV (6900 Å) for sodium, just below the interband transition threshold.

HODGSON [1963], also using an ellipsometric method, with multiple reflexions at the quartz/metal interface, immediately showed that the values of optical conductivity  $\sigma = c\epsilon_2/2\lambda = cnk/\lambda$  could differ, for different quartz-sodium interfaces, by up to 20%. The dotted curve in Fig. 4 representing one of the spectral distributions he obtained for sodium confirms the existence of Mayer's anomalous band but locates it at about 1.4 eV (8900 Å).

SMITH [1969, 1970] carried out his research on opaque films (approximating to bulk metal) of Na, K, Rb and Cs, deposited by vaporization and condensation on a sheet of copper or on one or both surfaces of a plate of fused silica (Suprasil). To counteract re-evaporation of the metal

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1) with a single reflection of the polarized incident beam at the metal/vacuum interface of the deposit on copper;

2) with four reflections at a Suprasil/metal surface;

3) with seven reflections between two Suprasil/metal surfaces.

Smith's results of measurements at the Suprasil-sodium surface are included in Fig. 4. It will be noted that they agree well with Hodgson's results in the infrared for energies lower than 1.2 eV ( $\lambda > 10 300 \text{ Å}$ ). In this region the values are nevertheless distinctly higher than those corresponding to Drude absorption; the discrepancy may be due to a very irregular surface, even though both authors used the Suprasil/metal interface. These values agree well with those of R. W. and R. C. Duncan, between 2 and 3 eV (6100-4100 Å) for both sodium and potassium. The presence of interband transitions is also clearly revealed by Smith's curve; on the other hand, neither Hodgson's anomalous band nor that found by Mayer et al. are present.

Smith attempts to explain this disagreement as primarily due to the fact that his measurements were made on thick films deposited by volatilization whereas Mayer operated with surfaces of bulk metal. He also believes that the anomalous band may be due to an abnormal skin effect, since "a quick calculation shows that the mean free path of electrons is comparable with the classical skin depth".

In point of fact Smith would probably have repeated Mayer's result in his experiments using a single metal/vacuum surface if he had worked at ambient temperature instead of cooling the copper substrate to the boiling point of liquid nitrogen.

The films investigated by MONIN [1972, 1973] and by MONIN and BOUTRY [1974] were prepared on a substrate at 77 K and then reheated. The results given in Figs 4, 5 and 6 were obtained after reheating to 293 K for sodium and to 195 K for potassium, rubidium and cesium.

The method of measurement was ellipsometric, operating on the metal/vacuum interface; the results are fairly close to Smith's even though the latter used the metal/quartz interface. The agreement is not so close for potassium or rubidium, especially at the low photon energies. If, however, the film is measured before reheating (that is, at 77 K), when according to Smith it still retains microcrystallites, the absorption curve

shows a very pronounced peak, at least as prominent as that found by Mayer et al., although not coincident with it.

In the case of cesium the curves show a minimum for energies slightly higher than the plasma energy (3.05 eV at 195 K).

PALMER and SCHNATTERLY [1971] also used an ellipsometric method, usually operating on the metal/vacuum surface of thick films (200 nm) deposited on sapphirc substrates held at 77 K. They measured the reflected complex relative amplitudes, with the obliquely incident beam p-polarized and s-polarized.

For sodium (Fig. 4), the authors agree reasonably well with IVES and BRIGGS [1937, 1938] (metal/vacuum interface) but not with SMITH [1967, 1969, 1970] (metal/Suprasil interface), MAYER and HIETEL [1965, 1966] (metal/vacuum interface) or HODGSON [1963, 1968] (metal/quartz interface). However, when a metal/glass interface was used the agreement with Smith's results is closer.

In the case of potassium (Fig. 5), while agreement with Smith's results is relatively close in the region of 2 eV, it is less good at higher photon energies.

Quite recently WHANG, ARAKAWA and CALLCOTT [1972] have studied the optical properties of potassium between 4 and 10.7 eV and have compared them with those of rubidium and cesium, which they had already determined, and with Sutherland's values for sodium. The optical constants were calculated from measurements of reflection and transmission at various angles of incidence. Potassium was deposited on the plane face of a semicylinder of slightly cooled MgF<sub>2</sub>. Reflection factors were measured at the metal/support interface through the support.

The results, together with those relating to other alkali metals, are shown in Fig. 7 as continuous traces. The broken-line curves were calculated from values of n and k derived from a smoothed interpolation between the values given separately by Smith and Sutherland.

The maxima occurring between 4.5 and 10 eV could be due to oneelectron transitions between the d and f bands.

Before proceeding to a discussion of the latest results it is appropriate at this point to look at the results of some experiments on very thin granular films.

# b) Experimental results for granular films of alkali metals.

We have seen that anomalous bands occurring in the absorption spectra of bulk alkali metals were also found in the spectra of certain metals,

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Fig. 7. Optical conductivity versus photon energy of Na, K Rb and Cs. Solid lines for K, Rb, and Cs are from WHANG, ARAKAWA and CALLCOTT [1972] and the two solid lines for Na are from Sutherland's data with different films. The dash-dotted lines are calculated from n and k values obtained by a smoothed interpolation between Smith's and Sutherland's data.

particularly gold, silver, and copper, when the metals were presented as two-dimensional distributions of small aggregates on a plane dielectric substrate. This discovery raised the question whether anomalous bands would also be found when the alkali metals were themselves examined as very thin granular or porous films.

It has already been noted that measurement of the optical properties of the alkali metals in the massive state is beset with serious difficulties stemming from their extremely reactive nature and, in the case of potassium, rubidium, and cesium, from their relatively high vapour pressure at ambient temperature. The difficulties are aggravated when these metals are in the form of porous films or of minute granules (dimensions of the order of a few tens of ångstroms) distributed over a flat dielectric surface (granular films).

This explains why serious quantitative study of these films had to await the development of evacuation techniques capable of attaining vacua of the order of  $10^{-10}$  torr.

The films must in fact be kept in the vacuum in which they were

prepared while their properties are measured: this vacuum must be as high as possible during both deposition and measurement, the latter being done as rapidly as possible. Moreover, in order that the results from films of different thicknesses may be strictly comparable, it is important that the various films be prepared and measured under conditions that are truly identical, which can only mean simultaneous deposition and measurement. Finally, the only way to obtain stable films, that is, films that do not immediately re-evaporate at pressures of the order of  $10^{-10}$  torr, is to cool their substrates.

In an article by ROUARD and BOUSQUET [1969] will be found a survey of research carried out before 1969 on thin granular films of the alkali and alkaline earth metals. A short resume of that article now follows.

The optical properties of very thin granular and porous films of sodium, potassium, rubidium, and cesium have been studied, at near-normal incidence, in particular by BLANC, R. PAYAN and RIVOIRA [1965]; R. PAYAN and ROUX [1967, 1968, 1969] and by R. PAYAN [1969].

The optical absorption of the films was determined by means of WOLTER's equation [1939]:

$$\frac{2nkd}{\lambda} = \varepsilon_2 \frac{d}{\lambda} = \frac{1}{2n} \frac{n_0 n_2}{n_2 - n_0} \frac{R - R'}{T} = \frac{n_0}{2\pi} \frac{1 - R' - T}{T} = \frac{n_2}{2\pi} \frac{1 - R - T}{T}$$

where  $n_2$  is the refractive index of the transparent dielectric substrate,  $n_0$  the refractive index of the transparent medium in contact with the outer surface of the film, that is, the vacuum, and  $\lambda$  the wavelength of the monochromatic radiation used for the measurements d and  $\varepsilon_2$  represent respectively the thickness and the imaginary part of the dielectric constant of a continuous film optically equivalent to the granular film, R and R' are the reflexion factors on the vacuum side and the substrate side at near normal incidence, and T is the transmissivity. This was, therefore, a photometric method.

Figures 4, 5 and 6 give the results for three of the metals examined. Taken in ascending order the curves relate to increasing thicknesses ranging from a few nanometers to several tens of nanometers.

An examination of these diagrams reveals two features of importance.

1) In the absorption spectra of granular films of sodium, potassium, rubidium, and cesium there are, between  $1.12 \text{ eV} (11\,000 \text{ Å})$  and 5.3 eV (2300 Å), two very prominent absorption bands.

The first, towards the higher energy region, has a peak of which the

position changes little as the film thickness increases. This peak lies at about 3.3 eV for sodium, 2.34 eV for potassium, 2.14 eV for rubidium, and 1.9 eV for cesium; thus, it shifts towards the lower photon energies in the progression from sodium to cesium.

The other band has a peak which also changes its spectral position towards the lower energies in going from sodium to rubidium, passing from about 2.25 eV for sodium to 1.55 eV for rubidium. R. Payan has suggested that in the case of cesium the band is very probably in the infrared at 1.12 eV (11 000 Å), and hence beyond the spectral limit of the experiment. This band would then be the same as that observed by Smith (Fig. 7).

This second band has a close resemblance to the anomalous band which appears in the spectra of granular films of copper, gold and, particularly, silver.

On the other hand, the source of the first band was thought by R. Payan, agreeing here with Mayer, to be due to interband transitions. The basis for his suggestion is essentially that its position does not change with film thickness, the opposite being true of the low-frequency, or anomalous, band as Figs. 4, 5 and 6 show. It would seem however that, as MEESSEN [1972] has shown, the position and shape of this band do not correspond with the theoretical distribution for interband transitions. We shall see later that Mccssen ascribes the two bands to collective oscillations induced in the metal granules of thin films and in the surface irregularities of bulk metals.

2) For a given alkali metal the position of the anomalous band present when the metal is in granular-film form moves towards the lower energies as the mass thickness increases. But, contrary to the case with copper, gold, and particularly silver, R. Payan has shown that under certain experimental conditions this band persists in even the thickest films and that its peak reaches its limit of displacement at the position of the anomalous band found by Mayer and his co-workers in bulk metal (Fig. 4). It seems therefore that we must be confronted with the same band; this is an important conclusion for, as we shall see, it leads to a much more soundly based explanation of the origin of this anomalous band than any other put forward up to now.

## c) Recent experimental results.

Having been struck by the relationship, to which R. Payan drew attention, between the anomalous band observed by Mayer et al. in bulk alkali metals and the anomalous band found in granular aggregates of н, §1]

these same metals, MEESSEN [1972] developed a theory according to which the anomalous absorption, both in the specimens of bulk alkali metals studied by Mayer et al. and in the granular films studied by R. Payan and Roux, is due to collective oscillations parallel to the bulk metal surface or to the surface of the substrate bearing the granular film. In other words, the anomalous absorption shown by bulk alkali metals is ascribed to roughness of the surfaces on which measurements are made and not to a volume property, the ellipsometric method giving rise to a systematic error when the surface of the metal is covered by a sufficiently dense distribution of small metallic granules.

These conclusions have been corroborated by G. and M. RASIGNI [1973] working with granular films and thick films of lithium.

While quite a large number of authors have concentrated on the optical properties of the alkali metals, very little research has been devoted to lithium (a particularly reactive metal) apart from that of HODGSON [1966], MATHEWSON and MYERS [1972], and CALLCOTT and ARAKAWA [1974].

M. and G. Rasigni, studied the surface structure of granular films and very thick films of lithium prepared and measured at 293 K in a static vacuum at  $10^{-10}$  torr. They found that in reality these surfaces were not "mirror-like", as had hitherto been explicitly or implicitly assumed, but were composed of a two-dimensional distribution of granular elevations rising from a continuous metal base (Fig. 8).



Fig. 8. Electron micrograph of the surface of a thick film of lithium deposited on SiO<sub>2</sub>. Shadowing angle, 50° (——represents 0.5 nm). (M. and G. RASIGNI [1973].)

These lithium films, whether granular or very thick, displayed a marked anomalous absorption, just as with the other alkali metals, in the form of a very intense absorption band varying in position from 2.1 eV for the thinnest films to 1.5 eV for the thickest films.

The problem now is to explain why, for instance, a thick film of silver with a surface that is not perfectly smooth does not show the phenomenon of anomalous absorption.

According to M. and G. Rasigni the surface of silver in either massive or thick-film form appears to possess a structure quite different from that of lithium or the other alkali metals, all of which have comparatively low melting points; the difference in structure can be seen by comparing Figs. 8 and 9.

The alkali metal specimens, bulk metal or very thick film, are all prepared by evaporation and condensation in an ultra-high vacuum. They tend, as we have seen, to have a rough metal/vacuum surface and to contain various types of internal defect. This is especially true when they are prepared at room temperature, which is not far below their melting point.



Fig. 9. Electron micrograph of the surface of a thick film of silver deposited on SiO<sub>2</sub>. Shadowing angle 65° (——represents 0.5 nm). (M. and G. RASIGNI [1973].)



Fig. 10. Optical absorption of a thin sodium film. Angle of incidence, 45°. Solid line:  $T_{\perp}$ . Broken line:  $T_{\parallel}$ . (J. C. PAYAN and ROUX [1971].)

Silver at room temperature is, on the contrary, far below its melting point, a condition that limits migration of surface atoms, changes in structure, and condensation on the specimen of atoms re-evaporated from the walls of the measurement chamber. Herein may perhaps lie the explanation for the absence of abnormal phenomena in silver, condensed at room temperature.

Further evidence comes from the work of J. C. PAYAN and ROUX [1971] on the optical absorption of plane-polarized light at oblique incidence by very thin granular films of sodium (Fig. 10). The absorption band reaching a maximum at about 3.3 eV, already observed in bulk sodium by MAYER and HIETEL [1966] and in granular films at normal incidence by R. PAYAN and ROUX [1969], was found to be accompanied by two anomalous bands. The first, with a maximum in the region of 1.9 eV, had already been brought to light by R. PAYAN, using normal incidence. It is identical with Mayer and Hietel's anomalous band (Fig. 4) and is observable in p- or s-polarized light at any angle of incidence: it could be due to collective oscillations parallel to the coated substrate surface. The second band, which had never previously been described, has a peak at a photon energy lying between 3 and 4.3 eV, depending on its mass thickness, that is, on the macroscopic structure of the particular film. It only appears at oblique incidence in p-polarized light: it could be the result of plasma oscillations taking place in a direction perpendicular to the film plane. Similar results were obtained by J. C. PAYAN and ROUX for potassium [1972] and rubidium [1973] (Fig. 11).

It seemed that Meessen's ideas were being verified and that anomalous optical properties were due to the state of division of the metal or to the



Fig. 11. Optical absorption of a thin rubidium film. Angle of incidence, 45°. Solid line:  $T_{\perp}$ . Broken line:  $T_{\parallel}$ . (J. C. PAYAN and ROUX [1971].)

roughness of its surface layer, when, in a series of recent publications, MAYER and VON AUFSCHNAITER [1972], MAYER and BLANARU [1972], MAYER and HIETEL [1972], STEFFEN and MAYER [1972], and HIETEL and MAYER [1973] announced the results of determinations of the optical properties of Na, K, Rb, and Cs. The specimens were in the form of bulk-metal mirrors and of thin films, prepared at the same time and measured *in situ* in a static ultra-high vacuum at  $10^{-10}$  torr. The parameters were calculated from measurements of the intensity and polarization of monochromatic radiation reflected by the metal surface; the bulk metals were measured at temperatures between 90 K and 370 K (hence in both solid and liquid state) and with radiation of wavelengths covering the range 0.3 to 2.5  $\mu$ m. Mayer et al. believed that "the completely uncontaminated, mirror-like, surfaces suffered no distortion from any treatment"; the purity of the metals used was checked by measuring the residual resistance at liquid helium temperature.

By analyzing the results so obtained, they were able to distinguish, and give values to, the absorption effects due to different mechanisms and to determine some of the quantities describing the behaviour of free electrons.

Figure 12 shows, for bulk sodium, variations of the difference  $\varepsilon_2$  (total absorption) –  $\varepsilon_2$  (Drude absorption) as a function of photon energy at four temperatures: 90 K, 195 K, 293 K and 375 K. It is clear that at 90 K the anomalous band is completely absent, which incidentally confirms results obtained by BÖSENBERG [1959]. As the temperature rises a well-



Fig. 12. Difference between total absorption and Drude absorption as function of photon energy for various temperatures (HIETEL and MAYER [1973]).

defined band develops and increases in strength; its peak stands at about 1.7 eV and its low-energy edge moves downwards from about 1.4 eV at 90 K, reaching 1.2 eV at 373 K, while its half-width broadens.

Since this band persists when the metal is molten, Mayer concludes that any possibility of ascribing its origin to a roughness of the sodium mirror must be dismissed. He also shows that an analysis of the results that Smith obtained by the same method reveals an absorption process at energies above about 1 eV which differs from Drude absorption.

Mayer thinks, with Hodgson, that this band is due to indirect transitions, or more precisely that it must be "attributed to transitions of Fermi surface electrons from the point of symmetry  $N_1$  in the first Brillouin zone to the second zone".

Figure 12 also shows very clearly that at about 2.2 eV a new absorption mechanism comes into action, reaching its peak between 2.4 and 2.7 eV, but here, in contrast to the former effect, the absorption is intensified as the temperature is lowered. Joos and KLOPPFER [1954], ROBERTS [1960], and OTTER [1961] had already observed a similar effect in gold, silver and copper. According to Mayer this is an effect belonging to the region of interband transitions for which he puts the limit at about 2.15 eV (5750 Å).

To sum up, then, the wavelength region between 0.3 and  $2.5 \,\mu m$  exhibits, according to Mayer, three different absorption mechanisms:

1) an intraband, or Drude, absorption;

2) an anomalous absorption, attributed by Mayer to indirect transitions, but of which the origin is still in dispute;

3) an absorption due to interband transitions which is, as we shall see later, also the subject of debate.

STEVENSON [1973] has contributed an examination of the possibility of explaining the disagreement between experiment and theory without abandoning the formalism of the single particle. He considered quantitatively the effect of phonons on absorption, basing his work on that of STURM [1972], MISKOVSKY and CUTLER [1972], and KARAKASHIAN and BARDASIS [1971], who had emphasized the importance of phonons.

The results obtained by Stevenson by means of the Nettel formalism appear to support Smith's experimental findings for sodium and potassium but they are incapable of explaining the existence of the anomalous band observed by Mayer and Hietel in these two metals.

Stevenson came to the conclusion that "for the alkali metals at least, the common procedure of analyzing absorption curves as the sum of an  $\omega^{-2}$  Drude term and a direct-interband term is invalid".



Fig. 13. Variation of transmissivities  $T_{\perp}$  (s-polarized) as function of incident photon energy for thin sodium films prepared and measured *in situ* at 80 K, then reheated and measured at 293 K. Angle of incidence, 45°. (J. C. PAYAN and ROUX [1971].)



Fig. 14. Variation of transmissivities  $T_{\parallel}$  (p-polarized) as function of incident photon energy for thin sodium films prepared and measured *in situ* at 80 K, then reheated and measured at 293 K. Angle of incidence, 45°. (J. C. PAYAN and ROUX [1971].)

In order to elucidate this question, J. C. PAYAN and ROUX [1974] pursued their experiments on continuous and granular films. The continuous films were prepared by depositing sodium on a substrate cooled to 80 K, while the granular films were obtained by heating the continuous films to 293 K. The anomalous band was found to be present at about 1.9 eV in the granular films for both s- and p-polarized radiation incident at  $45^{\circ}$ , but there was no trace of this band in the continuous films (Figs. 13 and 14). This confirms Mayer and Hietel's findings for bulk sodium at 90 K and seems to show that the anomalous optical properties of granular sodium films are determined by the state of granulation of the film rather than by the nature of the bulk metal, and that the anomalous band shown by the bulk metal is due, as Meessen supposes, to the roughness of the surface used for the ellipsometric measurements.

Moreover, MAYER, ZEMBOLD and STEFFEN [1974], in a paper on the determination of volume plasma frequencies, find evidence of an analogous dependence on film structure. They noted that values of  $\hbar\omega_p$  derived by previous authors from optical transmission measurements on thin potassium films condensed at 10 K and 80 K varied between 3.58 and 3.88 eV, though by calculation the value should be  $\hbar\omega_p = 4.21 \text{ eV}$ ; then, having shown that  $\omega_p$  was independent of thickness for films condensed at 10 K but decreased with thickness for those prepared at 80 K, they

concluded that: "This variation, as well as the difference between the values of  $\omega_p$  determined by various authors, are attributed to varying degrees of surface roughness of the film used".

It does now seem that despite all the precautions taken by Mayer et al. in their first experiments, the surfaces of their bulk metals were in fact not mirror-like, because of the time taken for the measurements (in the region of four hours) and the temperature of the specimens during measurement.

It is, indeed, important to make all measurements in as short a time as possible and at as low a temperature as possible (4 to 10 K) if all contamination and surface migration of atoms is to be avoided; these conditions are equally necessary for the supression of structural modifications and recrystallization effects in the surface layer. These precautions are of fundamental importance in measuring optical constants since such processes can in fact induce changes in surface roughness and hence cause variations in any optical properties measured by ellipsometry. Optical properties can also be affected by adsorption of residual gas. Finally, the surface under measurement may undergo a continuous process of renewal due to a secondary condensation of sodium atoms re-evaporated from the cooler walls of the vacuum chamber.

## 1.4.3. Conclusions

It will have been apparent that the experimental values of optical constants for the alkali metals obtained by various workers show a very wide spread.

How is this lack of agreement to be explained?

The majority of present-day authors work with high-purity metals in thick layers deposited in ultra-high vacua on substrates of fused silica, quartz, sapphire, etc. Mayer's school, alone, has used bulk metals, though even these are prepared by evaporation and condensation.

Now, the alkali metals are very reactive and hence very easily contaminated. It is therefore essential that the vacuum be not only as good as possible, it must also be *static*, that is to say, the atmosphere in the chamber must not change. This condition is satisfied in some experiments, such as those of Mayer or Rasigni for example. In other cases, however, the vacuum is maintained by means of powerful and continuous pumping: with measurements occupying several hours this most certainly leads to contamination of the surface layer.

Most measurements are made on thick films of which the structure is

not necessarily that of the bulk metal. Some authors, Smith for instance, who have worked with films at ambient temperature, projected the metal in a continuous stream onto the substrate throughout the duration of measurement to combat rapid re-evaporation. Under such conditions, with a film that could be called *dynamic* since it is in a state of constant evolution, is it really possible to be sure that the structure is that of the bulk metal?

It is, furthermore, usually assumed implicitly or explicitly that a surface produced by evaporation and condensation is truly plane. Experience shows that it is nothing of the sort and that there are transition layers at both faces of the film. In particular, the alkali metals, which are very close to their melting point at normal temperatures and under ultra-high vacuum, have a tendency to develop a roughness on the exposed surface and to contain various internal defects of structure.

These difficulties can be avoided by working with a substrate cooled to as low a temperature as possible and by using the metal/substrate interface, which is more effectively protected from contamination. It must not be forgotten that the results will usually vary with the substrate used and that the substrate surface carrying the film is not strictly plane but is scratched and rough on both micro- and macro-scales, defects to which ellipsometric methods are very sensitive.

Internal defects are much more difficult to characterize and to avoid but their effects could be studied by changing the experimental conditions (rate of evaporation, baking, etc.).

A very thin granular film may show an extra absorption band which seems to be essentially due to plasma oscillations taking place within the granules. When a film is thick and continuous, or when the surface of a bulk metal is rough, this extra absorption band may correspond to the optical excitation of surface plasmons, a phenomenon arising in submicroscopic surface irregularities not more than a few tens of ångstroms in height. It could also be due, in part, to an anomalous skin effect or to other phenomena induced by these micro-irregularities.

A study of the behaviour of surface plasmons under a range of experimental conditions would seem to promise considerable help not only in resolving the major problem of the accurate determination of optical constants and hence of the real and imaginary parts of bulk metal dielectric constants but also in understanding the physical properties of metal surfaces themselves. Some recent research, particularly that of BARKER [1973], is interesting in this context.

Before adding more columns of figures to those that have already been published, it is therefore necessary to proceed to a very thorough analysis of the phenomena that result from the incidence of electromagnetic radiation on a metal surface, in order to be sure that experimental results genuinely relate to bulk metal, that is to say that the measurements have been carried out on the truly plane and uncontaminated surface of a perfectly pure metal, and that the real and assumed structures of the surface are identical. Modern experimental techniques, using as high a vacuum as possible, are designed to produce truly flat surfaces and to eliminate the influence of the nature of the substrate and of irregularities in its surface. Even these precautions, coupled with methods of measurement that are insensitive to residual surface defects, are probably still insufficient to ensure that true bulk-metal properties are measured. It is therefore not impossible that the results so far obtained could be bettered, particularly by operating in the neighbourhood of absolute zero.

It is only when all this has been done that the tables of constants will be meaningful and that theoreticians and practical workers alike will be able to base their work on a truly reliable foundation.

## § 2. Excitation of Collective Oscillations in Thin Metal Films

#### 2.1. INTRODUCTION

The optical properties of *bulk metals* are of considerable interest, since they provide informations about the behaviour of the electrons within their host metals. A free electron would actually be unable to absorb a photon, since the energy and the momentum conservation requirements cannot be fulfilled simultaneously, unless the electron is scattered by some "third body" while the photon is being absorbed. This allows us to consider two kinds of photoexcitation processes, resulting respectively from electron-lattice interactions (interband transitions) and from electron-phonon or electron-lattice defect interactions (intra-band transitions or Drude absorption). But the optical properties of continuous or discontinuous *thin metal films* are equally interesting, since they allow the appearance of other photoexcitation processes, resulting from surface effects, which can even overshadow the volume effects. First of all, it is evident that the absorption of a photon by a single electron can also be assisted by *electron-surface scattering*. This effect may be described as being equivalent to a reduction of the electronic mean-free-path, and therefore to an increase of the Drude absorption, with respect to its value in the bulk metal. These *individual particle* excitation processes have also to be taken into consideration, when one defines the complex dielectric constant  $\varepsilon$  of the electronic gas that is contained within any piece of metal. Higher order surface effects, requiring electron-surface-lattice interactions (indirect transitions and excitation towards surface states) or electron-surface-phonon interactions (anomalous skin effect) are certainly possible, but usually much smaller.

The predominant feature which appears in the optical properties of thin metal films corresponds, however, to the excitation of collective oscillations of the conduction electrons by the electric field of the incident light wave. Maxwell's equations allow actually for the propagation of two kinds of waves within any homogeneous metal: transverse electromagnetic waves of arbitrary frequency  $\omega$ , and longitudinal plasma waves of frequency  $\omega_p$ , determined by the condition  $\varepsilon(\omega_p) = 0$ , where  $\varepsilon$  is the frequency dependent dielectric constant of the bulk metal. But Maxwell's equations provide no coupling of these waves with one another, so that it is impossible to convert a photon into a plasmon within the bulk of a metal. The longitudinal and transverse waves are coupled, however, through the boundary conditions at the metal surfaces. This means that an optical excitation of plasma waves can arise under particular circumstances always implying a surface effect.

The nature of this surface effect can be clarified, by recalling that the boundary conditions, which have to be imposed on the electric field at any metal surface, actually express the fact that the polarization of the metal by an applied electric field E leads necessarily to the appearance of *surface charges*. These surface charges generate a secondary electric field E', which also contributes to the polarization density within the metal, and therefore to the actual surface charge. Such a feed-back process allows the occurrence of a *resonance*, since the action of the surface charges can amplify the action of the applied field, when this field oscillates at some particular frequency. The polarization density within the metal can always be attributed to a displacement of the conduction electrons (at least formally). We can therefore consider the resonance as an excitation of collective oscillations of the electrons within the metal, with corresponding oscillating surface charges. This surface effect was

already known at the beginning of this century for the particular case of very small metal particles, where the "wave" aspects of the collective oscillations can be neglected.

FARADAY [1857] had already recognized that finely divided metals display very peculiar optical properties, but WOOD [1902] became the first to realize that the optical properties of thin granular metal films imply the existence of "a new type of absorption", resulting from "an electrical resonance in minute metal particles". Although he did not discuss the resonance mechanism, Wood stated that one observes the light which is "emitted by the resonators, as a result of their forced vibrations". This reminds us of RAYLEIGH's theory [1871, 1881, 1897] for the scattering of light waves by very small obstacles. It is well known that Rayleigh explained the colour and polarization of light scattered by the sky and by turbid media. He assumed that the electric field of the incident light wave (only) induces an *electric dipole moment* within each polarizable particle, oscillating at the frequency of the incident light, so that the scattered light can be considered as the radiation which is emitted by these oscillating dipoles. This model was transposed by MAXWELL-GARNETT [1904] to the case of a dense distribution of very small spherical metal particles, suspended in a transparent medium (coloured glasses). He attributed the strong absorption band of these colloids to the fact that the induced dipole moment will oscillate with great amplitude, when the frequency of the incident light is close to a particular frequency. Moreover, he defined optical constants for the colloid, by considering an effective dielectric constant, that takes into account only the average effect of all metal particles within a volume of small dimensions compared to the wavelength of the incident light. This procedure is analogous to the definition of the dielectric constant for an ensemble of polarizable molecules in a gas, and implies that the metal particles are very small and that their distribution is sufficiently dense. Maxwell-Garnett suggested that these concepts should also be applicable to thin granular metal films, formed by condensing the metal on a transparent substrate.

The "dipole approximation" and the definition of an "effective dielectric constant" for a metal colloid had a profound influence on all further discussions of the so called *anomalous optical properties* of thin granular metal films. But these concepts required progressive refinements and corrections. Considerable experimental and theoretical progress has now been achieved, especially during the last decade. It would therefore seem useful to review the state of our present understanding, in order to

## 2.2. THE DIPOLE APPROXIMATION

The theory of the interaction of light with small metal particles is enormously simplified, when it is possible to adopt the "dipole approximation", introduced by Rayleigh. This approximation is actually based on two assumptions: (i) the particles have to be very small with respect to the wavelength  $\lambda$  of the incident light, and (ii) their shape has to be ellipsoidal. This includes the particular case of spheres and spheroids, or ellipsoids of revolution. The first assumption allows us to consider the electric field of the incident light as being spatially constant over a relatively large domain, surrounding any given particle, so that the induced dipole moment can be evaluated by means of electrostatic methods, although the electric field actually oscillates at the frequency  $\omega$ of the incident light wave. This "quasi-static approximation" is equivalent to neglecting all retardation effects, since we assume that  $\lambda \sim c/\omega \sim \infty$ . It is also necessary, however, as pointed out by VAN DE HULST [1957], that the index of refraction n of the metal should not be too large, since the wavelength  $\lambda' = \lambda/n$  within the metal could otherwise become too small, even when  $\lambda$  is large enough. We could also consider a correction, resulting from the relatively small wavelength of longitudinal plasma waves within the metal. The condition concerning the shape of the particles has to be introduced, to exclude the induction of multipoles, which would occur for particles of arbitrary shape.

Let us consider a homogeneous ellipsoidal particle of dielectric constant  $\varepsilon$  and volume V, surrounded by vacuum and subjected to the action of a spatially constant field E. The components of the polarization density within this particle are then given by

$$P_i = \alpha (E_i + E'_i) \quad \text{where} \quad E'_i = -4 \pi f_i P_i. \tag{1}$$

These components are defined with respect to the principal axes of the ellipsoid, designated by the index i = 1, 2, 3.  $\alpha = (\varepsilon - 1)/4\pi$  is the intrinsic polarizability of the material within the particle, while  $E_i$  and  $E'_i$  are, respectively, the *i*-components of the applied field E and the depolarizing field E', which results from the induced surface charges. We expect, of

course, that the form factor  $f_i$  has a small value when the extension of the particle along the *i*-axis is large, and a large value when the extension of the particle along the *i*-axis is small, since the particle acts like a condensor. JONES [1945] derived the expression of  $E'_i$  from consideration of the potential within two identical ellipsoids, that are slightly displaced relative to one another and that are filled with a uniform space-charge, of equal magnitudes but opposite signs. The same result can be obtained by solving Poisson's equation inside and outside the particle, with the adequate boundary conditions at the interface, as is shown in many textbooks. The general expressions of  $f_i$ , given by OSBORN [1945], satisfy the sum rule  $\sum_{i} f_{i} = 1$ . In the particular case of a sphere, we therefore obtain  $f_i = \frac{1}{3}$ . The case of spheroids had already been treated by RAYLEIGH [1897], GANS [1912] and DAVID [1939], who provided the analytical expressions which determine  $f_i$  as a function of the ratio of the semi-axes. Instead of recalling these formulas, we calculated the resulting values of  $f_1$  and  $f_2 = f_3$ , when  $a_1$  and  $a_2 = a_3$  are the values of the semi-axes of the spheroid, with  $z = a_1/a_2$  (see Table 1). We note that  $f_1 = 1$  and  $f_2 = 0$  in the limiting case of a disc (z=0), while  $f_1=0$  and  $f_2=\frac{1}{2}$  in the limiting case of a needle.

z	$f_1$	$f_2 = f_3$	z	$f_1$	$f_2 = f_3$
0.0	1.000	0.000	1.0	0.3333	0.3333
0.1	0.8608	0.0696	1.1	0.3082	0.3459
0.2	0.7502	0.1249	1.2	0.2860	0.3570
0.3	0.6612	0.1694	1.3	0.2664	0.3668
0.4	0.5876	0.2062	1.4	0.2488	0.3756
0.5	0.5272	0.2364	1.5	0.2330	0.3835
0.6	0.4758	0.2621	1.6	0.2188	0.3906
0.7	0.4324	0.2838	1.7	0.2058	0.3972
0.8	0.3944	0.3028	1.8	0.1940	0.4030
0.9	0.3606	0.3197	1.9	0.1832	0.4082

<b>FABLE</b>	1
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The components of the induced dipole moment are simply given by  $p_i = VP_i$ , since the polarization density is constant throughout the volume V of the ellipsoidal particle. Solving (1) for  $P_i$ , we get

$$p_i = V \alpha'_i E_i$$
, where  $\alpha'_i = \frac{\alpha}{1 + 4\pi \alpha f_i}$  (2)

defines the effective polarizability of the ellipsoidal particle. JONES [1945] showed that it is sufficient to perform the substitutions  $\varepsilon \rightarrow \varepsilon/\varepsilon_a$  and

 $E_i \rightarrow \varepsilon_a E_i$  in the expressions which are valid for a particle surrounded by vacuum, to get those which are valid when the same particle is *embedded* in a homogeneous medium of dielectric constant  $\varepsilon_a$  and that these expressions remain valid also when  $\varepsilon$  and  $\varepsilon_a$  are tensors (anisotropic media). We note that (2) can be generalized for coated particles, as GÜTTLER [1952] did for concentric spheres and RICHARD and DONNADIEU [1968] for confocal ellipsoids. RICE, SCHNEIDER and STRÄSSLER [1973] showed, on the other hand, that the potential profile is smoothed out at the metal surface, when the screening effect of the plasma in the metal is taken into account, but it is still sufficient to consider only an induced dipole moment.

The effective dielectric constant of a colloid, composed of N identical and equally oriented particles per unit volume, suspended in vacuum, is defined by the components of the electric displacement vector  $\varepsilon'_i E_i = E_i + 4\pi N p_i$ . It thus follows from (2) that

$$\varepsilon_i' = 1 + \frac{q(\varepsilon - 1)}{1 + (\varepsilon - 1)f_i}.$$
(3)

q = NV is the *filling factor* of the colloid, or the total volume of metallic material per unit volume of the colloid. To account for the effect of an embedding medium, it is only necessary to perform the substitutions

$$\varepsilon \to \varepsilon/\varepsilon_{\rm a}$$
 and  $\varepsilon'_i \to \varepsilon'_i/\varepsilon_{\rm a}$ . (4)

Expressions (3) and (4) have been used by GANS [1912] for three dimensional colloids, with an additional randomization for the possible orientations of the ellipsoids, and by DAVID [1939] for thin granular metal films, with a simple correction, to account for the variability of the volumes and shapes of the individual particles. David's model, which has been applied to the analysis of many experimental results, was actually based on the following assumptions: (i) the metal "islands", formed by condensation on a transparent substrate, have a symmetry axis, that is normal to the plane of the film, and (ii) the shape of perfect spheroids; (iii) the effect of the substrate is equivalent to that of an embedding medium of dielectric constant  $\varepsilon_a = (\varepsilon_s + 1)/2$ , corresponding to the average of the dielectric constants of the substrate and the vacuum; (iv) the interaction between the polarized metal particles can be neglected. The first assumption is justified for very thin films, where coalescence is not yet important, but the other assumptions are rather questionable. Recent progress actually corresponds to an improvement of the model with regard to these assumptions. David's model remains very useful, nevertheless, since it allows us at least to account for the essential features of the optical properties of thin granular films. To show this, we introduce the complex dielectric constant  $\varepsilon = \varepsilon_1 + i\varepsilon_2$  of the metal in (3), so that

$$\varepsilon_i' = 1 + \frac{q[(\varepsilon_1 - 1) + (\varepsilon_1 - 1)^2 f_i + \varepsilon_2^2 f_i] + iq\varepsilon_2}{[1 + (\varepsilon_1 - 1)f_i]^2 + [\varepsilon_2 f_i]^2}.$$
(5)

Since  $\varepsilon_a$  is real, we can perform the substitutions (4) in the real and imaginary part of  $\varepsilon$  and  $\varepsilon'_i$ . It is now evident that the colloid behaves like an anisotropic homogeneous medium, and that its optical properties display "giant resonances", to use the terminology of nuclear physics. The real and imaginary part of  $\varepsilon'_i$  can be written in the form

$$\varepsilon_{i1}' = 1 + \frac{A_i(\omega_i - \omega)\gamma_i/2}{(\omega - \omega_i)^2 + (\gamma_i/2)^2}, \qquad \varepsilon_{i2}' = \frac{A_i(\gamma_i/2)^2}{(\omega - \omega_i)^2 + (\gamma_i/2)^2}$$
(6)

when the resonance is sufficiently sharp, as indicated by MEESSEN [1972]. It is sufficient, indeed, to consider a linear expansion of  $\varepsilon_1(\omega)$  near the resonance frequency  $\omega_i$ , determined by the condition

$$1 + (\varepsilon_1 - 1)f_i = 0$$
, while  $A_i = \frac{q}{\varepsilon_2(\omega_i)f_i^2}$  and  $\gamma_i = \frac{2\varepsilon_2(\omega_i)}{(d\varepsilon_1/d\omega)\omega_i}$ . (7)

 $A_i$  is the amplitude and  $\gamma_i$  the width of the absorption maximum, characterized by  $\varepsilon'_{i2}$ . We see that the resonance is particularly strong, when  $\omega_i$  is situated in a spectral region where the absorption of the bulk metal  $\varepsilon_2$  is small. On the other hand, it follows from (5) that the colloid becomes transparent in the far infrared, where the absorption of the bulk metal is very strong, since  $\varepsilon_2 = 4\pi\sigma(\omega)/\omega \to \infty$  when  $\omega \to 0$ , while  $\varepsilon'_{i1} \to 1 + q/f_i$  and  $\varepsilon'_{i2} \to 0$ . The colloid can only reproduce the behaviour of the bulk metal (with  $\varepsilon'_{i2} = q\varepsilon_2$ ), when  $(\varepsilon_1 - 1)f_i \ll 1$  and  $\varepsilon_2 f_i \ll 1$ . For a *free-electron metal*, we know that

$$\varepsilon_1 = 1 - \omega_p^2 / \omega^2$$
 and  $\varepsilon_2 = \omega_p^2 \gamma / \omega^3$ , (8)

at optical frequencies, where  $\omega_p = (4\pi ne^2/m^*)^{\frac{1}{2}}$  is the plasma frequency of the bulk metal, while *n* is the density and *m*<sup>\*</sup> the effective mass of the conduction electrons.  $\gamma = 1/\tau$  is Drude's damping constant. It follows from (7) and (8) that

$$\omega_i = \omega_p \sqrt{f_i}, \qquad A_i = q \omega_p^2 / \omega_i \gamma \qquad \text{and} \qquad \gamma_i = \gamma.$$
 (9)

These expressions are also valid below the threshold for interband transitions, even when a dielectric constant  $\varepsilon_c$  has to be included in the expression of  $\varepsilon_1$ , to account for the polarizability of the ion cores in the metal, as long as  $(\varepsilon_c - 1)f_i \ll 1$ . DAVID [1939] had already clearly stated that the resonance is associated with an oscillation of the electrons, but the concept of "plasma oscillations" in small metal particles was not used until MÖGLICH and ROMPE [1949] explicitly emphasized the analogy with gaseous plasmas. HAMPE [1952] noted that Drude's theory allows us to describe the average motion of the conduction electrons by the equation

$$m^*(\ddot{x}_i + \gamma \dot{x}_i) = -e(E_i + E'_i),$$

where  $x_i$  is the average displacement of the electrons, defining the polarization density  $P_i = -enx_i$ .  $E_i$  is the applied field and  $E'_i$  the depolarizing field, defined by (1). The effect of the surface charge is thus equivalent to a restoring force, and we actually obtain the equation of motion of a forced harmonic oscillator, of eigenfrequency  $\omega_i = \omega_p \sqrt{f_i}$ .

It is evident that the forced oscillations in the *i*-direction and the corresponding  $\omega_i$  resonances can only be excited when the electric field of the incident light wave has a non-vanishing component  $E_i$  along this direction. It is customary to define the polarization of the incident light wave with respect to the plane of incidence, by using the symbols s or  $\perp$ and p or ||, respectively when the electric field is normal and parallel to the plane of incidence. It is more convenient, of course, to define the directions of oscillations within the metal particles with respect to their principal axes, which are related to the plane of the film. To avoid any confusion, we intend to use the notations i = n and i = t, respectively, (instead of  $i = \bot$  and  $i = \parallel$ ) for the directions which are normal and tangential to the plane of the film. For spheroidal particles, with their symmetry axis normal to the plane of the film, we thus get  $f_n = f_1$  and  $f_1 = f_2 = f_3$  in Table 1, so that the resonance frequency  $\omega_1 \ll \omega_n$  for very flat ellipsoids, according to (9). In the limiting case of a thin continuous film  $(f_n = 1)$ , it follows from the resonance condition (7) that  $\omega_n$  is equal to the plasma frequency  $\omega_p$  of the bulk metal, defined by  $\varepsilon_1 = 0$ . At normal incidence and for s-polarized light, at oblique incidence, it is only possible to excite the low frequency  $\omega_t$  resonance, but with *p*-polarized light, we excite the  $\omega_t$  as well as the  $\omega_n$  resonance, the latter appearing more strongly for large angles of incidence. The experimental results are at least in good qualitative agreement with these predictions (see § 2.5).

#### 2.3. THE OPTICAL SIZE EFFECT

W. PLANCK [1914] and POGANY [1914, 1916] observed that the optical absorption as well as the d.c. resistivity, increases, when the film thickness is reduced below a certain value, which is of the order of the electronic mean-free-path in the bulk metal. They therefore suggested that both effects should be attributed to the same cause. The optical absorption  $\varepsilon_2$ and the static resistivity  $\rho$  are, indeed, proportional to the Drude damping constant  $\gamma = v_F/\Lambda$ , where  $v_F$  is the electronic velocity at the Fermi-level and  $\Lambda$  the electronic mean-free-path which is limited by the film thickness d.

FUCHS [1938] provided a successful theory for the film thickness dependence of the static conductivity of thin continuous metal films, where the electric field is applied parallel to the plane of the film. He actually solved Boltzmann's transport equation with the assumption that all electrons are diffusely reflected, and then amended this calculation for the case where a fraction p of these electrons are specularly reflected. Y1-HAN KAO [1966] applied this method of calculation to predict the optical properties of thin continuous metal films at normal incidence, for completely diffuse electron-surface scattering (p=0). We deduce from his calculation that  $\Lambda = 8d/3$ , at optical frequencies, when the film thickness d is much smaller than the electronic mean-free-path in the bulk metal. But the classical theory of Fuchs would predict that there is no absorption for completely specular reflection, even when the electric field oscillates normally to the plane of the film. This is in flat contradiction with the quantum-mechanical calculations, effected by ESPOSITO, BLOOMFIELD and MULDAWR [1968, 1969], SANDER [1968] and MEESSEN [1968]. The boundary condition for Boltzmann's probability function is not equivalent, indeed, to the boundary condition for the electronic wave-function, allowing for interference effects, as already suspected by GREEN [1966]. Meessen showed that single electrons can absorb a photon through electron-surface scattering, within a distance of the order of  $v_{\rm F}/\omega$  from the scattering surface, even in the case of a semi-infinite metal. But the total optical absorption in a thin metal film, with perfectly plane and parallel surfaces, is equivalent to a Drude absorption with  $\Lambda = 2d/3$ , when  $\hbar v_{\rm F}/d \ll \hbar \omega \ll E_{\rm F}$ . At lower frequencies, one gets a discrete spectrum, corresponding to the "quantum size effect", and when  $\hbar\omega$  approaches the value of the Fermi energy  $E_{\rm F}$ , interband transitions will always become predominant. The same value for  $\Lambda$  can be deduced from the

calculation of Esposito et al., while Sander's result is erroneous by a factor 2.

For small metal particles, we have to expect a similar increase of the Drude absorption, corresponding to an increase of the value of  $\gamma$  in (8) and (9). This enlargement of the plasma resonance with respect to the predictions which result from the value of  $\varepsilon_2$  in the bulk metal, has been observed by FRAGSTEIN and ROEMER [1958], ROEMER and FRAGSTEIN [1961], FLECHSIG [1963], DOREMUS [1964, 1965], KARLSSON and BECK-MAN [1967], KLEEMANN [1968], KREIBIG and FRAGSTEIN [1969], CARLAN [1969], SMITHARD [1973], KREIBIG [1974] and other authors. Doremus demonstrated, in particular, that the amplitude and the inverse of the width of the resonance for very small spherical particles of Au and Ag, forming a three-dimensional colloid, are both proportional to the radius of these particles, as should be expected according to (9). KREIBIG [1974] showed that the electronic mean-free-path  $\Lambda$  in small spherical Ag particles is practically equal to the radius R of these particles. This agrees with the result of EULER [1954], who simply evaluated the average value for all possible chords of the sphere. The quantum-mechanical calculation of KAWABATA and KUBO [1966] for the individual particle excitation of free electrons in a sphere, with a perfectly smooth surface, vielded, however, the result  $\Lambda = \pi^2 R/6 \approx 3R/2$  (corrected by a factor  $\pi$ ). This indicates that the surface is not smooth. For totally diffuse surface scattering, we found, indeed, that  $\Lambda = 3R/4$ , by applying the method of FUCHS [1938] to a sphere of radius R.

## 2.4. PARTICLE INTERACTIONS AND SUBSTRATE EFFECTS

Since the definition of an effective dielectric constant implies that the average distance L between the particles has to be much smaller than the wavelength  $\lambda$  of the incident light, it is evident that the mutual interactions between the polarized particles cannot be neglected. MAXWELL-GARNETT [1904] treated this problem by analogy with the Lorentz-Lorenz theory for molecules in a gas. The analytic properties of the resulting Clausius-Mossotti relation have been analysed in detail by MARTON and LEMON [1971, 1973], for free-electron metals. COHEN, CODY, COUTTS and ABELES [1973] recognized that the theory of Maxwell-Garnett has to be generalized for ellipsoidal particles, by considering the Lorentz field in a cavity that is congruent with the (average)

shape of the particles. Although this theory only applies to threedimensional colloids, it is useful to develop it briefly, generalizing the usual expressions, in order to evaluate the influence of the variability of the volumes and shapes of the individual particles. For simplicity, we consider only the case where the particles are equally oriented. We also assume that they are suspended in vacuum, since the effect of an embedding medium is easily taken into account by means of the substitutions (4). The total dipole moment per unit volume of the colloid is then defined by the components

$$\mathcal{P}_i = \sum_k V_k P_{ik} \quad \text{with} \quad P_{ik} = \alpha_{ik} (E_i + E'_{ik} + E''). \quad (10)$$

The index k refers to individual particles and the sum is extended over all particles per unit volume of the colloid.  $V_k$  and  $P_{ik}$  are respectively the volume and the *i*-component of the polarization density within a given particle k.  $\alpha_{ik}$  is the intrinsic polarizability of the metal, including the effect of the reduced mean-free-path for the *i*-direction in a particle k.  $E_i$  is the *i*-component of the applied field,  $E'_{ik}$ , the corresponding depolarizing field and  $E''_i$ , the average interaction field.  $E'_{ik}$  depends on the form factor  $f_{ik}$  of the chosen particle, according to (1), and  $E''_i$  can be evaluated by considering the Lorentz field in an ellipsoidal cavity, characterized by the average form factors  $\overline{f}_i$ , so that the effect of the surface charge appearing on the walls of this cavity. This means that

$$E'_{ik} = -4\pi f_{ik} P_{ik}$$
 and  $E''_i = 4\pi \bar{f}_i \mathcal{P}_i.$  (11)

Substituting (11) in (10), we get an expression for  $P_{ik}$ , leading to the equation

$$4\pi \mathscr{P}_i = G_i(E_i + 4\pi \overline{f}_i \mathscr{P}_i)$$
 with  $G_i = \sum_k \frac{V_k(\varepsilon - 1)}{1 + (\varepsilon - 1)f_{ik}}$ .

The effective dielectric constant, which is defined by  $\varepsilon'_i E_i = E_i + 4\pi \mathscr{P}_i$ , will thus be given by

$$\varepsilon'_i = 1 + \frac{G_i}{1 - \overline{f_i}G_i}$$
 with  $G_i = q \int \frac{g(f_i)(\varepsilon - 1) \, \mathrm{d}f_i}{1 + (\varepsilon - 1)f_i}$ . (12)

q is the filling factor of the colloid and  $g(f_i)$  is the weighted distribution for the average volume of the particles of form factor  $f_i$ . This function was introduced by DAVID [1939], who neglected, however, the mutual interactions between the particles, so that the effective dielectric constant (12) was reduced to  $1 + G_i$ . Since the distribution function  $g(f_i)$  cannot be determined experimentally (without stereoscopic electronmicrographs), it is customary to resort to hypothetical functions. SCHOPPER [1951], HEN-DERSON and WEAVER [1966] and YOSHIDA, YAMUGUCHI and KINBARA [1972] proposed various examples. But David actually introduced this distribution function  $g(f_i)$  to explain the observed, relatively large width of the optical resonances, without considering the optical size effect. To get a simple expression of the form (3), it is usually assumed that the particles have *nearly identical shapes*. To evaluate the limit of applicability of this approximation, it is sufficient to perform the integration (12) for a Lorentzian distribution  $g(f_i)$ , characterized by a width  $\sigma$  at half the maximum value and centered on the average value  $\overline{f_i}$ . We then get the simple result

$$G_i = \frac{qM_i}{1 + (\sigma M_i)^2}$$
 with  $M_i = \frac{\varepsilon - 1}{1 + (\varepsilon - 1)\overline{f_i}}$ 

when  $\varepsilon$  is assumed to depend only on  $\overline{f}_i$ . It thus follows from (12) that

$$\varepsilon_i' = 1 + \frac{q(\varepsilon - 1)}{1 + (\varepsilon - 1)F_i}$$
 with  $F_i = \overline{f}_i(1 - q) + \sigma^2 M_i$ . (13)

Considering the maximum value of  $|M_i|$ , according to (7), we see that the variability of the shapes of the particles can (only) be neglected when  $\sigma^2 \ll \varepsilon_2(\omega_i) \bar{f}_i^3(1-q)$ , or  $\sigma^2 \ll \gamma \bar{f}_i(1-q)/\omega_p$  for free electrons.

For a thin granular metal film, it is necessary to evaluate the interaction field  $E_i''$ , by considering only a two-dimensional distribution of polarized metal particles. S. YAMAGUCHI [1960, 1962] and BOUSOUET [1968] calculated the sum of the dipole fields which act on a given particle, by considering the dipole density per unit area  $Q_i$  as being constant outside a circle of radius a and zero within this circle. We get then a different result for i = n and i = t:

$$E_{n}'' = -Q_{n} \int_{a}^{\infty} \frac{2\pi r \, dr}{r^{3}} = \frac{-2\pi}{a} Q_{n};$$
$$E_{t}'' = Q_{t} \int_{a}^{\infty} \int_{0}^{2\pi} \frac{(3\cos^{2}\phi - 1) \, d\phi r \, dr}{r^{3}} = \frac{\pi}{a} Q_{t}.$$
 (14)

r is the length of the radius vector in the plane of the film and  $\phi$  is the angle between this radius vector and the direction of polarization of the

particles in the plane of the film.  $E_t''$  can also be evaluated by considering only the effect of the charge which appears on the rim of a circular hole. But the result is only identical to (14) when the radius of this circle is equal to a/2. S. Yamaguchi and Bousquet assumed that  $a \approx L/2$ , where L is the average distance between the particles. It is more correct, however, to set  $a \approx L$ , as can be confirmed by performing a summation for a discrete distribution of dipoles, instead of an integration. T. YAMAGUCHI, YOSHIDA and KINBARA [1974] applied this method, but the result depends then, of course, on the assumed lattice structure and the assumed orientation of the dipoles with respect to this lattice. S. YAMAGUCHI [1962] took into account the modulation of the amplitudes of the dipoles, resulting from the finite wavelength  $\lambda$  of the incident light, but he neglected the retardation effects for the dipole fields, which should have been considered in this case. Even this leads only to corrections of the order of  $(L/\lambda)^2$ , which can be safely neglected under normal conditions.

David's assumption that the effect of the substrate can be described by means of the substitutions (4) with  $\varepsilon_a = (\varepsilon_s + 1)/2$ , was only introduced for reasons of simplicity. T. YAMAGUCHI, YOSHIDA and KINBARA [1974] therefore introduced a different model, where the "dipole approximation" can also be maintained. It is sufficient, indeed, to assume that the metal "islands" can be regarded as *perfect spheroids*, situated slightly above the substrate, so that each particle is subjected to a nearly homogeneous field, resulting from the applied field in the surrounding vacuum and the field of the image of the polarized particle. Each dipole moment p, situated symmetrically with respect to the substrate-vacuum interface. The components of the image-dipole are given by

$$p'_{t} = -\mu p_{t}$$
 and  $p'_{n} = \mu p_{n}$  with  $\mu = \frac{\varepsilon_{s} - 1}{\varepsilon_{s} + 1}$ , (15)

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where  $\varepsilon_s$  is the dielectric constant of the substrate. An isolated particle is thus subjected to the applied field  $E_i$ , the depolarizing field  $E'_i$  defined by (1) and the image field

$$\hat{E}_i = \nu_i (\mu V/l^3) P_i$$
, where  $\nu_t = 1$  and  $\nu_n = 2$ . (16)

V is the volume of the particle and l the distance between the center of the particle and its image. But we have also to take into account the interaction field  $E_i''$ , resulting from the neighbouring polarized particles and their images. Since the dipole moment p and its image p' act

together, at sufficiently large distances, like a single dipole moment p'' = p + p', it follows from (14) that

$$E_i'' = \beta_i (\pi N' V/L\varepsilon_a) P_i$$
 with  $\beta_t = 1$  and  $\beta_n = -2\varepsilon_s$ . (17)

We now assume that the particles have nearly identical shapes and volumes, while  $N' = 1/L^2$  is the density of particles per unit area, and  $\varepsilon_a = (\varepsilon_s + 1)/2$ . Evaluating the polarization density  $P_i = \alpha(E_i + E'_i + \hat{E''_i} + E''_i)$ , with (16) and (17), we get the effective dielectric constant

$$\varepsilon_i' = 1 + \frac{q(\varepsilon - 1)}{1 + (\varepsilon - 1)F_i}$$
 with  $F_i = f_i^* - \beta_i d_m C$  (18)

where  $f_i^* = f_i - \nu_i \mu V/4 \pi l^3$  and  $C = 1/4 \varepsilon_a L$ , while  $d_m = N'V$  is the mass thickness of the film, or the volume of metallic material deposited per unit area of the substrate. The effective thickness d of the granular film is defined by the height of the metal particles, so that the average number of particles per unit volume of the granular film is N = N'/d. Since the filling factor q = NV, we get the relation  $d_m = qd$ . The effective dielectric constant (18) has the same form as (3), where we have only to replace the form factors  $f_i$  by the effective form factors  $F_i$ , satisfying the sum rule

$$F_{n} + 2F_{t} = 1 - \mu [(V/\pi l^{3}) - (V/L^{3})].$$
<sup>(19)</sup>

BOUSQUET [1968] neglected the substrate effect ( $\mu = 0$ ) and found thus the same sum rule as for individual spheroids. BÖESENBERG [1969] and T. YAMAGUCHI, S. YOSHIDA and KINBARA [1973] discovered that this sum rule is actually not satisfied for thin granular K and Ag films. The theoretical result of T. YAMAGUCHI [1974] differs only slightly from (19).

# 2.5. THE PLASMA RESONANCE ABSORPTION IN THIN GRANULAR METAL FILMS

Wood [1902] noted that three different situations can arise in alkali metal films, condensed on a transparent substrate: (i) Coarse particles, distinguishable by means of an optical microscope, produce a "silky lustre" and (ii) minute particles, far apart from one another, lead to a low intensity "fluorescent" appearance of the surface. In both cases, the light is simply scattered. But (iii) a dense distribution of minute particles yields a regular reflection, "the particles being so close together that interference, as imagined by Huyghens, takes place". Such a film is brightly coloured, since there exists a strong absorption band, resulting from the excitation of collective oscillations.

It has generally been assumed that a thin granular metal film should be optically equivalent to a continuous film, with plane parallel surfaces and optical constants, corresponding to those of a colloid. But S. YAMAGUCHI [1962] considered directly the interference effect for the radiation, which is emitted by an aggregate of oscillating dipoles, distributed over the surface of a transparent substrate. He obtained Snell's law, but the reflected and transmitted wave does not have exactly the same amplitude as would be expected for a thin continuous film of thickness *d*. BEDEAUX and VLIEGER [1973, 1974] performed similar calculations and compared them to the effect of a very thin surface layer. The results of S. YAMAGUCHI [1962] can be rewritten in the form

$$r_k = \frac{1 - A_k + iB_k}{1 + A_k - iB_k^+}$$
 and  $t_k = \frac{2}{1 + A_k - iB_k^+}$ 

 $r_k$  and  $t_k$  are respectively the amplitudes of the reflected and transmitted light, when the incident light has unit amplitude and a polarization k = sor p. The coefficients  $A_k$  and  $B_k^{\pm}$  are determined by the values of the angle of incidence  $\theta$ , the angle of refraction within the substrate  $\theta_s$ , the index of refraction  $n_s$  of the substrate and the effective polarizability  $\alpha'_i = (\varepsilon'_i - 1)/4 \pi q$  of the metal particles as well as the wavelength  $\lambda$  of the incident light:

$$A_{s} = \frac{n_{s} \cos \theta_{s}}{\cos \theta}, \qquad A_{p} = \frac{\cos \theta_{s}}{n_{s} \cos \theta}, \qquad B_{s}^{\pm} = \frac{2\pi d}{\lambda \cos \theta} (\varepsilon_{t}' - 1)$$
$$B_{p}^{\pm} = \frac{2\pi d}{\lambda \cos \theta} [(\varepsilon_{n}' - 1) \sin^{2} \theta \pm (\varepsilon_{t}' - 1) \cos \theta \cos \theta_{s}/n_{s}].$$

The density of the metal particles is taken into account through the effective film thickness  $d = d_m/q$ . When we calculate the reflection coefficient  $R_k$  and the transmission coefficient  $T_k$ , we get the relations

$$\frac{1-R_{\rm s}-T_{\rm s}}{T_{\rm s}} = \frac{2\pi d}{n_{\rm s}\cos\theta_{\rm s}} \varepsilon_{12}^{\prime}$$
(20)

$$T_{\rm s} = 1 - R_{\rm s}^{\rm o} - \frac{4\pi d\varepsilon_{\rm t2}^{\prime}}{\lambda \left(\cos\theta + n_{\rm s}\cos\theta_{\rm s}\right)} \tag{21}$$

$$T_{\rm p} = 1 - R_{\rm p}^{\rm o} - \frac{4\pi d(\varepsilon_{\rm n2}' \sin^2 \theta + \varepsilon_{\rm t2}' \cos \theta \cos \theta_{\rm s}/n_{\rm s})}{\lambda(\cos \theta + \cos \theta_{\rm s}/n_{\rm s})}.$$
 (22)

 $R_k^{\circ}$  is the reflection coefficient of the substrate. It was assumed that the film thickness d is very small, so that one only has to consider terms of the first order in d.

The "anomalous" optical absorption of thin granular metal films has been studied extensively by ROUARD and his collaborators, using reflection and transmission measurements at *normal incidence*. Since the electric field of the incident light wave then vibrates tangentially to the plane of the film,  $\omega_t$  resonance only can be observed. But since  $\omega_t \ll \omega_p$ , one gets an absorption maximum in the visible or the infrared, for practically all metals. The use of Wolter's relation is also justified, according to (20), as for a continuous film. The experimental curves for  $\varepsilon'_{12}d$ , obtained by this method, disclose a *characteristic shift* of the "anomalous" absorption peak towards low frequencies, when the mass thickness  $d_m$  of the granular films is increased (see Figs. 2, 4b). This effect would have to be attributed to a progressive flattening of the metal particles, if the resonance frequency  $\omega_t$  and the amplitude  $A_t$  were simply given by (9). But we have to replace  $f_t$  by  $F_t$ , according to (18). For  $d_m \rightarrow 0$ , we get then the displacement law

 $(\varepsilon_{12}'d)_{\max} = A_1 d = K(\omega_1^0 - \omega),$ 

with

 $K = 8 \varepsilon_{\rm a} L / \gamma$  and  $\omega_{\rm t}^0 = \omega_{\rm p} \sqrt{f_{\rm t}^*}$ .

Similar relations could be obtained with respect to the wavelength  $\lambda$ . Experimentally, one very often gets such a linear relationship for the peak value of  $\varepsilon'_t d$ , as noted by MEESSEN [1972], who indicated that this effect results essentially from the *mutual interactions* between the metal particles. The flattening of the metal particles will become predominant, however, for larger values of  $d_m$ , as a result of coalescence. The influence of the mutual interactions on the  $\omega_t$  resonance has actually been demonstrated directly by FLECHSIG [1962] and T. YAMAGUCHI, YOSHIDA and KINBARA [1972, 1973, 1974], who deposited the metal particles on a stretchable polyvinyl substrate.

According to (21) and (22), the separate optical excitation of the  $\omega_t$  and  $\omega_n$  resonances can be demonstrated, by performing transmission measurements for s- and p-polarized light at oblique incidence. The results of N. and A. EMERIC [1967] and YOSHIDA, YAMAGUCHI and KINBARA [1972]

provide an excellent illustration of the appearance of one minimum at  $\omega_t$ in  $T_s$  and two minima at  $\omega_t$  and  $\omega_n$  in  $T_p$  (see Fig. 3). FLEISCHMAN [1963] and DEICHSEL [1963] compared  $1 - T_p$  to  $1 - T_s$  for various alkali metal films, and showed that  $\omega_n < \omega_p$  in granular films, while  $\omega_n = \omega_p$  in continuous films condensed on low temperature substrates. The occurrence of the  $\omega_n$  resonance has also been demonstrated by means of  $T_p$  and  $T_s$ measurements, performed on continuous or nearly continuous K films by BRAMBRING [1967], BÖSENBERG [1969] and MAYER, ZEMBOLD and STEF-FEN [1974], and on Ag films by KRETSCHMANN [1969] and SCHROEDER [1969]. The  $\omega_n$  resonance is actually responsible for the "vectorial selective photoelectric effect" of alkali metals, studied by Ives and BRIGGS [1936, 1938] as well as other authors, and attributed for a long time to a "surface photoelectric effect", corresponding to the individual excitation of electrons through electron surface interactions. The parallelism between this effect and the optical resonance absorption was demonstrated by MAYER and THOMAS [1957]. MONIN and BOUTRY [1974] also found this plasma resonance effect in the photoelectric emission of alkali metal films.

The most important recent result is the discovery of new features which cannot be explained by means of the "dipole approximation". R. PAYAN [1967, 1968, 1969] found, indeed, that  $\varepsilon'_{12}$ , determined by (20) at normal incidence, displays two maxima for various alkali metals (Figs. 4, 5, 6). BÖSENBERG [1967, 1969] confirmed this result by measuring  $T_p$  and  $T_s$  for thin K films. The existence of (at least) two minima in the spectral distribution of  $T_s$  (as well as  $T_p$ ) was also established beyond any doubt by J. C. PAYAN and ROUX [1971, 1972, 1973] for Na, K and Rb (see Figs. 10, 11, 13, 14), and by M. and G. RASIGNI [1973] for Li. These authors suggest that the low frequency  $\omega_t$  resonance, which is shifted for increasing values of  $d_{\rm m}$ , corresponds to the usual "anomalous" absorption in thin granular metal films, while the absorption peak at a somewhat higher frequency  $\omega'_t$  should be attributed to interband transitions. This maximum could reveal, however, a much more interesting effect. In this connection, we have first to recall the astonishing discovery of MAYER and EL NABY [1963], MAYER and HIETEL [1965], confirmed recently by MAYER and HIETEL [1972], MAYER and VON AUFSCHNEITER [1972] and HIETEL and MAYER [1973], who measured the optical constants of practically semiinfinite alkali metals by means of the ellipsometric method. They found an unexpected absorption maximum below the threshold for interband transitions. But MEESSEN [1972] showed that the ellipsometric method can lead to an error of interpretation when one ignores the possibility that the

metal surface could be roughened, as a result of a delayed condensation of small metal particles of the same metal. MARTON [1971] proposed a similar explanation, in a more qualitative form. Mayer put forward a fundamental objection against this interpretation, resulting from the fact that the "anomalous" absorption peak does not vanish when the temperature of Na is very slightly raised above its melting point. But his objection is perhaps not so fundamental as it may appear at first sight. The surface of a liquid is only plane, indeed, on the average. On the time scale for optical excitation of collective oscillations, we should expect, on the contrary, that the surface of a liquid metal would display an irregular structure, since the atoms form temporary associations, and since these aggregates move and deform themselves at a relatively low pace, as compared to the frequency and the life-time of plasma oscillations. It may be worthwhile to note that an unexplained supplementary absorption band just below the threshold for interband transitions has also been observed, by means of other methods, in Au by SHLYAREVSKII and YAROVAYA [1966], HODGSON [1968] and THEYE [1970], and in Ag by DUJARDIN and THEYE [1971], HUNDERI and MYERS [1972].

MEESSEN [1972] showed that the apparent absorption curve, determined by ellipsometry, is the sum of the absorption  $\varepsilon_2$  of the bulk metal and the absorption  $\varepsilon'_{12}$  resulting from the excitation of collective oscillations in small metal particles, tangentially to the surface on which they are deposited. This argument indicated that  $\varepsilon'_{12}$  displays two maxima in agreement with the result of R. Payan. But the position and the shape of the secondary maximum do not correspond to that expected for interband transitions. We verified also that the application of (3) or (18) does not yield a secondary maximum like the one observed, when one takes into account the (enhanced) Drude absorption and the interband absorption of the bulk metal. The infrared behaviour of the granular alkali metal films shows, however, that these formulas should be applicable, unless the "dipole approximation" is no longer valid for these films. The recent experimental results of J. C. PAYAN [1972, 1973] actually indicate that there exists a sequence of secondary maxima of decreasing amplitude above  $\omega_t$  for  $\varepsilon'_{t2}$  and below  $\omega_n$  for  $\varepsilon'_{n2}$ , so that we have rather to look for multipole effects.

## 2.6. MULTIPOLE EFFECTS

To find out if the secondary maxima can be attributed to a breakdown

н, § 2]

of the "dipole approximation", we have evaluated the influence of three possible modifications: (i) the particles could become relatively *large* with respect to the wavelength  $\lambda$  of the incident light, so that it is no longer possible to assume that the electric field is spatially constant within the particle, or (ii) the metal particles do not exactly have the form of perfect ellipsoids of revolution. One could have, for instance, *slightly truncated* spheroids. But it is even more probable that (iii) they do not at all have the shape of spheroids, but rather the shape of *hemispheres*, as one would expect for metal droplets, deposited on a transparent substrate.

The general problem of the interaction of a plane light wave with a sphere of arbitrary radius a was solved by MIE [1908]. Applying the adequate boundary conditions to the general solution of Maxwell's equations, inside and outside the sphere, he found that the incident radiation induces electric and magnetic multipoles, and that higher order effects become more and more important when the size parameter  $x = 2\pi a/\lambda = ka$  increases. This allows us to evaluate the limit of applicability of the dipole approximation, by considering only the first order corrections in x, with respect to Rayleigh's result. This means that we have to consider the Mie coefficients

$$\hat{a}_1 = 2x^3 u_1 \frac{\varepsilon - v_1}{\varepsilon + 2w_1}, \qquad \hat{a}_2 = -\frac{x^5}{6} u_2 \frac{\varepsilon - v_2}{\varepsilon + \frac{3}{2}w_2} \text{ and}$$
 $\hat{p}_1 = -2x^3 u_1 \frac{1 - v_1}{1 + 2w_1},$ 

where  $\varepsilon$  is the dielectric constant of the metal inside the sphere, surrounded by vacuum, while  $u_n$ ,  $v_n$  and  $w_n$  are functions of  $\varepsilon$  and x, which are all equal to 1 when x = 0. The coefficients  $\hat{a}_1$ ,  $\hat{a}_2$  and  $\hat{p}_1$  define, respectively, the amplitude of the induced electric dipole, electric quadrupole and magnetic dipole moment. Following GANS and HAPPEL [1909], we can define the effective dielectric constant  $\varepsilon'$  and the effective magnetic permeability  $\mu'$  of a colloidal suspension of such metal spheres, by means of the equations

$$\varepsilon' E_x = E_x + 4\pi N \left( p_x - \frac{\partial}{\partial z} q_{xz} \right)$$
 and  $\mu' H_y = H_y + 4\pi N m_y$ . (23)

N is the number of (non-interacting) particles per unit volume, and  $E_x = E_x^0 \exp(ikz - i\omega t)$  is the electric field of the incident light wave, while  $H_y$  is the corresponding magnetic field.  $p_x$ ,  $q_{xz}$  and  $m_y$  are the relevant components of the induced electric dipole, electric quadrupole and

magnetic dipole moments, so that

$$\varepsilon' = 1 + 2\pi N(\hat{a}_1 - \hat{a}_2)/k^3$$
 and  $\mu' = 1 - 2\pi N\hat{p}_1/k^3$ .

 $\hat{p}_1$  is of the order of  $x^5$  and does not lead to a resonance effect, while  $\hat{a}_1$  and  $\hat{a}_2$  are respectively of the order of  $x^3$  and  $x^5$ , with a resonance frequency  $\omega_1$  and  $\omega_2$ , determined by the conditions

$$\varepsilon_1(\omega_1) + 2 + \frac{12}{5}x^2 = 0$$
 and  $\varepsilon_1(\omega_2) + \frac{3}{2} + \frac{15}{42}x^2 = 0$ ,

for  $x \rightarrow 0$ . GANS and HAPPEL [1909] neglected the x dependence of these resonance frequencies, as pointed out by DOYLE and AGARWAL [1965]. MEESSEN and VAN PARYS-DESAEDELEER [1975] evaluated in this way also the amplitudes  $A_1$  and  $A_2$  of the electric dipole and electric quadrupole resonances, and found that

$$A_1 = 9q(1 + \frac{7}{5}x^2)/\varepsilon_2(\omega_1)$$
 and  $A_2 = \frac{35}{56}x^2q/\varepsilon_2(\omega_2)$ 

This shows that the enlargement of the sphere leads only to the appearance of a very small secondary maximum in the absorption spectrum of the colloid, as long as x is relatively small. For x = 0.2, for instance, we get  $A_2 = 0.08A_1$ , in the case of free electron metals. The quadrupole effect will be more important in very oblate spheroids, where this problem can be treated by means of the perturbation method of STEVENSON [1953]. But the experimental results of R. and J. C. PAYAN show that the secondary maximum is already well developed in very thin granular films, while this should not be the case if the secondary maximum had to be attributed to the enlargement of the particles.

To evaluate the influence of a slight change of the *shape* of the particles, we have considered the particular case of a small sphere, with an axially symmetric deformation. MEESSEN and VAN PARYS-DESAEDELEER [1975] found that the components of the induced dipole moment are given by

$$p_i = \frac{\varepsilon - 1}{\varepsilon + 2} \left[ 1 + \frac{2}{\varepsilon + 2} \left( A_i + \varepsilon B_i \right) \right] a^3 E_i, \quad \text{when} \quad r = a \left[ 1 + \sum_{l=0}^{\infty} c_l P_l(\cos \theta) \right]$$

is the radius of the sphere, with small perturbation coefficients  $c_i$ .  $\theta$  is the angle with respect to the direction i = n that is normal to the plane of the film. The coefficients  $A_i$  and  $B_i$  are then determined in general by the relations

$$A_n = 2(c_0 - c_2/5), \quad B_n = 6c_2/5, \quad A_t = 2c_0 + c_2/2, \quad B_t = -3c_2/5.$$

The values of  $c_l$  are very small for a slightly truncated sphere. Even when the radius of the circular base is equal to a/2 only we get  $c_0 = -0.0039$  and  $c_2 = -0.0111$ . The correction of the induced dipole moment thus remains remarkably small. Moreover, no secondary resonance appears for small particles, since quadrupole effects would have to be evaluated by means of (23), so that they are always proportional to the factor  $a/\lambda$ .

The situation is very different, however, for hemispherical particles. BERREMAN [1967] has already solved the quasi-static problem for a homogeneous small sphere of dielectric constant  $\varepsilon$ , that is half immersed in a semi-infinite medium of dielectric constant  $\varepsilon_m$  while the other half is surrounded by vacuum. The case of hemispherical bumps or pits on the surface of a semi-infinite metal is then treated by setting  $\varepsilon = \varepsilon_m$  or  $\varepsilon = 1$ . It was evident that a whole set of resonances will appear in a spectral region of finite width, although the equations were only solved outside this region. MEESSEN and VAN PARYS-DESAEDELEER [1975] solved the analogous problem for hemispherical metal particles on a transparent substrate, including the resonance structure. In this case, the problem can indeed be simplified since the frequency-dependent dielectric constant  $\varepsilon$ of the metal appears only in the final equations through the parameter  $\lambda = (\varepsilon + \varepsilon_s)/(\varepsilon - 1)$ , where  $\varepsilon_s$  is the dielectric constant of the substrate. The amplitudes  $x_n$  of the induced multipole moments of order  $n \ge 1$  are actually determined by a set of linear algebraic equations

$$\sum_{n} (A_{mn} - \lambda B_m \delta_{mn}) x_n = F_m.$$
<sup>(24)</sup>

The coefficients  $A_{mn}$ ,  $B_n$  and  $F_m$  are determined by the boundary conditions and depend on  $\varepsilon_s$ , which can be considered as a parameter, while  $F_m$  is proportional to the amplitude of the applied electric field. The problem is thus equivalent to the description of the motion of an ensemble of *coupled harmonic oscillators*, which are set into forced vibrations by a force, acting on each of them with some particular strength, but the same frequency, determining the value of  $\lambda$ . We know that such a system will display N possible "modes of vibration" for N coupled oscillators, corresponding to well defined "eigenvalues"  $\lambda_r$  for  $\lambda$ , defined by the possible solutions of (24) when  $F_m = 0$ . By changing the frequency of the applied force, or the value of  $\lambda$ , we thus get N possible resonances for such a system. But the important point, in our case, is the fact that (nearly all) these resonances can be detected by observing the amplitude EXCITATION OF COLLECTIVE OSCILLATIONS

of the forced vibrations of any particular oscillator. We know, indeed, that we can only observe the optical properties which result from the induced dipole moment, in the case of small particles. But the multipole effects can be observed *indirectly*, through the resonances which appear in the induced dipole moment  $x_1$ . It actually follows from (24), in all generality, that the components of the induced dipole moment are given by

$$p_i = \frac{V}{4\pi} \sum_r \frac{D_{ri} E_i}{\lambda - \lambda_{ri}}.$$
 (25)

The index i = n, t takes into account the fact that we get a different set of equations (24) when the electric field is normal or tangential to the surface of the substrate. V is the volume of the particle, so that the effective dielectric constant of N non-interacting hemispherical particles is given by

$$\varepsilon_i' = 1 + \sum_r \frac{qD_{ri}(\varepsilon - 1)/(1 + \varepsilon_s)}{1 + (\varepsilon - 1)f_{ri}}$$

where  $f_{ri} = (1 - \lambda_{ri})/(1 + \varepsilon_s)$  is an effective form factor, allowing us to consider this system as being equivalent to an aggregate of spheroids of different shapes. q = NV is the filling factor of the colloid, but we note that the dependence of  $D_{ti}$  and  $\lambda_{ti}$  on the dielectric constant  $\varepsilon_s$  of the substrate does not simply correspond to the effect of the substitution (4) with  $\varepsilon_{\rm a} = (\varepsilon_{\rm s} + 1)/2$ , as postulated in David's theory. In the particular case where  $\varepsilon_s = 1$ , we get three resonances by considering a coupling among the three dominant multipole oscillations. These resonances are situated respectively at the frequencies  $\omega_t = 0.48 \omega_p$ ,  $\omega'_t = 0.56 \omega_p$  and  $\omega''_t = 0.76 \omega_p$ for a free electron metal and for oscillations that are tangential to the base of the hemispherical particles (i = t). The low frequency resonance has the largest amplitude, while the amplitudes of the  $\omega'_t$  and  $\omega''_t$  resonances reach, respectively, 28% and 4% of the amplitude of the  $\omega_t$ resonance. This is in good qualitative agreement with the experimental results concerning the appearance of secondary maxima in the absorptance of thin granular alkali metal films and rough alkali metal surface (see § 2.5). A preliminary account of these calculations was given by VAN PARYS and MEESSEN [1972], while the details of the method and the numerical results for the complete set of equations, for various cases, will be presented elsewhere.

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### 2.7. EXCITATION OF PLASMA WAVES IN CONTINUOUS METAL FILMS

An extremely flat ellipsoid can be considered as a very thin continuous metal film. This means that we have to expect two possible optical resonances for such a system, corresponding to  $\omega_t \rightarrow 0$  and  $\omega_n \rightarrow \omega_p$ , when the wavelength  $\lambda$  of the incident light wave is much larger than the film thickness d. The same conclusions were actually reached by a completely different route, starting with the concept of longitudinal plasma waves in bulk metals. These waves cannot be excited optically and were observed by the "characteristic energy losses" of fast electrons, passing through metal foils. But these experiments require a very high energy resolution. FERRELL [1958] suggested therefore that one should rather observe the radiation that is emitted, since the plasma waves which are excited in a thin film acquire a degree of transversality, allowing them to radiate. FERRELL [1958] actually specified the possible modes of collective oscillation within a metal film of arbitrary thickness d, by adopting the quasi-static dielectric treatment, introduced by RITCHIE [1957] for the description of the energy loss in thin metal films. Considering the equations for the (electrostatic) potential, one finds that surface charges with symmetric or antisymmetric distributions of the following type can exist:

These charge distributions are induced by collective oscillations of the electrons (or more generally, by a polarization of the metal) and correspond to "surface plasma waves", characterized by the wavevector  $k' = 2\pi/\lambda'$  in the plane of the film. The frequency of oscillation depends then, however, on the wavevector k' and the film thickness d, according to the dispersion laws

$$\varepsilon(\omega_{-}) = -\operatorname{ctgh}(k'd/2)$$
 and  $\varepsilon(\omega_{+}) = -\operatorname{tgh}(k'd/2),$  (26)

where  $\varepsilon(\omega)$  is the frequency dependent dielectric constant of the metal, which is assumed to be in contact with vacuum on both sides of the metal foil. The low frequency  $\omega_{-}$  corresponds to the symmetric mode of oscillation and the high frequency  $\omega_{+}$  to the antisymmetric mode. It follows from (26) that  $\varepsilon(\omega_{\pm}) = -1$ , or that  $\omega_{\pm} = \omega_{\rm s} = \omega_{\rm p}/\sqrt{2}$  for free electrons, when  $k'd \rightarrow \infty$ , and that  $\omega_{-} = 0$  while  $\omega_{+} = \omega_{\rm p}$  when  $kd \rightarrow 0$ . But the momentum conservation condition  $k' = k \sin \theta$ , where  $\theta$  is the angle of emission of the light wave with respect to the film normal, implies that a surface plasmon can only be converted into a photon when  $k' \leq k$ . We have thus to expect the emission of light of frequency  $\omega \approx \omega_p$ and wavelength  $\lambda \approx \lambda_p$  when the film thickness  $d \ll \lambda_p \leq \lambda'$ . It is actually necessary to distinguish between *radiative* surface plasmons (k' < k) and *non-radiative* surface plasmons (k' > k). RITCHIE and ELDRIDGE [1962] and KLIEWER and FUCUS [1967] showed that these surface plasmons have separate sets of dispersion relations, when *retardation* effects are taken into account. (26) is then replaced, indeed, by

$$\varepsilon(\omega_{-}) = -\frac{u}{v} \operatorname{ctgh}(ud/2)$$
 and  $\varepsilon(\omega_{+}) = -\frac{u}{v} \operatorname{tgh}(ud/2)$ 

where  $u^2 = k'^2 - \varepsilon k^2$  and  $v^2 = k'^2 - k^2$ . The non-radiative surface plasmons  $(k' > k = \omega/c)$  correspond to two curves for  $\omega_{\pm}$ , increasing from 0 to  $\omega_s$ , when k' varies from 0 to  $\infty$ . These plasma waves can only be coupled to light waves by means of special accommodations, while the radiative (or virtual) modes correspond to k' < k, with the limiting values  $\omega_{\pm} \rightarrow 0$  and  $\omega_{\pm} \rightarrow \omega_p$  when  $k' d \rightarrow 0$ .

If a surface plasmon can be converted into a photon, the inverse process is also allowed, of course. This means that we get an optical resonance absorption for  $\omega_{-} \rightarrow 0$  and  $\omega_{+} \rightarrow \omega_{p}$ , corresponding to the resonances  $\omega_{t} \rightarrow 0$  and  $\omega_{n} \rightarrow \omega_{p}$  for very flat ellipsoids. MCALISTER and STERN [1963], MATSUDAIRA [1963] and HATTORI, YAMADA and SUZUKI [1963] noted that it is possible to describe the "plasma resonance absorption" for p-polarized light at a frequency  $\omega \approx \omega_{p}$  by directly applying the usual formulas for the reflection and transmission coefficients to the case of very thin films ( $d \ll \lambda$ ). One then gets

$$R_{\rm p} = \frac{\gamma_{\rm r}^2}{4(\gamma - \gamma_{\rm p})^2 + (\gamma_{\rm r} + \gamma_{\rm d})^2} \quad \text{and} \quad T_{\rm p} = 1 - \frac{\gamma_{\rm r}(\gamma_{\rm r} + 2\gamma_{\rm d})}{4(\omega - \omega_{\rm p})^2 + (\gamma_{\rm r} + \gamma_{\rm d})^2},$$
(27)

where

$$\gamma_{\rm r} = \frac{2 \pi d \sin^2 \theta}{\lambda (d \varepsilon_1 / s \omega) \omega_{\rm p} \cos \theta}$$
 and  $\gamma_{\rm d} = \frac{2 \varepsilon_2 (\omega_{\rm p})}{(d \varepsilon_1 / d \omega) \omega_{\rm p}}$ .

The total width of the  $\omega_p$  resonance is thus given by  $\gamma_r + \gamma_d$ , according to Maxwell's equations and the Fresnel boundary conditions for transverse waves. Comparing this result with (6), we see that the "dipole approximation" implied that  $\gamma_r \ll \gamma_d$ , which is justified by the fact that  $\gamma_r$ 

is proportional to  $d/\lambda$ .  $\gamma_r$  is actually the inverse of the lifetime of the surface plasmon with respect to its conversion into a photon, while  $\gamma_d$  is the inverse of the lifetime of the plasmon with respect to the excitation of an electron. It is interesting to note, however, that the width of the resonance absorption for small metal particles can be enlarged through radiative effects, and that CROWELL and RITCHE [1968] predicted that  $\gamma_r = 2a^3\omega_1^4/3c^3$  for metal spheres of radius *a* and eigenfrequency  $\omega_1 = \omega_p/\sqrt{3}$ .

The excellent review article of STEINMANN [1968] already indicated that the study of the "plasma resonance absorption" and of related effects in continuous thin metal films has attracted the attention of many authors during the last decade (see also § 2.5). We note here only that SCHULZ and ZURHEIDE [1968] studied the dependence of the  $\omega_p$  resonance on the temperature, thickness and structure of thin Ag films, while NILSON, LINDEAU and HAGSTRÖM [1970] considered this resonance in thin films of Ag alloys.

A very remarkable new development arose from the observation that Fresnel's formulas are actually incorrect, since they are based on the assumption that there can only exist *transverse* electromagnetic waves inside the metal, while there can only exist *longitudinal* waves of frequency  $\omega_p$ . SAUTER [1967] and FORSTMANN [1967] pointed out that the boundary conditions have to be modified, even at the surface of a semi-infinite metal, to include the effect of these longitudinal waves. MELNYK and HARRISON [1968, 1970] studied this effect very thoroughly for continuous metal films of thickness d, and concluded from the modified expression of  $R_p$  and  $T_p$  that small additional resonances will show up at frequencies  $\omega > \omega_p$ . This fine structure, which is superposed on the broad  $\omega_p$  resonance, results from the creation of stationary longitudinal waves. The dispersion relation for longitudinal waves and transverse waves is, indeed, given by

$$\omega^{2} = \omega_{p}^{2} + \frac{3}{5}v_{F}^{2}k^{2}$$
 and  $\omega^{2} = \omega_{p}^{2} + c^{2}k^{2}$ ,

for  $k \rightarrow 0$ . The first relation results from Lindhard's expression for the longitudinal wavelength and frequency dependent dielectric constant, with the condition  $\varepsilon_{\rm L}(\mathbf{k}, \omega) = 0$ . The second relation corresponds to  $(ck/\omega)^2 = \varepsilon_{\rm T}(k, \omega) \approx 1 - \omega_{\rm p}^2/\omega^2$ . It follows that  $\lambda_{\rm L}/\lambda_{\rm T} \sim v_{\rm F}/c \sim 1/100$  at a given frequency  $\omega$ , so that it is possible to realize the condition  $\lambda_{\rm L} < d \ll \lambda_{\rm T}$ , with an interference effect when the film thickness  $d = n\lambda_{\rm L}/2$ , where *n* is an odd number. LINDAU and NILSSON [1971] verified experimentally the

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existence of this effect by means of thin Ag films, with "supersmooth" plane parallel surfaces, where small additional minima appear in the spectral distribution of the transmission coefficient  $T_{\rm p}$ .

JONES, KLIEWER and FUCHS [1969] also predicted the occurrence of additional structures in the absorptance of thin metal films for p-polarized light, at frequencies  $\omega \sim 0.2 \omega_p - 0.8 \omega_p$ . According to KLIEWER and FUCHS [1970], an oscillatory structure should even appear in the absorptance of thin metal films for s-polarized light at frequencies  $\omega \sim 0.01 \omega_p - 0.1 \omega_p$ . Although these predictions are not yet confirmed experimentally, they demonstrate very clearly that the search for "anomalous" optical resonances in thin metal films is now a field of particular interest.

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