SOME OPTICAL PROPERTIES OF THIN FILMS OF SILVER AND OTHER METALS

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Abstract

In the last fifteen years there has been a considerable increase in the knowledge of the optical properties of metal layers less than 1000 A thick, and the use of layers produced by evaporation or cathodic sputtering has become increasingly common for the determination of the optical constants of metals.

In this work the interferometric method, originally due to Tolansky, for the determination of the relative phase changes occurring on reflexion at the surface of a metal layer has been further developed, and, coupled with a simple photoelectric device for the measurement of intensity changes, has been applied to the study of reflexion at a number of surfaces.

The method requires slightly transparent layers of the metal to form a transmission interferometer, and it is therefore of particular importance to determine within what thickness limits the optical properties of these layers can be taken as characteristic of the metal in bulk form. To this end, a study of the variation with thickness of the characteristics of non-normal reflexion at thin silver layers has been made for thicknesses between 100 and 1000 A.

Measurements have also been made using the technique of the optical constants of copper, tin, speculum, and a new tin-nickel alloy. Some interesting anomalies in the optical properties of evaporated layers of tin have been observed.

The thesis commences with a treatment of the theory of reflexion at metal surfaces and layers, and the previous work in this field is reviewed, with particular reference to measurements on evaporated layers, and the variation of their properties with thickness. The evaporation equipment and procedure used are described, and the measurement of layer thicknesses critically discussed. The optical techniques are then described, the interferometric technique being analysed in detail. Finally the results of the experiments are mentioned and discussed.

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PART I

THEORETICAL AND HISTORICAL REVIEW

REFLEXION AT THE SURFACE OF AN ABSORBING MEDIUM

Chapter I.

If a beam of light, plane polarised at 45° to the plane of incidence, is reflected at the surface of an absorbing medium, the reflected light is in general elliptically polarised. Both the amplitudes and the phases of the components of the incident light polarised parallel and perpendicularly to the plane of incidence are changed by reflexion, the amount of the change in each quantity varying with the angle of incidence.

In order to explain these phenomena, the classical electromagnetic theory must be extended from the simpler case of wave propagation in isotropic transparent media, and reflexion at the boundaries of such media, to the more general case of propagation in and reflexion at the boundaries of isotropic absorbing media. The change necessary in Maxwell's equations for an electromagnetic field is that in addition to the "displacement current" term in the equations for the electric vector existing in a dielectric, account must also be taken of a "conduction current" varying with the applied field, in the case of conducting (i.e. absorbing) media.

It can be shown(1, 2, 3) that when the equations for wave propagation in an absorbing medium are developed, reflexion and refraxion at the boundary between an absorbing and a transparent medium can be completely determined by the usual equations for reflexion and refraxion between two transparent media provided that a refractive index having real and imaginary parts is assigned to the absorbing medium.

The equation for the propagation of an electromagnetic wave in the direction of an axis, z, in an absorbing medium is of the form

$$X = A.e^{-2\pi k z/\lambda}.e^{2\pi i\left(\frac{t}{T} - z/\lambda\right)}$$

where λ is the wavelength in vacuo. The term $A.e^{-2\pi k.z/\lambda}$ represents the amplitude of the vibration, which, after the wave has travelled a distance λ in the medium is reduced by a factor $e^{-2\pi k}$. The constant k is termed the Absorption Coefficient of the medium.

If we call the ratio of the velocity of propagation in vacuo to the velocity of propagation in the medium, the Refractive Index, n, then the medium is completely characterised by the Complex Refractive Index given by

$$N = n(1 - ik) \qquad 1.1$$

The quantity N is related, in dispersion theory, to the dielectric constant, ε, and the conductivity, σ, by the equations

$$\varepsilon = n^2(1-k^2)$$

and $\sigma = n^2 k . \nu$

where ν is the frequency of the incident radiation. The quantities n and k are the Optical Constants of the medium.

Consider the reflexion of a beam of light, polarised either parallel or perpendicularly to the plane of incidence, at the boundary between a transparent medium of refractive index n_1 , and an absorbing medium of refractive index N (figure 1). Let the incident wave front be plane, of amplitude unity and phase zero immediately before reflexion, and let the angle of incidence be θ .

The angle of refracion into the absorbing medium, η , is given, by Snell's Law, in the equation

$$n_1 \sin\theta = N \sin\eta \qquad 1{\cdot}21$$

But since we have seen that N is a complex quantity for an absorbing medium, it follows also that the angle of refraxion, η , must also be complex. The physical significance of this complex angle of refraxion has been discussed by Fry(4). When an electromagnetic disturbance is travelling in a non-absorbing medium, the wavefronts, i.e. the planes of equal phase, are also planes of equal amplitude. When the wave is travelling in an absorbing medium, however, the planes of equal phase remain perpendicular to the direction of propagation of the wave, but

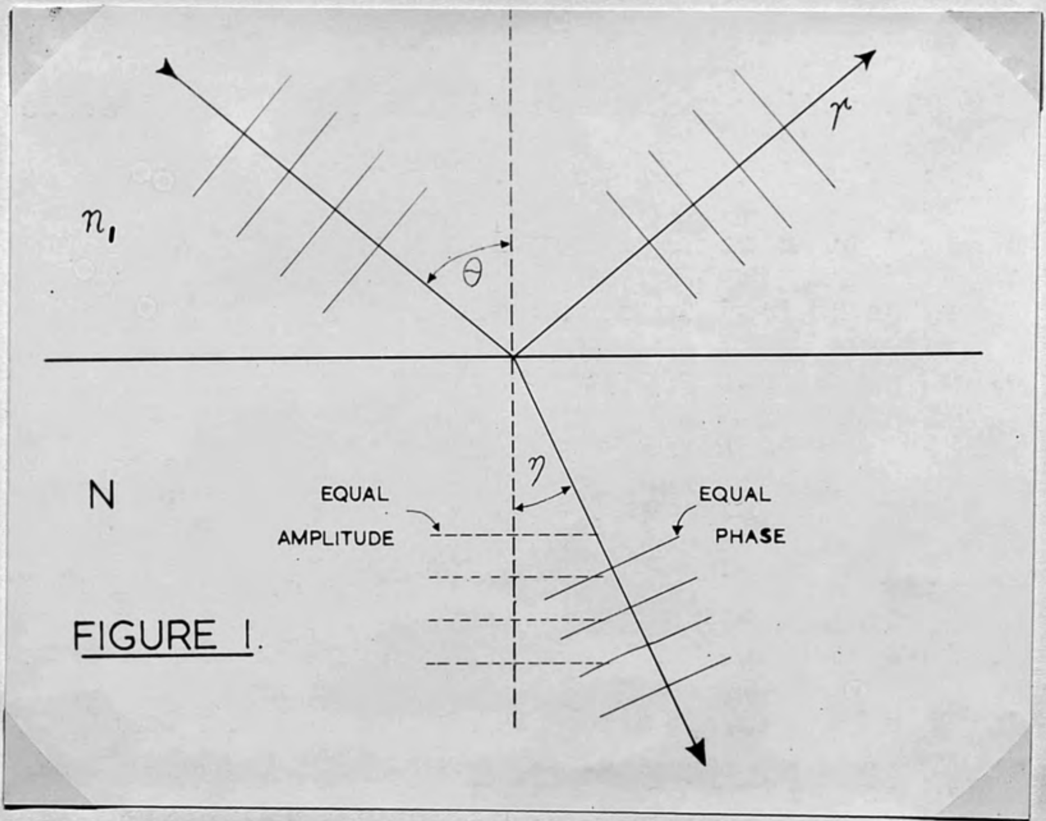

FIGURE I.

the planes of equal amplitude are not necessarily coincident with them. A vector representing the direction of maximum damping of the vibration is not necessarily parallel to the vector representing the direction of propagation of the vibration in an absorbing medium.

In the case of refraxion into an absorbing medium as in Figure 1, the planes of equal phase remain perpendicular to the direction of propagation, this direction varying of course with the angle of incidence, but the planes of equal amplitude lie parallel to the surface of the medium, whatever the angle of incidence. Hence they are only coincident with the planes of equal phase when the light is incident normally on the surface of the absorbing medium.

It is possible to define the optical constants in such a way that the angle η is real, with a numerical value of some significance as is obviously not the case with a complex angle of refraxion. The constants defined in this manner vary with the angle of incidence, as mentioned by Wood(2), but are not the fundamental constants related to the dispersion theory. The constants are also treated in this way by Schuster and Nicholson(3), who define constants η_θ and k_θ, where θ is the angle of incidence. The treatment given here necessitates the introduction of a complex angle of refraxion in every application of Snell's

Law, but seems more satisfactory in that the optical constants on this definition are characteristic of the medium alone, and do not vary with the angle of incidence.

The reflected beam in Figure 1 can be described by the complex quantity r, related to the angles of incidence and refraxion by Fresnel's equations. If r is expressed as $r = \gamma . e^{-i\phi}$, then the amplitude factor on reflexion is γ, and the phase change ϕ. If the incident light has equal components parallel and perpendicular to the plane of incidence, these can each be taken as unity and the reflected beam has two components given by

$$\left.\begin{array}{ll} \text{Parallel Component} & r_p = \gamma_p . e^{-i\phi_p} = \dfrac{N\cos\theta - n_1\cos\eta}{N\cos\theta + n_1\cos\eta} \\[2ex] \text{Perpendicular Component} & r_s = \gamma_s . e^{-i\phi_s} = \dfrac{n_1\cos\theta - N\cos\eta}{n_1\cos\theta + N\cos\eta} \end{array}\right\} \quad 1{\cdot}3$$

The optical constants, n and k, can be found from measurements on the reflected beam. For a given angle of incidence, equations 1·1, 1·2, 1·3 can be combined and n and k found from measurements of γ_p, γ_s, ϕ_p, and ϕ_s. In practice, however, the elliptically polarised reflected beam is usually analysed by some form of optical compensator, and the constants n and k determined from measurements of the ratio r_p/r_s, i.e. from measurements of the ellipticity of the reflected beam, $\gamma_p/\gamma_s = \rho$ and on the relative phase difference between the components $\phi_p - \phi_s = \Delta$.

From the equations for the reflexion of an electromagnetic wave, we can write

$$r_p/r_s = \gamma . e^{-i\Delta} = \cos(\theta+\eta)/\cos(\theta-\eta) \qquad 1{\cdot}4/$$

Then, if $\rho = \tan\psi$, and we put $Z = e^{i\Delta}.\tan\psi$ Fry has shown (with a correction by Emberson[5]) that

$$N^2 = \tan^2\theta\left\{1 - \frac{4Z\sin^2\theta}{(1+Z)^2}\right\} \qquad 1{\cdot}5/$$

In order to calculate n and k from given values of θ , ρ and Δ, equation 1·5 must be split into real and imaginary parts. The computation involved is quite lengthy and most workers make some substitutions.

The one most commonly used is due to Drude$^{(1)}$, who gave the equations

$$\begin{array}{lrcl} \text{If} & \tan Q &=& \sin\Delta\tan 2\psi \\ & \cos 2P &=& \cos\Delta\sin 2\psi \\ & S &=& \sin\theta\tan\theta\tan P \\ \text{Then} & k &=& \tan\chi/2 \\ \quad\text{where} & \tan\chi &=& S^2\sin 2Q/(S^2\cos 2Q + \sin^2\theta) \\ \quad\text{and} & n^2(1-k^2) &=& S^2\cos 2Q + \sin^2\theta \end{array} \qquad 1{\cdot}6/$$

Starting from an equation equivalent to 1·5, Price$^{(6)}$ has recently developed the equations

$$N^2 = A + iB$$

where

$$A = \tan^2\theta - \frac{2\sin^2\theta\tan^2\theta(\cos\Delta + \sin 2\psi)}{\sin 2\psi(\cos\Delta + \operatorname{cosec} 2\psi)^2}$$

$$B = \frac{2\sin^2\theta\tan^2\theta\sin\Delta}{\tan 2\psi(\cos\Delta + \operatorname{cosec} 2\psi)^2} \qquad 1.7$$

In most textbooks on Optics, approximate equations are given. For most metals $n^2(1+k^2)$ can be regarded as much greater than $\sin^2\theta$ [$n^2(1+k^2)$ lies between 8 and 30(2)] and if $\sin^2\theta$ is neglected in a term of the form $(N^2 - \sin^2\theta)^{1/2}$, then the approximate equations can be given as

$$n = \sin\theta\tan\theta\cos 2\psi / (1 + \cos\Delta\sin 2\psi)$$

$$k = \sin\Delta\tan 2\psi \qquad 1.8$$

As an alternative to measurements of ρ and Δ for a given value of θ, measurements are often made of the angle of Principal Incidence, defined as that angle of incidence at which the relative phase change $\Delta = \pi/2$ and of the corresponding value of ψ, the angle of Principal Azimuth.

If these angles are denoted by $\bar{\theta}$ and $\bar{\psi}$, then a rigorous treatment by Ketteler (presented by Konig(7)) gives the equations for n and k

$$n^2 k = \sin^2\bar{\theta}\tan^2\bar{\theta}\sin 2\bar{\psi}\cos 2\bar{\psi} \qquad 1.9$$

$$n^2 = \tfrac{1}{2}\tan^2\bar{\theta}\left[1 - 2\sin^2\bar{\theta}\sin^2 2\bar{\psi} + (1 - \sin^2\bar{\theta}\sin^2 2\bar{\psi})^{1/2}\right]$$

The set of equations chosen to determine n and k in any particular experiment depends on the quantities measured in the experiment and the personal choice of the observer as to ease of computation. For example the equations developed by Price (1·7) are stated to be especially suitable for computations made at a fixed angle of incidence for different wavelengths.

In addition to the quantities ρ and Δ , the normal incidence Reflexion Coefficient is often measured for absorbing media. This Coefficient is the ratio of the intensity reflected at normal incidence from the surface of the medium, to the incident intensity. It can readily be shown that it is related to the optical constants n and k by the equation

$$R = \frac{n^2(1+k^2)+1-2n}{n^2(1+k^2)+1+2n} \qquad 1{\cdot}10/$$

The experimental methods used to determine n and k , and the results found by previous workers will be discussed in Chapter III. In the next chapter (Chap. II) the theory discussed above will be extended to the treatment of thin layers of metals, transparent to visible light.

REFLEXION AT A THIN METALLIC LAYER

Chapter II.

The equations given in the first chapter enable the optical constants of any metallic, or other absorbing medium to be determined from measurements on the state of polarisation of light reflected from the surface of the medium. In the treatment given it was tacitly assumed that the media on either side of the boundary were infinite in extension in all directions.

If, however, the metal is in the form of a thin layer - in this treatment the term 'thin' will be used to describe layers not more than half a wavelength of light thick - then the equations of Chapter I no longer serve to define a beam reflected from such a layer. In extending the treatment to the case of a thin layer, account must be taken not only of rays reflected at the upper surface of the layer, i.e. the first surface which the incident beam strikes, but also of rays suffering multiple reflexions within the film, and of the interference relationships between these rays.

The problem has been treated in the general case of any incidence angle by several early workers, notably Machaurin(8) and Forsterling(9). A treatment roughly following that of Machaurin will be briefly discussed here.

It is assumed that the metallic layer is isotropic and bounded by two parallel surfaces, and that it is infinite in extension parallel to these surfaces. Let us consider a layer of thickness d and refractive index N (complex, given by 1·1), bounded on one side by a vacuum, and on the other side by a transparent medium of refractive index μ (see Figure 2).

Let the reflexion factor for the interface between the vacuum and the film, when the incident beam is in the vacuum, be r , this interface will be termed the interface $1 \rightarrow N$. Let the coefficient for the interface $N \rightarrow \mu$ be r' , These quantities r , r', are of course complex, and are given by equations of the form of 1·3

Consider a bundle of parallel rays incident on the interface $1 \rightarrow N$ at an angle θ . Let the complex angle of refraxion of the rays into the film be η , and into the transparent medium ϑ (real).

The intensity and phase of a ray reflected at any point such as E (Figure 2) is determined by the summation of the various rays (1, 2, 3, etc.) which have undergone several reflexions in the film.

In the case of a non-absorbing film, these rays can be treated by the well-known Airy summation$^{(10)}$, and it is possible in that treatment, to distinguish between amplitude factors, caused by reflexion, and phase factors,

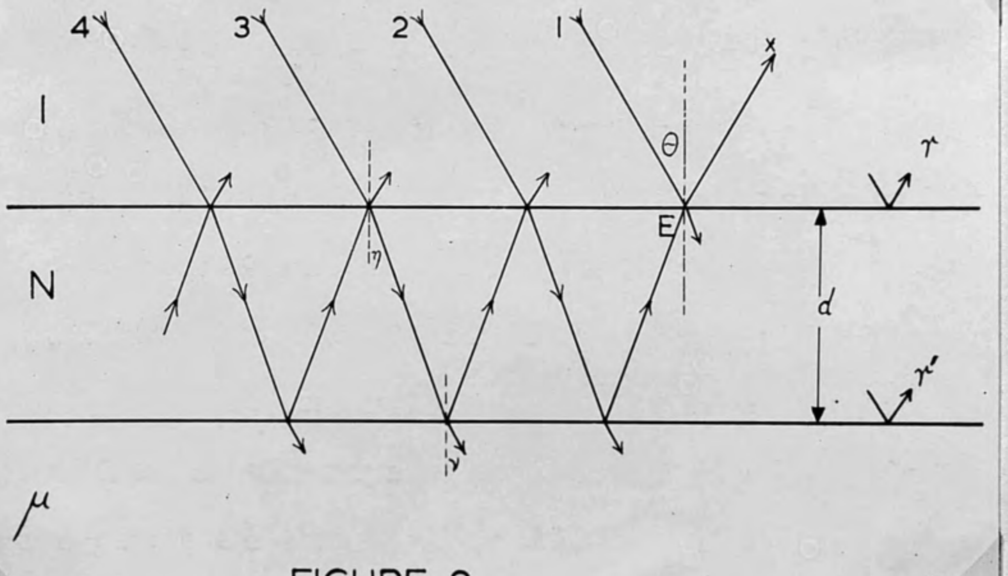

FIGURE 2.

associated with passage through the film. In this case, however, since the film is absorbing, this is not possible, since both reflexion and passage through the film will modify both the amplitude and the phase of a ray.

Taking the amplitude of the first ray (ray 1, Figure 2) to be unity, and its phase zero at a point just before reflexion at E, then after reflexion the contribution to the total reflected along the path Ex, due to the first ray is described in amplitude and phase by the factor r.

The next ray, (ray 2), after refraxion into the film, passage through it, reflexion at $N \rightarrow \mu$, and final emergence along Ex, gives a contribution given by the factor

$$(1-r).r'.(1+r).e^{-i\delta} = (1-r^2).r'.e^{-i\delta}$$

where $$\delta = \frac{2\pi}{\lambda}.2dN\cos\eta \qquad 2\cdot1$$

The third ray, after two reflexions at $N \rightarrow \mu$, and one at $N \rightarrow 1$, emerges along Ex as

$$-(1-r^2).r.r'^2.e^{-2i\delta}$$

The fourth ray gives

$$+(1-r^2).r^2.r'^3.e^{-3i\delta}$$ and so on.

The reflected ray at E, is then given in amplitude and phase by the complex quantity R where

$$R = r + (1-r^2).r'.e^{-i\delta}\left[1 - rr'e^{-i\delta} + r^2r'^2e^{-2i\delta} - \ldots\ldots\right]$$

which reduces to

$$R = \frac{r + r'.e^{-i\delta}}{1 + rr'.e^{-i\delta}} \qquad 2{\cdot}2$$

This expression has been developed without regard to the plane of polarisation of the incident beam. Obviously there must be two quantities R_p and R_s, for the components polarised parallel and perpendicularly to the plane of incidence, given by the equation 2·2 where r and r', have the appropriate suffixes and are given by the appropriate equations of 1·3

If, following Chapter I, the reflexion factors are expressed in the form $r = \gamma . e^{-i\phi}$, and if $e^{-i\delta}$ (which has real and imaginary parts since $N\cos\eta$ is complex (2·1)) is expressed as $m.e^{-in}$ then R is given by

$$R = \frac{\{\gamma.e^{-i\phi} + \gamma'm.e^{-i(\phi'+n)}\}\{1 + \gamma\gamma'm.e^{-i(\phi+\phi'+n)}\}}{1 + 2\gamma\gamma'm.\cos(\phi+\phi'+n) + (\gamma\gamma'm)^2} \qquad 2{\cdot}3$$

Equation 2·3 gives the amplitude and phase of the light reflected from a thin layer in terms of the amplitude factors γ, γ', m and the phase angles ϕ, ϕ', n. These factors themselves are functions of the film's thickness, the angle of incidence, the plane of polarisation of the incident light, and of the optical constants of the material of which the film is composed. The factor R can be determined experimentally, or, as in the case of experiments on reflexion at bulk metal surfaces, the quantity R_p/R_s can be determined, for given values of the variables quoted. Then from these measurements the optical constants of the layer can be calculated.

Unfortunately, however, the form of equation 2·3 is such that in the general case of non-normal incidence, it is not possible to develop straightforward equations relating n and k to the observables R_p, R_s or R_p/R_s. This means that in order to determine n and k for any particular layer, the quantities R_p, R_s etc. must be calculated for various values of n and k, and these results compared with experiment. The procedure is long and laborious, and it is perhaps for this reason that most experimental work on the optical properties of thin films has been restricted to normal incidence where matters are much simplified since $R_p = R_s$.

In the work of Murmann(11), Ornstein(12), Krautkramer(13), and many others, graphs relating the Reflexion Coefficient at normal incidence to the thickness d of the layer were computed for various values of n and k, and the experimentally determined curves compared with these graphs. The intersections of the theoretical and experimental curves give the values of n and k for any particular thickness. However, recent work by Perrot(14) on the determination of the amplitude factor on normal reflexion at thin layers of chromium, and later by Perrot and Cotton(15) on the phase change at normal reflexion, has greatly simplified the treatment of the results of experiments carried out at normal incidence. These workers have developed a graphical treatment whereby the values of n and k for a given layer can be determined directly from the experimentally observed values for the amplitude and phase changes on normal reflexion.

No such simplification appears possible, however, in the case of non-normal incidence, and determinations of n and k from measurements of the ellipticity ρ and relative phase change Δ, involve the computation from equations such as 2·3 of values of ρ and Δ for various thicknesses for various values of n and k, and comparison of the results of these computations with experiment. Calculations along these lines have been made by Essers-Rheindorf(16) on the basis of the work of Forsterling(9).

More recently an example of this form of calculation has been made by Winterbottom(17), whose work was actually concerned with the study of transparent or slightly absorbing films deposited on to a highly reflecting base, e.g. film of oxide on metals. It can be seen that a theoretical discussion would be similar in some respects to the one we have discussed, except that the third medium, which we have considered to be transparent, would in this case have a complex refractive index. A large number of investigators have studied this type of thin layer e.g. Tronstad and Feachem(18), who studied films of fatty acids spread on mercury, Lucy(19), who studied surface layers on metals, and Leberknight and Lustman(20). The last-named workers introduced an approximate treatment, in which only two beams were considered to interfere within the film. This approximation leads to some simplification of the calculations, but it is only applicable in cases where either the absorption is very high, or the reflexion coefficient of at least one surface of the film is very low (e.g. the case of an oxide film on a metal). In general the approximation is not applicable to the study of thin layers of metal which have an appreciable light transmission, since the reflexion coefficients of both surfaces of these films are usually high.

The experimental methods used to determine the optical characteristics of metallic surfaces and layers, will be discussed in the next two chapters, together with the result of such measurements and the applicability of the ideal theoretical equations developed in this chapter and the previous one.

THE OPTICAL CONSTANTS OF METALLIC SURFACES

Chapter III.

Among the earliest experimental determinations of the refractive indices and absorption coefficients of the metals were those of Kundt(21) and Drude(1). The work of Kundt is unique in that it is the only recorded attempt to measure the refractive index of a metal directly by the use of a prism. Very thin transparent prisms of metal were prepared by cathodic sputtering or chemical deposition, the wedge angle being of the order of a few minutes of arc only, and the deviation of a beam of light passing through the prism was measured directly.

The work of Drude remains the classic example of the "katoptric" methods for the determination of optical constants, i.e. the methods dependent on the analysis of the state of polarisation of the light reflected from a surface in relation to the state of the incident light. He allowed light which was plane polarised at 45° to the plane of incidence to fall on to the surface of the metal under investigation. The relative phase difference, Δ , between the two components of the elliptically polarised reflected light was then determined using a Soleil-Babinet compensator, and the azimuth ($\psi = \tan^{-1}\rho$) of the resulting plane polarised light (the azimuth of restored polarisation) was determined by the use of an analyser. This method has formed the basis of nearly all the determinations of optical constants carried out since, a typical optical arrangement for the method is shown in Figure 3.

Drude observed that the values found for the optical constants depended critically upon the manner in which the reflecting surface was prepared, and also upon the existence of thin layers of impurity on the surface. He showed that the effect of a thin layer of grease, oxide or other impurity had the effect of lowering the observed value of the phase difference, Δ , very considerably, and that the value of the azimuth, ψ , was slightly raised. He developed a set of equations which have been extensively used since (e.g. by Tronstad and Feachem (loc. cit.)) by means of which the optical characteristics of the impurity layers could be determined by measuring the changes in Δ and ψ observed when a clean surface was covered with such a layer. If the nature of the layer was known then alternatively the equations could be used to correct the values of n and k calculated from measurements on an impure surface.

Drude also pointed out that the accuracy of the values of n and k found from experiments of this nature was greatest when the experiments were made at angles of incidence such that Δ was of the order of $\pi/2$. This led to the adoption of the measurement of the angle of Principal Incidence and the Principal Azimuth, these measurements giving more accurate values for n and k than measurements of ψ and Δ for any other incidence angle.

Since the work of Drude there have been many determinations made of the optical constants of most of the metals. The results on the whole are very discordent and it appears that most of the differences must be considered to arise from differing methods of preparation of the reflecting surfaces. A complete review of this work will not be attempted here, but a few investigations of special note will be described, to illustrate some of the methods of surface preparation, with particular reference to the metals which have been studied in the present work, and to describe noteworthy experimental methods other than the usual method of Drude.

Typical of the measurements on bulk material, the measurements by Tool(22) in 1910 are of interest. Using a variation of the Drude polarisation method, he measured the change in optical constants with wavelength over the visible region. The reflecting surfaces were prepared by first filing the surface, then grinding it with fine emery, and finally polishing it with rouge. The conditions of the optical measurement were such that a value of ρ of 0·02 could be measured to an accuracy of

1%. However the variations arising from surface conditions were such that the maximum sensitivity of the instrument was not employed, and the statement is made that the optical constants cannot be measured to an accuracy of greater than 2 or 3 per cent.

In an effort to avoid the difficulties associated with the scratches caused by mechanical polishing, Kent(23) in 1919 used the surfaces of molten metals as the reflecting surfaces. Measurements were made on bismuth, cadmium, tin, lead, and their alloys.

A systematic investigation of the effect of method of surface preparation on the value obtained for the optical constants of copper and copper-nickel alloys was carried out by Lowery and his co-workers(24, 25, 26) between 1932 and 1936. Three methods of preparation were used, mechanical polishing, electrolytic polishing, and thermal evaporation in vacuo. When a mechanically polished surface was removed by the electrolytic polishing process, the value of the refractive index was found to decrease, and the absorption coefficient to increase. These changes in the optical constants continued after the Beilby Layer caused by mechanical polishing had been removed (thickness 30-40), and a layer of up to ·003 cm. had to be removed before no further change in the constants was observed. If the mechanical polishing process affects surfaces to this extent

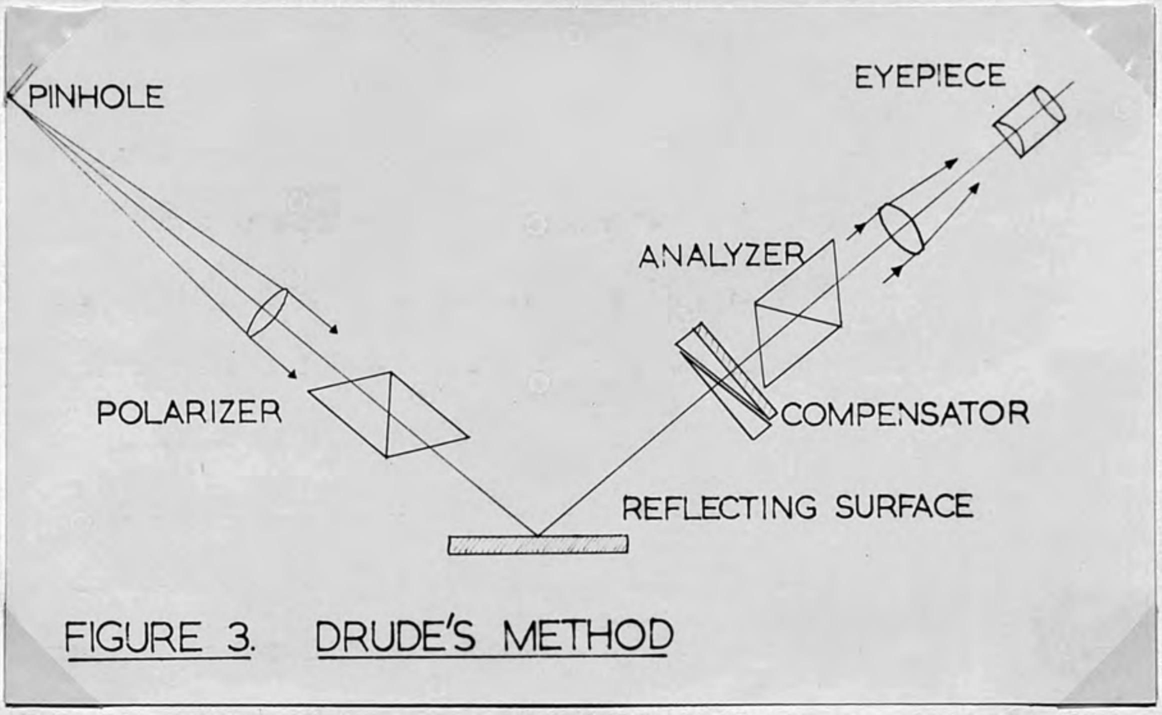

FIGURE 3. DRUDE'S METHOD

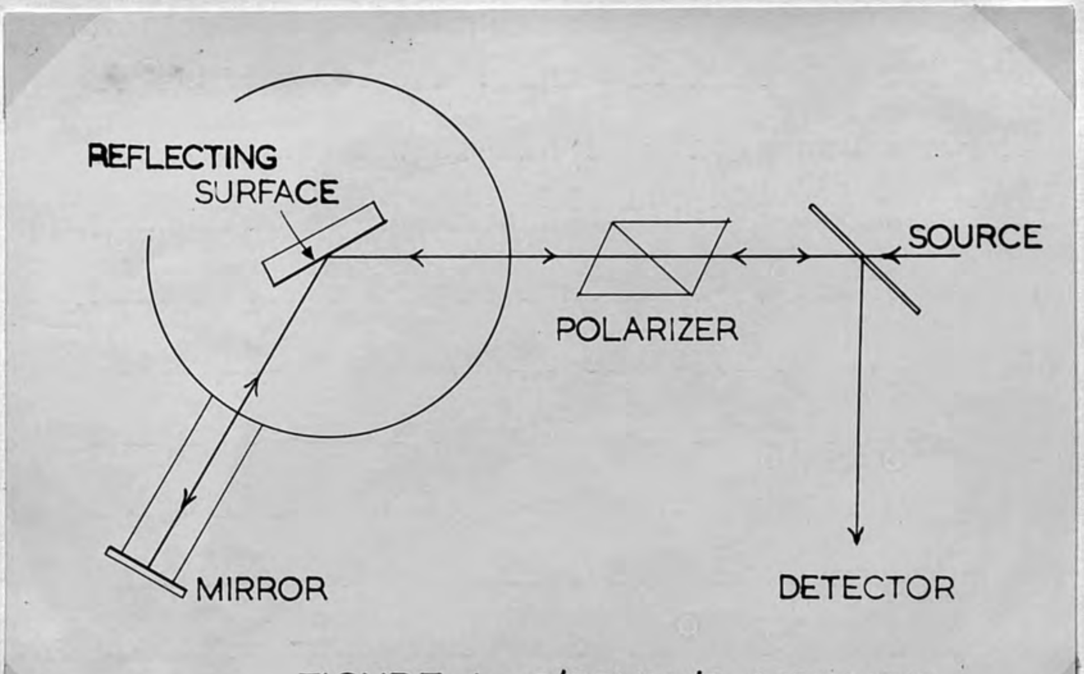

FIGURE 4. O'BRYAN'S METHOD

it is obvious that the comparison of the results obtained by various workers using this process would be extremely difficult, and Lowery, Wilkinson and Smare[26] state that even a single observer cannot reproduce surface conditions by mechanical polishing to any degree of accuracy.

This appears to be the first investigation in which the production of surfaces characteristic of the bulk metal was attempted by the vacuum evaporation process. The results for the evaporated surfaces agree more closely with those for the mechanically prepared surfaces in Lowery's investigation, than with those produced by electrolytic polishing. This is attributed to the probable micro-crystalline structure of the evaporated layers, which is said to approximate to the structure of the Beilby layer formed by mechanical polishing.

In the same year as Lowery's work was concluded, 1936, an account was published by O'Bryan[27] of a determination of the optical constants of a number of metals by a method based on one originally due to Brewster. The reflecting surfaces were prepared by evaporation in vacuo, and the method represented a considerable advance on previous work in that the surfaces of the evaporated layers were examined in vacuo, and then the formation of surface impurities was avoided. O'Bryan's method is quite different from that of Drude, and worthy of a brief mention.

When plane polarised light is reflected at a metal surface at the angle of principal incidence, it is converted into circularly polarised light ($\Delta = \pi/2$). If the beam is then again reflected at the same surface at the same angle of incidence, it is converted into plane polarised light again but of opposite azimuth to the incident beam. If, therefore, this beam is passed through the polariser (acting as analyser to the returning reflected beam) it will be extinguished. In O'Bryan's apparatus this was effected by the optical arrangement shown in Figure 4. The evaporated layer was deposited on to a glass slide mounted on a central turntable. The incident light passed through a polariser, was reflected at the specimen and then returned over its own path by normal reflexion at a plane mirror mounted on arm geared to the turntable by a two-to-one motion. The polariser, turntable, and plane mirror were all included inside the vacuum chamber, and the adjustment consisted of rotating the specimen and polariser until the returning beam was of minimum intensity. The angle of incidence was then the angle of principal incidence, and the two positions of the polariser found to give minimum intensity were separated by an angle equal to the angle of principal azimuth.

Besides avoiding atmospheric contamination, this method has the additional advantages that no expensive polarimetric compensators are required, and the method is suitable for extension into the infra-red if the positions of minimum intensity are observed with the aid of an infra-red detector. O'Bryan states that the angles of principal incidence and azimuth could be measured to an accuracy of ± $0{\cdot}1^{\circ}$, this gives values of n and k subject to an error due to experimental causes of ± 1 or 2%.

Values of the optical constants were again obtained from measurements on evaporated layers whilst they were still in a high vacuum by Hass(28). The measurements in this case were made by the standard method of Drude, the specimen alone being situated in the vacuum chamber. The observations were made at a fixed angle of incidence (70°), the light entering and leaving the chamber through glass ports. The danger in experiments of this kind is that on fastening the ports to the chamber, they are made subject to some stress, and hence acquire birefringent properties which affect the state of polarization of light passing through them. In this case, the ports were 'wrung' on to ground surfaces, the seal being made with grease only, to avoid heating them, and any errors associated with strain in the glass were less than the overall errors elsewhere in the experiment.

The accuracy with which the angle of principal incidence can be measured can be improved by the application of electronic techniques to the problem. We have seen that when plane polarised light is reflected at the angle of principal incidence, it is transformed into circularly polarised light. Kent and Lawson(29) allowed the reflected beam to pass through an analyserwhich was continually rotating at constant speed, and then to fall on to a photo-electric cell. The output from the cell was amplified, and the angle of incidence at which the alternating component of this output was zero could be very accurately detected. An improvement on this method, together with a comprehensive survey of the various methods for determining optical constants, is described in a recent work by Archard(30).

In conclusion it seems that two main factors enter into any accurate measurement of the optical constants of a metal:

1. The state of the surface (i.e. state of preparation, cleanliness etc.) must be clearly defined, and reproducible, and

2. The accuracy required of the optical measurements is governed by the reproducibility of the surfaces, since the latter is the limiting factor.

In this latter connection it appears that the methods of O'Bryan and Kent and Lawson represent an advance over the older polarimetric methods, since the experiments can be carried out more rapidly, less expensive apparatus is needed with no loss of accuracy, and they are more susceptible to refinement by modern techniques.

Production of the surfaces by evaporation appears at first sight to be superior to other methods in that polish marks, Beilby layers, etc. are avoided, and also the process lends itself to direct optical measurements on the surfaces in vacuo. It is essential, however, to bear in mind that the structure of an evaporated layer may not be the same as that of a metal in bulk. The technique of evaporation does not make it easy to deposit layers of thickness greater than, say, 2000A, without added complications such as multiple evaporating sources, etc., and it must be decided for each case whether layers of the order of thickness used can be regarded as typical of the material as a whole. The minimum thickness required, from the optical point of view, is that the beams reflected at the back surface of the layer shall not have sufficient intensity to affect the intensity and phase of the beam directly reflected at the front surface to an extent which would be detectable by the experimental method used.

The question of the structure of the evaporated layers will be considered in more detail in the next chapter, when the optical behaviour of metallic layers in relation to their thickness will be discussed.

THE OPTICAL BEHAVIOUR OF METALLIC LAYERS

Chapter IV.

Using Drude's values for the optical constants of silver and gold, MacLaurin(8) calculated the variation of the ellipticity and the relative phase retardation or reflexion at thin layers of these metals to be expected as their thickness varied from one tenth to one hundredth of the wavelength of the incident light. The mathematical expressions used were of a similar form to those developed in Chapter II. In addition, MacLaurin tabulated values of the normal incidence reflexion coefficients of thin layers.

These theoretical values were experimentally tested by Hagen and Rubens(31), who measured the reflexion coefficients of gold layers for incident light of various wavelengths. The thinnest layer actually measured was of the order of 300Å in thickness, but the experimental curves were extrapolated to zero reflexion coefficient for zero thickness, and these curves agreed very well with the theoretical predictions of MacLaurin. This work led to the assumption of a linear, or near-linear, relation between reflexion coefficient and thickness from the thinnest layers up to a limiting value for the reflexion coefficient equal to that of the bulk metal. The optical constants of the material of which the layer was composed were considered to be those of the bulk metal, and the phenomena associated with the variation of thickness of metallic layers appeared completely explained.

This view was held for a number of years. In 1927, Fabry(32) gave a formula relating the optical density, i.e. the logarithm of the reciprocal of the transmission coefficient, of a thin metallic layer to the thickness, which was assumed to hold down to layers of zero thickness. An investigation of the optical characteristics of thin films of iron, prepared either by cathodic sputtering or by thermal evaporation in vacuo, was described by Cau(64) in 1929, in which the phenomena observed could be completely explained using the values of the optical constants for iron in bulk. Again, in this investigation, the thinnest layers considered were of the order of 300A in thickness.

However, between 1932 and 1937 three separate investigations were made by Rouard(33) not reported till 1937 , Goos(34) and Murmann(11), of the variation of the optical characteristics of sputtered layers of silver with their thickness. In each case measurements were made of the reflexion and transmission coefficients of the layers for thicknesses down to about 20A , and it was found that the properties of layers less than about 200A thick could not be explained in terms of the optical constants of the bulk metal. The reflexion coefficient of the layer, seen from the air as distinct from through the support, was found to decrease more rapidly than predicted by the classical theory, below 200A, and the reflexion coefficient on the support, or substrate side showed a completely unexpected minimum value at a thickness of about 30 to 40A. The form of the curves relating the reflexion coefficient to the thickness as found by these investigators is shown in Figure 5.

In this figure (due to Rouard) the dotted lines represents the values of the reflexion coefficients (air-side and glass-side) to be expected from the classical theory, using the massive metal constants. It is seen from the figure that the anomalous behaviour of the layers begins when the thickness of the layer falls below 150A, and below this value of the thickness, the layer must be assumed to have optical constants differing from those of the massive metal in order to explain the experimental results; the values of the constants chosen must also be assumed to vary with the thickness of the layer in this region.

The work of Rouard has formed the basis for a large number of investigations, carried out in France, with the object of determining the variation of the optical constants of metallic layers with their thickness. The experimental methods used, and much of the earlier and wartime work has been summarised by Arons(35). The procedure in the earlier work was to measure the reflexion coefficients with results as described above, and from them to calculate the optical constants by the graphical method due to Murmann(11) which has already been mentioned (Chap. II). These values of n and k were then used to calculate the phase changes occurring on normal reflexion, and the results of the calculations compared with direct experimental measurements of the phase changes.

The improvement in ease of computation made by the introduction of the direct graphical method for determining n and k from the measurements on reflexion coefficients and phase changes made by Perrot(14) and Perrot and Cotton(15) has already been discussed (Chap. II) A further advance has since been made by Perrot and Rouard(36, 37) who have developed a still more direct method by which n and k can be determined from the position of the minimum in the curve for the reflexion coefficient on the support side of the layer, and the variation in position, with respect to thickness, of this minimum with wavelength. The most recent summary of this work was by Rouard(38) in 1949.

A study of the work of the French School in this subject tends to lead to the opinion that the problems

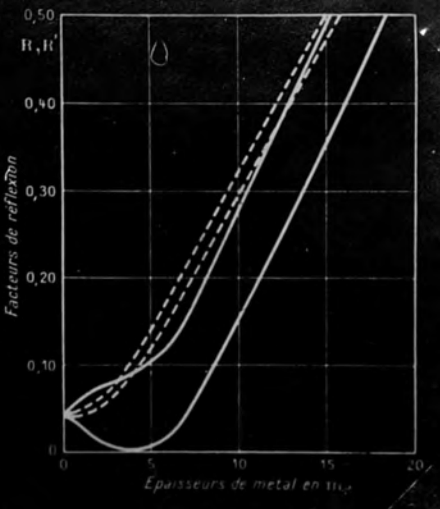

Fig. 3. — Argent : Comparaison des facteurs de réflexion pour λ = 5 780 Å —

a) déterminés expérimentalement (trait continu).

b) calculés à partir des constantes du métal massif (trait discontinu).

FIGURE 5

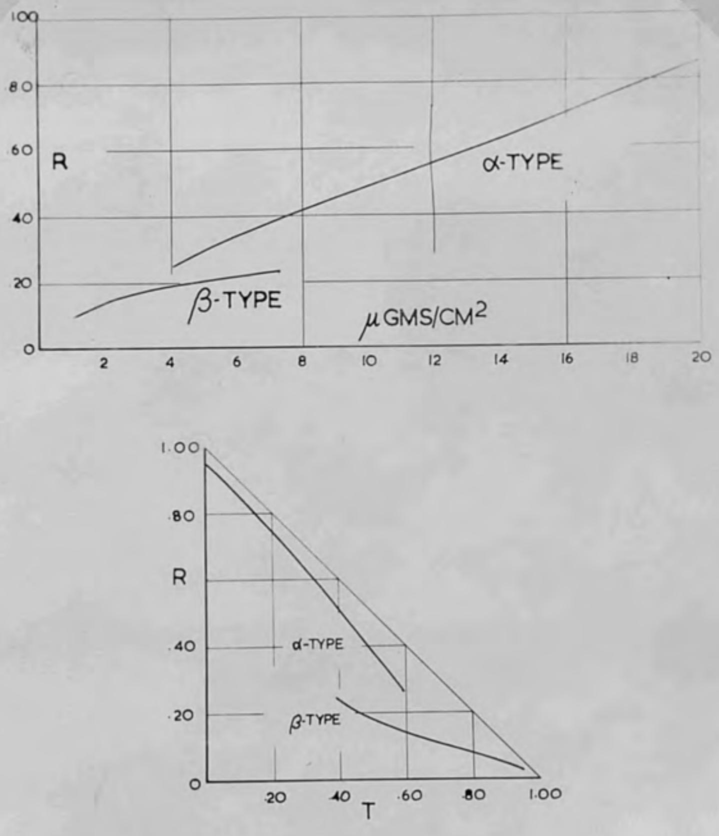

FIGURE 6. STRONG AND DIBBLE

associated with very thin metallic layers have now been settled, and that the results quoted are reproducible without difficulty. However, this view was dispelled when a very exhaustive treatment by Strong and Dibble(39) in 1940 is considered.

These workers measured the reflexion (air-side only) and transmission coefficients of 142 silver layers, of varying thicknesses, produced by thermal evaporation in vacuo. Their results indicate that, under the conditions of their experiment, two distinct types of silver layer could be formed. In Figure 6 (a) and (b), curves showing Strong and Dibble values for reflexion coefficient related to transmission coefficient and to thickness are given.

The thicker films ($d > 100A$) measured by Strong and Dibble, their α-type films, show a variation of reflexion coefficient, R , and transmission coefficient, T , with thickness, similar in form to the variations observed by Rouard and his co-workers, though they differ markedly from the films produced by the latter in that their light absorption, A , given by $A = 1 - (R+T)$ is considerably greater. The thinner films, the β-type films, are also characterised by a very large absorption, much greater than that observed by Rouard for a corresponding thickness. There is a certain thickness region in which films may occur in either of these two types.

The existence of these two types of layer has nowhere been observed in the work of the French school, or in other measurements of the reflexion and transmission coefficients carried out elsewhere. Strong and Dibble suggest that this may be due to the small number of films usually measured, and they state that if only a score or so of films are investigated the results may easily indicate a continuous variation of reflexion coefficient with thickness from which erroneous conclusions may be drawn.

In discussing these results it must be realised that it is very difficult to make a satisfactory critical comparison of the results obtained by various workers in this field for two reasons.

The first reason is that the methods used for the measurement of the thickness of the layers is different in the various cases. A more detailed discussion of the measurement of thin film thicknesses will be given in Part II, Chap. II, of this thesis, but it may be said here that the two most commonly used methods are estimation of the layer thickness by direct weighing, and the measurement of the thickness of the film by an interferometric method. Each of these methods is subject to large experimental errors, of as much as 10% or more, in the region where the optical behaviour of the layers is anomalous.

The thickness of the layers used by Strong and Dibble was esimated from considerations of the rate of evaporation of the silver and the geometry of the evaporation system. This method was checked in a few cases by direct weighing and the thicknesses as found by the latter method were found to be larger than the others by a factor of 1·35. The values by direct weighing were divided by this factor to obtain consistent results. However, comparison of their values for the α-type films with that of Rouard (Figure 5) shows that the reflexion coefficient for a given thickness in Strong and Dibble's case is considerably greater than that quoted by Rouard. If the direct weighings made by Strong and Dibble are taken as correct, and the thicknesses obtained by the other method multiplied by the factor 1·35, the agreement between the two sets of curves is much improved. That this latter procedure is perhaps more justifiable than that used by Strong and Dibble will appear later, when certain results obtained in this investigation are discussed.

In this way the α-type films may be said to have similar properties to those of Rouard, as far as the variation with thickness is concerned. However, as we have seen, the absorption in the former films is much higher than in films produced by the French workers. The explanation for this is probably to be found in the second reason why a comparative study is difficult. As in the case of measurements of n and k for bulk materials, the method of preparation of the films and their history after preparation is of extreme importance in determining their optical characteristics. The effect of exposure to the atmosphere after preparation is particularly important when the films are of metals which oxidise rapidly on exposure to air, as is shown by the recent work of Cabrera and Terrien(40) on aluminium films. Silver films are known to oxidise comparatively slowly in air and in this case an explanation for differences in properties lies more probably in differences in the method of preparation. Of the work we have discussed, the films of Goos and Rouard were prepared by cathodic sputtering, the latter using an atmosphere of anthracene. Murmann prepared his films by thermal evaporation, as have all the workers in the French school since Rouard's original experiments. To these may be added Krautkramer(13), who examined the properties of evaporated layers of silver and gold in 1938, and Strong and Dibble.

The characteristic of films which is most susceptible to differing methods of formation is their light absorption. This absorption is best seen from the experimental measurements of R and T if they are plotted one against the other, as Strong, and Cabrera and Terrien have done, rather than if they are both plotted against an independent axis of thickness measurements which may themselves be subject to considerable errors. This is done for the results of Goos, for sputtered layers, and Krautkramer and Strong and Dibble for evaporated layers in Figure 7. It is seen at once from this figure that Krautkramer's films, which are similar to those prepared by the French workers, have less absorption for a given transmission or reflexion coefficient, than the films of either Strong or Goos.

It is not unexpected that films made by cathodic sputtering should show a greater absorption than films produced by evaporation (Krautkramer), since the sputtering process may produce layers containing relatively large quantities of occluded gases. However the absorptions of the layers of reflexion coefficients greater than 70% or less than 35% made by Strong by evaporation are of the same order as those of Goos made by sputtering. The explanation for this seems to be that Krautkramer, in common with Murmann and other more recent workers, produced the high vacua necessary by the use of mercury diffusion pumps and liquid-air, and this high vacuum must be regarded

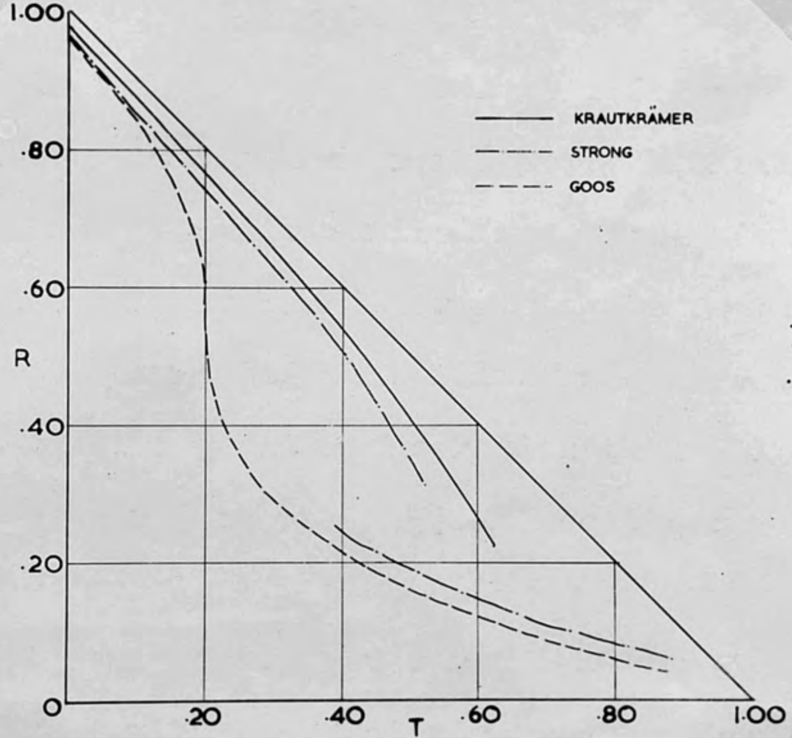

FIGURE 7

as altogether purer than the vacua (of the same order of total pressure) produced by untrapped oil diffusion pumps by Strong. This point will be borne out by some observations on the operation of an evaporation plant using an oil diffusion pump, quoted in Part II, Chapter I.

It is also obvious that the cleanliness of the substrates on to which the films are deposited will critically affect the purity and hence the light absorption of the films. In this respect, however, the techniques used by all workers appear materially the same.

Whilst this impurity hypothesis may explain the high absorption of Strong's α-type films, it is difficult to appreciate how it can account for the existence of two distinct types of film as recorded by Strong and Dibble. In the absence of further evidence, it seems that the contention of these workers, that a continuous variation of reflexion coefficient with thickness may appear from a comparatively small number of measurements must be accepted, though it is extremely difficult to reconcile this with the excellent reproducibility of the results of other workers, quoted in recent summaries(35, 38, 40).

Whilst it is apparent from the foregoing discussion that the optical behaviour of thin metallic layers is not yet completely explained, it can be said with some certainty that the optical constants of the material comprising a layer, differ from those of the bulk material in layers of thickness 150Å or less. The cause of this variation is immediately apparent when the existing knowledge of the structure of thin layers is considered. It has been shown by a large number of workers using the techniques of the ultra-microscope(48, 49), electron diffraction(28, 13) and of the electron microscope(41, 42, 43) that films of metals of this order thickness are granular in structure, the granules being in the case of silver, crystalline(13, 44, 45, 46, 47) and more or less oriented in certain directions according to the nature and temperature of the substrate on to which they were deposited. These granules have a dimension parallel to the surface of the substrate of the order of 200-1000Å*, and it is immediately obvious that a film composed of such granules does not satisfy the fundamental assumptions of the classical theory discussed in Chapter II in relation to isotropic layers, bounded by parallel surfaces, and infinite in extension parallel to these surfaces.

Only one of the workers in the optical field, Krautkramer(13), has attempted to explain these variations of the optical constants in terms of a granular structure.

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* This figure was given by Prof. G. I. Finch in a private communication.

He based his attempt on earlier theoretical work by Maxwell Garnett$^{(50)}$, who calculated the optical properties of a layer supposed to consist of spheres of metal (each having the optical constants of the bulk metal), whose diameter was small with respect to the wavelength of the incident light. He considered the variation of the optical properties with a 'packing factor', defined as the ratio of the volume of the layer occupied by the spheres, to the volume of the whole layer. The treatment does not necessitate that the spheres are all of the same size, but rather that random distribution about a mean diameter exists. In making a comparison between Maxwell Garnett's calculations and his own experimental results, Krautkramer took the view that for a certain packing factor of $q\ (<1)$, the thickness of the layer, as measured by an interferometric method, was $1/q$ times too great, since the film was only q times as dense. Using this correction to his thickness measurements, Krautkramer obtained a qualitative agreement between his own results and those of Maxwell Garnett. It would, however, be very difficult to make any quantitative comparison using this theory, since the granules observed in thin films are not spherical, and since it is very difficult to make any accurate estimation of their mean size. The difficulties inherent in any such comparison have been recently treated by Cabrera and Terrien$^{(40)}$.

In the preceding chapter, the use of the surfaces of evaporated metallic layers for the determination of the optical constants of a metal was discussed, and the importance of ensuring that these layers had a similar structure to that of the bulk metal was stressed. From the optical measurements on thin films quoted in this chapter we can say that the optical characteristics of layers greater than, say, 250 A at the most, can be explained by the bulk metal constants, as far as the variation of reflexion coefficient with thickness is concerned, but that the absorption of the layers is critically dependent on the conditions of preparation. However, for the measurement of the optical constants by any of the methods suitable for bulk metals i.e. dependent on reflexion at a single surface, the beams reflected at the film-substrate interface must make a negligible contribution only to the intensity and phase of the beam reflected at the first surface, and so for film of the order of thickness required for this condition to be satisfied, the absorption is of no importance. Furthermore, the work of Picard and Duffendack(41), Scott and Hass(42), and Levinstein(43), using the electron microscope, has shown that for layers of high melting point metals, (e.g. Ag, Au, Al, Cr, Cu) their surface structure is equivalent to that of a bulk metal only when a thickness of 400-500 A is reached. Measurements of reflexion and transmission coefficients indicate that for films of this order of thickness, the optical properties in reflexion are practically equivalent to reflexion at a single surface, and so the figure of 450Å may be taken as a suitable minimum thickness required before a metallic layer can be taken as optically characteristic of a bulk material, for these metals.

In the case of low melting point metals (e.g. Cd, Zn), Picard and Duffendack and Levinstein have shown that evaporated layers of these metals are very difficult to form at room temperatures, and cannot reasonably be used as reflecting surfaces characteristic of the bulk material.

THE EXPERIMENTS TO BE DESCRIBED IN THIS THESIS

Chapter V.

In the preceding chapters, the use of evaporated metal layers to provide reflecting surfaces characteristic of the metal in bulk has been described, together with the variation of the optical characteristics of the layers with their thickness, at thicknesses below the minimum required for bulk metal characteristics.

We have seen that the measurements on thin metallic layers, in relation to their thickness, have been almost entirely of the reflexion and transmission coefficients at normal incidence, and that the absorption of the layers measured seems to vary considerably with the method of preparation. In this laboratory, layers of silver are used a great deal in connection with spectroscopy(51), and multiple beam interferometry(52), and a few measurements have been made of the normal incidence coefficients of silver and aluminium layers to assist with this work. The layers were produced by evaporation under the normal conditions prevailing with the laboratory equipment.

The main part of the work is concerned with the application of a new technique, for the measurement of the relative phase retardation on reflexion, to the study of the optical characteristics of metallic layers. An investigation into the non-normal incidence reflexion properties of layers of silver will be described. Measurements have been made of the properties of layers thick enough to represent bulk silver, and of the variation with layer thickness of the ellipticity and relative phase retardation on reflexion at thin layers. In addition to the work on silver, the new technique has been applied to the study of reflexion at thick layers of tin, copper, speculum, and a new tin-nickel alloy, and the optical constants of these metals and alloys have been determined. The results obtained will be compared with the previous investigations already described.

The new optical technique will be discussed in Part III of this Thesis, Part II which follows will consist of a description of the evaporation equipment and procedure used, together with a discussion and some experimental results on the measurement of thin layer thicknesses. The experimental results form the subject of Part IV.

PART II

THE PRODUCTION OF THE FILMS AND THE MEASUREMENT OF THEIR THICKNESS

PART II

THE EVAPORATION TECHNIQUE

Chapter I.

The deposition of thin layers by means of thermal evaporation is now a standard technique, used a great deal not only for the production of metallic layers for interferometry, spectroscopy etc., but also for the production of anti-reflexion coatings of dielectrics, of interference colour filters(53), and layers of dielectrics such as silicon monoxide(42) to protect front surface mirrors from atmospheric corrosion. The technique has been adequately described in a number of books, e.g. by Tolansky(51, 52), Strong(54) and Lewis(55), and for this reason the treatment here will be restricted to a relatively brief description of the plant and technique used in this investigation.

The Equipment Used.

The metallic films used were produced in either of two evaporation plants. The first measurements were made on films deposited in a commercial Coating Unit Type E3 manufactured by W. Edwards & Co. Later, to relieve the congestion in the laboratory caused by continual use of this plant, a second evaporating plant was constructed, embodying certain improvements over the commercial unit.

Messrs. Edward's plant is of the vertical type. The vacuum chamber is a large Pyrex bell-jar, 60 cms. high, resting on a massive steel baseplate, a vacuum seal being made by an ungreased rubber gasket on the lower edge of the bell-jar. A large diameter flap-valve set into the baseplate connects the chamber to a three stage oil diffusion pump, using silicone oil. A number of vacuum-tight insulated electrodes are fastened into the baseplate, between which the evaporation filaments and electrodes for high tension discharge are connected. The substrates to be coated are placed face downwards on a table, some 30 cms. above the filament. This distance is large enough for the variation in density of the deposit, from a point source, across a circle on the table of diameter 10 cms. to be less than 1%.

The voltage available for passing a high tension discharge between two rings situated between the filament and the specimen table is 3,300. The maximum filament heating current available is 150 amps.

The capacity of the bell-jar and speed of the pump are such that a complete evaporation process takes only half an hour. The pressure in the chamber is measured by a Philips-type ionisation gauge, a cold-cathode gauge. The evaporation is usually carried out when the pressure is below 10^{-4} mms. of Hg, but the gauge does not permit of any accurate estimation of pressures of this order. Figure 8 is a photograph showing the arrangement of the components on the baseplate.

This evaporation unit has been found to be admirable for the general work of the laboratory. It has been used for the production of at least three or four hundred silver layers for interferometric purposes over the past two years. However, from the point of view of the production of layers for the study of their own optical characteristics it suffers from two serious disadvantages. The first concerns the lower limit of pressure which may be measured, already mentioned as 10^{-4} mms. of Hg. If the mean free path of a particle evaporated from the source is taken to be the same as that of a molecule of residual gas at this pressure, it is 100 cms., only three times the filament-substrate distance. To produce pure, reproducible films it is advantageous to reduce the pressure much further, so that the mean free path is at least ten times this distance. The second disadvantage is that the light transmission of the film can only be roughly estimated during production in the commercial unit by looking through it at the heated filament. This is not a serious drawback when it is desired to produce films of only three or four per cent transmission, as is general practice for interferometry, but it makes the estimation of thinner layers very difficult indeed.

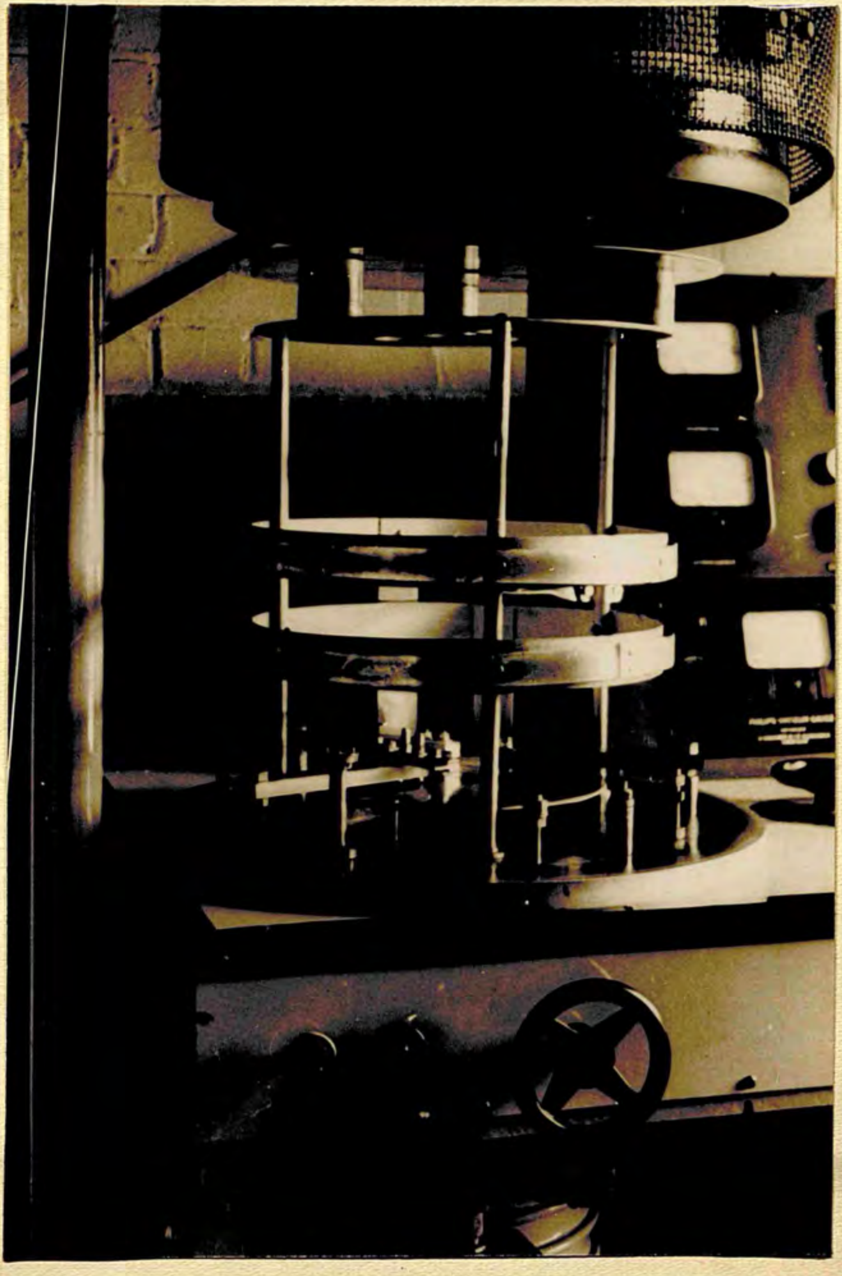

FIGURE 8

Accordingly, when it was decided to construct a second evaporation plant specially for this investigation, its design incorporated features overcoming these two main disadvantages. The design adopted was that of a horizontal unit, similar to that used by Ritschl(56). A schematic diagram of this plant is shown in Figure 9, and some photographs in Figure 10.

The substrates are fastened to two end plates which bolt on to a cylindrical metal vacuum chamber 35 cms. long. The filament electrodes are fastened to a plate which bolts on to a flange in the centre of this chamber, directly over the pipe leading to the Apiezon oil diffusion pumps. Two rings of aluminium wire near each end form the electrodes for the high tension discharge, the voltage being applied through two glass-metal seals in the wall of the chamber. The chamber is lined on each side of the filament with glass cylinders, which can easily be removed for cleaning. The pressure in the chamber can be adjusted by a needle valve, which is connected to a supply of dry nitrogen, so that no oxygen need be present during an evaporation.

The dimensions of the apparatus are such that a deposit, uniform in density to 1%, is obtained on a region 2 cms. in diameter at each end of the plant. This area is quite sufficient for the work to be described. The use of the horizontal system makes the estimation of film

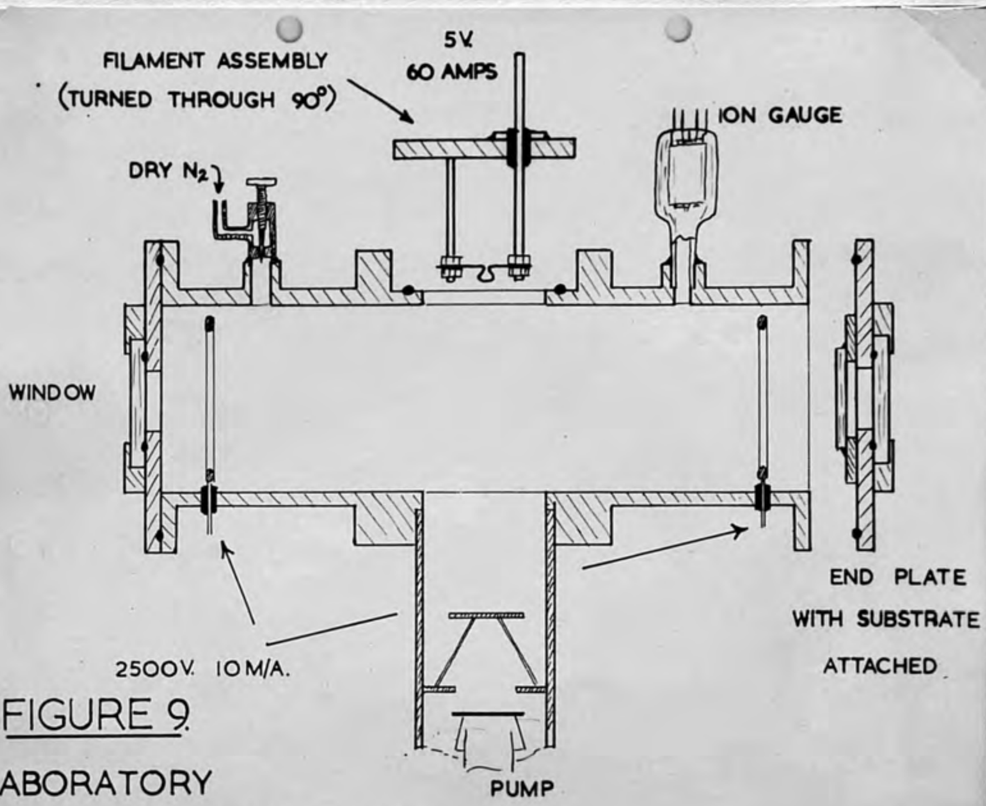

FIGURE 9.

LABORATORY
EVAPORATION PLANT

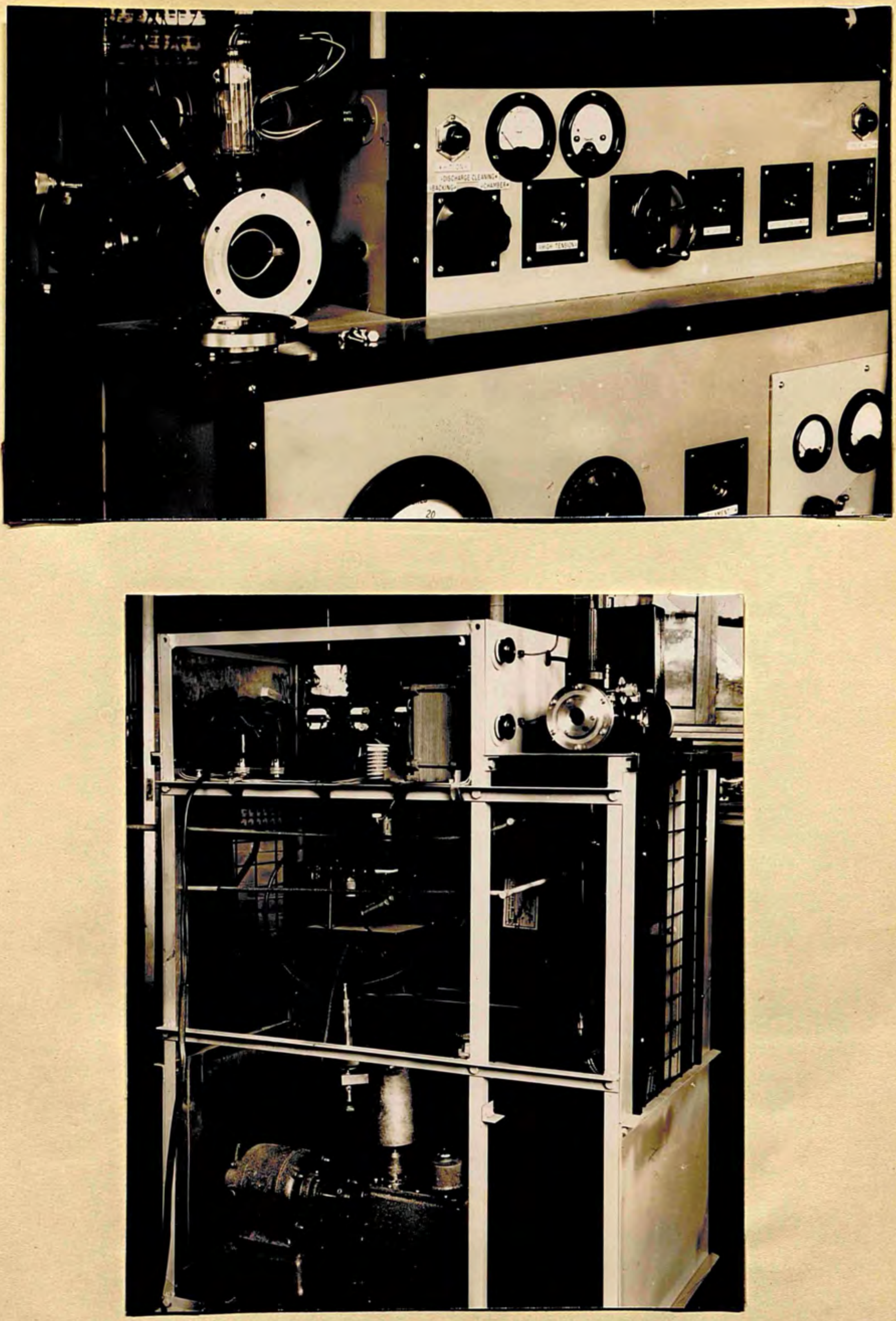

FIGURE 10

density during production much easier than in the vertical type. A constant light source can be viewed through the two films, and the density estimated very readily. If need be, a photo electric device could be employed to further improve the limits within which a film of given density can be prepared, but this was not found to be necessary.

The pressure in the chamber is measured in this plant by a hot filament ionisation gauge. An electronic control unit supplies the various potentials and amplifies the ion current, so that pressures down to 5×10^{-6} mms. of Hg can be easily measured, and rough estimations of pressures below this made. The gauge is attached to the system by a short tube, and this results in the pressure readings being incorrect to a certain extent due to the consumption of oil vapour, which is always present in varying amounts in the chamber, by decomposition at the hot filament(57). Because of this the readings of pressure must be taken as self consistent to a greater accuracy than as measurements of the actual pressure existing in the chamber. It was found from experience that in order to increase the speed of response of the gauge, the electrodes had to be outgassed by electron bombardment after each exposure to the atmosphere, and the electronic control unit for the gauge was suitably modified to allow an electron current of 50 milliamps to bombard either the accelerator or the collector of the gauge.

The pump used was a two-stage oil diffusion pump, using Apiezon 'B' oil, having a speed of 30 litres/sec. at pressures below 10^{-3} mms. of Hg. It is fitted with a baffle above the top jet, and in addition a second baffle plate was introduced into the short pipe leading from the pump to the chamber. The presence of these baffles is essential, since in the experience of the writer, the amount of oil-vapour streaming back from those pumps is quite large. It is estimated that the resultant pumping speed in the chamber is about 10 litres/sec.

With the system as described, before the outgassing procedure was adopted with the ion gauge, it was necessary to pump for six or seven hours before the gauge recorded pressures of the order of 10^{-5} mms. were reached, despite the fact that the leakage rate in the chamber was very small. When the outgassing procedure was adopted, the gauge recorded those pressures after three or four hours pumping. However, when the pumping was carried on for this length of time, despite the presence of the baffles in the pumping line, it was found that oil vapour was contaminating the substrates before deposition took place. Traces of oil were found in the chamber on completion of an evaporation. To combat this, a glass tube was attached to the side of the chamber, and its closed end was dipped into a freezing mixture of solid carbon dioxide and alcohol. This served as a pump for the oil-vapour, and it was found that the required pressures could then be reached in less than two hours, and all visible traces of contamination of the substrates disappeared.

The Evaporation Procedure.

The light absorption exhibited by metallic films is very dependent upon the cleanliness of the substrate prior to deposition. A number of different cleaning techniques have been proposed, for example the use of 'controlled contamination' by lanoline proposed by Strong(58). In order to obtain reproducible results in any one investigation the particular cleaning method chosen is less important than ensuring that the method used for each deposition is the same.

In this investigation all the layers considered have been deposited on to one of three or four glass discs, these discs being used repeatedly. The procedure adopted for cleaning the discs prior to a fresh deposition was as follows:

1. The old film was removed with concentrated acid (nitric acid for Ag, Cu, Sn, and the alloys, hydrochloric acid for Al).

2. The disc was dried with clean cotton wool and rubbed with pieces of cotton wool until the 'breath figures', formed by breathing gently on the surface, were uniformly grey in colour and disappeared in about one second or less.

3. The discs were then placed in the evaporation chamber of the plant being used, and the pressure reduced to about ·01 mms. by the mechanical rotary pump. A high tension discharge was then passed in the chamber to clean the specimen further by ionic bombardment. In the commercial unit, the discharge was passed for one minute in each case, about 250 milliamps passing in the discharge, at 1500 volts. In the laboratory built plant, the discharge electrodes are less than one inch from the substrate surface, and the cleaning may be expected to be more efficient than in the commercial unit. A discharge carrying 10 milliamps at 1500-2000 volts was passed for three separate periods of one minute in this plant.

After cleaning, the pressure in the chamber was reduced by the diffusion pump, evaporation being carried out in the commercial unit at a pressure (unknown) below 10^{-4} mms., and in the laboratory plant at a pressure below 2×10^{-5} mms .

The type of filament usually used for the evaporation differed in the two plants. In the commercial unit, the filament usually consisted of a strip of molybdenum, 2" x $\frac{3}{8}$" x ·008", in the centre of which a small depression, $\frac{1}{4}$" in diameter was punched to take the change of material. Evaporations from this type of filament were carried out at a heating current of 120 amps. In the laboratory plant the filament was a strip of molybdenum $\frac{1}{8}$" wide by ·004" thick, bent into the shape recommended by Tolansky(51), and shown in Figure 9. When the material fused, it formed a drop completely filling the 'U' section of the filament, and formed an evaporation source of about $\frac{1}{8}$" to 3/16" in diameter. The advantage of this form of filament is that the heat radiation in the direction the specimen is cut down, in comparison with the form used in the vertical plant, since the filament is viewed 'sideways' from the filament. The heating current used for this filament varied with the particular metal used.

A list follows of the various metals evaporated during the investigation, together with details of the type of filament used in either or both of the evaporation plants, if different from the standard molybdenum ones described. The heating current usually employed will be stated in each case, together with relevant details concerning the ease with which the metal evaporated. A very complete survey of the evaporations of metals has been made by Caldwell(59), and the writers experiences agree with the observations of Caldwell in the main, though one or two differences are noted below.

<u>Silver</u>. The metal was available in the form of 3 mm. diameter wire, spectroscopically pure, and was evaporated in both plants from the standard molybdenum filaments as described. The heating currents used were 120 amps. in the vertical plant and 40 amps. in the horizontal plant; with these currents an opaque layer could be formed easily in 30-45 seconds. The silver wetted the molybdenum when fused and, as is general experience, evaporated very readily.

<u>Aluminium</u>. Aluminium foil was evaporated, in the vertical plant only, from conical baskets of 1 mm. diameter tungsten wire, formed by winding the wire when red-hot on to an ordinary wood screw, about ½" in length, as a mandrel. The spiral was heated by the passage of a current of some 90 amps. As has been reported by Strong(54), the aluminium readily formed an alloy with the tungsten, and for this reason it was not usually possible to obtain an opaque layer before the filament itself fused. To overcome this two baskets were used, one after the other, an opaque layer being formed after two or three minutes. It is probable that the films produced by this process actually consist of an aluminium tungsten alloy.

Copper. The evaporation of copper was carried out in both plants, the conditions being the same as those for silver. No alloying took place between the metal and the filament. Since Copper has a lower absorption coefficient than silver, opaque layers took some two minutes to form, with the same heating currents as for silver.

Tin. 99·992% pure tin, in the form of small chips, was very kindly supplied by Dr. Hedges of the Tin Research Association. It was found to evaporate readily from molybdenum filaments, and was found to wet them, contrary to Caldwell's observations, provided that the tin was not fused until a low pressure (10^{-4} mms.) had been reached. At pressures above this, an oxide scum formed on melting, which prevented the metal from wetting the filament.

Dr. Hedges has suggested, in a private communication, that an alloy may be formed between tin and molybdenum. If this is so, it must be an alloy of a very low percentage of molybdenum, since one filament, ·004" thick, served to produce fourteen layers, without itself fusing. It was found that if the filament were heated beyond red-heat, the films produced had a marked 'bloom' on the surface, and their optical reflectivity was very low ($<$ 20%). Because of this, the heating currents employed were lower than for silver, not exceeding 90 amps. in the vertical plant, and

25-30 amps. in the horizontal plant. The horizontal plant was found to be superior for the evaporation of tin, due to the reduced heating effect of the filament, as has been mentioned.

Chromium. The metal was available in the form of small chips which were evaporated, in the vertical plant only, from tungsten baskets similar to those used for the evaporation of aluminium. It was found necessary to heat these baskets to white heat (130 amps. or more heating current) in order to fuse the metal, and then the evaporation took place only slowly, a thick layer taking at least three minutes to form. The metal was found to alloy with the filament, though not so readily as aluminium.

Zinc. Zinc was found to evaporate readily from molybdenum filaments, under similar conditions to those for silver. As is usual when zinc is evaporated on to substrates at room temperatures, the layers formed were non-uniform in density, and no optical measurements were made (cf. e.g.(41, 43)).

Speculum and Tin-Nickel Alloys. These alloys were again supplied through the courtesy of Dr. Hedges of Tin Research Association. They were in the form of a fine powder and hence could only be evaporated from the molybdenum filaments in the vertical plant. They were found to evaporate readily under identical conditions to those for silver. There was no alloying between speculum and molybdenum, but it is possible that the tin-nickel alloy forms an alloy with the filament to a certain extent.

THE MEASUREMENT OF THIN FILM THICKNESSES

Chapter II.

In the theoretical discussion of the optical properties of thin layers given in Part I, Chap. II, the layer was assumed to be homogeneous, and bounded by parallel surfaces separated by a distance d. However, as we have seen in Part I, Chap. IV, modern work on the structure of thin layers has shown that this assumption is incorrect, and that layers of less than 200-300 A in thickness are more accurately regarded as granular. In the light of this, it is very difficult to define the 'thickness' of a layer, and it will be appreciated when the various methods used to determine the quantity d are considered, that the definition of the thickness depends to a large extent on the method of measurement adopted.

A method frequently used to determine d (e.g. by Goos(34), Perrot(14), Strong and Dibble(39)), consists of measuring the mass of metal deposited upon a known area of substrate, by direct weighing with a microbalance. This method has the advantage that the microbalance can be introduced into the vacuum chamber without much difficulty and the measurements made as the film is produced. As an alternative to the use of a microbalance, colorimetric methods can be used to determine the mass of metal deposited. A colorimetric method for the estimation of silver has been described by Schoonover(60). The value for the thickness d, is obtained by dividing the mass of metal deposited per unit area of substrate by the density of the metal. It is seen at once that if the film is granular in structure, this will not yield correct results, since the density of the material of the film (mass per unit volume of film) is not the same as that of the metal in bulk. The error introduced by the assumption of bulk density for the film will be negligible for films of the order of 500A, and greater, in thickness, but will become very large, possibly 100% or more, for very thin layers less than 100A thick. A typical experimental measurement using a microbalance gives values for the thickness accurate to 10 or 20A(14).

A second method for the determination of d, used by Rouard(38), and Krautkramer(13) for silver films, relies on the chemical transformation of the metallic layer into a transparent layer of iodate or sulphate. The thickness of this layer can then be determined by the use of a Jamin interferometer, or similar method. While the results of Rouard and Krautkramer are as self-consistent as those obtained by workers using other methods, this method is open to several obvious objections. The main disadvantage is that there is no means of telling whether the iodate layer is of the same thickness as the original metallic layer. If the latter has a discontinuous structure, it is almost certain to be modified during a chemical transformation, and even if it is continuous, the layer of the salt is not necessarily of the same thickness. Also the refractive index of the iodate or sulphate must be known.

The third method is the interferometric method developed by Wiener(61), and until recently neglected, except by Cau(64). The method is the one that has been used in the present investigation, and it will be described and critically discussed in detail.

After the film has been deposited, a thin strip is carefully removed, leaving a clear strip of glass across the substrate, bounded on each side by steps of height equal to the thickness of the film. Over the whole an opaque layer of the same metal as the film is deposited, and the upper surface of this layer, following the contours underneath, has two steps in it. This arrangement of films is shown in Figure 11 (a). An optical flat is then placed with its surface very close to this opaque layer and in the air-film, between the flat and the layer, interference fringes of equal thickness are observed when the interferometer is illuminated with monochromatic light. The

USE OF MULTIPLE-BEAM INTERFEROMETRY TO DETERMINE THICKNESS OF THIN METALLIC COATINGS

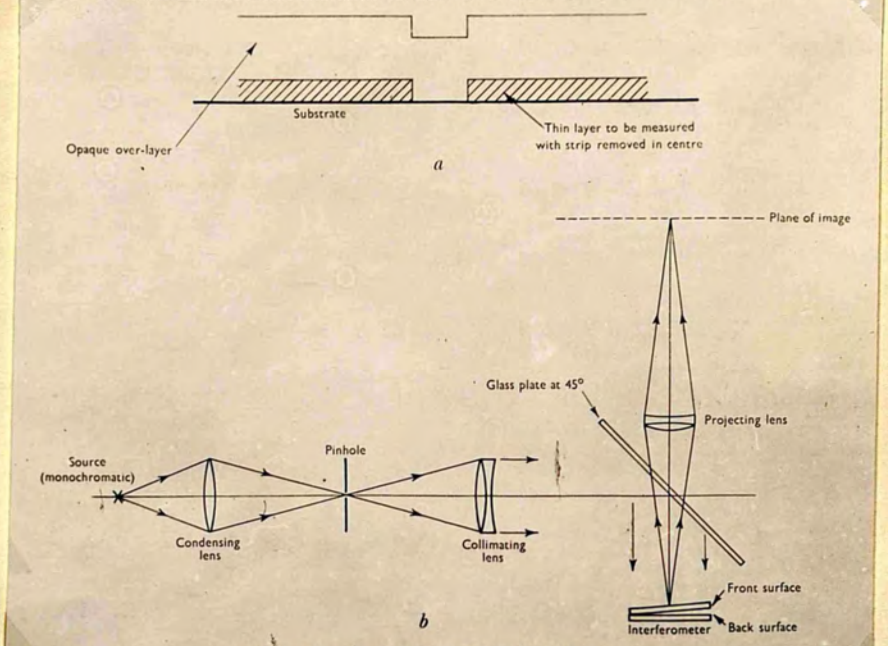

Fig. 11.—Measurement of the thickness of a thin film by Wiener.
(a) Arrangement of film during measurement.
(b) Optical arrangement.

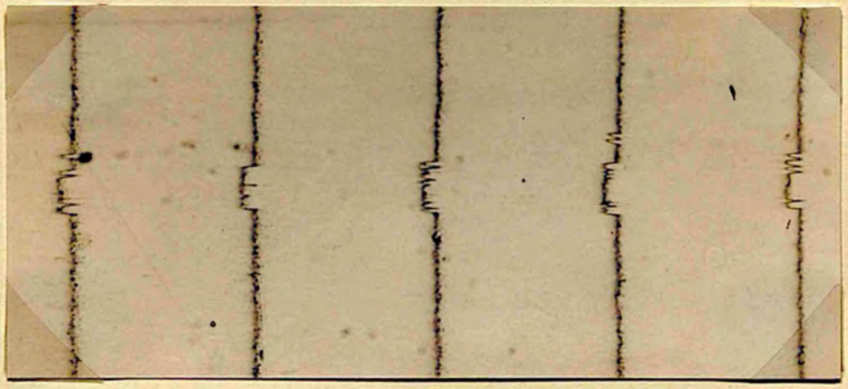

FIGURE 12

optical arrangement employed is shown in Figure 11 (b). The relative positions of the surfaces are adjusted so that the fringes run in straight lines perpendicular to the steps in the opaque layer, and from the displacement of the fringes as they pass over the step, the height of the step, and hence the thickness of the thin film can be measured.

It is of importance to appreciate fully the function of the opaque layer deposited over the thin film with its clear strip. If no opaque layer were present, the phase changes occurring when light is reflected at the thin film and the clear glass would be different, and the displacement of the fringes as they pass over the step would be due not only to the difference in gap of the interferometer caused by the removal of the thin film, but also to the difference in the phase changes on reflexion in the two cases. By depositing an opaque layer over the whole, the phase changes are made uniform throughout, and the displacement of the fringes is due solely to the steps in the opaque layer.

A very considerable advance upon the accuracy and usefulness of the technique as originally developed by Wiener has been made by applying the techniques of multiple beam interferometry developed by Tolansky and his co-workers(52).

Khamsavi and Donaldson(62), by coating the surface of the optical flat with a highly reflecting, slightly transparent silver layer, have used the greatly enhanced sharpness of multiple-beam fringes in conjunction with Wiener's method. The reflectivity of the layer on the interferometer front surface should be in the region of 80%, the exact values to give the best interference fringes have been discussed in a treatment of the reflexion interferometer by Holden(63). The optical arrangement employed is the same as that given in Figure 11 (b), but the conditions necessary for the best visibility and sharpness of the fringes are more stringent. The conditions for the optimum observation of multiple-beam interference fringes will be discussed in detail in Part III, Chap. III of this thesis, but briefly it may be said that the collimation of the incident parallel beam should be such as to give an angular spread in the beam of less than one or two degrees, and the numerical aperture of the lens used to project the fringes into an eyepiece or on to a photographic plate should be adequate. The effect of these factors on the sharpness and visibility of the fringes is greatly reduced if the separation of the interferometer surfaces is made as small as possible. The air gap in the interferometer should preferably be less than ·01 mm.

In Figure 12 a typical set of interference fringes taken to measure the thickness of a thin film using multiple beam methods is shown. The fringes are over a step in a silver film, the step being 176 ± 15 Å in height.

In the work quoted, Khamsavi and Donaldson also used white light fringes of equal chromatic order to measure the step height, in addition to monochromatic Fizean fringes of equal thickness. This procedure involves focussing a very small section of the interferometer on to the slit of a spectroscope , and thus has the disadvantage that local variations in the film's thickness may cause erroneous results. The use of monochromatic fringes of equal thickness involves taking measurements over at least one centimetre of the film step, so a desirable averaging effect is achieved. The average experimental error obtainable with a good interferometric technique is about ± 15 Å for films of the order of 200 Å in thickness and greater, and ± 10 Å for films of the order of 100 Å thick.

It would seem at first sight that the interferometric method is superior to the other two methods discussed, in that the value obtained for d would be a measure of the 'mean maximum' thickness of a layer having a granular structure, and that for continuous films d

is given directly, no knowledge of the density being required. Khamsavi and Donaldson used the colorimetric method of Schoonover to determine the mass per unit area in a number of silver films, the thickness of which had been measured by the interferometric method. They then calculated the density of the film and found that it appeared to be constant and equal to the value for bulk silver, 10·6, down to quite small thicknesses (122 Å).

In the light of the electron microscope and electron diffraction experiments previously mentioned, this result is strange, since films of this order of thickness have been shown to be granular, and hence could be expected to have a density differing from that of the bulk metal. Khamsavi and Donaldson themselves suggest, however, that this might be a necessary result of the method. They suggest that the result may be due to the fact that when the opaque layer is deposited over the thin one, the particles of the opaque layer first fill up the interstices between the particles of the thin film before building up on top of it. The effect of the particles packing together in this way would be that the step on the surface of the opaque layer would correspond to that which would be produced by a film having the same mass per unit area as the one actually present, but having the density of the opaque layer, i.e. of the bulk metal. If this is so, it seems that for films with a definite granular structure, the interferometric method can only safely be used for the determination of the mass per unit area in a film, rather than its metrical thickness.

If the hypothesis of Khamsavi and Donaldson is correct, then the interferometric method is only superior to the other methods in that it gives a direct value for the thickness of thin layers, but for thinner ones, it can only be used to determine the mass per unit area, as with a microbalance.

An experiment has been carried out, and will now be described, which tends to confirm this view. It was considered that if this 'packing-in effect' occurred, it would be to a different extent in the case where the superposed layer and the thin film were of different metals, from the usual case where they are of the same metal.

Accordingly a number of thin films of silver were prepared, most on glass substrates, but some on substrates of silver (previously prepared by evaporation to a thickness of 1000 Å or more). A strip was removed across the film in the usual way, and two opaque layers deposited, side by side, over this strip. One of the layers was of silver, and the other of a different metal. Two other metals were used, chromium, and speculum alloy. In all cases it was found that the apparent thickness of the film with an unlike superposed layer was greater than the apparent thickness with a silver layer superposed.

The actual results with chromium and speculum are given below in the table. B_1, is the apparent thickness with a silver overlayer, and B_2 the apparent thickness with an unlike overlayer

Substrate	B_1	B_2		$\ell = B_2 - B_1$	ℓ / B_1 x 100
Silver	247	312	Cr	65	26
Silver	470	569	Cr	99	21
Glass	202	279	Cr	77	38
Glass	377	504	Cr	127	34
Glass	198	239	Spec.	41	21
Glass	288	317	Spec.	29	10

Owing to the fairly low reflectivity of Chromium (50%), the accuracy of the measurements on the fringes with a chromium overlayer was fairly poor, ± 25 A, but with the speculum overlayer (reflexion coefficient = 64%), the experimental error was ± 15 A. Figure 13 shows the fringes used in one of the experiments with a speculum overlayer.

The magnitude of the effect observed is not sufficiently greater than the experimental error for any quantitative conclusions to be drawn, but it is significant that in all cases the apparent thickness with unlike overlayers was greater than with an overlayer of the same metal.

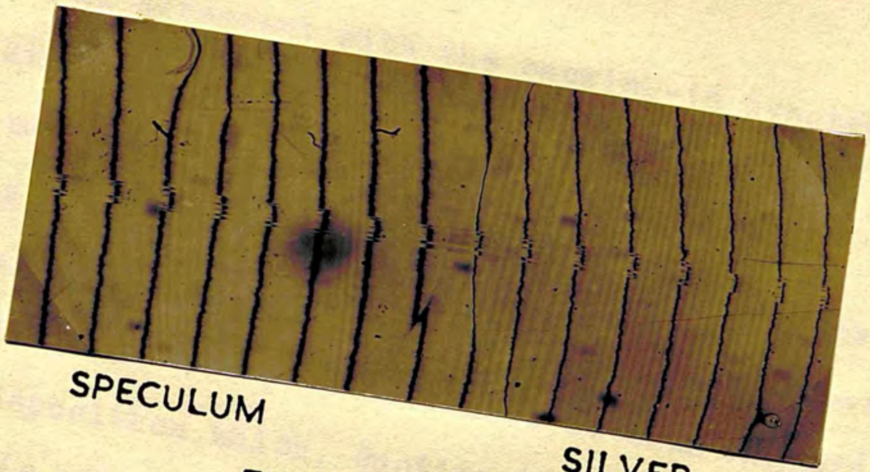

FIGURE 13

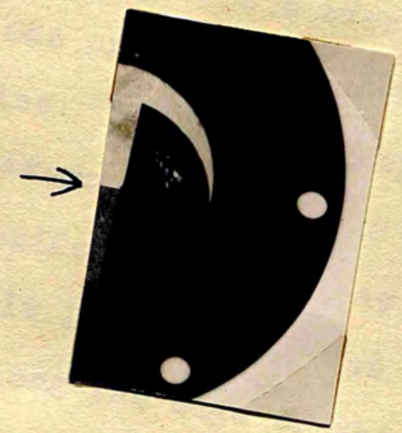

FIGURE 14

This is in general agreement with the packing-in hypothesis, since the packing could be expected to be most complete when the same metals were used.

It is not suggested that this experiment represents a complete investigation into the problem. No account has been taken of the possibility of extensive lateral migration of atoms after deposition which, quoting Picard and Duffendack(41), is not greater than 500 Å in the case of the higher melting point metals, but in the case of low melting point metals and alloys may be quite considerable. An interesting phenomenon was observed during some preliminary experiments on this question which is an indication of the aspects of the process of forming layers over one another, which remain unresolved. One of the metals first tried for the second overlayer was zinc. When it was deposited over the edge of a silver film, in several cases it was observed that the zinc deposit was quite uniform where it lay on top of the thin silver film, where it lay on the glass it was patchy in appearance, but exactly along the edge of the thin silver film there was no zinc at all. Figure 14 is a photograph made by simply exposing a piece of photographic paper through the combination of films, and the line of uncovered glass at the edge of the silver film can be clearly seen. A similar phenomenon has been observed by Heavens* when

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* O. S. Heavens, Univ. of Reading. Private Communication.

chromium was deposited over the edge of a silver film, but the writer never observed this.

In addition to this phenomenon, the results of the experiment quoted show that the percentage difference between the two apparent thicknesses is of the order of 30% for layers 500A thick. This is very difficult to explain purely on a packing theory, since these layers are generally assumed to be continuous.

To conclude, the interferometric method for determining the thickness of metallic layers is SLIGHTLY superior in accuracy to other methods, and may safely be used to give direct measurements of the thickness of layers which can be assumed to have a continuous structure. In the case of measurements on thin films, however, the work of Khamsavi and Donaldson and the results quoted here combine to suggest that the method can only be used without reserve for the determination of mass per unit area, rather than thickness, and in this respect is no advance over the direct weighing method. It is a debatable question however, in the light of the knowledge of the structure of these thin layers, whether the term 'thickness' can be applied to them at all, since they probably consist of a collection of small crystallites of varying sizes. It seems that the mass per unit area contained in such a film is a quantity having much more physical meaning than a 'thickness' defined in a rather arbitrary manner, such as the 'mean maximum' thickness of the granules.

PART III

THE OPTICAL TECHNIQUES

PART III

THE MEASUREMENT OF INTENSITY COEFFICIENTS AND ELLIPTICITY

Chapter I.

In the work discussed on the measurement of the normal incidence reflexion and transmission coefficients of metallic layers, the methods used for the measurement of these coefficients can be grouped roughly into three classes. The intensity reflected or transmitted by the layer can be compared with some standard intensity (such as reflexion from a glass surface) by the use of a suitably calibrated photographic plate, as was done by Rouard(33). In a second method, the intensity to be measured can be compared with a standard intensity in a form of half-shade device, as in the absorbing wedge photometer used by Cau(64), or the method of Fabry and Buisson, used also by Rouard. Finally, following Perrot(14), Strong and Dibble(39) and Krautkramer(13), the reflected or transmitted intensity can be directly compared with the incident intensity using a photoelectric cell.

In deciding upon a method to be used in the present work, in addition to considerations of accuracy, it was important to choose a method which was capable of easy extension to the measurement of the coefficients at all angles of incidence. This ruled out the method of Fabry and Buisson, and an absorbing wedge photometer to work at any angle of incidence would involve very complicated optical paths. The choice then lay between the use of a photographic plate as a recorder of intensities, and the use of a photoelectric cell. Of the two the latter is greatly to be preferred, since the use of a photographic plate involves the careful provision of density marks, etc., for each plate, and the subsequent use of a microphotometer, whereas the photoelectric method enables an intensity coefficient to be obtained directly from the ratio of two galvanometer readings. The photoelectric method was therefore adopted.

The experimental arrangement is quite simple. The glass substrates on to which the layers are deposited are permanently attached to brass rings. With the aid of these rings, the substrate can be mounted in a vertical plane on a turntable which enables it to receive light at any angle of incidence, the angle being measured by a graduated circle on the turntable reading to one tenth of a degree. Mounted to pivot about the same axis as the film is an arm carrying a photoelectric cell in a housing, which can be turned to receive either the light reflected from or the light transmitted through the film. A diagram of this instrument, together with its associated optical system is shown in Figure 15.

As source a 12 volt. 48 watt tungsten filament lamp is used, mounted so that the filament is vertical. The light from this is condensed on to a pinhole and a magnified image of this pinhole is focussed on to a shutter placed in the front of the photoelectric cell housing. The mounting for the substrate is such that the axis of rotation of the arm carrying the photocell is contained in the plane of the front of the substrate, and so the image of the pinhole on the shutter is in focus both for direct light, and when the beam is reflected at any angle of incidence. The magnification employed is such that the cone of light forming the image has a semi-angle of less than half a degree, so that any effect that non-parallelism of the beam may have on the correct measurement of the incidence angle can be neglected to this approximation.

The use of a focussed image, instead of a parallel beam is necessary since, when a parallel beam is used its cross-sectional area will vary with incidence angle after reflexion, and this means that the light in concentrated on to less of the available photosensitive cathode area, which may lead to incorrect results. With an image of the pinhole focussed at or near the cathode, the light passing through the pinhole forms an image of the same size, irrespective of incidence angle. The image is not actually focussed on the cathode, but, as stated, on to a shutter some 3 cms. in front of it. This means that the cathode is illuminated with a diffuse image, and a larger area of the cathode used than would otherwise be the case.

The photoelectric cell used is an RCA 931A electron multiplier phototube, having a blue sensitive cathode with maximum sensitivity at a wavelength of approximately 4000 A .

The particular wavelength desired is selected by the use of 'Wratten' filters. The filters used are Nos. 47, 62, and 27, giving mean wavelengths of 4,500, 5,400, and 6,100 A respectively, and a combination of Nos. 22 and 58, giving a mean wavelength of 5,700 A. The wavebands transmitted by these filters extend to approximately 150 A on either side of the mean, and since the variation of the sensitivity of the photocathode with wavelength is not accurately known, it is possible that values of the coefficients obtained using these filters, correspond to wavelengths slightly shorter than the mean values quoted above.

The errors in values for the reflexion and transmission coefficients of the films measured with this system can be discussed under two headings.

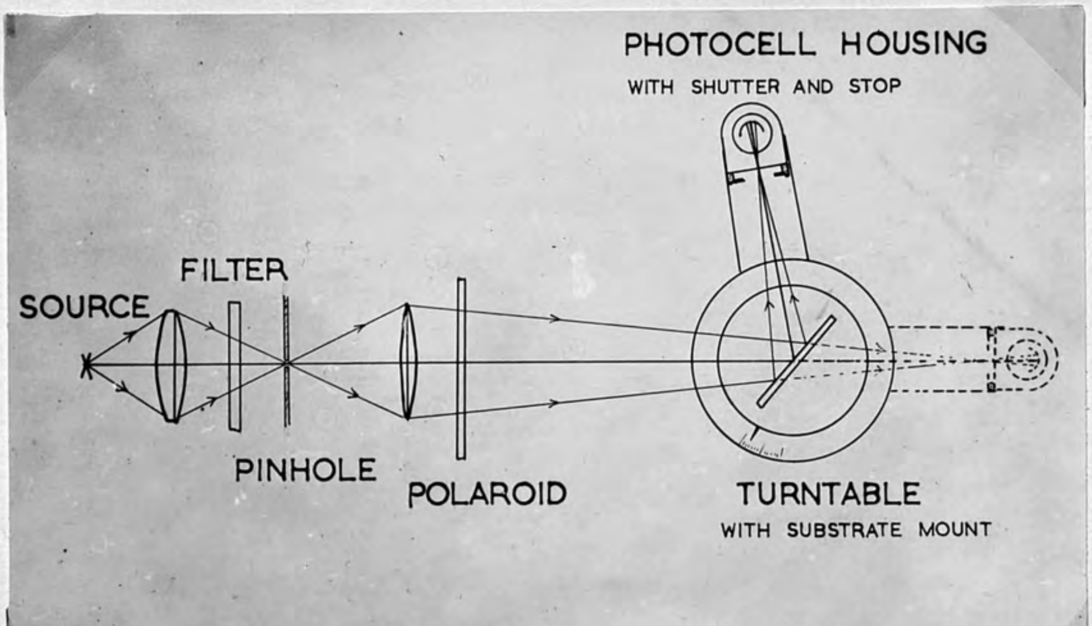

FIGURE 15. PHOTOMETER

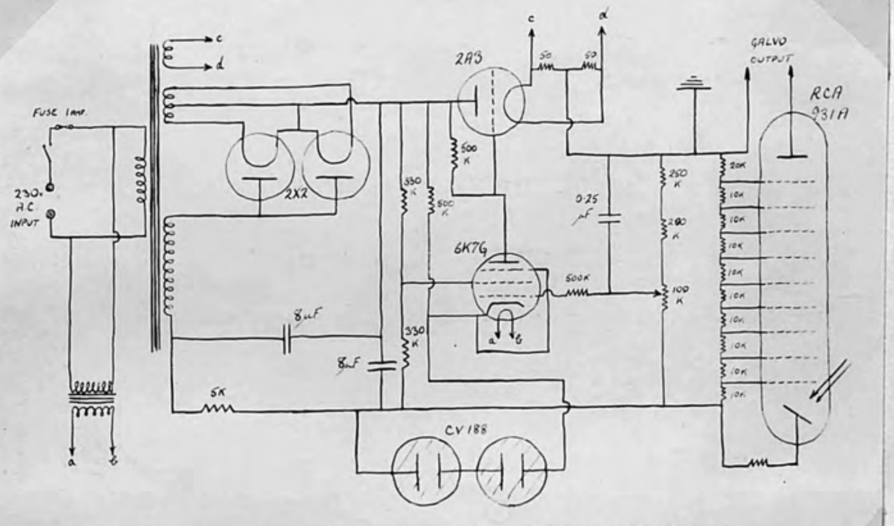

FIGURE 16. PHOTOCELL SUPPLY CIRCUIT.

The first class of errors arise from any lack of stabilisation of the incident light intensity, and of the potentials supplied to the electron multiplier. The tungsten filament lamp is supplied by a transformer, the primary of which is fed from the output of a constant voltage transformer, giving a voltage constant to one per cent. The potentials on the various electrodes of the electron multiplier are supplied by an electronic control unit comprising a rectifier and stabilising unit. This circuit is shown in Figure 16 and follows standard design for high voltage power units, except that, as is standard practice with electron multiplier tubes, the positive side of the system is at earth potential. The potentials are taken from points along a 'bleeder' chain, taking 10 milliamps with 1200 volts across it, and the final photocurrent is measured on a microammeter, provided with some necessary shunt resisters. The system was normally arranged so that the incident beam provided a current from the final collector of about 0·8 milliamps (maximum permissible 1·0 milliamps). When the source and the stabiliser circuit had reached thermal equilibrium, which took about 45 minutes, it was found that the reading of the microammeter was steady to much less than ± 1% over periods of several minutes, and only varied by ± 1% in periods of twenty minutes or more.

The second source of errors lies in the variation of photosensitivity over the surface of the photocell cathode. This means that if the beam does not fall on exactly the same area of the cathode each time, an apparent variation of intensity is recorded. When the instrument had been in use for some time, it was found that the substrates did not always set exactly in a vertical plane on being placed in the holder, on the turntable, and it was feared that this might be the cause of considerable errors. An analysis of the variation of photosensitivity with position on the cathode surface of a 931A tube has been made by Kessler and Wolfe(65), who found that the variation of sensitivity with movement of the beam in a vertical direction was quite large. To overcome the errors introduced from this source, an adjustable stop was fitted on to the photocell housing immediately behind the shutter. This stop was adjusted so that when the incident beam fell directly on to the photocell, it just passed through the stop. Any deviation of the beam from the horizontal plane after reflexion at the film on the turntable could then immediately be detected by the appearance of part of the image at the edge of this stop.

However, even with this precaution taken, it is likely that most of the experimental error in the results comes from the second cause. As a rule, three measurements of incident and reflected or transmitted intensity, in turn, were made for the determination of any coefficient. The results of a large number of such determinations show that the values of the coefficients measured in this way, are accurate to .01, i.e. to one per cent of the value of the incident intensity (1·00). The coefficients are thus accurate to one per cent of their own value for values greater than 0·6, the accuracy decreasing to five per cent for values of about 0·2.

The coefficients thus measured are not the true reflexion or transmission coefficients for the layer, but are the coefficients of the reflecting system formed by the layer and substrate combined. A correction must be made for the beam, which after transmission through the layer is reflected at the rear surface of the substrate. Some measurements on reflexion and transmission by uncoated substrates showed that to the accuracy of this experiment these factors could safely be calculated assuming the value for reflexion at the glass-air interface given by the simple Fresnel relationships. The correction factors vary with the angle of incidence and are, of course, different for the two planes of polarisation.

If the reflexion coefficient of the rear surface of the substrate is r_g, the observed transmission of the layer, T', is related to the true transmission, T, by

$$T = T'/(1-r_g)$$

The true reflexion coefficient, R , can be obtained from the observed coefficient, R' , by the relation

$$R = R' - r_g . T^2$$

From these relations it can be seen that whilst the correction must always be applied to measurements of the transmission coefficient, the correction to the observed reflexion coefficient only becomes of the order of the experimental error when the value of $r_g . T^2$ approaches or exceeds 0·01.

The ellipticity of the light reflected from a film at any angle of incidence is defined by the ratio of the amplitudes of the components of the vibration in the two planes of polarisation. This ratio is clearly equal to the square root of the ratio of the reflexion coefficients for the two planes of polarisation at that angle of incidence. To determine the ellipticity with this system, the incident beam is polarised, using a piece of 'Polaroid', and the reflexion coefficients determined, for each angle of incidence, for the cases when the incident beam is polarised parallel and perpendicularly to the plane of incidence. The accuracy with which the ellipticity can be determined is equal to half the sum of the errors in the measurements of the two reflexion coefficients R_p and R_s , i.e. to ± 0·01.

Values of the ellipticity with experimental errors of this order are obviously inferior to values obtained with the usual polarimetric technique, described in Part I, Chap. III, where Tool(22) is quoted as claiming to measure an ellipticity of 0·02 to one per cent. But as was pointed out in that chapter, this order of accuracy is not required for the determination of optical constants, since there are other factors introducing far greater errors, and values of ellipticity accurate to ± ·01 are probably adequate for the determination of the constants in all but investigations where the highest accuracy is essential. The method has the advantage that it is quite simple and requires little expensive equipment and, in addition, values of the reflexion coefficients themselves are obtained, which is not the case with the polarimetric method.

THE INTERFEROMETRIC METHOD FOR DETERMINING RELATIVE PHASE CHANGES

THEORY

Chapter II.

In a paper published in 1944, Tolansky$^{(66)}$ described the appearance of the multiple beam interference fringes formed between a highly silvered lens and a plate, when the angle of incidence of monochromatic light on to the interferometer varied from zero to 80°. At normal incidence the fringes were rings, similar to Newton's rings, but of course very much finer since they were formed in an interferometer with highly silvered surfaces. As the angle of incidence increased, the fringes became double, the separation of the doublet increasing continuously as the incidence angle increased. The components of the doublets were shown to be polarised in mutually perpendicular directions, and the origin of the doubling was shown to be the effective difference in gap of the interferometer for the two components, due to the difference between the phase changes suffered on reflexion by the components polarised parallel and perpendicularly to the plane of incidence. It was immediately apparent that this was possibly a powerful method for the measurement of the relative phase change on reflexion, the quantity Δ of Part I of this thesis, and some measurements were made by Tolansky of the relative phase changes on reflexion at the silver films of the interferometer.

No further use was made at that time of this phenomenon for the measurement of the relative phase change Δ . In the present investigation the method has been studied in greater detail, to a small extent simplified, and used to measure the values of Δ for the metals studied. The original work by Tolansky was part of a series of investigations developing the technique of multiple beam interferometry, and since the work in this field has recently been summarised(52) it is not intended to give any detailed treatment of the theoretical basis of multiple beam interferometry, such as a treatment of the properties of the Airy summation, etc. The account which follows will be restricted to a description and critical discussion of the application of the established techniques of multiple beam interferometry to the relative phase changes on reflexion at metallic films.

In Tolansky's original experiments, the Newton's rings were fringes of equal thickness, formed with monochromatic light, and at normal incidence were localised in or very near to the air gap of the interferometer. At non-normal incidence, however, the fringes were no longer localised in the gap, but on a curved surface in space near the interferometer. This surface was not perpendicular to the optical axis of the system, and in consequence only a very small section of the fringe system could be projected on to a photographic plate or into an eyepiece. This represented an immediate serious disadvantage when it was desired to measure the separation between the components of the doubled fringes, and in order to overcome this difficulty, the lens and plate combination was discarded in favour of a simple wedge interferometer. It can be shown(67, 52) that if the apex of an interferometer of two plane surfaces forming a wedge is parallel to the axis of rotation of the interferometer, and if both are perpendicular to the direction of the incident light, then the fringes formed in the system are always localised in a plane perpendicular to the direction of the incident light. At normal incidence this plane is contained in the air gap of the interferometer, and as the incidence angle increases, the plane moves away from the interferometer. With this arrangement, the whole field of the interferometer can be brought into focus at one time. The question of the precise position of the plane of localisation will be dealt with in greater detail later.

Considering the case of a wedge interferometer as described, it is necessary to develop equations relating the separation of the components of the doubled fringes to the relative phase change on reflexion, Δ, in order to use the doubling to measure that quantity.

Consider the general equation to the locus of points forming an interference fringe in any interferometer[*]. They are points such that

$$n\lambda = 2\mu t\cos\theta + 2\Phi(\theta, \lambda, \omega) \qquad 2.1$$

Here λ, μ, and θ have their usual significance, n is an integer, and ω represents the azimuth of the plane of polarisation of the incident light.

The interferometer is assumed to have identical reflecting surfaces, and the phase change on reflexion at either of these surfaces is represented by the function Φ, a function of θ, λ, and ω. We shall write Φ_p for Φ when $\omega = 0°$, and Φ_s when $\omega = 90°$.

Let us first consider the fringes of eual thickness formed in a wedge interferometer with an air-gap ($\mu = 1$), and at an angle of incidence θ, when the wavelength of the incident monochromatic light is λ.

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[*] I am greatly indebted to Mr. N. Barakat, of this department of Royal Holloway College, for much helpful discussion and advice in connection with the theory of interference fringes.

Since the fringes are formed at different points in the wedge, the value of t will be different from one fringe to another.

For two adjacent doublets we can write the equations

$$\left.\begin{aligned} n\lambda &= 2t_p.\cos\theta + 2\Phi_p(\theta,\lambda) \\ n\lambda &= 2t_s.\cos\theta + 2\Phi_s(\theta,\lambda) \end{aligned}\right\} \qquad 2{\cdot}2/$$

$$\left.\begin{aligned} (n+1)\lambda &= 2t'_p.\cos\theta + 2\Phi_p(\theta,\lambda) \\ (n+1)\lambda &= 2t'_s.\cos\theta + 2\Phi_s(\theta,\lambda) \end{aligned}\right\} \qquad 2{\cdot}3/$$

From the two equations of 2·2 we get immediately

$$\Phi_p(\theta,\lambda) - \Phi_s(\theta,\lambda) = (t_s - t_p)\cos\theta$$

But the left hand side of this equation is the relative phase change, Δ, and we have

$$\Delta(\theta,\lambda) = (t_s - t_p)\cos\theta \qquad 2{\cdot}4/$$

From the parallel components of each doublet, the first members of 2·2 and 2·3 we have

$$\lambda = 2(t'_p - t_p)\cos\theta$$

and so 2·4 becomes

$$\Delta(\theta,\lambda) = \frac{\lambda}{2}\cdot\frac{t_s - t_p}{t'_p - t_p}$$

If now the fringes occur at distances x_s, x_p, x'_s, x'_p, etc., along the wedge, these distances can be measured, and the quantity Δ can be measured from the equation

$$\Delta(\theta,\lambda) = \frac{\lambda}{2}\cdot\frac{x_s - x_p}{x'_p - x_p} \qquad 2{\cdot}5/$$

An equation from which Δ may be found can also be derived in the case of fringes of equal chromatic order. These fringes are formed when the interferometer is illuminated with white light, and a small section of the interferometer is focussed on to the slit of a spectrograph. The section is small enough for the value of t to be assumed constant over the section, if the wedge apex is parallel to the spectrograph slit. In the focal plane of the spectrograph fringes appear which are the locus of points having the same value of t/λ, in the present case they are straight lines perpendicular to the wavelength axis.

Let the wavelengths of the components of two adjacent doublets be λ_p, λ_s, λ'_p, λ'_s. Then we can write the equation for the doublets as

$$\left.\begin{aligned} n\lambda_p &= 2t\cos\theta + 2\Phi_p(\theta,\lambda) \\ n\lambda_s &= 2t\cos\theta + 2\Phi_s(\theta,\lambda) \end{aligned}\right\} \qquad 2.6$$

$$\left.\begin{aligned} (n+1)\lambda'_p &= 2t\cos\theta + 2\Phi_p(\theta,\lambda') \\ (n+1)\lambda'_s &= 2t\cos\theta + 2\Phi_s(\theta,\lambda') \end{aligned}\right\} \qquad 2.7$$

where

$$\lambda = \tfrac{1}{2}(\lambda_p + \lambda_s), \quad \lambda' = \tfrac{1}{2}(\lambda'_p + \lambda'_s)$$

It is seen that these equations are only valid when the separation of the doublet is small, and we are assuming that the variation of Δ with λ is small. This assumption is generally justified.

Then from the two components of 2·6 we can get

$$\Phi_p(\theta,\lambda) - \Phi_s(\theta,\lambda) = \Delta(\theta,\lambda) = \frac{n}{2}(\lambda_p - \lambda_s) \tag{2·8}$$

We can find Δ from measurements on λ_p and λ_s, if n is known. Now from the parallel components of each doublet, from 2·6 and 2·7, we can write

$$n\lambda_p - (n+1)\lambda'_p = 2\Phi_p(\theta,\lambda) - 2\Phi_p(\theta,\lambda') \tag{2·9}$$

In this case, since we are dealing with two fringes, and not two components of the same fringe, we cannot assume $\lambda = \lambda'$, and we see that n, and hence Δ, cannot be determined from measurements on fringes of equal chromatic order unless the form of the function Φ is known. No measurements have been reported of the variation of the quantity Φ with incidence angle and so fringes of equal chromatic order cannot be directly used for the determination of Δ.

It is possible however to make an assumption about the form of Φ and, by this, make use of fringes of equal chromatic order in this connection. Let us assume that $2\Phi_p(\theta,\lambda) = \beta\lambda$, and $2\Phi_p(\theta,\lambda') = \beta\lambda'$ Then as we have already assumed $\lambda_p \simeq \frac{\lambda_p+\lambda_s}{2} = \lambda$ we have from 2·9

$$n - \beta = \lambda' / \lambda - \lambda' \tag{2·10}$$

Now n, the order of the fringe, is integral, and so if the quantity $n - \beta$ for each fringe is determined from measurements on the wavelengths λ' and λ, in the general case $n-\beta$ is not integral. Suppose for example that for a number of fringes $n-\beta$ had the values 5·3, 6·2, 7·4, 8·4, 9·3.... In the absence of any knowledge of the form of the function Φ, and hence of the sign of β, we cannot tell whether β is negative, and n has values 5, 6, 7, 8, 9... or whether β is positive, and n has values 6, 7, 8, 9, 10....., assuming β is less than one.

However from measurements on Fizean fringes of equal thickness we can find Δ for a particular wavelength by the formula 2·5 . If then we choose n for a fringe of that wavelength to give a value of Δ equal to that given by the Fizean fringes, we can assign the correct values of n to the other fringes, and hence make use of fringes of equal chromatic order to measure the variation of Δ with wavelength.

The combination of Fizean fringes and fringes of equal chromatic order in this way could also be used to determine the nature of β . If it is found that to get the correct value of Δ from the measurements, β must be negative, then the original equation can be written

$$n\lambda = 2t\cos\theta - |\beta|.\lambda$$

This sign for β corresponds to a phase advance on reflexion. If on the other hand it is found that β must be positive, then

$n\lambda = 2t\cos\theta + |\beta|.\lambda$, corresponding to a phase retardation on reflexion. Little more than the sign of β could be determined in this way since the error in measuring the quantity $n-\beta$ is very large, since it involves the errors in measuring the fairly small wavelength shift $\lambda-\lambda'$. For fringes of order fifteen, this shift is only one or two hundred Angstrom Units, and with the average wavelength scale measurements can rarely be made to better than ±10A.

In the treatment of fringes of equal chromatic order we assumed that the difference $\lambda_p-\lambda_s$ was small enough for them each to be put equal to their mean. The error introduced by this assumption is obviously least when $\lambda_p-\lambda_s$ is least, i.e. when the wavelength separation of the fringes is small, and the order number n , large. In this case also, if n is of the order of 30 or 40, the error introduced by neglecting β altogether and taking n equal to the nearest integer to the value found for $n-\beta$, is only one part in 60 or 80. However, as will become apparent when the experimental technique is discussed in the next chapter, an upper limit on the value of n is placed by the necessity for having sharp fringes of good visibility.

From the equations developed in this chapter, the relative phase change $\Delta(\theta, \lambda)$ is expressed in terms of either the positions in the plane of localisation of the fringes of equal thickness, or the wavelengths of fringes of equal chromatic order. The experimental technique used to observe these fringes, and to make the necessary measurements to obtain Δ , together with a critical discussion of the technique, will form the subject of the next chapter.

THE INTERFEROMETRIC METHOD FOR DETERMINING RELATIVE PHASE CHANGES

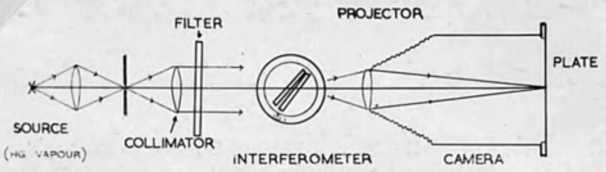
PRACTICE

Chapter III.

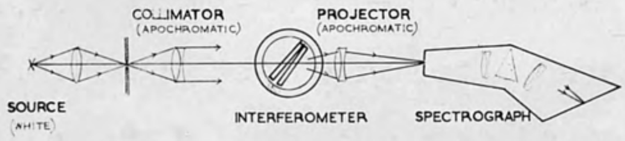
In the previous chapter equations were developed relating the doubling of an interference fringe, as the angle of incidence on the interferometer increased, to the relative phase change occurring between the two perpendicularly polarised components on reflexion at the surfaces of the interferometer. A simple wedge interferometer was considered, and the relations developed between the relative phase change and the linear separation of the doublet in Fizean fringes of equal thickness, and the wavelength separation of the doublet in white light fringes of equal chromatic order. In this chapter the experimental arrangement will be described, and the experimental conditions necessary for the best use of the interferometric technique discussed. The sources of errors arising in the measurement of relative phase changes by this method will be mentioned, and the limitations of the method considered.

The doubling of the interference fringes is nearly always observed by viewing the interferometer in transmission. The experimental arrangement for the Fizean fringe system is very simple, and the system for fringes of equal chromatic order scarcely less so. For Fizean fringes a high pressure mercury arc source is used (Figure 17 (a)), and the monochromatic radiation required selected by the appropriate 'Wratten' filters. Almost all the measurements have been made using the green line of wavelength 5461 . The light from this source is condensed on to a pinhole, and a collimating lens of 15 cms. focal length forms a parallel beam. This beam falls on to the interferometer, and the interference fringes, which are localised at or near the interferometer, are projected by a 5 cm. focal length lens on to a photographic plate. The lens and the plate-holder are incorporated in a simple camera which enables several exposures to be taken on one plate.

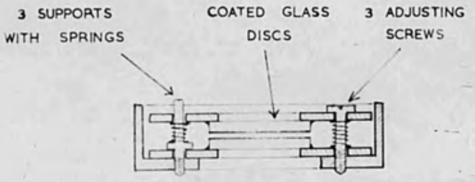
For observing fringes of equal chromatic order (Figure 17 (b)) the mercury arc source must be replaced by a white light source, here a 150 candle-power "Point-o-Lite" lamp was used. The parallel beam is formed in the same manner as for Fizean fringes, the only difference being that in this case it is essential that the lenses employed are achromatic for the wavelength range used. The interference fringes localised in the same position as the Fizean fringes are projected on to the slit of a spectrograph by a high quality achromatic lens. The image of the fringes then appears in the focal plane of the



A. FIZEAU FRINGES



B. FRINGES OF EQUAL CHROMATIC ORDER



C. INTERFEROMETER DETAIL

FIGURE 17

spectrograph. In these experiments two spectrographs were used, a Hilger medium-quartz instrument, in which the wavelengths of the fringes were determined using the wavelength scale provided, and a Hilger constant deviation instrument, fitted with a calibrated wavelength drum.

The interferometer itself was formed between two of the glass discs which had previously been coated with the film under examination. Figure 17 (c) shows the detail of the arrangement whereby they could be brought close to one another, so that their distance apart and the wedge angle between them could be varied at will. The interferometer unit as a whole could be mounted on the same turntable as was used for the intensity measurements (Chap. I of this part), and so the angle of incidence could be measured.

The visibility and the sharpness of multiple beam fringes are dependent upon a number of factors, primarily of course upon the reflexion coefficients of the two surfaces of the interferometer, but also upon the separation of the interferometer surfaces, the wedge angle between them, the parallelism of the incident beam, and, in the case of Fizean fringes, the monochromatism of the source. Since in this investigation we are concerned with the properties of the films forming the interferometer surfaces, their reflexion coefficients cannot be varied to give the best possible fringes, and so the other conditions must be fulfilled stringently to get the best results and they will be discussed in some detail.

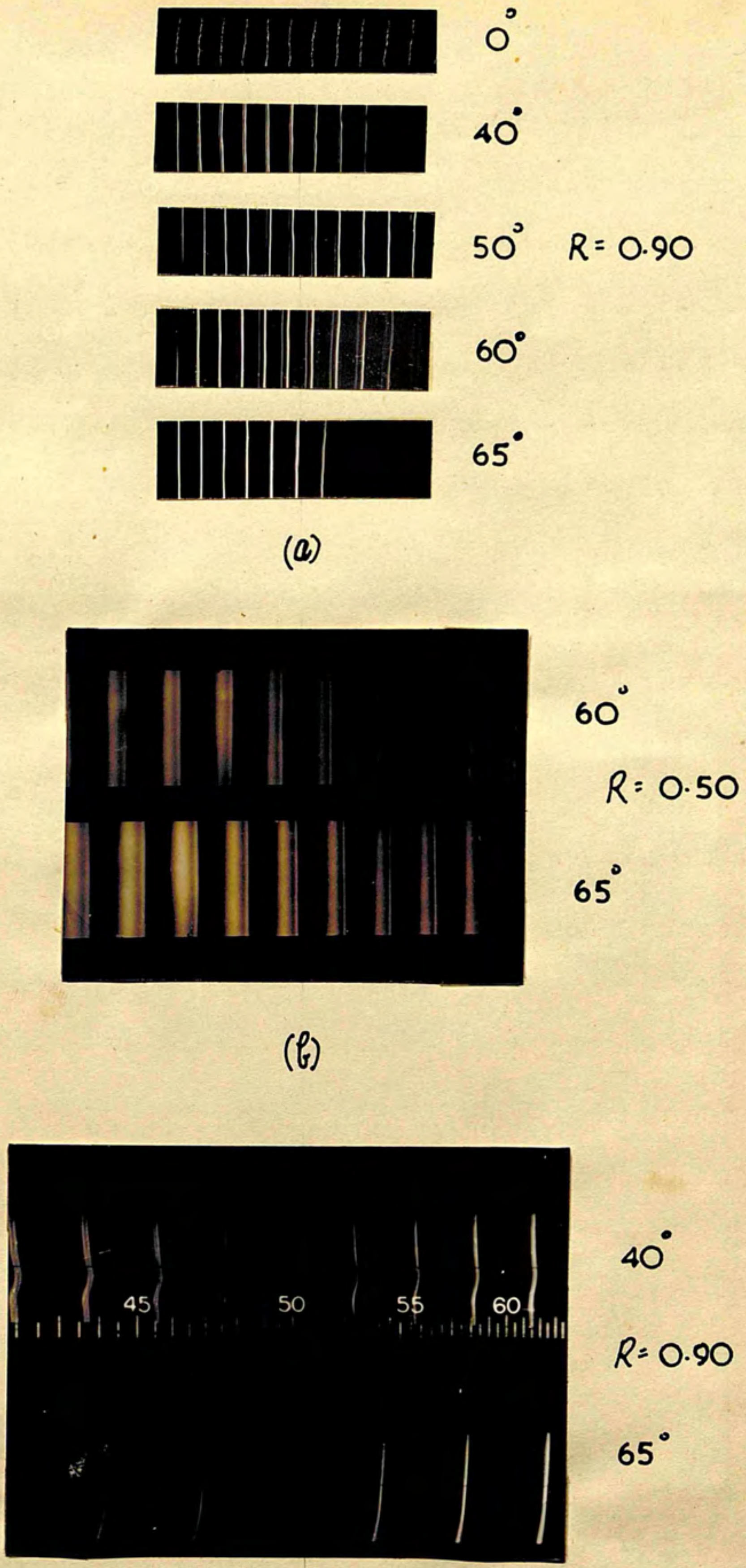
The ideal intensity distribution in a fringe formed by an infinite number of beams can be obtained by the use of the Airy summation (e.g.(10, 52)). In this summation it is assumed that the number of beams combining to form a fringe is infinite, and the fringe distribution observed in practice differs from the ideal by an amount depending on the actual number of beams which combine to form a given fringe. If the surfaces of the interferometer were perfectly plane and parallel to one another, the fringe intensity distribution would be the ideal one given by the Airy summation, the path difference between each pair of beams being $2t\cos\theta$ if the medium between the surfaces is air. If, however, the interferometer is a wedge, the phase difference between each pair of beams is slightly different from the ideal, and it can be shown(52) that for normal incidence to a rough approximation, the path difference between the 1st beam and the n^{th} is $2nt - \frac{4}{3}n^3\varepsilon^2 t$, where t is the separation of the surfaces at the position of the 1st beam, and ε is the wedge angle of the interferometer. Thus the beams of higher order tend to oppose the Airy summation, until, if

$\frac{4}{3}n^3\varepsilon^2t = \lambda/2$, this beam is directly opposed in phase to the 1st beam. The effect of this departure from the ideal condition is to broaden the fringes, and it is obvious that the sharpest fringes will be obtained when t and ε are as small as possible. The value of t , if the interference fringes are 1mm. apart, a customary value, should be of the order of ·01 mm. or less. An exact treatment of the deviation of the practical wedge interferometer from the ideal case is given by Brossel(68).

Another assumption in the theoretical treatment of an interferometer is that the incident beam is perfectly parallel. In practice of course this is never the case. The broadening of the fringes caused by lack of perfect collimation has been described by Fabry(69), and it can easily be shown that the broadening caused by a given variation in the incidence angle is least when the interferometer separation is small. When t is of the order of ·01 mm., a tolerance of $\pm 1^\circ$ in the collimation of the incident beam will not increase the fringe width by more than 1/200th of the separation between one fringe and the next. Similarly the theoretical treatment assumes the incident light to be perfectly monochromatic. The finite line width of the source used in practice will cause a broadening of the interference fringes by an amount which again is directly propertical to the separation of the interferometer surfaces, and which is therefore small when t is small.

If at normal incidence, the interferometer gap is ·01 mm., when the wedge angle is such that there is one fringe per millimetre along the interferometer surface, the fringe width will not exceed the theoretical width by more than $1/200^{th}$ of the order separation of the fringes, all the effects which cause fringe broadening being reduced for small values of t . At non-normal incidence however, another effect arises which cannot be removed. The beams which combine to form a fringe at normal incidence come from a very small region of an interferometer, for the values of t and ε given, the sixtieth beam comes from a point only ·025 mms. away from the first beam. However when the incidence angle is increased, obviously the linear displacement of the interfering beams is greatly increased, at 60° the sixtieth beam comes from a point 2 mm. away from the first beam. This means that where at normal incidence, a very sharp fringe will follow the smallest contours of the surface, e.g. polish marks on an optical flat, at non-normal incidence local structure is masked, and the fringes are broadened since the phases of the interfering beams no longer obey the strict theoretical law.

In Figure 18 some photographs of the fringe doubling using fringes of equal thickness and fringes of



(a)

(b)

(c)

FIGURE 18.

equal chromatic order are shown, the normal incidence reflexion coefficients of the interferometer surfaces being shown in each case. The increased doubling of the fringes as the angle of incidence increases from zero to the maximum obtainable with the turntable used, 70°, is clearly shown. In the Fizean fringes taken with a reflexion coefficient of 0·90, the loss of the surface detail apparent at normal incidence with consequent increase of fringe width as the incidence angle changes from 0° to 45° can be seen.

Two striking features of these fringes are immediately apparent. First the great difference in fringe width for the two components, at high angles of incidence, and second the reduction in the maximum intensity of the sharper fringes as the incidence angle increases. Figure 19 is a microphotometer trace of the fringes shown in Figure 18, for a reflexion coefficient at normal incidence of 0·50, in which the relative sharpness of the two components is clearly shown. It should be noted that the vertical axis in this trace is one of plate blackening, not of intensity, and so the relative intensities of the fringes cannot be compared by the trace. The difference in sharpness of the fringes is the result of the variation of the reflexion coefficient of the metallic layers with incidence angle for the two components. The reflexion coefficient for the component polarised parallel to the plane of incidence falls to a minimum value somewhere in the region of 55° to 75°, the minimum value and the angle at which it occurs varying with the metal, and with the thickness of the layer. The reflexion coefficient for the perpendicularly polarised component rises steadily with increasing angle of incidence. Thus the fringes for the parallel component are broader at high angles of incidence, whilst those for the perpendicular component are finer, than at normal incidence.

The reason for the difference in the maximum intensity of the two fringes is less obvious. It was suggested by Tolansky(66) that the metallic layers of silver used in his experiment exhibited a differential absorption, absorbing the perpendicularly polarised component more strongly than the parallel component. However measurements made with the photometer, described in Chapter I of this Part, on the transmission and reflexion properties of fairly thick silver layers show that this is not the case, and also enable the difference in intensities to be explained. Figure 20 shows the variation of the reflexion coefficient R, and the transmission coefficient, T, with the angle of incidence, as measured for the two components. The absorptions, $A = 1-(R+T)$ are also plotted. Now the maximum intensity of an interference fringe is given by $1/(1+A/T)^2$ and it is seen from Figure 20 that as the incidence increases, the absorptions for the two components remain

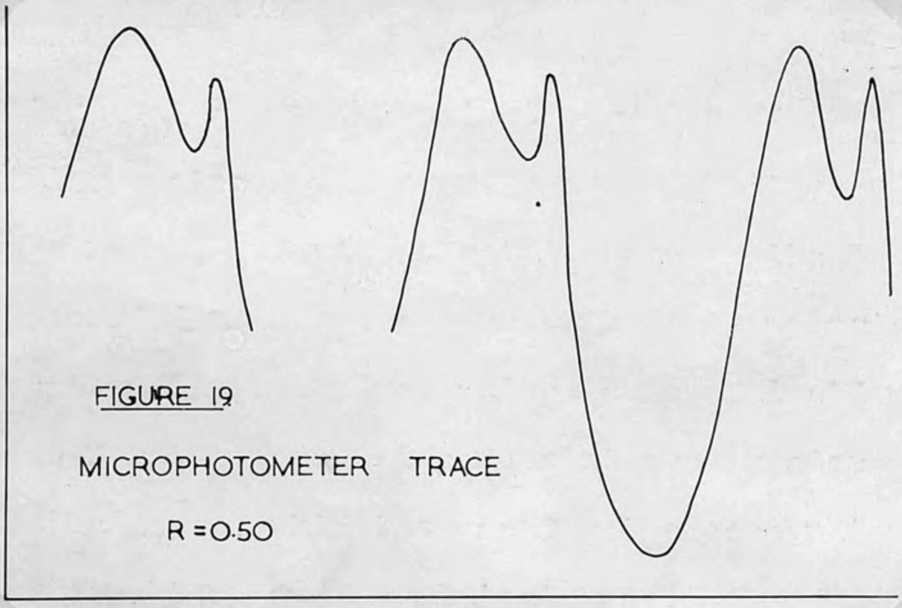


FIGURE 19

MICROPHOTOMETER TRACE

R = 0.50

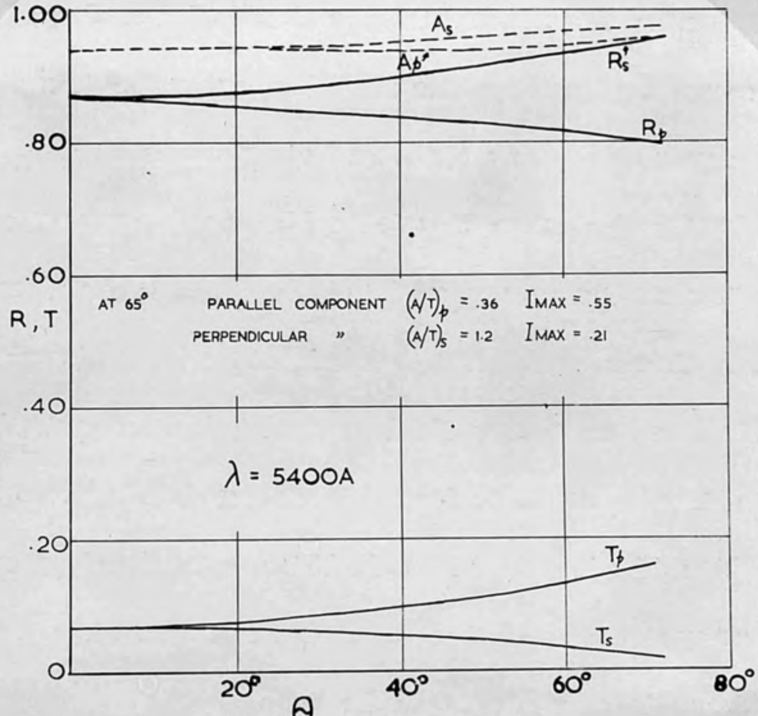


FIGURE 20.

roughly constant, but the transmission of the parallel component increases whilst that of the perpendicular component decreases. Thus it follows immediately that for the parallel component the ratio A/T decreases, and hence the maximum intensity increases, but for the perpendicular component, this ratio increases and the maximum intensity falls. It should also be noted that at high angles of incidence glass transmits the parallel component much more readily than the perpendicular one, and so the glass supports for the films account for some of the intensity difference.

In addition to the measurements on transmitted fringes in the manner described, it is also possible to observe the doubling in the reflected system of fringes. The experimental arrangement is obviously more awkward since either the collimating system or the camera system has to move round as the incidence angle changes. There is also a serious disadvantage inherent in the nature of reflected fringes. These fringes, for films of reflexion coefficient greater than 0·50, are fine dark lines on a bright background, and consequently the visibility of a system of doubled fringes is poor since the bright background for one component tends to obscure the dark fringe for the other. This difficulty can be partly overcome by the use of a device composed of two sheets of 'Polaroid' placed side by side with the line between them bisecting the incident beam. The axes of the sheets are arranged so that one half of the field is polarised in a direction perpendicular to the direction of polarisation in the other half. Each set of fringes is seen unobscured in one half of the field and measurements of the doubling can be made along the line of intersection of the two halves. Since, however, the Polaroids cannot be placed in the same plane as the fringes, this line of intersection is out of focus and there is some loss of visibility in the centre of the field. A photograph of some reflected fringes using this system is shown in Figure 21. The use of the reflected system is necessary in the case where measurements are carried out on an opaque metal surface, and this technique has been used in the present investigation, with results to be described later.

Before proceeding to a discussion of the sources of the errors of measurement in this technique, the question of the evaluation of the doubling from the actual measurements on the fringes of equal thickness must be mentioned. In the equation of the last chapter, 2·5 , the value of Δ was shown to be equal to $\frac{\lambda}{2} \cdot \frac{x_s - x_p}{x'_p - x_p}$, where x_p , x_s , x'_p , x'_s were the distances of the fringes from some arbitrary origin. This case was however derived for a

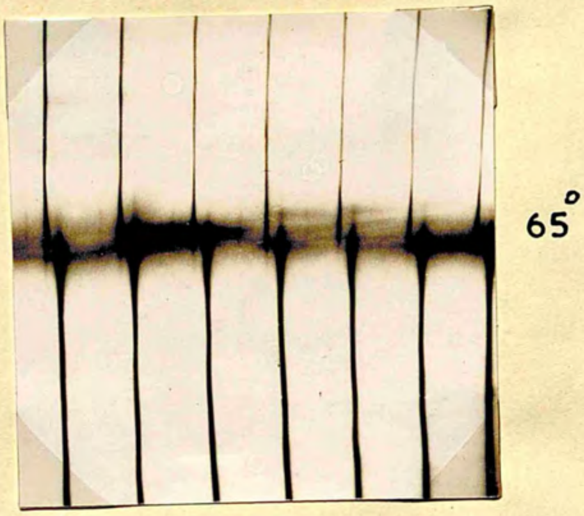


FIGURE 21

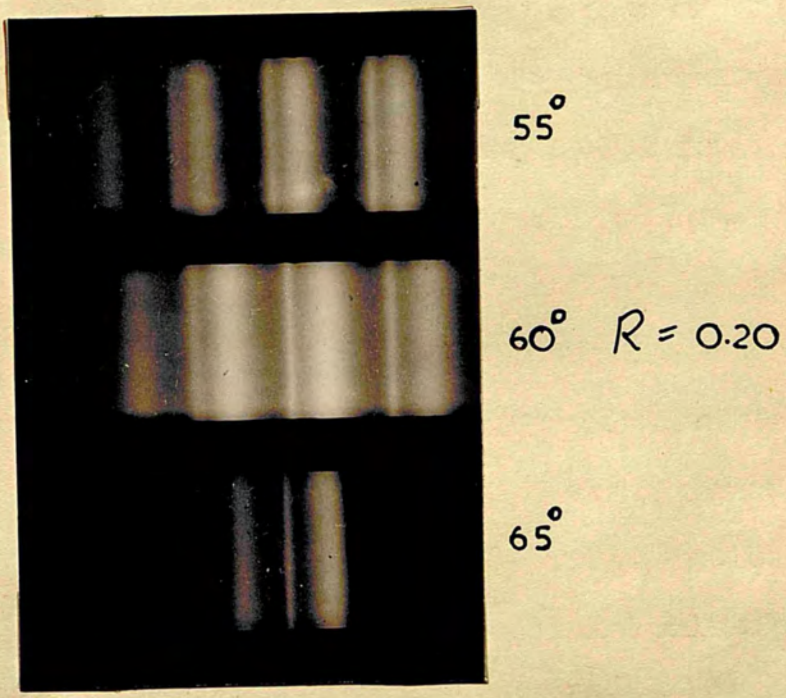


FIGURE 22

theoretical wedge interferometer, the separation between successive pairs of fringes being assumed to be constant. In practice, with the average optical flat, the pressure necessary to obtain the required small interferometer gap is generally sufficient to cause a slight buckling of the flats, with a consequent variation along the interferometer of the order separation, i.e. the quantity $x'-x$. It is therefore necessary to take the value of the order separation which holds at the doublet being measured, and to do this the average of the order separations for the two components is measured. If the doublet being measured is x_{2s}, x_{2p} in the series of fringes x_{1s}, x_{1p}, x_{2s}, x_{2p}, x_{3s}, x_{3p}, then the average order separation at the central doublet is $\frac{1}{2}(\overline{x_{1p}-x_{2p}} + \overline{x_{2s}-x_{3s}})$, and the value for Δ is $\frac{1}{2}(x_{2s}-x_{2p}) \Big/ \frac{1}{2}(\overline{x_{1p}-x_{2p}} + \overline{x_{2s}-x_{3s}})$. This method of approximation is the same as that due to McNair for the Lummer plate interferometer, quoted by Tolansky(52). It is important to note that it is only correct when the order separation between the various sets of fringes is either nearly constant, or varying slowly in a uniform manner, and if measurements are made under any other conditions serious errors are likely to result. It should be noted that this difficulty does not arise in the case of measurements with fringes of equal chromatic order, since in that case the section of the interferometer imaged at the spectroscope slit is of constant thickness, and hence the wavelength dispersion of the fringes is perfectly constant.

Measurements or fringes of equal thickness are made by setting the cross-wire in the eyepiece of an accurate comparator on to the centre of each fringe in turn. The accuracy with which this can be done obviously increases as the sharpness of the fringes increases, and so is greatest for fringes produced in interferometers with high reflexion coefficients. In the case of the measurement of relative phase change, this means that the accuracy of measurement on the fringes given by the parallel component is always the limiting factor, since these fringes are the broader of the two sets. In addition to the increased broadness of the fringes at low reflexion coefficients there is another source of increased errors in this case. When the reflexion coefficient of the parallel component is very low, it is so broad that it tends to impair the visibility of the sharp perpendicular component. It is seen in the microphotometer trace of Figure 19 that for a normal incidence value of R of 0·50, this is already happening to a certain extent. If the normal incidence reflexion coefficient is only 0·30, the reflexion coefficient at an angle of 60° may only be 0·10, and this effect then very seriously affects the accuracy of measurement. Figure 22 shows the doubling of fringes in an interferometer between two very thin silver layers, whose normal incidence reflexion coefficient was only 0·20. It can be seen that accurate measurement of this doubling is very difficult indeed.

Another source of error lies in the correct focussing of the image of the fringes on to the photographic plate. It has already been mentioned (Chapter II of this part) that for an ideal wedge interferometer the fringes are localised in a plane perpendicular to the axis of the system, and so all the fringes should be in focus at any one time on a photographic plate. In practice, however, the plates are generally very slightly curved, and the surface of localisation of the fringes is no longer a plane. This produces an apparent change in the doubling of the fringes in an image on a photographic plate as the plane of correct focus moves through the image of the fringes. This effect was totally unexpected and was found through a closer investigation of some apparent anomalies in the behaviour of thin layers. No attempt has been made to explain it theoretically but some experimental measurements of the magnitude of the effect were made.

The projecting lens, of 5 cm. focal length, was moved in 1 mm. steps through the position which appeared visually to give an image in correct focus, at a magnification of about four. A total movement of 6 mm. was made, and the doubling measured for each position for three different values of the wedge angle and interferometer gap. When the gap and wedge angle were such that there were twelve doublets per cm., the apparent change in doubling caused by the 6 mm. movement of the projecting lens was ·043 of the order separation. When there were seven doublets per cm., the movement of the lens produced an apparent change of ·031 of an order, and when there were four doublets per cm., a change of ·026 of an order. This effect is therefore least when the interferometer gap and wedge angle are at a minimum, and all measurements were subsequently made with a dispersion such that there were no more than four doublets per cm. of field.

When the reflexion coefficient of the surfaces was high, it was found that the position of correct focus could be estimated repeatedly to well within one mm. in the position of the projecting lens, and so the error introduced by this cause was less than ·004 of an order separation. When however the reflexion coefficient was very low, say less than 0·30, the position of correct focus of the fringes could not be estimated to any better than ± 2 mm., and so an error of ·01 of an order is introduced from this cause.

Both these sources of error have been shown to increase with decreasing reflexion coefficient of the surfaces of the interferometer. Using generally Fizean fringes of equal thickness, and occasionally fringes of equal chromatic order, at least forty determinations of the relative phase change have been made, for surfaces of reflexion coefficient varying between 0·20 and 0·94. Taking all these results into consideration, the experimental error in the determination of the relative change of phase by this method, expressed as a fraction of the wavelength of the incident light, varies from $\pm \cdot 002\lambda$ for the optimum case of $R > 0{\cdot}80$, to $\pm .005\lambda$ for $R < 0{\cdot}30$. If the relative phase change is expressed as an angle, this corresponds to $\pm\ 0{\cdot}7^\circ$ for the optimum case, and $\pm 2^\circ$ for the worst case. This compares unfavourably with the error in estimation of the angle of principal incidence by O'Bryan of $\pm\ 0{\cdot}1^\circ$, and the errors in determining the relative change of phase by Drude's method of $\pm \cdot 001\lambda$.

As a method for the determination of relative change of phase the interferometric technique has one main advantage over polarimetric methods in that the apparatus used is simple to construct, and inexpensive. It also has the additional advantage that the doublings can be recorded photographically and the measurements made at leisure, as opposed to the laborious visual observation necessary with most of the polarimetric methods. This is particularly the case when the variation of Δ with wavelength is required, since the whole visible range can be covered in one photograph of fringes of equal chromatic order, whilst the polarimetric method would require a dozen or more separate estimations with a half shade eyepiece or similar device.

As against these advantages, the technique has a number of serious limitations. The accuracy obtainable does not approach that obtainable by Drude's method, though from the point of view of the determination of optical constants this is not quite so serious a drawback as it seems, since we have seen that there is little need for very great accuracy in this connection. Perhaps the most severe limitation is the falling-off of accuracy with decreasing reflexion coefficient. The technique is little more than half as accurate for determining the relative changes of phase occurring on reflexion at metals such as Chromium or Copper, as it is for metals like Silver and Aluminium.

Another disadvantage in certain cases is that the technique requires two layers, one for each surface of the interferometer. Now it is not difficult to produce two layers of practically identical optical characteristics, if they are so thick as to have only a few per cent transmission. The optical properties of films of this kind, such as those used for general interferometric work, vary but slowly with thickness. However if it is desired to measure the variation of the relative change of phase with the thickness, it is found that the variation with thickness becomes appreciable at thicknesses below 350 A, and it is not an easy matter to produce two identical films. Even with the horizontal evaporation plant described in Part II, Chap. I, a small amount of oxide or other 'scum' on one side of the filament can cause a marked difference in the thickness and the properties of two very thin films produced at the same time in the plant.

One method of overcoming this difficulty is to match the thin film with a freshly prepared thick one whose properties, it will be shown, can be relied upon to be the same as others measured of the same order of thickness. The doubling is then due, not to twice the relative phase change at either of two identical films, but to the sum of the relative phase changes due to the thin film and the thick one. This process might at first sight appear to lead to an increased accuracy, since the fringes in the 'mixed' interferometer will be sharper than with one composed of two films of low reflection coefficients. However if the doubling in the former case can be measured to $\pm .004\lambda$, and thick films relative phase change is known to $\pm .002\lambda$, the value for the relative phase change at the thin film is only accurate to $\pm .006\lambda$.

A further disadvantage of the interferometric method is that it is not possible to carry out the measurements without removing the films from the vacuum in which it was deposited. This means that the films may be contaminated during the adjustment of the interferometer, etc., and false results ensue. It is generally possible to make the complete experiment for the measurement of relative phase change, including measurement of the variation with wavelength using fringes of equal chromatic order, within one hour, and so only metals which are rapidly contaminated in air will undergo any serious change during measurement. It may be possible completely to overcome this difficulty by covering the film with cedarwood or other oil of known refractive index immediately upon removal from the vacuum chamber, and forming the interferometer with this oil between the plates. It would of course be necessary to modify the interpretation of any results obtained to account for the refractive index of the oil.

From the point of view of the determination of the optical constants of the metals, it is seen immediately that this method is best suited to those metals of high reflexion coefficient. Since the measurements are most conveniently made in transmission, it follows that the metals must be in the form of layers having at least one or two per cent. transmission. It must be decided for each metal layer used whether or not the layers can be considered characteristic of the metal in bulk. The questions affecting this decision have been discussed in detail in Part I of this thesis.

PART IV

THE RESULTS OF THE EXPERIMENTS

PART IV

Introduction

The experiments that have been carried out using the optical techniques described, can be grouped under three headings, measurement of the normal incidence properties of silver and aluminium, a study of the non-normal incidence reflexion characteristics of silver layers, and the determination of the optical constants of layers of copper, tin, speculum and a tin-nickel alloy. Each of these sections will form the subject of a separate chapter, but since the overall experimental procedure was similar in each case, it can be described here.

All the layers used were deposited on to glass substrates in either of two evaporation plants described. The particular plant used will be described in the discussion of the results. After deposition, the coated substrates were removed from the vacuum chamber and the optical measurements carried out immediately. First each layer in turn was placed in the photometer and the intensity coefficients measured, both at normal incidence and at non-normal incidence for the determination of the ellipticity of the light reflected at these angles. The layers were then combined with each other (or with a freshly prepared thick layer of silver as described in Part III, Chapter III) to form an interferometer for the measurement of relative phase change.

In all cases the optical measurements were completed within two hours of the time of deposition. When these measurements were done, in those cases where the thickness of the layer was measured, a thin strip of the film was removed and an opaque layer deposited in the vertical evaporation plant in as short a time as possible.

Since these measurements were made in the minimum time in each case, no systematic investigation of the variation of the observed quantities with time has been made. The possible effect of any 'ageing' of the film during the measurements will be discussed in each particular case.

The measurements of the normal incidence reflexion coefficients will be discussed first, since they are not closely related to the application of the techniques described to the measurement of ellipticity and relative phase changes, which is the main purpose of the work.

NORMAL INCIDENCE PROPERTIES OF FILMS OF SILVER AND ALUMINIUM

Chapter I.

The reflexion and transmission coefficients at normal incidence of a number of films of silver and aluminium have been measured. Silver films were produced in both the evaporation plants, aluminium films in the vertical plant only. The angle of incidence at which the coefficients were measured was in practice 5°, but the variation of the coefficients with incidence for unpolarised light is such that in all cases the coefficients at this angle can be taken as the normal incidence coefficients within the accuracy of these measurements.

The intensity coefficients of the films of silver for incident light of mean wavelength 5400 A are shown in Figure 23. The reflexion coefficients are plotted as ordinates, the transmission coefficients as abscissae. The advantage of this method of representation over the more usual plot of the coefficients against a thickness axis has already been mentioned in Part I, Chapter IV of this thesis. The uncertainties in the thickness measurements are avoided, and the absorption of any particular layer can be quickly determined from the graph, since it is represented for any particular transmission coefficient, by the vertical distance from the point to the line of slope 45° which represents zero absorption.

In Figure 23, the points represent the films measured, the thick line is the mean of the observations of Strong and Dibble(39), showing the variation of reflexion with transmission coefficient for their α- and β-type films. It is clear at once from Figure 23 that the films measured here correspond quite closely to the films of Strong and Dibble.

It is also obvious from this figure that the scatter of the experimental points about a mean curve is very much greater than the experimental error associated with the measurements for each point, which is not greater than ± 0·01 in the value of either coefficient. The causes of these deviations were discussed when the results of previous workers were being compared. The scatter of the experimental points of Strong and Dibble is shown by the vertical dotted lines in Figure 23, and since they measured a very large number of films this order of deviation must be regarded as usual when films are produced in this manner. It must be noted, however, that despite the improvement in the pressure characteristics of the laboratory evaporation plant when the cold trap was added (see Part II, Chapter I), and the absence of any visible contamination, the scatter of points representing films produced in this plant is no less than for those produced in the vertical plant without any cold trap.

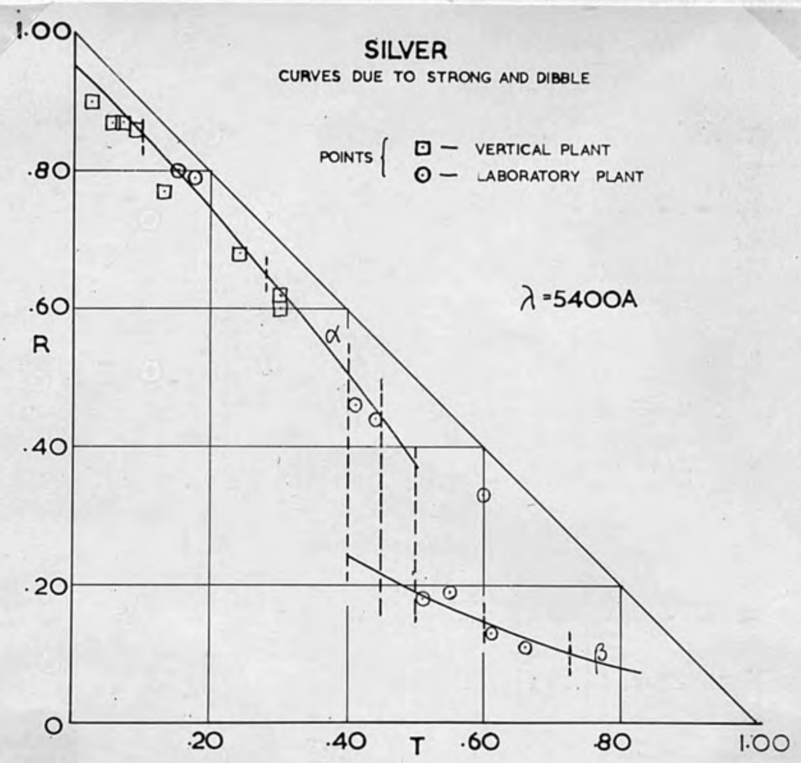


FIGURE 23.

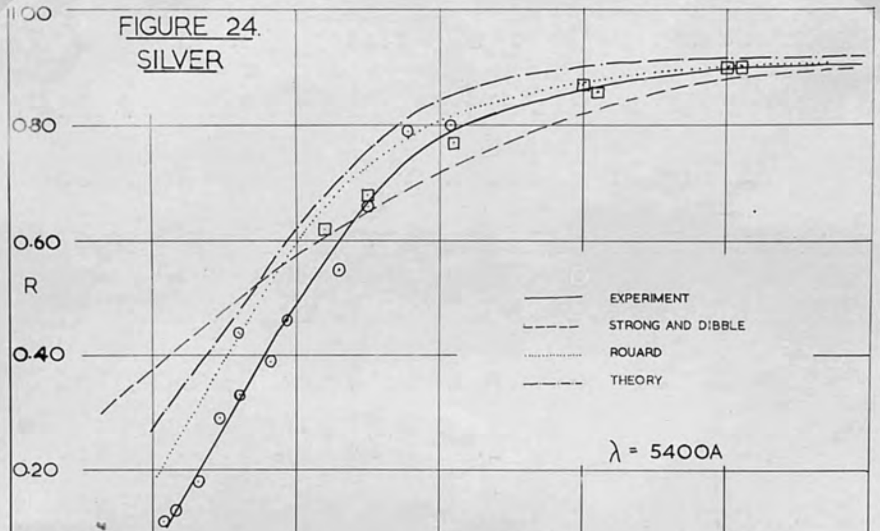


FIGURE 24.
SILVER

The fairly good agreement shown on this representation between the measured values and the values recorded by Strong, vanishes when the reflexion coefficients measured are plotted against a thickness measurement for the films, obtained in the manner described. This is done in Figure 24, the abscissae being values of the mass per unit area present in the film. Values of the thickness of the film, defined in the manner discussed in Part II, Chapter II, are also included. The continuous line represents the mean of the experimental points. The mean of the results of Rouard (cf. Figure 4) and Strong are also shown, together with a curve calculated from the values of the optical constants for opaque evaporated layers of silver, given by Hass(28). This latter curve was computed from the formulae given in Part I, Chapter II.

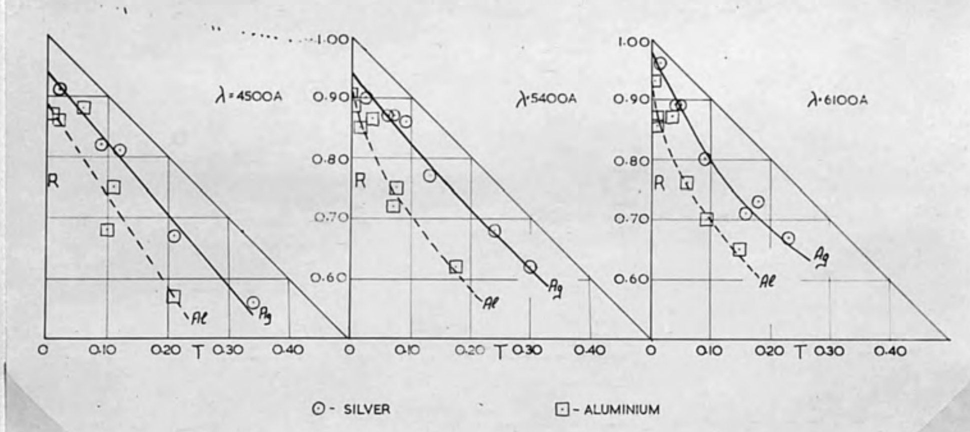
The agreement between the results of these experiments and the theory is poor, as is also the agreement between Strong's results and the theory. Here the values of the mass per unit area obtained by Strong by weighing are taken as correct . No doubt some of the discrepancy is due to the differing methods of thickness measurement employed, but a question which remains unresolved is the reason for the large differences between the work of Strong and the writer, and the work of Rouard, the latter's work agreeing fairly well with the theory for values of thickness greater than 150 Å. No further investigation of this phenomenon was made, since it lay outside the scope of this work.

The normal incidence measurements were primarily undertaken to be of assistance to workers in this laboratory using the techniques of multiple beam interferometry, and in this connection only values of reflexion coefficient greater than 0·50 are of interest. The representation of the results by plotting R against T is again the best from this point of view since the important factor, the absorption for a given transmission, can be directly observed, and no measurements of thickness are required to plot the curve.

Since, in all the interferometric done in this laboratory, the layers are deposited in the vertical evaporation plant, only films produced in that plant will be discussed from this point of view. Figure 25 shows the results for the reflexion and transmission coefficients for a number of silver and aluminium films produced in the vertical plant, for three different wavelengths, 4,500, 5,400 and 6,100 Å.

Now, the maximum intensity of an interference fringe formed in a transmission interferometer with reflectors of transmission T and absorption A is $1/(1+A/T)^2$.

FIGURE 25
SILVER AND ALUMINIUM



In order to obtain the maximum intensity, the ration must be as small as possible.

From the curves of Figure 25 it is seen at once that silver films are greatly superior to aluminium films at the wavelengths studied, the values of A/T for silver films being roughly half those for aluminium films. The values of A/T found for these silver films are in very close agreement with some measurements made using different optical techniques on films produced by evaporation by Bright, Jackson, and Kuhn(70).

Inspection of Figure 25 reveals however that these values of the ratio A/T taken from the mean curves are not reproducible to any great degree. The scatter of the experimental points is such that when successive films are evaporated in the plant under apparently identical conditions, variations in ratio A/T of up to 50% must be expected for silver films. It was at first thought that a large part of this variation was due to the fact that the actual pressure at which evaporation takes place in the vertical plant is not known, since the pressure gauge is insensitive below 10^{-4} mms. of Hg. However we have seen from Figure 23 that films produced in the laboratory plant, in which the pressures can be measured comparatively accurately, show variations of the same order.

The variations in the value of A/T for aluminium films are greater - of the order of 100% in some cases. A recent study of the optical effects of the oxidation of aluminium layers on exposure to the atmosphere, by Cabrera and Terrien(40), has shown that the variations are almost entirely due to this cause. The oxidation processes are only complete after several days, and the changes produced by them in the first two hours after production are very large.

The existence of these variations in the absorption means that in general use, this evaporation procedure cannot be relied upon to give strictly reproducible films for interferometric purposes. In the general applications of this technique in transmission, sources of high intensity are used, and an occasional highly absorbing film is not a serious handicap. However when an interferometer is used in reflexion the visibility of the interference fringes depends critically upon the absorption of the front surface of the interferometer(63), and it is occasionally found that a film is produced which is very poor for this purpose. Also because of these variations, it seems of little use to calculate values for functions relating the intensity efficiency of an interferometer to the reflexion coefficient of its surfaces, as Bright, Jackson, and Kuhn have done, since the values obtained are only reproducible between successive evaporations to ± 50%.

Another point of interest which arises from these results concerns the rate of evaporation. Strong and Dibble in their work calculated the thicknesses of their deposits from measurements on the time taken to deposit the layer and the geometry of the system. They then assumed these to be correct and 'corrected' values obtained by weighing to agree with these values. In the experiments described here, the time of deposition was measured in each case. A table is given below showing the time taken to deposit a layer and its reflexion coefficient.

Time (secs).	27	20	15	15	12	12	10	10
R	0·90	0·90	0·86	0·87	0·87	0·77	0·68	0·62

This table shows that measurements of the time taken to deposit the layer are only a very rough guide to the reflexion coefficients obtained. The reason for this, in the commercial plant, is that the silver wets the molybdenum and spreads out to a different area for each evaporation, and so the area of the source is different in each case. Strong and Dibble used a tungsten spiral coated with silver, and it might be expected that the source area in this case is more constant than with a molybdenum boat, but even so large variations in the reflexion coefficient of layers which take the same time to deposit might be expected. It was for this reason that the values given by Strong and Dibble were changed to a basis which assumed their weighings to be correct.

NON-NORMAL INCIDENCE PROPERTIES OF FILMS OF SILVER

Chapter II.

The ellipticity and relative phase change occurring on reflexion at layers of silver of various thicknesses between 100 and 600 A have been measured for angles of incidence of up to 70°. This study had two main objects. First, the variation of the quantities ρ and Δ with the thickness of a thin layer has not been previously examined. Secondly, it was desired to find whether the properties of layers of 'interferometric' thicknesses, that is only slightly transparent, were identical with those of the surface of a material in bulk, and also from the thickness variation to determine the limits of transmission and thickness, below which the properties of the layer diverged from those of the metal in bulk.

In Figure 26 the ellipticity of the light reflected from a silver layer (450 A thick, reflexion coefficient 0·90, transmission 0·04) is shown for various angles of incidence, the mean wavelength of the light being 5400 .. The experimental errors of ± 0·01 in any value of the ellipticity ρ are shown in the Figure. The values to be expected for reflexion at the surface of a bulk metal have been calculated from the formulae of Part I, Chapter I, Eqn. 1·3 , using the values for the optical constants of silver given by Hass(28), $n = 0{\cdot}177$, $k = 18{\cdot}60$, (λ = 5461A). These values are also plotted in Figure 26 and it is seen that for this film the variation of the measured ellipticity from the theoretical value for bulk solver only exceeds the experimental error of ±1% for angles of incidence above 68°.

The variation of the relative phase retardation Δ , expressed as a fraction of the incident wavelength (5461 A), with the angle of incidence is shown in Figure 27. The experimental values shown were those obtained using Fizean interference fringes in a number of interferometers, the common characteristic of which was that the transmission coefficient of the layers forming them never exceeded 0·07. No systematic variation of the relative phase retardation within these limits was observed. In Figure 27 the continuous line is not the mean curve through the points, but is the theoretical curve, computed for the case of reflexion at bulk silver, using the values of the optical constants quoted. The variation of a curve through the experimental points from the theoretical curve would not exceed the experimental error of $\pm \cdot 002\lambda$ for angles of incidence less than 60° and only by very little more than this for the higher angles of incidence less than 60° and only by very little more than this for the higher angles of incidence. The angle of principal incidence found by O'Bryan(27) is also plotted,

FIGURE 26.

SILVER

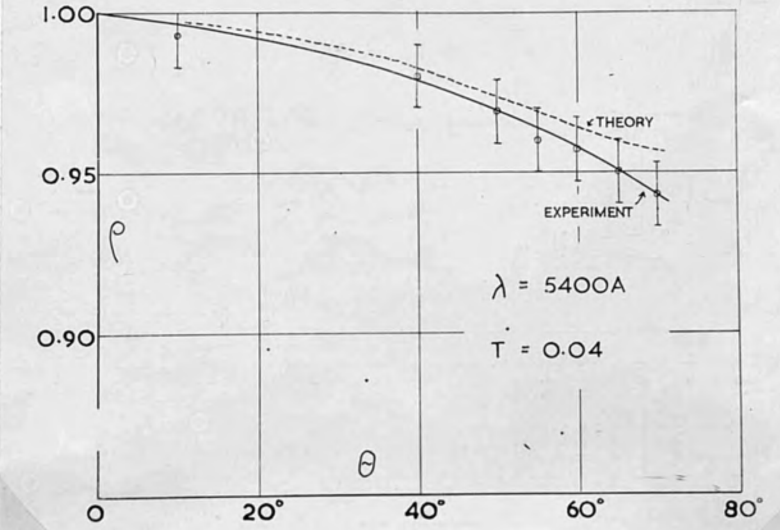
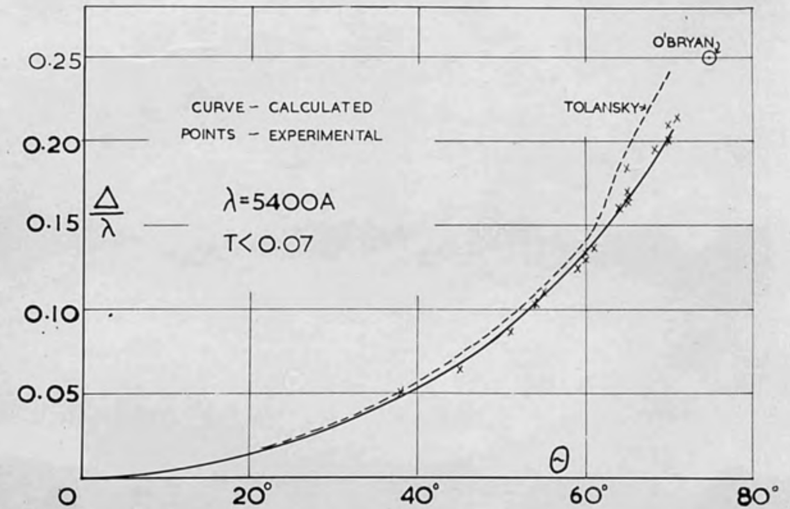


FIGURE 27.

SILVER



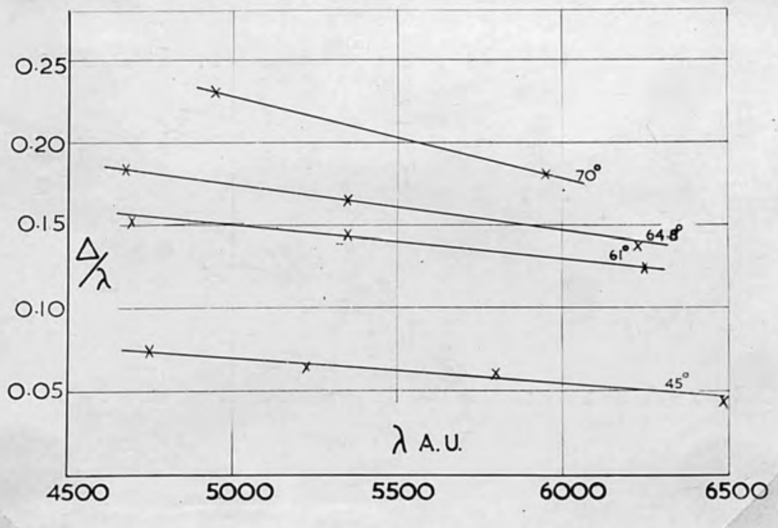
and an extrapolation of a curve through the experimental points would pass very near to this point.

It should be noted that values of Δ shown in Figure 27 and in succeeding figures are expressed as a fraction of the incident wavelength, and are directly calculated from the fractional order separation of the doubled interference fringes. These curves indicate a value of $\Delta = 0$, for $\theta = 0^\circ$. However, it can readily be shown from the theory given in Part I, Chaps. I and II (cf. Drude(1), Winterbottom(11), Born(71)) that for $\theta = 0^\circ$, $\Delta = \pi$, and that if the values of Δ given here are transformed into angular measurement, then the angle corresponding to a given fringe shift is equal to ($\pi - \Delta$) radioms. This is of importance when these measurements are used to calculate values for the optical constants, since the angular measure of Δ is required for substitution in the formulae of Part I. In passing it may also be mentioned that the shift of the dark bands in a Babinet compensator, used in Drude's method for determining Δ, when transformed into an angle is also equal to ($\pi - \Delta$), the interferometric and polarimetric methods being alike in that one cannot distinguish between a relative phase shift of zero and one of π ($\lambda / 2$).

Also shown dotted in Figure 27 is the curve obtained by Tolansky in the original work using the interferometric technique(66). This curve follows the present values very closely for incidence angles of up to 60° and then suddenly diverges from the theoretical curve. The reality of this divergence was carefully checked by Tolansky, but a thoroughly satisfactory explanation for it has not been found. One possible explanation is that it is an 'ageing' effect. The films used by Tolansky in the original experiment were several months old, and it was suggested that the effect may have been caused by the presence of a fairly thick layer of oxide on the surface. Some films used in the present investigation were left in the open laboratory for periods of up to three weeks and re-measured, but no change was ever observed of the order of magnitude of this effect.

The variation of Δ with wavelength for films of this order of thickness was measured very early in the investigation, using fringes of equal chromatic order. The results are shown in Figure 28. When Δ is expressed as a fraction of a wavelength, it decreases steadily towards the red for all angles of incidence, but if it is expressed as an angle, it remains nearly constant. The calculation of Δ from the measured wavelength was made assuming the term β in the equation 2·10 of Part III to be zero, and

FIGURE 28. SILVER



the fairly close agreement between the values taken from the fringes of equal chromatic order (Fig. 28) for $\lambda = 5461 A$, and the values from the Fizean fringes (Fig. 27) show that in fact the term β for silver must be very small. The experimental errors in these early measurements in Figure 28 are too large for any further conclusions as to the magnitude or sign of the quantity β to be drawn.

The variations of ρ and Δ with the thickness of the layer, at a fixed angle of incidence for a wavelength of 5400 A, are shown in Figures 29 and 30. The incidence angle was 65°. This angle was chosen as a compromise between the desire for as high an incidence angle as possible to decrease the percentage errors in the measurement of Δ, and the decrease in effective size of the interferometer for the measurement of Δ with increasing incidence angle.

Consider first the measurements of the ellipticity, ρ, Figure 29. The errors of measurement both of ρ and of the thickness, d, are shown in the figure, together with a theoretical curve calculated using equation 2·3 of Part I. A comparison of the theoretical and experimental curves shows that for values of d between 300 and 200 A, the experimental values are higher than the theoretical by a slight, but significant, amount, and for values of d less than 150 A, the experiemental values are considerably below

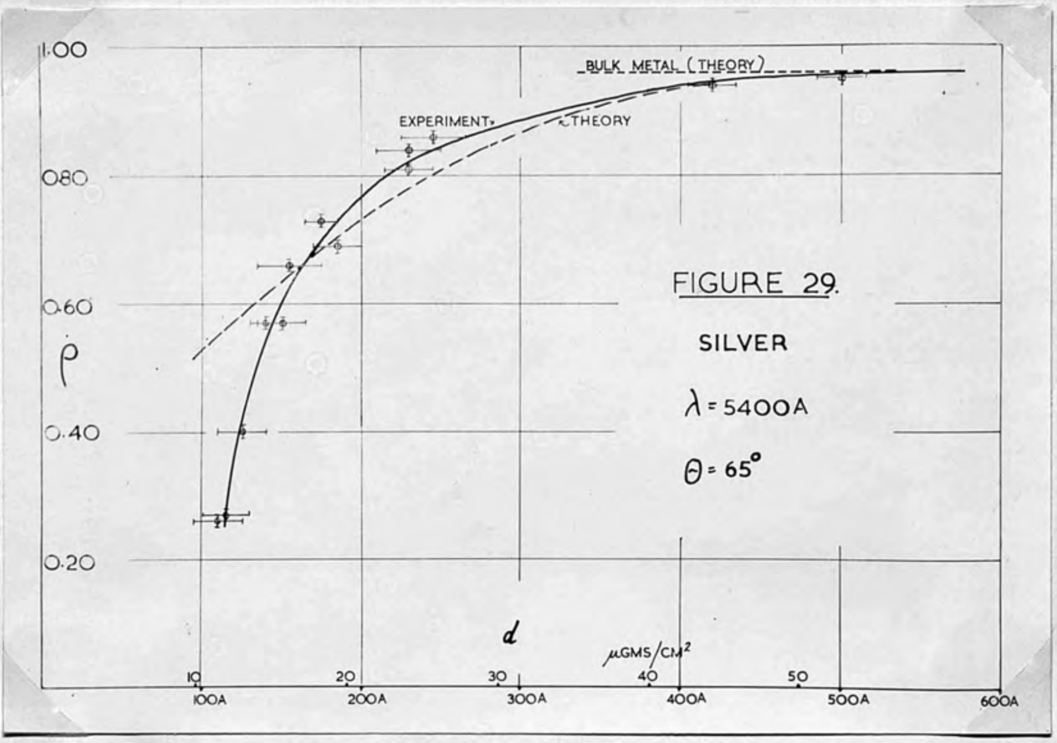


FIGURE 29.

SILVER

$\lambda = 5400A$

$\theta = 65^\circ$

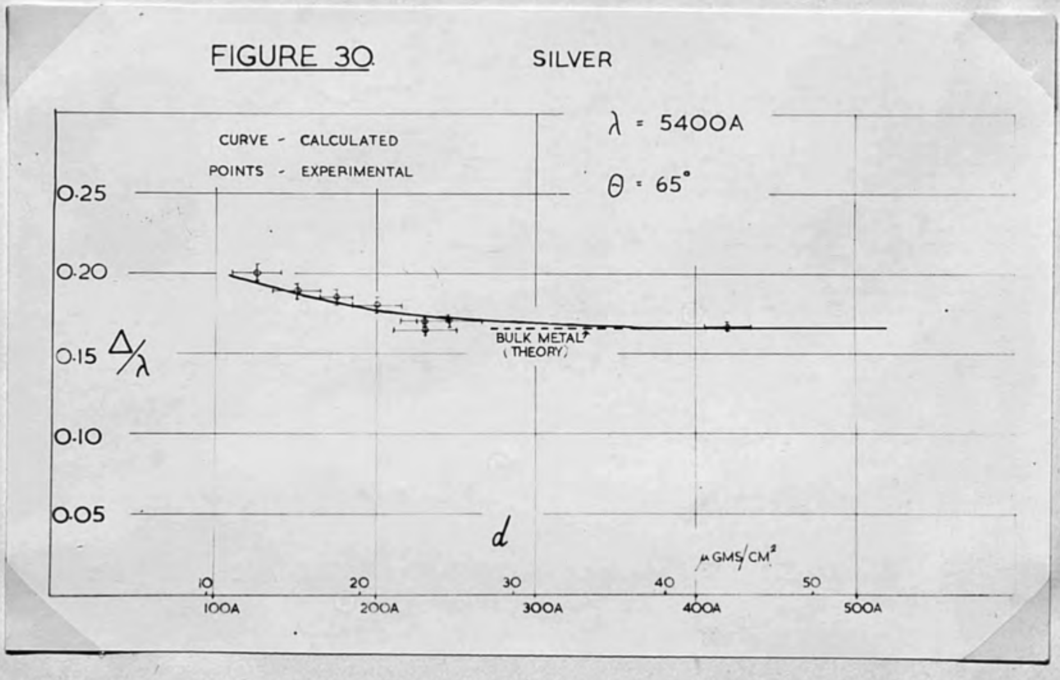


FIGURE 30.

SILVER

$\lambda = 5400A$

$\theta = 65^\circ$

the theoretical ones. It appears likely that the marked divergence of the values of ρ from the theoretical curve for very thin layers is due to a change in the optical constants of the layer similar to that observed by Rouard, Krautkramer, etc., for the normal incidence reflexion coefficients.

The variation of ρ with d in Figure 29 shows that for a layer to give ellipticities identical to within ± 1% with those given by reflexion at a bulk metal surface it must be at least 450 A thick. Using the data of the previous chapter (Figures 23 and 24) this means that the layer must have a reflexion coefficient greater than 0·90 and a transmission less than 0·04 (cf. Fig. 26).

Figure 30 shows the variation of the relative phase change, Δ , with the thickness, d . It is seen that within the limits of accuracy of the experiment there is no significant difference between the experimental points and the theoretical curve down to the smallest thicknesses measured, 125 A. It should be noted that the experimental error increases with decreasing thickness for the reasons discussed in Part III, Chapter III. Some of these points were obtained using an interferometer composed of two layers of nearly identical thickness, the mean thickness being given in the graph, and others using one layer of the thickness shown, and one layer greater than 400Å thick, for which a value of Δ taken from Figure 27 was used. It can be seen from the graph that the value of Δ for reflexion at a layer of thickness not less than 350Å is the same as the value of Δ for reflexion at the surface of bulk silver to within ± 1%.

In considering the use of the techniques described in this work for the determination of the optical constants of bulk materials, using evaporated layers as characteristic surfaces, the conclusion to be drawn from these measurements is that whilst the layers used in the interferometer can have transmissions of up to 0·07 and still yield values of Δ equal to the bulk metal values, the values of ρ obtained decrease fairly rapidly from the bulk metal value as the value of the transmission increases beyond 0·04. When the technique is used with metals, such as silver, which shows a comparatively low absorption in transparent layers, measurements on ρ and Δ can both be made on the same layers, of transmission say 0·02. However, if highly absorbing metals are to be investigated, a transmission of only 0·02 yields a very low value for the maximum intensity of the interference fringes used in the measurement of Δ (dependent upon $1/(1+A/T)^2$). For metals of this kind a more satisfactory procedure would be to prepare a number of opaque or very nearly opaque layers for the measurement of the ellipticity, and to prepare layers of transmission about 0·05, for the measurement of the relative phase change.

Finally, it can be mentioned that the optical measurements given here, suggesting a minimum thickness of 450 Å for layers of silver to be characteristic of the bulk metal, is in agreement with the observations of workers using other techniques, quoted in Part I, Chap. IV.

THE OPTICAL PROPERTIES OF Cu, TIN, SPECULUM AND A TIN-NICKEL ALLOY

Chapter III.

The techniques described have been used to investigate the optical properties of copper, tin, speculum, and a new alloy believed to be Ni_3Sn_2. The measurements were made on thick evaporated layers of these metals and alloys, and the optical constants calculated from the measurements. In order that the optical properties observed could be taken as those of the bulk material, the layers were deposited to the orders of thickness (as indicated by the transmission) suggested by the results described in the previous chapter on the variation of the properties of silver layers with their thicknesses.

The different metals and alloys will be discussed separately.

Copper.

Measurements were made on eight thick layers of copper, produced by evaporation in the horizontal evaporation plant. Four of these layers were opaque, or very nearly so ($T <$ 0·01), and four had a transmission of about 0·05. The opaque layers were used for the measurement of the ellipticity, ρ , and the slightly transparent ones for the measurement of the relative phase change, Δ .

The variation of the reflexion coefficients for the parallel and perpendicular components with the angle of incidence for one of the opaque layers is shown in Figure 31. A comparison of this figure with the variation of reflexion coefficient with incidence for silver layers as shown in Figure 20, shows at once that the difference in the reflexion coefficients at a given angle of incidence is much greater for reflexion at a copper surface than at a silver one.

Correspondingly, the values of the ellipticity, ρ , at a given angle are much less for copper than for silver. The values of ρ obtained for the four opaque layers of copper are plotted against the angle incidence in Figure 32. The values of Δ obtained by matching the four slightly transparent layers for two interferometric determinations are shown in Figure 33.

From the values of ρ and Δ thus obtained, the optical constants of these layers were determined. The formulae due to Drude, quoted in Part I, Chap. I, Eqn 1·6 , were used, the calculations being made for four angles of incidence 50°, 55°, 60°, and 65°. The various stages in the calculation are shown in the table below. Also in this table is included a column showing the magnitude of the errors arising in the various quantities involved in the

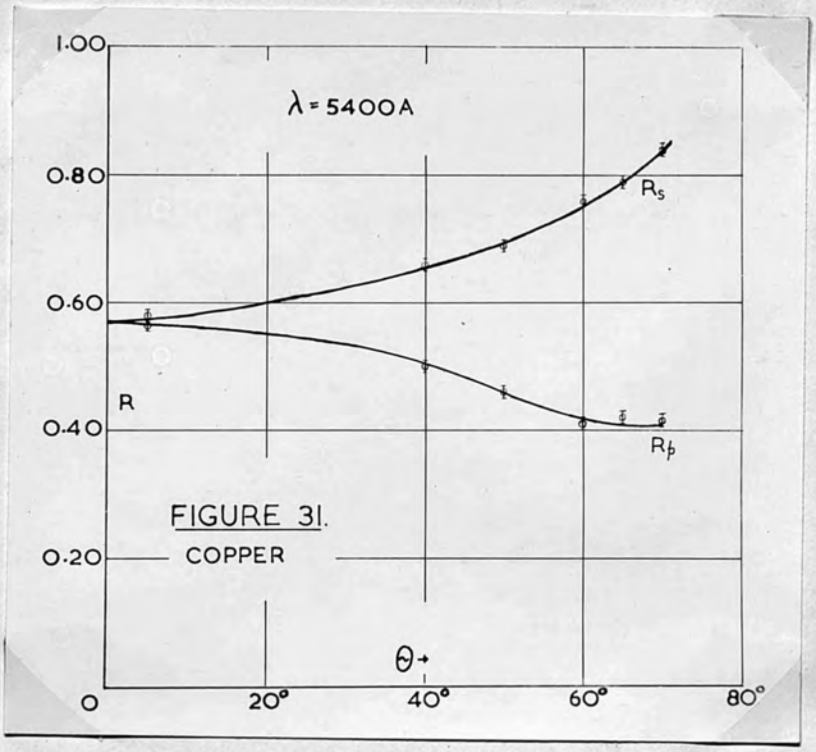


FIGURE 31.
COPPER

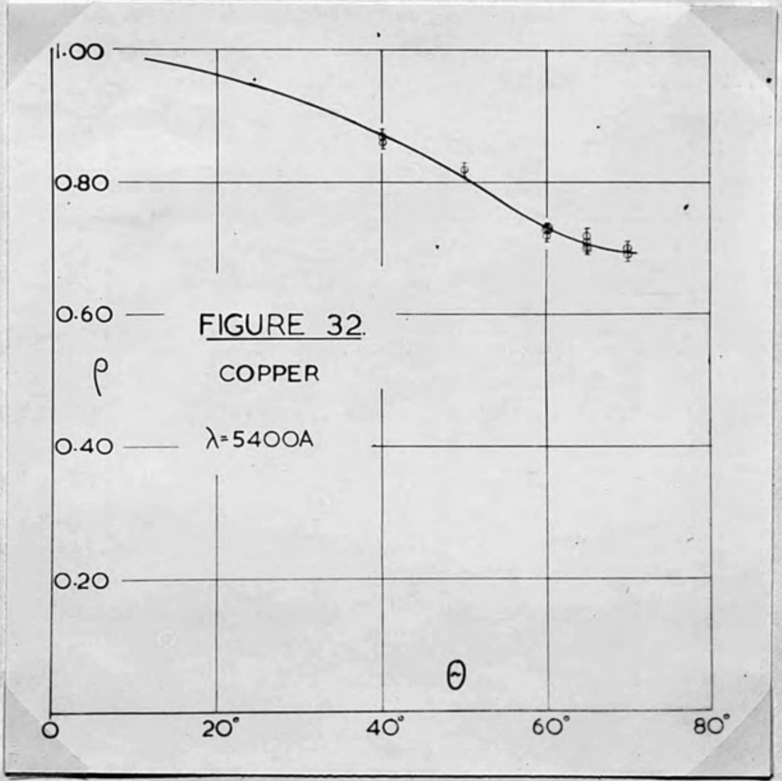


FIGURE 32.
COPPER

calculation, and in the final values for n and k, arising from errors of ± 0·01 in the value for ρ, and ± $\cdot 003\,\lambda$ in the value for Δ.

θ	50°	55°	60°	65°	
Δ	$\pi - 33°$	$\pi - 40°$	$\pi - 53°$	$\pi - 67°$	± 1°
2ψ	78°·20′	75°·30′	72°·10′	70°·44′	± 30′
Mean for Q	68°·47′				± 40′
P	72°·19′	68°·38′	62°·31′	55°·49′	± 40′
S	2·86	2·97	2·88	2·87	± 0·08
Mean for $n^2(1-k^2)$	$-5{\cdot}47$				± 0·4
k =	$2{\cdot}3 \pm 0{\cdot}1$				
n =	$1{\cdot}10 \pm 0{\cdot}07$				

The values found, $n = 1{\cdot}10$, $k = 2{\cdot}3$, for the optical constants of copper for $\lambda = 5400$ Å, can be checked roughly by calculating from them a value for the normal incidence reflexion coefficient, R, by the formula 1·10 of Part I, Chapter I, and comparing this with experiment. From calculations, the value for R is 0·59 ± 0·04 and, from Figure 31, experiment gives $R = 0{\cdot}57 \pm {\cdot}01$, and so within the accuracy of the calculations there is agreement.

The error of ± $\cdot 003\,\lambda$ quoted for the measurement of Δ is greater than the ± $\cdot 002\,\lambda$ quoted for the measurements on thick films of silver. This is because of the much lower reflexion coefficient of the parallel component in this case, and consequent loss of accuracy in the measurement of doublet separation. This point is better illustrated by a comparison of Figure 35, which shows some interference fringes used for measuring Δ for these copper films, with Figure 18 (a), the corresponding fringes with highly reflecting silver films.

In the curve of Δ against angle of incidence, θ, shown in Figure 33 two values obtained by Lowery, Wilkinson, and Smare$^{(26)}$ are also plotted. It is seen that there is excellent agreement between these values and the values obtained here. However, from their results, Lowery and his co-workers calculate the optical constants for copper to be $n = 0{\cdot}90$, $k = 2{\cdot}1$. The reason for the difference appears to be in the fact that these workers have not taken into account the fact that the shift of interference fringes or bands in a polarimetric compensator caused by the relative phase change is equal to an <u>angle</u> of $\pi - \Delta$, not Δ, as was mentioned in the previous chapter. Lowery, Wilkinson and Smare only made measurements at one angle of incidence, 70°, and this angle is near to the angle of principal incidence, i.e. Δ is near to $\pi/2$, and so the error introduced is comparatively small.

FIGURE 33.

COPPER

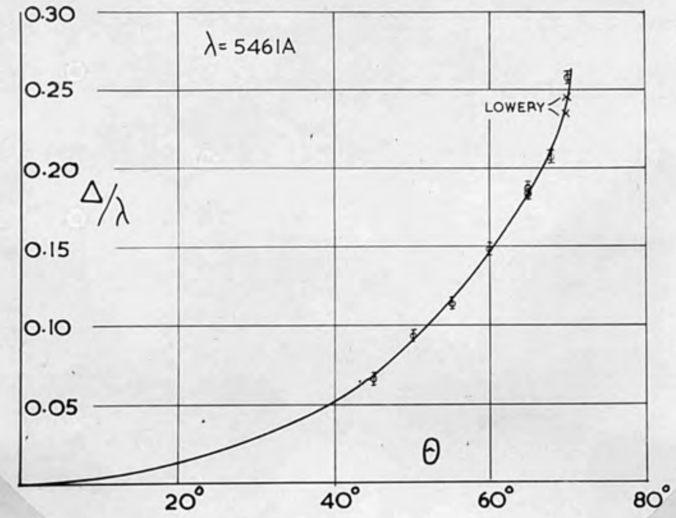


FIGURE 34.

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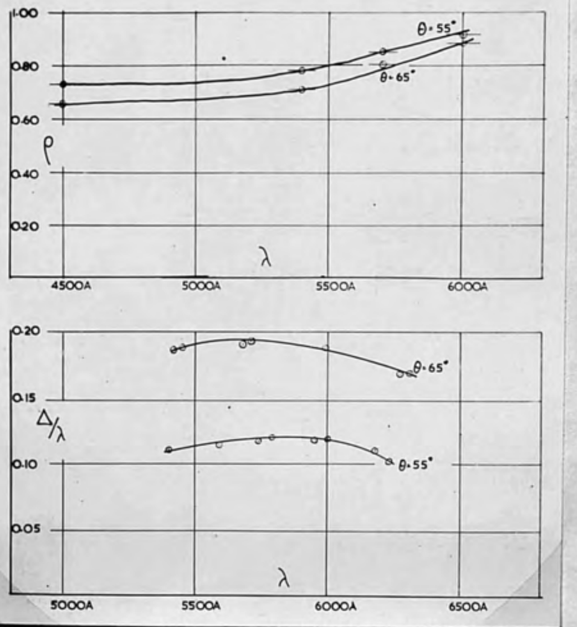

The variation of the quantities ρ and Δ with wavelength has also been measured for two angles of incidence, 55° and 65°. These variations are shown in Figure 34. The values for ρ are subject to considerable error owing to the uncertainty of the mean wavelengths given by the filters in the system used. The values for Δ were obtained by the use of fringes of equal chromatic order, each wavelength being accurate to ± 5 A.

The values obtained for the optical constants of these evaporated layers of copper are in good agreement with the values given for the bulk metal, for $\lambda = 5400$ A, in the International Critical Tables, $n = 1{\cdot}07$, $k = 2{\cdot}25$. However Lowery and his co-workers$^{(24,\ 25,\ 26)}$ have demonstrated the extreme sensitivity of measurements on copper surfaces to differing methods of surface preparation, and so in a sense the degree of agreement obtained must be regarded as fortuitous. However values have been obtained$^{(72)}$ for electrolytically deposited copper of $n = 1{\cdot}38$, $k = 1{\cdot}78$ ($\lambda = 5400$ A), and for cathodically sputtered layers$^{(73)}$ $n = 0{\cdot}90$, $k = 2{\cdot}70$, and so it seems that layers produced by evaporation resemble the structure of the massive metal more closely than layers made by electrolytic deposition or by cathodic sputtering.

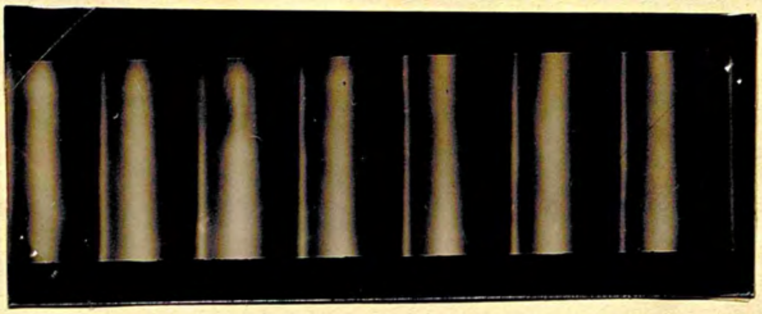

FIGURE 35 COPPER 65°

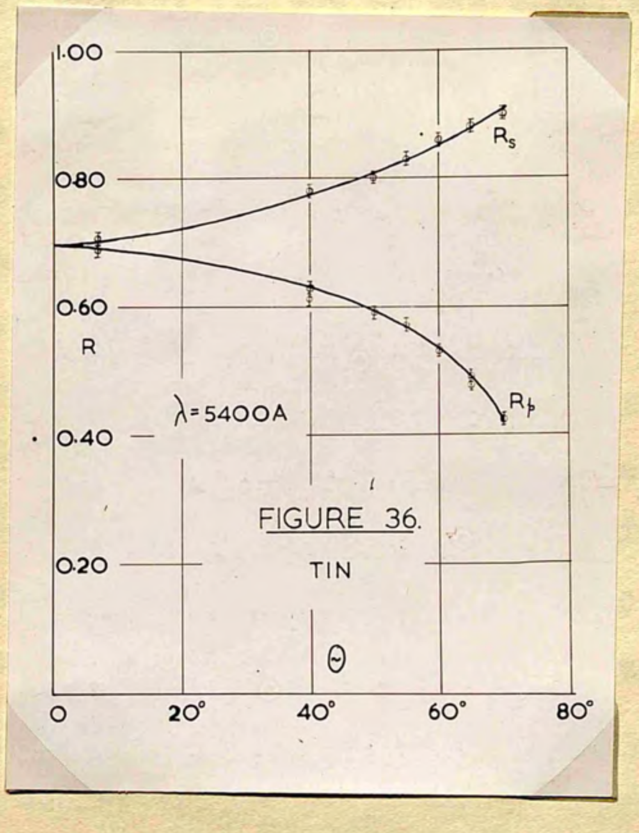

FIGURE 36.

TIN

Tin

A similar procedure to that employed for the determination of the optical constants of the evaporated layers was followed for measurements on eight evaporated layers of tin. The only difference between the two experiments was that in this case the values of ρ and Δ were only determined for one angle of incidence, 65°.

The variation of the reflexion coefficients with incidence angle was measured for one of the films and is shown in Figure 36. One of the sets of fringes used for the determination of Δ for these layers is shown in Figure 37, and from this it can be seen that the order of accuracy of these measurements is the same as that for the measurements on the copper films.

The mean values for the ellipticity and relative phase retardation on reflexion at an angle of 65° at these layers were $\rho = 0{\cdot}73 \pm {\cdot}01$, and $\Delta = {\cdot}106\lambda \pm {\cdot}003\lambda$. Using the same formulae as for the determination of the constants for copper, it was found that for these tin layers $n = 2{\cdot}4 \pm 0{\cdot}2$, $k = 1{\cdot}9 \pm 0{\cdot}1$ for $\lambda = 5400A$. The accuracy of the copper values cannot be claimed for these, since they were made at a single angle of incidence only. The value of the normal incidence reflexion coefficient calculated from these values is 0·70, which agrees with experiment.

Now the values of the optical constants for bulk tin are(74) $n = 1{\cdot}0, k = 4{\cdot}2 = \lambda\, 5400\, A$), and even allowing for considerable variations in the values for the bulk metal (tin is an extremely soft metal, and so its surface would be very susceptible to conditions of polish etc.) there exists a great difference between the optical constants of the layers and of the bulk.

The constants for the bulk metal yield theoretical values for ρ and Δ of $0{\cdot}82$ and $\cdot 130\,\lambda$. These values were checked experimentally. Some plane surfaces of tin were prepared by allowing drops of the molten metal to fall on to a hot glass plate, and to cool there slowly. When separated from the glass, if done carefully, the tin surfaces had the finish of the glass plate, and also were presumably free from any distortion due to cold-working. The ellipticity of the light reflected from these surfaces was measured using the photometer in the usual way, and the relative phase change was determined using the interferometric technique in reflexion, as described in Part III, Chapter III.

A photograph of the interference fringes obtained by reflexion in an interferometer formed between a freshly prepared silver surface ($R = 0{\cdot}87$, $T = 0{\cdot}07$) and the cast tin surface ($R = 0{\cdot}80$), is shown in Figure 38. Obviously the accuracy of measurement on these fringes does not approach the accuracy obtainable by measurements on the

FIGURE 37 TIN (EVAP)

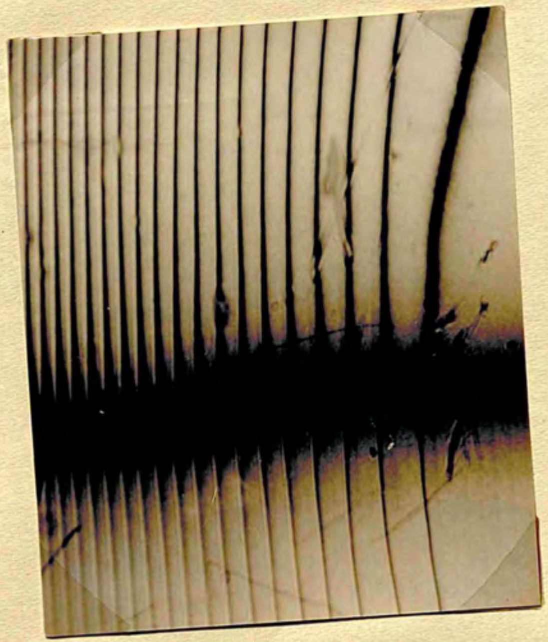

FIGURE 38 TIN (CAST)

fringes obtained in transmission in the usual way, but it is sufficient for this case.

The results of this experiment, together with the experimental values for the layers, and the theoretical values for bulk tin are included in the table below.

		ρ	Δ	R	n	k
THEORY	BULK	0·84	·133	0·82	1·0	4·2
EXP.	BULK	0·82 ± ·01	·13 ± ·01	0·80		
EXP.	LAYERS.	0·73 ± ·01	·106 ± ·003	0·70	2·4	1·9

The only conclusion that can be drawn from these results is that the surface structure of the evaporated layers of tin is quite different from that of the metal in bulk. Three possible explanations present themselves.

The first possibility is that the 'bloom' which was occasionally observed on evaporated films of tin was actually present in all cases in a sufficient amount to affect the optical characteristics of the surface. Against this must be placed the fact that if the effect is there it is remarkably constant, considering that the amount of heat radiated from the filament to the layer during production may vary considerably from one case to the next, since the quantity of tin on the filament and hence the effective source area may vary by at least ten per cent.

The second possibility is that an alloying action between the tin and the molybdenum filament did in fact take place (as suggested by Dr. Hedges, of Part II, Chapter II). It has already, however, been mentioned that the percentage content of molybdenum in any alloy must have been very small, since fourteen films in all were produced from the same filament.

The third, and perhaps the most probable, source of the difference is that tin, being a low melting point metal, must be classed with cadmium and zinc in that the structures of layers deposited at room temperatures, even when they are opaque, do not resemble the structure of the metal in bulk. Some slight evidence of an irregular surface structure was observed when freshly prepared layers were microscopically examined at high magnifications (x 1000) with dark ground illumination. With freshly prepared silver layers, the field of view of the microscope appeared of uniform intensity but with the tin layers a very slight 'speckled' effect was observed. The effect was very small, and could not be photographed, and so cannot be taken as definite evidence.

Speculum and Tin-Nickel

Measurements have been made on a few evaporated layers of speculum and tin-nickel. These alloys were evaporated only in the vertical plant, and only three or four films of each alloy were made.

The speculum alloy was composed of 58% Cu, 42% Sn. The value found for the normal incidence reflexion coefficients of the layers for incident light of wavelength 5400A was 0·65. This is close to the value of 0·64 quoted in the International Critical Tables for the reflectivity of bulk speculum of composition 68% Cu, 32% Sn. It is, however, nearly ten per cent less than the values found by Tolansky and Donaldson(65) for evaporated layers of an alloy composed of 55% Cu, 45% Sn.

The ellipticity and the relative phase change on reflexion at these layers were measured for an incidence angle of 65°. Since only four films were measured in all, a rigorous calculation of the optical constants from these figures was not justified. A calculation was made using the approximate formulae given in Part I, Eqn. 1·8, and the constants were found to be $n = 2{\cdot}0$, $k = 2{\cdot}3$. These figures are not accurate to better than ten per cent.

One interesting feature of these evaporated layers was that their structure and composition, after evaporation, was the same as that of the alloy before evaporation. This was found from an X-ray investigation carried out by the Tin Research Association, and is rather remarkable since the component metals of the alloy have widely differing melting points (Copper 1000° and Tin 230°).

Measurements were also made of the reflexion coefficients, ellipticity, and relative phase changes for three evaporated layers of a new Tin-Nickel alloy, supplied in December 1949, by the Tin Research Association. This alloy was believed to be the intermetallic compound $Ni_3 Sn_2$

The layers were produced in the vertical evaporation unit, and the average normal incidence reflexion coefficient for $\lambda = 5400 A$, for the three films was 0·53. None of the layers was opaque, their transmission coefficients being about 0·05. This comparatively high value of the transmission coefficient means that the values of the ellipticity for reflexion at a completely opaque layer would be greater than that measured by two or three per cent.

The ellipticities and relative phase changes were measured for reflexion at three angles of incidence 55°, 60°, and 65°, and from the measurements values for the optical constants were obtained using the approximate formulae as for the speculum constants. The measured quantities and the values found are included in the table below.

θ	55°	60°	65°
Δ	$\pi - 25°$	$\pi - 34°$	$\pi - 47°$
ρ	0·73	0·67	0·61

$n = 2{\cdot}4, \quad k = 1{\cdot}4$

These values for the constants are only accurate to ten per cent, and can only be taken as applying to the present case since, as has been mentioned in Part II, Chapter I, it was believed that some alloying action took place between the molybdenum filament and the tin-nickel.

The interference fringes used for the measurement of Δ in this case are shown in Figure 18 (b).

No worthwhile conclusions can be drawn from the rough measurements made on these alloys, but they are included as an indication of possible useful extensions of the technique, since these alloys are often only available in a powder form and optical measurements can only be made on layers produced either by evaporation or electrodeposition.

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