

XIV

Optics of metals

So far we have been concerned with the propagation of light in nonconducting, isotropic media. We now turn our attention to the optics of conducting media, more particularly to metals. An ordinary piece of metal is a crystalline aggregate, consisting of small crystals of random orientation. Single crystals of appreciable size are rare, but can be produced artificially; their optical properties will be studied in Chapter XV. A mixture of randomly oriented crystallites behaves evidently as an isotropic substance, and as the theory of light propagation in a conducting isotropic medium is much simpler than in a crystal, we shall consider it here in some detail.

According to §1.1, conductivity is connected with the appearance of Joule heat. This is an irreversible phenomenon, in which the electromagnetic energy is destroyed, or more precisely transformed into heat, and in consequence an electromagnetic wave in a conductor is attenuated. In metals, on account of their very high conductivity, this effect is so large that they are practically opaque. In spite of this, metals play an important part in optics. Strong absorption is accompanied by high reflectivity, so that metallic surfaces act as excellent mirrors. Because of the partial penetration of light into a metal, it is possible to obtain information about the absorption constants and the mechanism of absorption from observations of the reflected light, even though the depth of penetration is small.

We shall first consider the purely formal results arising from the existence of conductivity, and then briefly discuss a simple, somewhat idealized, physical model for this process, based on the classical theory of the electron. This model accounts only roughly for some of the observed effects; a more precise model can only be obtained with the help of quantum mechanics and is thus outside the scope of this book. The formal theory will be illustrated by applications to two problems of practical interest: the optics of stratified media containing an absorbing element, and the diffraction of light by a metallic sphere.

A particularly attractive mathematical feature of the theory is that the existence of conductivity may be taken into account simply by introducing a complex dielectric constant (or complex index of refraction), instead of a real one. In metals the imaginary part is preponderant.

14.1 Wave propagation in a conductor

Consider a homogeneous isotropic medium of dielectric constant ϵ , permeability μ , and conductivity σ . Using the material equations §1.1 (9)–(11), viz. $\mathbf{j} = \sigma \mathbf{E}$, $\mathbf{D} = \epsilon \mathbf{E}$,

$\mathbf{B} = \mu\mathbf{H}$, Maxwell's equations take the form

$$\text{curl } \mathbf{H} - \frac{\varepsilon}{c} \dot{\mathbf{E}} = \frac{4\pi}{c} \sigma \mathbf{E}, \quad (1)$$

$$\text{curl } \mathbf{E} + \frac{\mu}{c} \dot{\mathbf{H}} = 0, \quad (2)$$

$$\text{div } \mathbf{E} = \frac{4\pi}{\varepsilon} \rho, \quad (3)$$

$$\text{div } \mathbf{H} = 0. \quad (4)$$

It is easy to see that for an electromagnetic disturbance, incident from outside onto the conductor, one may replace (3) by $\text{div } \mathbf{E} = 0$. For if we take the divergence of (1) and use (3) we obtain

$$-\frac{\varepsilon}{c} \text{div } \dot{\mathbf{E}} = \frac{4\pi\sigma}{c} \frac{4\pi}{\varepsilon} \rho.$$

Also, differentiation of (3) with respect to time gives

$$\text{div } \dot{\mathbf{E}} = \frac{4\pi}{\varepsilon} \dot{\rho}.$$

Eliminating $\text{div } \dot{\mathbf{E}}$ between the last two equations one obtains

$$\dot{\rho} + \frac{4\pi\sigma}{\varepsilon} \rho = 0, \quad (5)$$

giving on integration

$$\rho = \rho_0 e^{-t/\tau}, \quad \text{where } \tau = \frac{\varepsilon}{4\pi\sigma}. \quad (6)$$

Any electric charge density ρ is thus seen to fall off exponentially with time. The *relaxation time* τ is exceedingly small for any medium having appreciable conductivity. For metals, this time is very much shorter (typically of the order of 10^{-18} s) than the periodic time of vibration of the wave. We may, therefore, assume that ρ in a metal is always sensibly zero. Consequently (3) may be written as

$$\text{div } \mathbf{E} = 0. \quad (7)$$

From (1) and (2) it follows by elimination of \mathbf{H} and the use of (7) that \mathbf{E} satisfies the wave equation

$$\nabla^2 \mathbf{E} = \frac{\mu\varepsilon}{c^2} \ddot{\mathbf{E}} + \frac{4\pi\mu\sigma}{c^2} \dot{\mathbf{E}}. \quad (8)$$

The term in $\dot{\mathbf{E}}$ implies that the wave is damped, i.e. it suffers a progressive attenuation as it is propagated through the medium.

If the field is strictly monochromatic, and of angular frequency ω , i.e. if \mathbf{E} and \mathbf{H} are of the form $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$, $\mathbf{H} = \mathbf{H}_0 e^{-i\omega t}$, we have $\partial/\partial t \equiv -i\omega$ so that (1) and (2) may be re-written as

$$\text{curl } \mathbf{H} + \frac{i\omega}{c} \left(\varepsilon + i \frac{4\pi\sigma}{\omega} \right) \mathbf{E} = 0, \quad (9)$$

$$\operatorname{curl} \mathbf{E} - \frac{i\omega\mu}{c} \mathbf{H} = 0, \quad (10)$$

and (8) becomes

$$\nabla^2 \mathbf{E} + \hat{k}^2 \mathbf{E} = 0, \quad (11)$$

where

$$\hat{k}^2 = \frac{\omega^2 \mu}{c^2} \left(\varepsilon + i \frac{4\pi\sigma}{\omega} \right). \quad (12)$$

These equations are formally identical with the corresponding equations for nonconducting media if in the latter the dielectric constant ε (which, to a good approximation, was shown to be real except for frequencies ω that are close to a resonance — see §2.3.4) is replaced by

$$\hat{\varepsilon} = \varepsilon + i \frac{4\pi\sigma}{\omega}. \quad (13)$$

The analogy with nonconducting media becomes closer still if, in addition to the complex wave number \hat{k} and the complex dielectric constant $\hat{\varepsilon}$, we also introduce a complex phase velocity \hat{v} and a complex refractive index \hat{n} which, in analogy with §1.2 (8), §1.2 (12), and §1.3 (21), are defined by

$$\hat{v} = \frac{c}{\sqrt{\mu\hat{\varepsilon}}}, \quad \hat{n} = \frac{c}{\hat{v}} = \sqrt{\mu\hat{\varepsilon}} = \frac{c}{\omega} \hat{k}. \quad (14)$$

We set

$$\hat{n} = n(1 + i\kappa), \quad (15)$$

where n and κ are real, and we call κ *the attenuation index*.* The quantities n and κ may easily be expressed in terms of the material constants ε , μ and σ . Squaring (15) we have

$$\hat{n}^2 = n^2(1 + 2i\kappa - \kappa^2). \quad (15a)$$

Also, from (14) and (13),

$$\hat{n}^2 = \mu\hat{\varepsilon} = \mu \left(\varepsilon + i \frac{4\pi\sigma}{\omega} \right). \quad (16)$$

Now σ , just like ε , is not a true constant of the medium, but depends on the frequency. We will see later (§14.3) that for sufficiently low frequencies (long wavelengths) σ is, to a good approximation, real. Assuming that ε is also real, we obtain in this case, upon equating the real and imaginary parts in (15a) and (16), the following relations:

$$n^2(1 - \kappa^2) = \mu\varepsilon, \quad (16a)$$

$$n^2\kappa = \frac{2\pi\mu\sigma}{\omega} = \frac{\mu\sigma}{\nu}. \quad (16b)$$

From these equations it follows that

* The term 'extinction coefficient' is also used.

$$n^2 = \frac{1}{2} \left(\sqrt{\mu^2 \varepsilon^2 + \frac{4\mu^2 \sigma^2}{\nu^2}} + \mu \varepsilon \right), \quad (17a)$$

$$n^2 \kappa^2 = \frac{1}{2} \left(\sqrt{\mu^2 \varepsilon^2 + \frac{4\mu^2 \sigma^2}{\nu^2}} - \mu \varepsilon \right). \quad (17b)$$

The positive sign of the square roots is taken here, since n and $n\kappa$ are real, and consequently n^2 and $n^2\kappa^2$ must be positive.

Eq. (11) is formally identical with the wave equation for a nonconducting medium, but the wave number is now complex. The simplest solution is that of a plane, time-harmonic wave

$$\mathbf{E} = \mathbf{E}_0 e^{i[\hat{k}\mathbf{r}\cdot\mathbf{s} - \omega t]}. \quad (18)$$

If, in accordance with (14) and (15), we substitute for \hat{k} from the relation $\hat{k} = \omega \hat{n}/c = \omega n(1 + i\kappa)/c$, (18) becomes

$$\mathbf{E} = \mathbf{E}_0 e^{-\frac{\omega}{c} n \kappa \mathbf{r} \cdot \mathbf{s}} e^{i\omega \left[\frac{n}{c} \mathbf{r} \cdot \mathbf{s} - t \right]}.$$

The real part of this expression, viz.

$$\mathbf{E} = \mathbf{E}_0 e^{-\frac{\omega}{c} n \kappa \mathbf{r} \cdot \mathbf{s}} \cos \left\{ \omega \left[\frac{n}{c} \mathbf{r} \cdot \mathbf{s} - t \right] \right\}, \quad (19)$$

which represents the electric vector, is a plane wave with wavelength $\lambda = 2\pi c/\omega n$ and with attenuation given by the exponential term. Since the energy density w of the wave is proportional to the time average of \mathbf{E}^2 , it follows that w decreases in accordance with the relation

$$w = w_0 e^{-\chi \mathbf{r} \cdot \mathbf{s}}, \quad (20)$$

where

$$\chi = \frac{2\omega}{c} n \kappa = \frac{4\pi\nu}{c} n \kappa = \frac{4\pi}{\lambda_0} n \kappa = \frac{4\pi}{\lambda} \kappa, \quad (21)$$

λ_0 being the wavelength in vacuum and λ the wavelength in the medium. The constant χ [denoted by α in §4.11 (6)] is called *the absorption coefficient*.

The energy density falls to $1/e$ of its value after the wave has advanced a distance d , where

$$d = \frac{1}{\chi} = \frac{\lambda_0}{4\pi n \kappa} = \frac{\lambda}{4\pi \kappa}. \quad (22)$$

This quantity is usually a very small fraction of the wavelength (see Table 14.1).*

Returning to (17) we see that, when $\sigma = 0$, the first equation correctly reduces to Maxwell's relation §1.2 (14) $n^2 = \mu\varepsilon$, and the second gives $\kappa = 0$. For metals $\sigma \neq 0$ and is in fact so large that in (17) ε may be neglected in comparison with $2\sigma/\nu$. To get an idea of the orders of magnitude involved let it be remarked that for most metals the conductivity at frequencies up to about the infra-red region of the spectrum

* This phenomenon of penetration to a depth that is a small fraction of the wavelength is well known in the conduction of alternating currents and is known to engineers as the 'skin effect.'

Table 14.1. The 'penetration depth' d for copper for radiation in three familiar regions of the spectrum, calculated with the static conductivity $\sigma \sim 5.14 \times 10^{17} \text{ s}^{-1}$ and $\mu = 1$.

Radiation	Infra-red	Microwaves	Long radio waves
λ_0	10^{-3} cm	10 cm	$1000 \text{ m} = 10^5 \text{ cm}$
d	$6.1 \times 10^{-7} \text{ cm}$	$6.1 \times 10^{-5} \text{ cm}$	$6.1 \times 10^{-3} \text{ cm}$

($\lambda \geq 10^{-3} \text{ cm}$) is of the order of 10^{17} s^{-1} . Thus, for example, with $\lambda = 10^{-3} \text{ cm}$ ($\nu \sim 3 \times 10^{13} \text{ s}^{-1}$), one then has $\sigma/\nu \sim 3000$. The dielectric constant ϵ of a metal cannot be measured directly, but as we shall see it can be deduced from optical experiments. However, as the mechanism of electric polarization in metals is not fundamentally different from that of a dielectric, it may be assumed that ϵ is of the same order of magnitude. Hence, provided the wavelength is not too short, one may suppose that

$$\frac{\mu\sigma}{\nu} = n^2\kappa \gg \mu\epsilon. \quad (23)$$

Eqs. (17) and (22) now reduce to

$$n \sim n\kappa = \sqrt{\frac{\mu\sigma}{\nu}}. \quad (24)$$

$$d \sim \frac{\lambda_0}{4\pi} \sqrt{\frac{\nu}{\mu\sigma}} = \frac{1}{4\pi} \sqrt{\frac{c\lambda_0}{\mu\sigma}} = \frac{c}{\sqrt{8\pi\mu\sigma\omega}}. \quad (25)$$

A perfect conductor is characterized by infinitely large conductivity ($\sigma \rightarrow \infty$). Since according to (16), $\epsilon/\sigma = (1 - \kappa^2)/\nu\kappa$, we have in this limiting case $\kappa^2 \rightarrow 1$, or by (16a), $n \rightarrow \infty$. Such a conductor would not permit the penetration of an electromagnetic wave to any depth at all and would reflect all the incident light (see §14.2 below).

Whilst the refractive index of transparent substances may easily be measured from the angle of refraction, such measurements are extremely difficult to carry out for metals, because a specimen of the metal which transmits any appreciable fraction of incident light has to be exceedingly thin. Nevertheless Kundt* succeeded in constructing metal prisms that enabled direct measurements of the real and imaginary parts of the complex refractive index to be made. Usually, however, the optical constants of metals are determined by means of katoptric rather than dioptric experiments, i.e. by studying the changes which light undergoes on reflection from a metal, rather than by means of measurements on the light transmitted through it.

14.2 Refraction and reflection at a metal surface

We have seen that the basic equations relating to the propagation of a plane time-harmonic wave in a conducting medium differ from those relating to propagation in a transparent dielectric only in that the real constants ϵ and k are replaced by complex

* A. Kundt, *Ann. d. Physik*, 34 (1888), 469.

constants $\hat{\epsilon}$ and \hat{k} . It follows that the formulae derived in Chapter I, as far as they involve only linear relations between the components of the field vectors of plane monochromatic waves, apply also in the present case. In particular, the boundary conditions for the propagation of a wave across a surface of discontinuity and hence also the formulae of §1.5 relating to refraction and reflection remain valid.

Consider first the propagation of a plane wave from a dielectric into a conductor, both media being assumed to be of infinite extent, the surface of contact between them being the plane $z = 0$. By analogy with §1.5 (8) the law of refraction is

$$\sin \theta_t = \frac{1}{\hat{n}} \sin \theta_i. \quad (1)$$

Since \hat{n} is complex, so is θ_t , and this quantity therefore no longer has the simple significance of an angle of refraction.

Let the plane of incidence be the x, z -plane. The space-dependent part of the phase of the wave in the conductor is given by $\hat{k}\mathbf{r} \cdot \mathbf{s}^{(t)}$, where [see §1.5 (4)]

$$s_x^{(t)} = \sin \theta_t, \quad s_y^{(t)} = 0, \quad s_z^{(t)} = \cos \theta_t. \quad (2)$$

From (1) and (2) and §14.1 (15)

$$s_x^{(t)} = \sin \theta_t = \frac{\sin \theta_i}{n(1 + i\kappa)} = \frac{1 - i\kappa}{n(1 + \kappa^2)} \sin \theta_i, \quad (3a)$$

$$\begin{aligned} s_z^{(t)} &= \cos \theta_t = \sqrt{1 - \sin^2 \theta_t} \\ &= \sqrt{1 - \frac{(1 - \kappa^2)}{n^2(1 + \kappa^2)^2} \sin^2 \theta_i + i \frac{2\kappa}{n^2(1 + \kappa^2)^2} \sin^2 \theta_i}. \end{aligned} \quad (3b)$$

It is convenient to express $s_z^{(t)}$ in the form

$$s_z^{(t)} = \cos \theta_t = q e^{i\gamma} \quad (4)$$

(q, γ real). Expressions for q and γ in terms of n, κ and $\sin \theta_i$ are immediately obtained on squaring (3b) and (4) and equating real and imaginary parts. This gives

$$\left. \begin{aligned} q^2 \cos 2\gamma &= 1 - \frac{1 - \kappa^2}{n^2(1 + \kappa^2)^2} \sin^2 \theta_i, \\ q^2 \sin 2\gamma &= \frac{2\kappa}{n^2(1 + \kappa^2)^2} \sin^2 \theta_i. \end{aligned} \right\} \quad (5)$$

It follows that

$$\begin{aligned} \hat{k}\mathbf{r} \cdot \mathbf{s}^{(t)} &= \frac{\omega}{c} n(1 + i\kappa)(x s_x^{(t)} + z s_z^{(t)}) \\ &= \frac{\omega}{c} n(1 + i\kappa) \left[\frac{x(1 - i\kappa)}{n(1 + \kappa^2)} \sin \theta_i + z(q \cos \gamma + iq \sin \gamma) \right] \\ &= \frac{\omega}{c} [x \sin \theta_i + znq(\cos \gamma - \kappa \sin \gamma) + inzq(\kappa \cos \gamma + \sin \gamma)]. \end{aligned} \quad (6)$$

We see that the surfaces of constant amplitude are given by

$$z = \text{constant}, \quad (7)$$

and are, therefore, planes parallel to the boundary. The surfaces of constant real phase are given by

$$x \sin \theta_i + znq(\cos \gamma - \kappa \sin \gamma) = \text{constant}, \quad (8)$$

and are planes whose normals make an angle θ'_i with the normal to the boundary, where

$$\left. \begin{aligned} \cos \theta'_i &= \frac{nq(\cos \gamma - \kappa \sin \gamma)}{\sqrt{\sin^2 \theta_i + n^2 q^2 (\cos \gamma - \kappa \sin \gamma)^2}}, \\ \sin \theta'_i &= \frac{\sin \theta_i}{\sqrt{\sin^2 \theta_i + n^2 q^2 (\cos \gamma - \kappa \sin \gamma)^2}}. \end{aligned} \right\} \quad (9)$$

Since the surfaces of constant amplitude and the surfaces of constant phase do not in general coincide with each other, the wave in the metal is an *inhomogeneous wave*.

If we denote the square root in (9) by n' , the equation for $\sin \theta'_i$ may be written in the form $\sin \theta'_i = \sin \theta_i / n'$, i.e. it has the form of Snell's law. However, n' depends now not only on the quantities that specify the medium, but also on the angle of incidence θ_i .

We may also derive expressions for the amplitude and the phase of the refracted and reflected waves by substituting for θ_t the complex value given by (1) in the Fresnel formulae (§1.5.2). The explicit expressions will be given in §14.4.1 in connection with the theory of stratified conducting media. Here we shall consider how the optical constants of the metal may be deduced from observation of the reflected wave.

Since we assumed that the first medium is a dielectric, the reflected wave is an ordinary (homogeneous) wave with a real phase factor. As in §1.5 (21a) the amplitude components A_{\parallel} , A_{\perp} of the incident wave and the corresponding components R_{\parallel} , R_{\perp} of the reflected wave are related by

$$\left. \begin{aligned} R_{\parallel} &= \frac{\tan(\theta_i - \theta_t)}{\tan(\theta_i + \theta_t)} A_{\parallel}, \\ R_{\perp} &= -\frac{\sin(\theta_i - \theta_t)}{\sin(\theta_i + \theta_t)} A_{\perp}. \end{aligned} \right\} \quad (10)$$

Since θ_t is now complex, so are the ratios $R_{\parallel}/A_{\parallel}$ and R_{\perp}/A_{\perp} , i.e. characteristic phase changes occur on reflection; thus incident linearly polarized light will in general become elliptically polarized on reflection at the metal surface. Let ϕ_{\parallel} and ϕ_{\perp} be the phase changes, and ρ_{\parallel} and ρ_{\perp} the absolute values of the reflection coefficients, i.e.

$$r_{\parallel} = \frac{R_{\parallel}}{A_{\parallel}} = \rho_{\parallel} e^{i\phi_{\parallel}}, \quad r_{\perp} = \frac{R_{\perp}}{A_{\perp}} = \rho_{\perp} e^{i\phi_{\perp}}. \quad (11)$$

Suppose that the incident light is *linearly polarized* in the azimuth α_i , i.e.

$$\tan \alpha_i = \frac{A_{\perp}}{A_{\parallel}}, \quad (12)$$

and let α_r be the azimuthal angle (generally complex) of the light that is reflected. Then*

* We write $-i\Delta$ rather than $+i\Delta$ in the exponent on the right-hand side of (13) to facilitate comparison with certain results of §1.5.

$$\tan \alpha_r = \frac{R_{\perp}}{R_{\parallel}} = -\frac{\cos(\theta_i - \theta_t)}{\cos(\theta_i + \theta_t)} \tan \alpha_i = P e^{-i\Delta} \tan \alpha_i, \quad (13)$$

where

$$P = \frac{\rho_{\perp}}{\rho_{\parallel}}, \quad \Delta = \phi_{\parallel} - \phi_{\perp}. \quad (14)$$

We note that α_r is real in the following two cases:

- (1) For normal incidence ($\theta_i = 0$); then $P = 1$ and $\Delta = -\pi$, so that $\tan \alpha_r = -\tan \alpha_i$.
- (2) For grazing incidence ($\theta_i = \pi/2$); then $P = 1$ and $\Delta = 0$, so that $\tan \alpha_r = \tan \alpha_i$.

It should be remembered that in the case of normal incidence the directions of the incident and reflected rays are opposed; thus the negative sign implies that the azimuth of the linearly polarized light is unchanged in its absolute direction in space. It is also unchanged in its absolute direction when the incidence is grazing.

Between the two extreme cases just considered, there exists an angle $\bar{\theta}_i$ called the *principal angle of incidence* which is such that $\Delta = -\pi/2$. At this angle of incidence, linearly polarized light is, in general, reflected as elliptically polarized light, but as may be seen from §1.4 (31b) (with $\delta = \pi/2$), the axes of the vibration ellipse are parallel and perpendicular to the plane of incidence. If, moreover, $P \tan \alpha_i = 1$, then according to (13) $\tan \alpha_r = -i$, and the reflected light is *circularly* polarized.

Suppose that with linearly polarized incident light an additional phase difference Δ is introduced between R_{\parallel} and R_{\perp} by means of a suitable compensator (see §15.4.2). The total phase difference is then zero, and, according to (13) the reflected light is linearly polarized in an azimuth α'_r such that

$$\tan \alpha'_r = P \tan \alpha_i. \quad (15)$$

The angle α'_r is, for obvious reasons, called *the angle of restored polarization*, though it is usually defined only with incident light that is *linearly polarized* in the azimuth* $\alpha_i = 45^\circ$. The values of α'_r and P relating to the principal angle of incidence $\theta_i = \bar{\theta}_i$ will be denoted by $\bar{\alpha}'_r$ and \bar{P} respectively. If we imagine a rectangle to be circumscribed around the vibration ellipse of the (uncompensated) reflected light obtained from light that is incident at the principal angle, with its sides parallel and perpendicular to the plane of incidence, then the sides are in the ratio $\bar{P} \tan \alpha_i$ and the angle between a diagonal and the plane of incidence is $\bar{\alpha}'_r$ (see Fig. 14.1).

For the purpose of later calculations it is useful to introduce an angle ψ such that

$$\tan \psi = P; \quad (16)$$

the value of ψ corresponding to the principal angle of incidence will be denoted by $\bar{\psi}$.

Using (10) and (1) we can compute the quantities $P (= \tan \psi)$ and Δ in terms of θ_i , if the constants n and κ of the metal are known. Fig. 14.2(a) shows their dependence on θ_i in a typical case. In Fig. 14.2(b) analogous curves relating to reflection from a transparent dielectric are displayed for comparison. The sudden discontinuity from $-\pi$ to 0 in the value of Δ which occurs when light is reflected from a transparent dielectric

* Then α'_r is equal to the angle ψ introduced in (16).

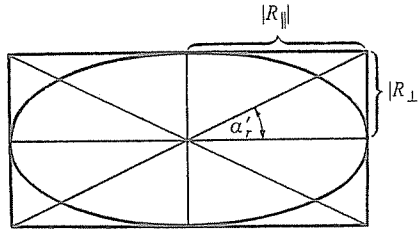


Fig. 14.1 Vibration ellipse of light reflected from a metal at the principal angle of incidence.

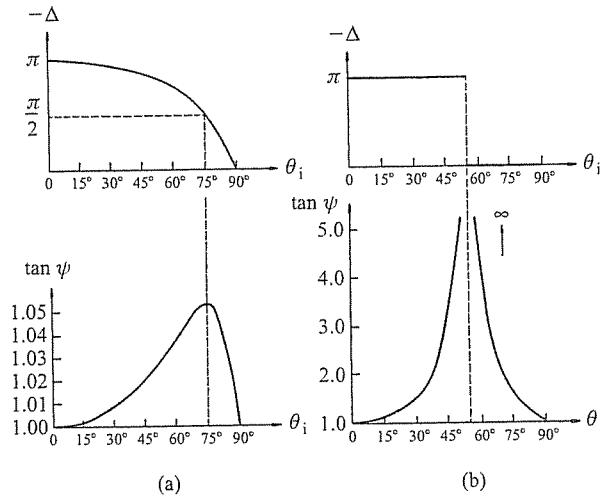


Fig. 14.2 The quantities $-\Delta = \phi_{\perp} - \phi_{\parallel}$ and $P = \tan \psi = \rho_{\perp}/\rho_{\parallel}$, which characterize the change in the state of polarization of light on reflection from a typical metal surface (a) and from a transparent dielectric (b).

at the polarizing angle is absent when light is reflected from a metal surface. The sharp cusp when $\tan \psi$ becomes infinite is likewise absent, and the curve is replaced by a smooth curve with a comparatively broad maximum. The angle of incidence at which this maximum occurs is sometimes called the *quasi-polarizing angle*; it is nearly equal to the principal angle of incidence $\bar{\theta}_i$. It is commonly assumed that this maximum is actually at $\bar{\theta}_i$, which is almost exactly true if $n^2(1 + \kappa^2) \gg 1$, as is usually the case (cf. Table 7.3). In general the two angles are, however, different; for example, in the case of silver at the ultra-violet wavelength 3280 Å; the quantity $n^2(1 + \kappa^2)$ is small; then $\bar{\theta}_i = 47.8^\circ$ and $\psi = 31.8^\circ$, whereas $\psi_{\max} = 29.5^\circ$ and occurs at $\theta_i = 40^\circ$, approximately.

Generally speaking the problem is not to find ψ and Δ from known values of n and κ , but to determine n and κ from experimental observations of the amplitude and phase of light reflected from the metal.

As the quantities R_{\parallel} , R_{\perp} , ϕ_{\parallel} , ϕ_{\perp} , ψ and Δ are all functions of θ_i , and of n and κ , measurement of any two of these quantities for a specific value of the angle of

incidence θ_i will in general permit the evaluation of n and κ . Since in many experiments one determines the last two of these quantities, we shall derive the fundamental expressions for n and κ in terms of ψ and Δ . From (13) and (1)

$$\frac{1 - Pe^{-i\Delta}}{1 + Pe^{-i\Delta}} = -\frac{\cos \theta_i \cos \theta_t}{\sin \theta_i \sin \theta_t} = -\frac{\sqrt{\hat{n}^2 - \sin^2 \theta_i}}{\sin \theta_i \tan \theta_i}. \quad (17)$$

Since $P = \tan \psi$, the left-hand side of (17) may be expressed in the form

$$\frac{1 - Pe^{-i\Delta}}{1 + Pe^{-i\Delta}} = \frac{1 - e^{-i\Delta} \tan \psi}{1 + e^{-i\Delta} \tan \psi} = \frac{\cos 2\psi + i \sin 2\psi \sin \Delta}{1 + \sin 2\psi \cos \Delta}. \quad (18)$$

From (17) and (18),

$$\frac{\sqrt{\hat{n}^2 - \sin^2 \theta_i}}{\sin \theta_i \tan \theta_i} = -\frac{\cos 2\psi + i \sin 2\psi \sin \Delta}{1 + \sin 2\psi \cos \Delta}. \quad (19)$$

Now if, as is usually the case in the visible region,

$$n^2(1 + \kappa^2) \gg 1, \quad (20)$$

$\sin^2 \theta_i$ may be neglected in comparison with \hat{n}^2 and we obtain

$$\frac{\hat{n}}{\sin \theta_i \tan \theta_i} = \frac{n(1 + i\kappa)}{\sin \theta_i \tan \theta_i} \sim -\frac{\cos 2\psi + i \sin 2\psi \sin \Delta}{1 + \sin 2\psi \cos \Delta}. \quad (21)$$

Equating the real parts, we obtain

$$n \sim -\frac{\sin \theta_i \tan \theta_i \cos 2\psi}{1 + \sin 2\psi \cos \Delta}. \quad (22a)$$

Equating the imaginary parts and using (22a) we find that

$$\kappa \sim \tan 2\psi \sin \Delta. \quad (22b)$$

These expressions permit the calculation of the optical constants n and κ from measurements of ψ and Δ at any angle of incidence. In the particular case of observation at the principal angle of incidence $\bar{\theta}_i$ one has $\Delta = -\pi/2$, $\psi = \bar{\psi}$ and (22a) and (22b) reduce to

$$n \sim -\sin \bar{\theta}_i \tan \bar{\theta}_i \cos 2\bar{\psi}, \quad (23a)$$

$$\kappa \sim -\tan 2\bar{\psi}. \quad (23b)$$

Other formulae relating to n and κ are sometimes useful. Without assuming (20) we have, on squaring (19),

$$\frac{\hat{n}^2 - \sin^2 \theta_i}{\sin^2 \theta_i \tan^2 \theta_i} = \frac{\cos^2 2\psi - \sin^2 2\psi \sin^2 \Delta + i \sin 4\psi \sin \Delta}{(1 + \sin 2\psi \cos \Delta)^2}. \quad (24)$$

If we substitute $\hat{n}^2 = n^2(1 - \kappa^2) + 2in^2\kappa$ and equate real and imaginary parts we obtain

$$n^2(1 - \kappa^2) = \sin^2 \theta_i \left[1 + \frac{\tan^2 \theta_i (\cos^2 2\psi - \sin^2 2\psi \sin^2 \Delta)}{(1 + \sin 2\psi \cos \Delta)^2} \right], \quad (25a)$$

$$2n^2\kappa = \frac{\sin^2 \theta_i \tan^2 \theta_i \sin 4\psi \sin \Delta}{(1 + \sin 2\psi \cos \Delta)^2}. \quad (25b)$$

In particular, at the principal angle of incidence ($\theta = \bar{\theta}_i$, $\Delta = -\pi/2$), these equations reduce to*

$$n^2(1 - \kappa^2) = \sin^2 \bar{\theta}_i (1 + \tan^2 \bar{\theta}_i \cos 4\bar{\psi}), \quad (26a)$$

$$2n^2\kappa = -\sin^2 \bar{\theta}_i \tan^2 \bar{\theta}_i \sin 4\bar{\psi}. \quad (26b)$$

The formulae (25) do not yield n and κ directly but in the combinations $n^2(1 - \kappa^2)$ and $n^2\kappa$. On reference to §14.1 (16) we see that these quantities have a direct physical significance. With $\mu = 1$ (as is always the case at optical wavelengths), $n^2(1 - \kappa^2)$ is the dielectric constant, and $n^2\kappa$ the ratio of the conductivity and the frequency. From the magnitude of these quantities, and particularly from their variation with frequency, information may be obtained about the structure of the metal (see §14.3 below).

So far our analysis has centred round the amplitudes of the components of the reflected light, but, as we shall see shortly, useful information may also be obtained from comparison of the intensity of the reflected light with that of the incident light, especially at long wavelengths. If we consider normal incidence ($\theta_i = 0$), the distinction between R_{\parallel} and R_{\perp} disappears, the plane of incidence then being undetermined, and we may write

$$\mathcal{R} = \left| \frac{R_{\parallel}}{A_{\parallel}} \right|^2 = \left| \frac{R_{\perp}}{A_{\perp}} \right|^2. \quad (27)$$

If we substitute from (1) and (10) (or if we replace n by \hat{n} in §1.5 (23)), we obtain

$$\mathcal{R} = \left| \frac{\hat{n} - 1}{\hat{n} + 1} \right|^2 = \frac{n^2(1 + \kappa^2) + 1 - 2n}{n^2(1 + \kappa^2) + 1 + 2n}. \quad (28)$$

The optical constants of many metals have been determined from measurements of reflected light. In Table 14.2 values of the constants as found by various observers are given for a wavelength in the yellow region of the visible spectrum. The metals are arranged in order of their reflectivity \mathcal{R} . We note that in all cases $n < n\kappa$ so that according to §14.1 (16a) $\mu\varepsilon$ and consequently (since $\mu \sim 1$ at optical wavelengths) ε is negative. At first sight it might appear that no physical significance can be attached to a negative dielectric constant. We shall see later that this is not the case and that the negative value of ε can be explained from certain simple assumptions concerning the electron mechanism of conductivity. From the table it would appear that values† $n < 1$ are associated with high reflectivity but in general this is not the case.

* Equations such as (23) and (26), which involve measurements only at the principal angle of incidence, are simpler than the more general expressions (22) or (25), and for this reason alone many experimenters have restricted themselves to measurements at this angle. At other angles of incidence experimental accuracy may be greater. Convenient choice of the angle of incidence is discussed in P. Drude, *Ann. d. Physik*, **39** (1890), 504; J. R. Collins and R. O. Bock, *Rev. Sci. Instr.*, **14** (1943), 135; I. Simon, *J. Opt. Soc. Amer.*, **41** (1951), 336; D. G. Avery, *Proc. Phys. Soc.*, **65** (1952), 425; R. W. Ditchburn, *J. Opt. Soc. Amer.*, **45** (1955), 743.

† When $n < 1$, the real phase velocity c/n exceeds the velocity of light in vacuum, but as explained at the end of §1.3.3 this is not in contradiction with the theory of relativity.

Table 14.2. *The optical constants of metals, for light of wavelength $\lambda = 5893 \text{ \AA}$ (sodium D lines).*

Metal	n	$n\kappa$	\mathcal{R}	Observer	
Sodium, solid	0.044	2.42	0.97	Duncan	1913
Silver, massive	0.20	3.44	0.94	Oppitz	1917
Magnesium, massive	0.37	4.42	0.93	Drude	1890
Potassium, molten	0.084	1.81	0.92	Nathanson	1928
Cadmium, massive	1.13	5.01	0.84	Drude	1890
Aluminium, massive	1.44	5.23	0.83	Drude	1890
Tin, massive	1.48	5.25	0.83	Drude	1890
Gold, electrolytic	0.47	2.83	0.82	Meier	1910
Mercury, liquid	1.60	4.80	0.77	Lowery and Moore	1932
Zinc, massive	1.93	4.66	0.75	Meier	1910
Copper, massive	0.62	2.57	0.73	Oppitz	1917
Gallium, single crystal	3.69	5.43	0.71	Lange	1935
Antimony, massive	3.04	4.94	0.70	Drude	1890
Cobalt, massive	2.12	4.04	0.68	Minor	1904
Nickel, electrolytic	1.58	3.42	0.66	Meier	1910
Manganese, massive	2.41	3.88	0.64	Littleton	1911
Lead, massive	2.01	3.48	0.62	Drude	1890
Platinum, electrolytic	2.63	3.54	0.59	Meier	1910
Rhenium, massive	3.00	3.44	0.57	Lange	1935
Tungsten, massive	3.46	3.25	0.54	Littleton	1912
Bismuth, massive	1.78	2.80	0.54	Meier	1910
Iron, evaporated	1.51	1.63	0.33	Meier	1910

Condensed from H. H. Landolt and R. Börnstein, *Phys. Chem. Tabellen*, (5 Aufl., Berlin, 1923; 1-3 Ergänzungsbd, Berlin, 1927-1936).

The values of n and $n\kappa$ displayed in Table 14.2 cannot be expected to be in agreement with calculations based on the approximate formulae §14.1 (17). These formulae were derived on the assumption that the conductivity σ is real and as we will see in §14.3 this assumption is fulfilled to a good approximation only at low frequencies. It will become clear from the considerations of §14.3 where we examine the frequency dependence of σ from an elementary model, that at the high frequencies ($\omega \sim 3.2 \times 10^{15} \text{ s}^{-1}$) corresponding to the sodium D lines, to which Table 14.2 refers, σ is complex, and its imaginary part is, in fact, appreciably larger than its real part. Indeed the dependence of the optical constants of metals on the wavelength, determined from experiments, shows a much more complicated behaviour than our formulae predict (see Fig. 14.3).

It appears from investigations of Hagen and Rubens* and subsequent workers that the reflectivity of many metals, calculated from the elementary theory that we outlined and with σ approximated by its static value, is in good agreement with results of experiments, provided the wavelength of the radiation λ is not shorter than about 10^{-3} cm . If we substitute for n and $n\kappa$ from §14.1 (24), (28) becomes (taking $\mu = 1$),

* E. Hagen and H. Rubens, *Ann. d. Physik* (4), 11 (1903), 873.

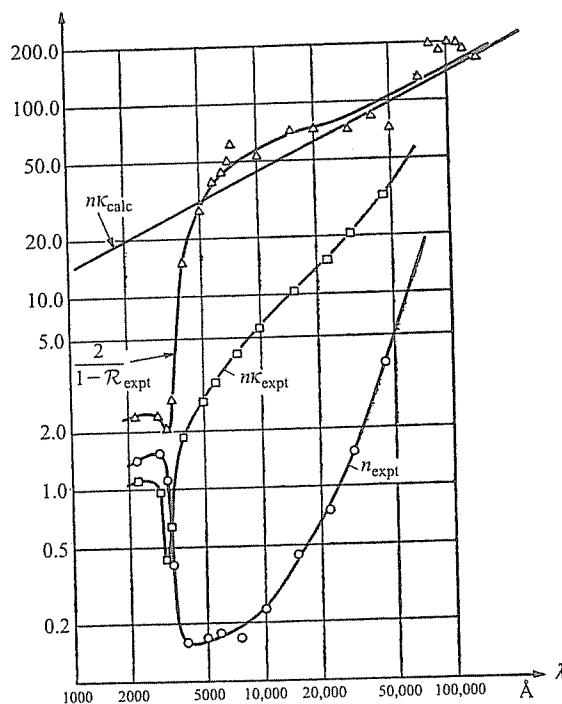


Fig. 14.3 The optical constants of silver as functions of the wavelength. Subscript 'expt' refers to data obtained from experiment. The scales are logarithmic.

$$\mathcal{R} = \frac{2\frac{\sigma}{\nu} + 1 - 2\sqrt{\frac{\sigma}{\nu}}}{2\frac{\sigma}{\nu} + 1 + 2\sqrt{\frac{\sigma}{\nu}}}. \quad (29)$$

When ν/σ is sufficiently small, we may neglect 1 in comparison with the other terms and may develop (29) in powers of $\sqrt{\nu/\sigma}$. We then obtain

$$\mathcal{R} \sim 1 - 2\sqrt{\frac{\nu}{\sigma}} + \dots \quad (30)$$

Hagen and Rubens found that, at wavelength $\lambda = 1.2 \times 10^{-3}$ cm, one has for copper $1 - \mathcal{R} = 1.6 \times 10^{-2}$, whilst on substituting for σ the static value of the conductivity, (30) gives $1 - \mathcal{R} = 1.4 \times 10^{-2}$.

As the wavelength is increased further, \mathcal{R} becomes so nearly equal to unity that it is difficult to measure $1 - \mathcal{R}$ with any accuracy. Hagen and Rubens obtained, however, useful estimates by an indirect method. According to *Kirchhoff's law* of heat radiation* the ratio of the emissive power E_ν to the absorptive power A_ν of a body† depends only

* See, for example, M. Planck, *Theory of Heat* (London, Macmillan, 1932), p. 189; or A. Sommerfeld, *Thermodynamics and Statistical Mechanics*, eds. F. Bopp and J. Meixner (New York, Academic Press, 1956), p. 136.

† By emissive power is meant the radiant energy emitted by the body per unit time, by absorptive power the fraction which the body absorbs of the radiant energy which falls upon it.

on the frequency ν and on the temperature T of the body and not on the nature of the body, i.e.

$$\frac{E_\nu}{A_\nu} = K(\nu, T), \quad (31)$$

where $K(\nu, T)$ is a universal function of ν and T . Evidently K is equal to the emissive power of a body whose absorptive power is unity, a so-called *black body*. Now suppose that radiation falls on a metal specimen of such a thickness that all the incident energy that is not reflected is absorbed in its interior. Then

$$A_\nu = 1 - \mathcal{R}, \quad (32)$$

and from (30), (31) and (32)

$$A_\nu = \frac{E_\nu}{K(\nu, T)} = 2\sqrt{\frac{\nu}{\sigma}}, \quad (33)$$

or

$$\sqrt{\sigma} E_\nu = 2\sqrt{\nu} K(\nu, T). \quad (34)$$

The right-hand side of this equation is independent of the nature of the metal. It is a well-known function of ν and T , the function $K(\nu, T)$ being precisely known both from experiment and theory, and represented by the celebrated formula of Planck.*

It follows that the validity of the formula (30) may be tested even when \mathcal{R} is very close to unity by determining the conductivity σ and the emissive power E_ν as functions of the frequency and temperature and examining whether the product $\sqrt{\sigma} E_\nu$ satisfies (34). Hagen and Rubens confirmed that this is so at long infra-red wavelengths, using for this purpose the so-called *residual rays*. These are rays left over from a wider spectral range after repeated reflections from certain crystals, e.g. fluorite, rock-salt or sylvine. These substances have pronounced absorption maxima in the spectral region $\lambda = 22.9 \mu\text{m}$ to $63 \mu\text{m}$, and hence [see (28)] highly selective reflectivity for such wavelengths.

In Fig. 14.3 curves are given, illustrating, for the case of silver, the dependence of n and $n\kappa$ on the wavelength, as determined from experiment. For comparison the theoretical curve computed from the formula §14.1 (24) is also shown. The scales are logarithmic so that the theoretical curve is the straight line

$$\ln n \sim \ln n\kappa \sim \frac{1}{2} \ln \lambda + C,$$

where $C = \ln \sqrt{\mu\sigma/c}$. From §14.1 (24) and from (30) we may also express n and $n\kappa$ in terms of the reflectivity (for long waves):

$$n \sim n\kappa \sim \frac{2}{1 - \mathcal{R}}. \quad (35)$$

The function $2/(1 - \mathcal{R})$ is also displayed in the figure for comparison. We see that the experimental curve for $n\kappa$ has a sharp minimum near $\lambda = 3000 \text{ \AA}$ and that the curve for n has a much flatter minimum near $\lambda = 5000 \text{ \AA}$. At about $\lambda = 3300 \text{ \AA}$ the reflectivity of the silver is seen to be very poor.

* See, for example, M. Born, *Atomic Physics* (London and Glasgow, Blackie and Son, 5th ed., 1951), p. 238.

With increasing wavelength the experimental curves approach the theoretical curve calculated from the conductivity measured electrically.

14.3 Elementary electron theory of the optical constants of metals

We pointed out in the previous sections that the conductivity σ , just as the dielectric constant ϵ and the magnetic permeability μ , is not a true constant of the medium, but that it depends on the frequency ω of the field. We will now present a rough, simple model (due to P. Drude) from which the frequency dependence of σ may be derived, at least for sufficiently low frequencies.

Let us recall first that the response of a dielectric medium to an external electromagnetic field is largely determined by the behaviour of electrons that are bound to the atomic nuclei by quasi-elastic forces (see §2.3.4). In a conducting medium (such as a metal), unlike in a dielectric, not all the electrons are bound to the atoms. Some move between the molecules and are said to be *free* electrons, to distinguish them from the other electrons that are bound to the atoms, just as in a dielectric. In the absence of an external electromagnetic field, the free electrons move in a random manner and hence they do not give rise to a net current flow. When an external field is applied the free electrons acquire an additional velocity and their motion becomes more orderly, even though occasionally the electrons still collide with the (essentially stationary) atoms. This more orderly motion of the electrons gives rise to the induced current flow.

We cannot enter into a detailed discussion of this process which has to be treated by means of statistical methods of the kinetic theory of gases. The very plausible result is that the averaged total effect is the same as that of a damping force proportional and opposite in direction to the velocity of a model electron that represents the average behaviour of the whole set of electrons. The equation of motion of this model electron in an electric field \mathbf{E} is, therefore,

$$m\ddot{\mathbf{r}} + m\beta\dot{\mathbf{r}} = e\mathbf{E}, \quad (1)$$

where m is the mass, e the charge of the electron and β the damping constant referred to unit mass. Unlike the equation of motion for a bound electron [§2.3 (33)] which contains on the right-hand side an 'effective field' \mathbf{E}' , (1) contains on the right-hand side the macroscopic electric field \mathbf{E} , which is believed to represent more closely the field that acts on a free electron in a conductor.

In order to understand the meaning of the damping constant β in (1), consider first the case where no electric field is present. If $\mathbf{E} = 0$, we have

$$\ddot{\mathbf{r}} + \beta\dot{\mathbf{r}} = 0, \quad (2)$$

with the solution

$$\mathbf{r} = \mathbf{r}_0 - \frac{1}{\beta}\mathbf{v}_0 e^{-\beta t}, \quad \dot{\mathbf{r}} = \mathbf{v} = \mathbf{v}_0 e^{-\beta t}, \quad (3)$$

we see that in this case the model electron starting with the velocity \mathbf{v}_0 is slowed down in an exponential way, with β as decay constant. The time $\tau = 1/\beta$ is called the *decay time*, or the *relaxation time*. It is typically of the order of 10^{-14} s.

Let us now assume a time-harmonic field $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$. The solution of (1) is then

the sum of two terms, one representing the decaying motion [solution of the homogeneous equation (2)] and the other representing a periodic motion

$$\mathbf{r} = -\frac{e}{m(\omega^2 + i\beta\omega)}\mathbf{E}. \quad (4)$$

This periodic motion gives rise to a current in the medium. If there are N free electrons per unit volume, the current density \mathbf{j} is given by

$$\mathbf{j} = Ne\dot{\mathbf{r}} = \frac{Ne^2}{m(\beta - i\omega)}\mathbf{E}. \quad (5)$$

Comparing (5) with the constitutive relation §1.1 (9), viz. $\mathbf{j} = \sigma\mathbf{E}$, we see that

$$\sigma = \frac{Ne^2}{m(\beta - i\omega)}. \quad (6)$$

As we have already mentioned, τ is typically of the order of 10^{-14} s, so that β is then of the order 10^{14} s $^{-1}$. It is thus clear, from (6), that when $\omega \ll \beta$, σ may be approximated by its static value $\sigma_0 = Ne^2/m\beta$ which, of course, is real. On the other hand, when $\omega \gg \beta$ (which is usually the case at optical frequencies), the imaginary part of σ will become large compared to its real part. It is, therefore, evident that only for frequencies $\omega \ll \beta$ is one justified in separating the real and imaginary parts of the complex dielectric constant in the manner that leads to the formulae §14.1 (16) and §14.1 (17).

According to §14.1 (16), the frequency dependence of the complex dielectric constant $\hat{\epsilon}$ and of the complex refractive index \hat{n} arises from the dependence on frequency not only of the conductivity σ (contribution from free electrons), but also of the real dielectric constant ϵ (contribution from bound electrons). At low enough frequencies the contribution from the bound electrons may be shown to be small compared to the contribution from the free electrons. Under these circumstances we may replace ϵ by unity and σ by the expression (6) in §14.1 (16). We then obtain, if we assume the conductor to be nonmagnetic ($\mu = 1$), the following expression for $\hat{\epsilon}$:

$$\hat{\epsilon} \equiv \hat{n}^2 = 1 - \frac{4\pi Ne^2}{m} \frac{1}{\omega(\omega - i\beta)}. \quad (7)$$

On separating the real and imaginary parts in (7), and on making use of §14.1 (15a), viz. $\hat{n}^2 = n^2(1 + 2i\kappa - \kappa^2)$, we obtain the formulae

$$\text{Re } \hat{\epsilon} \equiv n^2(1 - \kappa^2) = 1 - \frac{4\pi Ne^2}{m(\omega^2 + \beta^2)}, \quad (8a)$$

$$\text{Im } \hat{\epsilon} \equiv n^2\kappa = \frac{2\pi Ne^2/\beta}{m\omega(\omega^2 + \beta^2)}. \quad (8b)$$

We may readily deduce from (8a), that if β is sufficiently small, the real part of $\hat{\epsilon}$ is negative for low enough frequencies, but is evidently positive when ω is large. The critical value ω_c of the frequency at which the real part of $\hat{\epsilon}$ changes sign is given by

$$\omega_c^2 = \frac{4\pi Ne^2}{m} - \beta^2. \quad (9)$$

We may re-write (8) in terms of this critical value and obtain

$$\operatorname{Re} \hat{\epsilon} \equiv n^2(1 - \kappa^2) = 1 - \frac{\omega_c^2 + \beta^2}{\omega^2 + \beta^2}, \quad (10a)$$

$$\operatorname{Im} \hat{\epsilon} \equiv n^2\kappa = \frac{\beta(\omega_c^2 + \beta^2)}{2\omega(\omega^2 + \beta^2)}. \quad (10b)$$

We shall now assume that ω_c^2 is much larger than β^2 , so that in place of (9) we may write

$$\omega_c^2 \sim \frac{4\pi Ne^2}{m}. \quad (11)$$

If we also restrict ourselves to sufficiently high frequencies ($\omega^2 \gg \beta^2$), we obtain, in place of (10), the simpler formulae

$$\operatorname{Re} \hat{\epsilon} \equiv n^2(1 - \kappa^2) \sim 1 - \left(\frac{\omega_c}{\omega}\right)^2, \quad (12a)$$

$$\operatorname{Im} \hat{\epsilon} \equiv n^2\kappa \sim \frac{\beta}{2\omega} \left(\frac{\omega_c}{\omega}\right)^2. \quad (12b)$$

It follows from (12a) that when $\omega^2 < \omega_c^2$ (but still $\omega^2 \gg \beta^2$), the real part of $\hat{\epsilon}$ is negative and $\kappa > 1$. The negative value of the real part of $\hat{\epsilon}$ reflects the fact that under these circumstances the vibrations of the electrons are out of phase by a quarter of a period with the exciting field, as is evident from (5). For sufficiently low values of ω , the attenuation index κ becomes large compared to unity and the reflectivity [given for normal incidence by §14.2 (28)] is readily seen to have a value close to unity. On the other hand, when $\omega^2 > \omega_c^2$ (but $\omega^2 \gg \beta^2$), the real part of $\hat{\epsilon}$ is evidently positive, so that $\kappa < 1$, and, when ω is sufficiently large, κ becomes small compared to unity and the imaginary part of $\hat{\epsilon}$ becomes small compared to its real part. The metal must then be expected to behave essentially as a dielectric.

The alkali metals exhibit precisely these phenomena, for in the long wavelength region they are opaque and highly reflecting, whereas at some critical wavelength in the visible or ultra-violet they become transparent, and have comparatively low absorption. Table 14.3 shows in the second row the experimentally determined wavelengths at which this transition occurs. The third row contains these critical wavelengths $\lambda_c = 2\pi c/\omega_c$ determined from the approximate formula (11), where the number of free electrons is taken to be the same as the number N of atoms in the unit volume. It is seen that the values in the two rows are different, except for sodium. The last row gives the ratio of number N_{eff} of electrons that are 'effective' and the number of atoms, determined from the formula

$$\frac{N_{\text{eff}}}{N} = \frac{(\lambda_c)_{\text{calc}}^2}{(\lambda_c)_{\text{obs}}^2}. \quad (13)$$

It is seen that this number is of the order of unity though (except for sodium) considerably smaller. Thus the elementary theory gives the correct order of magnitude of the parameters, but does not describe the phenomena in detail.

The theory can be somewhat improved by using in place of the crude approximations (12) the more accurate formulae (10), which contain the decay constant β . However, because of the complexity of the physical processes involved in the inter-

Table 14.3. *The critical wavelengths λ_c below which the alkali metals become transparent, and above which they are opaque and highly reflecting.*

Metal	Lithium	Sodium	Potassium	Rubidium	Cesium
$(\lambda_c)_{\text{obs}}$	2050 Å	2100 Å	3150 Å	3600 Å	4400 Å
$(\lambda_c)_{\text{calc}}$	1500 Å	2100 Å	2900 Å	3200 Å	3600 Å
$\frac{N_{\text{eff}}}{N}$	0.54	1.00	0.85	0.79	0.67

action of a high-frequency electromagnetic field with a metal, it is not possible to extend appreciably the range of validity of the elementary classical theory that we outlined in this section by a simple modification. A completely satisfactory theory of the optical properties of metals can only be obtained on the basis of quantum mechanics.

14.4 Wave propagation in a stratified conducting medium. Theory of metallic films

In §1.6 we have studied the propagation of electromagnetic waves in stratified dielectric media, that is, in dielectric media with optical properties depending on one Cartesian coordinate only. We shall now briefly discuss the extension of the theory to stratified media that contain absorbing elements. Thus we assume that in addition to ϵ and μ being functions of only one coordinate, there may be a finite conductivity σ which likewise is a function of this coordinate alone.

As explained at the beginning of §14.2, the formulae of Chapter I as far as they involve only linear relations between the components of the field vectors of a time-harmonic wave retain their validity for conducting media, provided that the real dielectric constant ϵ and the real wave number k are replaced by the complex dielectric constant $\hat{\epsilon} = \epsilon + i4\pi\sigma/\omega$ and by the complex wave number $\hat{k} = \omega\sqrt{\mu(\epsilon + i4\pi\sigma/\omega)}/c$, respectively. Hence we may take over the basic formulae of the theory of stratified dielectric media as developed in §1.6, provided we make this formal change in the appropriate formulae. It follows, in particular, that a stratified absorbing medium may be characterized by a two-by-two matrix. In contrast to the case of a dielectric stratified medium, the elements of this matrix are no longer real or pure imaginary numbers but are complex numbers that contain both real and imaginary parts.

We shall illustrate the theory by studying in detail two cases of practical interest.

14.4.1 An absorbing film on a transparent substrate

Consider a plane-parallel absorbing film situated between two dielectric media (Fig. 14.4). The formulae relating to the reflection and transmission of a plane monochromatic wave by the film are obtained from §1.6 (55)–(58) on replacing n_2 by $\hat{n}_2 = n_2(1 + i\kappa_2)$. It is convenient to set

$$\hat{n}_2 \cos \theta_2 = u_2 + iv_2, \quad (1)$$

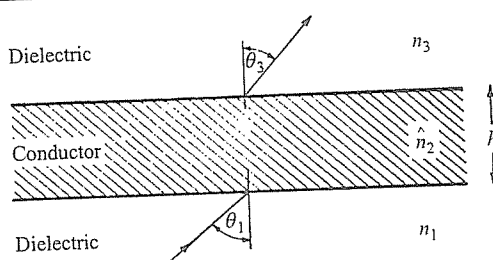


Fig. 14.4 An absorbing film situated between two dielectric media.

where u_2 and v_2 are real. We can easily express u_2 and v_2 in terms of the angle of incidence and the constants which characterize the optical properties of the first and the second medium. It follows, on squaring (1) and using the law of refraction $\hat{n}_2 \sin \theta_2 = n_1 \sin \theta_1$, that

$$(u_2 + iv_2)^2 = \hat{n}_2^2 - n_1^2 \sin^2 \theta_1. \quad (2)$$

On equating real and imaginary parts this gives

$$\left. \begin{aligned} u_2^2 - v_2^2 &= n_2^2(1 - \kappa_2^2) - n_1^2 \sin^2 \theta_1, \\ u_2 v_2 &= n_2^2 \kappa_2. \end{aligned} \right\} \quad (3)$$

From (3) we find that

$$\left. \begin{aligned} 2u_2^2 &= n_2^2(1 - \kappa_2^2) - n_1^2 \sin^2 \theta_1 + \sqrt{[n_2^2(1 - \kappa_2^2) - n_1^2 \sin^2 \theta_1]^2 + 4n_2^4 \kappa_2^2}, \\ 2v_2^2 &= -[n_2^2(1 - \kappa_2^2) - n_1^2 \sin^2 \theta_1] + \sqrt{[n_2^2(1 - \kappa_2^2) - n_1^2 \sin^2 \theta_1]^2 + 4n_2^4 \kappa_2^2}. \end{aligned} \right\} \quad (4)$$

Next we must evaluate the reflection and transmission coefficients for the interfaces 1-2 and 2-3 respectively, for these coefficients enter the formulae for the reflection and transmission coefficients of the film. We consider separately the cases when the electric vector of the incident wave is perpendicular, or parallel, to the plane of incidence.

Electric vector perpendicular to the plane of incidence (TE wave)

In this case we have, on replacing $n_2 \cos \theta_2$ by $\hat{n}_2 \cos \theta_2 = u_2 + iv_2$ in §1.6 (55),

$$r_{12} = \rho_{12} e^{i\phi_{12}} = \frac{n_1 \cos \theta_1 - (u_2 + iv_2)}{n_1 \cos \theta_1 + (u_2 + iv_2)}. \quad (5)$$

We shall later need explicit expressions for the amplitude ρ_{12} and the phase change ϕ_{12} . From (5) we have:

$$\rho_{12}^2 = \frac{(n_1 \cos \theta_1 - u_2)^2 + v_2^2}{(n_1 \cos \theta_1 + u_2)^2 + v_2^2}, \quad \tan \phi_{12} = \frac{2v_2 n_1 \cos \theta_1}{u_2^2 + v_2^2 - n_1^2 \cos^2 \theta_1}. \quad (6)$$

For transmission at the first interface, we have from §1.6 (56)

$$t_{12} = \tau_{12} e^{i\chi_{12}} = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + u_2 + i\nu_2}, \quad (7)$$

which gives

$$\tau_{12}^2 = \frac{(2n_1 \cos \theta_1)^2}{(n_1 \cos \theta_1 + u_2)^2 + \nu_2^2}, \quad \tan \chi_{12} = -\frac{\nu_2}{n_1 \cos \theta_1 + u_2}. \quad (8)$$

In a strictly analogous way we obtain the following expressions relating to reflection and transmission at the second interface:

$$\rho_{23}^2 = \frac{(n_3 \cos \theta_3 - u_2)^2 + \nu_2^2}{(n_3 \cos \theta_3 + u_2)^2 + \nu_2^2}, \quad \tan \phi_{23} = \frac{2\nu_2 n_3 \cos \theta_3}{u_2^2 + \nu_2^2 - n_3^2 \cos^2 \theta_3}, \quad (9)$$

$$\tau_{23}^2 = \frac{4(u_2^2 + \nu_2^2)}{(n_3 \cos \theta_3 + u_2)^2 + \nu_2^2}, \quad \tan \chi_{23} = \frac{\nu_2 n_3 \cos \theta_3}{u_2^2 + \nu_2^2 + u_2 n_3 \cos \theta_3}. \quad (10)$$

Since, according to the law of refraction $n_1 \sin \theta_1 = \hat{n}_2 \sin \theta_2$, $\hat{n}_2 \sin \theta_2 = n_3 \sin \theta_3$, the angle θ_3 is determined from θ_1 by means of the formula

$$n_3 \sin \theta_3 = n_1 \sin \theta_1. \quad (11)$$

Electric vector parallel to the plane of incidence (TM wave)

As explained in §1.6.3 the formulae for the reflection and transmission coefficients for a TM wave can be obtained from those for a TE wave simply by replacing the quantities $p_j = n_j \cos \theta_j$ by $q_j = \cos \theta_j / n_j$, it being assumed that the media are nonmagnetic. The quantities r and t now refer to the ratios of the magnetic, not the electric vectors. In particular we have from §1.6 (55),

$$\begin{aligned} r_{12} = \rho_{12} e^{i\phi_{12}} &= \frac{\frac{1}{n_1} \cos \theta_1 - \frac{1}{\hat{n}_2} \cos \theta_2}{\frac{1}{n_1} \cos \theta_1 + \frac{1}{\hat{n}_2} \cos \theta_2} = \frac{\hat{n}_2^2 \cos \theta_1 - n_1 \hat{n}_2 \cos \theta_2}{\hat{n}_2^2 \cos \theta_1 + n_1 \hat{n}_2 \cos \theta_2} \\ &= \frac{[n_2^2(1 - \kappa_2^2) + 2in_2^2\kappa_2] \cos \theta_1 - n_1(u_2 + i\nu_2)}{[n_2^2(1 - \kappa_2^2) + 2in_2^2\kappa_2] \cos \theta_1 + n_1(u_2 + i\nu_2)}. \end{aligned} \quad (12)$$

From (12) we find after a straightforward calculation

$$\left. \begin{aligned} \rho_{12}^2 &= \frac{[n_2^2(1 - \kappa_2^2) \cos \theta_1 - n_1 u_2]^2 + [2n_2^2 \kappa_2 \cos \theta_1 - n_1 \nu_2]^2}{[n_2^2(1 - \kappa_2^2) \cos \theta_1 + n_1 u_2]^2 + [2n_2^2 \kappa_2 \cos \theta_1 + n_1 \nu_2]^2}, \\ \tan \phi_{12} &= 2n_1 n_2^2 \cos \theta_1 \frac{2\kappa_2 u_2 - (1 - \kappa_2^2)\nu_2}{n_2^4(1 + \kappa_2^2)^2 \cos^2 \theta_1 - n_1^2(u_2^2 + \nu_2^2)}. \end{aligned} \right\} \quad (13)$$

For the ratio t_{12} we obtain from §1.6 (56) on replacing $n_j \cos \theta_j$ by $\cos \theta_j / n_j$,

$$t_{12} = \tau_{12} e^{i\chi_{12}} = \frac{\frac{2}{n_1} \cos \theta_1}{\frac{1}{n_1} \cos \theta_1 + \frac{1}{\hat{n}_2} \cos \theta_2} = \frac{2[n_2^2(1 - \kappa_2^2) + 2in_2^2\kappa_2] \cos \theta_1}{[n_2^2(1 - \kappa_2^2) + 2in_2^2\kappa_2] \cos \theta_1 + n_1(u_2 + iv_2)}. \quad (14)$$

From (14) we find that

$$\left. \begin{aligned} \tau_{12}^2 &= \frac{4n_2^4(1 + \kappa_2^2)^2 \cos^2 \theta_1}{[n_2^2(1 - \kappa_2^2) \cos \theta_1 + n_1 u_2]^2 + (2n_2^2 \kappa_2 \cos \theta_1 + n_1 v_2)^2}, \\ \tan \chi_{12} &= \frac{n_1 [2\kappa_2 u_2 - (1 - \kappa_2^2) v_2]}{n_2^2(1 + \kappa_2^2)^2 \cos \theta_1 + n_1 [(1 - \kappa_2^2) u_2 + 2\kappa_2 v_2]}. \end{aligned} \right\} \quad (15)$$

In a similar way we obtain the following formulae for the reflection and transmission coefficients relating to the second interface:

$$\left. \begin{aligned} \rho_{23}^2 &= \frac{[n_2^2(1 - \kappa_2^2) \cos \theta_3 - n_3 u_2]^2 + [2n_2^2 \kappa_2 \cos \theta_3 - n_3 v_2]^2}{[n_2^2(1 - \kappa_2^2) \cos \theta_3 + n_3 u_2]^2 + [2n_2^2 \kappa_2 \cos \theta_3 + n_3 v_2]^2}, \\ \tan \phi_{23} &= 2n_3 n_2^2 \cos \theta_3 \frac{2\kappa_2 u_2 - (1 - \kappa_2^2) v_2}{n_2^4(1 + \kappa_2^2)^2 \cos^2 \theta_3 - n_3^2(u_2^2 + v_2^2)}, \end{aligned} \right\} \quad (16)$$

and

$$\left. \begin{aligned} \tau_{23}^2 &= \frac{4n_3^2(u_2^2 + v_2^2)}{[n_3 u_2 + n_2^2(1 - \kappa_2^2) \cos \theta_3]^2 + (n_3 v_2 + 2n_2^2 \kappa_2 \cos \theta_3)^2}, \\ \tan \chi_{23} &= \frac{n_2^2 [(1 - \kappa_2^2)^2 v_2 - 2\kappa_2 u_2] \cos \theta_3}{n_3(u_2^2 + v_2^2) + n_2^2 [(1 - \kappa_2^2)^2 u_2 + 2\kappa_2 v_2] \cos \theta_3}. \end{aligned} \right\} \quad (17)$$

From the knowledge of the quantities ρ_{12} , ϕ_{12} , etc., the complex reflection and transmission coefficients of the film may immediately be evaluated. It will be useful to set

$$\eta = \frac{2\pi}{\lambda_0} h, \quad (18)$$

so that

$$\beta = \frac{2\pi}{\lambda_0} \hat{n}_2 h \cos \theta_2 = (u_2 + iv_2)\eta. \quad (19)$$

The equations §1.6 (57)–(58) now become

$$r = \rho e^{i\delta_r} = \frac{\rho_{12} e^{i\phi_{12}} + \rho_{23} e^{-2v_2\eta} e^{i(\phi_{23} + 2u_2\eta)}}{1 + \rho_{12}\rho_{23} e^{-2v_2\eta} e^{i(\phi_{12} + \phi_{23} + 2u_2\eta)}}, \quad (20)$$

$$t = \tau e^{i\delta_t} = \frac{\tau_{12}\tau_{23} e^{-v_2\eta} e^{i(\chi_{12} + \chi_{23} + u_2\eta)}}{1 + \rho_{12}\rho_{23} e^{-2v_2\eta} e^{i(\phi_{12} + \phi_{23} + 2u_2\eta)}}. \quad (21)$$

From (20) we obtain, after straightforward calculation, the following expressions for the reflectivity \mathcal{R} and for the phase change δ_r on reflection:

$$\mathcal{R} = |r|^2 = \frac{\rho_{12}^2 e^{2v_2\eta} + \rho_{23}^2 e^{-2v_2\eta} + 2\rho_{12}\rho_{23} \cos(\phi_{23} - \phi_{12} + 2u_2\eta)}{e^{2v_2\eta} + \rho_{12}^2 \rho_{23}^2 e^{-2v_2\eta} + 2\rho_{12}\rho_{23} \cos(\phi_{12} + \phi_{23} + 2u_2\eta)}, \quad (22)$$

$$\tan \delta_r = \frac{\rho_{23}(1 - \rho_{12}^2) \sin(2u_2\eta + \phi_{23}) + \rho_{12}(e^{2v_2\eta} - \rho_{23}^2 e^{-2v_2\eta}) \sin \phi_{12}}{\rho_{23}(1 + \rho_{12}^2) \cos(2u_2\eta + \phi_{23}) + \rho_{12}(e^{2v_2\eta} + \rho_{23}^2 e^{-2v_2\eta}) \cos \phi_{12}}. \quad (23)$$

These formulae are valid for a TE wave as well as for a TM wave. In the former case one must substitute for ρ and ϕ the values given by (6) and (9), in the latter case those given by (13) and (16).

In a similar way we obtain from (21) the following expressions for the transmissivity \mathcal{T} and for the phase change δ_t on transmission:

$$\mathcal{T} = \frac{n_3 \cos \theta_3}{n_1 \cos \theta_1} |t|^2 = \frac{n_3 \cos \theta_3}{n_1 \cos \theta_1} \frac{t_{12}^2 t_{23}^2 e^{-2v_2\eta}}{1 + \rho_{12}^2 \rho_{23}^2 e^{-4v_2\eta} + 2\rho_{12}\rho_{23} e^{-2v_2\eta} \cos(\phi_{12} + \phi_{23} + 2u_2\eta)}, \quad (24)$$

$$\tan[\delta_t - \chi_{12} - \chi_{23} + u_2\eta] = \frac{e^{2v_2\eta} \sin 2u_2\eta - \rho_{12}\rho_{23} \sin(\phi_{12} + \phi_{23})}{e^{2v_2\eta} \cos 2u_2\eta + \rho_{12}\rho_{23} \cos(\phi_{12} + \phi_{23})}. \quad (25)$$

For a TM wave the factor $n_3 \cos \theta_3 / n_1 \cos \theta_1$ must be replaced by $(\cos \theta_3 / n_3) / (\cos \theta_1 / n_1)$. For a TE wave the values given by (6), (8), (9) and (10) are substituted in these formulae, and for a TM wave those given by (13), (15), (16) and (17).

It may be worthwhile to recall that the phase change on reflection (δ_r) is referred to the first boundary (1-2), whereas the phase change on transmission (δ_t) is referred to the second boundary.

Eqs. (22)–(25) allow the computations of the four basic quantities that characterize reflection and transmission by an absorbing film of known optical properties and of prescribed thickness. Fig. 14.5 illustrates, for some typical cases, the dependence of the reflectivity and transmissivity on the thickness of the film.

For a nonabsorbing film \mathcal{R} and \mathcal{T} are periodic functions of the film thickness h , with a period of one wavelength. Absorption is seen to reduce the amplitude of the successive maxima and to give rise to a displacement of the maxima in the direction of smaller thickness. At optical wavelengths absorption of metals is so large that the thickness at which there is appreciable transmission is well below a quarter wavelength* (see Table 14.1, p. 739). With transmitted light maxima and minima are therefore not observed.

In optics, metal films are chiefly used to attain high reflectivities, for example in connection with the Fabry–Perot interferometer (§7.6.2). Such films used to be

* Simplified formulae relating to such thin films may be obtained by expanding the numerator and denominator (22)–(25) into series in powers of the film thickness, and retaining terms in the first few powers only (see F. Abelès, *Rev. d'Optique*, **32** (1953), 257).

The optical properties of thin metallic films in the visible and infra-red spectral region are thoroughly discussed by L. N. Hadley and D. M. Dennison, *J. Opt. Soc. Amer.*, **37** (1947), 451; **38** (1948), 483.

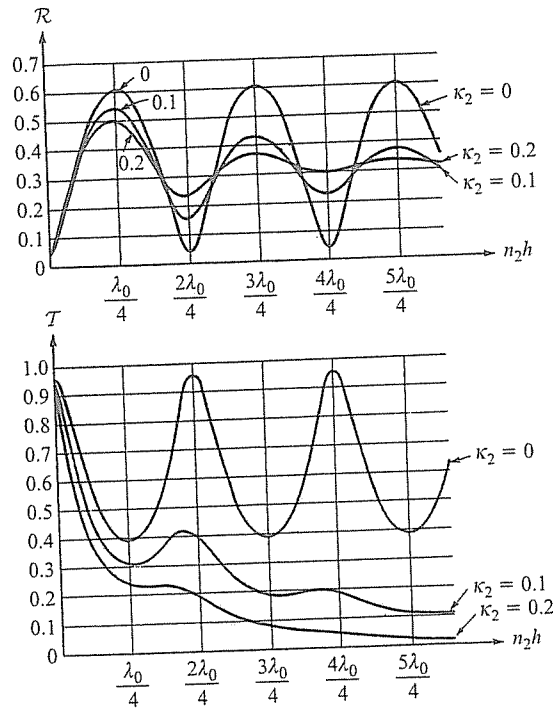


Fig. 14.5 The reflectivity \mathcal{R} and transmissivity \mathcal{T} of a metallic film as functions of its optical thickness. [$n_1 = 1, n_2 = 3.5, n_3 = 1.5, \kappa_1 = \kappa_3 = 0; \theta_1 = 0.$] (After K. Hammer, *Z. Tech. Phys.*, 24 (1943), 169.)

produced by chemical deposition but this method has in more recent times been superseded by the techniques of high-vacuum evaporation.*

Finally let us briefly consider reflection and transmission with a ‘thick’ film. If the thickness h and consequently the parameter η are sufficiently large all the terms in (22)–(25) which do not contain the multiplicative factor $\exp(2v_2\eta)$ may be neglected. For example, if $\exp(2v_2\eta) \geq 100$ this neglect does not, as a rule, involve an error of more than a few per cent. For such a film, one has at normal incidence $4\pi hn_2\kappa_2/\lambda \geq \ln 100 = 4.61$, or (dropping the suffix 2),

$$\frac{h}{\lambda} \geq \frac{0.37}{n\kappa}. \tag{26}$$

For a silver film, for example, $n\kappa \sim 3.67$ at $\lambda = 5780 \text{ \AA}$, and (26) gives $h \geq \lambda/10 \sim 5.8 \times 10^{-6} \text{ cm}$.

For a thick film, we have from (22) and (24)

$$\mathcal{R} \sim \rho_{12}^2, \quad \mathcal{T} = \frac{n_3 \cos \theta_3}{n_1 \cos \theta_1} t_{12}^2 t_{23}^2 e^{-4v_2\eta}. \tag{27}$$

We see that the reflectivity of a ‘thick’ film is almost that of an infinitely thick one, and

* See, for example, S. Tolansky, *Multiple-beam Interferometry of Surfaces and Films* (Oxford, Oxford University Press, 1948), p. 26; or O. S. Heavens, *Optical Properties of Thin Solid Films* (London, Butterworths, 1955).

that its transmissivity decreases exponentially with the thickness. The phase changes are immediately obtained from (23) and (25):

$$\delta_r \sim \phi_{12}, \quad \delta \sim \chi_{12} + \chi_{23} + u_2 \eta. \quad (28)$$

Formulae (27) and (28) interpret our definition of a 'thick' film in somewhat more physical terms, implying that in such a film the effect of multiple beam interference is negligible.

14.4.2 A transparent film on an absorbing substrate

As a second example, consider reflection from a transparent film on an absorbing substrate (Fig. 14.6).

In this case r_{12} is real whilst r_{23} is complex. The amplitude ratio ρ_{23} and the phase change ϕ_{23} are given by (6) or (13), with suffixes 1 and 2 replaced by 2 and 3 respectively. According to §1.6 (57) we now have

$$r = \frac{r_{12} + \rho_{23} e^{i(\phi_{23} + 2\beta)}}{1 + r_{12}\rho_{23} e^{i(\phi_{23} + 2\beta)}}. \quad (29)$$

This expression is identical with §1.6 (57) if 2β is replaced by $2\beta + \phi_{23}$ and r_{23} by ρ_{23} . Thus without any calculation we may at once write down the expression for the reflectivity and the phase change on reflection, simply by making this substitution in §1.6 (59) and §1.6 (61); we then obtain

$$\mathcal{R} = \frac{r_{12}^2 + \rho_{23}^2 + 2r_{12}\rho_{23} \cos(\phi_{23} + 2\beta)}{1 + r_{12}^2\rho_{23}^2 + 2r_{12}\rho_{23} \cos(\phi_{23} + 2\beta)}, \quad (30)$$

and

$$\tan \delta_r = \frac{\rho_{23}(1 - r_{12}^2)\sin(\phi_{23} + 2\beta)}{r_{12}(1 + \rho_{23}^2) + \rho_{23}(1 + r_{12}^2)\cos(\phi_{23} + 2\beta)}. \quad (31)$$

Thin transparent films on absorbing substrates have many practical uses. They are employed, for example, to protect metallic mirrors and to increase their reflectivity. They may also be used to reduce the reflectivity of a metal surface. We have mentioned on p. 68 that one may design a polarizer consisting of a dielectric film on a dielectric substrate for which $\mathcal{R}_{\parallel} = 0$ and \mathcal{R}_{\perp} is quite large. With a metallic substrate one may have either* $\mathcal{R}_{\parallel} = 0$ or $\mathcal{R}_{\perp} = 0$.

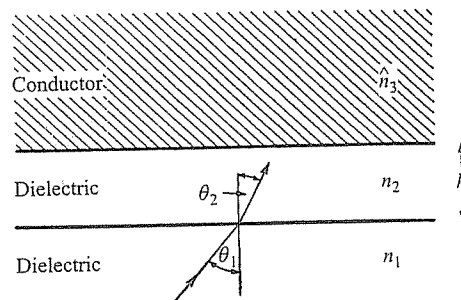


Fig. 14.6 A transparent film on an absorbing substrate.

* See H. Schopper, *Optik*, **10** (1953), 426.