The shortening of the metal–halogen bond has been previously observed in the results of electron-diffraction studies of metal halide molecules in the vapor state. It has been pointed out by several observers (Schomaker & Stevenson, 1941; Burawoy, 1943; Warhurst, 1949) that a decrease in bond distance is to be expected as the bond acquires more ionic character. Another explanation (Pauling, 1940, p. 228) attributes the shortening to partial double-bond character of the bond. Either explanation is applicable to $AlCl_4$.

Table 4. *Interatomic distances (in Ångström units)*

Distances in the $AlCl_4^-$ tetrahedron

Cl_I –Cl_{II}	3·48	Al–Cl_I	2·16
Cl_I –Cl_{III}	3·51	Al–Cl_{II}	2·11
Cl_I –Cl_{IV}	3·54	Al–Cl_{III}	2·13
Cl_{II} –Cl_{III}	3·49	Al–Cl_{IV}	2·12
Cl_{II} –Cl_{IV}	3·46		
Cl_{III}–Cl_{IV}	3·39		

Other distances

Na–Cl_I	3·08	Cl_I–Cl_{II}	3·85	Cl_{II}–Cl_I	3·85
Cl_I	3·20	Cl_{II}	3·86	Cl_I	3·86
Cl_{II}	2·88	Cl_{II}	4·03	Cl_I	4·03
Cl_{II}	3·72	Cl_{III}	3·77	Cl_{III}	3·74
Cl_{III}	2·79	Cl_{III}	3·95	Cl_{III}	3·91
Cl_{III}	3·29	Cl_{IV}	3·69	Cl_{IV}	3·74
Cl_{IV}	2·96	Cl_{IV}	3·81	Cl_{IV}	3·79
Cl_{IV}	3·06	Cl_{IV}	3·92	Cl_{IV}	4·06

Cl_{III}–Cl_I	3·74	Cl_{IV}–Cl_I	3·69
Cl_I	3·77	Cl_I	3·81
Cl_I	3·95	Cl_I	3·92
Cl_{II}	3·91	Cl_{II}	3·74
Cl_{III}	3·74	Cl_{II}	3·79
Cl_{III}	3·74	Cl_{II}	4·06
Cl_{IV}	3·78	Cl_{III}	3·78

The sodium ions are located in the empty spaces between the tetrahedra. All the sodium–chlorine distances are larger than the sum of ionic radii, 2·76 A. The sodium atom has seven chlorine neighbors from 2·79 to 3·29 A. distant with one chlorine atom much farther away at 3·72 A. Interatomic distances are listed in Table 4.

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Rotatory Power and Other Optical Properties of Certain Liquid Crystals

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A group of liquid crystals, mainly derivates of cholesterol, shows remarkable optical properties, including strong rotatory power and selective reflexion of circularly polarized light in a narrow region of wave-lengths. In this paper it is shown how these properties can be explained by the assumption that the molecules are arranged in a special way, so that the electrical axes rotate screw-like. It is inessential whether this occurs in small steps or continuously. When the axes make one revolution over a thickness p, then light in a region around $\lambda = pn$ will be reflected (n = refractive index). The second important parameter is the value of the double refraction $\alpha = (n_2 - n_1)/n$. From p and α all optical properties can be calculated. No accurate data for testing the theory are available but qualitatively the agreement is complete.

1. Description of the phenomena

From a monograph by Friedel (1922), we may summarize the phenomena occurring for a group of liquid crystals, mainly cholesterol derivates, as follows:

(1) Strong rotatory power (see Fig. 1). It amounts to more than ten and even to hundreds of revolutions per mm., whereas quartz gives only 24°/mm.

(2) Whereas in normal substances wave-length regions of opposite sign of the rotatory power are separated by a region of *absorption*, the liquid crystals have a region of *reflexion* of circularly polarized light. One circularly polarized component of the incident beam is completely unaffected; for the substance characterized by Fig. 1 (type 'dextro') it is only the

circularly polarized beam with anticlockwise rotating electrical vector which is reflected.* For substances of the type 'laevo' all signs are reversed.

(3) The electrical vectors of the incident and the reflected light rotate in opposite directions,* whereas the direction of rotation is unaffected by reflexion at normal substances.

(4) The mean wave-length, λ_0, of the reflexion band depends on the angle of incidence ϕ (the angle between the surface and the incident beam). Approximately the relation is represented by $\lambda = 2d \sin \phi$. Apparently a kind of Bragg reflexion occurs on internal planes with a distance d of several thousand Ångström units.
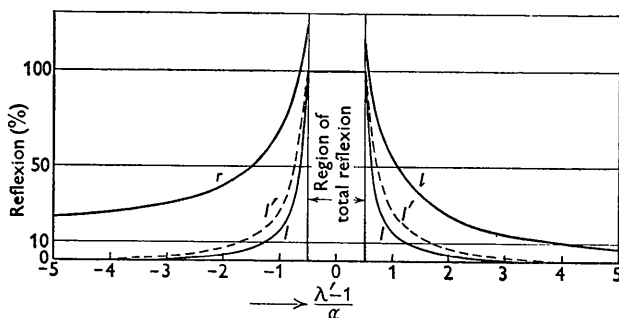
Fig. 1. Reflexion and rotatory power as a function of the wave-length $\lambda' = \lambda/\lambda_0$. A normal wave-length scale can be obtained by inserting for λ_0 and α some numerical value; say 550 mμ and 0·05. Curve r, right-handed rotation; l, left (arbitrary scale; sign of rotation according to *normal* usage). I, reflexion by a thick layer. I', intensity in the maxima (see also Fig. 5).

(5) Planes of Grandjean. When the substance fills a wedge-shaped space bright and dark lines appear, which follow the lines of equal thickness. Some authors interpreted these dark lines as intersections of *planes* in the crystal with the boundaries. It is remarkable that the distance d which can be found from these experiments agrees with d mentioned in the preceding paragraph.

2. Qualitative development of the model

The points (4) and (5) of the foregoing section suggest that these liquid crystals consist of a large number of thin layers, and that the light is reflected at the successive boundaries. Needless to say, however, reflexion at the boundary of two layers which make optical contact can only occur when there is a difference of the refractive indices of the layers. Suppose therefore that the crystal consists of thin *anisotropic* layers, and let the electrical axis in successive layers be turned through an angle ϕ. Similar piles of thin double-refracting sheets have often been discussed, but the reflexion was always neglected. Qualitatively this model easily explains several phenomena. The reflexion follows from the fact that both linear components of the wave in one layer

*Contrary to ordinary usage we refer all signs of rotation to an observer who looks in the direction of the incident light, i.e. the positive z axis used in the theory (unless stated otherwise).

will experience a change of refractive index when passing into the next layer. The fast component will be reflected with phase reversal; the other component is reflected without reversal. This involves that the sense of rotation of the electrical vector of circularly polarized light changes sign by the reflexion. The quantitative treatment in the next two sections will show that the angle ϕ between two successive layers is inessential for the phenomena, when at least the thickness p of the pile of layers in which the electrical axes make one complete revolution remains the same. Therefore the rigorous treatment in §§ 5–14 deals with a continuous rotation of the principal directions. Nevertheless, the elementary model is very useful since it gives a better insight into the mechanism.

3. Quantitative treatment of the reflexion between two anisotropic layers

We confine ourselves to perpendicular incidence. The x and y axes are laid along the electrical axes of the first layer. (Dielectric constants ϵ_1 and ϵ_2 respectively; $\epsilon_1 < \epsilon_2$.) The ξ and η axes are along the corresponding directions of the second layer (Fig. 2), which is turned through an angle ϕ (see § 2). Suppose the incident wave to be linearly polarized (electrical vector E). The x component of the wave is given by

$$E_x \exp[2\pi i(t/T - n_1 z/\lambda) + i\delta_x]. \quad (1)$$

Here $E_x = E \cos \beta$ (Fig. 2); $n_1 = $ refractive index $= \sqrt{\epsilon_1}$; $\lambda = $ wave-length *in vacuo*; $\delta_x = $ the phase constant, which can be chosen zero for the incident wave by
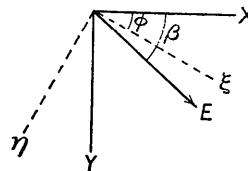

Fig. 2. Co-ordinate system used.

appropriate choice of t (so $\delta_x = \delta_y = 0$). A priori we do not know the phase constant δ for the reflected and transmitted waves. The formulae are very much simplified by combining these phase factors with the amplitude into a complex amplitude e. Then the formula (1) is converted into

$$e_x \exp[2\pi i(t/T - n_1 z/\lambda)]. \quad (1a)$$

Appropriate choice of t makes e_x and e_y real. For the y components n_2 should be substituted for n_1. For the reflected waves $-nz/\lambda$ is to be replaced by $+nz/\lambda$. Their amplitudes will be denoted by primes, e'_x, e'_y, etc. The reflexion can be calculated in the normal way from the boundary conditions at the plane between the two layers. The tangential components of E and H must be the same at both sides. H is calculated from

$$\frac{1}{c}\frac{\partial H_y}{\partial t} = -\frac{\partial E_x}{\partial z}, \quad \frac{1}{c}\frac{\partial H_x}{\partial t} = \frac{\partial E_y}{\partial z}. \quad (2)$$

Combining (1) and (2) we can express H in terms of E. In the plane $z=0$ all exponential factors in (1) or (1a) are the same, so that they can be omitted from the boundary conditions:

$$\begin{aligned}
\text{For } E_x: & \quad e_x + e'_x = e_\xi \cos\phi - e_\eta \sin\phi, \\
\text{For } E_y: & \quad e_y + e'_y = e_\xi \sin\phi + e_\eta \cos\phi, \\
\text{For } H_x: & \quad n_2 e_y - n_2 e'_y = n_1 e_\xi \sin\phi + n_2 e_\eta \cos\phi, \\
\text{For } H_y: & \quad n_1 e_x - n_1 e'_x = n_1 e_\xi \cos\phi - n_2 e_\eta \sin\phi.
\end{aligned} \tag{3}$$

We give here only the amplitudes of the reflected wave

$$e'_x = (-e_x \sin\phi + e_y \cos\phi)\frac{n_2 - n_1}{2n}\sin\phi.$$

Here some simplification has been made, which is justified when $(n_2 - n_1)$ is small; this is generally the case. We have further put $n_1 + n_2 = 2n$. This formula, as well as the exact one, involves that there is no phase shift between the incident and the reflected wave; e'_x is real, since e_x and e_y could be chosen real. A phase reversal will be expressed by the sign of e'_x.

In the notation of §6 $(n_2 - n_1)/n = \alpha$. Inserting, furthermore, $e_x = E\cos\beta$ and $e_y = E\sin\beta$ (see Fig. 2), one obtains

$$\begin{aligned}
e'_x &= E\sin(\beta - \phi) \cdot \tfrac{1}{2}\alpha\sin\phi, \\
\text{and similarly } e'_y &= E\cos(\beta - \phi) \cdot \tfrac{1}{2}\alpha\sin\phi.
\end{aligned} \tag{4}$$

Obviously e'_x and e'_y are components of a vector e', which makes an angle $\beta' = 90 - \beta + \phi$ with the x axis. Its length is $\tfrac{1}{2}\alpha E\sin\phi$.

4. The interference of the reflected waves (discrete layers)

In order to find the combined effect of a pile of thin layers it should be noted that, approximately, the vector E has a constant length and direction throughout the system. This means that β decreases by ϕ for the successive layers, since we make use of a rotating coordinate system. Consequently β' increases by ϕ (see equation (3)), and relative to a fixed direction e' rotates 2ϕ at subsequent boundaries. When the waves arrive at the surface they have relative orientations as given in Fig. 3. (Multiple reflexions are neglected.) The phase difference of two successive waves is $2nb$, b being the thickness of one layer. It will be clear from Fig. 3 that there will be a maximum of intensity when E'_1 and E'_7, E'_2 and E'_8, etc., are in phase. This requires that $\frac{2\pi}{2\phi} 2nb = \lambda$. The same formula is obtained when $\frac{2\pi}{2\phi}$ is not an integer. The thickness, p, of a pile in which there is a complete revolution of the principal directions equals $\frac{2\pi}{\phi} b$, so that the condition for a maximum becomes

$$pn = \lambda. \tag{5}$$

It should be noted that 2λ would not fit, since in this case E_1 and E_4, etc. would compensate each other. The next possibility is 7λ, 13λ, etc., but this leads to unreasonably large values of p.

According to (5) the wave-length λ of maximum reflexion depends on p only, whereas the value of b is inessential. The only value of b which would give special results is $b = \tfrac{1}{4}p$ and $\phi = \tfrac{1}{2}\pi$. In this case all partial waves E' have the same direction, and the resulting reflected wave will be linearly polarized. When $\phi \neq \tfrac{1}{2}\pi$ it can be proved that the resulting wave is circularly polarized. This can be understood qualitatively from Fig. 3. First E_1 reaches its maximum; then E_2, etc. So we see the maximum rotate in a *clockwise* direction, i.e. the sense in which the subsequent principal directions rotate. The length of the resulting vector is $\tfrac{1}{2}kE'$, k being the number of layers in the pile, and E' the amplitude of one partial wave. $E' = \tfrac{1}{2}\alpha E\sin\phi$. For small values of ϕ the amplitude of the circular wave reduces to

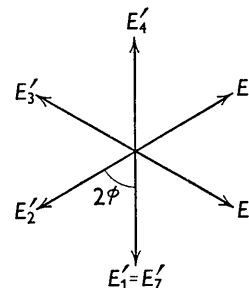$$\tfrac{1}{4}\alpha E k\phi = \tfrac{1}{2}\alpha \pi d\lambda^{-1} nE,$$

where $d = kb$.

Fig. 3. The partial waves E'_1, etc., from successive planes of reflexion, for $\phi = 30°$.

Here again the result does not depend on the thickness of one layer. For this reason we shall proceed in the following sections with a model in which the electrical axes turn continuously, though part of the results to be obtained there could perhaps also be derived from the present model.

Only one implication of the present theory has still to be mentioned. When the incident beam is circularly polarized with a clockwise rotating vector it is easily seen that the two reflected circular waves originating from its linear components just cancel out, whereas an incident beam with anticlockwise rotating vector gives waves reflected in phase with a clockwise rotating vector. This agrees with the properties summarized in §1. When the length of the rotating vector is E, the amplitude of the reflected wave is twice the value found above, i.e.

$$E' = \alpha\pi d\lambda^{-1} nE. \tag{6}$$

5. Rigorous treatment for continuously changing electrical axes

It was shown that the thickness b of one (hypothetical) layer was inessential for the phenomena. Moreover, the existence of a well-defined thickness would require a special explanation. It seems therefore more reasonable to assume continuous rotation of the principal directions. When the substance reflects visible light, p equals about 0.5μ and the rotation of the principal directions is about $1°$ for a monomolecular layer. This must be related

with the form and the arrangement of the molecules in some way, but it is beyond the scope of the present paper to explain this. I have found that a similar continuous rotation was already supposed to exist in azoxyphenetol by Mauguin (1911). This substance showed remarkable optical properties when the cover-glass was rotated through an angle ϕ. These phenomena could be explained by supposing that the cover-glass dragged the principal directions of the adhering layer of the crystal with it, so that the crystal acquired a screw structure in which the electrical axes change their orientation continuously from the lower glass to the cover-glass. Our hypothesis for the cholesterol derivates differs from the model of Mauguin in two ways: (1) spontaneous rotation, (2) a large number of revolutions with a pitch $p \approx \lambda$, whereas the rotation in Mauguin's experiments was smaller than 90° and $p \gg \lambda$.

6. The normal waves in the screw structure

The well-known relations between D and E for a wave in the direction of the z axis are given by

$$\frac{1}{c^2}\frac{\partial^2 D_x}{\partial t^2} = \frac{\partial E_x}{\partial z^2}, \quad \frac{1}{e^2}\frac{\partial^2 D_y}{\partial t^2} = \frac{\partial^2 E_y}{\partial z^2}, \quad D_z = 0. \quad (7)$$

The relations between D and E have a simple form in the ξ-η system (see Fig. 2), where the axes ξ and η are perpendicular to the z axis and in the direction of the electrical axes of the crystal. We suppose the angle ϕ between ξ and x to depend on z, $\phi = 2\pi z/p$ (see also §2). Here p stands for the pitch of the 'screw'. In this system we have $D_\xi = \epsilon_1 E_\xi$, $D_\eta = \epsilon_2 E_\eta$. Suppose $\epsilon_2 > \epsilon_1$.

In order to use the relations (7) it is necessary to transform them into the ξ-η system. According to Fig. 2 one can write

$$\begin{aligned} E_x &= E_\xi \cos 2\pi z/p - E_\eta \sin 2\pi z/p, \\ E_y &= E_\xi \sin 2\pi z/p + E_\eta \cos 2\pi z/p. \end{aligned} \quad (8)$$

Similar relations hold for D. With these values (7) takes the form

$$\begin{aligned} \frac{\epsilon_1}{c^2}\frac{\partial^2 E_\xi}{\partial t^2} &= \frac{\partial^2 E_\xi}{\partial z^2} - \frac{4\pi}{p}\frac{\partial E_\eta}{\partial z} - \frac{4\pi^2}{p^2}E_\xi, \\ \frac{\epsilon_2}{c^2}\frac{\partial^2 E_\eta}{\partial t^2} &= \frac{\partial^2 E_\eta}{\partial z^2} + \frac{4\pi}{p}\frac{\partial E_\xi}{\partial z} - \frac{4\pi^2}{p^2}E_\eta. \end{aligned} \quad (9)$$

As a solution we try

$$\left.\begin{aligned} E_\xi &= A \\ E_\eta &= iB \end{aligned}\right\} \exp\left[2\pi i\left(\frac{t}{T} - \frac{mz}{\lambda}\right)\right]. \quad (10)$$

This is an elliptically polarized wave in the ξ-η system. It would be misleading to call m the refractive index, though it plays this role in (10). It has very uncommon properties, since (10) describes the wave motion in a 'screwed' system. By substituting (10) in (9) one obtains

$$\begin{aligned} A\frac{\epsilon_1}{\lambda^2} &= A\frac{m^2}{\lambda^2} + 2B\frac{m}{\lambda p} + \frac{A}{p^2}, \\ B\frac{\epsilon_2}{\lambda^2} &= B\frac{m^2}{\lambda^2} + 2A\frac{m}{\lambda p} + \frac{B}{p^2}. \end{aligned} \quad (11)$$

Eliminating B/A,

$$m^4 - m^2(\epsilon_1 + \epsilon_2 + 2\lambda^2/p^2) + (\epsilon_1 - \lambda^2/p^2)(\epsilon_2 - \lambda^2/p^2) = 0. \quad (12)$$

The treatment of these equations is simplified by introducing 'reduced' quantities: $\lambda' = \lambda/(p\sqrt{\epsilon})$; $m' = m/\sqrt{\epsilon}$. According to (5) reflexion occurs for $\lambda' = 1$. ϵ stands for the mean dielectric constant ($\epsilon = \frac{1}{2}(\epsilon_1 + \epsilon_2)$). $(\epsilon_2 - \epsilon_1)/(2\epsilon) = \alpha$ is a measure of the double refraction. $\alpha = 0 \cdot 05$ fits rather well the data reported by Friedel (1922).

Equation (12) in its 'reduced' form is

$$m'^4 - 2m'^2(1 + \lambda'^2) + (1 - \alpha - \lambda'^2)(1 + \alpha - \lambda'^2) = 0. \quad (12a)$$

Finally

$$f = \frac{B}{A} = \frac{1 - \alpha - m'^2 - \lambda'^2}{2m'\lambda'}. \quad (13)$$

Apart from the notation, these formulae were also given by Mauguin (1911).

7. Discussion of the equations

Equation (12) gives two values for m'^2. The larger one, $m_2'^2$, proves to be positive for all values of λ'. The other root, m_1^2, is negative if $1 - \alpha < \lambda'^2 < 1 + \alpha$. (For these values of λ'^2 the product of the roots of (12a) is negative.) This implies that m_1' is imaginary in the region where the reflexion occurs according to equation (5). This reflexion will be dealt with in §§ 8 and 9. For m' one of the roots of m'^2 can be chosen. One is inclined to take the positive root since (10) has to represent a wave in the positive direction of the z axis. It will be shown, however, in §§ 7 and 8 (footnotes) that m_1' has to be negative when $\lambda'^2 > 1 + \alpha$. A positive value would give a wave in the wrong direction.

For part of the discussion we want explicit expressions for m_1' and m_2'; these are obtained by expanding in series:

$$\left.\begin{aligned} m_1' &= 1 - \lambda' - \frac{\alpha^2}{8\lambda'(1 - \lambda')} + \dots, \\ m_2' &= 1 + \lambda' + \frac{\alpha^2}{8\lambda'(1 + \lambda')} + \dots. \end{aligned}\right\} \quad (14)$$

For $\lambda'^2 < \alpha$ and $\lambda' \approx 1$ other expansions should be used. Each value of m corresponds to a normal wave with an ellipticity B/A which is obtained from (13). B_2/A_2 is always real and negative, corresponding to an electrical vector which rotates in clockwise direction. B_1/A_1 is real and negative except for the region of total reflexion (see Fig. 1). The values of B/A and m' are given graphically in Fig. 4.

The first wave in the region $|1 - \lambda'^2| < \alpha$ requires special discussion. Substituting in (9) an imaginary value of m', $m' = -i\mu$, where μ stands for a real number, one obtains

$$\left.\begin{aligned} E_\xi &= A_1 e^{-2\pi\mu z/\lambda} \cos 2\pi t/T, \\ E_\eta &= iB_1 e^{-2\pi\mu z/\lambda} \cos 2\pi t/T. \end{aligned}\right\} \quad (15)$$

It follows from (13) that iB/A is real in this region so that the resulting wave is linearly polarized. Its

This is, in our notation, a formula given by Pockels (1906, p. 291) and simplified by supposing that the angle ϕ between subsequent layers is small. It differs from our formula (17) just by the important factor $(1-\lambda'^2)$ in the denominator.

Finally, it can be remarked that the formula does not apply to substances like quartz which have a screw axis on an atomic scale. Inserting reasonable values for α and p, one arrives at very small rotatory powers. Moreover $d\psi/dz$ would be proportional to λ^{-4}, whereas it should be proportional to λ^{-2}. These rotatory powers have already been explained in a quite different way.

9. Calculation of the reflexion at the boundaries of a liquid crystal

On both sides of the boundaries E and H must be the same; this gives again the relations between incident and reflected waves. H can be expressed in terms of E by combining (10), (8) and (2).

One finds

$$\left.\begin{array}{l}H_\xi = -iA[\lambda/p+mf] \\ H_\eta = \quad A[m+(\lambda/p)f]\end{array}\right\} \exp\left[2\pi i(t/T - mz/\lambda)\right]. \quad (18)$$

These formulae become more comprehensible when the factor $[m+(\lambda/p)f] = (\sqrt{\epsilon})(m'+\lambda'f)$ is considered in more detail. It can be shown that $(m'+\lambda'f)$ is nearly unity, except for the first wave in the region $\lambda' \approx 1$. This means that $m+(\lambda/p)f$ is nearly the normal refractive index. Furthermore, $\lambda'+m'f = \dfrac{f}{\lambda'f+m'}$. (This can be proved from (12) and (13).) Denoting $\lambda'f+m'$ by q, (18) reduces to

$$H_\xi = -\frac{\sqrt{\epsilon}}{q}E_\eta \quad \text{and} \quad H_\eta = q\sqrt{\epsilon}\,E_\xi. \quad (18a)$$

The only difference from the corresponding formulae for a normal substance (see (19)) is the factor q which is exactly unity for normal substances. These formulae demonstrate once more that m does not play the role of the refractive index.*

A. *The boundary glass–crystal*

The components of the incident and the reflected wave in the cover-glass are represented by

$$\left.\begin{array}{l}\left.\begin{array}{l}E_x = e_x \\ E_y = ie_y\end{array}\right\} \exp\left[2\pi i(t/T - n_0 z/\lambda)\right] \\ \left.\begin{array}{l}E'_x = e'_x \\ E'_y = ie'_y\end{array}\right\} \exp\left[2\pi i(t/T + n_0 z/\lambda)\right]\end{array}\right. \quad \left.\begin{array}{l}H_y = \quad n_0 E_x, \\ H_x = -n_0 E_y, \\ H'_y = -n_0 E'_x, \\ H'_x = \quad n_0 E'_y.\end{array}\right\} \quad (19)$$

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* Formula (18a) enables the calculation of the Poynting vector $\mathbf{P} = \dfrac{c}{4\pi}[E, H]$ which gives the direction and the magnitude of the propagation of energy. P is zero for the first wave in the region of total reflexion, since the imaginary value of q causes a phase shift of 90° between E and H. The sign of P depends on the sign of m, chosen in § 7. It was anticipated there that m'_1 had to be chosen negative for $\lambda'^2 > (1+\alpha)$. A positive value would have given a negative P; this means that the wave would propagate in the direction of the negative z axis.

It has been explained already in § 3 that the amplitudes e may be complex in order to account for phase shifts. Since the waves turn out to be elliptically polarized we have denoted the y amplitudes by ie_y so that e_y will in general be real.

In order to avoid the normal reflexion at the boundary we will suppose n_0 of the glass to be equal to $\sqrt{\epsilon}$ of the crystal. The boundary conditions for E and H can now be written as

$$\left.\begin{array}{ll}e_x+e'_x=A, & e_y+e'_y=fA, \\ e_x-e'_x=qA, & e_y-e'_y=\dfrac{f}{q}A.\end{array}\right\} \quad (20)$$

It is supposed here that the incident wave is chosen so that only *one* normal wave in the crystal results.

The equations are solved by

$$\left.\begin{array}{l}2e_x = \quad A(1+q) \\ 2e_y = \quad Af(1+q)/q \\ 2e'_x = \quad A(1-q) \\ 2e'_y = -Af(1-q)/q\end{array}\right. \text{and} \left.\begin{array}{l}\dfrac{e_x}{e_y} = -\dfrac{e'_x}{e'_y} = \lambda'+\dfrac{m'}{f}, \\[2mm] \dfrac{e'_x}{e_x} = -\dfrac{e'_y}{e_y} = \dfrac{1-q}{1+q}.\end{array}\right\} \quad (21)$$

B. *The boundary crystal–glass*

This can be treated in a similar way. It should be noted that m, f and q for the reflected wave change sign (see (13)). The first important result is that the first normal wave in the crystal gives rise to a reflected wave which also consists of the first normal wave only. The same holds for the second wave. Therefore we can confine ourselves to *one* incident normal wave. The results are

$$A' = -\frac{1-q}{1+q}A, \quad e''_x = \frac{2q}{1+q}A, \quad e''_y = f\frac{2}{1+q}A. \quad (22)$$

Here A' stands for the amplitude of the reflected wave; e''_x and e''_y represent the amplitudes of the outgoing wave in the glass.

10. Reflexion at the boundaries (discussion)

A. *The polarization of the waves*

According to (21) and (22) $\dfrac{e_x}{e_y} = \dfrac{e''_x}{e''_y} = \lambda'+\dfrac{m'}{f}$. When $\lambda' > \alpha$ (i.e. the region we are interested in) this is approximately equal to $1+\frac{1}{2}\alpha/\lambda$ for the first wave, or $-1+\frac{1}{2}\alpha/\lambda$ for the second wave ((12) and (13)). This means that the waves in the glass are nearly circularly polarized. The waves in the glass which correspond to the first wave in the crystal and which move in the direction of the incident light have an anticlockwise rotating electrical vector. The deviations from circularity are in opposite directions for both waves, but they are very small whereas these deviations for the waves in the crystal may be very large (see Fig. 4). It is easily found from the formulae that the sense of the rotation is reversed by the reflexion.

B. *The phase relations*

Except for the first wave in the region $|1-\lambda'^2|<\alpha$, the 'refractive index' q is real. According to (21) and (22) this means that the ratios e'_x/e_x, etc., are real, so that there is no phase shift. In the region of total reflexion, however, the first wave has an imaginary q and $e'_x/e_x=(1-q)/(1+q)$ is complex. If arc tan $|q|=\phi$, there is a phase shift of 2ϕ between the incident and the reflected wave. Of course this phase shift is of no direct importance in the measurements. It is only a serious complication of the calculations when one does not make use of complex amplitudes.

C. *The intensity of the reflected wave*

According to (21) and (22) the reflexion is governed by the factor $(1-q)/(1+q)$. It can be shown that $(1-q)$ is approximately equal to $\tfrac{1}{2}\alpha/m$. This approximation does not hold for the first wave in the region $\lambda'\approx 1$, where $m'\approx 0$; this region will be considered separately. Since α is very small, and $m'\approx 1$ or even larger, the amplitude of the reflected wave is at most $\tfrac{1}{4}\alpha$ times the amplitude of the incident wave. For very large wave-lengths, λ', the reflexion goes to zero since $m'\approx 1\pm\lambda'$ (see (14)). This is reasonable since, for a long wave-length, only the mean refractive index, n_0, is of interest. We have chosen n_0 equal to the refractive index of the cover-glass so that the normal reflexion vanishes. The intensity of the reflected wave is proportional to the square of the amplitude. Since the latter is small the former can be neglected completely.

D. *The reflexion of the first wave in the region $\lambda'\approx 1$*

For $|1-\lambda'^2|<\alpha$, q is imaginary. The absolute value of $e'_x/e_x=(1-q)/(1+q)$ equals unity. This means that the wave is completely reflected. For $\lambda'^2<(1-\alpha)$ or $\lambda'^2>(1+\alpha)$, but not too far from $\lambda'=1$, the reflexion is still appreciable (see Fig. 1).

Of course both reflexions at the upper and the lower boundary of the crystal have to be taken into account, as well as multiple reflexions of the wave in the crystal. This will be done in the next section.

11. Reflexion at thin layers

According to § 10 we can confine ourselves to the first wave with an anticlockwise rotating electrical vector and the region $\lambda'\approx 1$. We have found already that all reflected waves have an electrical vector which rotates clockwise. Generally, however, there is a phase difference. Beyond the region of total reflexion, this is a consequence of the difference in optical path, d, traversed. In the region of total reflexion the phase difference results from the reflexion. Moreover, there is a difference in amplitude. In the region of total reflexion this results from a decrease of amplitude *in* the layer, beyond this region it is caused by reflexion at the boundaries. When the amplitude of the incident circularly polarized wave e_x equals unity, the amplitude of

the first reflected wave e'_x equals $(1-q)/(1+q)$, whereas $A_1=2/(1+q)$ (equation (22)). At the second boundary this amplitude is $A_1\exp[-2\pi i m'_1 d\lambda^{-1}\sqrt{\epsilon}]=A_1s$. Here s represents the absorption when m'_1 is imaginary, and the phase shift when m'_1 is real. Each of the successive waves which leave the crystal is obtained from the foregoing one by multiplication by $\{s(1-q)/(1+q)\}^2$. Summing the geometric series the total amplitude of the reflected wave is:

$$R=\frac{(1-q^2)(1-s^2)}{(1+q)^2-s^2(1-q)^2}. \qquad (23)$$

R is complex. Since we are only interested in the amplitude, we consider its absolute value.

(1) *Beyond the region of total reflexion*

Here q is real and s^2 is complex. Therefore s^2 can be represented by $s^2=\cos 2\delta+i\sin 2\delta$, where δ stands for the phase shift in the layer d, or $\delta=2\pi m'_1 d\lambda^{-1}\sqrt{\epsilon}$. The intensity R^2 of the reflected wave is then

$$R^2=\frac{(1-q^2)^2\sin^2\delta}{(1-q^2)^2\sin^2\delta+4q^2}. \qquad (24)$$

The intensity R^2 is thus a periodic function of the thickness d. When $\delta=0°$, $180°$, etc., the reflected wave vanishes; R^2 reaches a maximum for $\delta=90°$, $270°$, etc.
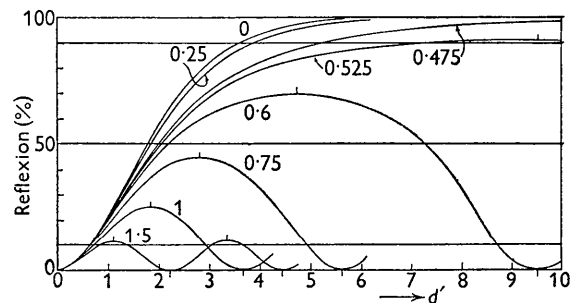
Fig. 5. The reflexion as a function of the reduced thickness $d'=2\pi d\lambda^{-1}\alpha\sqrt{\epsilon}$. The wave-length is $\lambda'=1-m\alpha$, m being given in the figure. For $m>0·5$ the curves are periodic; the maxima and minima have been marked by vertical lines.

The relation (24) is represented in Fig. 5. It is seen that the fluctuations become slower when λ' approaches unity. This also follows from the simple reasoning of § 4. When λ' is close to the right value, the deviation makes itself perceptible only when the wave is reflected on a large number of layers.

(2) *Inside the region of total reflexion*

Here s is real and q becomes imaginary (q^2 negative). One finds now

$$R^2=\frac{(1-s^2)^2(1-q^2)^2}{(1-s^2)^2(1-q^2)^2-16s^2q^2}. \qquad (24)$$

This function is also represented in Fig. 5. The first parts of all curves are seen to be nearly identical and can be derived from the formulae that the amplitude R for thin layers equals $\pi\alpha d\lambda^{-1}\sqrt{\epsilon}$. This formula was derived in § 4 in an elementary way (equation (6)).

12. Numerical calculations

Strictly speaking numerical calculations can be performed only if a special value of α is chosen. The parameter p is eliminated by making use of the reduced wave-length $\lambda' = \lambda/(p\sqrt{\epsilon})$. For small values of α, however, one can find very good approximations, in which α is also eliminated. For these small values of α the reflexion is symmetrical at both sides of $\lambda' = 1$; therefore we confine ourselves to $\lambda' \leqslant 1$. Introducing Δ, so that $\lambda'^2 = 1 - \alpha(1 + \Delta)$, one finds by expanding in series:

$$m_1'^2 \approx \left(\frac{\alpha}{2}\right)^2 (2\Delta + \Delta^2), \quad f_1 \approx \sqrt{\frac{\Delta}{2+\Delta}}, \quad q^2 = \frac{\Delta}{2+\Delta}.$$

In the region of total reflexion Δ varies from -1 to 0, so that m_1' and f_1 are imaginary. In the expression for s (see § 10) the exponent $2\pi i m_1' d\lambda^{-1} \sqrt{\epsilon}$ can be 'normalized' by introducing $d' = 2\pi\alpha d\lambda^{-1} \sqrt{\epsilon}$. Here d' will be called the reduced thickness. The exponent becomes now $d'\sqrt{(2\Delta + \Delta^2)}$. So there is only one parameter Δ left.

13. The planes of Grandjean

The phenomena predicted in the foregoing sections do not include the periodic bright and dark lines described in § 1 (5). It seems to us, therefore, that these lines are caused by periodical disturbances of the screwlike structure. It is probable that the orientation of the molecules in the two boundaries is prescribed by the structure of the surfaces—especially when the wedge consists of mica, which is often used. When the pitch, f, of the screw exactly fits the width, w, of the wedge the screwlike structure can develop. This requires that w equals $\frac{1}{2}kp$, or perhaps kp (k integer). Of course there are other parts of the wedge where the structure does not fit in w, so that the normal arrangement is disturbed and dark lines appear between crossed nicols. This hypothesis also explains why the planes of Grandjean are less pronounced when a wedge of glass is used since, generally, glass will not show these preferred directions. It is important to know, however, that the study of liquid crystals has often revealed the existence of preferred orientations even on glass (see Mauguin, 1911).

If this explanation is correct the planes of Grandjean should not be visible in light containing only the second normal wave, which is unaffected even when the screwlike structure is present. This has in fact been found. The experiments should, however, be repeated in monochromatic light.

14. Comparison with the experiments

In the course of the discussions it has been shown already that qualitatively the predictions of the theory agree with the experimental results summarized in § 1. No complete data are available to test the theory quantitatively. The measurements would not be difficult to make, however, since the theory contains only three constants, p, α and the refractive index n, which can be determined in various ways. The quantity p is determined from the wave-length λ_0 of the central part of the reflexion band ($pn = \lambda_0$). The wave-lengths can be reduced to λ' by dividing them by λ_0 ($\lambda' = \lambda/\lambda_0$). The quantity α can be determined from the width of the band (see Figs. 1 and 5). Then the rotatory power and the intensity of the reflected beam can be calculated as a function of λ; they depend only on α (see Fig. 5). The interesting fluctuations, shown in Fig. 5, have not yet been observed.

Finally, α appears in the ellipticity of the reflected beam. When α is not too small the ellipticity can be determined, as well as the directions of the axes. The latter are interesting with respect to the occurrence of fixed orientations on the cover-glass mentioned in § 12.

We have confined ourselves to perpendicular incidence. Oblique incidence may give rise to new phenomena which perhaps have been observed already though they still lack an explanation.

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