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ELECTRIC DOUBLE-REFRACTION IN RELATION TO THE POLARITY AND OPTICAL ANISOTROPY OF MOLECULES.—PART II. LIQUIDS.

Electric Double-Refraction in Relation to the Polarity and Optical Anisotropy of Molecules.—Part II. *Liquids.* *By* Prof. C. V. Raman, *F.R.S.*, *and* K. S. Krishnan.

1. *Introduction.*

In Part I.† the electric double-refraction (Kerr effect) in gases and vapours was discussed in relation to the optical anisotropy of molecules as determined from observations on light-scattering. It was found that in the case of electrically non-polar molecules their electrostatic anisotropy is sufficient to account for the orientative couple exerted by the field on them, and thus for the observed double-refraction. On the other hand, in the case of molecules known to be electrically polar, the orientative couple is in a large measure due to the permanent doublets present in them, and the actual magnitudes involved were shown in certain simple cases to be in quantitative agreement with what one should expect from Born's theory of the Kerr effect. In this part we propose to extend the discussion to the case of liquids. Here, of course, owing to our imperfect knowledge of the liquid state, the problem is more complicated. There are, however, certain prominent features of the phenomenon which are of interest, and admit of at least an approximate comparison between observation and theory.

2. *Kerr Constant Data in Liquids.*

The electric double-refraction in liquids has been studied extensively by Schmidt ‡, Leiser §, McComb ‖, and others, while data for the scattering of light in some 65 liquids (chiefly organic) are available from measurements made by K. S. Krishnan ¶. In the following Table (I.) are given the data for some typical cases. Column 2 gives the relative values of the Kerr constant, carbon bisulphide, as usual, being taken as 100; column 3 gives the factor of depolarization of the scattered light; and column 4 the values of the dielectric constant.

† *Suprà*, p. 713.

‡ W. Schmidt, *Ann. der Physik*, vii. p. 142 (1902).

§ For collected data, see H. Kauffmann, 'Beziehungen zwischen physikalischen Eigenschaften und chemischer Konstitution,' Enke, Stuttgart, 1920, pp. 385–389.

‖ H. E. McComb, Phys. Rev. xxix. p. 525 (1909).

¶ K. S. Krishnan, Phil. Mag. l. p. 697 (1925).

TABLE I.

Liquid.	Kerr constant, $CS_2 = 100$.	Depolarization factor, $r \times 100$.	Dielectric constant δ at 20° C.
Hexane	1·73	9·9	1·729
Cyclohexane	2·30	8	2·05
Heptane	3·26	11·4	.. ...
Octane	4·21	12·9	1·945
β-iso amylene	7·9	25·8	2·191
Propyl chloride	234	16·3	7·70
Methylene chloride	−36	31	8·3
Ethylene chloride	146	36	9·96
Chloroform	−103	24·0	4·853
Carbon tetrachloride	2·3	5·3	2·190
Carbon bisulphide	100	68·5	2·593
Acetic acid	130	45·5	6·02
Propionic acid	43	41	3·12 (at 18° C.)
Ethyl ether	−19·2	8·0	4·351
Benzene	18·4	47	2·284
Toluene	23·3	51	2·368
Ethyl benzene	23·4	53	2·417
m-Xylene	26·6	56	2·392
p-Xylene	22·6	58·3	2·15
Chlorobenzene	280	57·5	5·65
Bromobenzene	280	63·5	5·2
Nitrobenzene	7900	74	36·95
Aniline	−38	60	6·936
o-Nitrotoluene	5400	82	26·2
m-Nitrotoluene	5520	83	23·6
Benzyl alcohol	−477	62	13·0
Water	123	8·5	80·5
Methyl alcohol	30	6·0	31·2
Ethyl alcohol	23·8	5·3	25·8
Propyl alcohol	−78	7·1	22·2
Butyl alcohol	−113	9·3	19·2
Isobutyl alcohol	−111	7·3	20·0
Trimethyl carbinol	154	4·1	11·4
Ethyl formate	138	21·3	8·27
Ethyl acetate	52	23·0	6·11
Acetone	505	20·0	22·58

It will be seen that, just as in the case of vapours, all the liquids which have a large Kerr constant are characterized by the possession of strongly polar molecules, as will be evident from the dielectric constant data in column 4. In fact, the variations in the values of the Kerr constant are even more pronounced than in the case of vapours. This is really what we should expect from theoretical considerations. The influence of the electrical polarity of the molecules on the Kerr effect is here twofold. One is its direct contribution to the orientative couple exerted on the molecule by the external field, just as in the gaseous state. The other arises in the following way: owing to the influence of neighbouring molecules, the actual field tending to orientate any particular molecule is $\frac{\delta+2}{3}$ times the external imposed field, where δ is the dielectric constant. Since, in the case of polar molecules, the value of the dielectric constant is large, and since the double refraction varies as the square of the acting field, the enormous influence of the polarity of the molecules on the magnitude of the Kerr effect is readily understood.

The theoretical expression for the Kerr constant of a liquid is

$$K = \frac{\pi\nu(n_0^2+2)^2}{3n_0\lambda}\left(\frac{\delta+2}{3}\right)^2(\theta_1+\theta_2), \quad . \quad . \quad . \quad (1)$$

where the different letters have the same significance as in Part I., θ_1 and θ_2 being given, as before, by the relations

$$\theta_1 = \frac{1}{45kT}[(A-B)(A'-B') + (B-C)(B'-C') + (C-A)(C'-A')], \quad . \quad (2)$$

$$\theta_2 = \frac{1}{45k^2T^2}[(A-B)(\mu_1^2-\mu_2^2) + (B-C)(\mu_2^2-\mu_3^2) + (C-A)(\mu_3^2-\mu_1^2)]. \quad . \quad (3)$$

For convenience we shall denote the term on the right-hand side of equation (1), which is proportional to θ_1, by K_1, and the term proportional to θ_2 by K_2, so that

$$K = K_1 + K_2.$$

3. *Non-Polar Molecules.*

In the case of non-polar molecules $\theta_2 = 0$, and with the assumptions of Gans regarding the relation between the

constants of electrostatic and optical anisotropy, viz., $\frac{A'}{A}=\frac{B'}{B}=\frac{C'}{C}$, this ratio $=\frac{\delta-1}{\delta+2}\Big/\frac{n_0^2-1}{n_0^2+2}$, and hence the expression for θ_1 reduces to

$$\theta_1=\frac{1}{45kT}\frac{\delta-1}{\delta+2}\cdot\frac{n_0^2+2}{n_0^2-1}[(A-B)^2+(B-C)^2+(C-A)^2]. \quad (4)$$

It remains to evaluate the constants of optical anisotropy in the above expression from scattering measurements. It might be imagined that the anisotropic constants would be characteristic of the molecule, and could thus be easily evaluated from the vapour state, as in Part I.; but, as a matter of fact, owing probably to temporary molecular groupings, the optical anisotropy calculated from the liquid state is, in general, found to be less than that calculated from the vapour; and in any discussion concerning the liquids it is only appropriate that we should use the former value for the optical anisotropy. Two slightly different expressions have been proposed connecting the depolarization factor r with the constants of optical anisotropy—

$$r=\frac{6[(A-B)^2+(B-C)^2+(C-A)^2]}{10kT\beta\nu\left(\frac{n_0^2+2}{3}\right)^2(A+B+C)^2+7[(A-B)^2+(B-C)^2+(C-A)^2]} \quad (5a)$$

and

$$r=\frac{6[(A-B)^2+(B-C)^2+(C-A)^2]}{10kT\beta\nu(A+B+C)^2+7[(A-B)^2+(B-C)^2+(C-A)^2]}, \quad (5b)$$

where β is the isothermal compressibility and $(A+B+C)$ is given by the relation

$$\frac{n_0^2-1}{n_0^2+2}=\frac{4\pi}{3}\nu\frac{A+B+C}{3}. \quad (6)$$

Since the experimental data available at present are not sufficient to decide definitely between the two expressions *, we shall use both of them here. From (4) and (5) we thus have

$$\theta_1=\frac{9\beta(\delta-1)(n_0^2-1)}{8\pi^2\nu(\delta+2)(n_0^2+2)}\cdot\left(\frac{n_0^2+2}{3}\right)^2\cdot\frac{r}{6-7r} \quad (7a)$$

or

$$\theta_1=\frac{9\beta(\delta-1)(n_0^2-1)}{8\pi^2\nu(\delta+2)(n_0^2+2)}\cdot\frac{r}{6-7r}, \quad (7b)$$

* See K. S. Krishnan, Proc. Ind. Assn. Sc. ix. p. 251 (1926).

and hence

$$K = \frac{\beta(n_0^2-1)(n_0^2+2)(\delta-1)(\delta+2)}{24\pi n_0 \lambda}\left(\frac{n_0^2+2}{3}\right)^2 \cdot \frac{r}{6-7r} \quad (8\,a)$$

or

$$K = \frac{\beta(n_0^2-1)(n_0^2+2)(\delta-1)(\delta+2)}{24\pi n_0 \lambda} \cdot \frac{r}{6-7r} \cdot \quad . \quad . \quad . \quad (8\,b)$$

Table II. shows the values of the Kerr constant calculated according to these expressions for all the non-polar liquids for which we have the necessary data.

TABLE II.

Liquid.	$\frac{r}{\times 100.}$	n_0.	δ.	Kerr constant $\times 10^7$. Calculated according to (8 *a*)	Calculated according to (8 *b*)	Observed.
Pentane	7·5	1·356	...	0·082	0·050	0·050
Isopentane	5·6	1·353	...	0·059	0·036	0·050
Hexane	9·9	1·375	1·729	0·074	0·044	0·045 0·056
Cyclohexane	8	1·427	2·05	0·080	0·044	0·074
Heptane	11·4	1·386	...	0·102	0·060	0·071 0·105
Octane.....	12·9	1·397	1·945	0·116	0·067	0·077 0·136
Carbon tetrachloride.	5·3	1·461	2·190	0·068	0·036	0·074
Carbon bisulphide ...	68·5 64·0	1·627	2·593	9·79 7·24	4·08 3·02	3·226
Benzene	47	1·501	2·284	1·45	0·72	0·593
m-Xylene	56	1·497	2·392	2·20	1·10	0·858
p-Xylene	58·3	1·496	2·15	1·96	0·98	0·74 0·73

All the constants refer to the D line and 20° C.

Considering the uncertainties in the evaluation of the anisotropic constants from r, the agreement between the calculated and observed values in Table II. should be considered satisfactory. Equation (8 *b*), which corresponds to the relation (5 *b*) for the optical anisotropy, gives better agreement in the case of highly refractive liquids. In the

following discussion we shall use the same expression for the anisotropy consistently ; the main conclusions, however, will not be seriously affected when the relation (5 *a*) is used.

Polar Molecules.

Here also θ_1 can be evaluated in the same way as for non-polar molecules, the ratio $\frac{A'}{A} = \ldots$ being now equal to $\frac{\epsilon-1}{\epsilon+2}\Big/\frac{n_0^2-1}{n_0^2+2}$, where ϵ is given by Debye's relation

$$\frac{\delta-1}{\delta+2} = \frac{\epsilon-1}{\epsilon+2} + \frac{4\pi}{3}\nu\frac{\mu^2}{3kT}. \quad \ldots \quad (9)$$

μ is the "effective value" of the permanent electric moment of the molecule, which is different in general from the real moment of the individual molecules, owing to the well-known phenomenon of association of polar molecules ; its actual magnitude varies naturally with temperature. Hence ϵ can not be evaluated easily from the temperature dependence of the dielectric constant, as in the vapour state ; but it is possible to calculate it on the basis of Debye's dipole-theory from dielectric constant measurements at different temperatures of very dilute solutions of the liquid in a non-polar solvent like benzene, carbon bisulphide, or carbon tetrachloride *. However, for the purpose of our present discussion we can take ϵ to a first approximation to be equal to the square of the refractive index extrapolated for zero frequency.

Thus we obtain the relation

$$K_1 = \frac{\beta(n_0^2-1)(n_0^2+2)(\epsilon-1)(\delta+2)^2}{24\pi n_0\lambda(\epsilon+2)}\frac{r}{6-7r}. \quad (10)$$

The problem of determining θ_2, however, is very complicated. It is possible to evaluate θ_2 only when we know the form of the optical ellipsoid and the position of the permanent electric moment. Even in the gaseous state, where these quantities refer to the *individual molecules*, our information regarding them extends only to very simple cases. When, on the other hand, we have to deal, as in the liquid state, with certain "effective values" of these quantities which, we have *prima facie* reasons to believe, can no longer be identified with the values for the individual molecules, the problem is naturally very complicated. We

* See P. Debye, *Handbuch der Radiologie*, Bd. vi. p. 633.

have therefore to limit ourselves to a more or less general discussion.

Let us first consider a somewhat simple case, say chloroform. It has already been shown in Part I. that the optical ellipsoid of the $CHCl_3$ molecule is an oblate spheroid of revolution, with the permanent doublet along its axis.

The value of the permanent moment calculated according to equation (9) from the dielectric constant for the liquid at 20° C., taking ϵ to be equal to the square of the refractive index extrapolated for infinite wave-length, comes out to be equal to $1{\cdot}07 \times 10^{-18}$ e.s.u., which is slightly less than the value $1{\cdot}25 \times 10^{-18}$ calculated by Smyth * from the vapour.

Also the optical anisotropy, defined by, say,

$$\frac{(A-B)^2+(B-C)^2+(C-A)^2}{(A+B+C)^2},$$

calculated from the liquid state $=\cdot 017$, as against $\cdot 028$ from the vapour.

For reasons already indicated we shall take the former value and assume that the axis of the electric moment has the same position in the molecule as in the state of vapour. On calculation we get

$$K_1 = 0{\cdot}47 \times 10^{-7} \quad \text{and} \quad K_2 = -5{\cdot}9 \times 10^{-7},$$

$$\text{and therefore} \quad K = -5{\cdot}4 \times 10^{-7},$$

as compared with the observed value $-3{\cdot}32 \times 10^{-7}$. The assumption made in the calculation that the permanent doublet is along the direction of minimum optical polarizability would give to the calculated Kerr constant the maximum possible negative value. If, however, owing to molecular association in the liquid state, the position of the effective moment is altered, the calculated value of the Kerr constant would be diminished, and would then agree better with the observed value. Even as it stands, the results of the calculation furnish strong support to Born's expression for the Kerr constant in preference to that due to Langevin. The latter gives for chloroform the value $+1{\cdot}02 \times 10^{-7}$, which has the wrong sign, and is also numerically much smaller than the observed value.

A negative value for the Kerr constant cannot be explained on the basis of Langevin's theory unless we make the improbable assumption that the maximum electrostatic polarizability of the molecule is along directions of smaller

* C. P. Smyth, Journ. Am. Chem. Soc. xlvi. p. 2151 (1924).

optical polarizability—an assumption which cannot be reconciled with the ideas of Bragg regarding the cause of electrostatic and optical anisotropy, viz., as being due to atomic interaction.

5. *The General Case.*

In general there is considerable uncertainty both as regards the form of the optical ellipsoid and the position of the permanent moment, even for the individual molecules. For the present we shall, for the purpose of tentative calculations, assume that the effective optical ellipsoid is a spheroid of revolution whose axis coincides with the axis of the permanent doublet, the spheroid being taken as prolate or oblate according as the Kerr constant is positive or negative. This would obviously be far from the truth in most cases, and it is not surprising that we find in several cases large differences between the calculated and observed values as shown in Table III. It is significant, however, that the calculated values are always numerically higher than the observed, which is what we should expect, as the assumptions made are such as make the calculated value of the Kerr constant numerically a maximum.

TABLE III.

Liquid.	$K_1 \times 10^7$.	$K_2 \times 10^7$.	Kerr constant $\times 10^7$.	
			Calculated $= K_1 + K_2$.	Observed.
Propyl chloride	0·72	16·3	17·0	7·55
Methylene chloride ...	1·26	−9·6	−8·3	−1·16
Ethylene chloride	2·12	35·5	37·6	4·71
Acetic acid	1·18	12·2	13·4	4·19
Propionic acid	0·38	2·3	2·7	1·39
Ethyl ether.....	0·22	−1·49	−1·27	−0·618
Ethyl formate	0·74	18·2	18·9	4·45
Ethyl acetate	0·49	10·4	10·9	1·68
Acetone	3·6	120	124	16·3

6. *Monohydric Alcohols.*

Since the value of the Kerr constant depends on the angle between the axis of the electric moment of the molecule and its optic axis, which in its turn depends on the chemical structure of the molecule, we should expect certain

similarities in the behaviour of molecules of the same type. That is actually what we find, for instance, in the case of the monohydric alcohols. Table IV. shows in column 2 the observed values of K; column 3 gives the values of K_1 calculated according to equation (10); column 4 gives $K-K_1=K_2$; and the last column gives the values of K_2 directly evaluated on the assumption that the optical ellipsoid is a prolate spheroid of revolution with the permanent moment perpendicular to the axis of the spheroid.

TABLE IV.

Liquid.	$K\times10^7$ observed.	$K_1\times10^7$.	$K-K_1=K_2\times10^7$.	$K_2\times10^7$ calculated directly.
Methyl alcohol	0·97	1·41	−0·44	−40
Ethyl alcohol.....	0·768	0·96	−0·19	−32
Propyl alcohol	−2·52	0·99	−3·51	−31
Butyl alcohol.....	−3·65	1·01	−4·66	−29
Isobutyl alcohol	−3·58	0·90	−4·48	−29

It will be seen that the values of K_2 in column 4 are far smaller numerically than the values calculated according to the above assumptions. Theoretically the contribution from the permanent moment to the Kerr constant will be nothing when it makes an angle of 54° 44′ with the axis of the optical spheroid (corresponding to the condition $2\cos^2\alpha-\sin^2\alpha=0$). The small values of K_2 in column 4 therefore suggest that in the case of the alcohols the permanent moments, instead of being perpendicular to the optical axis, are inclined to it at an angle not much greater than 55°. Indeed, there is reason to believe that in the monohydric alcohols the OH group, which is chiefly responsible for the polarity, is inclined to the hydrocarbon chain at an angle which may vary slightly with the length of the chain.

7. *Some Benzene Derivatives.*

Let us take another example—simple derivatives of benzene. As in Part I., the optical ellipsoids of these molecules can be roughly considered to be oblate spheroids of revolution. Table V. gives the calculations for some of

these molecules, assuming that the permanent moment is in the plane of the ring. In the case of aniline and benzyl alcohol, for which the Kerr constant is negative, the moment is taken to be perpendicular to the plane, a supposition which, however, is *a priori* much less probable than that of a moderate inclination to the plane of the ring.

TABLE V.

Liquid.	$K_1 \times 10^7$.	$K_2 \times 10^7$.	Kerr constant $\times 10^7$.	
			Calculated $= K_1 + K_2$.	Observed.
Toluene	0·80	0·31	1·11	0·753
Ethyl benzene	0·84	0·42	1·26	0·754
Chlorobenzene	3·15	10·3	13·5	9·1
Bromobenzene	3·99	10·0	14·0	9·1
Nitrobenzene	184	770	950	256
Aniline	3·74	−29	−25	−1·23
Benzyl alcohol	12·0	−130	−118	−15·4

For toluene and ethyl benzene the contribution from the electrical polarity of the molecule is very small. In other cases the calculated values of the Kerr constant are numerically larger than the observed values, thus pointing to an inclination of the permanent moments to the plane of the ring. Whether this inclination arises from a distortion, due to the heavy substituents, of the benzene ring, which is otherwise plane, or whether it is due to the fact that ths ring is puckered, and consequently the substituent atoms like Cl or Br are attached to the ring at an angle, cannot be decided without further data, especially for the vapour.

8. *Temperature Dependence of the Kerr Constant.*

We now come to the question of the variation of the Kerr constant of liquids with temperature. We have seen that the value of the optical anisotropy and of the permanent moment calculated from the liquid state is less than that calculated from the vapour. As the temperature is raised, the values continually approach the value for the vapour.

Therefore any discussion of the temperature dependence of the Kerr constant of liquids must naturally take this variation into account. However, since the scattering measurements are not available at different temperatures, we shall, to a first approximation, assume the anisotropic constants to be independent of temperature, and shall only take into consideration the change in the effective value of the permanent moment μ, as given by eqn. (9). We shall also suppose that when the effective value of μ changes, its position with respect to the optic axes is not altered. With these assumptions the expression for the Kerr constant can be written in the form

$$K \propto \frac{(n_0^2-1)(n_0^2+2)(\delta+2)^2}{n_0 T}\left(1+\phi\frac{\mu^2}{T}\right), \quad . \quad (11)$$

where ϕ is a constant independent of temperature. ϕ can be evaluated from the known values of the quantities involved, at 20° C.

Table VI. includes all the liquids whose Kerr constant has been investigated over a long range of temperature. Column 3 gives the ratio of the values of K at the extreme limits of the range of temperature over which they have been studied, calculated according to (11). The observed values of the ratio are given in column 4 for comparison.

TABLE VI.

Liquid.	Limits of the range of temperature over which investigated.		Kerr const. at t_2° C. / Kerr const. at t_1° C.		Observer *.
	t_1 (0° C.).	t_2 (0° C.).	Calculated.	Observed.	
Toluene	−78·5	18	0·56	0·58	L. W.
	−20	100	0·51	0·59	B.
Chlorobenzene ...	−20	100	0·30	0·39	B.
Bromobenzene ...	−20	100	0·33	0·41	B.
Nitrobenzene	5·5	25	0·76	0·74	S.
Ethyl ether.....	−78·5	18	0·17	0·26	L. W.
Chloroform	−20	55	0·40	0·42	B.

* L. W.—N. Lyon and F. Wolfram, *Ann. der Phys.* lxiii. p. 739 (1920).
B.—C. Bergholm, *Ann. der Phys.* lxv. p. 128 (1921).
S.—G. Szivessy, *Zeit. f. Phys.* ii. p 30 (1920).

Considering the nature of the assumptions made, the agreement between the calculated and the observed values is quite satisfactory, so that measurements on the temperature dependence of the Kerr constant of liquids, far from disproving Born's expression, actually support it.

9. *Summary.*

1. In this part the discussion of the available data on electric double-refraction in relation to the polarity and optical anisotropy of the molecules is extended to the liquid state.

2. It is found that, just as in the case of vapours, all the compounds which exhibit a large Kerr effect are characterized by the possession of electrically polar molecules, the influence of the polarity on the Kerr constant being here even more pronounced than in the case of vapours.

3. In the case of non-polar molecules the moments induced in the molecules when placed in an electrostatic field are sufficient to account quantitatively for the observed double-refraction.

4. In simple cases of polar liquids like chloroform, where we have definite information regarding the form of the optical ellipsoid and the position of the electric moment, the observed Kerr constant is in numerical agreement with that calculated on the basis of Born's theory, which takes into account also the orientative couples exerted by the external field on the permanent doublets present in the molecules.

5. Even in the general case there is nothing to throw doubt on the validity of Born's theory. In the case of alcohols, for instance, the contribution from the permanent moments to the Kerr constant is found to be very small, and this is explained on the assumption of suitable positions for the permanent moment, which are not improbable from our knowledge of their structure. In the cases of benzene derivatives, also, the moments are apparently inclined to the plane of the ring.

6. Measurements on the dependence on temperature of the electric double-refraction of liquids support the validity of Born's expression for the Kerr constant.

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The Diffraction of Light by Metallic Screens.

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THE DIFFRACTION OF LIGHT BY METALLIC SCREENS.

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The Diffraction of Light by Metallic Screens.

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1. *Introduction.*

Gouy* discovered that when a metallic screen with a sharp and highly-polished edge is held in the path of a pencil of light, its boundary appears as a luminous line diffracting light through large angles, both into the region of shadow (interior diffraction) and into the region of light (exterior diffraction). He noticed further that this diffracted light is strongly polarised, but in perpendicular planes in the two regions mentioned; the colour of the diffracted light and its state of polarisation depend in a remarkable manner on the material of the screen and on the extent to which its edge is rounded off in the process of polishing. When the edge is viewed through a double-image-prism from within the shadow, only that image appears coloured which is more intense and is polarised with the magnetic vector parallel to the edge. The second image which is fainter and is polarised with the electric vector parallel to the edge, appears perfectly white. When the incident light is polarised in any arbitrary azimuth, the diffracted light is found to exhibit elliptic polarisation. These and other results have been confirmed by later observers.†

Gouy's experimental results were discussed by Poincaré on the basis of the electromagnetic theory of light in two memoirs published in the "Acta Mathematica."‡ The special case of an ideal screen (plane or wedge-shaped), supposed perfectly-reflecting and having a sharp edge, is amenable to complete theoretical treatment, and was dealt with by Poincaré himself, and later in a rigorous manner by Sommerfeld,§ and following him by numerous other mathematicians. The behaviour of actual metallic screens, however, differs considerably from that found theoretically for this ideal case. Though attempts have been made by Poincaré himself in the memoirs quoted, and later also by Epstein,|| to take the nature of the screen and the rounding of its edge into account, it cannot be said that Gouy's observations have so far received a complete or satisfactory explanation. We propose in this paper to discuss more particularly the

* 'Ann. Chim. et Physique,' vol. 8, p. 145 (1886).

† W. Wien, 'Wied. Ann.,' vol. 28, p. 117 (1886).

‡ 'Acta Mathematica,' vol. 16, p. 297 (1892), and vol. 20, p. 313 (1896).

§ 'Math. Annalen,' vol. 47, p. 317 (1896).

|| 'Diss. Munich'; also 'Encyklop. d. math. Wissensch.,' vol. V (3), p. 491.

influence of the material of the screen on the diffraction by a sharp edge, and to show how it may be explained in a very simple manner. The case of rounded edges is reserved for discussion in a separate paper.

In the fifth section of his first memoir, Poincaré discussed the electromagnetic boundary conditions at the surface of an imperfectly conducting screen, and made the important remark that the extreme smallness of the depth to which an optical disturbance penetrates into any actual metal, should considerably simplify the theory. In his actual attempt, however, to discuss the problem of diffraction by an imperfectly conducting screen, he made no use of the elegant mathematical methods and results contained in the earlier parts of his memoir, and contented himself with a qualitative discussion on the basis of the Kirchhoff formulation of Huygens' Principle. The treatment given does not, as was indeed remarked by Poincaré himself, appear capable of leading to quantitative results. In the course of our paper, we shall show how it is possible to apply the Fresnel-Huygens' Principle with success to the problem of diffraction by imperfectly-conducting screens. It is more convenient, however, to base our treatment in the first instance on a modification of the known exact solutions for the case of perfectly-reflecting screens or wedges.

2. *Theory.*

Sommerfeld's solution of the wave-equation in cylindrical co-ordinates for the case of a semi-infinite screen which is a perfect reflector and lies in the xz-plane, with its edge along the z-axis, is

$$u = \mathrm{F}(\rho, \phi, \phi_0) \mp \mathrm{F}(\rho, \phi, -\phi_0). \tag{1}$$

The upper (minus) sign refers to the case in which the plane of polarisation and the plane of incidence are parallel to each other; (we shall refer to this as the $\|^l$ case), and u then denotes the electric force parallel to the edge. The lower (plus) sign refers to the case in which the plane of polarisation of the incident light is perpendicular to the plane of incidence (we shall refer to this as the $\perp^r$ case), u then denoting the magnetic force parallel to the edge.

$$\mathrm{F}(\rho, \phi, \phi_0) = \left(\frac{i}{\pi}\right)^{\frac{1}{2}} e^{i\frac{2\pi t}{\mathrm{T}}} e^{ik\rho\cos(\phi-\phi_0)} \int_{-\infty}^{\tau} e^{-i\lambda^2}\, d\lambda, \tag{2}$$

where

$$\tau = \sqrt{2k\rho}\,.\cos\tfrac{1}{2}(\phi - \phi_0).$$

The expression (2) has the property that when τ is positive and sufficiently large, which is the case when $\pi + \phi_0 > \phi > 0$, the function tends to the limiting value $e^{i\frac{2\pi t}{\mathrm{T}}}\, e^{ik\rho\cos(\phi-\phi_0)}$, which represents a train of plane waves incident on

the screen in a direction making an angle ϕ_0 with its plane ; when τ is negative and sufficiently large, which is the case when $\pi + \phi_0 < \phi < 2\pi$, the function tends to the limit zero. F $(\rho, \phi, -\phi_0)$ is obtained by writing $-\phi_0$ for ϕ_0. When $\pi - \phi_0 > \phi > 0$ it tends to the limit $e^{i\frac{2\pi t}{T}} e^{ik\rho\cos(\phi+\phi_0)}$, which represents a plane train of waves reflected from the screen. When $\pi - \phi_0 < \phi < 2\pi$, F $(\rho, \phi, -\phi_0)$ tends to the limit zero.

Now the solutions (1) satisfy the conditions $u = 0$ and $\frac{\partial u}{\partial \phi} = 0$ respectively, on both faces of the screen, supposed to be infinitely thin and perfectly reflecting, that is, when $\phi = 0$ and also when $\phi = 2\pi$. Now any actual screen to be opaque must be of finite thickness, hence a solution of the form (1) or any simple modification of it cannot be expected to represent the behaviour of such screens *completely*. Nevertheless, as already mentioned above, a metallic screen of a thickness which is only a small fraction of a wave-length, is practically opaque, and this makes it possible to represent its behaviour with a high degree of accuracy by a comparatively simple modification of (1). Consider expressions of the form

$$u = \mathrm{F}(\rho, \phi, \phi_0) - (\mathrm{C}_s + i\mathrm{D}_s) \,.\, \mathrm{F}(\rho, \phi, -\phi_0) \qquad (3)$$

and

$$u = \mathrm{F}(\rho, \phi, \phi_0) + (\mathrm{C}_p + i\mathrm{D}_p) \,.\, \mathrm{F}(\rho, \phi, -\phi_0) \qquad (4)$$

in which the (numerical) factors $\mathrm{C}_s + i\mathrm{D}_s$ and $\mathrm{C}_p + i\mathrm{D}_p$ are so chosen that they represent the amplitude of the wave reflected at the illuminated face of the particular screen used, for the particular angle of incidence under consideration. Equation (3) refers to the $\|^l$ case, and (4) to the $\perp^r$ case. Since $\mathrm{C}_s + i\mathrm{D}_s$ and $\mathrm{C}_p + i\mathrm{D}_p$ are functions only of the angle of incidence ϕ_0, (3) and (4) continue to satisfy the wave-equation and represent distributions of light and shadow of the same general character as those indicated by (1), with this difference, however, that the disturbance on the illuminated face of the screen expressed by (3) and (4) will have the actual values corresponding to the screen used, while (1) corresponds to a screen with properties which cannot be physically realised. We are therefore justified in expecting that (3) and (4) would represent the disturbance throughout the whole field in the actual problem much more accurately than the Sommerfeld formulæ.

To understand the physical significance of the formulæ, it is best to use the asymptotic expressions for the functions for large values of ρ. We have, when $\cos\frac{1}{2}(\phi - \phi_0)$ is positive,

$$\mathrm{F}(\rho, \phi, \phi_0) \backsim e^{i\frac{2\pi t}{T}} e^{ik\rho\cos(\phi-\phi_0)} + \frac{i^{3/2} e^{i\frac{2\pi t}{T}} e^{-ik\rho}}{2\sqrt{2\pi k\rho} \,.\, \cos\frac{1}{2}(\phi - \phi_0)}, \qquad (5)$$

while when $\cos \frac{1}{2}(\phi - \phi_0)$ is negative, there is a similar expression in which the first term is missing. Similarly when $\cos \frac{1}{2}(\phi + \phi_0)$ is positive, we have

$$F(\rho, \phi, -\phi_0) \backsim e^{i\frac{2\pi t}{T}} e^{ik\rho\cos(\phi+\phi_0)} + \frac{i^{3/2} e^{i\frac{2\pi t}{T}} e^{-ik\rho}}{2\sqrt{2\pi k\rho} \cdot \cos \frac{1}{2}(\phi+\phi_0)}, \tag{6}$$

and a similar expression in which the first term is missing, if $\cos \frac{1}{2}(\phi + \phi_0)$ is negative. The general expression for the light diffracted by the edge is either

$$E_z = \frac{i^{3/2} e^{i\frac{2\pi t}{T}} e^{-ik\rho}}{2\sqrt{2\pi k\rho}} \left[\frac{1}{\cos \frac{1}{2}(\phi-\phi_0)} - \frac{C_s + iD_s}{\cos \frac{1}{2}(\phi + \phi_0)}\right] \tag{7}$$

or

$$H_z = \frac{i^{3/2} e^{i\frac{2\pi t}{T}} e^{-ik\rho}}{2\sqrt{2\pi k\rho}} \left[\frac{1}{\cos \frac{1}{2}(\phi-\phi_0)} + \frac{C_p + iD_p}{\cos \frac{1}{2}(\phi + \phi_0)}\right]. \tag{8}$$

3. *An Alternative Treatment.*

The formulæ (7) and (8) may also be derived in the following manner based on the Fresnel-Huygens' Principle. It is readily shown that the wave-equation in cylindrical co-ordinates,

$$\frac{\partial^2 u}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial u}{\partial \rho} + \frac{1}{\rho^2}\frac{\partial^2 u}{\partial \phi^2} + \frac{\partial^2 u}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0, \tag{9}$$

is exactly satisfied by putting

$$u = e^{i\frac{2\pi t}{T}} \frac{e^{-ik\rho}}{2\sqrt{2\pi k\rho}} \cos \tfrac{1}{2}(\phi + \varepsilon), \tag{10}$$

which represents a cylindrical wave of Poisson's type diverging from the z-axis. A plane wave incident on the xz-plane in the direction ϕ_0 is transmitted through the part of the plane to the left of the edge and is reflected from the part on the right. To find the disturbance diverging from the edge of the screen, at any point very distant from it, we divide the area of the xz-plane adjacent to the edge into half-period strips parallel to it on either side, and show in the usual way that the effect of the transmitted wave reduces to one-half of the first half-period strip on one side of the edge, and that the effect of the reflected wave reduces to that of a similar strip on the other side. Assuming that each of these strips is the origin of a cylindrical wave of the type appearing in (10), we may write the total disturbance at (ρ, ϕ) diverging from the origin, in the form

$$u = e^{i\frac{2\pi t}{T}} \frac{e^{-ik\rho}}{2\sqrt{2\pi k\rho}} [A_0 \cos \tfrac{1}{2}(\phi + \alpha) + B_0 \cos \tfrac{1}{2}(\phi + \beta)], \tag{11}$$

where A_0, B_0, α and β have to be so chosen as to give the amplitudes and phases of the divergent waves correctly. Now the width of either half-period strip is easily shown to be

$$\frac{\lambda}{4\cos\frac{1}{2}(\phi-\phi_0)\cos\frac{1}{2}(\phi+\phi_0)},$$

and we may assume, as is usual in the elementary diffraction theory, that the amplitudes A_0 and B_0 are proportional to this width. It is necessary that the term in (11) proportional to A_0, contributed by the transmitted wave, remains finite when $\phi = \pi - \phi_0$, and that proportional to B_0, contributed by the reflected wave, remains finite when $\phi = \pi + \phi_0$, as these directions do not coincide with the respective directions of travel of these waves. We are thus obliged to assume that $\alpha = \phi_0$ and that $\beta = -\phi_0$. The equation (11) then reduces to

$$u = e^{i\frac{2\pi t}{T}}\frac{e^{-ik\rho}}{2\sqrt{2\pi k\rho}}\left[\frac{A}{\cos\frac{1}{2}(\phi-\phi_0)}+\frac{B}{\cos\frac{1}{2}(\phi+\phi_0)}\right], \qquad (12)$$

where A and B are suitably chosen constants. As in the elementary diffraction theory we write

$$A = e^{-i\frac{\pi}{4}} = i^{3/2},$$

which expresses the difference of path of $\lambda/8$ between a parent plane wave and the divergent cylindrical wave from a laminar strip cut out of it. The value of B relatively to A evidently depends on the change of amplitude and phase occurring in reflection at the surface of the screen. We write therefore

$$B/A = -(C_s + iD_s) \quad \text{or} \quad +(C_p + iD_p),$$

according to the state of polarisation of the incident beam. The formulæ (7) and (8) are then reproduced.

4. *Explanation of Ellipticity of the Diffracted Light.*

From expressions (7) and (8) the ellipticity of the light diffracted through large angles, when the incident light is polarised in any arbitrary azimuth, follows as an immediate consequence. We shall consider first the case of normal incidence on a plane screen. We have then

$$C_s + iD_s = C_p + iD_p = \frac{n(1-i\kappa)-1}{n(1-i\kappa)+1}.$$

Taking for the case of a steel edge and for $\lambda = 5{\cdot}80 \times 10^{-5}$ cm., $n\kappa = 3{\cdot}24$ and $n = 2{\cdot}46$, we have $C_s + iD_s = C_p + iD_p = 0{\cdot}69 - i \times 0{\cdot}29$. With these numerical values and writing the expressions in the square brackets on the right-

hand side of (7) and (8) in the form $F_s + iG_s$ and $F_p + iG_p$ respectively, the values of $F_s^2 + G_s^2$ and of $F_p^2 + G_p^2$ for various angles of observation, and the phase differences between these two components are shown in Table I.

Gouy noticed that with a sharp steel edge, the light diffracted into the region of shadow shows no sensible ellipticity when the deviation is less than 45°. For larger deviations, it becomes sensible, the $\|^l$ component being in advance of the $\perp^r$ component, the difference of path being, however, always numerically less than $\lambda/4$. It will be seen that this is in general agreement with the figures for the difference of path shown in the fifth column of Table I. The table also indicates the interesting result that in the region of exterior diffraction, the path difference changes sign and increases in a continuous manner up to the boundary of reflection, when it becomes half a wave-length, while according to the Sommerfeld formulæ there is a sudden reversal of phase when the diffracted ray lies in the continuation of the plane of the screen.

Table I.—Diffraction by Steel Edge : Normal Incidence.

$\|^l$ and $\perp^r$ indicate plane of polarisation parallel and perpendicular respectively to the plane of incidence.

$\lambda = 5{\cdot}80 \times 10^{-5}$ cm.

Region of observation.	Direction of diffracted ray ϕ.	Intensity of $\|^l$ component $F_s^2+G_s^2$.	Intensity of $\perp^r$ component $F_p^2+G_p^2$.	Difference of path between the components $\frac{\delta_p-\delta_s}{\lambda}$.	Difference of path according to Sommerfeld formulæ.
	°				
Boundary of reflection....	90	—	—	0·50	0·50
Exterior diffraction (region of illumination)	120	15·0	3·9	0·45	0·50
	150	6·7	0·38	0·35	0·50
	180	5·9	0·36	0·15	—
	210	8·0	1·55	0·06	0
	240	21·1	10·0	0·03	0
Boundary of shadow.....	270	—	—	0	0
Interior diffraction (region of shadow)	285	49	70	−0·01	0
	300	10·0	21·1	−0·03	0
	315	3·6	11·4	−0·04	0
	330	1·55	8·0	−0·06	0
	345	0·72	6·4	−0·09	0
	360	0·36	5·9	−0·15	—

5. *Effect of Oblique Incidence.*

When the light is incident on the screen obliquely at an angle θ (measured as usual from the normal) we have

$$C_s + iD_s = -\frac{\cos\theta - \sqrt{n^2(1-i\kappa)^2 - \sin^2\theta}}{\cos\theta + \sqrt{n^2(1-i\kappa)^2 - \sin^2\theta}}, \tag{13}$$

and

$$C_p + iD_p = \frac{n^2(1-i\kappa)^2\cos\theta - \sqrt{n^2(1-i\kappa)^2 - \sin^2\theta}}{n^2(1-i\kappa)^2\cos\theta + \sqrt{n^2(1-i\kappa)^2 - \sin^2\theta}}, \tag{14}$$

At normal incidence (13) and (14) are equal, and at grazing incidence they are again equal but opposite in sign. At the principal incidence (which lies between 70° and 80° for most metals) the difference of path between the $\parallel$ and $\perp^r$ components of the reflected wave amounts to $\lambda/4$ and then rapidly diminishes to 0 as grazing incidence is approached. With the help of the formulæ (7), (8), (13) and (14) the intensity of the two components of the diffracted light and their phase-difference can be calculated for any angle of incidence and of observation. Let us first consider moderately oblique incidence. Two cases have naturally to be distinguished, viz., when the incidence is from the screen-side of the normal, and when it is from the farther side. Tables II and III give the values for a steel screen when $\phi_0 = 135°$ and 45°, respectively, for yellow light. It can be seen that the effects observed in interior and exterior diffraction are no longer similar to each other.

Table II.—Diffraction by a Steel Edge. $\phi_0 = 135°$.

Region of observation.	Direction of diffracted ray ϕ.	Intensity of $\parallel^r$ component $F_s^2+G_s^2$.	Intensity of $\perp^r$ component $F_p^2+G_p^2$.	Difference of path between the components $\frac{\delta_p-\delta_s}{\lambda}$.
	°			
	135	4·6	0·30	0·23
	180	3·8	0·35	0·14
Exterior diffraction	225	4·9	0·8	0·09
	270	12	4·0	0·04
	285	24	11	0·03
	300	75	48	0·02
Boundary of shadow.....	315	—	—	0
	330	41	75	−0·02
Region of shadow	345	6·0	27	−0·05
	360	0·7	18	−0·17

In the case considered in Table II, the region of shadow is of much smaller angular width, and the degree of polarisation and also the ellipticity increase rapidly as we approach the plane of the screen ($\phi = 360°$). On the other hand, in Table III the region of shadow is much wider, and the polarisation and ellipticity of the diffracted light increase less rapidly with increasing deviation of the diffracted ray. In exterior diffraction these effects are reversed.

Table III.—Diffraction by a Steel Edge. $\phi_0 = 45°$.

Region of observation.	Direction of diffracted ray ϕ.	Intensity of $\|\|^l$ component $F_s^2+G_s^2$.	Intensity of $\perp^r$ component $F_p^2+G_p^2$.	Difference of path between the components $\frac{\delta_p-\delta_s}{\lambda}$.
	°			
	135	—	—	0·45
Exterior diffraction	165	28	2·3	0·32
	195	31	8·4	0·06
Boundary of shadow	225	—	—	0
	255	9·6	22	−0·03
	285	1·5	7·0	−0·06
Region of shadow	315	0·5	4·2	−0·09
	345	0·2	3·3	−0·14
	360	0·1	3·1	−0·17

6. *Diminished Intensity of Diffracted Light.*

If we compare the figures shown in Tables II and III with those calculated from Sommerfeld's formulæ for a perfectly reflecting screen, we find that the effect of imperfect conductivity of the screen is not only to introduce elliptic polarisation, but also to diminish the total intensity of the diffracted light and the ratio of the components of vibration for specified angles of incidence and diffraction. In fact, these effects are all closely related to one another, and become the more striking when the incidence is very oblique.

In Table IV the case of oblique incidence on a steel edge has been worked out and shown. It is assumed that $\phi_0 = 170°$, that is, only 10° short of grazing incidence. The figures for the steel edge and for a perfectly reflecting screen are shown side by side for comparison, and it will be seen that the intensity of the $\perp^r$ component is diminished to one-fifth of its value, on the surface of the screen, by reason of the imperfect conductivity, while that of the $||^l$ component is very slightly increased. Nevertheless, the ratio of the $\perp^r$ and $||^l$ components remains large, showing that even at such incidences the polarisation remains large. We have to approach grazing incidence still more closely before the

Table IV.—Diffraction by a Steel Edge. $\phi_0 = 170°$.

Region of Shadow.

Direction of diffracted ray ϕ.	Intensity of $\parallel^l$ component for a *perfect conductor*.	Intensity of $\parallel^l$ component for *steel* $F_s^2+G_s^2$.	Intensity of $\perp^r$ component for *steel* $F_p^2+G_p^2$.	Intensity of $\perp^r$ component for a *perfect conductor*.	Difference of path between the components for *steel* $\frac{\delta_p-\delta_s}{\lambda}$.
°					
350	—	—	—	—	0
352	2590	2600	3100	4060	−0·01
354	460	480	750	1280	−0·02
356	119	128	313	746	−0·04
358	23	28	170	571	−0·07
360	0	0·9	109	527	−0·23

diminution of the $\perp^r$ component is such as to produce a striking diminution of the completeness of polarisation. From formulæ (7), (8), (13) and (14) it follows that, at grazing incidence, the diffracted light should be unpolarised at all angles.

The foregoing considerations help to explain, at least in part, the interesting observation of Gouy that for given directions of the incident and diffracted rays, the intensity of the diffracted light is a *maximum* when the plane of the screen bisects the angle between these two directions. According to Sommerfeld's formulæ the intensity should be a *minimum* for this position of the screen. Owing, however, to the imperfect conductivity of actual screens, as we have seen, the intensity falls off in approaching the extreme cases in which the light is incident grazingly on the screen from either direction. As we shall see later, other circumstances, as, for instance, the finite angle formed by the faces of the screen at the edge, or the actual rounding off of the latter, would also operate in the direction of diminishing the intensity of the diffracted light in the two extreme positions of the screen. Hence the intermediate position for the screen actually gives the maximum instead of the minimum intensity for the diffracted rays in the particular direction.

7. *Explanation of Diffraction Colours.*

The wave-length enters in the expression for the intensity of the diffracted light in two distinct ways. Referring to (7) and (8) it will be seen that the intensity is inversely proportional to k, that is, proportional to the wave-length. The longer wave-lengths would thus tend to be more prominent in

the light diffracted by the edge than in the incident light. This effect would operate both on the parallel and perpendicular components of vibration in the diffracted light. The colour of the diffracted light is also influenced, and in an entirely different way, by the factors $C_s + iD_s$ and $C_p + iD_p$ appearing in (7) and (8), which are, in general, functions of the wave-length of the incident light. If we confine ourselves to the case of normal incidence, $C_s + iD_s$ and $C_p + iD_p$ are identical in magnitude. But the former appears with a negative sign in (7) and the latter with a positive sign in (8). Hence, if a particular wave-length appears with a strengthened amplitude in (8) it will appear with a weakened amplitude in (7), and *vice versa*. This, taken together with the proportionality to λ already mentioned, furnishes an explanation of the difference in the colour of the parallel and perpendicular components of the light diffracted into the region of shadow, which was discovered by Gouy for metals such as copper and gold. It can easily be seen that in the region of shadow, the longer wave-lengths which are strongly reflected by the metal would be much enhanced in the perpendicular component, while the corresponding weakening in the parallel component would be almost insensible. In the region of exterior diffraction, these features are interchanged.

Table V.—Gold Screen. $\phi_0 = 90°$ (Normal Incidence).

Direction of diffracted ray ϕ.	$(F_s^2+G_s^2)\ \lambda \times 10^5$, for $\lambda \times 10^5 =$			$(F_p^2+G_p^3)\ \lambda \times 10^5$, for $\lambda \times 10^5 =$		
	4·20.	5·80.	7·00.	4·20.	5·80.	7·00.
°						
270	—	—	—	—	—	—
285	217	282	326	279	408	508
300	48·3	59·0	64·4	80·4	125	159
315	19·1	22·1	22·1	41·8	68·3	88·7
330	9·56	10·7	9·50	28·1	48·5	63·9
345	5·44	6·36	4·87	22·1	40·2	53·6
360	3·41	4·86	3·48	19·5	37·6	50·7

In Table V the intensity of the diffracted light has been calculated for the case of a gold screen using the following data :—

$$\lambda = 7{\cdot}00 \times 10^{-5}\,\text{cm.} \;;\; n = 0{\cdot}280 \;,\; n\kappa = 3{\cdot}800 \;;$$
$$\lambda = 5{\cdot}80 \times 10^{-5}\,\text{cm.} \;;\; n = 0{\cdot}415 \;,\; n\kappa = 2{\cdot}750 \;;$$
$$\lambda = 4{\cdot}20 \times 10^{-5}\,\text{cm.} \;;\; n = 1{\cdot}570 \;,\; n\kappa = 1{\cdot}800.$$

From the table it will be seen that in the region of shadow $(F_s^2 + G_s^2)\lambda$ has practically the same value for different wave-lengths, while $(F_p^2 + G_p^2)\ \lambda$

increases in value as we proceed towards the red end of the spectrum. The increase with wave-length is much more marked for large angles of diffraction than for small angles. Further, $F_p^2 + G_p^2$ is always greater than $F_s^2 + G_s^2$, the ratio between the two increasing with the angle of diffraction. From these facts, it follows that when the region of shadow is examined, the $\|^l$ component of the diffracted light will be perfectly white, while the $\perp^r$ component, which is in fact much stronger than the other, will exhibit an orange-yellow tint, the colouration being the more marked, the further we go into the region of shadow. The same colour effects will be noticeable also in the region of exterior diffraction, the $\|^l$ and $\perp^r$ components now, however, exchanging places.

8. *Intensified Colours at Oblique Incidences.*

While the variation with wave-length of the intensity of the $\perp^r$ component shown in Table V is marked enough, it is not exceptionally large, being in fact of the same order of magnitude as the variation of the reflecting power of the metal with wave-length. This is in agreement with observation, for Gouy found that the sharpest metallic edges do not show particularly vivid colours by diffraction. When, however, the incidence on the screen is made oblique, the colours of the $\perp^r$ component should become more lively. To understand why this should be the case, we have only to refer to section 6 above, in which it was shown that the imperfect reflectivity of the metal results in a diminution of the intensity of the diffracted light in comparison with the theoretical value for a perfectly reflecting screen, and that this diminution becomes the more marked as the incidence of the light on the screen becomes more oblique. Those wave-lengths, however, for which the reflecting power of the metal approaches unity, persist in nearly full strength in the $\perp^r$ component of the diffracted light, and hence determine its colour in increasing measure as the obliquity of the screen is increased. It is to be noted also that the colour should appear at smaller deviations of the ray in interior diffraction, and at larger deviations in exterior diffraction, or *vice versa*, according to the position of the screen.

In Table VI the case of a gold screen, for a position of the screen 10° short of grazing incidence, has been worked out and the intensities of the $\|^l$ and $\perp^r$ components are shown for six different wave-lengths, the direction of observation considered being along the surface of the screen in the region of shadow. The normal reflecting power of the metal for the same wave-lengths is also shown for comparison.

Table VI.—Gold Edge. $\phi_0 = 170°$, $\phi = 360°$.

$\lambda \times 10^5$ (cm.).	Intensity of $\|\|^l$ component $(F_s^2+G_s^2)\ \lambda \times 10^5$.	Intensity of $\perp^r$ component $(F_p^2+G_p^2)\ \lambda \times 10^5$.	The reflection coefficient.
4·00	9·9	200	0·360
4·60	12·5	210	0·358
5·20	17·5	240	0·608
5·80	10·5	470	0·827
6·20	8·8	650	0·889
7·00	7·1	1000	0·930

It will be noticed that the intensity of the $\|^l$ component varies but little with wave-length, while the $\perp^r$ component shows large intensities in the orange and red regions in the spectrum. The effect in the latter case is of a highly selective character, becoming pronounced only for the wave-lengths for which the reflecting power of the metal approaches unity.

When the figures shown in Table VI are computed after the manner employed by the late Lord Rayleigh* for discussion of the colours of thin plates, and plotted in Maxwell's colour-triangle, it is found that the $\|^l$ component is perfectly white, while the $\perp^r$ component is of a rich orange-yellow colour.

The case of other metals may be worked out in a similar manner. In Table VII are given the reflection-coefficients and the colour of the diffracted light as observed by Gouy and Wien, for a number of metals. The general relationship between them is fairly clear from the figures. In the case of the whiter metals, of course, the colour is largely determined by the factor λ appearing in the expression for the intensity of the diffracted light.

Table VII.—Reflection Coefficients and Diffraction Colours.

For $\lambda \times 10^5 =$	4·20	4·50	5·00	5·50	6·00	6·50	7·00	Colour of $\perp^r$ component of diffracted light.
Silver	0·866	0·905	0·913	0·927	0·926	0·935	0·946	Pale yellow.
Copper	0·33	0·37	0·44	0·48	0·72	0·80	0·83	Red.
Steel	0·52	0·54	0·55	0·55	0·55	0·56	0·58	Reddish white.
Platinum	0·518	0·547	0·584	0·611	0·642	0·663	0·69	Yellow.
Zinc	0·803	0·806	0·805	0·789	0·774	0·771	0·770	Colour insensible.
Tin	—	0·605	0·670	0·686	0·706	0·713	0·716	Greenish yellow.

* Lord Rayleigh, 'Scientific Papers,' vol. 2, p. 498.

9. *Diffraction by Metallic Wedges.*

Poincaré considered the case of a perfectly reflecting wedge in his first memoir, and showed that if the surfaces of the wedge are given by the angles $\phi = 0$ and $\phi = \chi$, the rays diffracted from its edge have an amplitude proportional to

$$\left[\frac{1}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi - \phi_0)} \mp \frac{1}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi + \phi_0)} \right]. \qquad (15)$$

As the result of a more elaborate analysis, Wiegrefe* found for the cylindrical wave diverging from a wedge-shaped edge the identical expression given by (15) with the multiplying factor

$$- i^{3/2} e^{i\frac{2\pi t}{T}} e^{-ik\rho} \sqrt{\frac{\lambda}{\rho}} \cdot \frac{\sin\frac{\pi^2}{\chi}}{2\chi}. \qquad (16)$$

On putting $\chi = 2\pi$, the formulæ (15) and (16) reduce to those for the case of a perfectly reflecting plane screen. In the case of an imperfectly conducting wedge, we modify expression (15) and write it in the form.

$$\left[\frac{1}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi - \phi_0)} - \frac{C_s + iD_s}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi + \phi_0)} \right], \qquad (17)$$

or

$$\left[\frac{1}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi - \phi_0)} + \frac{C_p + iD_p}{\cos\frac{\pi^2}{\chi} - \cos\frac{\pi}{\chi}(\phi + \phi_0)} \right], \qquad (18)$$

where C_s, D_s, C_p, D_p have the same significance as previously, and are functions of the angle of incidence of the light on the illuminated side of the wedge.

From formula (15) it appears that along the two surfaces of the wedge $\phi = 0$ and $\phi = \chi$, the diffracted light should be completely polarised with the intensity of the $\|^l$ component zero, and that of the $\perp^r$ component finite. As the rear surface of the wedge limits the region of shadow, it follows as a consequence that the polarisation-effects should usually appear at smaller deviations of the diffracted ray in the case of a wedge than for a plane screen. When the imperfect reflecting power of the metal is taken into account, as in formulæ (17) and

* A. Wiegrefe, 'Ann. d. Physik,' vol. 39, p. 449 (1912).

(18), it would also follow, for the reasons stated, that the colours of the diffracted light should also be observable at smaller deviations and be generally more striking than for a plane screen.

10. *Summary.*

1. The paper contains a discussion of the observations of Gouy on the intensity, colour and polarisation of the light diffracted through large angles by metallic screens and wedges with polished edges. The well-known expressions due to Poincaré and Sommerfeld referring to diffraction by perfectly-reflecting screens and wedges, are modified so as to take into account the changes of phase and amplitude which occur when light is reflected at the surface of a metal. The modified formulæ are then discussed.

2. The formulæ show that when the incident light is plane-polarised in any arbitrary azimuth, the light diffracted through large angles is elliptically polarised, the sign of the ellipticity being different in interior and exterior diffraction.

3. In interior diffraction, the component polarised in the plane of incidence is white, while the perpendicular component is coloured, the colour depending on the nature of the metal. In exterior diffraction, these effects are reversed.

4. The effect of imperfect conductivity is to make the intensity of the diffracted light less and less as the incidence becomes more and more oblique. This diminution is least for the wave-length for which the reflection-coefficient is largest. The colour-effects arise in this way and therefore become more prominent at oblique incidences.

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