

*Citation:*

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The greater deviations for  $Au_{II}$  at the lowest temperatures should be ascribed to the influence of impurities. The greater value of  $w$  already is an indication that  $Au_{II}$  is much less pure than  $Au_I$ . Further the same remarks apply here that have been made in § 6 about the resistance of  $Pt$  at helium-temperatures.

**Physics.** — “*The magnetic rotation of the plane of polarisation in titane tetrachloride*”. II. By Prof. L. H. SIERTSEMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 30, 1915).

In a preceding communication <sup>1)</sup> the results have been recorded of observations on the negative magnetic rotation of  $TiCl_4$  for different wavelengths, and an investigation was announced on the question whether the dispersion of rotation agrees with what was to be expected according to theory.

The theories of the magnetic rotation bring it in connection with the ZEMMAN-effect, and lead to formulae in which the rotation is represented as the sum of a number of terms, each corresponding to a free vibration of the substance. Similar formulae also hold for the index of refraction. An investigation as to whether the observations are in harmony with the theory will, therefore, have to lead to the drawing up of formulae of the form required by the theory, representing the observed indices of refraction and constants of rotation, and containing in both cases *the same* free frequencies.

For the theoretic formulae we shall have to start from those which have been derived by LORENTZ in the *Encykl. der math. Wiss.* <sup>2)</sup>, which will, however, be subjected to some modifications.

First of all we can keep in view that we shall only apply the formulae for wavelengths far from a free vibration, and that therefore we need not take absorption into consideration. This renders it possible for us to put the constant  $g$  in the formulae in question zero, which simplifies them considerably.

In another respect extension is, however, necessary. As here the formulae will be applied to liquids it is no longer allowed in the computation of the force acting on a charged particle to neglect the term proportionate to the polarisation, which must be added to the

<sup>1)</sup> These Proc. XVIII p. 101.

<sup>2)</sup> LORENTZ. Theorie der magneto-optische Phänomene. *Encykl. d. math. Wiss.* V. 3, p. 199.

electrical force<sup>1)</sup>. We shall take for this term  $\frac{1}{3} P$ , representing by  $P$  the dielectrical polarisation. In the formula mentioned in the cited treatise under (38)<sup>2)</sup> this modified value will then have to be taken under the sign of summation for the electrical force. Following the derivation further as it has been given in the treatise in §§ 49 and 50, we find for the index of refraction  $n$  outside the magnetic field:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3} S_{a_1 b_1 \dots} \frac{C}{v_0^2 - v^2} = \frac{1}{3} S$$

in which  $v$  represents the frequency of the considered light vibrations (number of vibrations in  $2\pi$  seconds),  $v_0$  free frequencies, while the constants  $C$  are in connection with LORENTZ's constants  $B$  through the relation<sup>3)</sup>:

$$C = \sum_{\nu_1} B^{(\nu_1)} = 2 \sum_{\nu_{2+}} B^{(\nu_{2+})} = 2 \sum_{\nu_{2-}} B^{(\nu_{2-})}$$

and  $S$  is introduced by way of abbreviation for the sum  $S_{a_1 b_1 \dots}$ .

Expressions for the magnetic rotation per unity of length are found from the values of the indices of refraction of circularly polarized light rays in the magnetic field by means of the known relation<sup>4)</sup>

$$\psi = \frac{v}{2c} (n_+ - n_-)$$

in which  $c$  denotes the velocity of light.

For the values of  $n_+$  and  $n_-$  we find in an analogous way as in § 57 of LORENTZ's treatise:

$$\frac{n_+^2 - 1}{n_+^2 + 2} = \frac{1}{3} S_{a_1 b_1 \dots} \sum_{\nu_{2+}} \frac{2B^{(\nu)}}{v_0^2 - (v - \delta^{(\nu)})^2} = \frac{1}{3} S_+$$

$$\frac{n_-^2 - 1}{n_-^2 + 2} = \frac{1}{3} S_{a_1 b_1 \dots} \sum_{\nu_{2-}} \frac{2B^{(\nu)}}{v_0^2 - (v - \delta^{(\nu)})^2} = \frac{1}{3} S_-$$

in which  $\delta^{(\nu)}$  represent the magnetic displacements through the ZEMMAN-effect. It follows from this that:

$$n_+^2 = \frac{1 + \frac{2}{3} S_+}{1 - \frac{1}{3} S_+}, \quad n_-^2 = \frac{1 + \frac{2}{3} S_-}{1 - \frac{1}{3} S_-}$$

Taking into account that  $n_+$  and  $n_-$  differ only little from  $n$ , and likewise  $S_+$  and  $S_-$  little from  $S$ , we find:

<sup>1)</sup> LORENTZ, loc cit. p. 228.

<sup>2)</sup> loc. cit. p. 229.

<sup>3)</sup> loc. cit. p. 236.

<sup>4)</sup> loc. cit. p. 245.

$$\psi = \frac{v}{4cn} (n_-^2 - n_+^2) = \frac{v}{4cn} \frac{S_- - S_+}{(1 - \frac{1}{3}S)^2}$$

Further :

$$S_- - S_+ = S_{a_1 b_1} \cdot \left[ \sum_{\nu_{2-}} \frac{2B^{(\nu)}}{v_0^2 - (v - d^{(\nu)})^2} - \sum_{\nu_{2+}} \frac{2B^{(\nu)}}{v_0^2 - (v - d^{(\nu)})^2} \right]$$

or a term  $\kappa_{2-}$  corresponding to every term  $\kappa_{2+}$ , for which  $B^{(\nu_{2+})} = B^{(\nu_{2-})}$  and  $d^{(\nu_{2+})} = -d^{(\nu_{2-})}$  :

$$S_- - S_+ = S_{a_1 b_1} \dots \frac{8v}{(v_0^2 - v^2)^2} \sum_{\nu_{2+}} B^{(\nu)} d^{(\nu)}$$

Moreover

$$1 - \frac{1}{3}S = 1 - \frac{n^2 - 1}{n^2 + 2} = \frac{3}{n^2 + 2}$$

so that we find :

$$\psi = \frac{2v^2(n^2 + 2)^2}{9cn} S_{a_1 b_1} \dots \frac{1}{(v_0^2 - v^2)^2} \sum_{\nu_{2+}} B^{(\nu)} d^{(\nu)}$$

If we call  $\Delta^{(\nu)}$  the magnetic displacement for the unity of magnetic force, we find for the constant of rotation  $\chi$  :

$$\chi = \frac{2v^2(n^2 + 2)^2}{9cn} S_{a_1 b_1} \dots \frac{1}{(v_0^2 - v^2)^2} \sum_{\nu_{2+}} B^{(\nu)} \Delta^{(\nu)}$$

Representing the sums  $\sum_{\nu_{2+}} B^{(\nu)} \Delta^{(\nu)}$  by  $D$  we come to a formula :

$$\chi = \frac{2v^2(n^2 + 2)^2}{9cn} S_{a_1 b_1} \dots \frac{D}{(v_0^2 - v^2)^2}$$

We shall now try to determine the constants  $C$  and  $D$  in such a way that these formulae represent the observations, the same free frequencies being taken for  $n$  and  $\chi$ .

We shall then have to fix how many free frequencies we shall assume, as the number of terms in the sum  $S_{a,b}$  corresponds with this. We can be led in this by what is known for the dispersion of the index of refraction. As was already mentioned in the first communication, it is found that the dispersion of transparent substances can be explained by assuming a small number of ultrared, and also one or more ultraviolet free frequencies. It must be tried, therefore, in the first place whether the assumption of one ultrared and one ultraviolet frequency leads to our purpose.

Then two terms must occur in the sum  $S$  for the index of refraction. In the usual way we shall suppose the red free frequency so small that  $-v^2$  may be substituted for  $v_0^2 - v^2$  for the frequencies

of the visible spectrum. We can omit the term for the ultrared altogether in the sum  $S$  for the constant of rotation, as for this term we may put  $\Delta^{(\prime)} = 0$ , so that then we find a one-term form for the constant of rotation, namely:

$$\rho = \frac{2v^2(n+2)^2}{9cn} \cdot \frac{D}{(v^2 - v_0^2)^2}.$$

This form has been examined for the constants of rotation of the first series of observations (preceding communication p. 103).

Observations of the index of refraction for different wavelengths have been made by H. BECQUEREL<sup>1)</sup>. He found:

$C$	$D$	$E$	$F$	$G$
$n = 1,5948$	$1,6043$	$1,6171$	$1,6293$	$1,6557$

By the aid of this an interpolation formula has been calculated, and with this the values of  $n$  for the wavelengths occurring in the two tables with results have been determined. Then the values of  $D$  and  $v_0$  have been determined by the method of the least squares for the first series. The agreement appeared unsatisfactory.

If it is further tried to represent BECQUEREL's values for the index of refraction with the found free frequency ( $v_0^2 = 40,381 \cdot 10^{10}$ ) by a form

$$\frac{n^2 - 1}{n^2 + 2} = -\frac{A}{v^2} + \frac{B}{v_0^2 - v^2}$$

it is found that this is only possible when a negative value is taken for  $A$ . This result must be rejected, as  $A = \frac{1}{3} \sum B^{(\prime)}$  must always be positive.

We shall therefore introduce an ultrared and two ultraviolet free frequencies, namely one far in the ultraviolet, so that  $v_0^2$  can be substituted for  $v_0^2 - v^2$  in the corresponding terms, and one at a moderate distance from the visible spectrum. Two terms must then occur in the sum in the expression for the constant of rotation, and we must therefore put,

$$\rho = \frac{2v^2(n+2)^2}{9cn} \left( D_a + \frac{D_b}{(v_b^2 - v^2)^2} \right),$$

whereas for  $n$  a form of three terms must be taken, viz.:

$$\frac{n^2 - 1}{n^2 + 2} = C_a + \frac{C_b}{v_b^2 - v^2} - \frac{C_c}{v^2}.$$

The values  $D_a$ ,  $D_b$  and  $v_b$  of the first form have been calculated

<sup>1)</sup> H. BECQUEREL. Ann. d. Ch. et d. Ph. (5) 12 p. 82 (1877).

by the method of least squares, and separately for the two series of observations. A preliminary investigation had namely shown that the observations with the mercury arc lamp (table p. 103) yield a dispersion curve which slightly deviates from that of the second series (table p. 105).

We found:

$$(I) \quad \varrho = \frac{2v^2(n^2+2)^2}{9cn} \left( 64,99 - \frac{302930 \cdot 10^{60}}{(47,485 \cdot 10^{30} - v^2)^2} \right) 10^{-25}$$

$$(II) \quad \varrho = \frac{2v^2(n^2+2)^2}{9cn} \left( 53,88 - \frac{298540 \cdot 10^{60}}{(48,161 \cdot 10^{30} - v^2)^2} \right) 10^{-25}$$

The agreement may be judged from the subjoined table, in which

$\lambda_{vac.}$	$P$	$Q$	$\varrho_{calc.}$ (min. per gauss. cm.)*	$\varrho_{observ.}$
(I) 0,5782	0,00668	— 0,02292	— 0,01624	— 0,01618
0,5462	0,00752	— 0,02771	— 0,02019	— 0,02023
0,5087	0,00874	— 0,03576	— 0,02702	— 0,02705
0,4806	0,00987	— 0,04463	— 0,03476	— 0,03468
0,4723	0,01024	— 0,04794	— 0,03770	— 0,03782
0,4359	0,01219	— 0,06859	— 0,05640	— 0,05633
(II) 0,6452	0,00441	— 0,01557	— 0,01116	— 0,01083
0,5956	0,00521	— 0,01983	— 0,01462	— 0,01471
0,5601	0,00592	— 0,02417	— 0,01825	— 0,01830
0,5245	0,00679	— 0,03030	— 0,02351	— 0,02349
0,5097	0,00722	— 0,03363	— 0,02641	— 0,02643
0,4889	0,00789	— 0,03941	— 0,03152	— 0,03170
0,4840	0,00806	— 0,04101	— 0,03295	— 0,03325
0,4723	0,00849	— 0,04528	— 0,03679	— 0,03689
0,4694	0,00861	— 0,04646	— 0,03785	— 0,03778
0,4688	0,00863	— 0,04670	— 0,03807	— 0,03843
0,4623	0,00889	— 0,04954	— 0,04065	— 0,04054
0,4495	0,00945	— 0,05601	— 0,04656	— 0,04686
0,4436	0,00973	— 0,05948	— 0,04975	— 0,04927
0,4355	0,01013	— 0,06481	— 0,05468	— 0,05439

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also the two parts of which  $\varrho$  is composed, have been given separately, namely :

$$P = \frac{2v^2(n^2+2)^2}{9cn} D_a \text{ and } Q = \frac{2v^2(n^2+2)^2}{9cn} \cdot \frac{D_b}{(v_0^2 - v^2)^2}$$

In this it should be borne in mind that every value of the series (I) is built up of the average of six determinations, those of the second series being derived from one determination. In the former greater accuracy is, therefore, to be expected.

At the same time the influence which the two free frequencies have on the constant of rotation, appears from the table. We see that that of the ultraviolet frequency at moderate distance by far preponderates.

We can compare the dispersion of the constant of rotation found here with H. BECQUEREL's determinations<sup>1)</sup>. He found for the relative values of the constant of rotation

$$\begin{array}{ccccccc} C & D & E & b & F & G & h \\ \varrho/\varrho_D = & 0,637 & 1,000 & 1,590 & 1,730 & 2,271 & 4,328 & 5,450 \end{array}$$

while from the formula found above for series (I) follows:

$$0,688 \quad 1,000 \quad 1,538 \quad 1,661 \quad 2,177 \quad 3,967 \quad 5,259$$

The dispersion found here is, therefore, considerably less than BECQUEREL's.

We can then try to represent BECQUEREL's five values of  $n$  by a formula

$$\frac{n^2-1}{n^2+2} = C_a + \frac{C_b}{v_b^2 - v^2} - \frac{C_c}{v^2}$$

taking for  $v_b^2$  first the value  $47,485.10^{30}$ , then  $48,161.10^{30}$ . These calculations too have been carried out by the method of least

	$n$	Observed	Calculated	
		$\frac{n^2-1}{n^2+2} =$	I	II
<i>C</i>	1,5948	0,33970	0,33966	0,33968
<i>D</i>	1,6043	0,34407	0,34413	0,34411
<i>E</i>	1,6171	0,34996	0,34997	0,34995
<i>F</i>	1,6293	0,35548	0,35547	0,35546
<i>G</i>	1,6557	0,36726	0,36723	0,36726

<sup>1)</sup> H. BECQUEREL, Ann. de Ch. et de Ph. (5) 12 p. 35 (1877).

squares. We found

$$(I) \quad \frac{n^2-1}{n^2+2} = 0,28204 + \frac{2,4850 \cdot 10^{30}}{47,485 \cdot 10^{30} - v^2} - \frac{0,04707 \cdot 10^{30}}{v^2}$$

$$(II) \quad \frac{n^2-1}{n^2+2} = 0,27587 + \frac{2,6182 \cdot 10^{30}}{48,161 \cdot 10^{30} - v^2} - \frac{0,04315 \cdot 10^{30}}{v^2}.$$

The agreement appears from the foregoing table which shows that a representation of the two quantities with the same free frequencies is possible.

It may be further examined in how far the found numerical values of the coefficients are in agreement with what theory would lead us to expect. For a comparison with the theory it is necessary to recalculate the constant of rotation in the new theoretical unities used by LORENTZ. We find then:

$$(I) \quad \chi = \frac{2v^2 (n^2+2)^2}{9cn} \left( 0,06702 - \frac{312,37 \cdot 10^{60}}{(47,485 \cdot 10^{30} - v^2)^2} \right) 10^{-25}$$

$$(II) \quad \chi = \frac{2v^2 (n^2+2)^2}{9cn} \left( 0,05556 - \frac{307,84 \cdot 10^{60}}{(48,161 \cdot 10^{30} - v^2)^2} \right) 10^{-25}.$$

A comparison with the above derived theoretical formulae yields first of all (the indices  $\kappa_2+$  being further omitted):

$$(I) \quad \frac{2}{3} \cdot \frac{1}{v_a^2} \sum B_a = 0,28204, \quad \frac{1}{v_a^4} \sum B_a \Delta_a = 0,06702 \cdot 10^{-25}$$

$$(II) \quad \quad \quad = 0,27587, \quad \quad \quad = 0,05556 \cdot 10^{-25}$$

or if we introduce a mean value  $\Delta_{am}$  for the different values  $\Delta_a$ :

$$(I) \quad \sum B_a = \frac{3}{2} \cdot 0,28204 v_a^2, \quad \Delta_{am} \sum B_a = 0,06702 \cdot 10^{-25} v_a^4$$

$$(II) \quad \quad \quad = \frac{3}{2} \cdot 0,27587 v_a^2, \quad \quad \quad = 0,05556 \cdot 10^{-25} v_a^4$$

from which follows

$$\Delta_{am} = (I) 1,584 \cdot 10^{-26} v_a^2, \quad \Delta_{am} = (II) 1,343 \cdot 10^{-26} v_a^2.$$

If we take for  $\Delta_{am}$  the normal value of the magnetic resolution

$$\Delta_{am} = 3,19 \cdot 10^7,$$

we find:

$$(I) \quad v_a^2 = 2014 \cdot 10^{30}, \quad \sum B_a = 852 \cdot 10^{30}$$

$$(II) \quad \quad \quad = 2376 \cdot 10^{30}; \quad \quad \quad = 983 \cdot 10^{30}$$

and from this the wavelength:

$$\lambda_a = (I) 0,0000042 \text{ cm.} \quad \quad \quad = (II) 0,0000039 \text{ cm.}$$

which really represents a wavelength very far in the ultraviolet.

The following terms give

$$(I) \quad \frac{2}{3} \sum B_b = 2,4850 \cdot 10^{30}, \quad \sum B_b \Delta_b = -312,37 \cdot 10^{35}$$

$$(II) \quad \quad \quad = 2,6182 \cdot 10^{30}, \quad \quad \quad = -307,84 \cdot 10^{35}$$



from which, again assuming a mean value  $\Delta_{bm}$ , follows:

$$(I) \quad \Sigma B_b = 3,73.10^{30}, \quad \Delta_{bm} = -0,838.10^7$$

$$(II) \quad \quad \quad = 3,93.10^{30}, \quad \quad \quad = -0,784.10^7$$

To

$$v_b^2 = (I) 47,485 \cdot 10^{30}, \quad = (II) 48,161 \cdot 10^{30},$$

correspond the wavelengths

$$\lambda_b = (I) 0,0000274 \text{ cm}, \quad = (II) 0,0000272 \text{ cm}.$$

From the third term can only be derived:

$$\Sigma B_c = (I) 0,0706 \cdot 10^{30}, \quad = (II) 0,0647 \cdot 10^{30}.$$

First of all we can draw the conclusion from these results that the found coefficients cannot lay claim to great accuracy. Small deviations in the dispersion curve from these series give already pretty great deviations in the coefficients and the values derived from them. Only  $\lambda_b$  agrees for the two series.

It further appears that really the dispersion of the index of refraction as well as that of the constant of rotation can be represented by the assumption of free frequencies:

1. one far in the ultraviolet, so that the corresponding terms can be considered constant, with a normal magnetic resolution,

2. one in the ultraviolet at a moderate distance from the visible spectrum,

3. one in the ultrared.

For the second wavelength, which gives terms which have a preponderating influence on the dispersion, we must assume a negative magnetic resolution of a value amounting to about a quarter of the normal value. As was already remarked in the first communication this negative magnetic resolution can be accounted for by assuming couplings between the electrons.

In LORENTZ'S theory the quantity  $B$  is an abbreviation for  $\frac{Ne^2}{A}$  <sup>1)</sup>,

in which  $A$  is closely connected with the mass of the vibrating particles. The fact that for  $\Sigma B_c$ , connected with the ultrared wavelength, a much smaller value is found than for the other wavelengths is in keeping with the view that the ultrared vibrations are executed by vibrating molecules, so that much larger masses come into play.

Taking everything together it may be said that the dispersion of  $\text{TiCl}_4$  can be explained by the theory of LORENTZ.

*\* Physical and electrotechnical laboratory  
of the Technical University.*

*Delft.*

<sup>1)</sup> LORENTZ, loc. cit. p. 229.