

**Physics.** — *The law of the para-magnetisation of a crystal and the law of the paramagnetic rotatory dispersion.* By JEAN BECQUEREL and W. J. DE HAAS. (Communication N<sup>o</sup>. 199a from the Physical Laboratory at Leiden.)

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I. *General considerations.* 1<sup>o</sup>. *Fundamental law of the para-magnetisation of a crystal.* 2<sup>o</sup>. R. LADENBURG's law of the paramagnetic rotatory dispersion.

In a recent paper <sup>1)</sup> we showed that the *paramagnetic* rotatory power of tysonite in the direction of the optical axis is represented with a great precision by the following law :

$$\varrho = \varrho_{\infty} \operatorname{tgh} \frac{\mu_B H}{RT} \dots \dots \dots (1)$$

where  $H$  is the magnetic field-strength,  $T$  the absolute temperature,  $R$  the gas-constant. The *saturation-rotation*  $\varrho_{\infty}$  is a function of the light-period (rotatory dispersion) and of the temperature.

$\mu_B$  is a magnetic moment which in the case of tysonite is found to be equal to the Bohr magneton. The law obtained by us is a magnetisation law in agreement, in this particular case at least, with the theoretical views of W. LENZ <sup>2)</sup> and of P. EHRENFEST <sup>3)</sup> on the mechanism of magnetisation. As it is impossible to reduce this law to a more simple form we are inclined to think, that it represents the most elementary mechanism of the para-magnetisation of a crystal.

An explanation however is due, why we found a simple law in a case which at first sight seems complex. In fact tysonite contains three paramagnetic ions :  $\text{Ce}^{+++}$ ,  $\text{Pr}^{+++}$ ,  $\text{Nd}^{+++}$ . Moreover the measurements of the magnetisation of oxides or of salts are interpreted by ascribing to these three ions different moments all greater than that of the Bohr magneton <sup>4)</sup>.

We first remember, that in our experiments the paramagnetic phenomenon becomes manifest by the unequal absorption of circular vibrations of opposite sign. It is evident that in a substance containing different paramagnetic ions the influence of each of these is proportional to its absorption. That is why the rotation is not proportional to the value of

<sup>1)</sup> JEAN BECQUEREL and W. J. DE HAAS, *Comm. Leiden* N<sup>o</sup>. 193a, 1928.

<sup>2)</sup> W. LENZ, *Phys. Z.S.* 21, 613, 1920.

<sup>3)</sup> P. EHRENFEST, *Comm. Leiden Suppl.* N<sup>o</sup>. 44b.

<sup>4)</sup>	$\text{C}^{+++}$	$\text{Pr}^{+++}$	$\text{Nd}^{+++}$	}	
	St. Meyer 13.8	17.3	17.5	}	Weiss magnetons.
	Cabrera 11.90	17.89	18.0	}	

the magnetisation which would have been obtained by means of magnetic measurements. It may be, that only one kind of ion is optically active or at least that its influence exceeds that of the other ions so far as to render the existence of these other ions negligible. This is precisely the case with tysonite as we shall establish in our investigations on the magnetic rotatory dispersion. We have already mentioned <sup>1)</sup> that long since one of us traced back to the paramagnetism both certain dissymmetries in the intensities, which are observed in the absorption of circular vibrations of opposite sign, and the connected effect of the magnetic rotation. The same author expressed the opinion, that the predominance of one of the directions of motion of the electrons is due to an orientation in the field <sup>2)</sup>. Recently R. LADENBURG proceeding from analogous ideas considerably advanced the question by giving the first quantitative mathematical theory of the paramagnetic rotatory dispersion. In combination with the quantum theory of dispersion previously developed by LADENBURG <sup>3)</sup> the new theory of this author enables us, among other important results, to predict under what circumstances the paramagnetic rotatory power can predominate over the diamagnetic rotatory power <sup>4)</sup> and to know the sense of the paramagnetic rotation. From the point of view of R. LADENBURG and W. PAULI Jr. two opposite senses are possible according as the variation of the internal quantum number  $j$  is equal to  $\pm 1$  or to 0.

In the first paper LADENBURG <sup>5)</sup> gave the following formula :

$$\varrho = \frac{lw(n^2 + 2)^2}{36cn} \left[ \sum_s \frac{(\varepsilon_{s-} + \varepsilon_{s+}) 2w O_L}{(w_s^2 - w^2)^2 - 4w^2 O_L^2} + \sum_s \frac{(\varepsilon_{s-} - \varepsilon_{s+}) (w_s^2 - w^2)}{(w_s^2 - w^2)^2 - 4w^2 O_L^2} \right] \quad (2)$$

in which  $l$  is: thickness traversed by the light;  $n$  index of refraction:  $c = 3.10^{10}$ ;  $w = \frac{2\pi c}{\lambda}$  frequency expressed in  $2\pi$  seconds ( $\lambda$  wavelength in vacuo);  $w_s$  natural frequency of the oscillators, in the *classical sense*,

giving the absorption band  $s$ ;  $O_L = -\frac{1}{2} \frac{e}{m} \frac{1}{c} H$  angular velocity of the

Larmor precession <sup>6)</sup>;  $\varepsilon_{s\mp} = 4\pi \mathfrak{N}_{s\mp} \frac{e^2}{m}$ , where  $\mathfrak{N}_{s-}$  and  $\mathfrak{N}_{s+}$  are the numbers, per unit of volume of the fictitious electrons  $s$  (Ersatzoszillatoren), of the classical dispersion theory, in circular motion of sign negative and positive with respect to the positive direction of the field.

<sup>1)</sup> JEAN BECQUEREL and W. J. DE HAAS, loc. cit. § I.

<sup>2)</sup> JEAN BECQUEREL C.R. de l'Ac. des Sc.; **143**, 24 déc. 1906.

<sup>3)</sup> R. LADENBURG, Zs. f. Phys. **4**, 451, 1921.

<sup>4)</sup> One of these circumstances is a sufficiently low temperature; already in 1907 one of us has pointed out this fact. It was even the very idea, that a rotation of paramagnetic origin much follows a law analogous to that of Curie for the magnetisation, which led to the introduction of the use of low temperatures in optical researches.

<sup>5)</sup> R. LADENBURG, Zs. f. Phys. **34**, 898, 1925.

<sup>6)</sup> R. LADENBURG considers here the normal Zeeman effect only.

A research of C. G. DARWIN, and W. R. WATSON <sup>1)</sup> led LADENBURG to a modification of his formula <sup>2)</sup>. He obtained the following result :

$$\varrho = \frac{lw^2}{2cn} \left( \frac{n^2 + 2}{3} \right)^2 \left[ \sum_s \frac{(\varepsilon_{s-} + \varepsilon_{s+}) 2 O_L}{(w_s^2 - w^2 + O_L^2)^2 - 4 O_L^2 w_s^2} + \sum_s \frac{1}{w_s} \frac{(\varepsilon_{s-} - \varepsilon_{s+}) (w_s^2 - w^2 + O_L^2)}{(w_s^2 - w^2 + O_L^2)^2 - 4 O_L^2 w_s^2} \right] \quad (3)$$

In both formulae (2) and (3) the first term in the brackets represents the diamagnetic rotation <sup>3)</sup> which was the only one considered in the old theory of Voigt. This rotation is the immediate consequence of the magnetic decomposition of the spectral rays and of the dispersion.

This effect is necessarily small.

The second term in the brackets is the *paramagnetic rotation* which is superposed on the diamagnetic rotation and which can become considerably greater. The condition for the existence of this rotation is, that by the phenomenon of the paramagnetic orientation  $\varepsilon_{s-}$  and  $\varepsilon_{s+}$  become different.

The difference  $(\varepsilon_{s-} - \varepsilon_{s+})$  is a function of  $\frac{H}{T}$ . The Larmor rotation also occurs in the paramagnetic term, but it is quite negligible for frequencies that are not lying in the neighbourhood of the proper frequency  $w_s$ .

It is interesting to remark, that the paramagnetic rotation need not be an exceptional phenomenon. The actual theory of the Zeeman effect shows that at least either in the initial or in the final state the atom necessarily possesses a magnetic moment and that generally the two states are paramagnetic. The Zeeman phenomenon, formerly considered as purely diamagnetic, is in reality paramagnetic as to its origin and diamagnetic as to the effect of precession. But the conditions favourable for the observation of the paramagnetic rotation are exceptional, a sufficiently high magnetic moment or a very low temperature being required and moreover a sufficiently intense absorption in the region of the active bands. In the formulae (2) and (3) the "damping" term of the classical theory is neglected; this is allowed at a distance from the rays (or bands) sufficiently large compared with their width.

## II. *Experimental verification of R. LADENBURG's law of paramagnetic rotatory dispersion.*

Before the investigation on the variation of the magnetic rotatory power as a function of the field-strength, we have measured at different temper-

<sup>1)</sup> C. G. DARWIN and W. R. WATSON, Proc. Roy. Soc. (A) **114**, 474, 1927.

<sup>2)</sup> R. LADENBURG, Zs. f. Phys. **46**, 168, 1927.

<sup>3)</sup> In the case of one single active band the term can be reduced, as a first approximation, to the formula of HENRI BECQUEREL:  $\varrho = \frac{lw}{c} \theta \cdot \frac{\partial n}{\partial w}$ , so that  $\theta$  becomes identical with the Larmor precession.

atures in a constant field, and for numerous wavelengths, the rotations of the crystals of tysonite, Parisite, Bastnaesite, Xénotime. Several results relating to the tysonite were published in 1925<sup>1)</sup>, but some rectifications of the numerical values are necessary. We gave 1.673 mm. for the thickness of the plate. Now it is true that with a plate of this thickness some measurements were made (1910) at the temperature of 291° K., but because of a mistake (due to the long interruption of the researches from 1914 to 1924) the plate used since 1924 is not the one mentioned before (this one has been lost). It is a plate of 1.866 mm. thickness. Moreover the constant field used in 1925 and mentioned as equal to 26.17 kilogauss is in fact equal to 26.73 kilogauss, as has been established by more accurate measurements made since then. Finally the measurements of the rotation at 4.2° K. may not be reduced to 10.000 gauss as we did, the rotatory power at that temperature being no longer proportional to the field. Thus all numbers must be corrected. At the end of this paper we give the definite results both for tysonite and for the other crystals. (See also comm. 199b.)

The measurements in a constant field refer to different regions of the visible spectrum and to the first part of the ultra-violet. They were made, either by noting (on cliché's the bands between crossed polariser and analyser, or as been described in the paper of 1925, by the fringe-method with a Babinet compensator combined with a quarter-wavelength-plate<sup>2)</sup>). The latter method is far from being as sensitive as that of the half shadow-polariser, but it gives a sufficient relative accuracy for the enormous rotations at low temperatures. By means of measurements on cliché's and of ten readings for each point, we obtain for the individual measurements a precision higher than 0.01 of a fringe (0.01 fringe corresponds to  $\frac{\pi}{100}$  or to 1.8°). The errors being accidental, the plotting of the curve for numerous measurements, taken from millimeter to millimeter (1 mm. of the cliché corresponds to about 25 Å in the 2<sup>nd</sup> spectrum) generally allows a better approximation in the definite result. The precision is always lower in the region of the short wavelengths, where the absorption becomes great; for, unless at exceedingly long exposures (impossible during the measurements at helium temperatures, which last only a few hours), the bands are wide.

This method has the advantage of going the whole of the rotations over a long spectral range and of showing at first glance the *local* disturbances

<sup>1)</sup> JEAN BECQUEREL, H. KAMERLINGH ONNES and W. J. DE HAAS, Comm. Leiden N<sup>o</sup>. 177 (1925).

<sup>2)</sup> An easy calculation shows that, when the plate is not exactly a quarter-wavelength-plate, the results do not contain an appreciable error. In fact the fringes practically keep the same position; theoretically the extinction is no longer total at the middle of the fringes, but this is not perceptible. For the whole spectrum three plates suffice. Those we used are of a quarter wavelength for 4000, 4500, 5800 Å.

due to some absorption bands <sup>1)</sup>. In the following we only consider the rotations in regions that are sufficiently distant from the bands to render these disturbances negligible ; we then have the principal effect due to the absorption in the ultra-violet.

We shall see, that the experimental results are represented by formula (3) and not by formula (2).

Let us consider formula (3) and suppose that the paramagnetically active band is the only one. At low temperatures the diamagnetic rotation vanished in comparison with the enormous paramagnetic rotation. Moreover we may neglect in the paramagnetic term the square  $O_L^2$  of the Larmor precession, the visible spectrum and even the first part of the ultra-violet being certainly sufficiently distant from the active band. Formula (3) may thus be written in the form :

$$\varrho = \frac{l}{2c} \frac{(n^2 + 2)^2}{9n} \frac{w^2}{w_s(w_s^2 - w^2)} \Delta \varepsilon_s ; \quad (\Delta \varepsilon_s = \varepsilon_{s-} - \varepsilon_{s+})$$

If we introduce the wavelength reduced to vacuum  $\left(\lambda = \frac{2\pi c}{w}\right)$  we get

$$\varrho = \frac{l}{4\pi c^2} \frac{(n^2 + 2)^2}{9n} \cdot \frac{\lambda_s^3}{\lambda^2 - \lambda_s^2} \Delta \varepsilon_s \quad \dots \dots \dots (3')$$

We eliminate  $\Delta \varepsilon_s$  with the aid of the ratio  $\frac{\varrho_1}{\varrho_2}$  of the rotations of two wavelengths  $\lambda_1, \lambda_2$  to which correspond the indices  $n_1, n_2$ . We have:

$$\frac{\varrho_1}{\varrho_2} = \frac{n_2}{n_1} \frac{(n_1^2 + 2)^2}{(n_2^2 + 2)^2} \cdot \frac{\lambda_2^2 - \lambda_s^2}{\lambda_1^2 - \lambda_s^2} \dots \dots \dots (4)$$

If we put: 
$$\alpha = \frac{\varrho_1}{\varrho_2} \cdot \frac{n_1}{n_2} \cdot \frac{(n_2^2 + 2)^2}{(n_1^2 + 2)^2}$$

we obtain

$$\lambda_s^2 = \frac{\alpha \lambda_1^2 - \lambda_2^2}{\alpha - 1} \dots \dots \dots (5)$$

If our assumption is true, that this is the only band, the measurement of the rotations for two wavelengths allows us to calculate the position of the band and the same result must be found whatever pair of radiations  $\lambda_1, \lambda_2$  may be chosen.

We have applied this calculation to tysonite, but here a difficulty arises : the plate in our possession being very small it was impossible to measure

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<sup>1)</sup> The method of the Babinet compensator combined with a quarter wave-length-plate, has an advantage over that of the compensator with two rotating quartzplates viz. it allows the obtaining of distinct fringes at the edges of the absorption bands and even in the interior of the circularly polarised components, it suffices to orientate the analyser accurately.

the refractive indices for the blue and violet radiations. GAUBERT found for the ordinary index with regard to air and for room temperature

$$\begin{aligned} 1.6128 & \text{ for } \lambda = 5893 \\ 1.6168 & \text{ ,, } \lambda = 5350 \text{ (thallium).} \end{aligned}$$

These two determinations are insufficient to obtain the exact law of dispersion.

The term  $\frac{n_1}{n_2} \cdot \frac{(n_2^2+2)^2}{(n_1^2+2)^2}$  is at all events nearly equal to one. If, as a first approximation, we replace it by one, we find from the results obtained at 1.95° K. and at 4.21° K., that the calculated quantity  $\lambda_s^2$  is constant within the limits of precision of the measurements of the rotations. The calculation, made for several pairs of values (chosen in such a way that  $\frac{\varrho_1}{\varrho_2}$  is nearly equal to 2) gives a wavelength about  $\lambda_s = 2420 \text{ \AA}$ .

If a law of dispersion is assumed within the allowed limits the constancy of  $\lambda_s^2$  remains equally good. This is the principal point for the verification of the law of LADENBURG, but the value found for  $\lambda_s^2$  depends on the admitted dispersion. The only thing we could do was to adopt the dispersion law of a kind of glass with very nearly the same indices as tysonite for the yellow and for the green rays. A little uncertainty remains, not in the essential result (i.e. in the verification of the formula of LADENBURG), but in the position of the active absorption band. Anyhow, by assuming this dispersion law, we certainly find a more exact value for  $\lambda_s$  than by supposing  $n$  to be constant; this value must even be exact within a few angströms, as the adopted dispersion law cannot be much different from the true law.

The wavelength  $\lambda_s$  having been determined in this way, we calculate with the aid of formula (3')  $\Delta \varepsilon_s$  for different values of  $\lambda$ . The values thus found for  $\Delta \varepsilon_s$  are remarkably constant.

As a result of our measurements we thus found :

$$\text{at } 4.21^\circ \quad \lambda_s = 2369 \text{ \AA} \quad l \Delta \varepsilon_s = -1.947 \cdot 10^{28}$$

for  $H = 26.73$  kilogauss and thickness 1 mm. at room temperature (the value of the thickness at 4.21° lies very near 0.1 cm.).

The figure represents the theoretical curve given by formula (3') with the above values. The marked points are points from the experimental curve. The agreement between theory and experiment is remarkable in the region distant from the groups of bands. In the neighbourhood of these groups we find the deviations, we could expect, due to the disturbances caused by the bands. Especially an enormous deviation is observed due to the presence of the intense band 5776<sup>1)</sup>. The agreement with the theo-

<sup>1)</sup> See Comm. Leiden N<sup>o</sup>. 177 (1925). The influence of this band is made manifest by a supplementary fringe in fig. 3 and by a strong curvature of the fringes in fig. 5.

retical curve becomes however better, when we go away from this band towards the red. We will give the verification of the formula at the

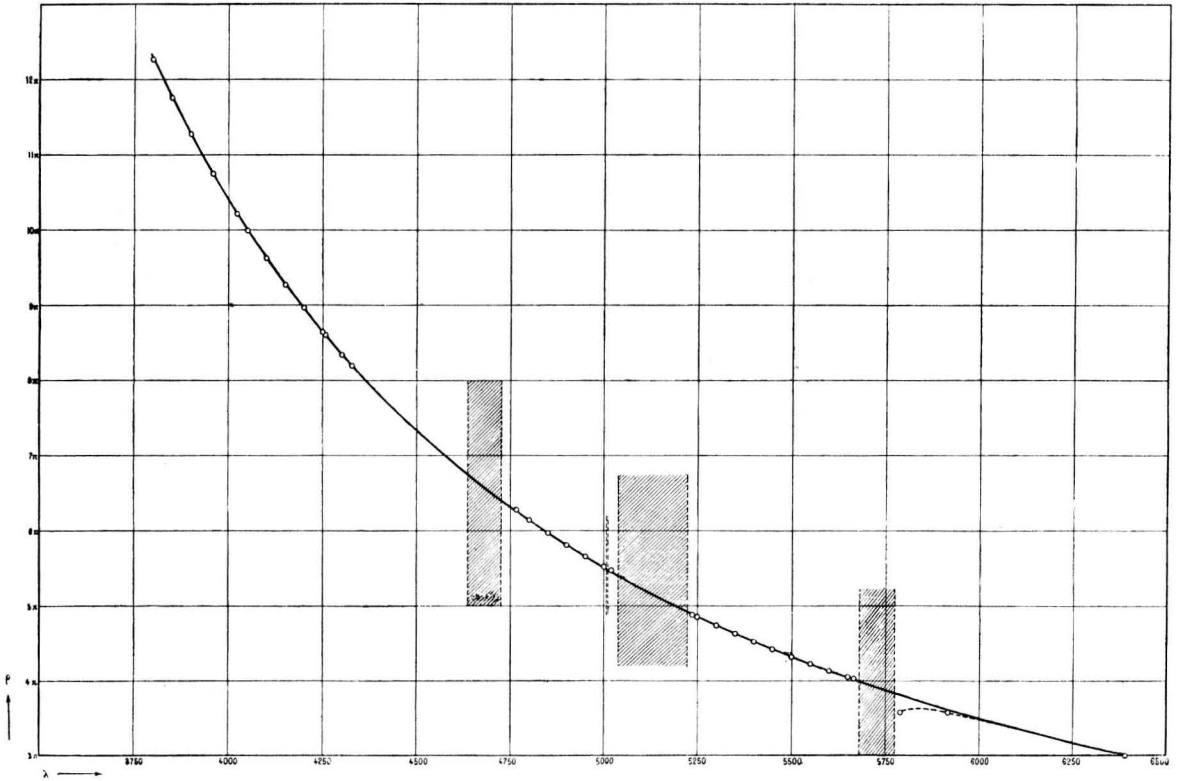


Fig. 1.

temperature of  $1.95^\circ \text{K}$ . from the ultra-violet to the blue. The rotations in a field of 26.73 kilogauss were measured with the method of the canalculated spectrum. The wavelengths of the fringes were determined by interpolation between the rays of tysonite and some rays of the arc-light. Table (1) gives the  $\lambda$  in air and reduced to vacuum, (the index having been estimated in the above mentioned way), the obtained rotations (reduced to a thickness of 1 mm. after application of a correction for the rotation due to the cryostat), and finally the rotations calculated by means of the formula with

$$\lambda_s = 2371 \text{ \AA} \quad \text{and} \quad l \Delta \epsilon_s = -2.9613 \cdot 10^{28}.$$

So formula (3') is verified to one *thousandth*. At the temperatures of  $4.2^\circ$  and  $1.95^\circ$  we practically find the same position for the active band, but this position was not determined very accurately, the calculated wavelength depending on the dispersion law, which remains uncertain. We can only say that the active band lies in the neighbourhood of  $2370 \text{ \AA}$ .

At the temperatures of liquid hydrogen and of liquid nitrogen, the verifications are still very good. For  $\lambda_s$  we took the same wavelength as

TABLE I. Tysonite  $T = \text{about } 1.95^\circ$ .  $H = 26.73$  kilo-gauss.  
Rotations reduced to a thickness of 1 mm at room temperature.

$\lambda_s = 2371 \text{ \AA} \quad \Delta \epsilon_s = 2.9613 \cdot 10^{28}$					
$\lambda$	$\lambda$ reduced to vacuum	$n$ adopted	$-\rho$ measured in multiples of $\pi$	$-\rho$ calculated	deviations
3830.4	3831.5	1.6389	18.265	18.256	+ 0.009
3864.2	3865.3	1.6379	17.728	17.732	- 0.004
3899.1	3900.2	1.6370	17.191	17.219	- 0.028
3939.9	3941.0	1.6358	16.654	16.648	+ 0.006
3979.5	3980.6	1.6348	16.117	16.124	- 0.007
4022.4	4023.5	1.6338	15.580	15.588	- 0.008
4068.7	4069.8	1.6328	15.043	15.042	+ 0.001
4116.6	4117.7	1.6318	14.506	14.510	- 0.004
4168.7	4169.8	1.6309	13.968	13.967	+ 0.001
4222.9	4224.1	1.6298	13.431	13.436	- 0.005
4282.2	4283.4	1.6288	12.894	12.892	+ 0.002
4344.8	4346.0	1.6278	12.357	12.358	- 0.001
4414.0	4415.2	1.6267	11.820	11.808	+ 0.012
4486.9	4488.1	1.6257	11.283	11.271	+ 0.012
4564.3	4565.6	1.6247	10.746	10.743	+ 0.003
4742.6	4743.9	1.6227	9.672	9.672	0.000

at  $4.2^\circ$  ( $2369 \text{ \AA}$ );  $\Delta \epsilon_s$  has been calculated from the experimental results. The rotations marked in table 2 as measured ones are those read for the indicated wavelengths on the experimental curve plotted according to the measurements.

In table 3 the  $\lambda$ 's are those, for which the measurements were made.

We see that at all temperatures the deviations are of the same order and within the limits of precision of the measurements according to what has been said above. The formula was also verified for parisite. We confined ourselves to the examination of the results at  $4.21^\circ$  K. As to the index we are here in still greater uncertainty than in the case of tysonite. For the rays  $D$  only the  $n$  has been determined ( $n_0 = 1.676$ ); as parisite is already very absorbing for violet rays, we assumed a dispersion higher than for tysonite. Using the indices from the 3<sup>rd</sup> column in table 4, we find the active band near  $\lambda_s = 2379 \text{ \AA}$ , that is nearly at the same place as



TABLE II. Tysonite. Thickness 1 mm at room temperature.			
$T = 20.4^\circ \text{ K.} \quad H = 26.73 \text{ Kilogauss} \quad \lambda_s = 2369 \text{ \AA} \quad l \Delta \epsilon_s = -0.48135 \cdot 10^{28}$			
$\lambda$ (air)	$-\rho$ measured	$-\rho$ calculated	deviation
3800	3.010 $\pi$	3.038 $\pi$	- 0.028
4200	2.212	2.213	- 0.001
4600	1.711	1.705	+ 0.006
4800	1.519	1.518	+ 0.001
5600	1.028	1.028	0.000
6600	0.699	0.691	+ 0.008

TABLE III. Tysonite. Thickness 1 mm at room temperature.			
$T = 77.5^\circ \text{ K.} \quad H = 26.73 \text{ Kilogauss} \quad \lambda_s = 2369 \text{ \AA} \quad l \Delta \epsilon_s = -0.14847 \cdot 10^{28}$			
$\lambda$ (air)	$-\rho$ measured	$-\rho$ calculated	deviation
3883.3	0.854 $\pi$	0.851	+ 0.003
4015.3	0.759	0.765	- 0.006
4046.6	0.746	0.746	0.000
4215.5	0.661	0.659	+ 0.002
4315.9	0.616	0.615	+ 0.001
4447.4	0.563	0.564	- 0.001
6597.7	0.224	0.208	+ 0.016

for tysonite. Making use of these results we find the following numbers : (See table 4, following page.)

In the well transparent regions of the blue and of the green, the deviations are of the same order as for tysonite. So we can say that the law has been well verified. The deviations that are somewhat larger in the violet must be due to the less high precision of the measurements because of the bad transparency of the crystal in this region. In the red the somewhat larger deviations can be ascribed to the influence of a group of intense bands in the yellow-orange region and to the weak absorption which spreads like a veil up to the beginning of the red.

TABLE IV. Parisite. Thickness 1 mm at room temperature.

$T = 4.21^\circ \text{ K.} \quad H = 26.73 \text{ Kilogauss} \quad \lambda_s = 2379 \text{ \AA} \quad l \Delta \epsilon_s = -0.92637 \cdot 10^{28}$					
$\lambda$ (air)	$\lambda$ (vacuum)	$n$ assumed	$-\rho$ measured	$-\rho$ calculated	deviation
4215	4216.2	1.7025	4.561 $\pi$	4.538	+ 0.023
4350	4351.2	1.6989	4.120	4.131	- 0.011
4500	4501.3	1.6955	3.741	3.745	- 0.004
4950	4951.4	1.6871	2.878	2.880	- 0.002
5300	5301.5	1.6825	2.419	2.411	+ 0.008
5600	5601.6	1.6790	2.100	2.098	+ 0.002
6300	6301.7	1.6726	1.535	1.576	- 0.041
6400	6401.8	1.6719	1.473	1.519	- 0.046

III. *The paramagnetic rotatory powers of tysonite and of parisite are caused by one single paramagnetic element.*

After the excellent agreement between experiment and formula (3') we are inclined to conclude that both tysonite and parisite give one single paramagnetically active band only. This has however not yet been proved. It is evident that just as good an agreement with formula (3) would have been found under the assumption of the existence of two bands and perhaps even of several active bands in the same spectral region as the one band we considered above (by assuming e.g. for tysonite at  $1.95^\circ$ .  $\lambda_{s_1} = 2366$ ,  $\lambda_{s_2} = 2376$ ,  $l \Delta \epsilon_{s_1} = -2.2653 \cdot 10^{28}$ ,  $l \Delta \epsilon_{s_2} = -0.7090 \cdot 10^{28}$ ).

But we shall show, according to experimental results, that if several bands exist, these are not independent.

The numbers in the tables, which will be given in another paper show that the ratio  $\frac{\rho_{\lambda_1}}{\rho_{\lambda_2}}$  of the rotations for two given wavelengths  $\lambda_1$ ,  $\lambda_2$  is rigorously the same at the different temperatures. The experiments described in the preceding paper <sup>1)</sup> allow a very exact verification. We mentioned, that (in the case of tysonite) the curves of the rotation  $\rho$  as a function of  $\frac{H}{T}$ , plotted for different wavelengths and for different temperatures, have ordinates that bear a fixed ratio to each other. The ratio of two ordinates belonging to two fixed wavelengths can be deter-

<sup>1)</sup> JEAN BECQUEREL and W. J. DE HAAS loc. cit.

mined very precisely by taking for each temperature the mean of the ratio's obtained for different values of  $\frac{H}{T}$ . In this way we found :

$$\begin{aligned} \text{at } 1.71^\circ \text{ K.} \quad & \frac{\varrho_{\lambda=4259}}{\varrho_{\lambda=5328.5}} = 1.8361 \\ \text{at } 4.21^\circ \text{ K.} \quad & \frac{\varrho_{4259}}{\varrho_{5328.5}} = 1.8383. \end{aligned}$$

The constancy of the ratio has thus been verified within one half-thousandth.

From these results it is evident, that the rotation is represented by an expression of the form :

$$\varrho = \varphi(\lambda) \psi(T) f\left(\frac{H}{T}\right) \dots \dots \dots (6)$$

Let us now suppose that there exist several paramagnetically active bands ; formula (3') is then replaced by a summation of analogous terms corresponding to the different bands  $s_1, s_2, s_3, \dots$ .

$$\varrho = \frac{l}{4\pi c^2} \frac{(n^2 + 2)^2}{9n} \left[ \frac{\lambda_{s_1}^3}{\lambda^2 - \lambda_{s_1}^2} \Delta \varepsilon_{s_1} + \frac{\lambda_{s_2}^3}{\lambda^2 - \lambda_{s_2}^2} \Delta \varepsilon_{s_2} + \dots \right] \dots (7)$$

At very low temperatures the thickness  $l$  varies no longer ; the term containing  $n$  varies so little, that with a close approximation it may be regarded as independent upon the temperature ; the same can be said of the  $\lambda_{s_i}$ . It is only through the  $\Delta \varepsilon_{s_i}$  that the relation is a function of  $T$  and of  $\frac{H}{T}$  and it is evident, that the expression (7) can only then take the form (6), if the  $\Delta \varepsilon_{s_i}$  are the same functions of  $T$  and of  $\frac{H}{T}$  but for constant factors : they are therefore not independent. This would not be the case, if the active bands belonged to different ions, for then we should have a superposition of rotations, varying independently of one another as functions of  $T$  and of  $\frac{H}{T}$ .

It is interesting with respect to the order of magnitude if the absorption, to calculate  $\Delta \varepsilon_{s_i}$  and  $(\mathfrak{N}_{s,-} - \mathfrak{N}_{s,+})$  in the supposition that the absorption band is the only one and further for the limiting value corresponding with the saturation.

Let us choose the wavelengths  $\lambda = 5328.5$  (5330 reduced to vacuum) : the above found values for the saturation rotations are :

$$\begin{aligned} \text{at } 1.71^\circ \text{ K.} \quad & \varrho_\infty = - 19.61 \pi \\ \text{at } 4.21^\circ \text{ K.} \quad & \varrho_\infty = - 21.81 \pi. \end{aligned}$$

with the thickness 1.866 mm measured at room temperatures.

As the chosen wavelength lies very near one of those for which the

index is known, we find by a safe extrapolation  $n = 1.617$  (1.6174 reduced to vacuum) at room temperature. Several measurements of the double-refraction of tysonite in directions oblique to the axis at temperatures down to the lowest have shown, that we may regard the double refraction as rigorously constant. Thus we can give for the index at the low temperatures the same value as at room temperature. For  $\lambda_{s_i}$  we assume the value 2370 Å. The contraction not being known we cannot take it into account. But at all events it is very small. In this way we find :

$$\begin{array}{ll} \text{at } 1.71^\circ \text{ K.} & (\epsilon_{s+} - \epsilon_{s-})_\infty = 4,37.10^{29} \quad (\mathfrak{N}_{s+} - \mathfrak{N}_{s-})_\infty = 1,37.10^{20} \\ \text{at } 4.21^\circ \text{ K.} & (\epsilon_{s+} - \epsilon_{s-})_\infty = 4,86.10^{29} \quad (\mathfrak{N}_{s+} - \mathfrak{N}_{s-})_\infty = 1,53.10^{20}. \end{array}$$

The following must be remarked. When in a magnetic field the band (which is supposed to be the only one) is not split up into a multiplet, but only into a doublet (which is the general case for the crystals of the rare earths)  $\epsilon_{s-}$  becomes zero in the limiting case of saturation and  $(\epsilon_{s+})_\infty$  becomes identical with the coefficient  $\epsilon_s$  that occurs in the expression of the index for a field-strength zero.

The old measurements <sup>1)</sup> of the variation of the index with the aid of the absorption bands of the visible spectrum of tysonite gave values  $10^5$  to  $10^6$  times smaller. Thus the enormous paramagnetic rotation of the tysonite is related to the presence, in the distant ultraviolet, of a band (or of a group of bands) far more intense than the visible bands.

The bands of the visible spectrum are characteristic for neodymium and praseodymium. Therefore it is nearly certain, that the very intense band (or the group) that produced the enormous rotation belongs to cerium<sup>+++</sup>. Tysonite contains a high percentage of cerium, only little neodymium and still less praseodymium. Moreover cerium-glass shows a strong paramagnetic rotation, while the rotation of praseodymium-glass and especially of neodymium-glass is very weak. It is therefore evident, that in tysonite the rotation due to the cerium so far predominates over the rotations due to the other rare earths, that the latter are negligible.

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<sup>1)</sup> JEAN BECQUEREL, *le Radium* 4, 383, 1907.