Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

G.J. Elias & Bois, H.E.J.G. du, The influence of temperature and magnetisation on selective absorption spectra. III, in: KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 839-850

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'

(839)

Physics. — "The influence of temperature and magnetisation on selective absorption spectra." III. By Prof. H. E. J. G. DU BOIS and G. J. ELIAS. (Communication from the Bosscha-Laboratory).

§ 20. Since our former communication (These Proc. March p. 734) we have obtained a number of samples, the crystallisation of which in reasonable sizes from solutions in water or amylic acetate was brought about only after many failures and many weeks of patience. Notices concerning the influence of the anion or the temperature only on the absorption spectrum, must be laid aside as being too extensive, though incidentally some details may appear about it. With respect to the ZEEMAN-effect we shall also confine ourselves to a choice from the profuse material, which for the present can be little more than an enumeration of the many ways in which the influence of the magnetisation may manifest itself; it must be reserved for further investigation to impart more order and regularity to the present rather unsystematic series of results.

As a rule we worked again in the spectrum of the first order; in some cases we had recourse to the second order, in which some special effect may sometimes be better judged, at least from a qualitative point of view; for measurements the first order proved preferable on the whole. As we have never to do with very fine lines, too great a dispersion is of no use here, and certainly of much less importance than a strong magnetic resolving power. Very thin crystal chips — some tenths of a mm. thick — already exhibiting jet-black absorption bands, particularly for neodymium salts, we could use these, and expose them to very strong fields, mostly of 38-42 kilogauss. The distinctness of the spectral image depends to some extent on the choice of the proper thickness for every salt. The fields were measured with a bismuth spiral; the disturbance by the narrow slits is certainly less than with the usual round bores; the increase of the - saturated - magnetisation values of the polar end-pieces on cooling them down to -190° is probably slight; it would be desirable to obtain further information concerning these points. We consider, however, the accuracy of our field-measurements of the same order as that of the readings in the spectrum. We again preferred the latter to a photographic reproduction; for with visual observation the identification of the lines with field on and field off, especially with erbium compounds, proved to be decidedly easier.

§ 21. Third series. We have investigated a few organic double salts of chromium and potassium with a view to a possible

ZEEMAN-effect, the absorption spectra of which were fully described at ordinary temperature by LAPRAIK¹). The so-called "blue" (dichroitic red-blue) chromium-potassium oxalate $[Cr_2K_6 (C_2O_4)_6 + 6 H_2O]$ mentioned in our first paper exhibited in liquid air a strong band 696,4—701,4 (cf. § 5), evidently still too broad to be taken into account. This oxalate may not be mistaken for the so-called "red" compound:

Chromium-potassium oxalate $[Cr_{2} K_{2} (C_{2} O_{4})_{4} + x H_{2} O;$ different authors consider x = 8, 10, 12]; this was obtained by CROFT in 1842, and its absorption-spectrum was investigated by BREWSTER²). Strongly dichronic (claret hue-bluish grey) probably monoclinic crystals. At -190° a number of fine bands and lines in the red are seen with the spectrometer, the most striking of which are a rather strong band 680,0, and a strong band 692,5 between the red ruby bands $R_{2} = 691,8$ and $R_{1} = 693,2$ (comp. §§ 7, 17).

A plate, 1.5 m.m. thick had to be examined with sunlight on account of its strong absorption; for the same reason the crystallographic orientation could not be determined. At --- 193° line 692,5 had a width with field off of 0,14 $\mu\mu$ with non-polarized light; in a field of 36,5 kgs. the widening amounted to about 0,05 $\mu\mu$.

Chromium-potussium malonate $[Cr_{s}K_{s}(C_{s}H_{s}O_{4})_{s} + 6H_{s}O]$, is evidently homologous with the "blue" oxalate. This could only be obtained as an interlaced dark crystal magma with irregular orientation, dichroïtic (grass green-sky blue). In the red at — 193° we find a strong band, the middle of which 693,3 coincides pretty nearly with the red ruby band R_{1} =693,2; and a broader rather faint band 698,3. A sample of a thickness of only 0,15 mm. exhibited band 693,3 with a width with field off of 0,8 $\mu\mu$ with unpolarized light; moreover it appears to have shifted 0,8 $\mu\mu$ towards the red with respect to the corresponding band of the oxalate above mentioned. In a field of more than 40 kgs. the band became distinctly vaguer and almost disappeared. We had no opportunity as yet to examine a malonate homologous with the "red" oxalate; perhaps the phenomenon would appear more clearly still in this case.

§ 22. Fifth series. We have now made a closer examination of some salts of the four metals Pr, Nd, Sm and Er, such as had been used in 1899.

Praseodymium sulphate $[Pr_2(SO_4)_8, SH_2O]$. Light green plate, containing both optical axes, 0,6 mm. thick. Exhibits several not

¹) W. LAPRAIK, Journ. f. prakt. Chemie (2) 47 p. 307, 1893.

²) A. ROSENHEIM, Zeitschr. f. anorg. Chemie 11 p. 196, 1896; and 28 p. 337, 1901.

(841)

very narrow bands at -193° in the violet and blue; in the orange some heavy broad bands, moreover a strong band 599,0-599,3, a pretty faint band 600,9-601,4. The plate was now investigated with the median line (dividing the acute angle formed by the axes into two equal parts) vertical in a field of 40 kgs.

With vertically polarized light band 599,0—599,3 appeared to be subject to a distinct widening of 0,1 $\mu\mu$; the other band also became wider and vaguer. With horizontally polarized light the phenomenon was analogous, but less distinctly to be seen; on the other hand some of the wider bands then show an unmistakable widening ¹).

Neodymium sulphate $[Nd_2(SO_4)_3, 8H_2O].$

§ 23. As a supplement to what was communicated in § 19 a number of plates of different thickness were more fully examined; they again contained both optical axes; the line dividing the acute angle was again placed in a vertical position.

Group of bands in the blue at -193° ; 8 of these bands were measured. For the sake of brevity we have been obliged to draw up the results in a table, where λ denotes the wave-length, β_0 the width with field off, β_1 the width in a field of x kgs., $d\beta$ the widening; in case a multiplet is formed, the distance of the centre-lines of the extreme components is denoted by $d\lambda$; the value of $d\lambda/\lambda^2$ is expressed in cm⁻¹, as is now usually done.

41 Ki	Kilogauss — Plane of polarisation horizontal — Thickness 0.3 mm								
	I	n	III	IV	v	VI	VII	VIII	
,	469.5	472.8	474 0	474.5	475 3	476.2	477.0	477.4	μμ
<i>β</i> o	0.26	0.26	0.14	0.05	0.035	0.16	0 .105	0.09	n
β ₄₁	0.26	0.35		0 105		0 195	0.21	0.23	н
d _i s	0	0.09		0.055		0.035	0.105	0.14	11
d.			0.22		0.18				n
$d\lambda/\lambda^2$			9.8		8.0				cm
	1	1			1	1	1		[

¹) From a copy that Prof. KAMERLINGH ONNES kindly sent us of the paper by himself and Mr. J. BECQUEREL (These Proc. X, p. 592) we now infer that the results given for the sulicates of Pr and Nd really apply to the sulphates; we had then nearly finished our observations; as, moreover, these were made at - 193° instead of - 253° and in a much stronger field, the two series of results are not directly comparable; but they may serve to complete each other. Here III formed an asymmetric doublet, of which the component on the red side was the narrower; V a faint doublet; for VI the middle became somewhat lighter.

With a vertical plane of polarisation all the bands became vaguer, most of them slightly shifting towards the red; in the field the bands widened or further faded away; now only IH gave a symmetrical doublet.

Band in the blue-green at -193° : with a horizontal plane of polarisation $\lambda = 511.9$, $\beta_0 = 0.13 \,\mu\mu$; in a field of 42 kgs. a doublet appeared: width of the lefthand line 0.13, of the righthand line 0.18, of the light interval 0.09 $\mu\mu$; the whole made the impression of perhaps being a quadruplet. With a vertical plane of polarisation the phenomenon was analogous but less clear.

Group of bands in the green at -193° : 6 bands were measured.

42 Kilogauss. — Plane of polarisation horizontal — Thickness 0,3 mm.							mm,
	I	II	III	IV	v	VI	
λ	521.2	523.0	523.9	525.3	526.0	527.5	ųų
ßo	0.49	0.105	0.355	0.10	0.13	0.195	*
β_{42}	0.58			0.15	0.275	0.275	*
dβ	0.09	—		0.05	0 145	0.08	>
d۷		0.26	0.29	-	-		*
d)/)2	-	9.5	10.5	-	-		cm—].

Band II gave an ordinary doublet; that of III remained rather dark in the middle, so that we may infer a more complex structure in this case also.

With a vertical plane of polarisation all this was less clearly visible, band II. still gave a clear doublet, for III only a trace of this could be perceived.

Group of bands in the yellow at -193° . Two rather sharply defined bands 576,0 ($\beta_0 = 0,3$) and 586,0 ($\beta_0 = 0,14$) exhibited a distinct widening of 0,05 $\mu\mu$ in a field of 42 kgs. The intermediate bands are too wide for this kind of observation.

Group of bands in the orange-red at -193° : 5 bands were measured.

1	843	1
١.	0.40	•

38 Kil	8 Kilogauss Plane of polarisation horizontal - Thickness 0,6 mm							
	I	11	, III	IV	v			
,	623.2	624.1	625 6	627.2	628.3	קק		
ßo	0.31	0.13	0.18	0.i3	0.08	n		
β_{88}	-	0.26	-	0 15	-	n		
dβ	_	0.13		0.02	-	»		
d۷	0.22*		0.46*	-	0.34	11		
$d\rangle/\rangle^2$	57	-	10.2		8.6	cm—1.		

Here I and III yielded very blurred doublets, of which the distances * of the extreme limits are given; V a distinct doublet with a shade between the components, perhaps a quadruplet.

With a vertical plane of polarisation the phenomenon was analogous and was confirmed with a thinner plate: I was a doublet, III was invisible here, with IV some light appeared in the middle with greater widening, structure probably complicated, V was again a very distinct doublet.

Group of bands in the red at -193° : Four bands, among which two rather sharp ones 674,4 and 676,2 showed a widening or a fading away in the field; the last-mentioned became a doublet, perhaps even a quadruplet, with plane of polarisation vertical.

Neodymium nitrate $[Nd(NO_3)_2 . 6 H_2 O]$.

§ 24. It appeared important to investigate crystals besides the amorphous nitrate (§ 9); with a much slighter thickness crystals show intense and narrow absorption bands; the natural monoclinic plates were directed perpendicularly to one of the optical axes, so that in this case a nicol could be done away with. The wave-lengths of the bands are on the whole slightly less — down to $3 \ \mu\mu$ — for the nitrate than for the sulphate.

Band in the blue-green at -193° . The wave-length now was $\lambda = 511,3 \ \mu\mu$; in a field of 41 kgs. a doublet appeared, the components of which had a distance of $0,22 \ \mu\mu$.

Group of bands in the green at -193° . 5 bands were measured in the spectrum of the second order.

(844)
------	---

41 Kilogauss. Thickness 0.2 mm.							
	I	II	III	IV	v		
)	521.3	522 3	523.1	524 6	525.0	יןין	
Po	0.155	0.11	0 18	0.09	0 045	53	
β_{41}	0 265	0 18	0.22		0.11	17	
ďјз	0 11	0.07	0.04	-	0.065	17	
d)			_	0.22	-	,,,	
$d_{1}/2$				8.0		cm1	

The doublet IV showed a shade in the middle.

Group of bands in the yellow at -193° . Two rather sharp bands 581,9 and 583,1 exhibited a widening of 0.05 $\mu\mu$ in a field of 42 kgs.; the others were too broad and too hazy.

Group of bands in the orange-red at -193°. 3 bands were measured.

40 Kilogauss.			Thic	kness 0.45	mm.
	I	II	III S	ш	
;	624.2	625.2	(626.7)	626.9	цц
β_0	0.265	0.18	(0.05)	0.14	n
d)	05	05	-	0.5	, , ,
d \rangle $)$ 2	12.8	12.8		12.8	cm-1

Doublets I and III were normal, II on the other hand was asymmetric, the component on the red side being weaker; the satellite III S was no longer visible in the field.

4	40 Kilogauss. Thickness 0.45 mm.						m.		
	1	11	111	IV	v	٧1	VII	VIII	
	671.0	672.0	673 3	674.3	675.2	675 8	676.6	677.2	µ,u
Fo	0.31	0.26	0.25	0.22	0.25	0.26	022	0.31	19
β_{40}	v.	0.52	0.45	0.32	v.	v.			
d_{l^3}	—	0.26	0.20	0.40		_	_		, »-
d).	—	_		_ ·		_	0.80	0.90	n
d^{γ}/γ^{2}			·	-	-		17.5	19.6	cm-1

Group of bands in the red at -193° : 8 bands were measured.

Band I, V and VI vanished in the field; with the field off II showed a dark core with shades on either side, which disappeared in the field. The two doublets VII and VIII gave the greatest resolution measured as yet $-1.5 \times (D_1 - D_2)$; with the field used the components facing each other happened to coincide, so that the pair of doublets looked like a very wide triplet with a heavy middle band. It ought to be possible to observe a phenomenon of this order of magnitude with every good spectroscope.

Finally we mention that the neodymium-magnesium nitrate of § 9 also occurs in hexagonal crystals; such optically uniaxial crystals are of great interest (§ 19); there also exists an isomorphous series of salts, which contain manganese, cobalt, nickel or zinc. Measurements on this subject have been made, partly they are still in preparation.

Samarium sulphate $[Sm_2(SO_4)_3 \cdot 8H_2O]$.

§ 25. We now examined a more transparent sample (cf. § 19), which again contained both optical axes, and was placed like the other sulphates; 4 bands in the green were measured at -193° .

40 Kilogauss — Plane of Polarisation horizontal — Thickness 0.8 mm.							
	I	II	111	IV			
;		_	558.2	559.1	μμ		
1 ³ 0	0.09	0 09	0.105	0.18	n		
1340	0.18	0.11	0 18	0.31	• <i>n</i>		
$d_{i} 3_{40}$	0.09	0.02	0 075	0.13	"		

The effect was apparently small here; the widened bands were vague. With a vertical plane of polarisation the phenomenon scarcely changed.

Erbiumyttrium sulphate $|(Er, Y)_2(SO_4)_3|$.

§ 26. We also examined an impure product obtained by treatment of the original minerals with sulphuric acid, in which erbium and yttrium occur in variable percentages, and the latter preponderates : the crystals were monoclinic. The group of bands in the green, yellow-green, and red showed peculiar and intricate effects of mag-

57

Proceedings Royal Acad. Amsterdam. Vol. X.

- 8 -

netisation; among others some bands which were hardly visible with field off were much more pronounced with the field on, in contrast to most of the other cases observed. Further measurements on this point are in progress.

It is quite probable that this product also contains other rare earth-metals (e.g. dysprosium and holmium); this is, moreover also rather likely for the other erbium salts.

Erbium nitrate $[Er(NO_3)_3, 6H_2O].$

§ 27. Here too, besides the amorphous salts (§ 10) monoclinic crystal plates of an average thickness of 0.6 m.m. were examined, containing both optical axes. The bands were finer than for any sample examined before. On account of the very complicated resolutions it was often somewhat difficult to ascertain to what bands the different components belonged; on exciting the field a sudden confusion was observed from which the single bands slowly emerged again on breaking the current. These observations were all made with unpolarized light.

The results are best arranged in a table in a way somewhat different from the above.

λ	β₀	Influence of a field of 39 Kilogauss.
516.4 517 2	.0.17 0.13	increases in width (not measured). gives a quadruplet, the outer lines of which are very fine, the middle ones (from violet to red) resp. 0.12 and 0.15 up wide, the distances of the
shade		middles amounting respectively to 0.08 ; 0.27 ; $0.08 \ \mu\mu$, while the middle of the outer components seems to have shifted about $0.01 \ \mu\mu$ towards the red with respect to the line with field off.
517.6 518.0 518.3 518.6	very narrow 0.06 0.11 0.07	no more visible. give a very complex set of lines, which ought to be further investigated.

Group of bands in the green at -193° .

(847)
~		

λ	βυ	Influence of a field of 39 Kilogauss.
519.1 519.7	0.10 0.16	gives a doublet (not measured). gives an asymmetric quadruplet, the extreme lines of which are very fine; those on the violet side are very faint; the middle ones are resp. (from violet to red) 0.11 wide (this one very faint) and 0.135 $\mu\mu$; the distances of the middles are resp. 0.07, 0.255, 0.13 $\mu\mu$, the middle between the ex- treme components sceming to have been displaced 0.05 $\mu\mu$ towards violet with respect to the line
520.2	0.17	with field off. gives an asymmetric doublet, of which the com- ponent on the violet side is $0.05 \mu\mu$ wide, the other very narrow; distance of the middles $0.175 \mu\mu$; the mean of these middles is not sensibly displaced with respect to the line with field off.
520.7	0.14	gives an asymmetric triplet (doublet with satellite on violet side); not measured.
521.3	0.11	gives an asymmetric quadruplet; outer component on violet side rather strong, on red side feeble; middle components stronger.

Ş	28.	Group	of	bands	in	the	yellow-green	at		193°
---	-----	-------	----	-------	----	-----	--------------	----	--	------

λ	$oldsymbol{eta}_{\mathfrak{o}}$	Influence of a field of 39 Kilogauss.
534.8	0.13 (faint)	widens and fades away, not measurable.
535.5	0.13	gives an asymmetric doublet, consisting of (from
shade ¹⁾		violet to red) first a shade of a width of 0.29 µµ,
535.8	0.09	then a strong band 0.18 $\mu\mu$ wide, then a shade, and at last a faint undefined band 0.26 $\mu\mu$ wide; the middle of the first component has shifted 0.17 $\mu\mu$ towards the violet side with respect to the original band 535.5, the place of the middle of the second component being 535.8.

¹) With a somewhat thicker crystal they form together a heavy band. 57*

(848)

~

.

-

λ	β	Influence of a field of 39 Kilogauss.
536.95	narrow	give together, seen in the first order, a triplet,
537.15	0.05	resp. 0.10; 0.05; 0.07 $\mu\mu$, wide, the first very faint, the last two stronger, and connected by a shade; the situation of the middles of the first two is shifted resp. 0.44 and 0.14 $\mu\mu$ towards the violet, that of the last 0.05 $\mu\mu$
		towards the red with respect to the band 537.15 with field off. Seen in the second order the line 536.95 be-
		comes a symmetric doublet, about $0.44 \ \mu\mu$ apart; the line 537.15 an asymmetric doublet, of which the component on the red side is very heavy.
537.35	narrow feeble	together give a triplet, the components of which (from violet to red) are resp. 0.08 ; 0.08 ; $0.10 \mu \mu$,
537.6	0.06	wide, the first two strong, and connected by a
537.8	narrow satellite some- what stronger than the former	shade, the last very faint; the place of the middle of the first component has moved $0.02 \mu\mu$ to- wards the violet, that of the two following ones resp. 0.07 and 0.34 $\mu\mu$ towards the red with respect to the original line 537.6.
538.5	narrow	gives a doublet (not measured).
539,15	0,09	gives a doublet, with components each 0.08 $\mu\mu$ wide, and distance of the middles 0.30 $\mu\mu$; on the violet side another shade is seen, where pos- sibly a third component is found; the middle of the two lines of the doublet seems to have shifted 0.03 $\mu\mu$ towards the violet with respect to the original line 539.15.
539.7	0.08	gives an asymmetric sextuplet of which the four outer components are faint, and very narrow, the two middle ones heavy, and resp. (from violet to red) 0.06 and 0.03 $\mu\mu$ wide, the distances of the middles amounting resp. to: 0.045; 0.05; 0.11; 0.17; 0.035, total 0.41 $\mu\mu$. The middle of the two outer components coin- cides with the line with field off. The two com-

(849)

λ	β _a	Influence of a field of 39 Kilogauss.
540.3	0.07	ponents on the violet side are connected by a shade. gives a somewhat vague band, $0.22 \mu\mu$ wide, in which lines could not be distinguished with cer- tainty : it may, however, be a triplet. The middle seems to have been displaced $0.03 \mu\mu$ towards the violet with respect to the line with field off
540.8	0.07	gives an asymmetric quadruplet, of which the three components lying on the violet side are rather strong, the fourth weak; the mutual distances of the components are very nearly the same, and amount to $0.18 \ \mu\mu$.

§ 29. Group of bands in the red at -193° .

λ	β	Influence of a field of 40 Kilogauss.
640.3	not mea- sured not mea-	gives an asymmetric doublet, (not measured).
640.9	sured	gives an asymmetric doublet, (not measured).
642.2	0.09	gives a doublet, consisting of a faint, thin line on the violet side, and a strong line, 0.11 $\mu\mu$ wide, the middle of which is at a distance of 0.09 $\mu\mu$ from the other faint line, and has moved
642.8	0.11	0.18 $\mu\mu$ towards the red with respect to the line with field off. Probably on the red edge of this strong line another faint line is found, which is connected with it, so that the whole would form a triplet. gives a triplet, the extreme components of which are weak, and very narrow, the middle ones strong, and 0.125 $\mu\mu$ wide; the distance of the middles (from violet towards red) amount resp. to 0.11 and 0.16 $\mu\mu$; the middle of the inner components has been displaced 0.035 $\mu\mu$ towards the red with respect to the line with field off.

•

I	(8	35	0)
	•			/

λ.	ßo	Influence of a field of 40 Kilogauss.
650.5	0.09 (some- what vague)	is widened; the width amounts to 0.35 $\mu\mu$, the band on the violet side is darker than the one lying towards the red; (possibly a quadruplet is formed, which, however, is uncertain); a displacement, however, was not observed.
651.3	0.09 (some- what vague)	increases in width and fades away; the width amounts to 0.40 $\mu\mu$; a shift towards violet seems to take place, but could not be ascertained.

§ 30. Seventh series. We now investigated.

Uranyl potassium sulphate $[UO_{g} K_{2} (SO_{4})_{2} + 2 H_{2}O]$.

A rhombic plate containing both axes, 0.7 m.m. thick, was examined in a field of about 40 kgs. with unpolarized light at -193° . The well-known bands appeared to be much more numerous and narrower than for uranyl nitrate (c.f. § 11), among others 487.8, 488.2, 488.8 and 490.5 in the blue. These bands seemed to fade somewhat in the field, but the phenomenon was uncertain here, and in any case the widening did not amount to more than $0.02 \,\mu\mu$. For the many bands in the violet no action of the field could be perceived.

Physics. — "The value of the self-induction according to the electrontheory." By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

Many physiciists refer to the existence of self-induction in order to make the existence of kinetic energy of electrons more intelligible. To a certain extent there is no objection to this, provided we keep in view, 1st that the kinetic energy consists for a large part electrical energy whereas for the calculation of the self-induction only the magnetical energy is taken into account, and 2nd that from a theoretical point of view it is the self-induction which is to be explained from the kinetic energy of the electrons, and not viceversa. It is this second point which occasions me to make the following remarks.

Let us imagine a piece of metal which contains a great number