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## **Physics.** — "Series in the spectra of Tim and Antimony". By T. VAN LOHUIZEN. (Communicated by Prof. P. ZEEMAN).

#### (Communicated in the meeting of April, 26 1912).

In my Thesis for the Doctorate, which will shortly appear, I have used a spectral formula, which expresses this fundamental thought: "For every series the curve obtained by using the parameters (1, 2, 3, etc.) as abscissae and the reciprocal values of the wave-lengths as ordinates, is exactly the same, only referring to another system of axes". This curve is the curve of the third degree :

$$y = -\frac{N}{x^2}$$

in which  $y = 10^{\circ} \lambda^{-1}$ , x is successively: 1, 2, 3 etc., and N is the universal constant which occurs in the formulae of **Rydburg**, **Ritz**, and **MOGENDORFF**—HICKS, the universality of which, somewhat more intelligible after the physical meaning which Ritz<sup>1</sup>) has given to it, can hardly be doubted any more. Transferred to one and the same system of axes the general spectral formula becomes for all series:

$$10^{\circ} \lambda^{-1} = b + (x-a) t g \gamma - \frac{N \sec \gamma}{[(x-a)\cos \gamma - b\sin \gamma - 10^{\circ} \lambda^{-1}\sin \gamma]^2}$$

in which a and b are the ordinates of the origin of the original system of axes, and  $\gamma$  the angle of rotation. As I shall demonstrate more at length in my Thesis, the formula may be reduced to:

$$10^{*} \lambda^{-1} = b - \frac{N}{[x + a' + c \lambda^{-1}]^{2}}$$

for small values of  $\gamma$ .

This approximated form closely resembles RITZ's formula, which may, therefore, be considered as an approximation of the one given by me. Also the formulae of RYDBERG (c = 0) and of BALMER for the 'hydrogen series (a' = 0 and c = 0) are implied in it as special cases. Accordingly it is also further closely related to the original formula of RYDBERG. This, too, expresses that the curve is the same for all series, but the important difference is that RYDBERG gives the system of axes only a translation, whereas according to my formula there generally appears a — mostly small — rotation of the curve.

The thought of one curve for all series has been embodied in a model which I have had constructed for this purpose, and which contains the most important part of the curve:

<sup>3</sup>) Magnetische Atomfeider und Serienspektren. Ann. d. Phys. 25 p. 660 et seg. 1908.

and also the axes of the system to which it refers. By a fine division with vernier it is possible to determine the first four figures of the oscillation frequencies expressed in five figures  $(10^{n} \lambda^{-1}, \lambda \text{ expres$  $sed in ÅU})$ .

It deserves notice that also RYDBERG has designed his curve by means of one model. He says<sup>1</sup>): "Toutes les courbes ont été tirées à l'aide du même calibre".

This model has proved to be a great help in detecting new series for elements for which no series had been observed up to now. For this investigation I have first chosen the spectra of those elements for which KAYSER and RUNGE<sup>3</sup>) had found "eine andere Art der Gesetzmässigkeit". KAYSER points out already there that when we pass from one MENDELEJEFF group to the next, the series move to the region of the small wave-lengths. He says<sup>3</sup>): "Es ist also recht gut möglich, dass für weitere Elemente, die Serien im unzugänglichen Gebiet der Schumannschen Strahlen liegen".

From what I have found, the results of which for *Tin* and *Antimony* I communicate here (I hope to publish the results for the other three elements Pb, As, and Bi later) I think I may infer that in general this conclusion is correct, but *that the beginning of* a great number of series is found in the already investigated region.

Whereas for the other elements the finding of series was facilitated, because the parts where the lines converge, had been observed, while later the first terms were added by the discoveries of PASCHEN and others in the ultra red, exactly the opposite takes place for the elements considered here. The initial terms have been observed, and they lie together of all kinds of series; the part where the series begin to converge clearly lies outside the region of observation. So the difficulty was to accomplish the discovery of the series from the few terms that have only been observed of most of these series. Only very few observations on the ZEEMAN-effect for Tin and Antimony have been made, so that at present they do not yet afford sufficient data for the finding of series. It would be desirable that investigations for these elements on the magnetical splitting up of the spectral lines lying more in the ultra violet were carried out. They 'might throw more light on the series found by me. So as these data were

<sup>1</sup>) Kon. Svensk Vetensk. Akad. Hand. Vol. 23 p. 152. 1890.

\*) Ueber die Spektren der Elemente VII. Abh. Berl. Akad. 1894. Cf. also KAYSER. Handbuch der Spektroskopie. Vol. 11, p. 573 et seq.
\*) 1. c. p. 578.

 $y = -\frac{109675.0}{-1}$ 

not at my disposal, I have tried to find the series by means of my model, somewhat led by the estimations of the intensity given by EXNER and HASCHEK<sup>1</sup>). As these authors give widely divergent and contradictory differences from those of KAYSER and RUNGE<sup>2</sup>), I have thought that I ought to prefer the former, because they extend over the whole of the spectrum observed by them.

The obtained results follow.

I must not omit mentioning that besides the said estimations of the intensity, also the constant frequency differences found by KAYSER and RUNGE<sup>3</sup>) have furnished a first basis for my investigation.

In the spectrum of Tin I have found a series which is represented by the formula:

$$10^{\circ} \lambda^{-1} = 45307.40 - \frac{109675.0}{(x+1.651360-657.42 \lambda^{-1})^2}$$

x = 1.2..

the results of which are:

x	λw	λĿ	λwλι	Limit of errors	Intensity
1	3655.92 4)	3655.92	0	0.03	5
2	2785.14	2785.14	0	0.03	3
3	2524.05	2524.05	0	0.05	1
4	2408.27	2408.71	0.44	0.03	I

No more terms have been observed of this series, which need not astonish us, if we consider that in their tables EXNER and HASCHEK indicate by 1 the lines of the least intensity, and that therefore the following lines have probably been too faint. Now this four-term series would have little conclusive force, if it was not in connection with other series, which I have called *Translation series* in my Thesis for the doctorate, because they are obtained by a pure y-translation of the curve, and so only differ in their asymptotes. Such translation series are easily shown, as I have proved there, in the spectra in which series are known. By a translation 5187.03 (one of the two differences of frequency discovered by KAYSER and

4) EXNER and HASCHEK, l. c.

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<sup>1)</sup> Die Spektren der Elemente bei normalem Druck, II, p. 232 and 235.

<sup>)</sup> l. c.

<sup>\*) 1.</sup> c.

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RUNGE), we get a series with the formula:

$$10^{\circ} \lambda^{-1} = 50494.43 - \frac{109675.0}{(x + 1.651360 - 657.42 \lambda^{-1})^{\circ}}$$

x = 1 . 2 ....

So the series differs from the others only in its asymptote. We find the following lines :

	^w	λδ	$\lambda_{w} - \lambda_{b}$	Limit of errors	Intensity
1		3073.15			
2	2433.58 <sup>1</sup> )	2433.57	+0.01	0.03	1
3	2231.80	2231.80	0	0.10	-
4	2141.1	2141.19	0.09	0.20	
5	2091.7	2092.30	0.60	0.50	
6	2063.8	2063.79	+ 0.01	0.50	-
	3 4 5	3     2231.80       4     2141.1       5     2091.7	2       2433.58 1)       2433.57         3       2231.80       2231.80         4       2141.1       2141.19         5       2091.7       2092.30	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

 $\lambda 3073.15$  for x = 1 does not occur in the arc-spectrum of tin. The spark-spectrum has the line  $\lambda 3071.9$ , which is given as diffuse and broad. There appears to be good agreement for this series. The terms for x = 7.8 etc. are outside the region of observation.

The translation 5618.84 gives the series with the formula:

$$10^{*} \lambda^{-1} = 50926.14 - \frac{109675.0}{(x+1,651360-657,42 \lambda^{-1})^{2}}$$
  
x = 1.2 . . .

which yields:

111	x	<sup>у</sup> w	۶b	λ <i>w-λ</i> δ	Limit of errors	Intensity
	1	3032.90 <sup>1</sup> )	3032.90	0	. 0.03	8
	2	2408.27	2408.27	0	0.03	1
	3	2209.78	2210.55	-0.77	0.10	
	4	2121.5	2121.57	0.07	0.20	
	5	2073.0	2073.50	-0.50	0.50	

For  $\lambda = 2209.78$  LIVEING and DEWAR found  $\lambda = 2210.7$ , which gives a difference of + 0.15. with the value found by me. There is

1) Exner and HASCHER l. c.

further again good agreement here, x = 6 falls just outside the region of observation.

The translation 6923.26 (the other difference of frequency found by KAYSER and RUNGE), yields:

	10	$\lambda^{-1} = 523$	330.66 — (4	$\frac{109675.0}{(x+1,651360-657.42\lambda^{-1})^2}$			
IV	<i>x</i>	= 1.2 .	• •	1	······································	1	
	x	×ω	۹۲	$\lambda_w - \lambda_b$	Limit of errors	Intensity	
	1		2917.48		·		
	2	2334.89	2334.93	0.04	0.03	1	
	3	2148.7	2148.59	+0.11	0.20		
	4	2063.8	2064.12	-0.32	0.50		

x = 5 is outside the region of observation.  $\lambda 2917.48$  has not been observed.

The translation 8199.87 yields the formula:

 $10^{\circ} \lambda^{-1} = 53507.27 - \frac{109675.0}{(x + 1.651360 - 657.42 \lambda^{-1})^2}$ 

x = 1.2 .

V	x	λισ	λj	$\lambda_{uv} - \lambda_b$	Limit of errors	Intensity
	1	2812.72 <sup>1</sup> )	2812.72	0	0.05	3
	2	2267.30	2267.33	0.03	0.05	1
	3	2091.7	2091.23	+0.47	0.50	

x = 4 is outside the region of observation.

The translation 8617.50 yields a series with the formula: 109675.0

VI	x	λw	۶۶	λω-λι	Limit of errors	Intensity
	1	2779.92	2780.06	0.14	0.03	4
	2	2246.15	2246.06	+0.09	0.10	-
	3	2073.0	2073.12	-0.12	0.50	-
1.1.1		1. ·		1	1	1

x = 4 is outside the region of observation.

1) EXNER and HASCHEK l.c.

x = 1.2 .

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Besides these six series, which are connected by a simple translation, I have found some more in the tin spectrum that are connected. The first series of this group may be represented by the formula:

x	<i>k</i> w	уP	λ <sub>w</sub> λb	Limit of errors	Intensity
1	3801.16	3801.16	. 0	0.05	30
2	2850.72	2850.72	0	0.03	10
3	2594.49	2594.49	0	0.03	3
4	2483.50	2482.53	+0.97	0.03	3
5	2421.78	2422.24	-0.46	0.03	5
6	2386.96	2385.98	+0.98	0.50	-

101 3 1 40005 00	109675.0
$10^{\circ} \lambda^{-1} = 43825.00 -$	$\overline{(x+1.384406+446.70 \ \lambda^{-1})^{s}}$

VП

Why EXNER and HASCHEK give so great an intensity for  $\lambda$  2421.78, whereas this line is fainter than any of the others according to KAYSER and RUNGE, I do not know. 2 2386.96 only occurs with KAYSER and RUNGE with the indication "sehr unscharf". EXNER and HASCHEK have not got this line at all, which is very strange, indeed, in connection with the intensity 5, which KAYSER and RUNGE give.

Of this series I have found two translation series, which correspond with the two differences of frequency found by KAYSER and RUNGE.

109675.0

The translation 5187.03 yields the series:

		$)^{8} 2^{-1} = 49$ = 1.2	012 03 - (	$\frac{109675.0}{(x + 1.3844!)6 + 446.70 \ 2^{-1})^2}$		
VIII '	x	λw	λĿ	×w->p	Limit of Errors	Intensity
	1	3175.12	3175.13	-0.01	0.03	100
	2	2483.59	2483.49	-4 0.01	0.03	3
~	3	2286.75 <sup>1</sup> )	2286.75	0.00	0.03	1
	4	2199.46	2199.32	+0.14	0.10	
	5	2151.2	2151.54	-0.34	0.20	· · · · ·
				A second second		

1) EXNER and HASCHEK I.c.

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The translation 6923.26 yields the formula:

$10^8 \lambda^{-1} = 50748.26 -$	109675.0
10	$\frac{1}{x+1.384406+446.70 \ \lambda^{-1})^2}{\lambda^{-1}}$
$x = 1.2 \ldots$	

IX	x	¢ω	λj	λ <i>ω</i> -λ6	Limit of Errors	Intensity
	1	3009.24	3009.24	0.00	0.05	50
	2	2380.82	2380.83	-0.01	0.05	1
	3	2199.46	2199.42	+0.04	0.10	

 $\lambda$  2118.43, which we found for x = 4 and the following lines have not been observed. Possibly their intensity is too slight.

These two groups of translation series are represented on the annexed plate, arranged in succession according to the vibration frequencies of the first lines of these series. The figures mean: freq.  $\times 10^3$ . The arrow indicates the limit of the region of observation.

The first line in the fourth red series for Tin must be dotted. The six series that were treated first, have been indicated by the same colour (viz. red), in the same way the three last by black. The succession is : VII, I, VIII, II, III, IX, IV, V, VI.

Not until further investigations on the ZEEMAN-effect have been carried out, will it be possible to determine further what place these series occupy in the whole system. In the arc-spectrum of Tin there are further indications for series, which have, however, not yet been examined by me.

In the spectrum of Antimony I have found a series which has as formula:

		${}^8 \lambda^{-1} = 453$ $= 1.2 \dots$	365.69 —	$59 - \frac{103013.0}{(x + 1.568667 + 237,63 \lambda^{-1})^2}$					
X	x	, no	уP	$\lambda_w - \lambda_b$	Limit of Errors	Intensity			
	-1	3383.24	3383.24	0.00	0.03	8			
	2	2692.35	2692.35	0.00	0.03	3			
	3	2480.50	2480.50	0.00	0.03	2			
	4	2383.73 <sup>1</sup> )	2383.93	-0.20	0.03	2+			
	5		2330.95	-	-				

1) EXNER and HASCHER l.c.

 $\lambda$  2330.95 has not been observed, its intensity is possibly too slight. It lies in the neighbourhood of  $\lambda$  2329.19 of KAYSER and RUNGE,

which, however, does not occur at all with EXNER and HASCHEK. The two following series are in connection with this by translation.

The former of them has as formula:

	$10^{8} \lambda^{-1} = 43296.20 - \frac{109675.0}{(x+1.568667+237,63 \lambda^{-1})^{2}}$ x = 1 2						
XI :	x	Ŷw	<i>`</i> b	$\lambda_w - \lambda_b$	Limit of Errors	Intensity	
	1	3637.94	3637.95	- 0.01	0.03	20	
	2	2851.20	2851.21	- 0.01	0.03	5	
	3	2614.74	2614.74	0.00	0.03	1	
	4	2507.90 <sup>1</sup> )	2507.74	+0.16	-		

 $\lambda 2507.74$  does not occur in the arc-spectrum.

In the spark-spectrum, however, we find  $\lambda = 2507.90$  which corresponds with this. Further terms have not been observed on account of their slight intensity.

The other translation-series has as formula:

$$\frac{10^8 \,\lambda^{-1} = 51908.81 - \frac{109675.0}{(x+1.568667 + 237,63 \,\lambda^{-1})^2}}{x = 1.2 \dots}$$

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(II	x	$\lambda_{w}$	۶,	×w-×P	Limit of Errors	Intensity
	1	2770.04	2770.04	• 0.00	0.03	10 u
	2	2289.09	2289.09	0.00	0.10	-
	3	2137.21	2135.97	+1.24	0.20	
	4	0. r. o.	2062.26			_
		1	1		1	

o.r. o. means outside the region of observation.

Further there are some more indications for other translation series, which lie further in the region of SCHUMANN, viz. that with the asymptotes:

53251.07 to which  $\lambda$  2673.73 (Int. 5) and  $\lambda$  2220.85 belong, and 54951.35 to which  $\lambda$  2554.72. (Int. 1) with  $\lambda$  2139.89 may be counted. For  $x = 3 \lambda$  2003.88 is therefore o. r. o.

1) EXNER and HASCHEK l.c. Vol. 111.

In the Antimony spectrum I found further a second group of translation series, the former of which has as formula:

$10^8 \lambda^{-1} = 47810.99 - x = 1.2 \dots$			810.99 — -	$\frac{10}{x+1.6165}$	99675.0 67 — 332,3'	$(\overline{\lambda})^2$
XIII	x	ک <sub>w</sub>	کې	$\lambda^m - \lambda^p$	Limit of Errors	Intensity
	1	3267.60	3267.60	0.00	0.03	30 u
	2	2574.14	2574.14	0.00	0.03	2
	3	2360.60	2360.60	0.00	0.03	1+

5 2212.54 2212.51  $\pm 0.03$  0.10 -Remarkable is the very great deviation for x = 4, while x = 5 is again in perfect harmony. Earlier investigators HARTLEY and ADENEY found  $\lambda$  2263.5 for this line, which lies just between the value found by KAYSER and RUNGE and mine.

-1.94

0.20

By translation we may obtain the series.

2264.49

2262.55

á

$$10^{\circ} \lambda^{-1} = 45741.50 - \frac{109675.0}{(x+1.616567-332.37 \ \lambda^{-1})^2}$$
  
$$x = 1.2 \dots$$

XIV Limit of x  $\lambda_w$ λb iw-ib Intensity Errors 1 3504.64 1) 3504.64 0.00 3 2 2719.00 2719.00 0.00 0.03 3 3 2481.81 2481.81 0.00 0.03 1 4 2375.74 o.r.o.

 $\lambda$  2375.74 lies near  $\lambda$  2373.78, which has been observed, and for which EXNER and HASCHEK remark: 2+, so diffuse. Possibly this diffuseness is caused by the faint line 2375.74 in the immediate neighbourhood.

Of a number of translation series, which lie for the greater part in the SCHUMANN region, indications are available, which I will give together in the following table with their respective asymptotes, and for each of them one calculated value in the as yet uninvestigated region.

1) EXNER and HASCHEK l. c. p. 822.

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AA	
TU	

XV- XIX	Asymptote	53986.13	54354.11	54905.34	55696.37	57039.02
	x = 1	2719.00	2692.35	<b>2652.7</b> 0	2598.16	2510.60
	<i>x</i> = 2	2220.85	2203.13	2175.99	2139.89	2079.55
	x = 3	2060.25	2044.78	2021.96	1990.20	1938.83

The values for x = 3 lie all in the not investigated region.

Further I have found a third group of translation series in the spectrum of Antimony, the first member of which has as formula:  $10^{s} \lambda^{-1} = 44790.00 - \frac{109675.0}{(x + 1.269826 + 1757,48 \lambda^{-1})^{s}}$ 

$$x = 1.2 \dots$$

 x
  $\lambda_w$ 
 $\lambda_b$ 
 $\lambda_w - \lambda_b$ 
 Limit of Errors
 Intensity

 1
 3232.61
 3232.61
 0.00
 0.03
 30

 2
 2652.70
 2652.70
 0.00
 0.03
 4

2477.45

2395.31

2349.50

XX \*

3

4

5

2478.40 1)

2395.31

n.o.

 $\lambda$  2349.50 has not been observed any more, which tallies with the course of the intensity, as 1 indicates the faintest lines according to EXNER and HASCHEK.

+0.95

0.00

?

0.03

2

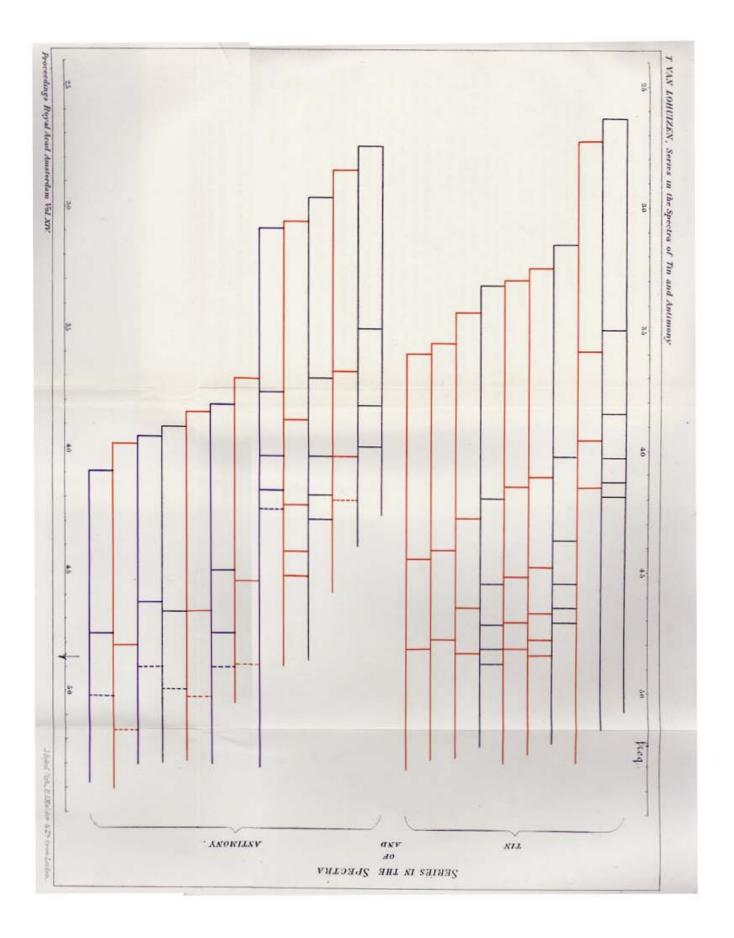
1

The following form was found as corresponding translation series:

$$\frac{10^{\circ} \lambda^{-1} = 52099.97}{x = 1.2} - \frac{109675.0}{(x + 1,269826 + 1757,48 \lambda^{-1})^2}$$

XXI	x	λ <sub>w</sub>	λb	λ <i>w</i> —λβ	Limit of Errors	Intensity
	1	2614.74	2614.74	0.00	0.03	1
	2	2222.10	2221.88	+0.22	0.10	
	3	2098.47 •	2097.76	+ 0.71	0.30	-
	4	o.r.o.	2038.40	_		

1) EXNER and HASCHER loc. cit. p. 232.



while there have been found two indications of series of translation in the region of SCHUMANN viz.

XXII and

37	37	٠	TT.	
v	×			
- A	~			

I	Asymptote =	53 <b>4</b> 02.61	54744.87
	x = 1	2528.60 (Int. 20)	2445.59 (Int. 2)
	x = 2	2159.32	2098.47
	x = 3	2042.40 (o.r.o.)	1987.30 (o.r.o.)

The found series in the Antimony is indicated on the annexed plate, coloured in groups, just as that of the Tin.

The first group of translation series is coloured black, the second group red, the last mentioned group blue. The succession of the black one is : XI, X, XII; that of the red one XIV, XIII, XV, XVI etc.; that of the blue one XX, XXI, XXII and XXIII.

So it appears from this investigation that in the spectra of Tin and Antimony the series have been considerably shifted towards the side of the small wave-lengths, and so that they lie for the greater part in the SCHUMANN region. At the same time it has appeared from it that the intensity of the lines of one and the same series greatly decreases, so that only a limited number of lines has been observed. But though the number of lines is limited, yet the mutual relation that exists between the different members of one translation group, sufficiently proves the existence of series in the same form <sup>1</sup>) as we meet with them for other elements. Though the series there are at once far more pronounced, yet the translation series exists there too, as I shall show more at length in my thesis for the doctorate.

How we must distinguish the series found as principal and subordinate series etc. cannot be decided for the present. Not until a sufficient number of magnetic splittings up have become known in the ultra-violet spectrum of these metals, this investigation can be undertaken. The few things that are known about the ZEEMAN-effect of Sn and Sb, have been found by PURVIS<sup>3</sup>). We will summarize it here.

PURVIS has measured the magnetic splitting up of the following lines in our tables.

<sup>&</sup>lt;sup>1</sup>) RYDBERG's statement, therefore (Rapports Paris 1900. T. II. p. 220) that Sn, Sb and some other elements present spectra built according to other laws, cannot be maintained.

<sup>&</sup>lt;sup>2</sup>) PURVIS Untersuchungen über die ZEEMAN-Phänomene. Physikal. Zeitschr. p. 594. 1907. and the literature mentioned there.

	λ	dì 71
Tin		
1 111	3032.90	+2.12 s 0 p -2.16 s
j	3801.16	+ 1.22 s 0 p - 1.22 s
	2850.72	+ 1.30 s 0 p - 1.30 s
	3175.12	+2.12 s 0 p -2.13 s
	3009.24	+2.00 s 0 p -2.02 s
Antim	ony	
	3637.94	$ \begin{array}{c} + 2.11 \ s \\ + 0.99 \ p \\ 0 \\ - 0.99 \ p \\ - 2.11 \ s \end{array} $
	3232.61	+ 1.76 s 0 p - 1.75 s
	2770.04	+ 1.20 s 0 p - 1.20 s
	3267.60	+ 1.17 s 0 p - 1.19 s
	2598.16	+ 1.60 s 0 p - 1.60 s
	2528.60	+ 1.59 s 0 p - 1.59 s

 $\mathbf{i}$ 

In this table s denotes vibrations normal to the field, p vibrations parallel to the field. Of the lines of the Table only Sn 3801 and Sn 2851 belong to the same series. They are both blurred, in connection with this the agreement in magnetic splitting up is sufficient. Sb 3638 becomes a quadruplet. According to PURVIS it is identical

with that of Cu 3274 and Ag 3383 and so of Na 5896. It will have to appear from the further investigation of the magnetic field whether this numerical result has a deeper meaning.

In conclusion I will point out some objections, which might be

raised when the above series are studied. In some cases we find, namely, a value given under  $\lambda_w$  which occurs in two series. The corresponding values of  $\lambda_b$  are then somewhat different as a rule. It is now the question :

"Do the observed lines belong to two series, or have we to do with two lines close together, one of which is difficult to distinguish from the other ?"

Before answering this question I will first draw attention to this that this phenomenon is also met with in the spectra of other elements. Thus we find in the spectrum of aluminium 1)  $\lambda$  2204,73 classed as n = 8 in the 1st subordinate series, and as n = 7 in the 2nd subordinate series; in that of Zinc<sup>2</sup>)  $\lambda$  2430,74 as n = 8 in the 2nd component of the 1st subordinate series, and as n = 9 in the 1st component of the same series. In the spectrum of Calcium<sup>3</sup>) we find  $\lambda$  3101,87 as n = 8 in the 3rd component of the 2nd subordinate series, and as n = 9 in the 1st subordinate series. These few examples may suffice to show that the phenomenon that presents itself a few times in the series found by me, is met with elsewhere.

Let us now try to answer the question raised led by the examples which present themselves in our case.

Let us begin with the spectrum of Tin.

For  $\lambda_w$  2483.50 we find  $\lambda_b = 2412.53$  in VII and  $\lambda_b = 2482.49$  in VIII<sub>2</sub>. Examining the observation of this line we find given by KAYSER and RUNGE<sup>4</sup>): "2 umgekehrt", and by EXNER and HASCHEK<sup>6</sup>): "3 unscharf, umgekehrt". It is not impossible that here two different lines must be observed. Also what follows pleads in favour of this: In VII we find successively the intensities: 30, 10, 3, 3. That for x = 4 the intensity is not found smaller than 3 may find its explanation in this, that two lines of slighter intensity give this increased intensity.

For  $\lambda_w$  2408,27, which is given in I<sub>4</sub> with  $\lambda_b = 2408,71$ , in III<sub>2</sub> with  $\lambda_b = 2508.27$ , a similar explanation may hold. KAYSER and RUNGE find '): "3 umgekehrt", EXNER and HASCHEK '): "1 unscharf." The course of intensity in I is: 5.3.1.1. Probably  $\lambda_b = 2408.71$  agrees therefore with a very faint line beside  $\lambda$  2408,27, which belongs to III.

 $\lambda_w$  2199.46, which has been given in VIII, with  $\lambda_b = 2199.32$ , and in IX, with  $\lambda_b = 2199.42$ , we find in KAYSER and RUNGE<sup>6</sup>) with the indication: "1 umgekehrt", and in EXNER and HASCHEK<sup>6</sup>) in the

<sup>1</sup>) KAYSER, Handbuch der Spectroscopie. Vol. II, p. 547.

<sup>2</sup>) l. c. p. 542.

<sup>3</sup>) l. c. p. 536.

4) Ueber die Spektren der Elemente. VII. Abh. Berl. Akad. 1894.

<sup>5</sup>) l. c. Vol. II.

<sup>6</sup>) l. c. Vol. III.

sparkspectrum (the arc-spectrum of Tin they have observed no further than  $\lambda 2267$ ):  $\lambda 2199.41$  "1 unscharf" and  $\lambda 2199.68$  "1 unscharf". So the two lines very clearly appear here very closely side by side.

 $\lambda_w$  2091.7 occurs with  $\lambda_b$  2092.30 in II<sub>s</sub> and with  $\lambda_b$  2091.23 in V<sub>s</sub>. This line has not been observed by EXNER and HASCHEK.

In KAYSER and RUNGE<sup>1</sup>) we find "3 umgekehrt (?)". So they doubt whether or no they have to do with a reversal here. So the surmise is justified that we have to do here with two separate lines, which surmise is supported if the course of the intensity in II is examined according to the observations of KAYSER and RUNGE. Starting from x = 2 this is namely 5, 3, 1, 3, 3. The increased intensity 3 for x = 5 is again accounted for by the assumption of two lines close together. In the same way the increased intensity of the line 2063.8, which as x = 6 occurs in the same series, may be accounted for by our finding  $\lambda_b = 2064,12$  in IV<sub>4</sub>, which is given there also with  $\lambda_w = 2063.8$ . It is a line which has been given by KAYSER and RUNGE<sup>2</sup>) with a limit of errors 0.50, so which could be observed less accurately.

After this extensive discussion of the spectrum of Tin, a few indications will suffice for that of Antimony.

 $\lambda 2719.00$  we find in XIV, and XV<sub>1</sub>. The intensity in XIV is 3.3.1, so somewhat too high for x = 2. This line is found in KAYSER and RUNGE reversed, but not in EXNER and HASCHEK<sup>2</sup>). This is also the case for  $\lambda 2692.35$ , which occurs in X, and XVI<sub>1</sub>, and with  $\lambda 2652.70$  in XX, and XVII<sub>1</sub>.

 $\lambda 2614.74$  we find as XI, and XXH. It occurs in both observers as a single line. Noteworthy, however, is the difference in intensity. In KAYSER and RUNGE<sup>3</sup>) this line is one of the strongest lines (intensity 5, while 6 is the greatest intensity that occurs), whereas in EXNER and HASCHEK<sup>4</sup>) it is one of the weakest (intensity 1, highest intensity 30).  $\lambda 2098.47$  has not been observed by EXNER and HASCHEK. We find it given in XXI, and XXIII,. In connection with the  $\lambda_b$ which I found for XXI, namely 2097.76 I still want to remark that this value lies between that found by KAYSER and RUNGE, and that of HARTLEY and ADENEY, who give for it:  $\lambda 2096.4$ .

I should further like to make another remark. When the list on

- <sup>1</sup>) l. c. Vol. III.
- <sup>2</sup>) l. c.
- <sup>3</sup>) 1, c.
- 4) l. c.

p. 42 with the given magnetic separation is examined, the question naturally rises :

"Why do  $\lambda$  3032.90 (III<sub>1</sub>) and  $\lambda$  3175.12 (VIII<sub>1</sub>) occur in different series for Tin, though they exhibit the same splitting-up?"

The same question applies also for Antimony  $\lambda 2770.04$  (XII<sub>1</sub>) and  $\lambda 3267.60$  (XIII<sub>1</sub>), and also for Antimony  $\lambda 2598.16$  (XVIII<sub>1</sub>) and  $\lambda 2528.60$  (XXII<sub>1</sub>).

To answer this question I have traced every time two lines as  $10^{8} \lambda^{-1}$  and examined by means of my model without giving it a rotation, what would be about the frequencies of the other terms of the series that is perfectly determined without rotation by these two points. In this way I have arrived at the following results:

If we consider  $Sn \lambda 3175.12$  as x = 3 and  $Sn \lambda 3032.90$  as x = 4, we get  $10^{s} \lambda^{-1} = \pm 28400$  for x = 1, which does not agree with any observed line. (The nearest lines have the frequencies 27353.20 and 30023.63).

If we consider these lines as x = 3 and x = 5, we find  $10^{s} \lambda^{-1} = \pm 32450$  for x = 4, which does not agree with any line. x = 2 yields  $10^{s} \lambda^{-1} = \pm 29500$ , which might then possibly be 30023.63. But this is not very probable either, for the line which

+1.79s

+1.22 p

agrees with this ( $\lambda$  3330.75) exhibits a quadruplet <sup>1</sup>) 0 in the

## -1.22 p

-1.79 s

magnetic field, and so very certainly does not belong to this eventual series. In this way I have ascertained that the lines in question cannot be ranged together with others in one and the same series.

I have obtained corresponding results with the other lines which show the same splitting-up. This has rendered it very probable that the rule: "All the terms of one and the same series present the same resolution in a magnetic field", cannot be reversed, and so it is my opinion that the argument that I have not ranged lines which present the same splitting up in the same series, cannot be advanced as an objection to the classification of the Tin- and Antimonyspectrum given by me.

1) PURVIS. Proc. Cambridge Phil. Soc. 14. 1907, p 220.

## Mathematics. — "New researches upon the centra of the integrals which satisfy differential equations of the first order and the first degree." (Second Part). By Prof. W. KAPTEYN.

8. Assuming in the third place

$$a' + c' = i (a+c)$$
  
 $aa' - cc' = (b-ib') (a+c)$   
 $2b' = 3a + 5c$ 

or putting  $b = i\beta$ 

$$2a' = -i (3a - 2\beta + 3c)$$
  

$$2c' = i (5a - 2\beta + 5c)$$
  

$$2b' = 3a + 5c.$$

We have

$$q_{1} = a' - i (3a + 2b') = -\frac{i}{2} (15a - 2\beta + 13c)$$

$$q_{2} = 2a + 3b' - ib = \frac{1}{2} (13a + 2\beta + 15c)$$

$$r_{0} = -\frac{i}{6} (86a^{2} + 26a\beta + 179ac - 4\beta^{2} + 28\beta c + 99c^{2})$$

$$r_{1} = -\frac{1}{4} (45a^{2} - 36a\beta + 84ac + 4\beta^{2} - 32\beta c + 39c^{2})$$

$$r_{2} = -\frac{i}{2} (130a^{2} - 6a\beta + 265ac - 4\beta^{2} - 8\beta c + 137c^{2})$$

$$r_{3} = -\frac{1}{12} (421a^{2} + 116a\beta + 972ac - 12\beta^{2} + 120\beta c + 567c^{2})$$

and for the coefficients of  $P_4$ 

$$s_{1} = (5a+2b') r_{0} + a' r_{1}$$

$$2s_{2} - 4s_{0} = (8b+2c') r_{0} + (4a+4b') r_{1} + 2a' r_{2}$$

$$3s_{3} - 3s_{1} = 3cr_{0} + (6b+3c') r_{1} + (3a+6b') r_{2} + 3a' r_{3}$$

$$4s_{4} - 2s_{2} = 2cr_{1} + (4b+4c') r_{2} + (2a+8b') r_{3}$$

$$-s_{3} = cr_{2} + (2b+5c') r_{3}.$$

To determine the next condition we introduce the two following polynomia

$$P_{s} = t_{0}x_{s} + t_{1}x^{4}y + t_{2}x^{3}y^{2} + t_{3}x^{2}y^{3} + t_{4}xy^{4} + t_{5}y^{5}$$

$$P_{s} = u_{0}x^{6} + u_{1}x^{5}y + u_{2}x^{4}y^{2} + u_{3}x^{3}y^{3} + u_{4}x^{2}y^{4} + u_{5}xy^{5} + u_{6}y^{6}.$$
The coefficients of the first are determined by the relations