

INTERPRETATION OF ZEEMAN PATTERNS OF Tb II - LINES

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ABSTRACT

Analysis of Zeeman patterns and wavenumbers in the long wave region of the spectrum of singly ionized terbium leads to the identification of the principal septet levels of the configuration $4f^9 5d$. Notwithstanding the perturbations by hyperfine structure, g -factors could be established with a precision of $\leq 1\%$. Although the spin-orbit interaction is of the same order of magnitude as the electrostatic effects, a Russell-Saunders description appears to be adequate. Especially 7H is a remarkably regular term, both with respect to level positions and g -values. There is no direct evidence, from the Zeeman effect, for the correctness of the Tb II system difference, but this is confirmed by combinations of the new $4f^9 5d$ - levels.

RESUMEN

El análisis de números de ondas y patrones Zeeman en la región de longitudes de ondas largas del espectro del terbio monoionizado conduce a la identificación de los niveles del septete principal de la configuración $4f^9 5d$. Teniendo en cuenta las perturbaciones de la estructura hiperfina han podido establecerse factores g con una precisión $\leq 1\%$. Aunque la interacción spin-orbital es del mismo orden de magnitud que los efectos electrostáticos parece ser adecuada una descripción Russell-Saunders. Especialmente el 7H es un término señaladamente regular tanto respecto de las posiciones de los niveles como de los valores g . Del efecto Zeeman no se deduce una evidencia directa de la corrección del sistema de diferencias del Tb II, pero éste está confirmado por las combinaciones de los nuevos niveles $4f^9 5d$.

1. INTRODUCTION

The first significant regularities in the Tb II spectrum were discovered by Miss Meinders some years ago, whereupon the basic structure was revealed (1,2). As she emphasized at the first EGAS conference (Orsay 1969), the Zeeman effect was of no use in identifying levels because of the wide hyperfine structure of the lines involved. Instead, the analysis was based on measurements of hyperfine structure (HFS) broadenings and resolved HFS patterns. While they gave conclusive evidence of the fundamental structure, only few levels beyond 10^4 Ky^* above the ground state could be established in the low configurations, and no levels with $J \leq 5$ were found at all.

(*) $1 \text{ Ky} = 1 \text{ cm}^{-1}$; the original symbol for the kayser was identical with the symbol internationally adopted for the kelvin in 1970.

On the other hand there are also numerous relatively sharp Tb II lines, and many of them show resolved or partly resolved Zeeman patterns corresponding to low J -values. So it is clear that an extension of the analysis is needed. The following is a report on results obtained in the system based on the parent term Tb III $4f^9 {}^6H$.

2. EXPERIMENTAL DATA

The Zeeman spectrograms available had been obtained by the author, at the Argonne National Laboratory, in a field of 2.4 T (3). They have been measured and evaluated systematically between 11230 and 5090 Å, and, as far as resolved patterns are concerned, also between 5090 and 3350 Å. Because the light source used, a TbI_3 -filled electrodeless discharge tube operated by means of a 2460 MHz magnetron oscillator, is known to emit light from the neutral and singly ionized atoms

only, a resolved Zeeman pattern uniquely determines the ionization stage. Comparison of intensities then reveals a magnetic enhancement of ion lines (4) that can be used to discriminate between Tb I and Tb II when the patterns are not resolved. This can be checked and extended by comparing intensities under different conditions of excitation without magnetic field, as was done by Dr. Meinders (2,5). Low power excitation favors the ionized state and the plates so obtained showed many previously unknown lines. It was found furthermore that the old wavelength spectrograms which had generated the present description of the Tb spectra, in addition to being superior in sharpness with respect to the field-free exposures on the Zeeman plates, correspond to conditions still less favorable to emission of Tb II lines. They had been obtained by means of a bigger size lamp, provided with a carrier gas (Ne). Nonetheless, most of the strong Tb II lines are faintly present and there are plenty of sharp Tb I lines in common with the new spectrograms so that calibration did not give rise to any problem.

Although the segregation into Tb II and Tb I is reliable for the stronger lines, there are cases in which neither the intensity behavior in magnetic fields nor that under different conditions of excitation in a field-free source is conclusive. One obvious reason is the interference of Tb I and Tb II lines in this exceedingly dense spectrum; in some cases the Zeeman pattern indeed reveals the existence of such nearly coincident lines. But

also there are gradual differences in the magnetic enhancement. Even without this variation the effect is difficult to evaluate because of the re-distribution of the intensity over the Zeeman components and the hyperfine structure components which, due to the endless variety in the absolute and relative spacings, gives rise to photographic densities which have no simple relationship to the total intensity. However, some lines stand out, as they are absent in field-free spectrograms and quite strong in the field. The lines in this category have not yet been classified. On the other hand, the analysis includes a number of faint lines whose Tb II origin cannot be proven from anything else than the fact that the wavenumbers match calculated transitions in the Tb II level scheme. There is no correlation between our assignments and those given in the NBS compilation of 1961 in the wavelength region of interest, i.e. above 5500 Å (6). The Zeeman data will be discussed further in section 5, in connection with some representative cases.

3. EXTENSION OF THE ANALYSIS OF TB II

In table I the newly detected levels belonging to the configuration $4f^9 5d$ have been collected. The level value in Ky with respect to the ground state $4f^9 ({}^6H) 6s^7H_8$ is followed by the J-value, the experimental g-factor, the interpretation, and the theoretical g-value on the basis of Russell-Saunders coupling.

Table I — Levels in the $4f^9 5d$ configuration of Tb II

Value (Ky)	J	g_{exp}			
11261.565*	8	1.36 ₈	$4f^9 ({}^6H) 5d$	7_H	1.375
12200.400*	7	1.33 ₉		7_H	1.330
13518.250	9	1.32 ₄		7_I	1.333
13605.220*	6	1.33 ₀		7_H	1.286
15023.800	6	1.44 ₂			7 _F 1.500
15212.590	5	1.22 ₁		7_H	1.200
15289.155	8	1.29 ₀		7_I	1.292
15844.440	7	1.37			7 _G 1.429
16384.330	10	1.30 ₄		7 _K	1.300
16475.050	4	1.05 ₈		7_H	1.050
16534.390	5	1.38			7 _G 1.367
17061.530	5	1.44 ₅			7 _F 1.500
17125.820	7	1.28 ₂		7_I	1.232
17475.200	3	0.78 ₀		7_H	0.750
17811.610	6	1.23 ₀		7_I	1.143

The level ${}^7K_{10}$ is to be regarded as provisional because it can have only one combination. The line chosen has the correct Zeeman splitting, but this is an unresolved pseudotriplet. All other levels are based on sufficient experimentally established Tb II data to be fully reliable. Not inserted in the table is a tentative level at 14397.595 Ky with $J = 6$, $g_{\text{exp}} = 1.385$ which could be the 7G_6 . The number of combinations is too low and there is only one Zeeman effect observation available. The level values marked with an asterisk have been reported previously (2), but without interpretation.

The level at 13518 Ky has been detected independently by Wyart et al (7), using the table in the NBS compilation (6). These authors give the value 13518.35 and propose the designation $f^9 ({}^6H_{15/2} d_{3/2})_9$. However, if one calculates the theoretical g -factor for this identification, one finds 1.244, which is at variance with the experimental value. On the contrary, the experimental value is very close to the Landé value and the relatively good overall agreement of g -factors in table I leads to the conclusion that there is no need for abolishing the Russell-Saunders notation in the (sub) configuration concerned.

The largest discrepancies occur for the $J = 6$ levels and the partial g -sum of the well-established levels has an excess of 0.073. This would be reduced to 0.053 by the tentative 7G_6 level mentioned above. For $J = 7$ the g -sum is correct within experimental error and for $J = 5$ there is a deficit of 0.021. The smallness of these departures indicates that the septet system is little perturbed by exterior states.

In fig. 1 the levels are arranged according to the value of J and the energies. It is seen that 7I and 7H , and perhaps 7F also, are well-behaved terms, despite the fact that they are overlapping largely. This is not unusual in rare earth spectra; especially the total value of the electronic spin, S , remains a fairly good quantum number, so that multiplicity is a significant property (8). The position of 7G_7 is quite irregular. The departure of its g -factor is nearly compensated by that of 7I_7 , but this partial sharing of identities cannot explain the strange position in a simple way.

As was expected, some of the even levels, found by means of their combinations with the $4f^9 ({}^6H) 7s$ group (1,2), could not be confirmed through the new odd levels. They will probably have to be dismissed, but the final proof will not be available before the Zeeman measurements will be concluded. Values which must be dropped already now, because of paucity of combinations, coincidences with Tb I transitions, for conflicting Zeeman data, are the following: 30068.295 ($J=6$), 30364.740 (7), 33767.290 (7), 35080.265 (8),

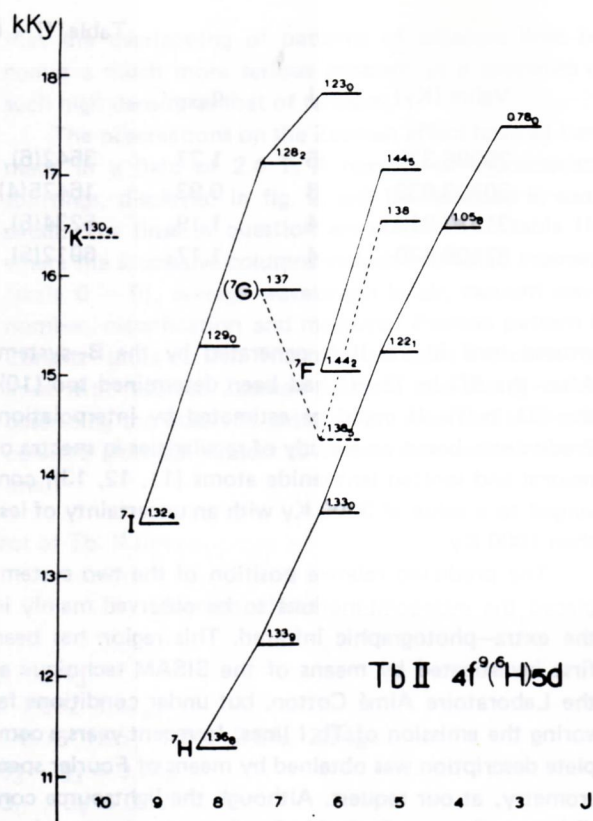


Fig. 1.—Level system of Tb II $4f^9 5d$, established with respect to $4f^9 6s {}^7H_8 = 0.000$.

35227.650 (5), 36602.005 (8) and 36861.990 (8).

On the other hand, the new low J levels found in $4f^9 ({}^6H) 5d$ permitted to establish some new even levels of low J , as recorded in table II. The search has not been exhaustive and only safe levels have been retained for the table. In the last column those odd levels are quoted with which a combination is found in the list of lines attributed to Tb II on experimental grounds. In only one case (marked with a $\sim$) the discrepancy between the experimental wavenumber and the one calculated from the level values is larger than 100 mKy. No quantum interpretations of the even levels are given; the most likely configuration is $4f^9 ({}^6H) 6p$ in which the p -electron is supposed to couple to the f^9 -core according to the J_{ij} -scheme.

4. SYSTEM DIFFERENCE IN TB II

The levels treated in section 3 belong to the system originally denoted B, and the A-system is based on the core $4f^8$. With the detection of the system difference (SD), i.e. the interval between the lowest levels in the two systems, in Tb I (9), it became obvious that the

Table II — New even levels in Tb II

Value (Ky)	J	g_{exp}	Combinations
29995.370	5	1.27	3542(6), 5234(5), <u>15212(5)</u> , 16475(4), $\sim$ 16534(5), <u>17811(6)</u>
30703.630	3	0.93 ₄	16475(4), <u>17475(3)</u>
31530.910	4	1.19 ₀	5234(5), 6912(5), <u>16475(4)</u> , 16534(5), <u>17475(3)</u>
37109.470	4	1.17 ₃	6912(5), 15212(5), 16475(4), <u>16534(5)</u> , <u>17061(5)</u> , 17475(3)

ground level in Tb II is generated by the B-system. After the SD in Tb III had been determined too (10), the SD in Tb II could be estimated by interpolation. Predictions, based on a study of regularities in spectra of neutral and ionized lanthanide atoms (11, 12, 13), converged to a value of 3300 Ky with an uncertainty of less than 1000 Ky.

The predicted relative position of the two systems placed the intercombinations to be observed mainly in the extra-photographic infrared. This region has been first investigated by means of the SISAM technique at the Laboratoire Aimé Cotton, but under conditions favoring the emission of Tb I lines. In recent years a complete description was obtained by means of Fourier spectrometry, at our request. Although the lightsource conditions again were favorable for the neutral state, six of the very strongest Tb II lines could be observed and identified as such on account of their wide hyperfine structure patterns. These lines could be explained as intercombinations if a SD of 3235.180 Ky was adopted (14). Because not only the barycenters of the lines were in accordance with these classifications, but also the hyperfine structure widths and signs were compatible with the known level structures (1,2), it was judged safe to merge the previously independent level systems.

Nonetheless it seemed of interest to investigate whether the connection found explains more observed lines. Between the two low groups of levels with opposite parity one finds 191 possible combinations falling in the range from 3040.495 to 15555.340 Ky. Including the 6 original ones 45 wavenumbers are indeed found in the list, 29 of which being connected with the new levels of table I or 4 new low levels established in the other system (not dealt with here). The noise level was found to be about 18 by trying arbitrary values for the SD around 3235 Ky. So some 20 lines may be actually due to intercombinations. It should be added that the lines involved are weak, that for none of them a Zeeman splitting is available and that they have not been attributed to an ionization stage. In the extreme infrared there is no such discrimination available and below 9500 Å it is very imperfect, certainly with regard to the weak lines. It is

obvious that the SD could not have been detected without the high resolution observations in the infrared. On the other hand it is clear that the statistics made afterwards lend support to the value established.

5. TB II LINE PATTERNS IN A MAGNETIC FIELD

The Zeeman spectrograms show a tremendous variety of hyperfine structure perturbed Zeeman patterns in Tb II, the analysis of which is not always unambiguously possible when the classification is not known. Once a line is classified and the J-values are fixed, consistent solutions for the g-values can be determined. In addition to the HFS perturbation the patterns are mostly also distorted by overlapping of other Tb lines, Tb I as well as Tb II. Asymmetries due to incipient Paschen-Back effects cannot be ruled out, but as a matter of fact they are quite rare because they require proximity of states rather than lines, and in addition the states must obey selective rules.

As is well-known the hyperfine interaction, if the field intensity is high enough, produces a splitting of each Zeeman component into $2I + 1$ equidistant sub-components, i.e. 4 in Tb. These arise from the HFS in the magnetic sublevels of the two combining states, which is proportional to M_J (Back-Goudsmit effect). Hence it is zero in the $O - O \pi$ -component, and widest in the outermost π -components. How this can give rise to an apparently sharp π -component in the centre, when $\Delta J = \pm 1$ and the g-factors differ little, has been discussed elsewhere (15). When $\Delta J = 0$, the picture is dominated by the wide HFS of the outermost π -components which for small Δg may become entangled. The width of this HFS is determined by the difference in the HFS interval constants of the two levels, ΔA . It may show up as a diffuse broadening or it may produce 4 sharp, equidistant sub-components, but in practically no case is the type of the π -pattern masked if it would not already be indiscernible without HFS. The strongest σ -components, in this case, are in the centres of the σ -wings; so they correspond to small values of M_J and are relatively

sharp. The increasing broadening of the weaker components may cause them to disappear gradually into the background so that no reliable check on J can be obtained, but again the type is not impaired. However, if $\Delta J = \pm 1$ the interplay between HFS and Zeeman splittings may give rise to inversion of intensity types in the σ -patterns (15) while the position of the strongest components may become obscure, especially when their HFS splittings are comparable with the Zeeman intervals. The impressive variety of patterns is further complicated by the fact that for high values of A in a level the condition for the Back-Goudsmit effect is not fulfilled in a given magnetic field so that the simple situation of 4 equidistant substates does no longer apply. Increasing the field, apart from technical difficulties, has the disadvantage

that the overlapping of patterns of adjacent lines becomes a much more serious problem in a spectrum of such high density as that of terbium.

The observations on the Zeeman effect have all been made in a field of 2.4 T. A number of characteristic splittings, displayed in fig. 2, will be discussed in some detail. The lines in question are collected in table III, where the successive columns include estimated intensity (scale 0 – 9), average wavelength in air, vacuum wavelength, classification and measured Zeeman pattern in Lorentz-units (L.U.). The table contains 4 unclassified lines with resolved Zeeman patterns and the g_J -values describing the observed patterns are recorded in the last column, although subject to certain reservations (see below).

Table III – Zeeman effect of Tb II lines

I	λ (Å)	σ (Ky)	Transition	Zeeman effect
6	5262.109	18998.50	22008(7) – 3010(7)	(... 0.11₈) 1.34 ₃
3	5322.117	18784.29		(0 0.504 1.002 1.47 ₈) ~0.75 1.25 ₇ 1.74 ₈ 2.24 ₅ 2.74 ₅ $g_4 = 1.26_3$; $g_3 = 0.76_9$
4	5470.252	18275.62	30476(7) – 12200(7)	(0) 1.33 ₀ ; $E_\pi = 0.17$
5	5470.403	18275.11		(0 0.43 ₈ * 0.90 ₂) -0.44₅ 0 0.44 ₅ 0.93 ₅ * 1.40 ₅ $g_3 = 0.45_0$; $g_2 = 0.90_0$
6	5476.956	18253.25		(~0.32* 0.631 0.952) 0.900 1.209 1.533 1.846 2.159 2.48 ₂ * $g_3 = 1.848$; $g_3 = 1.532$
5	5864.457	17047.15		(0.52 ₈ 1.02 ₁ 1.576) 0.25 ₀ 0.747 1.263 1.790 $g_3 = 1.26_5$; $g_3 = 0.74_5$
9	5967.305	16753.34	28014(8) – 11261(8)	(... 0.51₅) 1.32 ₈
3	5986.293	16700.20	19710(8) – 3010(7)	(0) 1.36
7	6077.810	16448.74	28649(7) – 12200(7)	(... 0.57₅) 1.27 ₆
5	6171.863	16198.08	29803(6) – 13605(6)	(0) 1.337
8	6331.630	15789.36	31078(8) – 15289(8)	(0) 1.278
6	6405.912	15606.27	30895(7) – 15289(8)	(0) 1.22 ₀
7	6785.114	14734.08	28339(6) – 13605(6)	(0.18 ₂) 1.34 ₇
4	7112.286	14055.71	31530(4) – 17475(3)	(0 0.418 0.823 1.264) ~ 0.75* ~ 1.19* 1.602 2.019 2.423 $g_4 = 1.19_5$; $g_3 = 0.78_5$
6	7311.335	13673.63	30148(5) – 16475(4)	(0 0.203 0.407 0.608 0.790) 1.29 1.46 ₂ 1.662 1.866 2.070 $g_5 = 1.258$; $g_4 = 1.055$
8	7348.605	13604.28	25804(7) – 12200(7)	(0.11 ₆) 1.34 ₉

Notes to table III:

1. π -components between brackets; strongest components in bold type
2. Depressed digit in Zeeman shifts not reliable
3. Depressed digit in g -values not representative for absolute accuracy but significant for g -difference
4. E = edge of unresolved structure
5. An asterisk marks a component that has been measured only on one side of the zero line position.

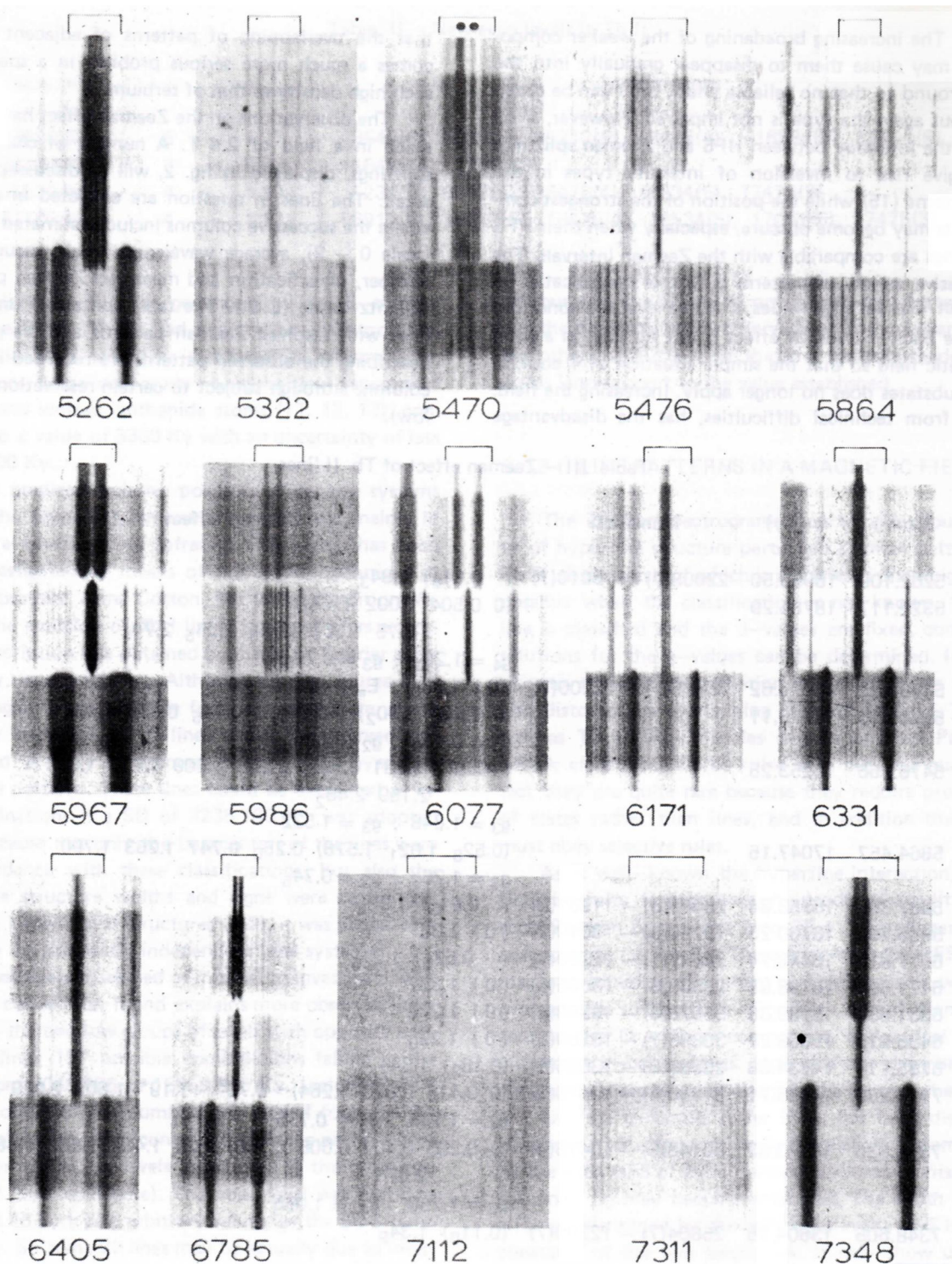


Fig. 2.— Spectrograms of 16 Tb II lines in a magnetic field of 2.4 T, obtained by means of 9m grating (ANL). Central strip shows zero field line, upper strips show π -polarized, lower strips σ -polarized pattern, with two different exposure times. Wavelength increasing from left to right in each picture, but on different scales: Pattern at $\lambda = 6785$ is from second order; pictures of $\lambda\lambda$ 5262 – 5476 are from fourth order; all others from third order. Brackets above each picture indicate normal σ -splitting, i.e. 2 Lorentz-units. Details about patterns in section 5.

5262.109 : A typical example of a HFS dominated π -pattern. Because the Zeeman splitting is small the 4 subcomponents of the strongest π -components overlap to such an extent that one sees 5 components in total, of different degrees of diffuseness. The distance between the two groups of 4 subcomponents can be regarded as the interval between the strongest π -components, while the weaker ones are responsible for the diffuseness. The σ -components have a relatively sharp appearance, due to the fact that the strong central components in each wing have narrow HFS and add up their intensities. The weaker components contribute a hazy background and since they are symmetrically arranged around the strong ones, they cannot influence the centre of gravity. Knowing the J-values the g-factors can be derived with a precision of 1% or better. They are 1.35₇; 1.34₀.

5322.117 : Almost free of HFS perturbation, but σ -pattern slightly affected by adjacent lines. It is not excluded that weakest components are lost in the background, in both polarizations. If the J's are correct, the g-factors are reliable to within 2%. The obvious classification, —on 17475(3) with $g = 0.78_0$ —, is not corroborated by other combinations.

5470.252 : A just resolved HFS in the field-free spectrogram. The reduction to a simple (pseudo) triplet in the field indicates that the g-factors cannot differ by more than about 0.02; the k-broadening is to be regarded as due to HFS mostly. Because the σ -components are sharper the average value of g should be reliable to within 1%. The extreme values of the g-factors are 1.34₀ and 1.32₀.

5470.403 : Without field, a resolved HFS is visible of a type corresponding to low J-values. The Zeeman effect is badly perturbed. The O—O component stands out, but the other π -components are diffuse and asymmetric as a result of HFS; the σ -wings get entangled because there are negative components involved, while strong interference from adjacent lines is present. The g-difference is estimated to be correct to 1%; the g-values, $g_3 = 0.45_0$ and $g_2 = 0.90_0$ should be accurate to 5% provided the interpretation is correct, otherwise they are phony.

5476.956 : A sharp line whose Zeeman splitting can be evaluated as if there were no HFS splitting at all; slightly perturbed only by adjacent lines, causing intensity asymmetries. Consequently the g-factors given can be trusted to within 1%.

5864.457 : The π -components are progressively broadened away from the centre due to a narrow HFS. Weakest σ -components lost; the innermost ones are negative and practically coincident with the first positive components. The g-values may be in error by as much

as 5%, but the g-difference is quite precise.

5967.305 : A relatively sharp line, broadened by overexposure only, and measured on a lower density spectrogram. Knowing the J-values one finds 1.36₀ and 1.29₆ for the g's, probably accurate to 2%; the average may be better still, since the σ -wings are symmetrical.

5986.293 : A wide, resolved HFS pattern in zero field. In the π -polarized pattern this HFS collapses into one reasonably sharp central component, proving that the g-values are nearly equal; the weak π -components are responsible for the haziness around the strong component. On the contrary a resolved HFS is visible in the σ -pattern, but the irregular intensity distribution prevents accurate measurement. In particular it is uncertain whether the measured splitting corresponds to the barycentre of the Zeeman splitting or to the strongest σ -component. Therefore an error of up to 8% must be admitted.

6077.810 : A relatively sharp line where the π -splitting does not cause any problem. However the σ -pattern is unsymmetrical due to an exterior perturbation on the component shifted to the lower wavelength side. On account of this the possible error in the g-factors of this 7—7 transition may be 4%. One finds 1.31₇ and 1.23₅.

6171.863 : A just resolved HFS causing a slight asymmetry in the σ -components. Because no splitting is seen in the π -image it is assumed that $\Delta g \leq 0.02$ so that the extreme values of the g-factors of this 6—6 transition are 1.34₇ and 1.32₇.

6331.630 : Intrinsically narrower than $\lambda = 6171$, but broadened by overexposure. The Zeeman splitting is quite similar and leads, for $J_1 = J_2 = 89$ to extreme values of 1.288 and 1.268 for the g's; the average should be better than 1%.

6405.912 : An example of a $\Delta J = \pm 1$ transition with a just resolved HFS producing a pseudotriplet in the field. From the π -picture it can be concluded that the g-values are quite close. The σ -components are only slightly broader than the field-free HFS pattern, but the intensity distribution gives no information on the relative value of the g-factors. From the measurement and the known g_8 (1.29₀) one obtains $g_7 = 1.31_0$ to account for the barycentre of the σ -wings. However, the σ -pattern should be of the shade-out type whereas it has the inverse appearance as a result of the HFS.

6785.114 : Negligible HFS, but unfortunately the longer wave σ -component is somewhat perturbed by the adjacent line at 6784.872 Å, a very sharp triplet in the field (at least the σ -components are very sharp), probably also to be attributed to Tb II. Due to this perturbation there may be a 2% error in the g-values,

which for $J_1=J_2=6$ turn out to be 1.36₆ and 1.32₈.

7112.286 and 7311.335 : Two specimen of relatively sharp, classified lines with resolved Zeeman patterns which do not give problems and allow g-factors to be determined with a precision better than 1% (see table).

7348.605 : Same character as $\lambda = 6785$. Despite overexposure g-factors will be reliable to within 1%. Given $J_1=J_2=7$ they are 1.36₀ and 1.33₉.

The preponderance, in table III, of $\Delta J = 0$ transitions is not accidental. More useful information on the Zeeman effect can be drawn from such lines than from $\Delta J = \pm 1$ transitions generally, because HFS is less perturbing in the former ones. This can be understood from the fact that in configurations with several 4f-electrons the HFS of levels is mainly due to the parent sub-configurations, in this case 4f⁹(⁶H), which is common to both combining levels (16). If the A-factors were equal we should expect zero HFS for $\Delta J = 0$, while for $\Delta J = \pm 1$ the difference $A_J(F_1 - F_2)$ should occur, which is A_J (This rough picture applies in the case of the strong

HFS components; for high J-values the satellites are indeed negligible). Now the outer electron(s) can only impose relatively small fluctuations on the A_J -factors so that for $\Delta J = 0$ the HF splittings generally remain narrow. As a result the Zeeman patterns are "cleaner" for this type of transitions. For $\Delta J = \pm 1$ the patterns are more likely to disappear into the background due to HFS, and, if they do not, they are more difficult to interpret and evaluate.

CONCLUDING REMARKS.

The progress in the Tb II analysis discussed in the sections 3 and 4 is incorporated in two compilations, appearing shortly (17, 18), which will give account of the complete level systems known presently.

This paper is dedicated to the memory of the late Dr. Rafael Velasco, who himself has been engaged in the interpretation of distorted Zeeman patterns and published classic papers on the subject.

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