

TERM VALUES IN THE SPECTRUM OF CHROMIUM II*

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ABSTRACT. Term values for the configurations $3d^5$, $3d^4.4s$, $3d^3.4s^2$ in CrII are calculated and compared with the experimental data due to Kiess. The values of the unidentified terms are predicted from these theoretical calculations.

INTRODUCTION

An extensive experimental analysis of the spectrum of CrII was recently published by Kiess (1951). The even terms arising out of the configurations $3d^5$, $3d^4.4s$ and $3d^3.4s^2$ were worked in fairly good detail and their values were given. A theoretical calculation of these term values appeared desirable for (a) checking the analysis and (a) predicting the terms yet to be established. The results of these calculations are presented and discussed in the following pages.

The theory of the calculations was first given by Slater (1929) and developed later by Van Vleck (1934). The working details were given by Rao (1948) in his paper on "Term values in Complex Spectra (Columbium I and II)". Tables I, II and III embody the results. The observed values of the terms are the statistical means of the multiplet levels of each term. The formulae used in the calculations are given in the last column. For the evaluation of the parameters F_0 , F_2 , F_4 and G_2 the method of normal equations was employed (Rao, 1948). Low lying terms are used for this purpose (marked in the table with asterisks) as their assignment is generally more certain.

In Table I the term values of the lowest configuration $3d^5$ of CrII are given. In the calculated values, the a^6S term is reduced to zero and correspondingly all the other terms shifted to that scale. The percentage of discrepancy, between observed and calculated values is given in column 4. There is in general good agreement. Considerable disagreement is found between the values for a^4P . Of all the quartet terms, this should be the highest according to Hund's rule (lowest 'L' value). However, the b^4D and b^4F terms are larger than a^4P . This involves a certain amount of perturbation in the term scheme which may possibly be due to slight deviation from rigorous R-S coupling assumed in theoretical considerations. Terms a^3D_+ and a^2P_+ are not identified in experimental work as these are considerably high. The lines arising out of these levels and an excited state generally lie in the far infrared and so was not obtained. These values could,

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in general, be only predicted from theory and fitted into the term scheme. Their values are given in column (3). Table II gives the results of calculation for the configuration $3d^4.4s$ of CrII which is the next higher configuration to the above one namely $3d^3$. In this, calculations are made in two ways. The values obtained by straight calculations with formulae (column 1) are given in column 5. In column 4 the data are obtained from calculations through ion data. The configuration $3d^4$ of CrIII is the ionic configuration of $3d^4.4s$ of CrII. Van Vleck (1934) gave the necessary theory for such a calculation and the working details may be found in Rao's paper (1948). This calculation helps us to verify CrII spectra as against Cr III spectrum. A good agreement between the two data indicates the consistency of assignments of both the spectra of the configurations dealt with. However, the calculation is limited by the number of terms known in $3d^4$ configuration in CrIII. The first column gives the base terms of $3d^4$ of CrIII on which those of CrII are built up by the addition of a $4s$ electron. Columns 6 and 7 give the percentage of discrepancy between the observed values on one hand and the calculated values from ion data (column 6) and from formulae (column 7) given in the last column. It is seen that where calculation could be made for ion data, the discrepancy is very small, confirming the assignments of terms in the configurations of both CrII and CrIII. In the calculated data from the formulae, it would be found that the percentage of discrepancy is more than in case of the $3d^3$ configuration, though in itself it is not much. However, this may be attributed to the fourth parameter G_2 entering the formulae. The deviation from R-S coupling may be considerable in the case of $3d^4.4s$ electrons.

Table III gives term values for the $3d^3.4s^2$ configuration of CrII. In this configuration the unit $3d^3$ is shielded by the complete subshell $4s^2$ and so the deviation from the R-S coupling may be considered to be much less than in the earlier configurations. The configuration gives rise to the same terms as $3d^3$ and values are given in column (3). The percentage of discrepancy is small. The terms, 2F , 2H , $^2D_+$ and $^2D_-$ are predicted in the spectrum. In view of the general good agreement it may be reasonably expected that these predicted values can lie within 4 percent of the values given. The formulae given in the last column of this table are obtained by neglecting the G 's in the formulae for the d^3s configuration by Bowman (1941).

TABLE I
Term values of chromium II
Configuration $3d^5$

Term symbol	Observed value	Calculated value (author)	Percentage of discrepancy	Formula (Laporte 1942)
a^6S^*	0.0	0.0	0.0	$10F_0 - 35F_2 - 315F_4$
a^4G^*	20516.0	20498.5	-0.1	$10F_0 - 25F_2 - 190F_4$
b^4F	32848.2	31666.7	-0.7	$10F_0 - 13F_2 - 180F_4$
b^4D^*	25039.9	25721.2	+2.7	$10F_0 - 18F_2 - 225F_4$
a^4P^*	21823.7	23475.2	+7.6	$10F_0 - 28F_2 - 105F_4$
a^3I^*	30147.2	29067.1	-3.5	$10F_0 - 24F_2 - 50F_4$
b^3H	35664.0	35774.3	+0.3	$10F_0 - 22F_2 - 30F_4$
a^3G	36197.9	37274.2	+3.1	$10F_0 - 13F_2 - 115F_4$
d^3G	52311.2	34426.8	+4.0	$10F_0 + 3F_2 - 155F_4$
a^3F	32459.2	33536.0	-3.3	$10F_0 - 25F_2 - 15F_4$
c^3F	39821.1	40258.6	+1.1	$10F_0 - 9F_2 - 165F_4$
d^3D	47361.4	49204.5	+3.9	$10F_0 - 4F_2 - 120F_4$
a^2D_-	31420.1	33018.5	+5.1	$10F_0 - 3F_2 - 90F_4$
a^2D_+		72096.9		$+ (513F_2^2 + 4500F_2F_4 + 2700F_4^2)^{1/2}$
a^2P		67110.5		$10F_0 + 20F_2 - 210F_4$
a^2S	44307.0	44735.2	+1.4	$10F_0 - 3F_2 - 195F_4$

$10F_0 = 62378.0 \text{ cm}^{-1}$,

$F_2 = 1118.6 \text{ cm}^{-1}$,

$F_4 = 74.5 \text{ cm}^{-1}$.

Note:—In this and the following tables the suffixes + and - indicate higher and lower of two similar terms and the corresponding formulae must be taken with the respective sign.

The terms Marked with asterisks are those taken for the calculation of the constants.

TABLE II
Configuration $3d^4.4s$.

Base term	Term symbol	Observed value	Calculated value (in data)	Calculated value (by formula)	Percentage discrepancy		Formula (Rao, 1948)
					(Ion data)	(Formula)	
3D	$^3D^*$	12295.0	12296.0	11476.7	0.0	-6.7	$6F_0 - 21F_2 - 189F_4 - 3G_2$
	$^3D^*$	19848.9	19850.8	20659.2	0.0	+4.1	$6F_0 - 21F_2 - 189F_4 + 2G_2$
3H	$^3H^*$	30286.3	3019.3	29732.0	+1.9	-1.8	$6F_0 - 17F_2 - 69F_4 - 2G_2$
	$^3H^*$	34731.2	35382.5	35261.5	+1.9	+1.5	$6F_0 - 17F_2 - 69F_4 + G_2$
3G	$^3G^*$	33592.2	34305.4	33920.5	+2.1	+1.0	$6F_0 - 12F_2 - 94F_4 + G_2$
	3G	39763.0	38830.5	39430.0	-2.3	-8.3	$6F_0 - 12F_2 - 94F_4 - 2G_2$
$^3F_+$	$^3F_+$			57131.2	+2.6	+3.4	$6F_0 - 5F_2 - 76.5F_4 - 2G_2$
$^3F_-$	$^3F_-$	31166.3	31961.3	32219.6			$\pm \frac{1}{2}(612F_2 + 20025F_4 - 4860F_4F_4)^{1/2}$
	$^3F_-$			52630.7			$6F_0 - 5F_2 - 76.5F_4 + G_2$
$^3F_-$	$^3F_-$	31166.3	31961.3	32219.6	+2.5	+6.0	$\pm \frac{1}{2}(612F_2 + 20025F_4 - 4860F_4F_4)^{1/2}$
	$^3F_-$	38309.1		39755.4		+3.8	$6F_0 - 5F_2 - 129F_4 - 2G_2$
3D	3D	42031.3		45265.9		+5.4	$6F_0 - 5F_2 - 129F_4 + G_2$
	3D			57593.6			$6F_0 - 5F_2 - 76.5F_4 - 2G_2$
$^3P_+$	$^3P_+$	39577.5	31054.3	31777.2	+1.5	+3.9	$\pm \frac{1}{2}(912F_2 + 38025F_4 - 9960F_4F_4)^{1/2}$

TABLE II (contd.)

Base term	Term symbol	Observed value	Calculated value (ion data)	Calculated value (by formula)	Percentage discrepancy		Formula (Rao, 1948)
					(Ion data)	(Formula)	
$^3P_+$	$^3P_+$			63073.1			$\left\{ \begin{aligned} &6F_0 - 3F_2 - 76.5F_4 + G_2 \\ &\pm 1/2(912F_2^2 + 38025F_4^2 - 9960F_2F_4)^{1/2} \end{aligned} \right.$
a^3P_-	a^3P_-	35181.9	35587.5	37585.7	+1.2	+6.0	
a^1I	b^3I	40214.1		39807.9		-1.0	$6F_0 - 15F_2 - 9F_4 - G_2$
$^1G_+$	$^3G_+$			66757.3		+2.1	$\left\{ \begin{aligned} &6F_0 - 5F_2 - 6.5F_4 - G_2 \\ &\pm 1/2(708F_2^2 + 30825F_4^2 - 6420F_2F_4)^{1/2} \end{aligned} \right.$
a^1G_-	b^3G_-	38539.5		39360.5		-2.8	
a^1F	d^3F	50675.8		49211.5			$6F_0 - 84F_4 - G_2$
$^1D_+$	$^3D_+$			82348.6			$\left\{ \begin{aligned} &6F_0 - 9F_2 - 76.5F_4 - G_2 \\ &\pm 1/2(1206F_2^2 + 30825F_4^2 - 10440F_2F_4)^{1/2} \end{aligned} \right.$
$^1D_-$	c^3D_-	45707.7		47002.6		+2.8	
$^1S_+$	$^3S_+$			104918.0			$\left\{ \begin{aligned} &6F_0 + 10F_2 + 6F_4 - G_2 \\ &\pm 1/2(30885F_2^2 + 133200F_4^2 - 20640F_2F_4)^{1/2} \end{aligned} \right.$
a^1S_-	a^3S_-	40415.3		42591.2		+5.4	

$G_2 = 1836.5 \text{ cm}^{-1}$.

$F_2 = 1501.7 \text{ cm}^{-1}$, $F_1 = 93.6 \text{ cm}^{-1}$,

$6F_0 = 62012.3 \text{ cm}^{-1}$,

TABLE III
Term values in chromium II.
Configuration $3d^3.4s^2$

Term	Observed value	Calculated value	Percentage of discrepancy	Formula
4P	55045.7	55658.9	+1.1	$F_0 - 147F_4$
2P	59112.8	57292.7	-3.2	$F_0 - 6F_2 - 12F_4$
4F	53574.4	52970.9	-1.1	$F_0 - 15F_2 - 72F_4$
2F		59980.7		$F_0 + 9F_2 - 87F_4$
2G	54576.2	56396.7	+3.3	$F_0 - 11F_2 + 13F_4$
2H		57292.7		$F_0 - 6F_2 - 12F_4$
$^3D_+$		62709.6		$F_0 + 5F_2 + 3F_4$
$^3D_-$		59430.2		$\left\{ \begin{array}{l} \pm \frac{1}{2}(193F_2^2 - 1650F_2F_4 \\ - 8325F_4^2)^{1/2} \end{array} \right.$

$$F_0 = 59451.5 \text{ cm}^{-1}$$

$$F_2 = 308.2 \text{ cm}^{-1}$$

$$F_4 = 25.8 \text{ cm}^{-1}$$

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