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MULTIPLETS IN THREE ELECTRON SYSTEMS OF THE FIRST LONG PERIOD

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ABSTRACT

Wave-lengths and relative positions of multiplets in the spectra of Sc (I), Ti (II), V (III), and Cr (IV).—Using the regular and irregular doublet laws as guides, it has been found possible, from the corresponding known multiplets in Sc (I) and Ti (II), to identify the triad of multiplets of V (III) designated as $^4F_{2,3,4,5}-^4G_{3,4,5,6}$; $^4F_{2,3,4,5}-^4F'_{2,3,4,5}$; and $^4F_{2,3,4,5}-^4D_{1,2,3,4}$. For these multiplets the initial state is given by one *4p* electron and two *3d* electrons. In the final state the *4p* electron has shifted to a *4s* orbit. The separations of the $^4F_{2,3,4,5}$ levels are found to be in the ratio 2.50:3.52:4.50, in very close agreement with Landé's interval rule. The relative intensities of the lines in these multiplets conform to the usual rule. A comparison of the data for one, two, and three electron systems of Sc, Ti, and V shows that the addition of first one and then a second *d* electron causes not only an increase in the multiplicity but also successive shifts in the radiated lines toward the longer wave-lengths by very nearly the same frequency interval. It has also been found possible to identify the $^4F_{2,3,4,5}-^4F'_{2,3,4,5}$ multiplet of Cr (IV).

IT HAS been shown[1] that for the one electron systems of the first long period from K(I) to Mn(VII) the first lines of the principal series follow very closely the regular and irregular doublet laws. Each of these lines results from an electron in a *4p* orbit jumping into a *4s* orbit. Similarly for two electron systems of this same period from Ca(I) to Cr(V), we have been able to show that when one of the electrons in a *4p* orbit jumps to a *4s* orbit in the presence of an electron in a *3d* orbit a triad of multiplets of the type $^3D_{1,2,3}-^3P_{0,1,2}$, $^3D_{1,2,3}-^3D'_{1,2,3}$, and $^3D_{1,2,3}-^3F_{2,3,4}$, also follow the regular and irregular doublet laws.[2]

In the three electron systems Sc(I), Ti(II), and V(III), three multiplets forming a triad of the type $^4F_{2,3,4,5}-^4D_{1,2,3,4}$; $^4F_{2,3,4,5}-^4F'_{2,3,4,5}$; and $^4F_{2,3,4,5}-^4G_{3,4,5,6}$, have been identified which obey these same laws. For these multiplets the initial state is given by one *4p* electron and two *3d* electrons. The final state finds one electron in a *4s* orbit and the other two in *3d* orbits. This transition may have taken place in two ways either by a one electron jump, *4p* to *4s*, or by a two electron jump, *4p* to *3d* and *3d* to *4s*. If the two electron jump takes place one electron has changed by $\Delta k=1$, and the other by $\Delta k=2$.

In either case the sums of the total quantum numbers for the initial and final states are equal, which is the necessary requirement that the resultant spectral lines follow the doublet laws.

Multiplets in the arc spectrum of scandium have been itendified by Catalan.[3] He reports three multiplets of the type $^4F_{2,3,4,5}-^4D_{1,2,3,4}$, $^4F_{2,3,4,5}$

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[1] R. C. Gibbs and H. E. White, Nat. Acad. Sci. Proc. **12**, 448 (1926).

[2] R. C. Gibbs and H. E. White, Phys. Rev. **29**, 426 (1927).

[3] Catalan, Ann. de Soc. Esp. Fis. Y Quim. p. 466 (Nov., 1923).

$-{}^4F'_{2,3,4,5}$, and ${}^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$, in the region of 5000A.U. The intensities, wave-lengths, and frequencies of the lines in these multiplets as well as the relative term values are given in Table I. In Ti(II) a similar triad of the same type in the region of 3000A.U. has been reported by Russell,[4] and by Meggers, Kiess, and Walters.[5] Their results are shown in Table II together with the relative values of the ${}^4F_{2,3,4,5}$, ${}^4D_{1,2,3,4}$, ${}^4F'_{2,3,4,5}$, and ${}^4G_{3,4,5,6}$ terms

TABLE I

Multiplet Triad in Sc(I) (*Catalan*)

$d^2p \rightarrow d^2s$

		${}^4F_5$		${}^4F_4$		${}^4F_3$		${}^4F_2$
		157.3	(67.1)	90.2	(52.5)	37.7	(37.7)	000
${}^4G_6$	17783.3	200 5671.83 17626.1						
	(113.6)							
${}^4G_5$	17669.7	15 5708.63 17512.5		150 5686.83 17579.6				
	(93.6)							
${}^4G_4$	17576.1	2 5739.21 17418.9		15 5717.29 17486.0		100 5700.18 17538.4		
	(73.2)							
${}^4G_3$	17502.9			1 5741.34 17412.7		15 5724.08 17465.2		100 5711.75 17502.9
${}^4F'_5$	19830.7	125 5081.57 19673.5		10 5064.32 19740.5				
	(75.3)							
${}^4F'_4$	19755.4	20 5101.08 19598.2		90 5083.70 19665.3		40 5070.21 19717.6		
	(59.6)							
${}^4F'_3$	19695.8			40 5099.20 19605.5		60 5085.53 19658.2		10 5075.81 19695.8
	(43.3)							
${}^4F'_2$	19652.5					30 5096.72 19615.0		50 5086.99 19652.5
${}^4D_4$	21231.5	40 4743.80 21074.3		8 4728.77 21141.2		0 4717.03 21193.9		
	(54.6)							
${}^4D_3$	21176.9			30 4741.02 21086.6		10 4729.21 21139.3		0 4720.77 21177.1
	(37.6)							
${}^4D_2$	21139.3					18 4737.65 21101.7		10 4729.21 21139.3
	(21.8)							
${}^4D_1$	21117.5							15 4734.10 21117.5

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[4] H. N. Russell, Astrophys. Jour. **61,** 254 (1925).

[5] Meggers, Kiess and Walters, J.O.S.A. **9,** 364 (Oct., 1924)

where the $^4F_2$ term, which is the lowest level of the normal state of the ionized atom, is taken as zero. Applying the irregular doublet law, i.e. a linear extrapolation of ν from each multiplet in Sc(I) and Ti(II), the corresponding multiplets were looked for in the spark spectrum of vanadium in the vicinity of 2500A.U. Three very strong multiplets have been identified in this part of the spark spectrum, the details for which are given in Table III. The wave-lengths in Tables I and II are given in I.A.(air) while those in

TABLE II

Multiplet Triad in Ti(II)[4,5]

$d^2p \rightarrow d^2s$

		$^4F_5$ 393.3 (167.7)	$^4F_4$ 225.6 (131.5)	$^4F_3$ 94.1 (94.1)	$^4F_2$ 000
$^4G_6$	30240.6	40 3349.41 29847.4			
	272.5				
$^4G_5$	29968.1	15 3380.28 29574.9	40 3361.22 29742.6		
	233.6				
$^4G_4$	29734.5	4 3407.20 29341.3	15 3387.83 29509.0	30 3372.80 29640.4	
	190.0				
$^4G_3$	29544.5		5 3409.80 29318.9	15 3394.57 29450.4	40 3383.76 29544.5
$^4F'_5$	31300.9	60 3234.52 30907.6	15 3217.04 31075.5		
	187.4				
$^4F'_4$	31113.5	20 3254.23 30720.4	50 3236.57 30888.0	15 3222.82 31019.8	
	154.8				
$^4F'_3$	30958.7		25 3252.85 30733.5	40 3239.03 30864.6	15 3229.18 30958.7
	122.1				
$^4F'_2$	30836.6			20 3251.89 30742.5	40 3241.97 30836.6
$^4D_4$	32767.3	60 3088.03 32373.9	30 3072.10 32541.7	?	
	69.1				
$^4D_3$	32698.2		45 3078.64 32472.6	30 3066.20 32604.3	?
	95.6				
$^4D_2$	32602.6			40 3075.22 32508.7	20 3066.36 32602.6
	70.1				
$^4D_1$	32532.5				40 3072.97 32532.5

Table III are in I.A.(vac). Assuming the regular doublet law to hold an extrapolation from the values of the $^4F_{2,3,4,5}$ separations for Sc(I), and Ti(II) enabled us to predict the $^4F_{2,3,4,5}$ separations for V(III) to be about

TABLE III

Multiplet Triad in V(III)

$d^2p \rightarrow d^2s$

		$^4F_5$	$^4F_4$	$^4F_3$	$^4F_2$
		705.1 (301.7)	403.4 (235.8)	167.6 (167.6)	000
$^4G_6$	42867.6	200 2371.76 42162.8			
	(503.1)				
$^4G_5$	42364.5	75 2400.40 41659.7	150 2383.18 41960.7		
	(431.0)				
$^4G_4$	41933.5	2 2425.51 41228.4	80 2407.90 41530.0	125 2394.27 41766.4	
	(351.6)				
$^4G_3$	41581.9		2 2428.43 41178.8	40 2414.62 41414.4	100 2404.89 41581.9
$^4F'_5$	43603.2	100 2331.09 42898.4	50 2314.81 43200.1		
	(325.8)				
$^4F'_4$	43277.4	30 2348.94 42572.4	75 2332.39 42874.5	40 2319.65 43109.9	
	(281.0)				
$^4F'_3$	42996.4		30 2347.78 42593.4	75 2334.87 42829.0	40 2325.78 42996.3
	(221.3)				
$^4F'_2$	42775.1			30 2347.00 42607.6	75 2337.80 42775.1
$^4D_4$	45479.2	70 2233.46 44773.6	25 2218.49 45075.7	2 2206.96 45311.2	
	(39.9)				
$^4D_3$	45519.1		40 2216.55 45115.2	20 2205.00 45351.5	2 2196.88 45519.1
	(267.7)				
$^4D_2$	45251.4			30 2218.09 45083.8	8 2209.88 45251.4
	(186.9)				
$^4D_1$	45064.5				30 2219.04 45064.5

$\Delta\nu = 172$, 246, and 310. These separations are found to be $\Delta\nu = 167.6$, 235.8, and 301.7 which is in very close agreement with the predicted values. According to Lande's interval rule these separations should have values in the ratio 2.5:3.5:4.5. The observed separations are in the ratio 2.50:3.52:4.50.

Owing to insufficient data on chromium in the extreme ultra-violet we have as yet been able to identify with certainty only the ${}^4F_{2,3,4,5}-{}^4F'_{2,3,4,5}$ multiplet and several lines of the ${}^4F_{2,3,4,5}-{}^4G_{3,4,5,6}$ multiplet.

The linear progression in frequency of each of the above multiplets with the atomic number, is brought out most clearly in Fig. 1 for the first three elements. It may be seen that by displacing the frequencies of each group of lines to the left by $\Delta\nu=12{,}000$ with respect to the spectral groups of the element just preceding it, corresponding multiplets are seen to lie very nearly one below the other. In this way the small departures from the irregular doublet law appear to be magnified.

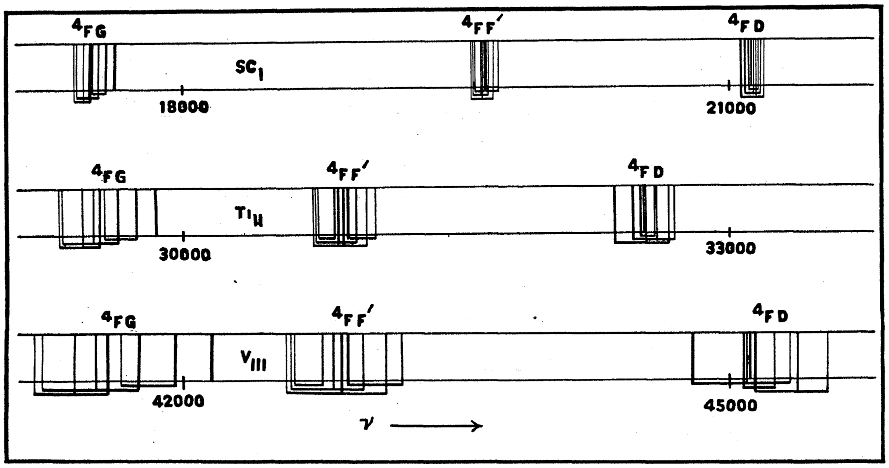

Fig. 1. Three electron systems of the first long period.

The increasing frequency separations of the ${}^4F_{2,3,4,5}$ levels, as may be seen in Fig. 1 follows directly from the regular doublet law which requires that $\Delta\nu=K(Z-s)$.[4] This law although derived for doublet separations is found to apply also to multiplet terms.[2] The screening constants as computed from the above relation are given in Table IV. If Fig. 1 had been plotted to a scale of wave-lengths in place of frequencies, the corresponding ${}^4F_{2,3,4,5}$ separations would have been almost the same for each multiplet in all three elements. This is also a consequence of the regular doublet law. This constancy of $\Delta\lambda$ between corresponding lines in each of these multiplets

TABLE IV

Regular doublet laws

	$\Delta\nu$ ${}^4F_5-{}^4F_4$	$(\Delta\nu/.0456)^{1/4}$	s	$\Delta_1\lambda$ $({}^4F_5F'_5-{}^4F_4F'_5)$	$\Delta_2\lambda$ $({}^4F_5F'_5-{}^4F_5F'_4)$
Sc(I)	67.1	6.193	14.807	17.25	19.51
Ti(II)	167.7	7.787	14.213	17.48	19.71
V(III)	301.7	9.018	13.982	16.28	17.85

is quite remarkable. Examples of this are given in the last two columns of Table IV. There are in a few cases departures from this rule just as there are occasional departures from the interval rule as given by Landé for term separations.

Starting with the one electron system of any of the elements given in Table V, it is seen that the screening effect due to the addition of first one and then a second *d* electron is to shift the spectral lines toward the longer wave-lengths by very nearly the same frequency interval, while at the same time the multiplicity is increased. The uniformity of this shift is more strikingly brought out in Fig. 2 where in passing downward along any of the light diagonals there is a successive addition of *d* electrons with a simultaneous decrease in effective core charge. Fig. 2 also serves to bring out the nearly linear displacement of multiplets when successive *d* electrons are added keeping the effective core charge nearly constant i.e. upward along the heavy diagonals. The irregular doublet law which holds here for isoelectronic systems, is illustrated by the almost equal intervals along the verticals. To show this screening effect, we have taken the strongest line in each electron system as representing the position in the spectrum of that system of lines. In the one electron systems the $4^2S_1-4^2P_2$ line is the strongest line of the doublet since *k* and *j* are changing in the same direction. For the two electron systems the strongest line of all three multiplets is the line $^3D_3-{}^3F_4$. Similarly for the three electron systems the line $^4F_5-{}^4G_6$ is the strongest.

TABLE V

Screening effect of d electrons.

Doublets $p\rightarrow s$ $4^2S_1-4^2P_2$		Triplets $dp\rightarrow ds$ $a^3D_3-a^3F_4$		Quartets $d^2p\rightarrow d^2s$ $a^4F_5-a^4G_6$
Sc(III)		Sc(II)		Sc(I)
37039.6	(9376.0)	**27663.6**	(10037.5)	**17626.1**
(11311.2)		(12070.1)		(12221.3)
Ti(IV)		Ti(III)		Ti(II)
48350.8	(8617.1)	**39733.7**	(9886.3)	**29847.4**
(11163.6)		(11837.7)		(12315.4)
V(V)		V(IV)		V(III)
59514.4	(7943.0)	**51571.4**	(9408.6)	**42162.8**
(11020.9)		(11994.9)		(12181.5)
Cr(VI)		Cr(V)		Cr(IV)
70535.3	(6969.0)	**63566.3**	(10778.0)	**54344.3**

It is interesting to note that in general the jump from the multiple level having the largest *k* value into a common lower multiple level gives the strongest lines in the triad of multiplets; the intensities of the other multiplets following in an order corresponding to their relative *k* values. In each multiplet the stronger lines appear where *k* and *j* are changing in the

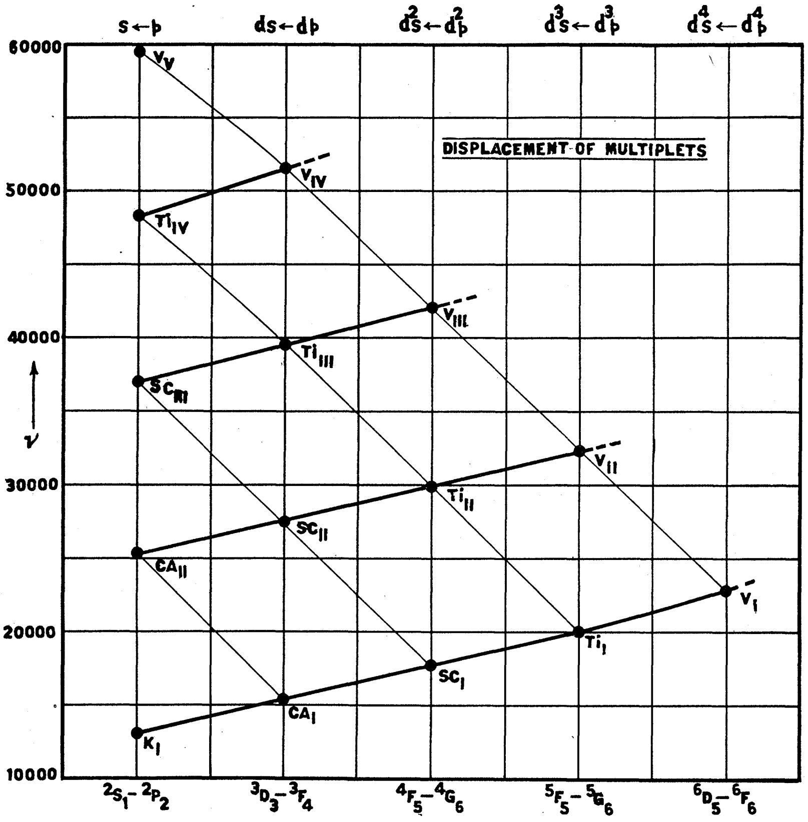

Fig. 2. Up heavy diagonals: successive addition of d electrons with constant core charge. Down light diagonals: successive addition of d electrons with simultaneous decrease in core charge. Up verticals: iso-electronic systems with successive increase in core charge.

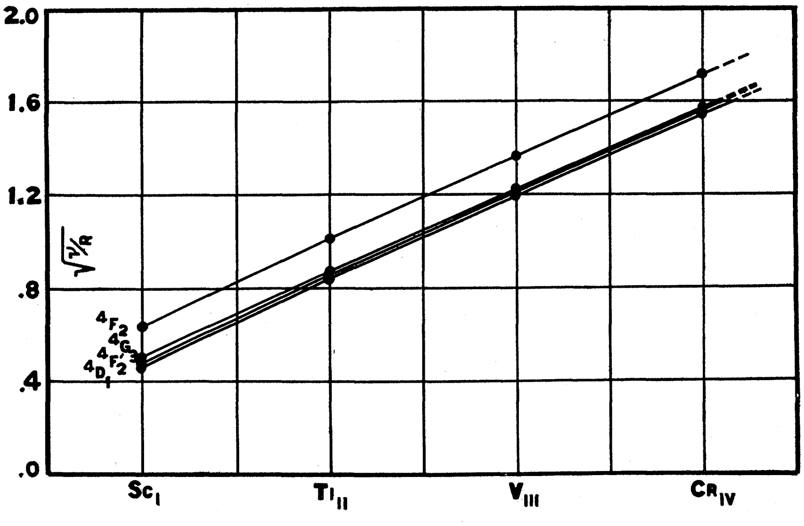

Fig. 3. Moseley diagram.

same direction. Of these stronger lines, which in Tables I, II and III are on the diagonals of each multiplet, the strongest line occurs for the transition involving the largest j values. From these intensity rules then it may be deduced that for a given electron configuration the most stable state occurs when the orbital axes and also the spin axes of all the valence electrons are as nearly as possible in the same direction. Furthermore when an electron transition takes place the most probable transition will be such that these axes retain as nearly as possible the same relative directions. The exceptions to this rule are probably accounted for, by ones inability to measure accurately the relative intensities of lines taken from different photographic plates, or from the failure of photography in general to record true relative intensities.

The lines on the Moseley diagram, Fig. 3, being parallel are a direct consequence of the irregular doublet law which requires $\Delta(\nu/R)^{1/2} = \text{constant}$, where ν is given in cm^{-1}. The values of $(\nu/R)^{1/2}$ were obtained by an extrapolation from terms already known in K(I), Ca(II), and Ca(I), Sc(II). It may here be pointed out that the regular and irregular doublet laws give an effective method of attack in the classification of spectra arising from higher states of ionization in iso-electronic systems of successive elements in any one Period.

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