

MULTIPLETS IN TWO ELECTRON SYSTEMS  
OF THE FIRST LONG PERIOD\*

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ABSTRACT

Wave-lengths and comparative positions of certain multiplets in the spectra of Ca<sub>I</sub>, Sc<sub>II</sub>, Ti<sub>III</sub>, V<sub>IV</sub>, Cr<sub>V</sub>.—When an electron in a  $4p$  orbit jumps to a  $4s$  orbit in the presence of another valence electron in a  $3d$  orbit, multiplets of the type  ${}^3D_{1,2,3}-{}^3P_{0,1,2}$ ;  ${}^3D_{1,2,3}-{}^3D'_{1,2,3}$ ;  ${}^3D_{1,2,3}-{}^3F_{2,3,4}$  appear. These multiplets for Ca<sub>I</sub>, Sc<sub>II</sub>, Ti<sub>III</sub> have already been recognized by other investigators. The same multiplets for V<sub>IV</sub> and Cr<sub>V</sub> have now been found and the wave-lengths of the lines have been measured. The progressive shift in the relative positions of these multiplets in passing from element to element has been noted. The *regular and irregular doublet laws* have been found to hold fairly accurately for two electron systems when one of the electrons jumps between two orbits,  $p$  and  $s$ , having the same total quantum number.

ACCORDING to the new theory of space quantization a single valence-electron gives rise to a system of doublet levels. In the presence of another valence-electron, however, the doublet levels are replaced by singlet and triplet levels, except when both electrons are in  $s$  orbits having the same total quantum number. These triplet levels in general give rise to groups of lines called multiplets.

Ca<sub>I</sub>, Sc<sub>II</sub>, Ti<sub>III</sub> etc., each contains two valence electrons and we should therefore expect to find such multiplets in their spectra and also that each of the three multiplets would have somewhat the same structure for all these atoms.

The Ca<sub>I</sub> spectrum is known from the work of Russell and Saunders,<sup>1</sup> in which they find the lowest level to be a  ${}^1S_0$  level. This  ${}^1S_0$  level is the resultant of two similar ( $s$ ) electrons in orbits of total quantum number 4, the normal state of the atom. When one of these ( $s$ ) electrons is excited to a  $3d$  orbit, the two electrons will then give rise to  ${}^1D_2$  and  ${}^3D_{1,2,3}$  levels. If the other ( $s$ ) electron is now displaced to a  $4p$  orbit, the two electrons, one in a  $3d$  orbit and the other in a  $4p$  orbit, will give rise to  ${}^1P_1$ ,  ${}^1D'_2$ ,  ${}^1F_3$ ,  ${}^3P_{0,1,2}$ ,  ${}^3D'_{1,2,3}$ ,  ${}^3F_{2,3,4}$  levels. When the electron in the  $4p$  orbit returns to the lower  $4s$  orbit there will result radiations corresponding to jumps from any one of the  ${}^1P_1$ ,  ${}^1D'_2$ ,  ${}^1F_3$ ,  ${}^3P_{0,1,2}$ ,  ${}^3D'_{1,2,3}$ ,  ${}^3F_{2,3,4}$  levels to any one of the  ${}^1D_2$  or  ${}^3D_{1,2,3}$  levels except those excluded by the selection principle ( $\Delta j=0, \pm 1$ ). The jumping

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<sup>1</sup> H. N. Russell and F. A. Saunders, *Astrophys. J.* **61**, p. 38 (1925).

of one electron from the  $4p$  orbit to the  $4s$  orbit, the stationary state of the other valence electron in the  $3d$  orbit remaining unchanged, will correspond exactly to the jumps in the one electron systems<sup>2</sup> except that here it is jumping in a field which is modified by the presence of another electron in a  $3d$  orbit. This causes not only a shift in the radiated frequency but an increase in the number of lines radiated.

Scandium in the normal state contains three valence electrons, two of them are in  $s$  orbits and the other in a  $d$  orbit, the latter being more tightly bound than either of the ( $s$ ) electrons. If now an electron be removed from the normal scandium atom it will probably be one of the ( $s$ ) electrons which is ejected. The two remaining electrons should then give rise to  $^1D_2$  and  $^3D_{1,2,3}$  levels as the lowest state in the first spark spectrum of scandium, with the  $^3D_{1,2,3}$  according to Hund,<sup>3</sup>

TABLE I  
*Titanium (III) triplets.* (H. N. Russell).

		$a^3D_3$ 361.69 (227.2)	$a^3D_2$ 134.48 (134.5)	$a^3D_1$ 000
$a^3D'_1$	39360.7	9 2564.17 38999.0	1 2549.32 39226.2	
	(257.6)			
$a^3D'_2$	39103.1	7 2581.21 38741.5	8 2566.16 38968.7	5 2557.35 39103.0
	(166.9)			
$a^3D'_3$	38936.2		6 2577.22 38801.5	7 2568.29 38936.4
$a^3F_4$	40095.4	10 2516.76 39733.7		
	(412.7)			
$a^3F_3$	39682.7	2 2543.17 39320.9	9 2528.56 39548.2	
	(324.7)			
$a^3F_2$	39358.0	0 2564.36 38996.0	2 2549.45 39224.1	8 2540.78 39357.9
$a^3P_2$	42959.8	8 2347.50 42598.5	3 2335.05 42825.7	0 2327.75 42959.8
	(85.3)			
$a^3P_1$	42874.5		5 2339.73 42740.0	1 2332.39 42874.5
	(5.9)			
$a^3P_0$	42880.4			3 2332.07 42880.4

<sup>2</sup> R. C. Gibbs and H. E. White, Proc. Nat. Acad. Sci. **12**, p. 448 (1926); **12**, p. 675 (1926).

<sup>3</sup> Hund, Zeits. f. Physik **33**, p. 345 (1925).

lying deeper than the  ${}^1D_2$  level. If now the (*s*) electron is displaced to a  $4p$  orbit, and the (*s*) electron is indeed more free to move than the (*d*) electron, we again get  ${}^1P_1$ ,  ${}^1D'_2$ ,  ${}^1F_3$ ,  ${}^3P_{0,1,2}$ ,  ${}^3D'_{1,2,3}$ ,  ${}^3F_{2,3,4}$  levels.

Similarly,  $\text{Ti}_{\text{III}}$ ,  $\text{V}_{\text{IV}}$  etc., will give these same types of levels when two, three, etc., valence electrons have been removed respectively, giving as before  ${}^1D_2$  and  ${}^3D_{1,2,3}$  as the lower levels, when one electron is in a  $3d$  orbit and the other is in a  $4s$  orbit, and  ${}^1P_1$ ,  ${}^1D'_2$ ,  ${}^1F_3$ ,  ${}^3P_{0,1,2}$ ,  ${}^3D'_{1,2,3}$ ,  ${}^3F_{2,3,4}$  levels when the (*s*) electron has been displaced to a  $4p$  orbit.

TABLE II  
*Vanadium (IV) triplets.*

		$a^3D_3$ 600.4 (385.0)	$a^3D_2$ 215.4 (215.4)	$a^3D_1$ 000
$a^3D'_1$	50656.9	6 1997.74 50056.6	1 1982.49 50441.6	
	(424.6)			
$a^3D'_2$	50232.3	5 2014.83 49632.0	5 1999.32 50017.0	3 1990.75 50232.3
	(310.2)			
$a^3D'_3$	49922.1		2 2011.80 49706.7	4 2003.12 49922.1
$a^3F_4$	52171.4	6 1939.07 51571.1		
	(712.9)			
$a^3F_3$	51458.5	0 1966.25 50858.2	6 1951.48 51243.1	
	(519.5)			
$a^3F_2$	50939.0	0 1986.54 50338.8	1 1971.47 50723.6	6 1963.13 50939.0
$a^3P_2$	54797.2	8 1845.09 54197.9	6 1832.07 54583.1	4 1824.91 54797.2
	(83.2)			
$a^3P_1$	54880.4		5 1829.28 54666.3	1 1822.10 54881.7
	(140.8)			
$a^3P_0$	55021.2			4 1817.48 55021.2

The lines caused by transitions from the  ${}^3P_{0,1,2}$ ,  ${}^3D'_{1,2,3}$ ,  ${}^3F_{2,3,4}$  states to the  ${}^3D_{1,2,3}$  states are characteristic multiplets of which  ${}^3D_{1,2,3} - {}^3D'_{1,2,3}$  is the easiest to recognize by its somewhat symmetrical configuration. This multiplet is composed of seven lines, while the other two  ${}^3D_{1,2,3} - {}^3P_{0,1,2}$  and  ${}^3D_{1,2,3} - {}^3F_{2,3,4}$  are made up of six lines

each. These multiplets in  $\text{Ca}_I$  are given by Russell and Saunders<sup>1</sup> in the visible region of the spectrum, and those for  $\text{Sc}_{II}$  by Meggers<sup>4</sup> in the ultra-violet region. Dr. Russell has very kindly put at our disposal his unpublished data of the corresponding multiplets of  $\text{Ti}_{III}$ . These three multiplets are given in Table I, with the relative term values of the levels, where the value of the  ${}^3D_1$  level is taken as zero. The intensities of the  $\text{Ti}_{III}$  lines are taken from our own photographs of these multiplets. The first two multiplets of  $\text{V}_{IV}$  recorded in Table II occur at the threshold of the air absorption limit of the ordinary grating spectrograph. The other multiplet,  ${}^3D_{1,2,3}-{}^3P_{0,1,2}$  of  $\text{V}_{IV}$  as well as all three multiplets of  $\text{Cr}_{V}$  lie still deeper in the ultra-violet and were obtained from plates very kindly taken for us by Dr. I. S. Bowen of the California Institute of Technology using a vacuum spectrograph.

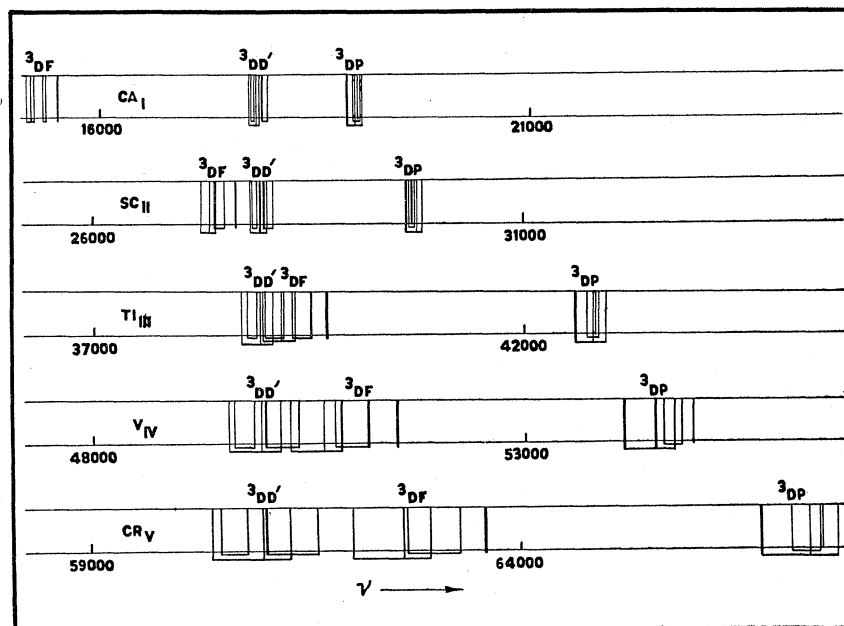


FIG. 1. Relative positions of multiplets.

Since we are here dealing with lines arising from an electron transition between orbits of the same total quantum number they would be expected to follow the irregular doublet law just as was found to be the case for the doublets of these elements<sup>2</sup> when their atoms contain only *one* valence electron. Fig. 1 is given for the purpose of showing the

<sup>4</sup> Meggers, Journal Wash. Acad. Sci. 14, p. 419 (1924).

application of the irregular doublet law to each group of lines, i.e. the almost linear progression of  $\nu$  with increasing atomic number, as well as the relative shifting of the  ${}^3DF$  and  ${}^3DP$  multiplets with respect to the  ${}^3DD'$  multiplet. It may be seen that the  ${}^3DF$  and  ${}^3DD'$  groups progress very regularly while the  ${}^3DP$  group shows small irregularities in going from element to element.

TABLE III  
*Chromium (V) triplets.*

		$a^3D_3$ 912.0 (596.7)	$a^3D_2$ 315.3 (315.3)	$a^3D_1$ 000
$a^3D'_1$	61943.6	6	0	
	(630.0)	1638.51 61031.0	1622.64 61628.0	
$a^3D'_2$	61313.6	2	5	1
	(488.2)	1655.60 60401.0	1639.40 60997.9	1630.96 61313.6
$a^3D'_3$	60825.4		2	4
			1652.63 60509.5	1644.05 60825.4
$a^3F_4$	64477.9	7		
	(895.5)	1573.16 63566.3		
$a^3F_3$	63582.4	1	4	
	(633.5)	1595.64 62670.8	1580.62 63266.3	
$a^3F_2$	62948.9	?	2	2
		(1611.95) 62036.7	1596.59 62633.5	1588.57 62948.9
$a^3P_2$	67669.7	8	5	0
	(230.2)	1497.97 66757.0	1484.67 67355.0	1477.75 67670.2
$a^3P_1$	67439.5		6	3
	(51.4)		1489.75 67125.3	1482.81 67439.5
$a^3P_0$	67490.9			5
				1481.68 67490.9

The regular doublet law, derived by Sommerfeld<sup>5</sup> from relativity considerations and by Heisenberg and Jordan<sup>6</sup> from the new quantum mechanics of the spinning electron, shows not only that the value of  $(\Delta\nu)^{1/4}$  should be a linear function of  $Z$ , but that  $\Delta\lambda$  should remain nearly constant for increasing atomic number. These laws are found

<sup>5</sup> Sommerfeld, *Atombau*, 4th German edition 1924, p. 144.

<sup>6</sup> W. Heisenberg and P. Jordan, *Zeits. f. Physik*, **37**, p. 276 (1926).

to hold even in these triplet systems except for possibly the Ca<sub>I</sub> multiplets. The values given in Table IV show how beautifully these relations are fulfilled. Using the same constant in Sommerfeld's

TABLE IV

$$\begin{aligned} \Delta_1\lambda &= (a^3D_3 - a^3D'_3) - (a^3D_2 - a^3D'_2) \\ \Delta_2\lambda &= (a^3D_3 - a^3D'_3) - (a^3D_3 - a^3D'_2) \end{aligned}$$

Element	$\Delta\nu$		$s$	$\Delta_1\lambda$	$\Delta_2\lambda$
	$a^3D_3 - a^3D_2$	$(\Delta\nu / .0456)^{1/4}$			
Ca <sub>I</sub>	21.9	4.681	15.32	6.63	12.43
Sc <sub>II</sub>	109.97	7.008	13.99	13.98	17.95
Ti <sub>III</sub>	227.2	8.400	13.60	14.85	17.04
V <sub>IV</sub>	385.0	9.585	13.41	15.25	17.09
Cr <sub>V</sub>	596.9	10.696	13.30	15.87	17.09

relativity formula as is used for doublets of the same period<sup>2</sup> the screening constants are found for every element to be larger, by a very nearly constant value, than they are for the corresponding one electron systems which is the effect to be expected from the addition of one more valence electron.

In these two electron systems it is found that the observed frequencies appear at very nearly the same region of the spectrum as do the corresponding doublets of the one electron systems in this same period.<sup>2</sup> This relation is shown in Table V using the  $4^2S_1 - 4^2P_1$  line in the doublet

TABLE V

*Shift due to the presence of a second valence electron.*

	Doublets $4^2S_1 - 4^2P_1$		Triplets $a^3D_3 - a^3F_4$	Diff.
Ca <sub>II</sub>	25191.6	Ca <sub>I</sub>	15525.9	9665.7
Sc <sub>III</sub>	36565.3	Sc <sub>II</sub>	27663.6	8901.7
Ti <sub>IV</sub>	47533.3	Ti <sub>III</sub>	39733.7	7799.6
V <sub>V</sub>	58249.9	V <sub>IV</sub>	51571.4	6678.5
Cr <sub>VI</sub>	68713.8	Cr <sub>V</sub>	63566.3	5147.5

systems and the  $a^3D_3 - a^3F_4$  line in the triplet systems. The consistently larger frequencies of the doublets as compared with those of the triplets suggests that this shift in frequency from one system to the other is caused by the screening effect of an additional electron, in this case an electron in a  $3d$  orbit.

One of the irregular doublet laws requires that the value of  $\Delta(\nu/R)^{1/2}$  be a constant for the corresponding term values of the stationary states between which a transition is taking place. The only term values known are those given by Russell and Saunders<sup>1</sup> for Ca<sub>I</sub>. The term values used to obtain the Moseley diagram Fig. 2 are merely extrapolated

values computed from the known values of the first element  $\text{Ca}_I$ , the slope of the extrapolated curve for  $(\nu/R)^{1/2}$  being so chosen as to yield a similar line for other levels when these other levels are obtained by adding or subtracting the observed frequencies of radiation from those of the extrapolated levels. Although these extrapolated term values may differ somewhat from their true values, yet the figure shows very well the way in which the different levels are changing in going from element to element, and when once started, serves as an aid in predicting the approximate positions of new lines.

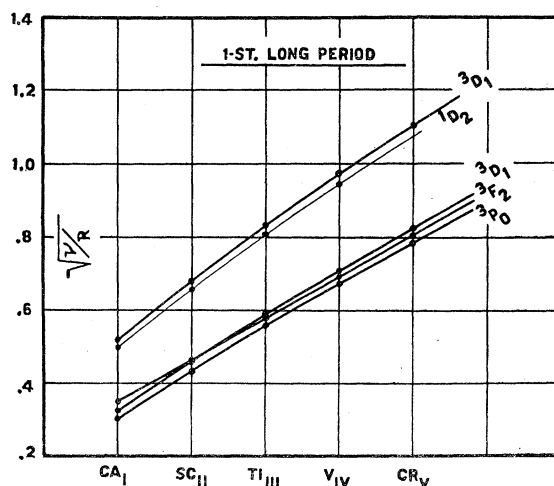


FIG. 2. Moseley diagram.

We have here been dealing with two valence electrons, the initial state of the atom having one electron in a  $4p$  orbit and the other in a  $3d$  orbit. The final state finds one electron in a  $4s$  orbit and the other in a  $3d$  orbit. It is interesting to note that this electron transition may take place in two ways, either one electron is jumping from a  $4p$  to a  $4s$  orbit, the  $3d$  electron remaining fixed, or two electrons are jumping, one from a  $4p$  orbit to a  $3d$  orbit and the other from a  $3d$  orbit to a  $4s$  orbit. In the latter case one electron is changing by  $k=1$  and the other by  $k=2$  which is in accordance with the usual quantum conditions of two electron jumps.<sup>7</sup> The sum of the total quantum numbers is the same in either of the above mentioned cases.

CORNELL UNIVERSITY,  
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<sup>7</sup> W. Heisenberg, *Zeits. f. Physik*, 32, 841 (1925).