

SPECTRAL RELATIONS BETWEEN CERTAIN ISO-ELECTRONIC
SYSTEMS AND SEQUENCES, PART III;
Ti I, V II, Cr III, Mn IV, AND Fe V

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ABSTRACT

Spectral relations between the iso-electronic systems, Ti I, V II, Cr III, Mn IV, and Fe V.—The removal of, one valence electron from neutral vanadium, two valence electrons from neutral chromium, three valence electrons from neutral manganese, and four valence electrons from neutral iron forms with neutral titanium the five iso-electronic systems Ti I, V II, Cr III, Mn IV, and Fe V.

The irregular doublet law.—The irregular doublet law, wherever applicable, proves to be a powerful method of attack in attempting to analyze the spectra arising from ionized atoms. In this report for the electron transition $3d^3 4p$ to $3d^3 4s$ about forty lines, and for the electron transition $3d^3 4d$ to $3d^3 4p$ about twelve lines, have been traced through the first three elements Ti I, V II and Cr III. In the first electron transition the multiplet ${}^5F' - {}^5G'$ has been traced as far as Fe V.

Term separations, The Landé interval rule, and Hund's rule.—The systematic increase in term separations is given for the ${}^6F'$ and ${}^6G'$ terms arising from the electron configurations $3d^3 4s$ and $3d^3 4p$ respectively. For these same terms the Landé interval rule is found to be in general agreement with observed separations. Hund's rule for relative term positions is followed for the terms thus far identified.

Energy levels and the Moseley law.—A new type of energy level Moseley diagram for Ti I to Fe V is compared with a similar diagram for the three sequences starting respectively with Sc I, Ca I, and K I. These four diagrams together with a similar diagram for V I, V II, V III, V IV, and V V are found to be almost identical. The constancy in the values of $\Delta\lambda$ between the diagonal lines of certain multiplets is traced through the first five elements of each of the four iso-electronic sequences starting with Ti I, Ca I, Sc I and K I.

THE neutral atoms of titanium, vanadium, chromium, manganese, and iron contain four valence electrons, $3d^2 4s^2$, five valence electrons, $3d^3 4s^2$, six valence electrons, $3d^4 4s$, seven valence electrons, $3d^5 4s^2$, and eight valence electrons, $3d^6 4s^2$, respectively. The removal of one of these electrons from vanadium, two from chromium, three from manganese, and four from iron, forms with neutral titanium the five iso-electronic systems Ti I, V II, Cr III, Mn IV, and Fe V.

Neutral titanium, Ti I. Identifications of singlet, triplet, and quintet terms and multiplets in the spectra of neutral titanium have been made by several investigators.¹ The most complete analysis, however, has been given by Russell² in which he has classified some 1400 lines involving about 364 energy levels.

Singly ionized vanadium, V II. The identification of a number of terms and multiplets in the first spark spectrum of vanadium, V II, has been

¹ Kiess and Kiess, Proc. of Wash. Acad. Sci. **13**, 270 (1923); Jour. Opt. Soc. Amer. **8**, 607 (1924). Gieseler and Grotrian, Zeits. f. Physik **25**, 342 (1924).

² Russell, Astrophys. J. **66**, 347-438 (1927).

made by Meggers.³ Most of these terms arise from the three lowest electron configurations in the singly ionized atom, $3d^4$, $3d^34s$, and $3d^34p$.

In a previous report on the sequence of iso-electronic systems Sc I to Mn V⁴ the quartet multiplet ${}^4F' - {}^4G'$ ($3d^24s - 3d^24p$), following very closely the irregular doublet law, was found to be displaced to higher frequencies by approximately $12,000 \text{ cm}^{-1}$ in going from one element to the next, (Fig. 7⁴ in the previous report). It was also found that the quartet multiplet ${}^4G' - {}^4H'$ ($3d^24p - 3d^24d$) was displaced to higher frequencies by approximately $20,000 \text{ cm}^{-1}$ in going from one element to the next. In the sequence of iso-electronic systems starting with Ti I the multiplet ${}^5F' - {}^5G'$ ($3d^34s - 3d^34p$) in going from Ti I to V II has been displaced to higher frequencies by approximately $12,000 \text{ cm}^{-1}$. By analogy with the preceding sequence it was predicted that the multiplet ${}^5G' - {}^5H'$ ($3d^34p - 3d^34d$) in going from Ti I to V II would be displaced to higher frequencies by some $20,000 \text{ cm}^{-1}$. This prediction is verified by the finding of the multiplet ${}^5G' - {}^5H'$ in the spark spectrum of vanadium, V II, approximately $20,000 \text{ cm}^{-1}$ higher than the corresponding multiplet in Ti I. The wave-lengths, relative intensities, and frequencies of the lines thus identified are given in multiplet form in Table XVI. The term values given in the table have been computed from the lowest term in the spectrum ${}^5D_0(3d^4)$ taken as zero.³

TABLE XVI. *Singly ionized vanadium, V II.*
 ${}^5G' - {}^5H'$ ($3d^34p - 3d^34d$)

		${}^5G_5'$ 290	${}^5G_5'$ 247	${}^5G_4'$ 201	${}^5G_3'$ 153	${}^5G_2'$
		35483.3	35192.9	34946.3	34745.5	34592.5
${}^5H_7'$	73018.1	100n 2664.19 37534.8				
	182.					
${}^5H_6'$	72835.6	20n 2677.20 37352.5	90n 2656.57 37642.6			
	157.					
${}^5H_5'$	72678.8	2?n 2688.39 37197.0	20n 2667.66 37486.0	80n 2650.24 37732.4		
	129.					
${}^5H_4'$	72549.7		2?n 2676.86 37357.2	20n 2659.32 37603.5	70n 2645.21 37804.2	
	102.			?		
${}^5H_3'$	72446.1			20n 37501.5	60n 2652.36 37702.3	2641.74 37853.8

Doubly ionized chromium, Cr III. Applying the irregular doublet law to the spectra of Ti I and V II, Gibbs and White⁵ were able to identify the quintet multiplet ${}^5F' - {}^5G'$ arising from the electron transition $3d^34p$ to

³ Meggers, Zeits. f. Physik **33**, 509 (1925); **39**, 114 (1926).

⁴ White, Phys. Rev. **33**, 681 (1929).

⁵ Gibbs and White, Proc. Nat. Acad. Sci. **13**, 525 (1927).

$3d^34s$ in doubly ionized chromium, Cr III. With the ${}^5G'_{2,3,4,5,6}(3d^34p)$ term separations thus known the ${}^5G' - {}^5H'(3d^34p - 3d^34d)$ multiplet (using again the irregular doublet law) was predicted and identified approximately $20,000 \text{ cm}^{-1}$ higher than the corresponding multiplet in V II.

The triad of triplet terms ${}^3D', {}^3F, {}^3G'(3d^34p)$ are found to combine strongly with b^3F' of $3d^34s$ and with a ${}^3F'$ and ${}^3G'$ of $3d^4$. The latter electron configuration gives the lowest terms in the spectrum, the ${}^5D_{0,1,2,3,4}$, terms of which have not yet been definitely identified. The relative term values for Cr III are given in Table XVII. Since the lowest terms, ${}^5D(3d^4)$ and intercom-

TABLE XVII. Term values of doubly ionized chromium, Cr III

Config. (Limit)	Term	Triplet Terms			Config. (Limit)	Quintet Terms			
		Value	Combinations	$(\nu)^{1/2}$		Term	Value	Combinations	$(\nu)^{1/2}$
$3d^4$ ($3d^3$) (${}^4F'$)	$a^3F'_2$	19000	${}^3D', F$	472	$3d^34s$ ($3d^3$) (${}^4F'$)	${}^5F'_1$	50000	${}^5G', {}^5F$	438
		56				${}^5F'_2$	50136		
	$a^3F'_3$	19056	${}^3G'$			${}^5F'_3$	50336		
		75				${}^5F'_4$	50559		
	$a^3F'_4$	19131				${}^5F'_5$	50918		
	3G_3	21250	${}^3F, {}^3G'$						
	148								
	3G_4	21398							
		146							
	3G_5	21544		469					
$3d^34s$ ($3d^3$) (${}^4F'$)	$b^3F'_2$	57194	${}^3D', {}^3F$	429	${}^5G'_2$	94273	${}^5F'$	383	
		342			${}^5G'_3$	94537			
	$b^3F'_3$	57536	${}^3G'$		${}^5G'_4$	94884			
		430			${}^5G'_5$	95309			
	$b^3F'_4$	57966			504				
$3d^34p$ ($3d^3$) (${}^4F'$)	${}^3D'_1$	97621	a^3F', b^3F'	375	$3d^34p$	${}^5G'_6$	95813	380	
		228			($3d^3$)	5F_1	97281		
	${}^3D'_2$	97849			(${}^4F'$)	5F_2	97428		
		378				5F_3	97628		
	${}^3D'_3$	98227				5F_4	97867		
		200				5F_5	98126		
	${}^3G'_3$	100384	$a^3F', {}^3G$						
		259							
	${}^3G'_4$	100643	b^3F'						
		323							
${}^3G'_5$	100966								
	3F_2	101988	$a^3F', {}^3G$	373	$3d^34d$ ($3d^3$) (${}^4F'$)	${}^5H'_3$	152694	${}^5G'$	298
		302				${}^5H'_4$	152878		
3F_3	102290	b^3F'				${}^5H'_5$	153107		
		354					280		
	3F_4	102644			${}^5H'_6$	153387			
						323			
					${}^5H'_7$	153710			

binations between triplet and quintet terms have not been identified with certainty, absolute term values have not been given in the table. For convenience only the $a^3F'_2(3d^4)$ term has been taken to be $19,000 \text{ cm}^{-1}$, and the ${}^5F'_1(3d^34s)$ taken to be $50,000 \text{ cm}^{-1}$, above the ${}^5D_0(3d^4)$ term. The values

of $(\nu)^{1/2}$ given in the fifth and tenth columns of this table are taken with respect to ${}^4F_5'(3d^3)$ of the once more ionized atom, and were obtained from an extrapolation of a Moseley diagram. The wave-lengths, relative intensities, frequencies and designations of the lines thus far identified in this report on Cr III are given in Table XVIII.

Triply ionized manganese, Mn IV. Extrapolating by means of the irregular doublet law the quintet multiplet ${}^5F' - {}^5G'(3d^34s - 3d^34p)$ was pre-

TABLE XVIII. Doubly ionized chromium, Cr III

$\lambda(\text{vac.})$	Int.	ν	Designation	Mult. No.	$\lambda(\text{vac.})$	Int.	ν	Designation	Mult. No.
2483.79	25	40261.0	$b^3F_4' - {}^3D_3'$	1	2104.05	20	47527.5	${}^5F_4' - {}^5F_5$	5
2480.53	22	40313.9	$b^3F_3' - {}^3D_2'$	1	2103.90	20	47530.8	${}^5F_3' - {}^5F_4$	5
2473.56	20	40427.5	$b^3F_2' - {}^3D_1'$	1	1735.89	25	57574.2	${}^5G_6' - {}^5H_6'$	6
2459.69	6	40655.5	$b^3F_2' - {}^3D_2'$	1	1730.16	20	57798.1	${}^5G_5' - {}^5H_5'$	6
2457.54	7	40691.1	$b^3F_3' - {}^3D_3'$	1	1727.19	100	57897.5	${}^5G_6' - {}^5H_7'$	6
2343.18	6	42677.1	$b^3F_4' - {}^3G_4'$	2	1724.31	15	57994.2	${}^5G_4' - {}^5H_4'$	6
2333.80	4	42848.5	$b^3F_3' - {}^3G_3'$	2	1721.82	90	58078.1	${}^5G_5' - {}^5H_6'$	6
2325.60	80	42999.6	$b^3F_4' - {}^3G_5'$	2	1719.51	15	58156.1	${}^5G_3' - {}^5H_3'$	6
2319.78	70	43107.5	$b^3F_5' - {}^3G_4'$	2	1717.54	80	58222.8	${}^5G_4' - {}^5H_5'$	6
2315.35	60	43190.0	$b^3F_2' - {}^3G_3'$	2	1714.08	70	58340.3	${}^5G_3' - {}^5H_4'$	6
2275.99	2	43936.8	${}^5F_3' - {}^5G_2'$	3	1711.74	60	58420.1	${}^5G_2' - {}^5H_3'$	6
2275.93	2	43938.1	${}^5F_4' - {}^5G_3'$	3	1271.90	15	78622.5	$a^3F_5' - {}^3D_1'$	7
2274.47	2	43966.3	${}^5F_5' - {}^5G_4'$	3	1269.19	20	78790.4	$a^3F_3' - {}^3D_2'$	7
2265.65	15	44137.4	${}^5F_2' - {}^5G_2'$	3	1268.23	tr	78850.0	$a^3F_2' - {}^3D_2'$	7
2262.40	15	44200.8	${}^5F_4' - {}^5G_3'$	3	1266.06	tr	78985.1	${}^3G_4 - {}^3G_4'$	8
2258.70	50	44273.2	${}^5F_1' - {}^5G_2'$	3	1264.27	25	79097.1	$a^3F_4' - {}^3D_3'$	7
2258.11	15	44284.8	${}^5F_4' - {}^5G_4'$	3	1264.27		79097.1	${}^3G_5 - {}^3G_4'$	8
2256.17	6	44322.9	$b^3F_4' - {}^3F_3$	4	1263.65	20	79135.8	${}^3G_3 - {}^3G_3'$	8
2252.70	15	44391.2	${}^5F_5' - {}^5G_5'$	3	1263.11	5	79169.6	$a^3F_5' - {}^3D_3'$	7
2252.18	60	44401.4	${}^5F_2' - {}^5G_3'$	3	1261.91	30	79244.9	${}^3G_4 - {}^3G_4'$	8
2249.62	8	44451.9	$b^3F_3' - {}^3F_2$	4	1259.52	8	79395.3	${}^3G_3 - {}^3G_4'$	8
2244.83	70	44546.8	${}^5F_3' - {}^5G_4'$	3	1259.10	40	79421.8	${}^3G_5 - {}^3G_5'$	8
2238.25	60	44677.6	$b^3F_4' - {}^3F_4$	4	1256.85	2	79564.0	${}^3G_4 - {}^3G_5'$	8
2236.62	80	44710.4	${}^5F_4' - {}^5G_5'$	3	1238.60	40	80736.3	${}^3G_3 - {}^3F_2$	9
2234.45	50	44754.8	$b^3F_5' - {}^3F_3$	4	1236.23	50	80891.1	${}^3G_4 - {}^3F_3$	9
2232.46	40	44793.6	$b^3F_2' - {}^3F_2$	4	1233.99	tr	81037.9	${}^3G_3 - {}^3F_3$	9
2227.40	100	44895.4	${}^5F_5' - {}^5G_6'$	3	1233.04	60	81100.3	${}^3G_5 - {}^3F_4$	9
2217.53	2	45095.3	$b^3F_2' - {}^3F_2$	4	1230.84	tr	81245.3	${}^3G_4 - {}^3F_4$	9
2216.92	2	45107.6	$b^3F_3' - {}^3F_4$	4	1229.52	10	81332.5	$a^3F_3' - {}^3G_3'$	10
2129.95	2	46949.4	${}^5F_5' - {}^5F_4$	5	1228.67	15?	81388.8	$a^3F_2' - {}^3G_3'$	10
2126.37	5	47028.6	${}^5F_4' - {}^5F_3$	5	1226.81	8	81512.2	$a^3F_4' - {}^3G_4'$	10
2123.50	5	47092.1	${}^5F_3' - {}^5F_2$	5	1225.69	20	81586.7	$a^3F_3' - {}^3G_4'$	10
2121.09	10	47145.6	${}^5F_2' - {}^5F_1$	5	1221.97	20	81835.1	$a^3F_4' - {}^3G_5'$	10
2118.27	60	47208.3	${}^5F_5' - {}^5F_5$	5	1205.79	2	82933.2	$a^3F_3' - {}^3F_2$	11
2115.60	50	47267.8	${}^5F_4' - {}^5F_4$	5	1204.97	30	82989.6	$a^3F_2' - {}^3F_2$	11
2115.00	20	47281.3	${}^5F_1' - {}^5F_1$	5	1202.49	8	83160.7	$a^3F_4' - {}^3F_3$	11
2114.50	60	47292.5	${}^5F_3' - {}^5F_3$	5	1201.41	40	83235.5	$a^3F_3' - {}^3F_3$	11
2114.50		47292.5	${}^5F_2' - {}^5F_2$	5	1200.61	2	83291.0	$a^3F_2' - {}^3F_3$	11
2108.43	10	47428.7	${}^5F_1' - {}^5F_2$	5	1197.42	50	83512.8	$a^3F_4' - {}^3F_4$	11
2105.61	15	47492.2	${}^5F_2' - {}^5F_3$	5	1196.33	2	83589.0	$a^3F_3' - {}^3F_4$	11

dicted and identified approximately $12,000 \text{ cm}^{-1}$ higher than the corresponding multiplet in Cr III. The wave-lengths, relative intensities, and frequencies of the lines thus identified are given in multiplet form in Table XIX. The quintet multiplet ${}^5G' - {}^5H'(3d^34p - 3d^34d)$ for Mn IV, although the frequencies of the radiated lines are quite accurately predictable in the region

of 1200 A.U., has not been definitely identified owing to its low intensity even with long exposures.

TABLE XIX. *Triply ionized manganese, Mn IV.*

		$({}^5F' - {}^5G'(3d^34s - 3d^34p))$				
		${}^5F_5'$ 475 1375	${}^5F_4'$ 394 900	${}^5F_3'$ 302 506	${}^5F_2'$ 204 204	${}^5F_1'$ 000
${}^5G_6'$	58775	200 1742.17 57399.7				
	786	90 1766.36 56613.6	150 1751.65 57089.0			
${}^5G_4'$	57328	661 tr 1787.21 55953.1	30 1772.17 56428.0	120 1759.87 56822.4		
	56793	535	1 1789.16 55892.1	30 1776.62 56286.6	100 1767.13 56588.9	
${}^5G_2'$	56383	410		0 1789.64 55877.2	10 1780.02 56179.1	90 1773.57 56383.4

Quadruply ionized iron, Fe V. Just as for Cr III and Mn IV the quintet multiplet ${}^5F' - {}^5G'(3d^34s - 3d^34p)$ was predicted and identified approximately 12,000 cm^{-1} higher than in the preceding element. The wave-lengths, re-

TABLE XX. *Quadruply ionized iron, Fe V.*

		${}^5F' - {}^5G'(3d^34s - 3d^34p)$				
		${}^5F_5'$ 669 1953	${}^5F_4'$ 573 1284	${}^5F_3'$ 427 711	${}^5F_2'$ 284 284	${}^5F_1'$ 000
${}^5G_6'$	71858	100 1430.51 69905.1				
	1152	30 1454.48 68753.1	80 1440.47 69421.8			
${}^5G_4'$	69735	971 ? 1475.32 67781.9	10 1460.89 68451.4	60 1448.77 69024.1		
	68960	775	? 1477.63 67675.9	5 1465.21 68249.6	45 1456.11 68676.1	
${}^5G_2'$	68375	585		? 1477.91 67663.1	5 1468.63 68090.7	30 1462.53 68374.7

lative intensities, and frequencies of the lines thus identified are given in multiplet form in Table XX.

The irregular doublet law. The irregular doublet law, wherever applicable, proves to be the most powerful method of attack in attempting to analyze the spectra arising from ionized atoms. The irregular doublet law is applicable to those radiated lines arising from electron transitions involving no

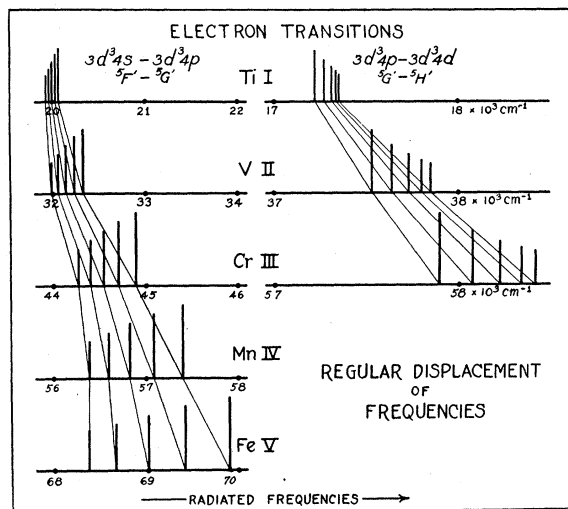


Fig. 8. Irregular doublet law.

change in total quantum number. For sequences of iso-electronic systems involving only one valence electron (i.e. K I, Ca II, Sc III, etc.) an electron transition gives rise to only two or three radiated lines. In the sequence starting with Ti I, however, where four valence electrons are involved and electron transition may give rise to over a hundred radiated lines. In this

TABLE XXI. *Irregular doublet law.*

Atom	$3d^3 4s - 3d^3 4p$ ${}^5F_6 - {}^5G_6 \Delta\nu$	$3d^3 4s - 3d^3 4p$ ${}^3F_4 - {}^3G_5 \Delta\nu$	$3d^3 4p - 3d^3 4d$ ${}^5G_6 - {}^5H_7 \Delta\nu$
Ti I	20068	15973	17224
V II	32321	30515	37535
Cr III	44895	42999	57897
Mn IV	57399	*55687	*78300
Fe V	69905	(68567)	(98734)

* Not definitely identified.

report on the latter sequence of iso-electronic systems only a few of the strongest lines have been traced through five elements. For the electron transition $3d^3 4p$ to $3d^3 4s$ about forty lines, and for the electron transition $3d^3 4d$ to $3d^3 4p$ about twelve lines, have been traced through the first three

elements, Ti I, V II, and Cr III. Examples of the almost linear progression in frequency of these radiated lines may be seen in Table XXI where the lines ${}^5F_5' - {}^5G_6'$ and ${}^3F_4' - {}^3G_5'$ are chosen to represent the electron transition $3d^34p$ to $3d^34s$ and the line ${}^5G_6' - {}^5H_7'$ chosen to represent the electron transition $3d^34d$ to $3d^34p$. This almost linear progression is best brought out graphically as in Fig. 8. Each frequency scale, although the same for each element and corresponding multiplet, has been displaced to the left of the one just preceding it by $12,000\text{ cm}^{-1}$ and $20,000\text{ cm}^{-1}$ for the two electron transitions respectively.

Term separations, the Landé interval rule, and Hund's rule. The systematic increase in term separations in going from one element to the next for one set of terms from each of the two electron configurations $3d^34s$ and $3d^34p$ is shown in Table XXII. In the lower half of the table it is seen that the Landé interval rule for quintet terms is in general in agreement with the observed separations.

TABLE XXII. *Quintet term separations.*

Atom	$3d^34s$				$3d^34p$			
	${}^5F_1'$	${}^5F_2'$	${}^5F_3'$	${}^5F_4'$ ${}^5F_5'$	${}^5G_2'$	${}^5G_3'$	${}^5G_4'$	${}^5G_5'$ ${}^5G_6'$
Ti I	42	62	82	100	70	93	116	148
V II	82	122	159	194	153	201	246	290
Cr III	136	200	263	319	264	347	425	504
Mn IV	204	302	394	475	410	535	661	786
Fe V	284	427	573	669	585	775	971	1152
Theor.	2.0	3.0	4.0	5.0	3.0	4.0	5.0	6.0
Ti I	2.1	3.1	4.1	5.0	2.8	3.8	4.7	6.0
V II	2.1	3.1	4.1	5.0	3.2	4.2	5.1	6.0
Cr III	2.1	3.1	4.1	5.0	3.1	4.1	5.1	6.0
Mn IV	2.1	3.2	4.2	5.0	3.1	4.1	5.0	6.0
Fe V	2.1	3.2	4.3	5.0	3.0	4.0	5.0	6.0

Hund's rule for relative term positions gives a satisfactory account of the terms thus far identified. All of the terms given in this report are built upon, and therefore have as a limit, the ${}^4F'(3d^3)$ terms of the once more ionized atoms.

Energy levels and the Moseley law. Combining the data now available for Ti I, and V II, and the data here given for Cr III, Mn IV, and Fe V, the same type of *energy level Moseley diagram* may be drawn for the triplet and quintet terms of these spectra as was drawn for the doublet and quartet terms of the sequence Sc I to Mn V, Fig. 5⁶ for the singlet and triplet terms of the sequence Ca I to Cr V, Fig. 4⁷ and for the doublet terms of the sequence K I to V V, Fig. 1⁷. This type of diagram is shown in Fig. 9 for all four of the above mentioned sequences.

For each electron configuration shown in the diagram, including the limits, a point has been plotted for the term involving the largest R , L ,

⁶ White, Phys. Rev. **33**, 672 (1929)

⁷ White, Phys. Rev. **33**, 538 (1929).

The multiplet structure of ${}^5F' - {}^5G'(3d^34s - 3d^34p)$. The characteristic wavelength separations and relative intensities of the diagonal lines in the

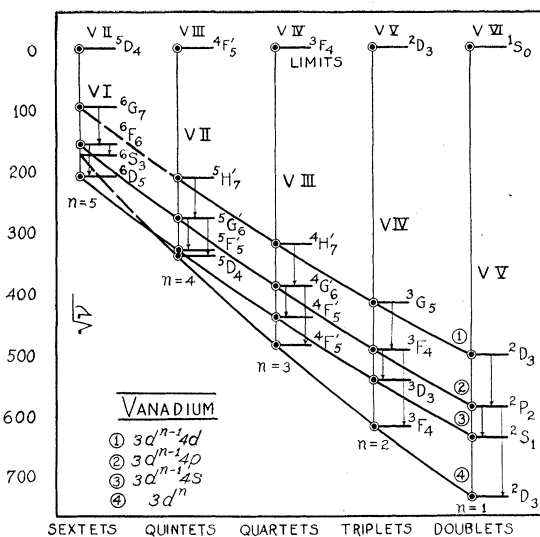


Fig. 10. A new energy level relation.

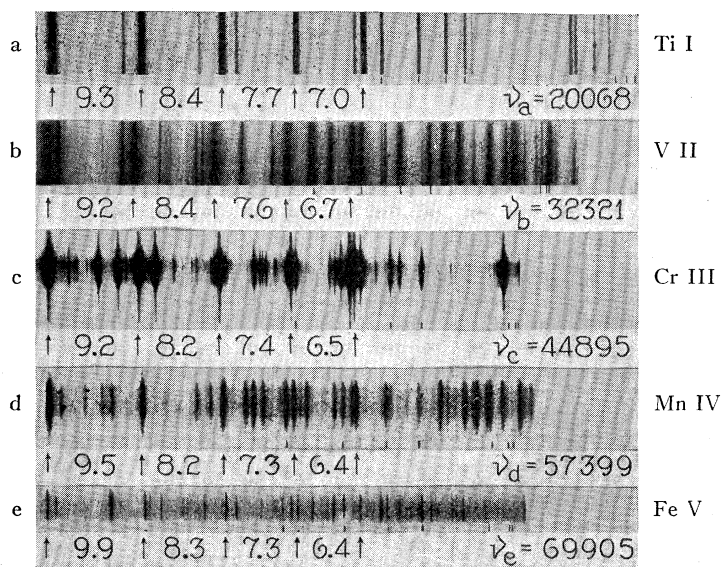


Fig. 11. Quintet multiplets.

${}^5F' - {}^5G'(3d^34s - 3d^34p)$ multiplet for Ti I to Fe V are almost identical. This multiplet is so easily recognized by sight that for Cr III, Mn IV and

Fe V the diagonal lines were identified on the spectrograms before any wave-length determinations were made. Owing to this striking similarity this multiplet, for each of the five elements Ti I, V II, Cr III, Mn IV, and Fe V, has been enlarged from the original plates to exactly the same scale of wave-lengths and reproduced in Fig. 11. It is interesting to note in this figure the different types of spectra present. The first three spectra, the titanium arc spectrum, the vanadium spark spectrum and the chromium vacuum spark spectrum were taken on the same apparatus with the same dispersion and have been enlarged about six times. The last two, spectra of manganese and iron were taken with a vacuum spectrograph and are enlarged about 15 times. The wave-numbers for the strongest line (given at the right and below each multiplet) are the ones given in Column 2, Table XXI, which indicates the almost linear progression of frequency with atomic number, Fig. 8. The constancy of $\Delta\lambda$ between the diagonal lines indicated in Fig. 11 is a characteristic which also appears in the corresponding quartets, triplets, and doublets of the sequences mentioned above starting with Sc I, Ca I, and K I. This constancy in the value of $\Delta\lambda$ for all four sequences is shown in Table XXIII.

TABLE XXIII. Wave-length separations of diagonal lines. ($\Delta\lambda$ in A.U.)

$3d^34s-3d^34p$ ${}^6F'-{}^6G'$				$3d^24s-3d^24p$ ${}^4F'-{}^4G'$				
Atom				Atom				
Ti I	9.3	8.4	7.7	7.0	Sc I	15.0	13.3	11.6
V II	9.2	8.4	7.6	6.7	Ti II	11.8	11.6	11.0
Cr III	9.2	8.2	7.4	6.5	V III	11.4	11.1	10.6
Mn IV	9.5	8.2	7.3	6.4	Cr IV	11.8	11.2	10.8
Fe V	9.9	8.3	7.3	6.4	Mn V	12.4	11.4	11.3

$3d4s-3d4p$ ${}^3D-{}^3F$			$4s-4p$ ${}^2S-{}^2P$	
Atom			Atom	
Ca I	23.5	3.12	K I	34.1
Sc II	16.9	12.0	Ca II	34.8
Ti III	11.8	12.0	Sc III	35.0
V IV	12.4	11.6	Ti IV	35.6
Cr V	12.0	11.5	V V	36.5

The analysis of complex spectra as exemplified by Ti I (the lines of which are nearly all accessible with existing high dispersion apparatus) when extended to Cr III, Mn IV, etc. must rely upon spectrograms taken with relatively small vacuum spectrographs. In working with these complex spectra of atoms in the higher states of ionization one cannot help but feel the need for vacuum spectrograms taken with much higher dispersion and resolving power. Since in the vacuum region the frequencies of lines increase so rapidly in going toward shorter wave-lengths, and since analysis of spectra depends upon the frequency separations, apparatus capable of giving higher disper-

sion and resolving power must be constructed before much progress can be made in identifying high frequency spectral lines.

The author wishes to take this opportunity to express his appreciation and indebtedness to Professor R. C. Gibbs for his valuable advice and criticism in carrying on this investigation as well as those of the two preceding papers under the same general title.

CORNELL UNIVERSITY,
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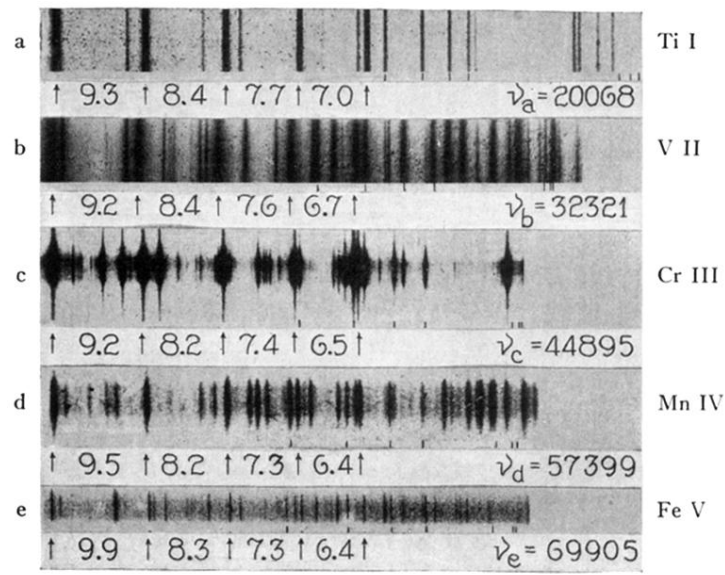


Fig. 11. Quintet multiplets.