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Series and Other Regularities in the Spectrum of Manganese

Miguel A. Catalan

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IV. *Series and Other Regularities in the Spectrum of Manganese.*

By Miguel A. Catalán, *D.Sc.* (*Madrid*); *Research Student, Imperial College, South Kensington.*

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1.—Introductory.

The discovery of the laws which govern the distribution of lines in spectra is of great importance in relation to the problem of the structure of the atom. Up to the present time nearly all the work on the regularity in the arrangement of spectral lines has dealt with spectra which have a relatively small number of lines. Important laws have

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been found which include most of the lines in these spectra, but in nearly all cases there remain some prominent lines whose relation to the regular series is not yet clear. It seemed possible that the careful study of a spectrum rich in lines would lead to the discovery of new or more general laws than those which have been found for elements comparatively poor in lines, and so enable us to classify many other spectra, and at the same time to interpret the lines which at present remain unclassified in those spectra with fewer lines. It was with this object that the present work was undertaken.

The spectrum of manganese was chosen, because there were already some indications of series in this spectrum, analogous to those found in other elements, and it would naturally seem to make a good starting point.

The results obtained have exceeded expectations. The study of the manganese spectrum has not only led to an interpretation of this spectrum itself, but has also indicated new view-points that will probably aid in the analysis of other spectra containing many lines, as well as of the unclassified lines in spectra for which the series are best known. The detailed evidence is set forth in the pages which follow.

2.—Bibliography.

The spectrum of manganese has been much studied. Kayser* has summarised the work published previous to 1910. Fuchs† has remeasured the arc spectrum, from λ2289 to λ7070, giving wave-lengths in I.A. to the third decimal place and has summarised the work during the period 1910 to 1915. Takamine and Nitta‡ have measured the spark spectrum, from λ1842 to λ2000. Randall and Barker§ have published infra-red measures of the arc spectrum, from λ8672 to λ17609, on the Rowland scale. Meggers and Kiess|| have given wave-lengths in I.A., to the second decimal place, from λ5500 to λ9600. Hemsalech¶ has studied the character of the light-radiations emitted by the vapour of manganese under selective actions of thermo-chemical and thermo-electrical excitations. Lately, while this investigation was in progress, the work of King** on the variation with temperature of the electric furnace spectrum of manganese came to hand.

3.—Experimental Procedure.

The following instruments have been used in the present work: (1) A spectrograph of the "Littrow" form having a glass prism, giving a linear dispersion of 16A. per mm. at λ6300 and 5·5A. per mm. at λ4700.

* 'Handbuch der Spectroscopie,' vol. 5, p. 726 (1910).

† 'Zeit. f. Wiss. Phot.,' vol. 14, pp. 239–248 and 263–280 (1915).

‡ 'Mem. College of Science,' Kyoto University, vol. 2, p. 131 (1917).

§ 'Astroph. Journ.,' vol. 49, p. 59 (1919).

|| 'Sc. Papers, Bureau of Standards,' No. 372 (1920).

¶ 'Phil. Mag.,' vol. 40, p. 296 (1920).

** 'Astroph. Journ.,' vol. 53, p. 133 (March, 1921).

(2) A "Littrow" spectrograph with quartz prism. The linear dispersion is 12A. per mm. at λ4000, 4·5A. per mm. at λ3000 and 2A. per mm. at λ2300.

(3) A concave grating of 10 feet radius having 14,438 lines per inch. The length of the ruled surface is 3·5 inches. This grating is arranged with the Abney mounting, giving a normal dispersion of 5·5A. per mm. in the first order. Photographs have been made in the first, second, and third orders.

The flame-arc, arc, and spark have been used as sources. For the arc, two electrodes of metallic manganese were found to be unsatisfactory because strong enhanced lines appeared mixed with the arc lines; also because the arc is very unsteady, the metal scattering in the air in small burning pieces. Better results were obtained by introducing a lump of manganese chloride (previously melted and desiccated) between carbon poles, the current being obtained from the 110-volt lighting circuit. The arc thus obtained consists of two regions; the inner part is blue-grey and very bright, while the surrounding outer part is green and not so bright. By mixing manganese chloride with sodium chloride and introducing a quantity of this into the carbon arc a very long arc-flame was obtained which was found to be very satisfactory for the detection of flame lines. For the spark spectrum electrodes of metallic manganese about 1 mm. apart were quite satisfactory. The plates used were "Imperial ordinary" for λ2400 to λ4500. In the green part of the spectrum Marion's "Iso-record" were found to be very sensitive, and for red, Wratten and Wainwright's "panchromatic" were used.

In general FUCHS's measures have been adopted because they were found to be sufficiently accurate. In some cases, however, the measures of KILBY,* or of EXNER and HASCHEK† have been employed. Some new lines have been measured and some existing measures have been amended. For these purposes the spectrum of the iron arc was photographed as a comparison, the wave-lengths being taken from BURNS.‡

The wave-lengths of the manganese lines were corrected to vacuum by the data given by MEGGERS,§ and from these the wave-numbers were calculated by taking reciprocals.

Impurities.—During the present work several lines were found in the tables which seem to be due to impurities, and it may be useful to give a list of them.||

* 'Astroph. Journ.,' vol. 30, p. 243 (1909).

† 'Tabelle der Bogenspectra,' Wien, 1904, and 'Tabelle der Funkenspectra,' Wien, 1902.

‡ 'Zeit. f. Wiss. Phot.,' vol. 12, p. 219 (1913), and 'Lick Obs. Bull.,' vol. 8, No. 247 (1913).

§ 'Bureau of Standards, Washington,' No. 327 (1918).

|| In BURNS's tables of the iron spectrum there are also some lines which seem to be due to impurities, namely :—

λ (BURNS).	Int.	Probable Element.	λ (I.A.)	Int.	Remarks.
3395·382	(1)	Co	3395·377	(8)	Wave-lengths by HAMM, measured in the nickel spectrum as impurity lines. ['Zeit. f. Wiss. Phot.,' vol. 13, p. 130 (1913).]
3433·049	(2b)	Co	3433·044	(10)	
3443·645	(1)	Co	3443·650	(10)	
3449·447	(1)	Co	3449·446	(10)	
3798·259	(1)	Mo	3798·259	(10R)	Wave-lengths by PUHLMANN. ['Zeit. f. Wiss. Phot.,' vol. 17, p. 97 (1917).]
3864·110	(1)	Mo	3864·115	(10R)	
3961·534	(1)	Al	3961·538	(10)	Wave-length by GRUNTER. ['Zeit. f. Wiss. Phot.,' vol. 13, p. 1 (1913).]

λ (Fuchs).	Int.	Probable Element.	λ (I.A.).	Int.	λ (Fuchs).	Int.	Probable Element.	λ (I.A.).	Int.
2795·525	(2)	Mg	2795·53	(10)	3961·534	(1)	Al	3961·538	(10R)
2833·056	(1*u*)	Pb	2833·066	(10R)	3968·471	(1)	Ca	3968·479	(10R)
2839·999	(1)	Sn	2839·985	(10R)	4226·728	(3)	Ca	4226·730	(10R)
3247·545	(2)	Cu	3247·552	(10R)	4302·527	(2)	Ca	4302·528	(10R)
3349·406	(1)	Ti	3349·409	(10R)	5183·625	(1)	Mg	5183·60	(10R)
3361·215	(1)	Ti	3361·219	(10R)	5889·929	(1)	Na	5889·965	(10R)
3371·458	(1)	Ir	3371·460	(8)	5895·924	(1)	Na	5895·932	(10R)
3502·289	(1)	Co	3502·285	(10R)	6122·248	(2)	Ca?, Co?	6122·24	(10)
3683·473	(1)	Pb	3683·474	(6R)	6162·199	(1)	Ca?, Co?	6162·18	(9)
3798·262*	(1)	Mo	3798·259	(10R)	6384·687	(3)	Ni	6384·690	(5*u*)
3864·107*	(3)	Mo	3864·115	(10R)	6707·836	(4)	Li	6707·82	(10R)
3933·663	(1)	Ca	3933·674	(10R)					

4.—The Spectrum of the Neutral Atom of Manganese.

According to Bohr's theory, all series lines which follow a formula of the type

$$\nu = \text{A} - \text{N}/[f(m)]^2,$$

in which N has nearly the same value as that deduced from the hydrogen series, namely

$$\text{N} = \frac{2\pi^2 e^2 m}{ch^3} e^2,$$

are produced under a comparatively low stimulus by the quantum changes of orbit of the outermost electron, the nucleus and the remaining electrons behaving as a simple positive charge. These lines include the flame lines and the majority of the lines which occur in the arc. This spectrum will be regarded as the spectrum of the *neutral atom.*

There is another spectrum constituted of lines which are only developed, or are developed with maximum intensity, when more violent methods of excitation are used. This spectrum consists of the enhanced lines, which relatively increase in strength in passing from the arc to the spark. Fowler† has shown that these lines form series of Rydberg type, but in the formula the constant " N " must be changed to " 4N." According to Bohr's theory this spectrum is emitted by the quantum changes of orbit of the now outermost electron of an atom which has lost an electron, the nucleus and the remaining electrons then behaving as a double positive charge, so that the constant becomes

$$\frac{2\pi^2 e^2 m}{ch^3} (2e)^2 = 4\text{N}.$$

This spectrum will be regarded as originating in the *ionised atom.*

* These lines are not found in Fuchs's tables, but are given by Kilby.

† 'Phil. Trans.,' A, vol. 214, p. 225 (1914).

(*a*)—*The Ordinary Triplet System and Combination Lines.*

In the arc spectrum of manganese KAYSER and RUNGE* found five triplets with separations about 173 and 129, and arranged them in two series, one sharp and one diffuse. The formulæ given by these observers were

$$\nu = 41223 \cdot 86 - 125229n^{-2} - 1377549n^{-4}; \text{ (Diffuse series)}$$
$$\Delta\nu_1 = 172 \cdot 07; \ \Delta\nu_2 = 129 \cdot 14;$$
$$\nu = 41222 \cdot 15 - 119890n^{-2} - 580770n^{-4}; \text{ (Sharp series)}$$
$$\Delta\nu_1 = 173 \cdot 78; \ \Delta\nu_2 = 129 \cdot 14;$$

An attempt has been made to extend these series, but a considerable difficulty arose from the fact that the manganese spectrum is very rich in lines and that such expected triplets would probably be very faint. Additional triplets, however, have been recognised, as shown in Table I.

Sharp series, $1p - ms$.—The first two triplets of this series were traced by KAYSER and RUNGE. The observations of JANICKI† on the structure of the manganese lines show the lines of the first triplet to be quite simple and sharp (see Plate 1, fig. 5). The lines are fairly strong at low temperatures and are present in many other spectra as impurity lines. The three lines were measured in the iron spectrum by KILBY‡ and the wave-lengths in the table have been quoted from his measurements. The wave-lengths for the second member of the sharp series (see Plate 1, fig. 4) entered in the table are quoted from FUCHS.

The first line of the third triplet is doubtful, because it is masked by another line very close to it; the other two lines as measured by FUCHS give the expected separation very accurately. The fourth triplet includes two lines observed by EXNER and HASCHEK and by FRITSCH§ which have now been remeasured; the third line is very faint and has not previously been recorded.

There are three other lines with separations very near to those of the triplet and at a position suitable for the fifth triplet of the sharp series, but the intensities are not in the usual order.

The following HICKS formula has been calculated from the first components of the first three triplets of the sharp series:

$$s(m) = 41217 \cdot 17 - \frac{109678 \cdot 3}{\left[m + 1 \cdot 427114 - \dfrac{0 \cdot 227155}{m+1}\right]^2}.$$

* 'Abh. Berl. Akad.' (1894).

† 'Ann. d. Physik,' vol. 29, p. 849 (1909).

‡ *Loc. cit.*

§ 'Ann. d. Physik,' vol. 16, p. 793 (1905).

TABLE I.—The Ordinary Triplet Series of Manganese.

PRINCIPAL.—$1s-mp$.
$1s=20506\cdot13$.

λ.	Int.*	ν.	Δν.	m.	$mp_{1,2,3}$.
—4823·522 —4783·432 —4754·048	(10R) (9R) (9R)	—20725·96 —20899·67 —21028·85	*173·71* *129·18*	(1)	41232·09 405·80 534·98
15263·1	—	6550·0	—	(2)	13956·1
7646·34 51·91 56·24	(3*n*) (3*n*) (2*n*)	13074·56 65·04 57·66	*9·52* *7·38*	(3)	7431·57 41·09 48·47
6315·064	(2)	15830·78	—	(4)?	4675·35

SHARP.—$1p-ms$.
$1p_1=41232\cdot09$ $1p_2=41405\cdot80$ $1p_3=41534\cdot98$

λ.	Int.	ν.	Δν.	m.	ms.
4823·522 4783·432 54·048	(10R) (9R) (9R)	20725·96 20899·67 21028·85	*173·71* *129·18*	(1)	20506·13
3178·508 61·055 48·192	(6) (5) (4)	31452·24 625·87 755·09	*173·63* *129·22*	(2)	9779·89
2818·09† 04·35 2794·23	(3) (2) (2)	35474·8 648·3 777·5	*173·5* *129·2*	(3)	5757·4
2670·22‡ 57·88‡ 48·79§	(2) (1) (1)	37439·0 612·8 741·8	*173·8* *129·0*	(4)	3793·1
2595·77 84·12 75·51	(4) (3) (5)	38512·7 686·4 815·6	*173·7* *129·2*	(5)?	2719·4

DIFFUSE.—$1p-md$.
$1p_1=41232\cdot09$ $1p_2=41405\cdot80$ $1p_3=41534\cdot98$

λ.	Int.*	ν.	Δν.	m.	$md^{1,2,3,4,5}$.
3570·034‖ 69·798‖ 69·499‖ 3548·180‖ 48·024‖ 47·792‖ 3532·110‖ 31·990‖ 31·833‖	(7R) (9R) (10R) (7·5R) (8R) (8·5R) (8R) (7·8R) (7·5R)	28002·97 004·82 007·16 28175·44 176·68 178·52 28303·68 304·58 305·85	*1·85* *2·34* *173·71* *1·24* *1·84* *129·17* *0·90* *1·27*	(2)	md^1=13224·93 md^2= 227·27 md^3= 229·12 md^4= 230·38 md^5= 231·30
2940·51 25·59 14·62	(7*n*) (6*n*) (6*n*)	33997·8 34171·2 34299·8	*173·4* *128·6*	(3)	7234·7
2726·15 13·35 03·98	(4*n*) (3*n*) (3*n*)	36670·9 844·0 972·6	*173·1* *128·6*	(4)	4561·8
2624·80 12·86 04·21§	(2) (2) (1)	38086·7 260·8 389·4	*174·1* *128·6*	(5)	3145·3

FUNDAMENTAL.—$2d-mf$.
$2d^1=13224\cdot93$.

λ.	ν.	m.	mf.
15964·9	6262·0	(3)	6962·9
11377·9	8786·6	(4)	4438·3

COMBINATION LINES.

λ.	Int.	ν.	ν calc.
3664·624	(1)	27280·18	$1p_1-2p=27276\cdot0$
3642·662	(1)	27444·65	$1p_2-2p=27449\cdot7$
7383·59	(1)	13539·82	$1s-3f=13543\cdot2$

* In this column, R=reversed, *n*=nebulous. † This line is masked by another line very close to it.
‡ Observed by EXNER and HASCHEK and by FRITSCH; now remeasured. § Observed by the Author.
‖ Remeasured in third order spectrum by the Author.

The residuals given by this formula in ν observed $-\nu$ calculated are

$$\begin{array}{rccccc} m = & 1 & 2 & 3 & 4 & 5\,? \\ \nu(\mathrm{O}-\mathrm{C}) = & +0\cdot01 & 0\cdot00 & +0\cdot01 & +8\cdot76 & +17\cdot51\,? \end{array}$$

It is interesting to note that the members of this series are not far removed from the corresponding members of the sharp triplet series of magnesium, the terms being closely similar in the two series.

Diffuse series, $1p-md$.—KAYSER and RUNGE traced the first three members of this series, as shown in Table I. The first in their list was composed of three lines, $\lambda\lambda$3569·95, 3548·16 and 3531·95 (Rowland scale), and it was remarked that the triplet was possibly more complex. There are in fact six other lines close to these three which must certainly be considered to form part of the diffuse triplet. The wave-lengths given for these lines by different observers differ considerably, as will be seen from Table II. A difficulty is caused by the fact that the lines are grouped together in sets of three, and in each set the lines are very close together; also the lines are very diffuse and with a strong tendency to reversal, so that their resolution is difficult. In a further attempt to improve the measures the best results were obtained in the third order spectrum, using the arc between carbon poles with a small quantity of manganese salt in order to prevent the reversal of the lines by the vapour round the crater. The results are shown in Plate 1, fig. 2. The original photograph is here enlarged about 12 diameters, but as the distances between the three sets are relatively very large, the groups are not shown in their true positions in the Plate, but are placed at distances proportional to their real separations.

The wave-lengths of these lines have been measured, and the results are compared with the values given by other observers in Table II.

TABLE II.—Wave-lengths of Components of First Diffuse Triplet.

λ CATALÁN. Int.	λ KILBY. Int.	λ FUCHS. Int.	λ E. & H.* Int.	λ BURNS.†	λ HAMM.‡	λ ROWLAND (in sun).§
3570·034 (7R)	·061 (4)	·101 (4)	·02 (4)	·024	·020	·033 (4)
69·798 (9R)	·796 (8)	·799 (8R)	·80 (10R)	—	—	·808 (2)
69·499 (10R)	·485 (5)	·495 (6R)	·46 (15R)	—	—	·499 (4)
48·180 (7½)	·187 (4)	·186 (4R)	·18 (4R)	—	—	·182 (5)
48·024 (8)	·025 (4)	·022 (4R)	·03 (10R)	·024	·020	·025 (3)
47·792 (8½R)	·790 (5)	·792 (5R)	·76 (10R)	—	·793	·791 (5)
32·110 (8R)	·128 (5)	·109 (5R)	·20 (5R)	—	—	·112 (3)
32·990 (7½R)	3·002 (5)	2·999 (5R)	2·94 (3)	—	—	2·993 (4)
31·833 (7½)	·839 (5)	·838 (4R)	—	—	—	·832 (3)

* EXNER and HASCHEK, corrected from Rowland scale to I.A.

† BURNS's measures in the arc spectrum of iron, 'Zeit. f. Wiss. Phot.,' vol. 12, p. 233 (1913).

‡ HAMM's measures in the arc spectrum of nickel, 'Zeit. f. Wiss. Phot.,' vol. 13, p. 130 (1914).

§ Measures of the corresponding Fraunhofer lines, corrected to I.A.

It will be noted that the new measures are in close accordance with those given by ROWLAND for the solar lines. The chief exception is the second line, differing by 0·010A., but the new measure agrees with the values given by KILBY and others. The lines λλ3548·024 and 3547·792 have nearly the same values in all the measures, but the remaining lines show considerable discordances.

The wave-numbers calculated from the new wave-lengths are stated in Table I. It will be seen that the separations of the first and fifth and of the fifth and ninth are practically identical with those of the first sharp triplet, $s(1)$, and that the same two intervals separate the second and sixth and the fourth and eighth lines. The diagram (fig. 1) illustrates these relations and shows also, for comparison, a diffuse triplet typical

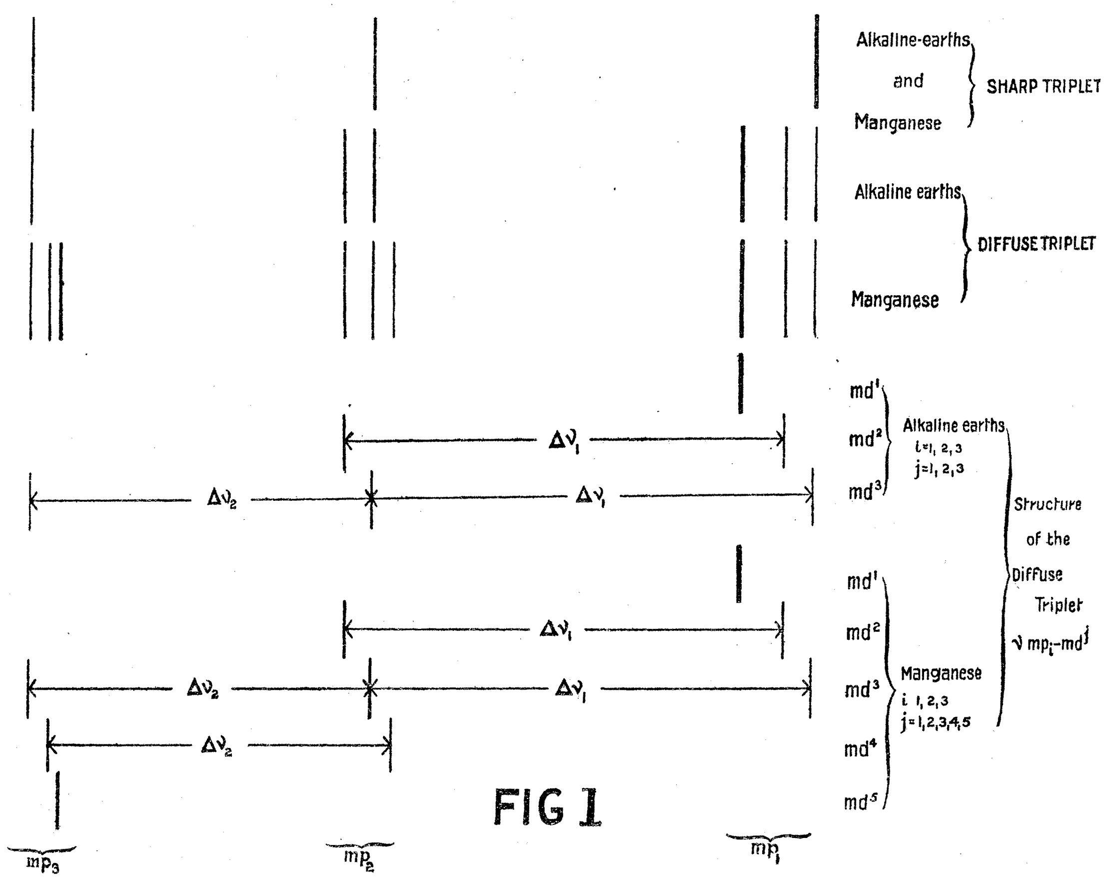

FIG 1

of alkaline-earth spectra. For clearness, the distances between the satellites have been magnified in the diagram, but their proportionality has been retained. For the same reason the diffuse triplet representing the alkaline-earth spectra is not an actual triplet, but has been drawn with arbitrary separations in order to make clearer the relation with manganese. The thicknesses of the lines are approximately proportional to the relative intensities. The structures of the two types of diffuse triplet are further shown by the analysis in the lower part of the diagram. The symbols $\Delta\nu_1$ and $\Delta\nu_2$ here represent the larger and smaller separations of the sharp triplet. The terms shown on the right of the diagram are those which originate the lines by combination with the terms indicated at the bottom. It is to be noted that in manganese the diffuse term has five values, as compared with three in the case of the more familiar triplets. All the possible combinations of the terms mp and md, however, do not occur as real lines. If for simplicity, j, i, denote the combination $mp_i - md^j$, the lines which actually appear have the following values of j, i:—

Alkaline-earths.			*Manganese.*				
		3,1			3,1	4,1	5,1
	2,2	3,2		2,2	3,2	4,2	
1,3	2,3	3,3	1,3	2,3	3,3		

Thus, using the actual values of the wave-numbers, the first diffuse triplet of manganese may be represented as follows :—

				(7½R)		(8R)		(8R)
				28305·85	*1·27*	28304·58	*0·90*	28303·68
				129·17		*129·14*		
		(8½R)		(8R)		(7½R)		
		28178·52	*1·84*	28176·68	*1·24*	28175·44		
		173·70		*173·71*				
(10R)		(9R)		(7R)				
28007·16	*2·34*	28004·82	*1·85*	28002·97				

The numbers in brackets represent the relative intensities of the lines, and those in italics the differences between the wave-numbers.

It will be observed that the most intense line is the combination 1,3, the faintest line is 3,3, and also that 5,1 is more intense than 3,1.

The lines of the second and third triplets in the diffuse series are broad and probably complex, but they have not been resolved. The values in Table I. are quoted from FUCHS's measures. There are two other lines in the tables which give the separation $\Delta\nu_1$, and these with another faint line, now measured for the first time, constitute the fourth diffuse triplet.

The first lines of the first three members of the diffuse series give the following formula :—

$$d^3(m) = 41247 \cdot 01 - \frac{109678 \cdot 3}{\left[m + 0 \cdot 913578 + \frac{0 \cdot 071699}{m}\right]^2}.$$

The residuals are :—

$m =$	2	3	4	5
ν (O−C) $=$	−0·01	0·00	0·00	+18·70

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In Table I., the adopted value of $1p_1$ is the mean of the limits deduced from the sharp and diffuse series ; thus

$$\left.\begin{array}{ll}\text{Calculated limit of diffuse series :} & 41217\cdot17 \\ \text{Calculated limit of sharp series :} & 41247\cdot01\end{array}\right\}\text{mean value } 41232\cdot09 = 1p_1,$$

and, taking $\Delta\nu_1 = 173\cdot71 = 1p_2 - 1p_1$ and $\Delta\nu_2 = 129\cdot18 = 1p_3 - 1p_2$, the values $1p_2 = 41405\cdot80$ and $1p_3 = 41534\cdot98$ are obtained. The values of the terms $2s$, $3s$,.... and also $3d$, $4d$, ..., shown in Table I., are the respective differences between these limits and the wave-numbers of the observed lines. The value $m = 2$ has been assigned to the first observed diffuse members as indicated by the formula, and also from analogy with the diffuse series of magnesium, in which the limits and terms are very similar.

Principal series, $1s - mp$.—The first member of this series is, of course, the first member of the sharp series taken with negative sign. Since $1p$ is known, a rough value of the term $2p$ can be calculated from RYDBERG'S* tables, and as the limit $1s$ of this series is known, the value of $p(2)$ can be obtained approximately. As $1p_1 = 41232\cdot09$, $2p_1$ from RYDBERG'S tables is about 14200 and $1s - 2p_1$ is about $\nu 6500$. The second member of the principal series should be a triplet with smaller separations than $\Delta\nu_1$ and $\Delta\nu_2$. There are several lines in the infra-red but no triplet at all suitable to be $p(2)$. The strong line $\lambda 15263\cdot1$ or $\nu 6550\cdot0$, however, has been adopted as the probably unresolved triplet in question. The third member of the principal series must be expected, from RYDBERG'S tables, to be near $\lambda 7650$. In MEGGERS and KIESS'S measures there are three lines of the same character forming a triplet with appropriate intensities and separations which has been adopted as $p(3)$. There is another line, $\lambda 6315$, which falls in series with the above and has been included as possibly representing the next member. There is, however, no strong evidence to support the arrangement of the principal series as here suggested. As in magnesium, it is not to be expected that the intensities in the principal series will be at all comparable with those in the principal series of the alkali elements.

Fundamental series, $2d - mf$.—The limit of this series is the variable part or " term " of the first member of the diffuse series. In the alkaline-earths the three elements calcium, strontium, and barium which possess the term $1d$ have very strong series, $1d - mf$, and also a weak parallel series, $2d - mf$. On the contrary, magnesium, which apparently has no term $1d$, has only a relatively weak series, $2d - mf$. By analogy, as the term $1d$ has not been found in manganese, only a series $2d - mf$ is to be expected. As a matter of fact in all spectra the terms $3f$ and $4f$ ($1f$ and $2f$ never appear) have values close to 6950 and 4420 respectively. In manganese it is therefore to be expected that the lines $2d - 3f$ and $2d - 4f$ will be not far from $2d - 6950 = \nu 6279$ and $2d - 4420 = \nu 8809$. In the infra-red the lines nearest to $\nu 6279$ are $\nu\nu 6550\cdot0$, $6262\cdot0$, and $5767\cdot0$, but neither

* 'Kgl. Svenska Vetensk. Akad. Handl.,' vol. 23, No. 11, and also A. DEL CAMPO and M. A. CATALÁN, 'Anales Soc. Esp. Fis. y Quim.,' vol. 18, p. 118 (1920).

ν6550 nor ν5767 give a value of $3f$ near 6950. For this reason the very strong line ν6262, *i.e.* λ15964·9 (value of RANDALL and BARKER corrected to I.A.), has been selected for $f(3)$. Near ν8807 there is only one line, relatively faint, at λ11397·9 or ν8786·6, and it is suitable for $f(4)$.

If it is supposed that ν6262·0 and ν8786·6 are two consecutive members of a series, the approximate limit of this series may be calculated from RYDBERG's tables, giving a value 13233. This is very close to the adopted value $1d = 13225$ and supports the earlier conclusions. An objection may be raised that the f series must be complex, because the diffuse term is quintuple. But this objection can hardly be maintained when it is considered that the components of the members of this series would be very close together, and very probably are unresolved in the infra-red observations.

Combination lines in the triplet system.—Following RITZ's principle, the terms of the main series can be combined in various ways, and other series of lines are then obtained which are called "combination series." In the present case only series with limits $1p$, $2p$, $2d$, and $1s$ are to be expected, because the other terms are too small to serve as limits of series in the observed region. In some spectra the combination series $1p-mp$ is fairly strong, but in the alkaline-earths it is very faint. In manganese two lines are found, given in Table I., which correspond approximately with the combinations $1p_1-2p$ and $1p_2-2p$. As the term $2p$ must be triple it must not be expected to give very concordant results. Another combination series, fairly strong in some spectra, is $1d-mp$, but as the term $1d$ has not been found in manganese this series is not likely to be present. The series $2d-mp$ is out of the range photographed, and $2d-3p$ may be too faint for infra-red measures. Most of the remaining possible combinations are probably absent for similar reasons. The combination $1s-3f$, however (see Table I.), may possibly be present. The agreement of the calculated and observed values of this line is fairly good, if it is remembered that the term $3f$ has been calculated from a line which is probably complex and unresolved. Further, in the spectrum of magnesium, in which the terms are very similar to those of manganese, the number of combination lines is also very small.

(*b*)—*The Intercombination Lines* $1S-1p_2$ *and* $1S-1p_3$.

In the arc spectra of the alkaline-earth elements, in addition to triplet series, there are series of singlets and also certain "intercombination" lines, which are formed by terms from the triplet series combined with terms from the singlet series. Special attention must be given to the intercombination lines $1S-1p_2$ and $1S-1p_3$. It is very important to note that the combination line $1S-1p_1$ never appears and that the line $1S-1p_2$ is always stronger than $1S-1p_3$, and further that the line $1S-1p_2$ often occurs alone. This line has important characteristics. In magnesium, the line (λ4571) has long been recognised as being especially characteristic of the flame, and KING* has

* 'Astroph. Journ.,' vol. 48, p. 13 (1918).

lately shown that it is strongly developed in the electric furnace spectrum at the lowest temperature. It seems that this condition of low temperature is valid for the appearance of the line in other elements. This line $1S-1p_2$ is also the "resonance line" in magnesium,* calcium,† and other elements.

Considering the above data, if the lines $1S-1p_{2,3}$ are expected in the manganese spectrum, two lines, strong at low temperatures and with separation about *129·17*, are to be looked for. The appropriate lines were first recognised in visual observations of the long flame of an arc in which a liberal supply of manganese chloride was maintained on carbon poles. In the visual part of the spectrum there were usually many lines which remained strong in the flame, but occasionally there were only two, namely :—

λ (Fuchs).	Int.	ν.	Δν.
5394·677	(7)	18531·65	
			129·20
5432·555	(5)	18402·45	

An attempt was made to photograph the spectrum when only these two lines were present, but the instability of the flame made it very difficult. However, by mixing the manganese chloride with sodium chloride, a method previously adopted by FOWLER‡ for obtaining arc-flame spectra, satisfactory photographs were obtained.

The results are shown in Plate 2, fig. 1, in which (*a*), (*b*), and (*c*) represent three successive stages of temperature. (*a*) is the ordinary arc spectrum, (*b*) is the spectrum of the middle part of the flame-arc, and (*c*) is the spectrum of one side of the flame-arc. The exposures, in the first order of the 10-ft. concave grating, were 1 minute, 8 minutes, and 20 minutes respectively. The three photographs were taken with Marion's "Iso-record" plates. In (*c*) it is evident that the only manganese lines present are λ5394·7 and λ5432·6, the line λ5341·1, which appears very strongly in (*a*) and in (*b*), having quite disappeared in (*c*). In (*b*) and (*c*) another strong line§ appears, but it is an impurity line due to barium, λ5535·53.

Confirmation of the above conclusions may be found in earlier observations. Thus LOCKYER|| observed the line λ5395 in the Bunsen flame spectrum of manganese, and the lines λ5395 and λ5433 were both noted by HAGENBACH and KONEN.¶ The same two lines also appear in the flame spectrum of manganese in EDER and VALENTA'S** atlas of spectra.

* MOHLER, FOOTE, and MEGGERS, 'Bur. of Standards,' vol. 15, p. 734 (1920).

† MOHLER, FOOTE, and STIMPSON, 'Phil. Mag.,' vol. 40, p. 73 (1920).

‡ 'Phil. Trans.,' A, vol. 209, p. 52 (1908).

§ This line represents in barium the first member of the principal series of singlets, $1s-1P$.

|| 'Roy. Soc. Proc.,' vol. 43, p. 117 (1887).

¶ 'Atlas der Emissions Spektra,' Jena (1905).

** 'Atlas Typischer Spektren,' Tafel VIII–6, Wien (1911).

When these conclusions were arrived at, the publication of KING,* "On the Variation with Temperature of the Electric Furnace Spectrum of Manganese," came to hand. It will be interesting to quote the following remarks (p. 142): "λ5433 and λ5395 are remarkable by their strength at low temperature. λ5341 is stronger than either of these at high temperatures but falls off rapidly below 2000°. The temperature of the furnace, especially in the lower range, may be closely gauged by the relative intensity of λ5341 as compared with λ5395 and λ5433." These results are in perfect agreement with those arrived at above.

From all these facts the conclusion may be drawn that the lines λ5395 and λ5433 represent in manganese the inter-combination lines $1S-1p_{2,3}$. As the values of $1p_2$ and $1p_3$ are known from the ordinary triplet series, 1S can be calculated. Thus,

$$\left.\begin{array}{l} 1S - 1p_2 = 18531\cdot65\,;\ 1S = 18531\cdot65+41405\cdot80 = 59937\cdot45 \\ 1S - 1p_3 = 18402\cdot51\,;\ 1S = 18402\cdot51+41534\cdot98 = 59937\cdot49 \end{array}\right\} \begin{array}{l}\text{mean value} \\ 59937\cdot47 = 1S.\end{array}$$

The value of 1S thus determined forms the starting point for the investigation of the singlet system.

(c)—*The Two Parallel Systems of Narrow Triplet Series and their Analogies with the Singlet Systems of Series in the Alkaline-earths.*

Naturally the first line to be looked for in the singlet system of series must be the first member of the principal series, 1S−1P. This line has characteristic properties, as known in other elements. It is extremely persistent at low temperatures; in the arc spectrum it is very easily and strongly reversed. If an element is present as an impurity in another, in very small quantity, the most likely line to appear is 1S−1P. In many elements 1P has a value not far from 24000, and a rough value of P(1) may therefore be calculated as follows, using the approximate value for 1S of 60000 already mentioned:—

$$60000-24000 = 36000 \quad \text{or} \quad \lambda 2780.$$

There is no single line at all in this part of the spectrum with the properties above mentioned; but very close to λ2780 there is a strong reversed triplet, namely:—

λ (FUCHS).	Int.	ν.	Δν.
2794·822	(10R)	35769·94	
			44·12
2798·273	(9R)	725·82	
			35·75
2801·076	(8R)	690·07	

In Plate 2, fig. 4, this triplet is shown, from a photograph in the second-order spectrum with a very narrow slit, as three strong reversed lines. The lines of this triplet are

* 'Astroph. Journ.,' vol. 53, p. 133 (March, 1921).

found as impurity lines in many other spectra, and it was felt, from the first, that they represented the member 1S−1P in the manganese spectrum. But here the term 1P is triple, whereas in alkaline-earth spectra it is single. The line 1S−1P is found in magnesium not very far from the position of the above triplet, at λ2852. If considered as the first member of the S series the line has a negative wave-number. Thus in manganese, if this line is represented by a triplet it will probably also be negative; that is, the faintest line and the smaller separation will be on the red side, and actually the above triplet λλ2795, 2798, 2801 is negative. Regarding this triplet as the first member of a sharp series, additional triplets of the sharp series with separations *44·1* and *35·8* would be expected.

PAULSON,* in his work on constant differences, has drawn attention to the separation *35·8* as found twice in the manganese spectrum (once already used in the above triplet). MEGGERS and KIESS† have also found this separation twice in the extreme red.

The possible association of *44·1* with *35·8* was therefore tested, with the following results:—

λ (MEG. & K.)	Int.	ν.	Δν.
7326·55	(7)	13645·25	
			44·13
7302·92	(6)	689·38	
			35·95
7283·80	(6)	725·33	
λ (FUCHS).			
5457·468	(1)	18318·44	
			44·11
70·640	(8)	274·33	
			35·85
81·395	(6)	238·48	

The intensities of the lines of the second triplet are not in the usual order, but the separations are very satisfactory. It will be shown later that these three lines form part of a more complex group.

The remaining separation of *35·8* given by PAULSON for the lines λλ5517, 5506, is definitely not associated with a separation *44·1*. It will be shown later that these lines form part of the same complex group as the preceding triplet.

Another triplet with separations *44·1* and *35·8* has also been found, namely:—

λ (FUCHS).	Int.	ν.	Δν.
6605·546	(3)	15134·62	
			44·17
6586·357	(2)	178·79	
			35·80
6570·830	(2)	214·59	

* 'Astroph. Journ.,' vol. 40, p. 300 (1914).

† 'Sc. Papers, Bureau of Standards,' No. 372 (1920).

The intensities and the separations are thus normal.

If it be supposed that the triplet $\lambda\lambda 2795$, 2798, 2801 is $1S-1P_{1,2,3}$, the calculated values of $1P_1$, $1P_2$, and $1P_3$ will be as follows :—

$$35769 \cdot 94 = 1S-1P_1\ ;\quad 1P_1 = 24167 \cdot 53$$
$$725 \cdot 82 = 1S-1P_2\ ;\quad 1P_2 = \quad 211 \cdot 65$$
$$690 \cdot 07 = 1S-1P_3\ ;\quad 1P_3 = \quad 247 \cdot 40$$

But all triplets with separations *44·1* and *35·8* must be combinations of terms $1P_1$, $1P_2$, and $1P_3$, with unknown terms $x, y, z, \ldots$. Calculating these terms for the triplets mentioned above the results are :—

$$\left.\begin{array}{ll} 15134 \cdot 62 = 1P_1 - x\ ; & x = 9032 \cdot 91 \\ 178 \cdot 79 = 1P_2 - x\ ; & x = \cdot 86 \\ 214 \cdot 59 = 1P_3 - x\ ; & x = \cdot 81 \end{array}\right\} \text{mean value } x = 9032 \cdot 86.$$

$$\left.\begin{array}{ll} 13645 \cdot 25 = 1P_1 - y\ ; & y = 10522 \cdot 28 \\ 689 \cdot 38 = 1P_2 - y\ ; & y = \cdot 27 \\ 725 \cdot 33 = 1P_3 - y\ ; & y = \cdot 07 \end{array}\right\} \text{mean value } y = 10522 \cdot 21.$$

The terms $1S = 59937 \cdot 47$ and $x = 9032 \cdot 86$ may be, from RYDBERG's tables, two non-consecutive terms of the same series, having between them another term with approximate value 18500. The line corresponding to this term would be

$$24200 - 18500 = 5700 \quad \text{or} \quad \lambda 17540.$$

RANDALL and BARKER, in their measures of the infra-red spectrum of manganese, give a strong line (the longest wave-length given in their tables) at $\lambda 17607 \cdot 5$ (corrected to I.A.) or $\nu 5677 \cdot 9$. This line is provisionally adopted as S(2), and strong evidence supporting this assignment will be given later.

The term $y = 10522 \cdot 21$ may be a diffuse term, probably 3D.

These conclusions are summarised on the left in Table III.

There are two well-known narrow triplets of manganese which next call for consideration. Their wave-lengths and wave-numbers are :—

λ (FUCHS).	Int.	ν.	$\Delta\nu$.
4030·760	(10)	24802·23	
			14·22
33·074	(9)	788·01	
			8·70
34·489	(9)	779·31	
6021·787	(10)	16601·78	
			14·21
16·636	(9)	615·99	
			8·72
13·484	(9)	624·71	

The first triplet has the same properties as $1S-1P_{1,2,3}$. It is a negative triplet, it is very strong in the flame, and in the arc it is usually reversed, as shown in Plate 1, fig. 1. It will be of interest to quote the following remarks from KING's work (p. 142): "The prominent low temperature group between λ4000 and λ4100 contains a very sensitive triplet λλ4031, 4033, 4034. These lines are of extreme persistence, occurring very generally as impurity lines in arc spectra. Their intensity in the furnace spectrum seems to depend very largely on the vapor density, and with an ordinary charge of manganese present they are always widely reversed . . . The intensities of this triplet given in the table therefore signify little relatively to the general run of manganese lines. At low temperature with very much vapor present they can be made much stronger than at high temperature with less vapor." At 1560° C. "the lines of the triplet are strong and well reversed. Evidently they are emitted at a considerably lower temperature than that used here."

The difference between the wave-numbers of the first lines of this triplet and that at λλ2795, 2798, 2801 (adopted as $1S-1P_{1,2,3}$) is

$$35769 \cdot 94 - 24802 \cdot 23 = \mathit{10967 \cdot 71}.$$

It is very nearly the same as that between the line adopted as S(2) and the first line of the strong red triplet at λ6022 (see Plate 1, fig. 5): thus

$$16601 \cdot 78 - 5677 \cdot 9 = \mathit{10923 \cdot 9}.$$

To determine whether this was or was not a mere coincidence, the difference *10967·7* was tested with all triplets which have separations *44·1* and *35·8* and the following interesting results were obtained. The first line of the triplet at λ6606 gives

$$15134 \cdot 62 + \mathit{10967 \cdot 7} = 26102 \cdot 3 \quad \text{or} \quad \lambda 3829 \cdot 99.$$

There is a line, measured now for the first time, λ3829·987 (2), and two more lines not previously recorded, which give the following triplet:—

λ (CATALÁN).	Int.	ν.	Δν.
8829·987	(2)	26102·37	
			14·20
27·904	(1)	116·57	
			8·71
26·698	(1)	125·28	

It is evident that these separations are the same as those of the triplet λλ4031, 4033, 4035.

The first line of the narrow triplet at $\lambda 7327$ gives

$$13645 \cdot 25 + \mathit{10967 \cdot 7} = 24613 \cdot 0 \quad \text{or} \quad \lambda 4061 \cdot 74.$$

There is actually a line at $\lambda 4061 \cdot 744$ and two more forming the following triplet :—

λ (FUCHS).	Int.	ν.	$\Delta\nu$.
4061·744	(3)	24613·03	
			14·23
59·399	(2)	627·26	
			8·73
57·959	(2)	635·99	

These three lines are mixed with many others, but KING's observations show that they belong to the temperature class IV. or V., while the adjacent lines belong to class I. or II. This triplet is shown in Plate 1, fig. 1.

The above considerations show that each triplet with separations *44·1* and *35·8* has a corresponding triplet with separations *14·2* and *8·7*, and between the first lines of the triplets there is a difference very close to *10967·7*.

The possibility that one of these series with separations *14·2* and *8·7* might be an F series was considered, but soon abandoned because there is no reason to expect an F series to be parallel to the series with separations *44·1* and *35·8*. Further, it is not possible to suppose that the series with separations *14·2* and *8·7* are combination series like $2P_{1,2,3} - m$S or $2P_{1,2,3} - m$D because $2P_{1,2,3}$ would then be greater than $1P_{1,2,3}$. Hence it must be accepted that in manganese there are two systems of narrow triplet series displaced from each other by a quantity $C = 10967 \cdot 7$. It is curious to note that this separation is very close to 1/10 of the RYDBERG constant 109678·3.

In Table III. the series with separations *14·2* and *8·7* are summarised and are compared with the other parallel series.

A general view of the series in manganese is given in fig. 2, in which each line represents a triplet.

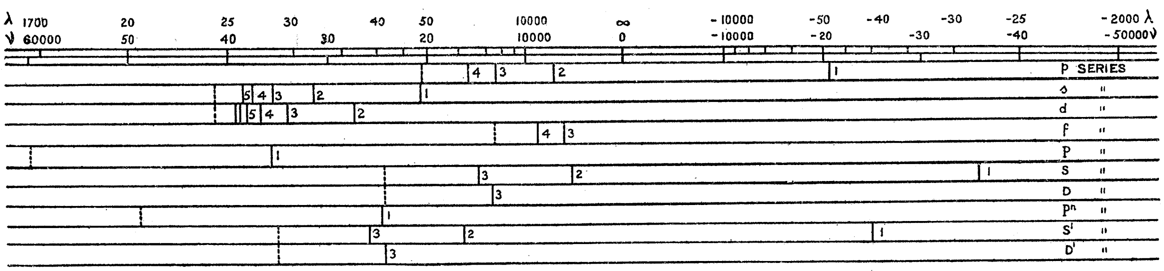

Fig. 2.

TABLE III.—The Two Parallel Systems of Narrow Triplet Series.

Principal 1S—*m*P. 1S=59937·47.

λ.	Int.	ν.	Δν.	*m*.	*m*$P_{1,2,3}$.
2794·822	(10)	35769·94	*44·12*	(1)	24167·53
2798·273	(9)	725·82	*35·75*		211·65
2801·076	(9)	690·07			247·40

Principal 1S—(*m*P+C).

λ.	Int.	ν.	Δν.	*m*.	Shift Number C.
4030·760	(10)	24802·23	*14·22*	(1)	*10967·71*
33·074	(9)	788·01	*8·70*		
34·489	(9)	779·31			

Sharp 1P—*m*S. $1P_1$=24167·53 $1P_2$=24211·65 $1P_3$=24247·40

λ.	Int.	ν.	Δν.	*m*.	*m*S.
—2794·822	(10)	—35769·94	*44·12*	(1)	59937·47
—2798·273	(9)	— 725·82	*35·75*		
—2801·076	(9)	— 690·07			
17607·5		(5644·0)*	*44·1*	(2)	18533·50
		(5678·1)	*35·8*		
		(5714·0)			
6605·546	(3)	15134·62	*44·11*	(3)	9032·89
6586·357	(2)	178·79	*35·80*		
6570·830	(2)	214·59			

Sharp (1P+C)—*m*S.

λ.	Int.	ν.	Δν.	*m*.	
—4030·760	(10)	—24802·23	*14·22*	(1)	*10967·71*
— 33·074	(9)	— 788·01	*8·70*		
— 34·489	(9)	— 779·31			
6021·787	(8)	16601·78	*14·21*	(2)	*10967·75*†
16·636	(8)	615·99	*8·72*		
13·489	(7)	624·71			
3829·987‡	(2)	26102·37	*14·20*	(3)	*10967·75*
27·904‡	(1)	116·57	*8·71*		
26·628‡	(1)	125·28			

Diffuse 1P—*m*D. $1P_1$=24167·53 $1P_2$=24211·65 $1P_3$=24247·40

λ.	Int.	ν.	Δν.	*m*.	*m*D.
7326·55	(7)	13645·25	*44·13*	(3)	10524·27
7302·92	(6)	689·38	*35·95*		
7283·80	(6)	725·33			

Diffuse (1P+C)—*m*D.

λ.	Int.	ν.	Δν.	*m*.	
4061·744	(3)	24613·03	*14·23*	(3)	*10967·78*
59·399	(2)	627·26	*8·73*		
57·959	(2)	635·99			

* This triplet has been calculated from the red triplet λλ6022, 6017, 6013 and the shift number C=*10967·75*. The strong infra-red line given by RANDALL and BARKER as λ17607·5 (I.A.) or ν5677·9 agrees very well with the second calculated line ν5678·1, but it is probable that the actual line ν5677·9 represents the triplet unresolved in infra-red measures.

† Used for calculation of the triplet in the infra-red.

‡ Lines not previously recorded.

(*d*)—*The Resonance and Ionisation Potentials of Manganese.*

A schematic representation of the possible orbits of the displaced electron in the manganese atom, as illustrated in fig. 3, can be constructed from the terms of the

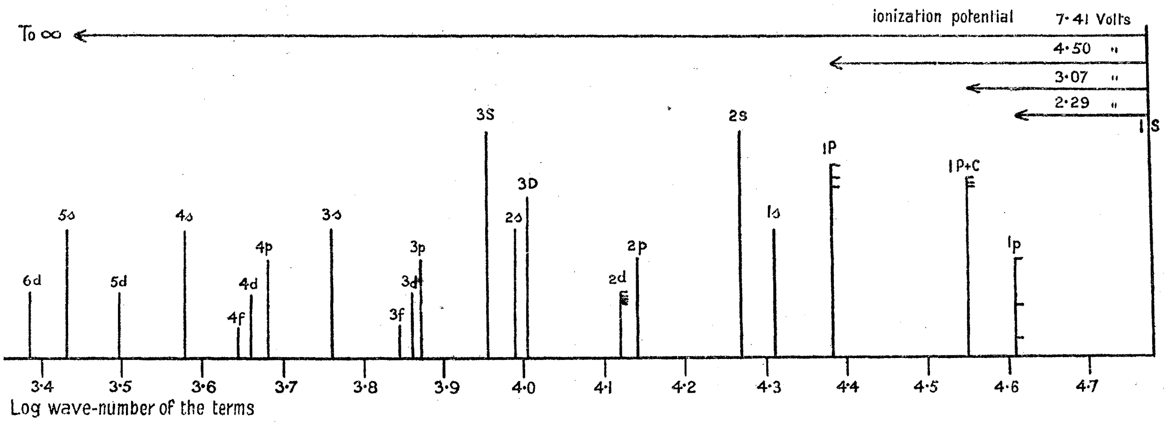

Fig. 3.

spectral series, adopting the method of BIRGE.* The only modification here introduced has been to represent the terms which have triple or quintuple values by the first of the values, with the addition of horizontal short lines at distances apart proportional to the differences of the different values, thus giving an approximate idea of the separations in the corresponding triplets.

The ionisation potential of manganese has been calculated by the formula†

$$V_I = \frac{c^2 h\,(1S)}{e}\,10^{-8},$$

V_I being the ionisation potential in volts, c the velocity of light, h PLANCK'S constant; and e the charge of an electron.

$$\left.\begin{aligned} c &= 3 \times 10^{10} \text{ cms. sec.}^{-1} \\ h &= 6\cdot55 \times 10^{-27} \text{ erg sec.} \\ e &= 4\cdot77 \times 10^{-10} \text{ e.s.u.} \\ 1S &= 59939\cdot53 \text{ cm.}^{-1} \end{aligned}\right\} V_I = 7\cdot41 \text{ volts.}$$

The resonance potential V_R may be calculated by the same formula, using instead of 1S the wave-number of the line $1S - 1p_2 = 18531\cdot65$. The value thus obtained is

$$V_R = 2\cdot29 \text{ volts.}$$

The other potentials calculated and given in fig. 3 are for the lines

$$1S - (1P_1 + C) = 24802\cdot23 \quad \text{and} \quad 1S - 1P_1 = 35769\cdot94,$$

which are $3\cdot07$ and $4\cdot50$ volts respectively.

* In a paper by MOHLER, FOOTE, and STIMPSON, 'Phil. Mag.,' vol. 40, p. 73 (1918).

† SOMMERFELD, 'Atombau und Spektrallinien,' p. 290 (1921).

These values may be compared with the corresponding values in magnesium,* namely :—

	Magnesium.	Manganese.
Resonance potentials	2·70 volts	2·29 volts.
	—	3·07 ,,
	4·33 ,,	4·50 ,,
1st ionisation potential	7·61 ,,	7·41 ,,

The values for magnesium are so close to those for manganese that the strong analogies between the arc spectra of the two elements might well be expected.

(*e*)—" *Multiplets.*"

Whilst the manganese series of ordinary type were under investigation, it was noted that there was a strong tendency for lines of similar character to appear in groups and that such groups included some of the most intense lines in the spectrum. In the blue region the lines are very numerous, but the nine strongest are apparently grouped together, as will be seen in Plate 2, fig. 2. At first glance, these nine lines present the appearance of a diffuse triplet, but with the satellites in the wrong order. The wave-lengths and the wave-numbers are :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
4455·019	(6)	22440·32	III
55·320	(6)	438·80	III ?
55·820	(5)	436·29	III
57·041	(5)	430·14	III
57·553	(6)	427·56	—
58·263	(6)	423·99	II
60·376	(3)	413·37	—
61·089	(6)	409·84	III
62·033	(8R)	405·85	III

All the separations between these nine lines, taken in pairs, were calculated and it was found that some of them appeared more than once. On the plan adopted for the schematic representation of *d* (2) (p. 135), the character of the group may be shown as follows :—

				(5) 22436·29	*2·51*	(6) 22438·80	*1·42*	(6) 22440·32
				8·73		*8·66*		
		(6) 22423·99	*3·57*	(6) 22427·56	*2·58*	(5) 22430·14		
		14·15		*14·19*				
(8R) 22405·05	*4·80*	(6) 22409·84	*3·53*	(3) 22413·37				

* Foote, Meggers, and Mohler, 'Phil. Mag.,' vol. 42, p. 1002 (1921).

It is to be noted that the separations *14·19* and *8·73* are the same as those of the series of narrow triplets shown on the right in Table III.

As will be seen later there are many " groups " of lines in the manganese spectrum with similar structure to that of the foregoing " group," and for this form of regularity the name " multiplet " is suggested.

The separation C = *10967·75* was next tested with the first line of the above multiplet, giving

$$22405\cdot05 - \mathit{10967\cdot75} = 11437\cdot30 \quad \text{or} \quad \lambda 8740\cdot92$$

In MEGGERS and KIESS's list there is a line at λ8740·91 (3) or ν11437·32, in practically exact agreement with the position calculated. Close to this line there are other lines, among which the following are the most intense :—

λ (MEG. and KI.).	Int.	ν.
8670·85	(2)	11529·71
72·08	(2)	528·09
74·01	(2)	525·53
99·13	(2)	492·24
8701·04	(2)	489·72
03·73	(3)	486·17
34·64	(1)	445·53
37·29	(2)	442·05
40·91	(3)	437·32

These nine lines form the following multiplet :—

				(2)		(2)		(2)
				11525·53	*2·56*	11528·09	*1·62*	11529·71
				35·81		*35·85*		
		(3)		(2)		(2)		
		11486·17	*3·55*	11489·72	*2·52*	11492·24		
		44·12		*44·19*				
(3)		(2)		(1)				
11437·32	*4·73*	11442·05	*3·48*	11445·53				

This multiplet thus shows as the main separations *44·1* and *35·8* identical with those of the series shown on the left in Table III. ; it is shifted from the multiplet with separations *14·1* and *8·7* by C = *10967·73*, which is identical with the relative displacement of the two series of narrow triplets. The smaller separations, as shown, are probably the same in both multiplets :—

	Separations.			
Blue multiplet	*4·80*	*3·57* *3·53*	*2·51* *2·58*	*1·42*
Extreme red multiplet . . .	*4·73*	*3·55* *3·48*	*2·56* *2·52*	*1·62*

The distribution of the intensities is the same in both multiplets, and very much the same as in d (2).

Attention has been drawn (p. 140) to a pair with separation *35·8* formed from the lines $\lambda\lambda$5517 and 5506, and to a triplet with separations *44·1* and *35·8* formed from the lines $\lambda\lambda$5481, 5471, and 5457. These could not be directly associated with the triplets given in Table III., because the pair was not associated with a *44·1* separation and the triplet had not the intensities of the lines in the usual order. This triplet and pair are not far apart and it seemed possible that they belonged to a multiplet analogous to those which have been described, but presenting, in combination with the separations *44·1* and *35·8*, another set of much larger separations. The five lines may be arranged as below, thus introducing a new separation of *116·96* :—

(6) 18238·48	*116·96*	(7) 18121·52
35·85		*35·86*
(8) 18274·33	*116·95*	(6) 18157·38
44·11		
(1) 18318·44		

Following the analogy of the previous two multiplets, this separation *116·96* must correspond with the separation *2·54*. If this be correct, a pair with the separation *44·1* should be found at a distance from the triplet in corresponding ratio with the separation *3·53*. Calling this distance x, we have

$$2{\cdot}54 : 3{\cdot}53 = 116{\cdot}96 : x \qquad x = 165.$$

An appropriate pair actually occurs, as shown by the following data :—

λ (Fuchs).	Int.	ν.	Δν.
5420·368	(6)	18443·82	
			44·15
07·432	(6)	487·97	

The distance from the pair to the triplet is

$$18487{\cdot}97 - 18318{\cdot}44 = 169{\cdot}53.$$

This value *169·53* is in sufficient agreement with the calculated $x = 165$, and the separation of the pair *44·15* is also in accordance with that expected.

If this multiplet be analogous to the previous two multiplets, two more lines are to be expected, at distances which may be calculated approximately as follows :—

$$2{\cdot}54 : 1{\cdot}5 \;\; = 116{\cdot}96 : y \qquad y = 69$$
$$3{\cdot}53 : 4{\cdot}76 = 169{\cdot}53 : z \qquad z = 229$$

Two very strong lines were found which satisfied these values, namely :—

λ (Fuchs).	Int.	ν.	
5537·749	(8)	18052·88	$y = 18121 \cdot 52 - 18052 \cdot 88 = \mathit{68 \cdot 64}$
5341·070	(10)	18717·64	$z = 18717 \cdot 64 - 18487 \cdot 97 = \mathit{229 \cdot 67}$.

The entire multiplet, therefore, includes the following lines :—

λ Fuchs.	Int.	ν.	Temp. Class (King).
5341·070	(10)	18717·64	IIIA
5407·432	(6)	487·97	IIIA
20·368	(6)	443·82	IIIA
57·468	(3)	318·44	IIA
70·640	(8)	274·33	IIA
81·395	(6)	238·48	IIA
5505·877	(4)	157·38	III
16·773	(7)	121·52	IIIA
37·749	(8)	052·88	III

with the schematic representation :—

				(6) 18238·48	*116·96*	(7) 18121·52	*68·64*	(8) 18052·88
				35·85		*35·86*		
		(6) 18443·82	*169·49*	(8) 18274·33	*116·95*	(4) 18157·38		
		44·15		*44·11*				
(10) 18717·64	*229·69*	(6) 18487·97	*169·53*	(3) 18318·44				

The intensities of the lines are distributed in much the same manner as in the other multiplets.

In this region of the spectrum there are additional strong lines, and it remained to be seen if these belonged to the above multiplet or not. Attention had already been given to this region when the lines $1S - 1p_{2,3}$ were under investigation (p. 137). In the provisional description given of fig. 1 in Plate 2, it was explained that (*a*), (*b*), and (*c*) represent three different stages of temperature, (*a*) corresponding to the highest temperature, (*b*) a middle stage, and (*c*) the lowest. In (*a*) there are many strong lines ; in (*b*) some of these lines are absent, and in (*c*) there remain only two Mn lines. These have already been shown to be $1S - 1p_{2,3}$; (*b*) shows these two lines, and in addition nine other lines (one is not visible in the reproduction on account of its low intensity). These are precisely the nine lines of the multiplet just described ; the strong arc lines not belonging to this multiplet *are not present* at this middle stage of temperature. Hence the preceding facts may be summarised as follows : At the lowest temperature two lines appear, namely $1S - 1p_{2,3}$; at the intermediate temperature the nine lines of this multiplet appear, while the lines $1S-1p_{2,3}$ begin to fall off in intensity in comparison; at the highest temperature the lines of the multiplet are strong, but many other strong lines are also present, and the lines $1S-1p_{2,3}$ have lost much of their intensity. When the previously mentioned work of KING came to hand these results were compared with those given by the electric furnace. From KING'S tables it would seem that at his lowest stage of temperature, which corresponds with the intermediate arc (*b*), there are only present the nine lines forming the preceding multiplet, with intensities varying from 1 to 4, and the two lines λ5395 and λ5433 ($1S-1p_{2,3}$) with intensities 35 and 40 respectively. The fairly strong arc lines λλ5378, 5400, and 5414, not belonging to the multiplet, are only developed at the highest stage of the furnace temperature.

A diagram of this multiplet is given in fig. 4.

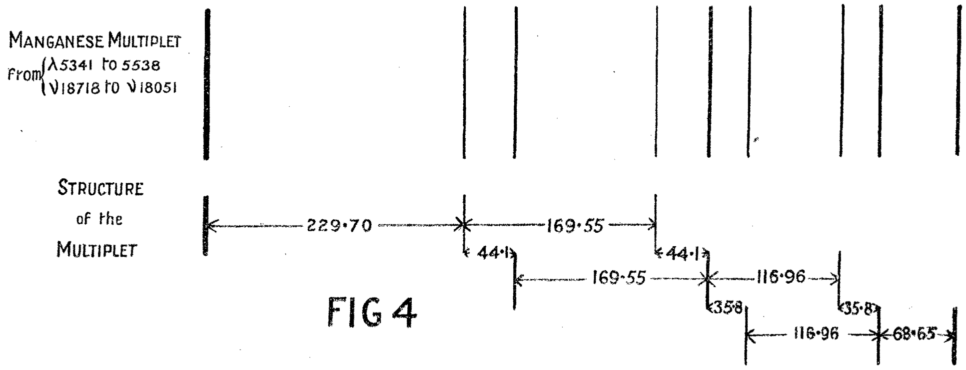

FIG 4

The constant difference C = *10967·75* was then applied to the first line of the preceding multiplet as follows:—

$$-18717\cdot 64+10967\cdot 75 = 7749\cdot 89 \quad \text{or} \quad \lambda 12899\cdot 9.$$

The wave-number 18717·64 is written with negative sign because the triplet with the separations *44·1* and *35·8* in this multiplet is negative, the strongest line λ5341 being on the violet side.

There is a line in the infra-red at λ12899·7 or ν7750·0. Near this there is another line λ13294·1 or ν7520·1, the separation between these lines thus being

$$7750\cdot 0-7520\cdot 1 = 229\cdot 9,$$

which is in agreement with the separation *229·7* found in the multiplet. Using some additional lines recorded in this region by RANDALL and BARKER, a multiplet similar to the preceding was traced. The observed lines of this multiplet are:—

λ (R. and B.).	Int.	λ (I.A.).	ν.
12900·3	(80)	12899·7	7750·0
13294·7	(50)	13294·1	7520·1
318·5	(30)	317·9	7506·7
626·3	(200)	625·7	7337·1
864·4	(100)	863·8	7211·1
997·6	(120)	997·0	7142·5

and the schematic representation is :—

						(100)		(120)
				(7328·3)	*117·2*	7211·1	*68·6*	7142·5
				8·8		*8·8*		
		(300)		(200)				
		7506·7	*169·6*	7337·1	*117·2*	(7219·9)		
		13·4		*14·1*				
(80)		(50)						
7750·0	*229·9*	7520·1	*168·9*	(7351·2)				

The lines in brackets are calculated, but the multiplet is considered to be completely defined for the following reasons: 1st, the line ν7750·0 is distant *10967·7* from the first line λ5341 of another multiplet; 2nd, with the actual lines the separations *229·9*, *169·6*, *68·6*, and *13·4* are found, which are close to the expected separations; and 3rd, the lines missing are expected to be the faintest of the multiplet by analogy with the other multiplet. It is to be noted that, as calculated, this multiplet is negative because the larger separation (14·1) is on the violet side.

Paulson has found the constant difference *229·7* three times. In one case, it was formed from the lines λ5341 and λ5407 and it has already been used in one of the multiplets. In a second example the constant difference *229·7* arose from the lines λ3578 and λ3607. In this region of the spectrum there are only nine strong lines, including these two, namely :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
3577·880	(6R)	27941·57	II
86·540	(5)	874·10	III
95·112*	(3)	807·64	III
3607·530	(6)	711·92	II
08·484	(6)	704·60	II
10·296	(6)	690·69	III
19·399	(4)	620·53	III
23·790	(4)	587·58	III
29·739	(3)	542·37	III

These nine lines form a multiplet which can be represented as follows :—

				(3)		(4)		(4)
				27807·64	*116·95*	27690·69	*68·67*	27622·02
				103·04		*103·11*		
		(4)		(6)		(4)		
		27874·10	*169·50*	27704·60	*117·02*	27587·58		
		162·18		*162·23*				
(6R)		(6)		(3)				
27941·57	*229·65*	27711·92	*169·55*	27542·37				

* Kilby's value.

The intensities are distributed very much in the same manner as in the foregoing multiplets. It is to be noted that the first line shows strong tendency to reversal, and that the lines belong to temperature class II. or III. This multiplet is shown in Plate 2, fig. 3.

The remaining separation of *229·7* given by PAULSON, between the lines λ4018 and λ4056, was next considered. In this region of the spectrum, in addition to these two lines, there are other very strong and also many weak lines. From nine of these lines, a multiplet showing the four separations *229·7*, *169·5*, *116·9*, and *68·6* was arranged, but was not considered very satisfactory because it did not present the intensities in the usual order of distribution; the first line of the multiplet being the weakest instead of the strongest. As in the case of the green multiplet having the first line at λ5341, some photographic observations were made of the spectrum of the flame-arc, and compared with the spectrum of the ordinary arc in this region. All the lines which retain their intensity at low temperatures were thus found to form a multiplet having a more complicated structure than the preceding multiplets, but showing the same four separations *229·7*, *169·5*, *116·9*, and *68·6*. The lines are :—

λ (FUCHS).	Int.	ν.	Temp. Class (KING).
4018·108	(8)	24880·32	I
35·730	(5)	771·69	I
41·366	(10R)	737·15	I
48·760	(4)	691·97	I
55·553	(8)	650·62	I
58·936	(2)	630·02	I
63·533	(4)	602·18	I
68·029	(2)	575·01	—
70·280	(2)	561·43	II
79·245	(6)	507·44	I
79·428	(6)	506·34	I
82·947	(6)	485·22	I
83·639	(6)	481·07	I

The wave-lengths are quoted from FUCHS's measures except for λ4068·029, which has now been remeasured because the values given by different observers differ considerably.

The scheme of the multiplet is :—

						(2)		(2)
						24630·06	*68·63*	24561·43
						55·05		*55·09*
				(4)		(2)		(6)
				24691·97	*116·96*	24575·01	*68·67*	24506·34
				89·79		*89·79*		
		(5)		(4)		(6)		
		24771·69	*169·51*	24602·18	*116·96*	24485·22		
		121·07		*121·13*				
(8)		(8)		(6)				
24880·32	*229·70*	24650·62	*169·57*	24481·05				
143·17		*143·18*						
(10R)		(6)						
24737·15	*229·71*	24507·44						

This multiplet is shown in Plate 1, fig. 1; (*a*) is the ordinary arc spectrum and (*b*) is the flame-arc spectrum.

The lines of this multiplet are, with two exceptions, classified by KING as of temperature class I. One of the exceptions is the faintest line of the multiplet (assigned to class II.) and the other, λ4068, is not mentioned in KING's tables. Mixed with the lines of the multiplet there are two triplets λλ4041, 4035, 4033 and λλ4062, 4059, 4058, already discussed, and many lines fairly strong in the arc but not present in the furnace spectrum. A diagram showing the structure of this multiplet is given in fig. 5.

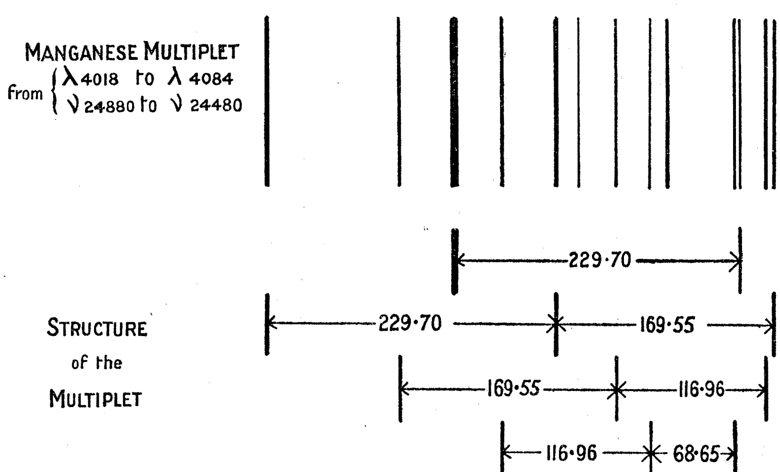

FIG 5

As the recognised constant differences found in the manganese spectrum were exhausted, a search for multiplets was commenced among the more intense lines, guided by the observations of the flame-arc and arc spectra, and some additional multiplets were then found.

One multiplet is formed by the following nine lines :—

λ (FUCHS).	Int.	ν.	Temp. Class (KING).
3044·573	(6)	32835·76	III
54·386	(5)	730·31	III
62·132	(4)	647·52	III
66·035	(3)	605·97	III
70·290	(5)	560·77	III
73·144	(4)	530·54	III
79·638	(5)	461·95	IV
81·347	(4)	443·94	IV
82·062*	(2)	436·42	—

The scheme of the multiplet is :—

				(4) 32647·52	*116·98*	(4) 32530·54	*68·59*	(5) 32461·95
				86·75		*86·60*		
		(5) 32730·31	*169·54*	(5) 32560·77	*116·83*	(4) 32443·94		
		124·34		*124·35*				
(6) 32835·76	*229·79*	(3) 32605·97	*169·55*	(2) 32436·42				

The intensities are distributed in the usual manner, as will be seen in Plate 1, fig. 4. The first line of the multiplet is mixed with many other lines, but can be detected very easily by its intensity and character.

Another multiplet is formed by the following lines :—

λ (FUCHS).	Int.	ν.	Temp. Class (KING).
3776·537	(1)	26471·79	—
90·215	(3)	376·19	III
99·256	(2)	313·49	III
3806·866	(10R)	260·93	I
09·599	(6)	242·07	II
16·746	(2)	192·93	III
23·515	(9R)	146·56	II
23·896	(5)	143·94	II
29·674	(2)	104·50	III
33·864	(6)	075·92	II
34·363	(8R)	072·58	II
38·329†	(2)	045·64	—
39·777	(4)	035·82	II
41·081	(5)	026·97	II
43·985	(4)	007·31	II

* The wave-length of the last line was measured by the author because it had not previously been recorded.

† KILBY'S value.

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The scheme of this multiplet is :—

								(2) 26045·64
								9·82
						(2) 26104·50	*68·68*	(4) 26035·82
						28·58		*28·51*
				(2) 26192·92	*117·00*	(6) 26075·92	*68·61*	(4) 26007·31
				48·98		*48·95*		
		(2) 26313·49	*169·65*	(5) 26143·94	*116·97*	(5) 26026·97		
		71·42		*71·36*				
(1) 26471·79	*229·72*	(6) 26242·07	*169·49*	(8R) 26072·58				
95·52		*95·51*						
(3) 26376·27	*229·71*	(9R) 26146·56						
115·34								
(10R) 26260·93								

Most of the lines of this multiplet are present at low temperature in the electric furnace, the exceptions being λ3777 and λ3838, which are absent probably on account of their small intensities. A schematic diagram showing the structure of this multiplet is given in fig. 6.

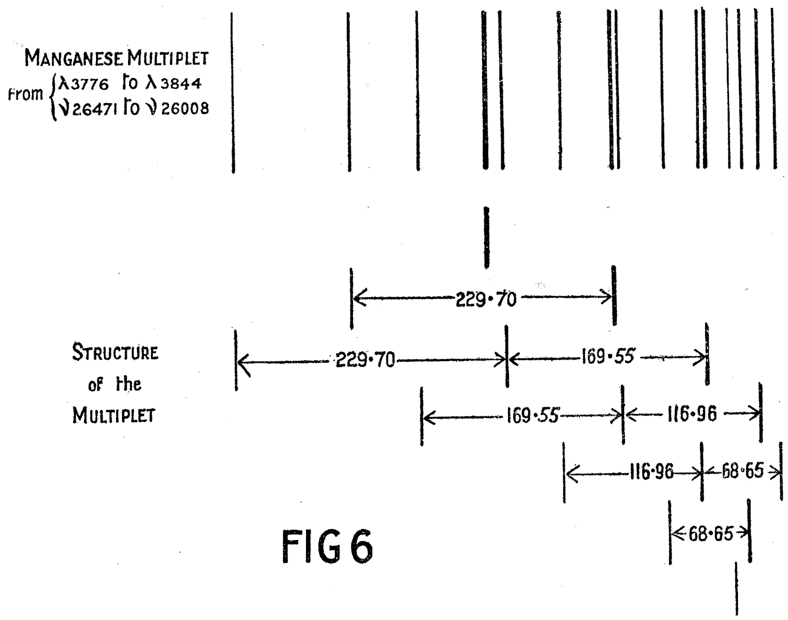

FIG 6

In the region near λ3200 there are very many lines of the same character and placed by KING in the low or medium temperature class. A multiplet may be arranged from the following thirteen of these lines:—

λ (FUCHS).	Int.	ν.	Temp. Class (KING).
3206·915	(3)	31173·64	IV
12·897	(6)	115·60	III
26·043	(2)	30998·81	IV
30·725	(3)	943·90	III
36·787	(6)	885·94	II
40·624	(3)	849·38	IV
43·784	(4)	819·32	III
48·521	(4)	774·38	III
51·139	(3)	749·60	IV
52·954	(4)	732·45	III
56·141	(4)	702·36	III
58·417	(4)	680·92	III
60·237	(4)	663·80	III

The scheme of the multiplet is:—

						(3) 30749·60	*68·68*	(4) 30680·92
						17·15		*17·12*
				(3) 30849·38	*116·93*	(4) 30732·45	*68·65*	(4) 30663·80
				30·06		*30·09*		
		(2) 30988·81	*169·49*	(4) 30819·32	*116·96*	(4) 30702·36		
		44·91		*44·94*				
(3) 31173·64	*229·74*	(3) 30943·90	*169·52*	(4) 30774·38				
58·04		*57·96*						
(6) 31115·60	*229·66*	(6) 30885·94						

Mixed with the lines of this multiplet there are some other lines of similar character which are also related to one another by the differences *229·7*, *169·5*, *116·9*, and *68·6*, namely :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
3240·408	(3)	30851·44	III
54·040	(2)	722·19	IV
64·713	(4)	621·76	III
78·553	(3)	492·49	IV
96·029	(2)	330·83	IV
96·884	(3)	322·97	IV
3308·791	(3)	213·83	—
16·324	(3)	145·32	IV
43·728	(2)	29898·18	IV
51·427	(1)	829·50	—

Their relations may be shown as follows :—

(3) 30851·44	*229·68*	(6) 30621·76						
(2) 30722·19	*229·70*	(3) 30492·49	*169·52*	(3) 30832·97				
				(2) 30330·83	*117·06*	(3) 30213·83	*68·51*	(3) 30145·32
						(2) 29898·18	*68·68*	(1) 29829·50

No connection between these lines and the previous overlapping multiplet, however, has been found.

There are still other lines strong at low temperatures, but it has not been found possible to arrange them in multiplets. There are, however, some common separations. In the region near λ4150 the following lines of the same character are found :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
4235·147	(6)	23605·30	II
35·300	(6)	604·45	I
39·729	(6)	579·79	II
57·659	(6)	480·49	II
59·329	(2)	471·29	—
61·294	(3)	460·47	—
65·920	(6)	431·03	II
81·097	(6R)	351·94	II

The following relations appear among these :—

		(2) 23471·29	*119·35*	(6R) 23351·94	*252·51*	(6) 23604·45
		108·50		*108·53*		
(6) 23480·49	*99·30*	(6) 23579·79	*119·32*	(3) 23460·47		

The separations *99·3* and *252·5* also occur among the following lines of similar type in the region near λ4500 :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
4414·887	(6)	22644·29	II
36·358	(6)	534·70	III
51·578	(8)	457·66	II
53·013	(4)	450·42	III
64·679	(6)	391·76	II
70·142	(6)	364·40	III
72·793	(6)	351·14	III
90·078	(5)	265·10	III
98·897	(6)	221·45	II
4502·223	(6)	205·01	II

and the relations found are :—

(5) 22265·10	*99·30*	(6) 22364·40
86·04		*86·02*
(6) 22351·14	*99·28*	(4) 22450·42

(6) 22205·01	*252·65*	(8) 22457·66
186·75		*186·63*
(6) 22391·76	*252·53*	(6) 22644·29

A few remaining strong lines are situated near λ4700, namely :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
4709·704	(6)	21226·83	III
27·462	(6)	147·10	III
39·001	(6)	095·81	III
61·527	(5)	20995·81	III
62·376	(8)	992·09	III
65·856	(5)	976·71	III
66·425	(5)	974·25	III

The only significant relation found among these is the separation *252·5*, as follows :—

(6) 21226·83 *252·58* (5) 20974·25

It should be observed that the multiplets which have been described do not exhibit either of the separations characteristic of the ordinary triplet system (*173·71* and *129·18*). Two of them, however, involve the respective separations of the narrower sets of triplets, and have other small separations in common; two which include the same triplet separations are associated with new and larger separations, which are in the same ratio as the smaller separations in the first two. In the remaining multiplets no triplet separations occur at all, but the larger separations just mentioned appear in all of them. The mutual relationships of the multiplets and their connections with the regular series are not yet clear, and the following summary is given to facilitate further investigation.

Table IV.—Multiplets of the Neutral Atom of Manganese.

Mul-tiplet.	Limiting νν.	No. of Lines.	Triplet Separations.		Separations.		Non-recurring Separations.	Remarks.
			14·2, 8·7.	*44·1, 35·8.*	*4·8, 3·5, 2·5, 1·4.*	*229·7, 169·5, 116·9, 68·6.*		
I.	22440—22405	9	×		×			Interval =10967·7.* (I.–II.)
II.	11437—11490	9		×	×			
III.	18718—18053	9		×		×		Interval =10967·7.* (III.–IV.)
IV.	7750—7142	9 ?	×			×		
V.	27942—27542	9				×	162, 103	
VI.	24880—24481	13				×	143, 121, 89, 53	
VII.	32836—32436	9				×	124, 86	
VIII.	26472—26007	15				×	115, 95, 71, 48, 28, 10	
IX.	31174—30664	13				×	58, 44, 30, 17	

5. The Spectrum of the Ionised Atom of Manganese.

The enhanced lines of manganese have been investigated by Lockyer† and by Baxandall,‡ in connection with the spectra of the different types of stars. In addition to the enhanced lines given in these papers there are many others which, in spite of being present as fairly strong lines in the arc, increase considerably in intensity on passing to the spark, and hence must be considered as enhanced lines.

* This is identical with the interval separating corresponding members of the two sets of narrow triplets.

† 'Solar Physics Committee, Tables of Wave-lengths of Enhanced Lines' (1906).

‡ 'Monthly Notices of R.A.S.,' vol. 74, p. 250 (1914).

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In order to distinguish these lines the spark and the arc spectra have been photographed side by side for comparison. The number of enhanced lines thus detected is very great and it is not possible at present to give a detailed study of their distribution. However, seeing that the preliminary results are of great interest, not only in the particular case of manganese, but also in their general bearing upon the relations between the lines of other elements, it is thought that the following remarks will be of value.

In the spectrum of the ionised atom of manganese (Mn^+) there are three very prominent lines, λλ2949, 2939, and 2933, apparently forming a triplet. These are present in the arc spectrum as fairly strong lines, but in passing from the arc to the spark their intensities increase considerably, as shown in Plate 1, fig. 3. It will be noticed that the diffuse arc triplet λλ2941, 2926, 2914 [*d* (3)] becomes very faint in the spark, while, on the contrary, the enhanced triplet λλ2949, 2939, 2933 is much stronger in the spark than in the arc. In the electric furnace, as shown by KING, the lines of the arc triplet are faint at medium temperatures, but the lines of the spark triplet are only present at high temperature, and then as very faint lines.

The wave-lengths and the wave-numbers, from measures in the *arc*, are :—

λ (FUCHS).	Int.	ν.	Δν.	Temp. Class (KING).
2949·207	(10)	33897·54		IV
			114·08	
39·315	(9)	34011·62		V
			72·45	
33·066	(8)	084·07		V

There are two other strong triplets in the ultra-violet. One of them is formed from three lines which are strongly reversed in the spark and appear also as fairly strong lines in the arc spectrum. This is a negative (or inverted) triplet, the wave-lengths and wave-numbers, from measures in the *arc*, being :—

λ (FUCHS).	Int.	ν.	Δν.
2576·116	(10R)	33806·52	
			263·58
93·734	(9R)	542·94	
			176·91
2605·695	(9)	366·03	

The other triplet is of the diffuse type and presents the same features as the diffuse triplet in the arc spectrum; that is, instead of being formed from six lines, as in the familiar diffuse triplets in the alkaline-earths, it is formed from nine lines. The wave-lengths and wave-numbers of the lines are :—

λ (Ex. and H.).	Int.	ν.
2427·43	(3)	41183·3
27·77	(4)	177·5
27·97	(4) ?	174·1
37·45	(5)	015·7
37·92	(3)	006·1
38·22	(3)	001·1
52·53	(10)	40761·9
53·17	(2)	751·3
53·65	(1)	743·0

and the scheme of the triplet is :—

				(3) 41183·3	*3·8*	(4) 41177·5	*3·4*	(4) ? 41174·1
				177·2		*176·4*		
		(5) 41015·7	*9·6*	(3) 41006·1	*5·0*	(3) 41001·1		
		264·4		*263·1*				
(10) 40761·9	*10·6*	(2) 40751·3	*8·3*	(1) 40743·0				

The wider separations of this triplet are practically identical with those of the negative triplet λλ2576, 2594, 2606.

A group of prominent enhanced lines is situated near λ3480. The lines of this group are of medium intensity in the arc, but, as shown in Plate 2, fig. 3, their intensities on passing from the arc to the spark increase considerably. It is very interesting to compare the behaviour of three characteristic groups in this photograph. In the middle there is the diffuse arc triplet, *d* (2), very strong in the arc and weak in the spark; on the right there is a multiplet of nine arc lines, almost disappearing in the spark, and on the left the multiplet of enhanced lines, present in the arc as lines of medium intensity and strengthened considerably in the spark.

The wave-lengths and the wave-numbers of this enhanced multiplet, from measures in the *arc*, are :—

λ (Fuchs).	Int.	ν.	Temp. Class (King).
3497·540	(6)	28583·37	V
96·815	(4)	589·30	V
95·840	(8)	597·26	V
88·618	(8)	655·89	V
82·918	(7)	703·37	V
74·139	(6)	775·90	V
74·050	(7)	776·65	V
60·332	(8)	890·71	V
41·999	(9)	29045·93	V

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These lines do not appear in the electric furnace, and so are classified by KING in temperature class V.

This multiplet can be schematically represented as follows :—

				(6) 28775·90	*120·01*	(8) 28655·89	*58·63*	(8) 28597·26
				72·53		*72·52*		
		(8) 28890·71	*187·34*	(7) 28703·37	*120·00*	(6) 28583·37		
		114·06		*114·07*				
(9) 29045·93	*269·28*	(7) 28776·65	*187·35*	(4) 28589·30				

The structure is similar to that of the arc multiplets of nine lines, and the intensities follow the same distribution law. Moreover, the separations *114·06* and *72·53* are identical with those of the enhanced triplet $\lambda\lambda$2949, 2939, 2933.

It is very interesting to compare the main separations of this multiplet with those of the arc multiplet thus :—

Separations in Mn . .	*229·70*	*169·55*	*116·96*	*68·75*
Separations in Mn^+ .	*269·28*	*187·34*	*120·00*	*58·63*

An attempt may be made to interpret the preceding regularities in the spectrum of Mn^+. The persistence of the reversed negative triplet $\lambda\lambda$2576, 2594, 2606 has been investigated by POLLOK,* MORROW,† and by HARTLEY and MOSS‡. POLLOK gives the lines of this triplet as the "ultimate" lines in the spark, and those which appear next are the components of the diffuse triplet $\lambda\lambda$2453, 2438, 2428. With this MORROW agrees, and HARTLEY and MOSS place the lines of these triplets among the most persistent lines of the spark. The negative triplet $\lambda\lambda$2576, 2594, 2606, thus seems to be the first member of the principal series $1s^+-mp^+$ and the triplet at $\lambda\lambda$2453, 2438, 2428 a member of the diffuse series $1p^+-md^+$. The observations of the extreme ultra-violet at present available are unfortunately insufficient for tracing the series further.

The strong enhanced triplet $\lambda\lambda$2949, 2939, 2933 is comparable in intensity with the narrow arc triplets forming the series S or D, so that it may be a member of the enhanced series S or D, equivalent to the arc singlets in the alkaline-earths.

The enhanced multiplet at λ3497, which shows the separations of the preceding triplet, seems to be analogous to the arc multiplet at λ5341, which contains the separations of the S and D arc series.

The present fragmentary evidence thus seems to indicate that the enhanced lines form a complex triplet system which is built up on the *same* plan as the arc spectrum.

* 'Proc. Roy. Dublin Soc.,' vol. 13, p. 202 (1912).

† 'Proc. Roy. Dublin Soc.,' vol. 13, p. 269 (1912).

‡ 'Roy. Soc. Proc.,' A, vol. 87, p. 38 (1912).

6. The Occurrence of "Multiplets" in other Spectra.

In Sections 4*e* and 5 it has been shown that in the spectra of the neutral atom and ionised atom of manganese many lines of the same character are related by certain separations and form clearly defined multiplets. The accuracy of the separations, some of them being identical with those of the ordinary series, together with the fact that the lines of each group are of the same character, strongly suggests that the multiplets have a real physical significance. Further evidence for their reality is afforded by the occurrence of similar multiplets in the spectra of other elements.

Chromium.—The spectrum of the normal atom of chromium has been examined in some detail, but the investigation is not completed, and no attempt will be made to describe the whole system of series and multiplets. It may be said, however, that the arc spectrum of chromium exhibits triplet series analogous to the series *p*, *s*, *d*, and *f* in manganese, and series of narrower triplets with separations about *8·8* and *5·6*, quite analogous to the series P, S, and D in manganese; further, there are multiplets of a similar character to those of manganese. It will suffice at present to give details of three of the groups. These were identified by a comparative study of the spectra of the flame and the arc. Also, the work of King* on the variation with temperature of the electric furnace spectrum has been utilised.

The wave-lengths (Exner and Haschek corrected to I.A.) and other data relating to the three multiplets are collected in the following table:—

Table V.—Multiplets of the Neutral Atom of Chromium.

Cr Multiplet I.				Cr Multiplet II.				Cr Multiplet III.			
λ (I.A.).	Int.	ν.	Temp. Class.	λ (I.A.).	Int.	ν.	Temp. Class.	λ (I.A.).	Int.	ν.	Temp. Class.
5247·55	(6)	19051·2	I	3883·33	(10)	25743·8	I	4337·58	(20)	23047·9	I
64·18	(6)	18991·0	I	85·21	(8)	731·4	I	39·46	(20)	037·9	I
65·73	(6)	18985·5	I	86·77	(8)	721·0	I	39·74	(12)	036·4	I
96·69	(5)	874·4	I	94·05	(7)	673·0	I	44·52	(25)	011·1	I
98·29	(7)	868·7	I	3902·90	(6)	614·8	II ?	51·05	(15)	22976·5	I
5300·71	(4)	860·2	I	03·14	(5)	613·3	II	51·85	(40)	972·5	I
45·80	(7)	701·1	I	08·76	(10)	576·4	II	59·65	(20)	931·2	I
48·31	(6)	692·3	I	16·26	(6)	527·3	I	71·31	(20)	870·1	I
5409·81	(8)	479·8	I	19·17	(12R)	508·4	II	73·25	(6)	859·9	I
				21·06	(9)	496·1	I	84·98	(20)	798·7	I
				28·67	(10)	446·7	I	91·76	(6)	763·4	I
				41·52	(10)	363·8	I	4412·27	(6)	657·7	Ia

A photograph of the green region in which the first multiplet appears has been given by King, showing the arc spectrum and the spectra obtained at three different stages

* 'Astroph. Journ.,' vol. 41 (1915).

of temperature of the electric furnace. At the lowest temperature there remain nine strong lines of the same character, while the other lines which are strong in the arc have greatly decreased in intensity. The multiplet is formed of these nine lines and may be represented as follows :—

				(5) 18874·4	*116·6*	(6) 18991·0	*60·2*	(6) 19051·2
				5·7		*5·5*		
		(7) 18701·1	*167·6*	(7) 18868·7	*116·8*	(6) 18985·5		
		8·8		*8·5*				
(8) 18479·8	*212·5*	(6) 18692·3	*167·9*	(4) 18860·2				

This multiplet includes the separations *8·5* and *5·7* of the series S and D, and also four separations which are surprisingly close to the four important separations in manganese, as shown by the following comparison :—

Cr (neutral atom)	*212·5*,	*167·8*,	*116·7*,	*60·2*
Mn (neutral atom)	*229·7*,	*169·5*,	*116·9*,	*68·6*
Mn^{+} (ionised atom)	*269·3*,	*187·3*,	*120·0*,	*58·6*

These four separations occur also in the second and more complex multiplet of chromium as shown in the following scheme :—

				(9) 25496·1	*117·2*	(5) 25613·3	*59·7*	(7) 25673·0
				118·7		*118·1*		
		(10) 25446·7	*168·1*	(6) 25614·8	*116·6*	(8) 25731·4		
		129·7		*129·0*				
(10) 25363·8	*212·6*	(10) 25576·4	*167·4*	(10) 25743·8				
144·6		*144·6*						
(12R) 25508·4	*212·6*	(8) 25721·0						

Mixed with the lines of this multiplet there are many other lines, but, with one exception, they belong to temperature classes III., IV., or V.; the outstanding line 3916·26 (I.A.), $= \nu 25534 \cdot 6$, belongs to class I., but it has not been found to have any connection with the multiplet.

The third multiplet of chromium is mixed with many other lines, but all the latter belong to classes III., IV., and V. The structure of the multiplet is shown in the following arrangement of the wave-numbers :—

				(6)		(15)		(12)
				22859·9	*116·6*	22976·5	*59·9*	23036·4
				71·3		*71·4*		
		(6)		(20)		(20)		
		22763·4	*167·8*	22931·2	*116·7*	23047·9		
		106·7		*106·7*				
(6)		(20)		(20)				
22657·7	*212·4*	22870·1	*167·8*	23073·9				
141·0		*141·0*						
(20)		(25)						
22798·7	*212·4*	23011·1						
173·5								
(40)								
22972·5								

Other elements.—A preliminary consideration of the spectra of other elements has shown the existence of multiplets in the arc spectra of magnesium, calcium, strontium, barium, silicon, and in the enhanced spectra of aluminium, scandium, yttrium, and lanthanum.* It results that when the diffuse triplets include six lines, as in the arc spectra of the alkaline-earths, the typical multiplet is also formed from six lines. On the other hand, if the diffuse triplets are formed from nine lines, as in manganese, the typical multiplet is also composed of nine lines.

The recognition of such multiplets is of importance as affording a means of determining the probable constitution of the series in some of the spectra which have not been resolved into series of the regular types. Such knowledge is of particular interest in the consideration of the spectra in relation to the periodic classification of the elements.

7. The Spectrum of Manganese and the Periodic Table.

It has long been recognised that there is a relation between the spectral structure of an element and its place in the periodic table. Rydberg† found that the elements with even valencies have triplet series, while those which have odd valencies have doublet series. There were two well-known exceptions: one of them being manganese, which, having an odd number valency, yielded triplet series. The other exception was the alkaline-earth elements, which give doublets in addition to the triplet series. The latter exception, however, is no longer valid, as it is now considered that these doublet

* The existence of groups of lines whose relations with the typical series were not clear was recognised by Saunders ('Astrophys. Journ.,' vol. 32, p. 166, 1910), in Ca, Sr, and Ba, and by Campo ('Asoc. Española Prog. Ciencias,' vol. 7, p. 351, 1921), in Ca. Popow ('Ann. d. Phys.,' vol. 45, p. 147, 1914) has also drawn attention to groups of lines in certain elements and has suggested that they may represent combinations of diffuse type.

† See Kayser, 'Handbuch der Spectroscopie,' vol. 2, p. 589.

series belong to the spectrum of the ionised atom, while the triplet series belong to the spectrum of the neutral atom. Hence it seems that the constitution of a spectrum by doublets or by triplets depends upon the number of the outer electrons in the atom. If this is an odd number the spectrum of the neutral atom will be composed of doublets, and if it is an even number it will be composed of triplets. Further, in the same element, if the spectrum of the neutral atom is composed of triplets, when the atom loses an electron and thus becomes ionised, its spectrum might be expected to contain doublets, as is the case with the alkaline-earths. Hence, as already recognised, some relation between the spectrum of the ionised atom of an element and that of the neutral atom of the preceding element in the periodic table may be expected. SOMMERFELD* and FUES† have indeed suggested certain numerical relations between the doublet series in the spectra of the ionised atoms of the alkaline-earths and the doublet series in the spectra of the alkali metals.

From the preceding remarks it might be expected that the manganese spectrum, by reason of its place in the periodic table (atomic number $Z = 25$, column VII), would present doublet series in the spectrum of the neutral atom and triplet series in that of the ionised atom. The present investigation, however, has shown that the manganese arc spectrum consists of triplets which follow a formula with the constant "N" of RYDBERG, and hence belong to the neutral atom. The spark series also seem to be formed of triplets. SOMMERFELD‡ remarks that the number of electrons in the outer ring of the manganese atom, and in the atoms of neighbouring elements in the periodic table, is *two,* as deduced by LADENBURG§ by chemical methods, and so the exception to the simple relation between arc spectra and the periodic table is explained. But seeing that the series of ionised manganese are also formed of triplets, it is necessary to suppose that when the manganese atom loses one of the two outermost electrons the remaining electron falls into the adjacent inner ring; or, more probably, that an electron from this ring *comes out* to the outermost ring. Otherwise the spectrum given by an atom having a single outermost electron would contain doublets, if the alternate rule of triplets and doublets were valid.

The second hypothesis is supported from another point of view, derived from the study and interpretation of the magnetic properties of the elements. CABRERA‖ concludes that the transference of an electron from the outermost ring to the adjacent inner one originates the changes in valency and in the magnetic properties of the paramagnetic elements of the iron group, Cr, Mn, Fe, Ni, Co. In the case of

* *Loc. cit.*, p. 299.

† 'Ann. d. Phys.,' vol. 63, p. 1 (1920).

‡ *Loc. cit.*, p. 304.

§ 'Naturwissenschaft,' vol. 8, p. 5 (1920).

‖ 'Asociación Española para el Progreso de las Ciencias, Congreso de Oporto,' Tomo II, p. 39 (1921).

Cr and Mn the arrangement of the electrons in the different rings may be as follows :—

Ring.	Chromium.		Manganese.	
	Trivalent.	Divalent.	Trivalent.	Divalent.
K	2	2	2	2
L	8	8	8	8
M	8	8	8	8
N	3	4	4	5
N (valency electrons)	3	2	3	2
	$Z = 24$		$Z = 25$	

Thus the trivalent chromium ($Z = 24$), by transference of an electron, gives the divalent chromium. The unstable trivalent Mn ($Z = 25$) resembles this, but has one more electron in the outermost ring and a correspondingly larger nuclear charge. The transference of this electron to the next ring gives rise to the very stable divalent manganese.

The spectrum of the neutral atom of manganese corresponds with that of the divalent manganese, which, having *two* electrons in the outermost ring, gives a spectrum containing *triplets*. When this atom loses an electron from the outermost ring, thus becoming ionised, it seems possible that one electron from the next ring, which possesses five, *comes out* to take its place, and hence the spectrum of the manganese ionised atom, having *two* electrons in the outermost ring, would also show *triplets* as actually observed.

It is also to be noted that the Mn^+ atom has a structure quite analogous to that of neutral Cr, the only difference being that the atom has a positive charge. The spectra of ionised manganese and neutral chromium would thus be closely similar, in accordance with the observed facts.

The preceding considerations are schematically represented in fig. 7.

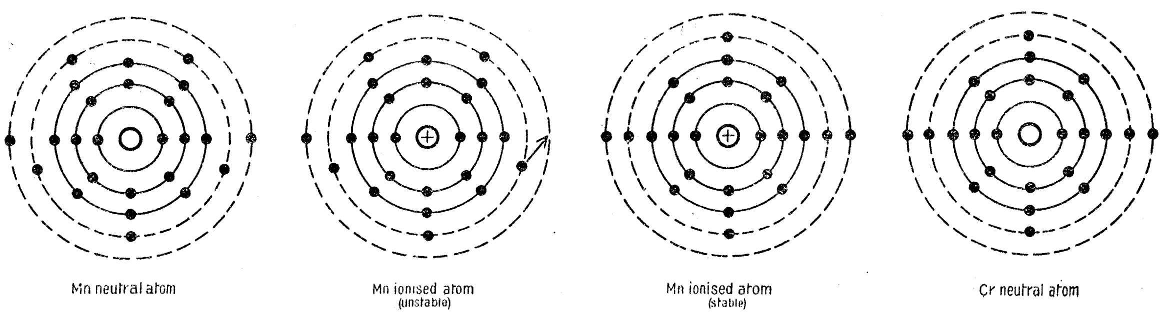


Fig. 7.

8.—Summary.

1. The flame, arc, and spark spectra of manganese, like those of other elements, are formed of two classes of lines, some belonging to the neutral atom and some to the ionised atom (Mn^+).

2. In the spectrum of the neutral atom, triplet series and combination lines have been found. The series follow a Hicks formula with the Rydberg constant "N" and may be classified as follows :—

(*a*) A system of four triplet series (sharp, diffuse, principal, and fundamental ; the last two being rather doubtful), analogous to the ordinary triplet systems of series in the alkaline-earths.

(*b*) A system of three narrower triplet series (sharp, diffuse, and principal) which have strong analogies with the singlet systems of series in the alkaline-earths.

(*c*) Another system of yet narrower triplets (sharp, diffuse, and principal) which is parallel to the preceding system, the shift number being $C = 10967 \cdot 75$.

3. The intercombination lines $1S - 1p_2$ and $1S - 1p_3$ ($\lambda 5394 \cdot 677$ and $\lambda 5432 \cdot 555$) between the first two systems are found as two lines very prominent at low temperatures, and losing very much of their intensity at high temperatures.

4. The ionisation and resonance potentials of manganese have been calculated from the term 1S and from the wave-number of the line $1S - 1p_2$. The values are 7·4 volts and 2·3 volts respectively.

5. The lines of ionised manganese ("enhanced" lines) also form triplets. The observations are not yet sufficiently complete to permit the series to be traced, but there is evidence that they include a system of triplets (sharp, diffuse, and principal), and also another system of narrower triplets, corresponding to the singlet systems in the alkaline-earths, as in the case of the neutral atom.

6. Each diffuse triplet, in neutral and ionised atom alike, is formed of *nine* lines, giving *five d* terms in contrast to the *six* lines giving *three d* terms which are found in the more familiar diffuse triplets of the alkaline-earths.

7. In the spectra of both the neutral and ionised atoms there are certain groups of prominent lines having the same character and showing similar variations with changes of temperature. The lines of each group are related by very exact numerical separations and it is suggested that the word "multiplet" be used to denote them.

8. It is pointed out that similar multiplets exist in the spectra of Mg, Ca, Sr, Ba, Al^+, Sc^+, Y^+, La^+, Si, and Cr, and that they may represent a form of regularity present in the spectra of many elements, and serve to indicate the most probable nature of the series in the spectra where the actual series have not been traced.

9. The spectrum of manganese in relation to the place of the element in the periodic table is discussed. It seems probable that the neutral atom of manganese has *two* electrons in the outermost ring, and that when this atom loses an electron, thus becoming ionised, another electron, from the next ring, comes out to take its place in the outermost ring, which again contains *two* electrons. The similarity of the spectra of the neutral and ionised atoms may thus be accounted for.

TABLE VI.—Classified Lines in the Spectrum of the Neutral Atom of Manganese.

λ (I.A.).	Int.	Temp. Class (KING).	ν.	Δν.	Series.
2575·51	5	—	38815·6	*129·2*	
84·12	3	—	686·4	*173·7*	s (5) ?
95·77	4	—	512·7		
2604·21	1	—	389·4	*128·6*	
12·86	2	—	260·8	*174·1*	d (5)
24·80	2	—	086·7		
48·79	1	—	37741·8	*129·0*	
57·88	1	—	612·8	*173·8*	s (4)
70·22	2	—	439·0		
2703·98	3U	—	36972·6	*128·6*	
13·35	3U	—	844·0	*173·1*	d (4)
26·15	4U	—	670·9		
94·23	2	—	35777·5	—	
94·822	10R	IV.	769·94	*44·12*	
98·273	9R	IV.	725·82	*35·75*; *129·2*	P (1)
2801·076	9R	IV.	690·07	*173·5*	
04·35	2	—	648·3	—	s (3)
18·09	3	—	474·8	—	
2914·62	6U	IV.	34299·8	*128·6*	
25·59	6U	IV.	171·2	*173·4*	d (3)
40·51	7U	IV.	33997·8		
3044·573	6	III.	32835·76		
54·386	5	III.	730·31		
62·132	4	III.	647·52	*229·7*	
66·035	3	III.	605·97	*169·5*	
70·290	5	III.	560·77	*117·0*	Multiplet VII.
73·144	4	III.	530·54	*68·6*	
79·638	5	IV.	461·95	*124·3*	
81·347	4	IV.	443·94	*86·7*	
82·062	2	—	436·42		
3148·192	4	IV.	31755·09	*129·22*	
61·055	5	IV,	625·87	*173·63*	s (2)
78·508	6	IV.	452·24		
3206·915	3	IV.	173·64		
12·897	6	III.	115·60		
26·043	2	IV.	30988·81		
30·725	3	III.	943·90		
36·787	6	II.	885·94	*229·7*	
40·408	3	III.	851·44	*169·5*	?*
40·624	3	IV.	849·38	*116·9*	
43·784	4	III.	819·32	*68·6*	Multiplet IX.
48·521	4	III.	774·38		
51·139	3	IV.	749·60	*58·0*	
52·954	4	III.	732·45	*44·9*	
54·040	2	IV.	722·19	*30·1*	?*
56·141	4	III.	702·36	*17·1*	
58·417	4	III.	680·92		
60·237	4	III.	663·80		

* These lines do not certainly belong to Multiplet IX.

TABLE VI. (continued).

λ (I.A.).	Int.	Temp. Class (KING).	ν.	Δν.	Series.
3264·713	4	III.	30621·76		?
78·553	3	IV.	492·49		?
96·029	2	IV.	330·83	*229·7*	?
96·884	3	IV.	322·97	*169·5*	?
3308·791	3	IV.	213·83	*117·0*	?
16·324	3	IV.	149·32	*68·6*	?
43·728	2	IV.	29898·18		?
51·427	1	—	829·50		?
3531·833	7·5R	III.	28305·85	*2·36*	
31·990	7·8R	III.	304·58	*1·85*	
32·110	8R	III.	303·68	*1·25*	
47·792	8·5R	III.	178·52	*0·90*	
48·024	8R	III.	176·68		*d* (2)
48·180	7·5R	III.	175·44		
69·499	10R	III.	007·16	*129·17*	
69·798	9R	III.	004·82	*173·71*	
70·034	7R	III.	002·97		
77·880	6R	II.	27941·57		
86·540	5	II.	874·10	*229·7*	
95·112	3	III.	807·64	*169·5*	
3607·530	6	II.	711·92	*117·0*	
08·484	6	II.	704·60	*68·6*	Multiplet V.
10·296	6	III.	690·69		
19·399	4	III.	620·53	*162·2*	
23·790	4	III.	587·58	*103·1*	
29·739	3	III.	542·37		
42·662	1	—	444·65	—	$1p_2—2p$?
64·624	1	—	280·18	—	$1p_1—2p$?
3776·537	1	—	26471·79		
90·215	3	III.	376·19		
99·256	2	III.	313·49		
3806·866	10R	I.	260·93	*229·7*	
09·599	6	II.	242·07	*169·5*	
16·746	2	III.	192·93	*117·0*	
23·515	9R	II.	146·56	*68·6*	
23·896	5	II.	143·94		
26·628	1	—	125·28	—	Multiplet VIII.
27·904	1	—	116·57	— *8·71*	
29·674	2	II.	104·50	*14·20*	S_c (3)*
29·987	2	—	102·37	—	
33·864	6	II.	075·92	*115·3*	
34·363	8R	II.	26072·58	*95·5*	
38·329	2	II.	045·64	*71·4*	
39·777	4	II.	035·82	*49·0*	
41·081	5	II.	026·97	*28·5*	
43·985	4	II.	007·31	*9·8*	

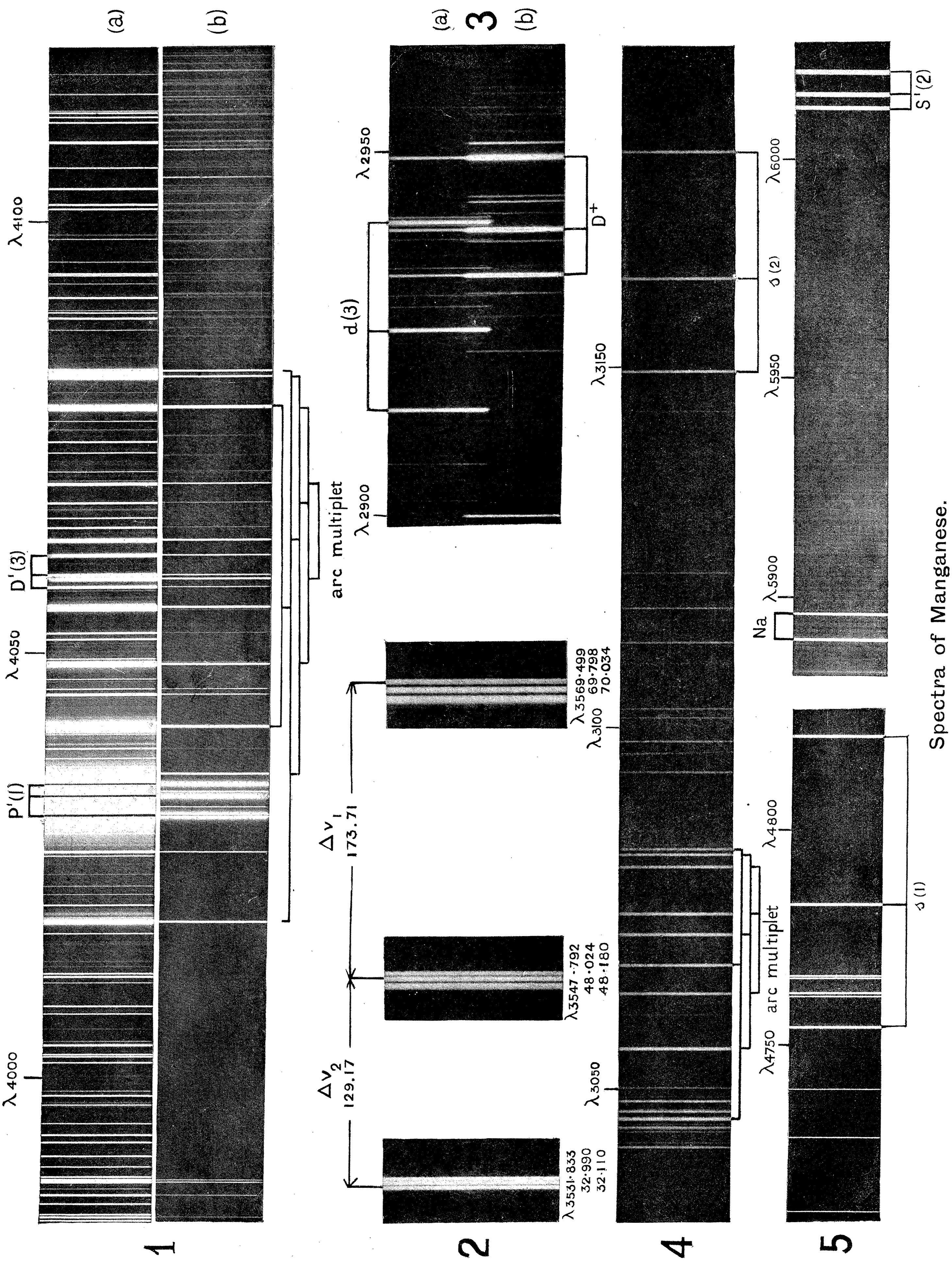
* Series S_c (*m*) denotes the series parallel to S (*m*), and the same notation is adopted for the remaining series of this system.

TABLE VI. (continued).

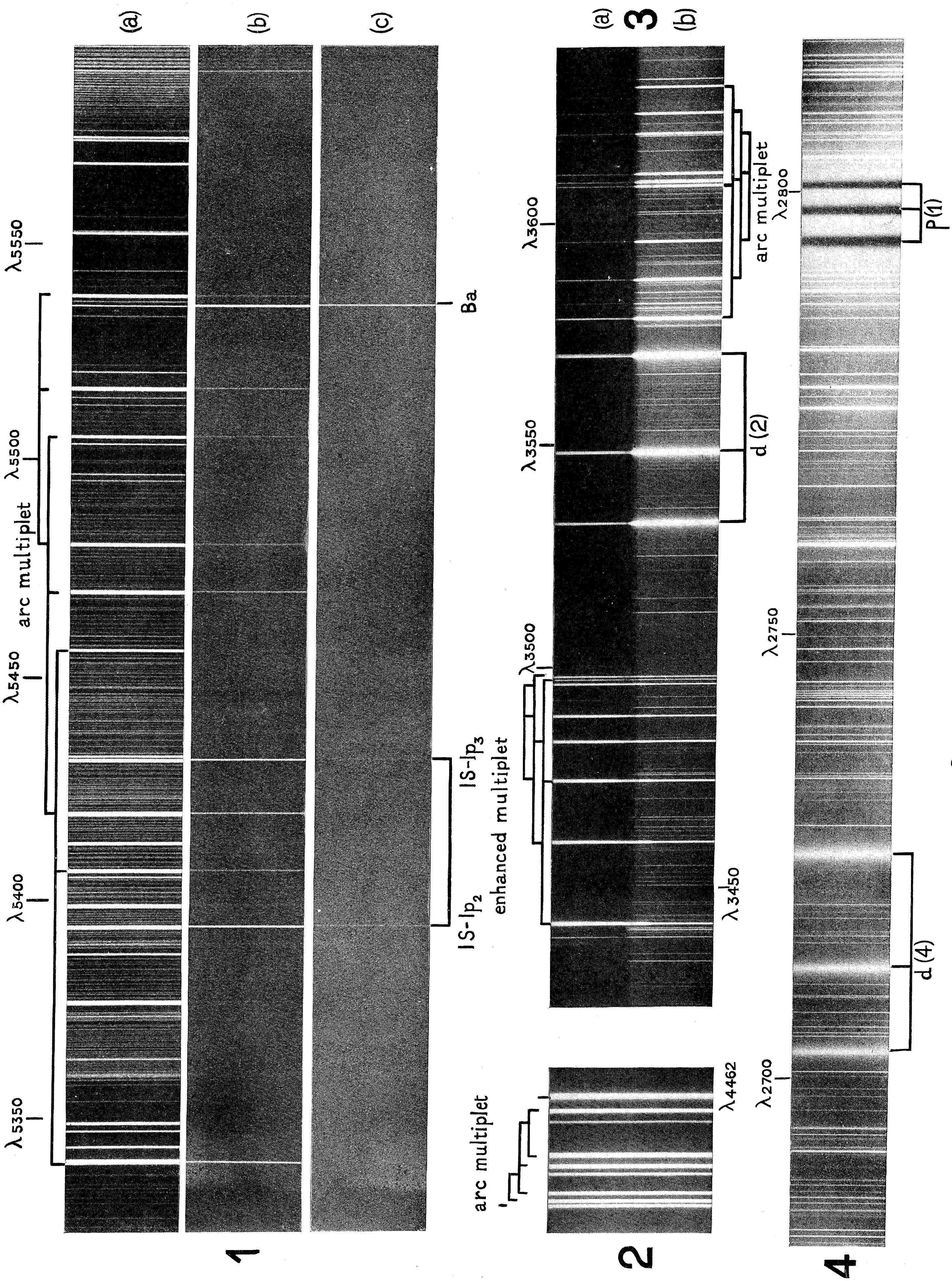
λ (I.A.).	Int.	Temp. Class (KING).	ν.	Δν.	Series.
4018·108	8	I.	24880·32		
30·760	10R	I.	802·23	— 14·22	
33·074	9R	I.	788·01	— 8·70	P_c (1)
34·489	9R	I.	779·31	—	
35·730	5	I.	771·69	*229·7*	
41·366	10R	I.	737·15	*169·5*	
48·760	4	I.	691·97	*117·0*	
55·553	8	I.	650·62	*68·6*	
57·959	3	V.	635·99	—	
58·936	2	I.	630·06	*8·73*	Multiplet VI.
59·399	2	IV.	627·26	— *14·23*	D_c (2)
61·744	2	V.	613·03	—	
63·533	4	II.	602·18	*143·2*	
68·029	2	—	575·01	*121·1*	
70·280	2	II.	561·43	*89·8*	
79·245	6	I.	507·44	*55·1*	
79·428	6	I.	506·34		
82·947	6	I.	485·22		
83·639	6	I.	481·07		
4455·019	6	III.	22440·32	*4·8*	
55·320	6	III. ?	438·80	*3·5*	
55·820	5	III.	436·29	*2·6*	
57·041	5	III.	430·14	*1·4*	
57·553	6	—	427·56		Multiplet I.
58·263	6	II.	423·99		
60·376	3	—	413·37	*14·2*	
61·089	6	III.	409·84	*8·7*	
62·033	8R	III.	405·85		
4754·048	9	I.	21028·85	*129·18*	
83·432	9	I.	20899·67	*173·71*	*s* (1)
4823·522	10	I.	725·96		
5341·070	10	III.A	18717·64		
94·677	7	I.A	531·65	—	1S—$1p_2$
5407·432	6	III.A	487·97	*229·7*	
20·368	6	III.A	443·82	*169·5* *129·20*	
32·555	5	I.A	402·45	*117·0* —	1S—$1p_3$
57·468	3	II.A	318·44	*68·6*	Multiplet III.
70·640	8	II.A	274·33		
81·395	6	II.A	238·48	*44·1*	
5505·877	4	III.	157·38	*35·8*	
16·773	7	III.A	121·52		
37·749	8	III.	052·88		
6013·484	7	III.	16624·71	*8·72*	
16·636	7	III.	615·99	*14·21*	S_c (2)
21·787	8	III.	601·78		
6315·064	2	—	15830·78	—	*p* (4)
6570·830	2	—	214·59	*35·80*	
86·357	2	—	178·79	*44·17*	S (3)
6605·546	2	—	134·62		
7283·80	6	—	13725·33	*35·95*	
7302·92	6	—	689·38	*44·13*	D (2)
26·55	7	—	645·25		
83·59	1	—	539·82	—	1*s*—3*f*

TABLE VI. (continued).

λ (I.A.).	Int.	Temp. Class (KING).	ν.	Δν.	Series.
7646·34	3	—	13074·56	*9·52*	
51·91	3	—	065·04	*7·38*	*p* (3)
56·24	2	—	057·66		
8670·85	2	—	11529·71	*4·8*	
72·08	2	—	528·09	*3·5*	
74·01	2	—	525·53	*2·6*	
99·13	2	—	492·24	*1·4*	
8701·04	2	—	489·72		Multiplet II.
03·73	3	—	486·17		
34·64	1	—	445·53	*14·2*	
37·29	2	—	442·05	*8·7*	
40·91	3	—	437·32		
11377·9	15	—	8786·6	—	*f* (4)
12899·7	80	—	7750·0	*229·7*	
13294·1	50	—	7520·1	*169·5*	
13317·9	30	—	7506·7	*117·0*	Multiplet IV.
13625·7	200	—	7337·1	*68·6*	
13863·8	100	—	7211·1		
13997·0	120	—	7142·5	*14·2*	
15263·1	200	—	6550·0	*8·7*	*p* (2)
15964·9	200	—	6262·0	—	*f* (3)
17607·5	20	—	5677·9	—	S (2)



Spectra of Manganese.



Spectra of Manganese.

Table VII.—Classified Lines in the Spectrum of the Ionised Atom of Manganese.

λ (I.A.).	Int.	Temp. Class (King).	ν.	Δν.	Series.
2427·43	3	—	41183·3	*10·6*	
27·77	4	—	177·5	*8·7*	
27·97	4 ?	—	174·1	*4·7*	
37·45	5	—	015·7	*3·4*	
37·92	3	—	006·1		
38·22	3	—	001·1	*176·9*	d^+ (?)
52·63	10	—	40761·9	*263·6*	
53·17	2	—	751·3		
53·65	1	—	743·0		
2576·116	10R	—	38806·52	*263·58*	
93·734	9	—	542·94	*176·91*	p^+ (1)
2605·695	9R	—	366·03		
2949·207	10	IV.	33897·54	*114·08*	
39·315	9	V.	34011·62	*72·45*	S^+ (?)
33·066	8	V.	084·07		or D^+ (?)
3497·540	6	V.	28583·37		
96·815	4	V.	589·30	*269·28*	
95·840	8	V.	597·26	*187·34*	
88·618	8	V.	655·89	*120·00*	
82·918	7	V.	703·37	*58·63*	Multiplet$^+$
74·139	6	V.	775·90		
74·050	7	V.	776·65	*114·07*	
60·332	8	V.	890·71	*72·53*	
41·999	9	V.	29045·93		

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Description of Plates.

Spectra of Manganese.

Plate 1. Fig. 1. (*a*) Arc; (*b*) flame-arc.
Fig. 2. Arc, showing first diffuse triplet, enlarged 12 times.
Fig. 3. (*a*) Arc; (*b*) spark.
Figs. 4 and 5. Arc.

Plate 2. Fig. 1. (*a*) Arc; (*b*) middle of flame-arc; (*c*) edge of flame-arc.
Figs. 2 and 4. Arc.
Fig. 3. (*a*) Spark; (*b*) arc.

Spectra of Manganese.

Spectra of Manganese.