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Bakerian Lecture: Series Lines in Spark Spectra

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VI. BAKERIAN LECTURE.—*Series Lines in Spark Spectra.*

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[PLATE 3.]

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§ 1. *Introductory.*

THE classical work of RYDBERG, and that of KAYSER and RUNGE, dealt mainly with series lines in spectra which are developed in the flame or electric arc, or in vacuum tubes with discharges of moderate intensity. The lines to be discussed in the present communication are some of those which belong to the class of *enhanced* lines as defined by LOCKYER; that is, they are relatively intensified in passing from arc to spark conditions.

In considering these lines it is necessary to take account of the fact that their behaviour in the arc is different for different elements. At least three classes may be recognised :—(I.) Enhanced lines like the H and K lines of calcium, which are well developed in the ordinary arc; (II.) Lines which only appear with small intensities in the arc, such as the enhanced lines of iron; (III.) Lines which do not appear in the ordinary arc (except very locally near the poles), but are strongly developed under spark conditions, as in the case of the well-known magnesium line at λ 4481.

Until very recently the only evidence that enhanced lines may belong to series was that afforded by RUNGE and PASCHEN's observations of the spectra of magnesium, calcium, strontium, barium, and radium, under the influence of a magnetic field. In the case of each of these elements, three pairs of lines of Class I. were observed, and though no series formulæ could be calculated for them, the magnetic resolutions proved that one pair belonged to the Principal series, another to the Sharp, and the third to the Diffuse series. Further discussion of these series has become possible through the valuable work of LYMAN in the Schumann region, published in 1912.

The present investigation was undertaken in connection with the new series of lines which were produced in 1912 by passing strong condensed discharges through helium tubes containing hydrogen as an impurity.* These lines, of which the strongest is at λ 4686, are of considerable importance in celestial spectroscopy because of their occurrence in the spectra of some of the nebulæ, and in stars which are generally regarded as representing the earliest stages of stellar condensation. One of the series, only feebly visible, was in apparent agreement with a series of lines first observed in ζ Puppis by PICKERING, and attributed to hydrogen because of their simple relation to the Balmer hydrogen series. The other was a strong series, which included the lines assigned by RYDBERG to the Principal series of hydrogen from analogy with the spectra of the alkali metals. In addition to the RYDBERG lines, however, the "4686" series included intermediate lines, which the then recognised formulæ suggested was a second Principal series related in a simple manner to the first. As the new lines could not be obtained from hydrogen alone, and in consideration of the occurrence of lines not anticipated by RYDBERG, it was soon felt that further inquiry should be made as to the value of the numerical evidence on which their assignment to hydrogen was chiefly

* 'Monthly Notices, R.A.S.,' vol, 73, p. 62 (December, 1912).

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founded. A search for other series of similar character was therefore undertaken, in the hope that some generalisation with regard to such series might be arrived at.

The mode of production of the "4686" lines suggested spark spectra as the most promising source of such series, and, shortly afterwards, experiments on magnesium yielded some new lines of that element which were obviously associated with the spark line 4481 in series of the kind looked for. No satisfactory evidence of relation to other series of magnesium lines, however, was then obtained, and it seemed possible that both the "4686" and the "4481" series were of a new type, having no necessarily simple relation to other known series in the respective spectra.*

The lines of the "4686" and the associated Pickering series have since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical investigations of Dr. BOHR.† Beginning with the "Rutherford" model of the atom, and introducing PLANCK'S quantum, Dr. BOHR has derived a formula for the hydrogen spectrum which excludes these lines, while agreeing closely with the hydrogen series about which there can be no doubt. The "4686" and Pickering series, however, are included in another formula, derived for the emission of helium atoms during the first stage of their reformation when both electrons are supposed to have been removed by the strong discharges employed. This formula is identical, in a first approximation, with that for hydrogen except that the Rydberg constant "N" (= 109,675 for ROWLAND'S scale) has four times its ordinary value. The two "Principal" series previously assigned to hydrogen were thus united in a single formula and attributed to helium, while the Pickering series was made to include intermediate lines coincident with the Balmer series of hydrogen. As the lines in question, whatever their origin, must be regarded as enhanced lines, it was evidently desirable to continue the general investigation of lines of this class.

Further investigation of magnesium, in particular, was also suggested by the discovery made by PASCHEN,‡ and by KING,§ that the line 4481 is a close doublet ($\delta\lambda$ = about 0·2 Å.U.), as it appeared that a valuable indication of the type of series to which it belongs might be obtained if other members could be resolved. Photographs with high dispersion have accordingly been taken for the resolution of the lines and to provide more accurate data for testing the formula for enhanced lines which was suggested by the work of BOHR. Other photographs, taken with smaller dispersion, have resulted in the detection of additional lines which clearly belong to series related to that beginning with 4481. The discussion of the new data for magnesium, and of the data for calcium and strontium given by other observers, has led to some conclusions which are probably of general application to enhanced line series.

The chief results of the investigation are summarised in § 14.

* 'Roy. Soc. Proc.,' A, 1913, vol. 89, p. 133.

† 'Phil. Mag.,' vol. 26, p. 1 and p. 476 (1913).

‡ Communicated privately (1913, August).

§ 'Astrophys. Jour.,' vol. 38, p. 327 (1913).

§ 2. *Wave-lengths of the "4481" Series of Magnesium.*

The members of the "4481" series are essentially spark, or enhanced lines, but they are most conveniently produced in an arc between magnesium poles *in vacuo*, and are best observed in the blue green patch in the region of the negative pole, viewed end-on. Under these conditions they are obtained as very narrow lines, well adapted for accurate measurement. The new determinations of wave-lengths have been based as far as possible on the interferometer values for the lines of iron, or upon grating determinations depending upon such standards, among which those given by Dr. KEIVIN BURNS* have been especially useful.

The Line 4481.—Previous photographs taken in the 1st order of a concave grating of 10 feet radius gave no indication of the resolution of 4481, but photographs recently obtained in the 3rd and 4th orders show it to consist of two clearly separated lines (Plate 3, fig. 6), of which the more refrangible is the stronger, as stated by KING. The lines have no close resemblance to the side components of a reversed line, as the space between them is considerably greater than the thickness of either of them, and, as pointed out by KING, the measured separation is the same in photographs taken with different lengths of exposure, and in different orders of the grating. Iron arc comparisons were exposed both before and after the magnesium, and the plates were measured in the usual way with red right and red left. The mean results from numerous measurements are :—

International scale.	Rowland scale.	$\delta\lambda$.
4481·327	4481·495	
		0·198
4481·129	4481·297	

Dr. KING's values for the two components on ROWLAND's scale are 4481·499 ± 0·001 and 4481·284 ± 0·001 ($\delta\lambda$ = 0·215), but from the reproductions given in his paper, the lines do not appear to have been as narrow as those from which the above results were obtained.

[*Note.*—The new measurements of λ 4481 as a doublet permits of a more satisfactory conclusion as to its presence among the Fraunhofer lines than has hitherto been possible. ROWLAND tabulates two lines, each of intensity "0" at 4481·298 and 4481·515, with an intermediate titanium line (intensity 1) at 4481·438. The agreement for the stronger component, which is a very distinct line in ROWLAND's map, may be considered exact, but the discordance on the less refrangible line exceeds the probable error of measurement, and the intensity is also a little too high in the sun. It may be, however, that both these discordances are caused by a still fainter solar line which is nearly superposed on that of magnesium, since such lines are very numerous. The presence of Mg 4481 as faint lines in the solar spectrum may therefore be considered

* 'Zeitsch. f. Wiss. Photog.,' 1913, XII., 6, p. 219; 'Lick Obs. Bull.,' vol. VIII., No. 247 (1913).

very probable, indicating a condition somewhat more advanced than the ordinary arc, in the direction of the spark.]

The Line 3104.—This line was easily resolved in the 4th order of the grating (Plate 3, fig. 7), and has two components exactly resembling those of 4481, but separated by less than one-tenth of an Ångström unit. The iron arc comparison was photographed through a glycerine solution of para-nitroso-dimethyl-aniline contained in a quartz cell, as recommended by Prof. R. W. Wood.* This solution absorbs the superposed 3rd order spectrum, but transmits the 4th order lines with reference to which the magnesium lines were measured. The mean results from three excellent plates with five comparison spectra are as follows :—

International scale.	Rowland scale.	$\delta\lambda$.
3104·805	3104·929	
		0·092
3104·713	3104·837	

The Line 2661.—On the assumption of a constant wave-number interval between the components of the resolved lines, the separation at 2661 would be about 0·07 Å.U. which is very near the limit of resolution of the grating. Hence with the exposures of 3 to 5 hours required in the 3rd and 4th orders, a very slight unsteadiness of conditions, such as might arise from small variations of temperature, would tend to mask any resolution which might otherwise be effected. Many 3rd order plates were taken, all of which show the line broadened, but only one suggests resolution, and on none of the 4th order plates was this result improved upon. Measurements of the best 3rd order plate gave the following wave-lengths :—

International scale.	Rowland scale.	$\delta\lambda$.
2660·821	2660·909	
		0·066
2660·755	2660·843	

These values are in good accordance with the mean of several determinations from 1st order plates, namely, 2660·785 (I.Å.), 2660·873 (R).

The Remaining Lines.—It has not been found possible to photograph beyond the first three lines in the higher orders of the grating, but the wave-lengths of the next two, 2449 and 2329, have been checked by a photograph in the first order, giving a dispersion of 5·5 Å.U. per mm. Wave-lengths of iron lines given by Burns were used for the line 2449, but were not available for 2329. The lines 2253, 2202, 2166 do not appear on any of the grating photographs, but are well shown on the original plates taken with a quartz spectrograph, giving an average dispersion in this region of about 6 Å.U. per mm. Further measurements have been made, but in the absence of better standards it has not been found necessary to modify the values given in the

* 'Phil. Mag.,' Series 6, vol. ~~6~~ 5, p. 257 (1903).

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previous paper. The reference spectrum for these lines was the copper arc, as given by KAYSER and RUNGE, and the lines are subject to an uncertainty of about 0·05 Å.U. in absolute value.

All the necessary details with regard to the "4481" series are brought together in Table I., the corrections to vacuum having been made from KAYSER's table.*

TABLE I.—The "4481" Series of Magnesium.

λ, wave-length (I.Å.).	Estimated limit of error in λ.	$\delta\lambda$.	n, wave-number (*in vacuo*).	Estimated limit of error in n.	δn.	Remarks.
4481·327	0·005	0·198	22,308·68	0·025	0·99	From 3rd and 4th order plates.
4481·129	0·005		9·67	0·025		
3104·805	0·005	0·092	32,198·99	0·05	0·94	From 4th order plates.
3104·713	0·005		9·93	0·05		
2660·821	0·01	0·066	37,571·43	0·14	0·94	From 3rd order plate.
2660·755	0·01		2·37	0·14		
2449·573	0·01		40,811·31	0·17		From 1st order plate.
2329·58	0·02		42,913·30	0·4		
2253·87	0·05		44,354·65	1·0		From quartz spectrograph.
2202·68	0·05		45,385·36	1·0		
2166·28	0·05		46,147·86	1·1		

From the separations of the three lines which have been resolved, it appears at once that the interval between the components, in wave-numbers, is sensibly constant, and that the series is therefore not of the ordinary Principal type. In a Principal series having a separation of 0·99 for the first member at 4481, the interval at 3104 would be reduced to 0·64, and at 2660 to 0·44, but there is no evidence of such contraction.

§ 3. *Formulæ for the* Mg "4481" *Series.*

The application to these lines of the ordinary formulæ of RYDBERG, RITZ, or HICKS, requires the division of the lines into two series by taking alternate lines, the two

* 'Handbuch der Spectroscopie,' Band II., p. 514.

series thus resembling the Diffuse and Sharp series which occur in the spectra of other elements. Two such series can only be included in a single formula in the special case when the fractional terms associated with the parameter m differ by exactly 0·5, the Rydberg constant N being then replaced by 4N, if m takes successive integral values. In the general case, an objection to this combination would be the smaller intensities of the lines of the Sharp as compared with those of the Diffuse series. The intensities of the "4481" lines, however, are graded as in an ordinary series, and the chief objection to uniting them in a single formula in the first discussion was the undesirability of introducing a new type of series formula for what seemed to be a special case, so long as the older formulæ could be employed. This objection is no longer valid, because, as will appear later, several other series of the same type, occurring in associated groups, have since been recognised.

From the formulæ previously given for the two divisions of the "4481" lines, it was evident that all the lines could be combined, at least very nearly, in one equation if desired. There were, however, small deviations, apparently systematic, which suggested that the union was not quite exact, but these have been removed by the new measurements, which became necessary when it appeared that the lines were doublets. It can no longer be doubted that the lines form a single series, differing from the more familiar series in that the lines occur twice as frequently; *i.e.*, if the ordinary formulæ involving the Rydberg constant N be employed, we find lines corresponding not only to the integral values m, but also to $m+\frac{1}{2}$. It will, however, be more convenient to employ formulæ in which m takes successive integral values only, N being then replaced by 4N or by a number of that order of magnitude.

As the positions of the lines have been determined with considerable precision, and the lines are fairly numerous, it seemed desirable to compare the accuracy of a variety of formulæ, some with N assumed the same as for hydrogen, and others with this term calculated from the lines themselves. The fact that not all the lines have been resolved, and the slight uncertainty as to the absolute positions of the last two or three lines of the series, renders the comparison to some extent wanting in finality, but the results may nevertheless be of interest.

For comparison of observed and calculated wave-numbers, the unresolved lines have been regarded as consisting of two components separated by 0·99, one having a wave-number greater by 0·33 than that of the unresolved line, and the other 0·66 less, since the more refrangible component is about double the intensity of the less refrangible. The wave-numbers adopted in the calculations for the less refrangible components, adjusted in this manner, are given in the first column of Table II. The wave-numbers are on the International scale, and have been corrected to vacuum. On this scale, the value of the Rydberg constant, according to an investigation by W. E. CURTIS* is 109,679·3.

* Not yet published.

The formulæ which have been calculated are as follows :—

I. RYDBERG'S, with N as for hydrogen,

$$n = 49{,}770{\cdot}45 - \frac{4 \times 109{,}679{\cdot}3}{(m + 0{\cdot}996943)^2} \qquad m = 3,\ 4,\ \ldots .$$

II. RYDBERG'S, with numerator calculated,

$$n = 49{,}781{\cdot}21 - \frac{4 \times 109{,}883{\cdot}9}{(m + 0{\cdot}999887)^2} \qquad m = 3,\ 4,\ \ldots .$$

III. HICKS', with N as for hydrogen,

$$n = 49{,}775{\cdot}20 - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 0{\cdot}994541 + \dfrac{0{\cdot}006170}{m}\right)^2} \qquad m = 3,\ 4,\ \ldots .$$

IV. RITZ'S, with N as for hydrogen,

$$n = 49{,}774{\cdot}76 - \frac{4 \times 109{,}679{\cdot}3}{\left(m - 0{\cdot}004714 + \dfrac{0{\cdot}021503}{m^2}\right)^2} \qquad m = 4,\ 5,\ \ldots .$$

V. RYDBERG'S, with numerator calculated, and $(m+\mu)$ assumed an integer

$$n = 49{,}781{\cdot}63 - \frac{4 \times 109{,}891{\cdot}8}{m^2} \qquad m = 4,\ 5,\ \ldots .$$

VI. Same as V.; least square solution, using all the lines,

$$n = 49{,}780{\cdot}44 - \frac{4 \times 109{,}885{\cdot}65}{m^2} \qquad m = 4,\ 5,\ \ldots .$$

The observed *minus* computed values resulting from these formulæ are shown in Table II.

TABLE II.—Less Refrangible Components of Mg "4481" Series.

Wave-number (I.Å.), *in vacuo.*	Estimated limit of error.	I.	II.	III.	IV.	V.	VI.	Remarks.
22,308·68	0·02	0·00*	0·00*	0·00*	0·00*	0·00*	−0·35	
32,198·99	0·05	−1·30	0·00*	0·00*	0·00*	+0·05	+0·25	
37,571·43	0·14	0·00*	0·00*	0·00*	0·00*	0·00*	+0·51	
40,810·65	0·17	+1·43	−0·15	+0·21	+0·25	−0·22	+0·47	Lines unresolved but wave-numbers adjusted.
42,912·64	0·4	+2·39	−0·63	+0·25	+0·34	−0·75	+0·05	
44,353·99	1·0	+3·48	−0·71	+0·70	+0·85	−0·88	0·00	
45,384·70	1·0	+4·11	−1·05	+0·86	+1·06	−1·26	−0·31	
46,147·24	1·1	+4·57	−1·37	+1·00	+1·23	−1·60	−0·62	
(46,727·2)†				(+1·15)				

* Used in calculation of constants.

† Calculated from equation III. assuming estimated error of formula.

It will be seen that the lines are very closely represented by any of the formulæ. Even the simple Rydberg equation (I.) leaves no error so great as a quarter of an Ångström unit, and it would require wave-lengths of still greater accuracy to test the relative merits of the other formulæ. In each case, however, the residuals, although very small, are sufficiently systematic to indicate that not one of the formulæ can be considered exact, unless some unrecognised source of systematic error in the determination of the wave-numbers may eventually be traced. In choosing between the different forms of equation it is accordingly necessary to be guided by experience of their application to other series of the same character, if they can be found. The result of such trials, as will presently appear, is to indicate that the Hicks form of equation is the one which most closely accords with the observations in general.

In the absence of an exact formula, a consideration of the residuals given in Table II. indicates that the limits of the "4481" series may be taken as 49778·0 and 49779·0 with very small probable error, and these values will be adopted in the subsequent discussion.

§ 4. *The Doublet Series of Calcium, Strontium, and Barium.*

Other series of lines apparently similar in character to the "4481" series of Mg were found in LYMAN'S observations of narrow doublets of Ca, Sr, and Ba in the Schumann region,* combined with SAUNDER'S observations in the ordinary ultra-violet. While the investigation was in progress, however, a discussion of the available observations of these series was published by E. LORENSER,† who also found that the ordinary formulæ could not be applied to them. LORENSER has further established that these series stand in the relation of Fundamental (F), or "Bergmann," series to the systems of series comprising the well-known wider doublets in the spectra of these elements, of which the H and K lines of calcium may be quoted as a familiar example. In each case the separation of the narrow doublets of the F series is identical with that of the first member and its satellite in the Diffuse (D) series of the wider doublets; and the limits of the F are apparently identical with the variable parts of the expressions for these lines.

Omitting Ba, which presents some difficulties, though generally conforming, LORENSER'S formulæ‡ are as follows, the Sharp series being indicated by S:—

* 'Astrophys. Jour.,' vol. 35, p. 341 (1912).

† 'Dissertation,' Tübingen (1913).

‡ Formulæ of this type were first employed for the doublets of Ba by SAUNDERS ('Astrophys. Jour.,' vol. 32, p. 164, 1910). In a later paper SAUNDERS also indicated a connection between the limits of the wide and narrow doublets ('Physical Review,' Series 2, vol. 1, p. 332, 1913).

Calcium—

Wide doublets . . . . .
$$\begin{cases} D(m) = \left.\begin{matrix}70{,}117\\70{,}340\end{matrix}\right\} - \dfrac{423{,}416}{(m-0{\cdot}69117)^2}, \\ S(m) = \left.\begin{matrix}70{,}117\\70{,}340\end{matrix}\right\} - \dfrac{421{,}559}{(m+0{\cdot}617844)^2}. \end{cases}$$

Narrow doublets . . . .
$$F(m) = \left.\begin{matrix}81{,}820{\cdot}0\\81{,}880{\cdot}8\end{matrix}\right\} - \frac{430{,}959}{(m-0{\cdot}039796)^2}.$$

Strontium—

Wide doublets . . . . .
$$\begin{cases} D(m) = \left.\begin{matrix}64{,}154\\64{,}954\end{matrix}\right\} - \dfrac{410{,}836}{(m-0{\cdot}59254)^2}, \\ S(m) = \left.\begin{matrix}64{,}154\\64{,}954\end{matrix}\right\} - \dfrac{415{,}157}{(m+0{\cdot}684636)^2}. \end{cases}$$

Narrow doublets . . . .
$$F(m) = \left.\begin{matrix}73{,}833{\cdot}5\\74{,}113{\cdot}2\end{matrix}\right\} - \frac{430{,}554}{(m-0{\cdot}056189)^2}.$$

The numeration of the members is shown in Tables III. and IV. (LOR. = LORENSER; FOW. = FOWLER).

The negative terms corresponding to $m = 3$ in the D series, and to $m = 1{\cdot}5$ in the S series (the latter giving the first P doublet), are given very erroneously by the formulæ, as is so often the case in the more familiar series. Nevertheless, LORENSER has fully established the connection of the F with the D series, through the usual relations, to which reference has already been made. There is sufficient evidence that the lines in question are to be regarded as enhanced lines, and, though LORENSER does not appear to have recognised this fact, his work proved that enhanced lines may form groups of related series which are generally similar to those occurring in arc spectra, but require modifications of the usual formulæ.

It will be observed that in LORENSER's formulæ the numerator is of the order of 4N as in those already found for the Mg "4481" series, and the question arises whether 4N may not be the universal constant for enhanced lines, as N is universal for series of lines produced under less violent excitation. The series are not long enough to give a very satisfactory comparison of the relative accuracy of different formulæ, but, so far as it goes, the evidence is distinctly in favour of the Hicks formula with 4N for the numerator. For the F series the formula may take the simpler Rydberg form with sufficient accuracy.

The formulæ for the above series are then as follows, the wave-numbers being on ROWLAND's scale to facilitate comparison with LORENSER's figures :—

Calcium—

Wide doublets . . .

$$D(m) = \begin{Bmatrix} 70{,}289{\cdot}2 \\ 70{,}512{\cdot}2 \end{Bmatrix} - \frac{4 \times 109{,}675}{\left(m + 0{\cdot}396204 - \frac{0{\cdot}106980}{m}\right)^2},$$

$$S(m) = \begin{Bmatrix} 70{,}289{\cdot}2 \\ 70{,}512{\cdot}2 \end{Bmatrix} - \frac{4 \times 109{,}675}{\left(m + 0{\cdot}222264 - \frac{0{\cdot}143832}{m}\right)^2}.$$

Narrow doublets . .

$$F(m) = \begin{Bmatrix} 81{,}948{\cdot}6 \\ 82{,}009{\cdot}4 \end{Bmatrix} - \frac{4 \times 109{,}675}{(m - 0{\cdot}013703)^2}.$$

Strontium—

Wide doublets . . .

$$D(m) = \begin{Bmatrix} 64{,}323{\cdot}3 \\ 65{,}123{\cdot}3 \end{Bmatrix} - \frac{4 \times 109{,}675}{\left(m + 0{\cdot}611476 - \frac{0{\cdot}283578}{m}\right)^2},$$

$$S(m) = \begin{Bmatrix} 64{,}323{\cdot}3 \\ 65{,}123{\cdot}3 \end{Bmatrix} - \frac{4 \times 109{,}675}{\left(m + 0{\cdot}344681 - \frac{0{\cdot}233220}{m}\right)^2}.$$

Narrow doublets . .

$$F(m) = \begin{Bmatrix} 73{,}968{\cdot}3 \\ 74{,}248{\cdot}0 \end{Bmatrix} - \frac{4 \times 109{,}675}{(m - 0{\cdot}028718)^2}.$$

The numeration of the members is shown in Tables III. and IV.

Details as to wave-lengths and wave-numbers of the lines involved, as quoted by LORENSER, are shown in Tables III. and IV., which also indicate the differences between the wave-lengths observed and those calculated from the two sets of equations.

An inspection of the tables will show that the observations are more closely represented in every case, and especially in the case of the negative terms, by the Hicks formula involving 4N than by the formula which has been employed by LORENSER. The superiority of the former is further shown in the greater accuracy with which it proves the identity of the limits of the F series with the variable parts of the expressions for the first line of the D series and its satellite. LORENSER has assumed this identity in determining the limits of the F series, thus—

$$\text{Ca}: \quad 70{,}117 + 11{,}703{\cdot}0 = 81{,}820{\cdot}0$$
$$70{,}117 + 11{,}763{\cdot}8 = 81{,}880{\cdot}8$$

$$\text{Sr}: \quad 64{,}154 + 9{,}679{\cdot}5 = 73{,}833{\cdot}5$$
$$64{,}154 + 9{,}959{\cdot}2 = 74{,}113{\cdot}2$$

If, however, the formulæ for the F series be calculated entirely from the F lines themselves we get the equations

TABLE III.—Calcium Doublets.

Wide—Diffuse series.						Wide—Sharp series.						Narrow—Fundamental series.				
λ (ROWLAND).	*n*.	*m*.		O – C (Δλ).		λ (ROWLAND).	*n*.	*m*.		O – C (Δλ).		λ (ROWLAND.)‡	*n*.	*m*.	O – C (Δλ).	
		LOR.	FOW.	LOR.	FOW.			LOR.	FOW.	LOR.	FOW.				LOR.	FOW.
– 8498·35* – 8542·47 – 8662·50	– 11,763·8 – 11,703·0 – 11,540·9	3	2	– 2195	– 1825	– 3933·83† – 3968·63†	– 25,413·5 – 25,190·6	1·5	2	– 259·5	– 130	1840·2 1838·0	54,341 54,406	4	0·0	0·0
3181·4* 3179·45 3158·98	31,423·8 31,443·0 31,646·8	4	3	0·0	0·0	3737·08 3706·18	26,751·4 26,974·5	2·5	3	0·0	0·0	1555·1 1553·5	64,304 64,370	5	0·0	0·0
2113·01 2103·47	47,311·2 47,525·8	5	4	0·0	0·0	2208·95 2198·03	45,256·6 45,481·4	3·5	4	0·0	0·0	1434·3 1433·1	69,720 69,778	6	– 0·65	– 0·27
1815·0 1807·8	55,096 55,316	6	5	– 0·08	+ 0·24	1851·3 1843·8	54,016 54,236	4·5	5	+ 0·2	+ 0·3	1370·6 1369·1	72,960 73,040	7	– 0·70	0·0
1680·5 1674·1	59,506 59,733	7	6	– 0·76	0·0	1698·9 1692·4	58,861 59,087	5·5	6	– 0·2	+ 0·3					

* Satellites.
† First doublet of Principal series.
‡ Wave-lengths *in vacuo*.

TABLE IV.—Strontium Doublets.

Wide—Diffuse series.						Wide—Sharp series.						Narrow—Fundamental series.				
λ (Rowland).	n.	m.		O – C (Δλ).		λ (Rowland).	n.	m.		O – C (Δλ).		λ (Rowland).‡	n.	m.	O – C (Δλ).	
		Lor.	Fow.	Lor.	Fow.			Lor.	Fow.	Lor.	Fow.				Lor.	Fow.
– 10,038·3*	– 9,959·2	3	2	– 5945	– 2823											
– 10,328·3	– 9,679·5					– 4077·88†	– 24,515·7	1·5	2	– 300·5	– 81	2166·11	46,151·6	4	0·0	0·0
– 10,915·0	– 9,159·2					– 4215·66†	– 23,715·7					2152·82	46,436·4			
3475·01*	28,768·8	4	3	0·0	0·0											
3464·58	28,855·4					4305·60	23,219·2	2·5	3	0·0	0·0	1778·8	56,217	5	0·0	0·0
3380·89	29,569·7					4161·95	24,020·6					1769·8	56,503			
2324·60*	43,005·2	5	4	0·0	0·0											
2322·47	43,044·6					2471·71	40,445·9	3·5	4	0·0	0·0	1620·7	61,702	6	– 1·4	– 0·96
2282·14	43,805·2					2423·67	41,247·4					1613·3	61,985			
1995·7	50,092	6	5	+ 1·30	+ 0·5	2053·3	48,687	4·5	5	+ 0·93	+ 0·7					
1965·2	50,869					2020·5	49,477									
1847·0	54,142	7	6	+ 0·06	0·0											
1820·0	54,945															

* Satellites.

† First doublet of Principal series.

‡ Wave-lengths *in vacuo*, except in case of first pair.

$$\text{Ca}: \ F(m) = \left.\begin{matrix} 82{,}044{\cdot}8 \\ 82{,}105{\cdot}6 \end{matrix}\right\} - \frac{444{,}561}{(m+0{\cdot}00586)^2},$$

$$\text{Sr}: \ F(m) = \left.\begin{matrix} 74{,}236{\cdot}6 \\ 74{,}516{\cdot}3 \end{matrix}\right\} - \frac{455{,}055{\cdot}1}{(m+0{\cdot}025265)^2}.$$

Thus, when LORENSER'S formula is used throughout the discrepancies are

$$\text{Ca}: \ 82{,}044{\cdot}8-81{,}820{\cdot}0 = 224{\cdot}8$$
$$\text{Sr}: \ 74{,}236{\cdot}6-73{,}833{\cdot}5 = 403{\cdot}1$$

The Hicks 4N formula gives the variable parts of the expressions for the first D lines and their satellites as

$$\text{Ca}: \ 70{,}289{\cdot}2+11{,}703{\cdot}0 = 81{,}992{\cdot}2$$
$$70{,}289{\cdot}2+11{,}763{\cdot}8 = 82{,}053{\cdot}0$$

$$\text{Sr}: \ 64{,}323{\cdot}3+ \ 9{,}679{\cdot}5 = 74{,}002{\cdot}8$$
$$64{,}323{\cdot}3+ \ 9{,}959{\cdot}2 = 74{,}282{\cdot}5$$

Comparing these values with the limits calculated from the observed F lines by means of the formula with 4N, we have the discrepancies reduced to

$$\text{Ca}: \ 81{,}992{\cdot}2-81{,}949 \quad = 43{\cdot}2$$
$$\text{Sr}: \ 74{,}002{\cdot}8-73{,}968{\cdot}3 = 34{\cdot}5$$

The discussion of the available data for calcium and strontium, therefore, leads to the conclusion that series consisting of enhanced lines may be represented by the formula of HICKS if the ordinary numerator N be replaced by 4N. It is, of course, to be understood that the formula is subject to the same limitations as the one involving N as applied to ordinary series.

There is, however, one important difference between the enhanced line series of Ca, Sr, and Ba, and the ordinary arc series of these and other elements, namely, that in the case of enhanced lines the first observed member of the Diffuse series appears with a negative sign, while in the corresponding ordinary series it has a positive sign. In each case the limit of the F series and the separation of the doublets are nevertheless derived from this first member taken with proper sign. This is the "new relation" discovered by SAUNDERS in connection with the wide and narrow doublets of Ca, Sr, and Ba, namely, "The convergence wave-number of the complex pair series (D) *plus* the wave-number of the first term equals the convergence wave-number of the narrow pair series (F)."

The modified Hicks formula may accordingly be employed with confidence in searching for possible relationships of the "4481" series with other series of enhanced lines of magnesium.

§ 5. *The Doublet System of Magnesium.*

The spectrum of magnesium, as is well known, also contains doublets similar to those occurring in calcium, strontium, and barium. They do not appear in the flame spectrum; they occur in the arc and are certainly intensified in the spark, and are therefore to be regarded as enhanced lines of Class I. LORENSER has discussed these lines, but has not identified any associated Fundamental series such as were found for the other three elements. The lines in question are indicated in Table V.

TABLE V.—Magnesium Wide Doublets.

Diffuse series.				Sharp series.			
λ (ROWLAND).	n.	m.		λ (ROWLAND).	n.	m.	
		LOR.	FOW.			LOR.	FOW.
				– 2795·63* – 2802·80*	– 35,759·9 – 35,668·4	1·5	1
2798·07 2790·88	35,728·7 35,820·7	3	2	2936·61 2928·74	34,043·1 34,134·6	2·5	2
1737·8 1735·0	57,544 57,637	4	3	1753·6 1750·9	57,025 57,113	3·5	3

Unfortunately, the observed lines are so few that the equations of the two series can only be determined completely by utilising all the lines in the calculation of constants, the limit derived from the Sharp series being assumed for the Diffuse. LORENSER'S formulæ with the numeration indicated in Table V. are

$$S(m) = \left.\begin{matrix} 84{,}893 \cdot 0 \\ 84{,}984 \cdot 5 \end{matrix}\right\} - \frac{413{,}202 \cdot 5}{(m+0 \cdot 35060)^2},$$

$$D(m) = \left.\begin{matrix} 84{,}893 \cdot 0 \\ 84{,}984 \cdot 5 \end{matrix}\right\} - \frac{423{,}376 \cdot 6}{(m+0 \cdot 065474)^2}.$$

The Hicks formulæ for these series, with the numeration shown under "Fow." in Table V., are

$$S(m) = \left.\begin{matrix} 85{,}479 \cdot 8 \\ 85{,}571 \cdot 3 \end{matrix}\right\} - \frac{4 \times 109{,}675}{\left(m+0 \cdot 938644 - \frac{0 \cdot 036421}{m}\right)^2},$$

$$D(m) = \left.\begin{matrix} 85{,}479 \cdot 8 \\ 85{,}571 \cdot 3 \end{matrix}\right\} - \frac{4 \times 109{,}675}{\left(m+0 \cdot 949439 - \frac{0 \cdot 040110}{m}\right)^2}.$$

* Also the first doublet of the Principal series.

These Mg doublets are analogous to the wider doublets of Ca, Sr, and Ba :—(1) They occur under precisely similar experimental conditions; (2) They show similar Zeeman effects (Runge and Paschen); (3) The separations of the components—Mg 91·5, Ca 223, Sr 801, and Ba 1691—are roughly proportional to the squares of the atomic weights; (4) The limits of the series follow a natural sequence, decreasing in the usual way as the atomic weight increases.

The analogy, however, is incomplete. In Ca, Sr, and Ba, the first negative terms of the D series, (given by $m = 2$ in the Hicks formula) correspond, as already mentioned, to observed lines (Tables III. and IV.) having satellite separations identical with those of the doublets in the associated F series; in these cases the satellite lies on the violet side of the more refrangible component of the D doublet, and not on the red side of the less refrangible component as in the positive terms of the same series. In Mg, on the other hand, the D pair given by $m = 2$ in the Hicks formula has a positive sign, and no lines have been observed near the position of the negative term (25,350 or about λ 3940) given by $m = 1$. An associated F series, by analogy, would be expected to have its limits near 110,830 (= 85,480+25,350), but there is no evidence of the existence of such a series.

The absence of a negative term in the observed D doublets of Mg suggests, as an alternative view, that the associated F series may be derived from the first line actually observed, namely λ 2798. In that case Lorenser's formula would give for the limit of the F series: 84,893·0−35,728·7 = 49,164·3, and the Hicks formula 85,479·8−35,728·7 = 49,751·1.

These figures at once suggest the limit 49,778 of the "4481" series; and the available data for the Wide doublets are, in fact, consistent with the assumption that the agreement is exact. It would seem then that the "4481" series may be a Fundamental series deriving its limits from the first positive line of the D series of Wide doublets. In that case the D line λ 2798 would be expected to have a satellite with the same separation as the lines of the "4481" series, namely, $\delta n = 0·99$. A special search for the satellite has been made in the photographs of the arc *in vacuo* taken in the fourth order of the grating, but it has not been directly observed. Indirect evidence of its possible existence, however, is afforded by careful measurements of the intervals of the Wide pairs. The new wave-lengths are given on the International Scale in Table VI. It will be seen that while the pairs of the P and S series are in close agreement, indicating a normal separation of 91·5, the interval of the D pair is not less, as would usually be the case if a satellite were present, but greater. This is confirmed by the recent measures of these lines by Nachen.* The measurements thus suggest that there is a satellite on the *more* refrangible side of the chief line, the separation being comparable with that in the "4481" series if we assume that the tabulated λ 2797·989 refers to the chief line itself. Such a reversal of the usual position of the satellite, however, would accord

* 'Zeitsch. f. Wiss. Photog.,' 1913, XII., 2, p. 59.

with the fact that the more refrangible component of the "4481" lines is also the stronger.

While it is thus probable that the "4481" series is numerically related to the D series of Wide doublets, there are objections to regarding it as directly derived from that series—

(1) The "4481" lines, unlike the doublets, do not occur in the ordinary arc; (2) The separation of the components of the "4481" lines is much too small compared with the F doublets of Ca, Sr, and Ba; the latter are roughly proportional to the squares of the atomic weights—Ca 65, Sr 285, Ba 575—and a corresponding F series of Mg would be expected to have a separation of about 20 in place of the 0·99 actually observed in the "4481" lines.

The probable nature of the relation, however, has been revealed by the discovery of a new system of doublets, with which the "4481" series appears to be directly associated. Before referring to these new lines it will be convenient to give further data for the Wide doublets, for comparison with similar data which will appear later for the new series. On the assumption that the variable part of the expression for the first observed pair of the D series is identical with one limit of the "4481" series, the corrected limit of the less refrangible components (I.Å.) becomes 49,779·0+35,729·6, or 49,778·0+35,730·6* = 85,508·6, and that of the more refrangible components, 85,508·6+91·5 = 85,600·1. These values have been utilised in the construction of Table VI. It is only necessary to explain that the symbols mD, mS,

TABLE VI.—Mg Wide Doublets. Revised Data.

Limits $\begin{cases} 85{,}508·6. \\ 85{,}600·1. \end{cases}$

m.	D series.				S series.			
	λ (I.Å.).	n.	δn.	mD.	λ (I.Å.).	n.	δn.	mS.
1					−2795·523†	−35,761·15	91·54	121,269·7
					−2802·698†	−35,669·61		121,269·7
2	2797·989	35,729·63 (35,730·6)‡	92·44	49,779·0 49,778·0	2936·496	34,044·44	91·48	51,464·2
	2790·768	35,822·07		49,778·0	2928·625	34,135·92		51,464·2
3		57,546 57,639		27,962·6 27,961·1		57,027 57,115		28,481·6 28,485·1

* Assumed wave-number of satellite to λ 2797·989.

† First P doublet.

‡ Wave-number of probable satellite.

in the convenient notation adopted by PASCHEN in his extensive researches on series, represent the differences between the wave-numbers of the observed lines and the limits of the series to which they belong. Thus, if the Hicks equation were exact, the symbol 3D would be an abbreviation for $4N\Big/\left(m+D+\frac{\Delta}{m}\right)^2$ when m has the value 3, and so on. Defects of formulæ are eliminated in evaluating the variable parts of the expressions in this manner, except as regards the determination of the limits. In the present case it is probable that the limits are also exact.

The differences between the two values of 3D, and between those of 3S are to be attributed to errors of observation.

§ 6. *A New System of Magnesium Doublets.*

Two conspicuous doublets, a little more refrangible than λ 4481 (Plate 3, fig. 2), were recorded in the magnesium arc *in vacuo* by FOWLER and PAYN in 1903.*

Following E. E. BROOKS,† who also investigated their occurrence in the magnesium spectrum, it will be convenient to designate these the "F and P" or "F.P." Doublets in order to distinguish them from the "Wide" Doublets which have already been discussed, and to avoid confusion with the term "Narrow" Doublets as applied to the F series of Ca, Sr, and Ba. The wave-lengths of these lines were given more accurately by FOWLER‡ in a later paper as 4434·20, 4428·20, 4390·80, and 4384·86 (ROWLAND), from which the wave-number intervals in the two doublets are 30·5 and 30·8 respectively.

The lines evidently form two related pairs, and the experimental conditions for their production are identical in every respect with those for λ 4481, thus differing from the Wide Doublets in the ultra-violet. It appeared, therefore, that the "F.P." Doublets might belong to series, the investigation of which would throw further light on the relationships of the "4481" series.

Six other doublets with the same interval were eventually traced, and an additional one in the infra-red has been recorded by LORENSER. The doublets occur in groups of two, the more refrangible being slightly the stronger in each group. They fall readily into two series, and as in the other enhanced line series which have been considered, it is necessary to employ the term 4N for the numerator in the formulæ.

The stronger doublets have been regarded as belonging to the Diffuse, and the weaker ones to the Sharp series. According to HICKS this classification is supported by the signs of the last terms of the denominators when his formula is employed.

Measurements of the lines have been made on photographs taken with the quartz spectrograph (Plate 3, figs. 4 and 5), with the exception of the doublets near λ 4481,

* 'Roy. Soc. Proc.,' 1903, vol. 72, p. 255.
† 'Roy. Soc. Proc.,' 1907, vol. 80, p. 220.
‡ 'Phil. Trans.,' A, 1909, vol. 209, p. 451.

TABLE VII.—New ("F.P.") Doublets of Magnesium.

m.	Diffuse series.					Sharp series.				
	λ (ROWLAND).	λ (I.Å.).	n, *in vacuo* (I.Å.).	δn.	O – C, Δn.	λ (ROWLAND).	λ (I.Å.).	n, *in vacuo* (I.Å.).	δn.	O – C, Δn.
2		– 10897·8* – 10934·2*	– 9,172·1* – 9,141·6*				– 9334·8* – 9361·5*	– 10,709·8* – 10,679·3*		
3	7896·63†	7896·37	12,660·6	30·9	0·0‡		8227·5*	12,154·4*		
	7877·39†	7877·13	12,691·5				8206·9*	12,184·9*		
4	4390·751	4390·585	22,769·73	30·86	0·0‡	4434·159	4433·991	22,546·84	30·53	0·0‡
	4384·809	4384·643	22,800·59			4428·163	4427·995	22,577·37		
5	3539·00	3538·86	28,249·8	30·5	0·0	3553·65	3553·51	28,133·3	30·9	0·0
	3535·18	3535·04	28,280·3			3549·75	3549·61	28,164·2		
6	3169·11	3168·98	31,546·9	30·3	0·0‡	3175·97	3175·84	31,478·8	30·3	0·0‡
	3166·07	3165·94	31,577·2			3172·92	3172·79	31,509·1		
7	2967·98	2967·87	33,684·5	30·5	+1·8	2971·81	2971·70	33,641·1	30·4	+1·5
	2965·30	2965·19	33,715·0			2969·13	2969·02	33,671·5		

* Calculated only.
† Observed by LORENSER.
‡ Used in calculation of constants.

the wave-lengths of which have been redetermined from plates taken in the 3rd and 4th orders of the grating. International standards were employed in the determinations but the wave-lengths on both scales are given in Table VII.

For these "F.P." doublets the small letters d, s, and p will be used for the Diffuse, Sharp, and Principal series respectively, D, S, and P being reserved for the corresponding series of Wide doublets.

Employing the less refrangible components of the first, second, and fourth doublets for the calculation of constants, the resulting equation for the d series is

$$d(m) = \left.\begin{matrix} 40{,}618{\cdot}45 \\ 40{,}648{\cdot}95 \end{matrix}\right\} - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 0{\cdot}947218 + \dfrac{0{\cdot}042317}{m}\right)^2}$$

and for the s series, assuming the same limits and calculating from the first and third of the less refrangible components

$$s(m) = \left.\begin{matrix} 40{,}618{\cdot}45 \\ 40{,}648{\cdot}95 \end{matrix}\right\} - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 0{\cdot}930{,}683 - \dfrac{0{\cdot}014220}{m}\right)^2}.$$

These equations represent all the observations very closely as will be seen from the columns "O – C" in Table VII.

§ 7. *Relation between the* "4481" *and the New Series.*

A connection between the "F.P." doublets and the "4481" series is indicated by the above equation for the d series, since $m = \dot{2}$ gives the variable part as 49,790·5 which is very close to the limits of the "4481" series. By analogy with the doublets of Ca, Sr, and Ba, this would be the case if the "4481" series were a Fundamental series forming part of the "F.P." system. Such an association would conform with the rule already indicated by the other three elements that the limit of the Fundamental series in the case of enhanced lines is derived from the first negative term of the d series, and not from the first positive as in arc line series.

For the complete establishment of this relation the lines of the d series should be found to have satellites; and in the case of the first member the separation of the satellite should be equal to that of 4481. The wave-length of the first line is given by the Hicks formula as near λ 10,900, a position which does not fall within the region which could be observed with the instruments available. The satellite separation should be $\delta\lambda = 1{\cdot}2$. The second d pair (λ 7896), which should have a satellite separation $\delta\lambda = 0{\cdot}25$, is also outside the region investigated. At the third (λ 4390·6) the satellite separation would be reduced to $\delta\lambda = 0{\cdot}04$ ($\delta n = 0{\cdot}21$) which is too small for resolution. There is, however, some evidence of a disturbance of the position of the third line (Table VII.). This part of the spectrum was photographed in the 3rd and 4th orders of the grating, and careful measurements have shown that the λ 4390 *d* doublet is slightly wider (0·3) than the neighbouring doublet of the *s* series. LORENSER's interval for the second *d* pair is also greater than that of the other doublets which have been measured. The intervals of the remaining pairs have been less accurately determined and cannot be used for such a comparison. As in the case of the corresponding line λ 2798 of the Wide doublet (D) series, the observations of the λ 4390 doublet suggest a satellite on the *more* refrangible side of the chief line, and this unusual position would accord with the greater strength of the *more* refrangible components of the "4481" series.

The "4481" series may accordingly be considered to be associated with either of the two systems of doublets, but a more direct connection with the "F.P." group is indicated by the fact that these lines occur under precisely the same experimental conditions as 4481. With this relation no difficulty arises with regard to the small interval of the "4481" lines, or to the limits of the series when compared with the corresponding figures for Ca, Sr, and Ba. It may therefore be concluded that the "4481" series is the Fundamental series of the "F.P." system.

§ 8. *The Principal Series of the New Doublet System.*

Associated with the "F.P." doublets a Principal series would also be expected. The approximate formula for the more refrangible components of these doublets, calculated in the usual way from that of the *s* series, is

$$p(m) = 51{,}328{\cdot}2 - \frac{4 \times 109{,}679{\cdot}3}{(m+1{\cdot}286480)^2}.$$

This indicates the neighbourhood of λ 9340 for the first *p* doublet (which should have $\delta n = 30{\cdot}5$) and λ 3643 for the second. The first is outside the range of the present observations, but the second is probably represented by one of two similar pairs of lines which are developed under the same conditions as the "F.P." lines. In each pair the more refrangible component is the stronger, as it should be in the *p* series, and the separations are about that which would be expected in the second member. Particulars of these lines are as follows:—

λ (I.Å.).	*n*.	δ*n*.	Remarks.
3850·40	25,964·1	14·6	Probable "combination" doublet (Plate 3, fig. 8).
3848·24	25,978·7		
3615·64	27,650·0	14·0	Probable *p* doublet.
3613·80	27,664·0		

It is evident that both pairs cannot belong to the *p* series, and the near equality of the intervals therefore suggests that one belongs to the p series while the other is a "combination" doublet. We have, in fact, the following numerical relations with the term $2d$ given by the limit of the more refrangible (stronger) components of the "4481" series:—

$$49{,}779{\cdot}0 - 25{,}978{\cdot}7 = 23{,}800{\cdot}3,$$
$$49{,}779{\cdot}0 - 25{,}964{\cdot}1 = 23{,}814{\cdot}9.$$

$$\left.\begin{array}{l} 23{,}800{\cdot}3 + 27{,}664{\cdot}0 = 51{,}464{\cdot}3 \\ 23{,}814{\cdot}9 + 27{,}650{\cdot}0 = 51{,}464{\cdot}9 \end{array}\right\} \text{mean } 51{,}464{\cdot}6.$$

The last number is not far from the approximate limit calculated for the p series, and it is suggested that the lines at λ 3615 form the p doublet while the other pair is a combination derived from this and the limit of the "4481" series ($f\infty - 3p$, or $2d - 3p$).

A striking confirmation of this conclusion is afforded by the fact that the term 2S for the Wide doublet series (Table VI.) is 51,464·2. This is not only in close accordance with the limit for p calculated above, but is an important indication of the intimate connection of the two systems of doublets. It will suffice for the present to note that the limit of the p series of "F.P." doublets appears to be given by the difference between the limit of the subordinate Wide doublets and the wave-number of the first observed S line which has a *positive* value; or, symbolically, $p\infty = 2S = S\infty - S(2)$.

The agreement is too close to be regarded as accidental, and assuming the relation to be true, the limit of the p series can be determined very exactly. The limit of the "4481" series (giving 2D and thence $S\infty$) has been found with considerable precision and the wave-number of the line λ 2936·496 giving S (2), has also been accurately determined. Hence, with very small probable error, the limit of the p series may be taken as 51,464·2. The limits of the d and s series (40,618·4 and 40,648·9) are probably also not far from the truth, and the wave-numbers of the components of the *first* p pair may therefore be deduced by the Rydberg-Schuster law. Hence, although only the second p doublet has been actually observed, there are sufficient data for the calculation of HICKS' formulæ for the series, namely,

$$p_2(m) = 51{,}464{\cdot}2 - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 1{\cdot}305940 - \dfrac{0{\cdot}041388}{m}\right)^2},$$

$$p_1(m) = 51{,}464{\cdot}2 - \frac{4 \times 109{,}679{\cdot}3}{\left(m + 1{\cdot}307258 - \dfrac{0{\cdot}041556}{m}\right)^2}.$$

The positions of the first four doublets calculated from these equations are as follows:—

TABLE VIII.—Principal Series of "F.P." Doublets.

Limit = 51,464·2.

m.	λ (I.Å.).	n.	mp_2. mp_1.	δn.	Remarks.
2	9243·7	10,815·3	40,648·9	30·5	Calculated.
	9217·7	10,845·8	40,618·4		
3	3615·64	27,650·0	23,814·2	14·0	Observed.
	3613·80	27,664·0	23,800·2		
4	2790·84	35,819·9	15,644·3	7·6	Calculated.
	2790·35	35,827·5	15,636·7		
5	2474·37	40,402·4	11,061·8	4·5	Calculated.
	2474·09	40,406·9	11,057·3		

The Principal series thus appears to be satisfactorily identified, but it is somewhat remarkable that it does not occur with greater intensity.

§ 9. *Relation between the Two Systems of Doublets.*

The connection of 4481 with the Wide doublets appears to arise from the fact that the two sets of doublets are themselves closely related. An indication of this has already been noted in connection with the limit of the p series. Further evidence is afforded by a comparison of other terms of the two systems. Thus, for the Wide doublets, including the case just mentioned, we have from Table VI.,

$$S_1\infty = 85{,}508{\cdot}6,$$
$$S_2\infty = 85{,}600{\cdot}1,$$

$$2D = 49{,}778{\cdot}0, \qquad 2S = 51{,}464{\cdot}2,$$
$$3D = 27{,}961{\cdot}8, \qquad 3S = 28{,}483{\cdot}3,$$

all of which are derived from actual observations, and are, therefore, unaffected by any imperfections of formulæ except as regards the limits of the "4481" series. The equations for the d, s, and p series of "F.P." doublets (pp. 244 and 246) give corresponding terms,

$$1p_1 = 85{,}462{\cdot}9,$$
$$1p_2 = 85{,}550{\cdot}2.$$
$$2d = 49{,}790, \qquad 2s = 51{,}328,$$
$$3d = 27{,}958, \qquad 3s = 28{,}464.$$

The calculated terms of the "F.P." doublets may thus be considered identical with the corresponding terms of the Wide doublets, within the possible limits of error. In that case the corresponding subordinate series would run parallel to each other in the two systems at distance apart of

$$S_1\infty - s_1\infty = 85{,}508{\cdot}6 - 40{,}618{\cdot}4 = 44{,}890{\cdot}2 = P_1(2) - P_1(1)$$

and

$$S_2\infty - s_2\infty = 85{,}600{\cdot}1 - 40{,}648{\cdot}9 = 44{,}951{\cdot}2 = P_2(2) - P_2(1).$$

A further important indication of a close connection between the two systems results from a consideration of the P series of Wide doublets, of which only the pair λλ 2802, 2795 falls within the region of observation. In view of the relations of the other series to which reference has been made, the limit of the P series is probably given exactly as 85,508·6+35,761·1, or 85,600·1+35,669·6 = 121,269·7 as shown in Table VI. With this limit, the formulæ for the two components of the series, derived from the observed pair are,

$$P_2(m) = 121{,}269{\cdot}7 - \frac{4 \times 109{,}679{\cdot}3}{(m+1{\cdot}263889)^2},$$

$$P_1(m) = 121{,}269{\cdot}7 - \frac{4 \times 109{,}679{\cdot}3}{(m+1{\cdot}265100)^2}.$$

From these equations we find for the P series the results shown in Table IX.

TABLE IX.—Principal Series of Wide Doublets (Preliminary Calculation).

Limit = 121,269·7.

m.	λ (I.Å.).	n.	mP_2. mP_1.	δn.	Remarks.
1	2802·698	35,669·6	85,600·1	91·5	Observed lines (Table VI.).
	2795·523	35,761·1	85,508·6		
2	1248·64	80,087·1	41,182·6	30·5	Calculated.
	1248·16	80,117·6	41,152·1		
3	1029·45	97,138·8	24,130·9	13·7	
	1029·31	97,152·5	24,117·2		

The first striking result derived from these calculations is that the separation of the second member is 30·5, which is exactly that of the *d* and *s* doublets of the "F.P." system. Hence it is suggested that the variable parts mP_1, mP_2 are really identical with corresponding terms of the *p* series (Table VIII.). The differences are in fact not too great to be attributed to defects of the simple formulæ employed. Thus the P and *p* series may also be considered as running parallel to each other at a distance apart of $P\infty - p\infty = 121{,}269{\cdot}7 - 51{,}464{\cdot}2 = 69{,}805{\cdot}5 = S(2) - S(1)$. Since the data for the *p* series depend upon more complete observational material than those for P, the latter may be corrected by the former, with the following results:—

TABLE X.—Corrected Principal Series of Wide Doublets.

Limit = 121,269·7.

m.	λ (I.Å.).	*n*.	mP_2. mP_1.	δ*n*.	Remarks.
1	2802·698	35,669·6	85,600·1	91·5	Observed lines (Table VI.).
	2795·523	35,761·1	85,508·6		
2	1240·37	80,620·8	40,648·9	30·5	Calculated.
	1239·90	80,651·3	40,618·4		Calculated.
3	1026·11	97,455·5	23,814·2	14·0	Calculated.
	1025·96	97,469·5	23,800·2		Calculated.

Even the second pair is beyond the region photographed by LYMAN in the case of magnesium, but it is not outside the limit of possible observation.

The foregoing considerations leave no doubt that while the limits and separations of the D and S series of Wide doublets are derived in the usual manner from the first doublet of the P series, those of the *d* and *s* series of the narrower "F.P." doublets are derived from the *second* P pair (Wide doublets). PASCHEN'S work on Combination series appears to justify the belief that the RYDBERG-SCHUSTER law of limits, and RUNGE'S law as to the derivation of the limit of the Fundamental series from the first line of the Diffuse series, are both exact, and the parallelism of the two systems thus permits the accurate calculation of data for both, since data lacking in one may be adopted from the other. For example, the term 2*s* of the "F.P." group is given by calculation as 51,328·2, and 1*s* as 119,449·3; both may be obtained with a much higher degree of precision by adopting the values 2S and 1S of the Wide doublet system (Table VI.), which are themselves independent of formulæ except as regards the determination of the limits of the "4481" series. The following table (XI.) may

TABLE XI.—The "F.P." Doublet System of Magnesium (Wave-numbers and "Variable Parts").

m.	*d* series. Limits {40,618·4. 40,648·9.		*s* series. Limits {40,618·4. 40,648·9.		*f* ("4481") series. Limits {49,778·0. 49,779·0.		*p* series. Limit, 51,464·2.	
	n.	*md.*	*n.*	*ms.*	*n.*	*mf.*	*n.*	mp_2. mp_1.
1		(110,836)		121,269·7*		(109,576·1)†	−34,135·9‡ −34,044·4‡	85,600·1 85,508·6
2		49,779·0		51,464·2*		(48,823·6)†		40,648·9 40,618·4
3	12,660·6 12,691·5	27,957·8		28,483·3*	22,308·7 22,309·7	27,469·3	27,650·0 27,664·0	23,814·2 23,800·2
4	22,769·7 22,800·6	17,848·7	22,546·8 22,577·4	18,071·6	32,199·0 32,199·9	17,579·0		15,644·3 15,636·7
5	28,249·8 28,280·3	12,368·6	28,133·3 28,164·2	12,485·1	37,571·4 37,572·4	12,206·6		11,061·8 11,057·3
6	31,546·9 31,577·2	9,071·5	31,478·8 31,509·1	9,139·6	40,811·3	8,967·4		
7	33,684·5 33,715·0	6,933·9	33,641·1 33,671·5	6,977·3	42,913·3	6,865·4		
8		(5,473·9)		(5,502·9)	44,354·7	5,424·0		
9					45,385·4	4,393·3		
10					46,147·9	3,630·8		
11						(3,050·8)†		

* From Table VI. (*m*S); 1*s* = P ∞.

† From HICKS' formula for "4481" series (equation III., p. 232).

‡ Observed S doublet (Table VI.), S (2); the variable parts in this case are $1P_2$ and $1P_1 = S_2\infty$ and $S_1\infty$.

accordingly be drawn up for the "F.P." system, it being understood that the variable parts of the p, d, and s series are equally applicable to the Wide doublets. In each case the terms md, &c., are given as derived from the observed wave-number of the less refrangible components; they would be the same for the more refrangible components if there were no errors of observation. The wave-numbers included are those which have been actually observed; others may readily be obtained from the limits and variable parts given. Terms depending wholly on calculation from formulæ are enclosed in brackets, and for simplicity the satellite has been disregarded. Further reference to this table will be made in the discussion of Combination series.

§ 10. *Combination Lines and Series of Magnesium.*

In the discussion of series, the wave-number of a line is represented by the difference of two other wave-numbers, the first of which (the limit) is constant for a given series, and the other variable, the limit itself appearing as one of the variable parts in an associated series. Combination lines and series, as is well known from the work of Ritz and Paschen, are formed by taking differences between the variable parts from different series. The Fundamental series was regarded by Ritz as a special type of Combination series, in which the variable part, in a doublet series, is given by $m\,(p_1-p_2)$, or $m\,\Delta p$, where p_1 and p_2 are taken from the formulæ for the two components of the Principal series, or derived from the constant separation in the Diffuse and Sharp series. This relation, however, is only approximate, and mf will be used to denote the variable part in the Fundamental series. It should be recalled that if there are no satellites in the D series, the F series consists of single lines, and that when satellites are present in a doublet system, the F lines are also doublets, with a separation equal to that of the satellite and chief line in the first member of the D series.

The whole of the "F.P." system may be considered to consist of Combination series derived from the Wide doublets, or *vice versâ*. Retaining the use of capital letters for the Wide, and small ones for the "F.P." doublets, and disregarding the satellites, we have the relations

$$p_2\,(m) = 2\mathrm{S}-m\mathrm{P}_2, \qquad \mathrm{P}_2\,(m) = 1s-mp_2,$$
$$p_1\,(m) = 2\mathrm{S}-m\mathrm{P}_1. \qquad \mathrm{P}_1\,(m) = 1s-mp_1.$$

$$s_1\,(m) = 2\mathrm{P}_1-m\mathrm{S}, \qquad \mathrm{S}_1\,(m) = 1p_1-ms,$$
$$s_2\,(m) = 2\mathrm{P}_2-m\mathrm{S}. \qquad \mathrm{S}_2\,(m) = 1p_2-ms.$$

$$d_1\,(m) = 2\mathrm{P}_1-m\mathrm{D}, \qquad \mathrm{D}_1\,(m) = 1p_1-md,$$
$$d_2\,(m) = 2\mathrm{P}_2-m\mathrm{D}. \qquad \mathrm{D}_2\,(m) = 1p_2-md.$$

$$f\,(m) = 2\mathrm{D}-mf \quad \text{or} \quad 2\mathrm{D}-m\,(\mathrm{P}_1-\mathrm{P}_2).$$

Either of the groups might be approximately determined in this way from the other, but an accurate knowledge of all the data for one of them can only be obtained by utilizing observations of both.

An interesting extension of the investigation of magnesium has been made possible by the production of a number of new lines of moderate intensity, which occur under the same experimental conditions as the "F.P." group (Plate 3, figs. 1, 2, 3). For some time the appearance of these lines seemed rather capricious, and it was thought that they might possibly be due to impurities. It was eventually found, however, that they could always be obtained in a small region near the negative pole of the arc *in vacuo*, provided a sufficiently heavy current (7 or 8 amperes) were employed. The lines were shown clearly in many photographs, where the only lines traceable to impurities were faint ones of Na, Ca, and Ba. No further doubt can be felt as to the magnesium origin of the lines, in view of the manner in which their positions can be calculated from the constants for the doublets, taken from Table XI.

One of the combination terms has already been utilised in the discussion of the p series. This is represented by the combination $2d-3p_1$, $2d-3p_2$, giving the lines λλ 3850·40, 3848·24, which form a well-marked doublet, shown very clearly in Plate 3, fig. 8.

In addition, two well defined Combination series have been identified. A few of the lines involved appear in a list given by LORENSER, but their connections were not then recognised. One of these series is somewhat stronger than the other and may be distinguished as Series A, the weaker being designated Series B. In each case the intensities degrade in the usual way in passing to the violet (Plate 3, figs. 1, 2, 3). Series A results from the combination $3d-mf$, and B from $3f-mf$. Details of the observations and comparisons with the calculations are given in Tables XII. and XIII.

TABLE XII.—Magnesium Combination Series A ($3d-mf$).

Limit, $3d$ = 27,957·8.

m.	λ (I.Å.) (FOWLER).	n (observed).	n (calculated).	O – C, Δn.	Remarks.
5	6346·67	15,752·0	15,751·2	+0·8	LOR. gives λ 6347·27 (Row.).
6	5264·14	18,991·3	18,990·4	+0·9	,, ,, λ 5264·2 ,,
7	4739·59	21,093·1	21,092·4	+0·7	
8	4436·48	22,534·2	22,533·8	+0·4	
9	4242·47	23,564·7	23,564·5	+0·2	,, ,, λ 4242·60 ,, Mg?
10	4109·54	24,326·9	24,327·0	−0·1	
11	4013·80	24,907·1	24,907·0	+0·1	

TABLE XIII.—Magnesium Combination Series B ($3f-mf$).

Limit, $3f = 27{,}469{\cdot}3$.

m.	λ (I.Å.) (FOWLER).	n (observed).	n (calculated).	O – C, Δn.	Remarks.
5	6545·80	15,272·8	15,262·7	+ 10·1	LOR. gives { λ 6546·77 (Row.). λ 6545·66 ,, }
6	5401·05	18,509·9	18,501·9	+ 8·0	,, ,, λ 5401·2 ,,
7	4851·10	20,608·2	20,603·9	+ 4·3	
8	4534·26	22,048·2	22,045·3	+ 2·9	
9	4331·93	23,078·1	23,076·0	+ 2·1	
10	4193·44	23,840·2	23,838·5	+ 1·7	
11	4093·90	24,419·8	24,418·5	+ 1·3	

It will be observed that in each case there is a systematic difference between observation and calculation. In Series A, however, the differences are very slight, and possibly negligible; but in Series B they are too large to be attributed to faulty observations. The terms mf have been derived from observations of a high order of accuracy, and in the case of Series B, the calculated wave-numbers would not be affected by any error in the adopted value of the limit of the f series. It is scarcely probable that Series B, with its limit so near to $3f$, is independent of the "F.P." system, and it would therefore appear that the combination principle is not exact in every case, except probably as regards the values of the limits.

Calculations of formulæ for the two series from the observed lines themselves confirm the values of the limits given by the combination terms. These formulæ are as follows:—

$$A\,(m) = 27{,}956{\cdot}48 - \frac{4\times 109679{\cdot}3}{\left(m+0{\cdot}993807+\dfrac{0{\cdot}008967}{m}\right)^2},$$

$$B\,(m) = 27{,}468{\cdot}38 - \frac{4\times 109679{\cdot}3}{\left(m+0{\cdot}994863+\dfrac{0{\cdot}014621}{m}\right)^2}.$$

The residuals (O – C) left by the formulæ on the observed wave-numbers are—

	$m =$	5	6	7	8	9	10	11
O – C {	Series A =	0·0*	+ 0·3	0·0*	+ 0·1	0·0	– 0·3	0·0*
	,, B =	0·0*	+ 1·8	0·0*	+ 0·1	0·0	0·0	0·0*

A general view of the enhanced line series of magnesium now identified is given in fig. 1, in which the doublet separations have been arbitrarily increased for greater clearness.

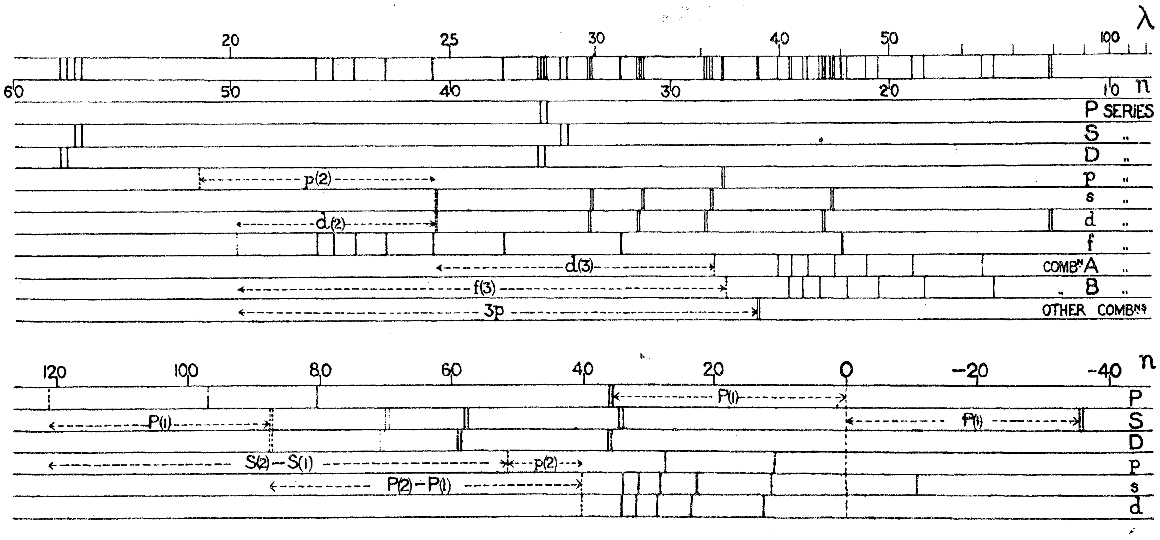

Fig. 1. Enhanced-line series of magnesium.

§ 11. *General Comparison of* Mg, Ca, Sr, *and* Ba.

One of the results of the investigation is to indicate that Mg behaves differently from Ca, Sr, and Ba in the spark. All are alike in having series of Wide doublets with separations related to the atomic weights, but the D doublet with negative frequency which occurs in the other three elements is lacking in Mg. While Ca, Sr, and Ba have strong Fundamental series with limits derived from the negative D doublet, the corresponding F series of Mg, like the negative term from which it should be derived, does not appear to exist. In Mg the equivalent of the F series of the other three elements is replaced by the whole system of "F.P." doublets (including the "4481" series as Fundamental), which has no analogue in the other three elements so far as is known at present. The "F.P." system itself is closely related to the family of Wide doublets, but although both consist of enhanced lines they do not necessarily co-exist; the wider system occurring in the ordinary arc, while the closer requires the conditions of the spark or its equivalent, the negative pole of an arc *in vacuo*.

The "4481" series is therefore established as a Fundamental series, but the system of which it forms a part is in some respects exceptional.

It is important to observe that no numerical relations between the enhanced and arc line series occurring in the spectra of any of the four elements have been recognised.

§ 12. *The Spectra of Hydrogen and Helium.*

The now demonstrated existence of series having 4N for the "universal" constant has an interesting bearing on the question of the origin of the special lines produced by strong discharges in helium tubes, to which reference has already been made. Some of these were at first regarded as being identical with the lines of the supposed P series of hydrogen calculated by RYDBERG on the assumption that the Pickering (ζ Puppis) lines formed the S series. The lines in question are compared with RYDBERG's values (Rowland scale) in the appended table :—

TABLE XIV.—The "4686" Series.

Observed λ (FOWLER).	Calculated λ (RYDBERG).	Difference $\Delta\lambda$.
4685·98	4687·88	1·90
3203·30		
2733·34	2734·55	1·21
2511·31		
2385·47	2386·50	1·03
2306·20		
2252·88	2253·74	0·86

In order to conform with RYDBERG's theory, and to adapt the formulæ then ordinarily employed, it was necessary, as in the first discussion of the Mg "4481" series, to divide the series into two parts by taking alternate lines. One series, as will be seen from the table, then agreed very closely with the calculated values for the P series of hydrogen, and the other was regarded as a second P series having a simple relation to the first.

The conditions of appearance of these lines in helium tubes indicates that they are enhanced lines, and calculation shows that they can be united in a single series of the 4N type, as in the case of the other series of lines of this class which have been discussed. Thus, the first line, which has been most accurately measured, gives the equation

$$n = 438{,}879{\cdot}1\left(\frac{1}{3^2}-\frac{1}{m^2}\right).$$

The differences O$-$C (Δn) for the seven observed lines are 0·0, $-$0·3, $+$1·4, $+$0·6, $+$1·0, $+$2·3, $-$1·4. All are within the estimated limits of error of observation, or very nearly so, except the third, and even in this case a correction of 0·1 Å.U. to the observed wave-length would reduce the difference to zero.

The "4686" series is accordingly a series of the enhanced line, or 4N, type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen which is of the arc, or N, type. The numerical relations indicated by RYDBERG's calculations are therefore not significant, and, in view of the experimental evidence, it must be concluded that the "4686" series is not due to hydrogen, but to helium, as first indicated by Dr. BOHR from theoretical considerations. This conclusion is further supported by EVANS's observation of the line 4686 in a helium tube in which the ordinary lines of hydrogen could not be detected.* In accordance with the convenient nomenclature of LOCKYER it is suggested that the lines in question should be designated "proto-helium" lines.

Analogy with the magnesium "4481" series suggests that the "4686" series should be regarded as one of the F type, and the question arises as to how the associated P, S, and D series are represented in the proto-helium spectrum. A knowledge of the F series alone does not permit the complete calculation of any of the three associated series, but only indicates the "variable part" of the first line of the D series. In the case of proto-helium, the limit of the "4686" series, $N'/3^2$, shows that the variable part of the D formula is identical with that of the F, but the limit of D remains undetermined. A consistent arrangement is possible, however, if the D be regarded as having the same limit as the F series, in which case the four series would coalesce in the formula

$$n = N'\left(\frac{1}{3^2} - \frac{1}{m^2}\right)$$

where $N' = 438{,}879 \cdot 1$. This only requires that the zero values of n given by $m = 3$ be regarded as negative terms, so that if the formula be taken to represent the coalesced D and S series, the limit of P derived from S, and that of F derived from D would also be $N'/3^2$. The lines of the four series would thus be coincident. The great strength of the "4481" series of magnesium as compared with that of the other series of the "F.P." group, however, suggests that the "4686" series is primarily of the F type.

As pointed out by BOHR, the substitution of 4 for 3 in the above formula for the "4686" series yields a series of lines of which the Pickering (ζ Puppis) lines, also formerly attributed to hydrogen, are alternate members, the remainder being nearly coincident with the Balmer lines of hydrogen. It is probable, therefore, that the Pickering lines are also due to proto-helium, as they have only been observed in association with 4686. The calculated wave-lengths of the earlier members of the extended series are compared in Table XV. with the Balmer series, and with the hypothetical "sharp" series of hydrogen calculated by RYDBERG.

TABLE XV.—The "Pickering" Series.

Proto-helium, "Pickering" series, λ (calculated).	Hydrogen, Balmer series, λ.	"Hydrogen," RYDBERG'S S series, λ (calculated).
6560·37	6563·07	
5411·74		5412·8
4859·53	4861·52	
4541·79		4543·3
4338·86	4340·64	
4200·02		4201·5

* 'Nature,' 1913, September 4, p. 5.

The astrophysical and experimental data have as yet given no proof of the existence of the lines adjacent to those of hydrogen, but there is no evidence against the supposition that they exist.

The assignment of these lines to proto-helium is supported by the observations of magnesium, which have shown analogous series associated with the "4481" series. The series A of magnesium, given by the combination $3d-mf$, would become $4D-mF$ in proto-helium—the numeration being slightly different in the two cases*—and this would be identical with the formula for the extended Pickering series. Series B of magnesium, given by $3f-mf$, would similarly become $4F-mF$ and would also coalesce into the Pickering series. Alternate lines of series B are in fact not far removed from the Balmer lines, while intermediate lines are near the observed Pickering lines, as will be seen by comparing Tables XIII. and XV.; lines near these positions might also be derived from the F series of other elements in which mF approximates to $4N/m^2$. The relative weakness of the Pickering series of proto-helium, as compared with 4686, is matched in magnesium by the relatively low intensities of the analogous combination series A and B.

The close relations between the lines of hydrogen (real and hypothetical) and some of those of proto-helium are simply accounted for by BOHR's theory of the origin of these spectra. The general formulæ, in which p and m can only take integral values, may be written

$$\text{Hydrogen:} \quad n = N\left(\frac{1}{p^2}-\frac{1}{m^2}\right) \qquad p = 2 \text{ for Balmer series.}$$

$$\text{Proto-helium:} \quad n = N'\left(\frac{1}{p^2}-\frac{1}{m^2}\right) \qquad \begin{cases} p = 3 \text{ for ``4686'' series,} \\ p = 4 \text{ for Pickering series.} \end{cases}$$

If N′ were exactly equal to 4N, alternate lines of the Pickering series would evidently coincide with the Balmer series; and the hypothetical P series of hydrogen, given by $p = 1{\cdot}5$ in the first formula, would fall on alternate lines of the "4686" series.

The hydrogen lines, according to the theory, are produced during the binding of an electron by an atomic nucleus having a single positive charge, and those of proto-helium during the binding of an electron by a nucleus having four times the mass and a double positive charge. If the mass of the electron were negligible in comparison with that of the nucleus, N′ would be equal to 4N, but BOHR has shown that when correction is made for the mass of the electron, the theoretical ratio for these constants is in nearly perfect agreement with that of the values deduced from the spectroscopic observations.† His expression for the constant of the hydrogen series may be written

$$N_H = 109{,}675 \equiv \frac{10^8 2\pi^2 E^2 e^2 Mm}{ch^3(M+m)}$$

* The numeration would be the same if m in the proto-helium formula were written $(m+1)$ to correspond with $(m+0{\cdot}99)$ of magnesium.

† 'Nature,' 1913, October 23, p. 231.

where c is the velocity of light, h is PLANCK's constant, e and m the charge and mass of the electron, and E and M the charge and mass of the nucleus of the hydrogen atom. In the case of proto-helium, the value of E is doubled and M is increased four times. The theoretical ratio between N′ and N is therefore

$$\frac{N_{p\text{He}}}{N_{\text{H}}} = \frac{16(M+m)}{4(M+m)}.$$

Introducing the recognised value $M/m = 1835$, the resulting ratio is 4·001635, as compared with 4·001632 derived from the observations.

A spectroscopic method of determining the mass of the electron, from the constants of the hydrogen and proto-helium series, is thus suggested. The value of N′ obtained from λ 4685·98±0·01 (ROWLAND's scale) is 438,879·1±1·0, and combining this with hydrogen 109,675, the resulting value for the mass of the hydrogen atom in terms of that of the electron is 1836±12. A similar calculation from wave-lengths on the International scale, using Mr. CURTIS's new value of the hydrogen constant (109,679·3) gives the ratio $M/m = 1855 \pm 12$. This result, however, is only to be regarded as provisional; more exact measures of the proto-helium lines may be possible, and the formula employed may require a small correction for the alteration in the mass of the electron due to its velocity.

The assignment of the "4686" series to proto-helium may nevertheless be considered to be independent of BOHR's theory. It really depends upon the recognition of the new class of series associated with enhanced lines, and the better accordance with experimental results. Apart from the theory it might still be considered possible that the hydrogen spectrum, under appropriate conditions, would include the Rydberg lines. The well-known line about λ 4686 which occurs in the solar chromosphere and, in some of the nebulæ, however, is undoubtedly the proto-helium line, and there are no indications in these spectra of another line near 4688 which would correspond with the hypothetical line of hydrogen. Until other evidence is forthcoming, it may therefore be considered that the line spectrum of hydrogen, as required by BOHR's theory, consists only of the Balmer series and parallel series in the infra-red and Schumann regions. These are all included in the simple formula previously given.

The proto-helium spectrum is apparently of the same simple character as that of hydrogen, but the series in the infra-red and Schumann regions have not yet been investigated.

§ 13. *Enhanced Lines in Relation to* BOHR's *Theory.*

The apparently successful application of BOHR's theory to the lines of proto-helium renders it desirable to consider briefly the implications of this theory as regards other systems of enhanced lines.

Since enhanced lines have been found to occur in families of series similar to those previously recognised in arc spectra, the only new theoretical problem presented by them is to account for the appearance of the series constant with four times the value associated with arc lines. Otherwise, the extension of the simple formulæ for proto-helium to enhanced lines in general is identical with the extension of BALMER'S formulæ for hydrogen to the ordinary systems of series of arc lines. Hydrogen and proto-helium may thus be regarded as limiting cases of the two kinds of series.

Independently of the series evidence there are numerous indications that enhanced lines originate in vibrating systems differing from those which give rise to arc lines. The mode of occurrence of the two sets of lines in the spectra of celestial bodies furnishes important evidence in favour of this view, and experimental evidence in the same direction is abundant. The extensive researches of HEMSALECH on the phenomena of the spark discharge, for example, have revealed striking differences in the behaviour of the two classes of lines.*

It has been shown that in a single discharge, the durations of the enhanced lines of Ca, Sr, and Mg, are much shorter with respect to their intensities than those of the arc lines of the same elements; and in another investigation it was shown that the velocities of the particles emitting the enhanced lines of Ca were nearly twice as great as those of the particles producing the arc lines.†

These experiments suggested that centres of emission of different constitution were concerned in the production of the two classes of lines, but HEMSALECH hesitated to adopt this view until other experiments had been made.

The series investigation not only points to the existence of different emitting systems, but, in the light of BOHR'S theory, may possibly give a clue to the nature of the difference. The appearance of 4N in the formulæ for series of enhanced lines suggests that, as in the case of proto-helium, such series are produced during the binding of an electron by each of the atoms from which two electrons have been removed by the exciting source; while arc series lines are emitted during the re-formation of atoms from each of which only one electron has been removed. Although the neutral atoms of different elements contain different numbers of electrons, the approximate constancy of N for arc series, according to BOHR, is explained by the fact that the force on an electron entering a system consisting of a positive nucleus and a number of electrons one less than that required to render it neutral would not be very different from the force in the case of the binding of an electron by a hydrogen atom. A similar explanation would evidently account for the constancy of 4N in the formulæ for series of enhanced lines. Variations from the simple series conditions presented by hydrogen and proto-helium would be expected in consequence of the presence of additional electrons, but these have not yet been worked out theoretically by Dr. BOHR.

* 'Comptes Rendus,' vol. 151, pp. 220 and 668 (1910).

† 'Comptes Rendus,' vol. 154, p. 873 (1912).

The varying facility with which enhanced lines can be produced in the spectra of different elements would seem to depend upon the intensities of the forces which bind the electrons to the nuclei. In some elements, such as lithium, no enhanced lines at all have been observed. The lithium atom is credited with three electrons, and BOHR's calculations indicate that while the outer electron is lightly bound, the inner two are very strongly bound as compared with the electron in an atom of hydrogen, and even more rigidly than the two electrons in a helium atom. Theory and experiment are thus in agreement, and the production of enhanced lines of lithium would appear to require more powerful spark discharges than those hitherto employed.

In the case of elements like calcium, which give enhanced lines of Class I., it may be supposed that one electron is lightly bound, so that even a flame may effect its removal, while a second is removable by the moderate increase in the energy of excitation when passing from the flame to the arc. The further increase in the intensities of the enhanced lines on passing to the spark may be attributed to the relatively greater number of atoms from which two electrons are simultaneously detached. In elements like iron, giving enhanced lines of Class II., the conditions may be supposed similar, except that the second electron is removed with somewhat greater difficulty.

Enhanced lines like Mg 4481 require a modified explanation. Although the series to which this line belongs is produced only under spark conditions (or their equivalents in modified arcs) it is important to bear in mind that the related system of Wide doublets, consisting of enhanced lines of Class I., is developed in the ordinary arc. Since the term 4N appears in the formulæ for both systems, BOHR's theory would lead to the supposition that in this case the greater energy of the spark does not result in the separation of a third electron from any of the atoms but merely produces some change in the configuration of the atomic systems. The experimental data are not sufficiently complete to justify the conclusion that such an explanation would be applicable to all enhanced lines of Class III.

If, by any means, three electrons could be separated from the nucleus, the appearance of lines for which the series constant was raised to 9N would be expected, if BOHR's theory is a safe guide. Great energy would apparently be needed to bring about this result, and no such series have yet been recognised. A sufficient increase in the energy of excitation would presumably yield series requiring still greater multiples of the constant N in the formulæ.

It will be observed that BOHR's theory gives a more definite conception to LOCKYER's earlier view that the varying spectra given by the same substance represent the vibrations of different "molecular groupings," such groupings being simplified by successive dissociations brought about by increase of temperature or electrical excitation.

It should be noted that some of the conclusions drawn by STARK from his experiments on canal-ray spectra are inconsistent with the views of BOHR. In the case of helium, STARK has found that the Döppler displacements are smaller for the doublet series (helium group) than for the single line series ("parhelium" group), and he infers that the atoms which act as carriers in the former case have a single positive charge, while in the second case there is a double positive charge.* Both sets of series, however, are of the "arc" type, with N for the series constant, whereas on BOHR's theory, one should be of the N, and the other of the 4N type if STARK's deduction is correct.

In the case of aluminium, STARK has similarly found evidence of atoms with one, two, and three positive charges.† The first is associated with the doublets of the arc spectrum, the second with a spark line at 4663·5, and the third with three spark lines at 4529·7, 4513·0, and 4480·0. Attention is drawn to the fact that the higher charges are connected with the enhanced lines, and differences in the behaviour of the two sets of spark lines when the spark is passed in hydrogen are indicated. The series to which the spark lines of aluminium belong have not yet been recognised, but STARK's results for this element are in general agreement with the conclusion indicated by BOHR's theory that enhanced lines are associated with atoms of greater positive charges than those giving rise to arc lines. In the case of helium it does not seem possible to reconcile STARK's conclusions with those of BOHR, since the doubly-charged atoms, on BOHR's theory, can only give rise to the system of series of which 4686 is the leading member.

STARK's conclusions are equally at variance with those of LENARD,‡ who found reason to believe that while principal series are produced by neutral atoms, the subordinate series originate in atoms which have become positively charged through the loss of one or more electrons. BOHR's theory differs from both in leading to the conclusion that all series having the same series constant should be produced by atoms having the same charge.

A knowledge of the charges of the atoms giving the arc and enhanced lines respectively would possibly aid in the interpretation of the peculiarities of the spectrum of the solar chromosphere, and further investigations bearing on this subject are very desirable.

Whatever may be its significance in connection with the atom, the change in the character of the series in passing from arc to spark lines suggests the spectra of "early-type" stars as a possible source of series requiring still greater multiples of the ordinary series constant in the formulæ representing them. In passing from the later to the earlier type stars, as shown by the work of LOCKYER and others, the arc lines of various metallic elements are gradually replaced by enhanced lines, while lines of hydrogen, helium, and other gases become more prominent. For such metallic elements as are known to belong to series, the change is definitely from series of the arc (N) type to series of the spark (4N) type. A considerable number of lines remain

* 'Ann. der Physik,' vol. 40, p. 540 (1913).

† 'Ann. der Physik,' vol. 42, p. 254 (1913).

‡ 'Ann. der Physik,' vol. 17, p. 197 (1905).

without identification, but a preliminary examination of these has given no certain evidence of series for which the series constant would be 9N.

The Wolf-Rayet ("bright-line") stars are of special interest in this connection, as they are generally considered to represent the first stage in the condensation of nebulous matter into stars, and in many of them the proto-helium lines are a prominent feature. NICHOLSON has suggested that some of the lines may belong to series which can be represented, in wave-lengths, by the formula

$$\lambda = 3646 \frac{(m \pm \frac{1}{3})^2}{(m \pm \frac{1}{3})^2 - 4},$$

where 3646 is the limit of the hydrogen series.* The lines were regarded as a possible extension of the hydrogen spectrum, but on the supposition that other lines associated with them may coincide with the Balmer series, Dr. BOHR has pointed out that all the lines might be united in a single series and might be attributed to lithium. The binding of an electron by a lithium atom from which the three electrons have been removed would, on the theory, give rise to such a series, namely,

$$\lambda = 3646 \frac{m^2}{m^2 - 36},$$

or

$$n = 27418 - \frac{9 \times 109675}{m^2}.$$

This hypothetical series would thus be of the "9N" type, but its existence in this form is not confirmed by the observational data. Omitting the lines which would coincide with the ordinary lines of hydrogen, the earlier members of the series would be 5697, 5193, 4633, 4466, 4243, &c. Of these only the first, third, and fourth are possibly represented in the Wolf-Rayet stars, and since the intensities should degrade in regular order in passing from red to violet, the absence of a line at 5193 is conclusive proof that the observed lines do not form a series of the "9N" type.

In a further discussion of the spectra of the Wolf-Rayet stars, NICHOLSON has arranged most of the lines in a number of series of a different character, in which the Rydberg constant is replaced by various *fractional* parts of its value for hydrogen.† The numerical relations traced in this way are very striking, but the individual series indicated are very fragmentary, and such lines do not always occur together in the same star. The suggested series are also remarkable as involving different fractional values of the Rydberg constant for series proceeding to the same limit.

The general progression from series of the N type to those of the 4N type in passing through the stellar sequence would suggest that further change, if any, would be in the direction of multiples, rather than fractions, of N in the series formulæ. It is

* 'Monthly Notices R.A.S.,' vol. 73, p. 382 (1913).

† 'Monthly Notices R.A.S.,' vol. 74, p. 118 (1914).

doubtful, however, whether any change beyond that represented by enhanced lines should be expected. It is now easy to produce a spectum in which the proto-helium line 4686 exceeds any of the ordinary helium lines in brightness, and from the persistence of the ordinary helium lines in many of the Wolf-Rayet stars it seems reasonable to infer that even in these stars the conditions are not indefinitely in advance of those obtainable in laboratory experiments.

§ 14. *Summary.*

(1) The enhanced (spark) lines of magnesium, calcium, strontium, and barium form series of doublets which occur in groups similar to those previously recognised in arc spectra. The formulæ representing these series, however, differ from those employed for arc lines in that RYDBERG's constant "N" (= 109675 for ROWLAND's scale) has a value equal to 4N.

(2) The Fundamental series, in the Doublet systems of calcium, strontium, and barium, as shown by SAUNDERS and LORENSER, derives its limit and the separation of its components from an observed negative term of the Diffuse series. In the case of magnesium, the corresponding negative term of the Diffuse series, and the Fundamental series which might have been expected, do not exist.

(3) A new group of series of narrower doublets has been found in magnesium, in which the separation of the Sharp and Diffuse pairs is identical with the (calculated) separation of the *second* pair of the Principal series of wider doublets. The new group is designated the "F.P." system; in addition to the ordinary series it includes two well-marked combination series, each consisting of seven observed lines.

(4) The "4481" series of magnesium consists of very close doublets with constant separation, and forms the Fundamental series of the "F.P." system. Its limits are derived from the first negative term of the Diffuse series.

(5) Corresponding series of the "F.P." and Wide doublet systems run parallel to each other, but notwithstanding this numerical relation, the two systems do not necessarily co-exist, the wider doublets occurring in the ordinary arc as well as in the spark, while the "F.P." group occurs only under spark conditions or their equivalent in the region of the negative pole of an arc *in vacuo*.

(6) No numerical relations have been traced between any of the enhanced line series and the series of arc lines of the same element.

(7) The "4686" series produced in helium tubes is of the enhanced line (4N) type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen, which is of the arc (N) type. It is concluded that these lines are due to helium, as indicated by Dr. BOHR from theoretical considerations. It is suggested that they should be designated "proto-helium" lines.

(8) Analogy with the "4481" series of magnesium indicates that the "4686" series

of proto-helium is primarily of the Fundamental type; the three associated series may be regarded as coincident with it.

(9) The "Pickering" lines associated with the "4686" series are also probably due to proto-helium, in which case the series would include lines nearly coincident with the Balmer series. The observational evidence on this point is incomplete, but the assignment of these lines to proto-helium is supported by the fact that one of the new combination series of magnesium is related to the "4481" series exactly as the extended Pickering series would be related to the "4686" series.

(10) The slight differences between the observed positions of alternate lines of the "4686" series and those calculated by RYDBERG for the "Principal" series of hydrogen are in very close agreement with BOHR's theoretical formulæ for hydrogen and proto-helium. Adopting these formulæ, the spectroscopic data give a provisional value for the mass of the hydrogen atom, in terms of that of the electron, as 1836 ± 12; or 1855 ± 12 when the data are corrected to the International scale of wave-lengths.

(11) The appearance of the Rydberg constant in enhanced lines series with four times its usual value may be explained on BOHR's theory by supposing that series of the arc type are produced when only one electron is removed from each of the atoms involved, while in the case of enhanced lines two electrons are removed.

(12) A preliminary examination of terrestrial and celestial spectra has given no indications of series requiring still greater multiples of the Rydberg constant in the formulæ representing them.

The author has pleasure in acknowledging his obligations to Mr. W. JEVONS, A.R.C.S., D.I.C., B.Sc., who has taken the new photographs of the magnesium spectrum, and has given much valuable assistance in other ways.

APPENDIX.

The wave-lengths (on the International scale) of the enhanced lines of magnesium, as observed in the arc *in vacuo* in the course of the foregoing investigation, are brought together in Table XVI. The letters indicating the series to which the lines belong have the significance given in the description of Plate 3. For completeness additional lines observed by LORENSER and by LYMAN are also included.

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TABLE XVI.—Enhanced Lines of Magnesium.

λ (I.Å.).	Inten-sity.	Series.	Remarks.	λ (I.Å.)	Inten-sity.	Series.	Remarks.
			Derived from LORENSER's values:—				
7896·37	—	} d	{ 7896·63 Rowland scale	3538·86	6	} d	
7877·13	—		7877·39 ,, ,,	3535·04	5		
6545·80	5	B	LORENSER { 6546·77 ,, ,,	3175·84	2	} s	
			{ 6545·66 ,, ,,	3172·79	1		
6346·67	5	A	,, 6347·27 ,, ,,	3168·98	3	} d	
5401·05	5	B	,, 5401·2 ,, ,,	3165·94	2		
5264·14	5	A	,, 5264·2 ,, ,,	3104·805	} 30	f	
4851·10	5	B		·713			
4739·59	5	A		2971·70	1	} s	
4534·26	4	B		2969·02	0		
4481·327	} 100	f	{ KING . . 4481·499 ,, ,,	2967·87	1	} d	
·129			,, . . ·284 ,, ,,	2965·19	0		
4436·48	5	A		2936·496	35	} S	{ NACHEN (Arc) 2936·516 (I.Å.)
4433·991	8	} s		2928·625	35		,, ,, 2928·636
4427·995	7			2802·698	50	P	,, ,, 2802·718
4390·585	10	} d		2797·989	40	D	,, ,, 2798·016
4384·643	8			2795·523	50	P	,, ,, 2795·545
4331·93	3	B		2790·768	40	D	,, ,, 2790·801
4242·47	4	A	LORENSER 4242·60 ,, ,,	2660·821	} 10	f	
4193·44	2	B		·755			
4109·54	3	A		2449·573	6	f	
4093·90	1	B		2329·58	5	f	
4013·80	2	A		2253·87	4	f	
3850·40	6	} C		2202·68	3	f	
3848·24	7			2166·28	2	f	
3615·64	3	} p				S {	LYMAN . . . 1753·6 Rowland scale
3613·80	4						,, . . . 1750·9 ,, ,,
3553·51	5	} s				D {	,, . . . 1737·8 ,, ,,
3549·61	4						,, . . . 1735·0 ,, ,,

Description of Plate.

The photographs are of the spectrum of the magnesium arc *in vacuo*. The letters indicate the series to which the lines belong, and have the following significance:—

Enhanced lines . .	P,	Principal series	Wide doublet system.
	D,	Diffuse ,,	Wide doublet system.
	S,	Sharp ,,	Wide doublet system.
	p,	Principal ,,	"F.P." doublet system.
	d,	Diffuse ,,	"F.P." doublet system.
	s,	Sharp ,,	"F.P." doublet system.
	f,	Fundamental series	"F.P." doublet system.
	A,	Combination ,, A	"F.P." doublet system.
	B,	,, ,, B	"F.P." doublet system.
	C,	Other combination lines	"F.P." doublet system.
Arc lines	R_1,	Rydberg series of single lines (Diffuse).	
	R_2,	,, ,, ,, ,, (Sharp).	
	T_1,	Diffuse series of triplets.	
	T_2,	Sharp ,, ,,	

1, 2, 3 show chiefly the two Combination series of enhanced lines and the "F.P." doublets near the Fundamental line λ 4481.

4, 5 show further members of the "F.P." system and the Wide doublets in the ultra-violet.

6, 7—Grating, 4th order—enlarged about eleven times. λ 4481 ($\delta\lambda = 0{\cdot}198$) and λ 3105 ($\delta\lambda = 0{\cdot}092$) respectively, each with a longer and a shorter exposure.

8, the "F.P." Combination doublet (λ 3850, λ 3848) near the Diffuse triplet.

Lines of impurities — Na, Hg, Ca, Ba, H.

Bands of magnesium hydride (5211, 4802).

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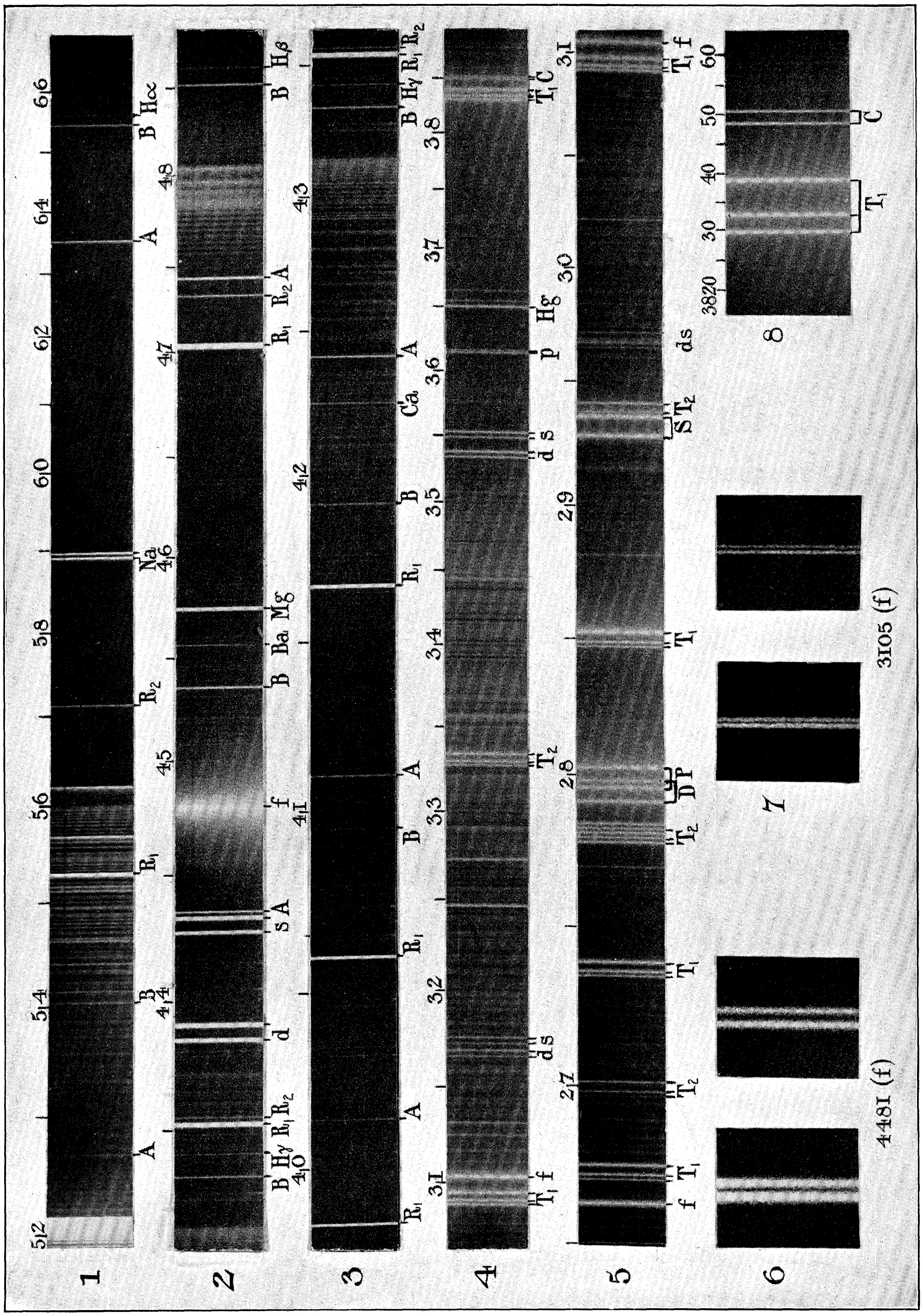

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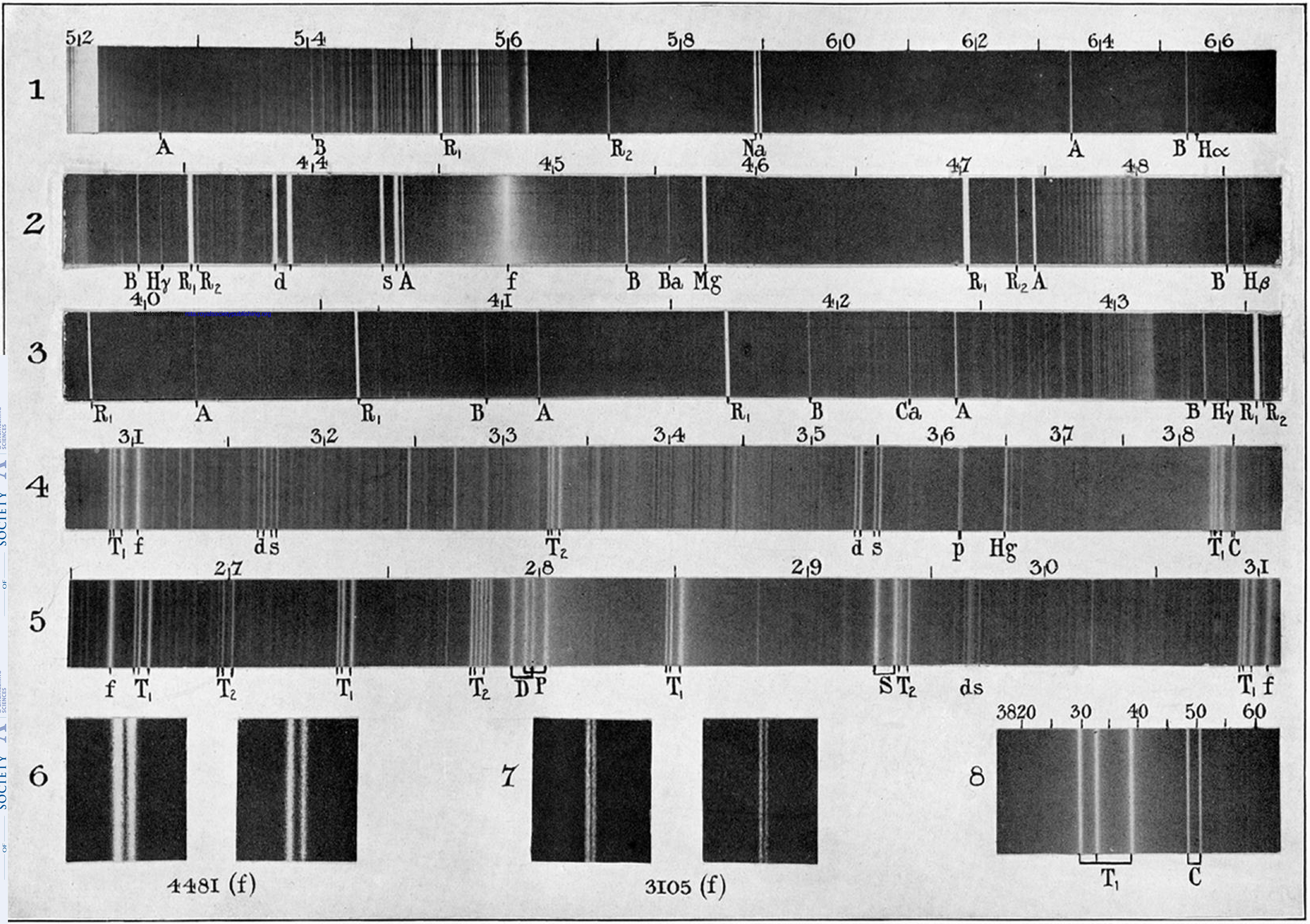
1
5·2 5·4 5·6 5·8 6·0 6·2 6·4 6·6
A B R1 R2 Na A B Hα
2
4·4 4·5 4·6 4·7 4·8
B Hγ R1 R2 d s A f B Ba Mg R1 R2 A B Hβ
3
4·0 4·1 4·2 4·3
R1 A R1 B A R1 B Ca A B Hγ R1 R2
4
3·1 3·2 3·3 3·4 3·5 3·6 3·7 3·8
T1 f d s T2 d s p Hg T1 C
5
2·7 2·8 2·9 3·0 3·1
f T1 T2 T1 T2 D P T1 S T2 ds T1 f
6
4481 (f)
7
3105 (f)
8
3820 30 40 50 60
T1 C