The Effect of Pressure upon Arc Spectra. No. 3. Silver, λ 4000 to λ 4600. No. 4. Gold

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Phil. Trans. R. Soc. Lond. A 1912 **211**, 33-73
doi: 10.1098/rsta.1912.0002

II. *The Effect of Pressure upon Arc Spectra.*

No. 3.—*Silver,* λ 4000 *to* λ 4600. *No.* 4.—*Gold.*

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Communicated by Arthur Schuster, *F.R.S.*

No. 3.—*Silver,* λ 4000 *to* λ 4600. [Plate 1.]

(Received January 9,—Read February 4, 1909.)

Contents.

1. *Preliminary.*—The effect of pressure upon arc spectra was first investigated by Humphreys and Mohler,[*] and later by Humphreys.[†] They found that, in general, the lines broadened, were displaced towards the red end of the spectrum, and showed a greater tendency towards reversal. Humphreys' work has dealt more fully with metals other than silver, of which the following table comprises all previous measurements under pressure:—

λ.	8 atmospheres.	9·75 atmospheres.	12·5 atmospheres.	13 atmospheres.
3280·80	0·029	0·028	0·032	—
3383·00	—	0·034	0·027	0·032

The displacements are in Ångström units.

The following investigation was undertaken for the purpose of extending the work to higher pressures. The spectrum of the silver arc has been photographed under pressures ranging from 1 to 201 atmospheres in the region λ = 4000 to λ = 4600 Å.U.

2. *The Apparatus.*—The arc was formed between silver poles, diameter $\frac{5}{8}$ inch, within the Pressure Cylinder (designed by Dr. Petavel, F.R.S.), which had previously been used for the investigation of the effect of pressure upon the Iron Arc,[‡] and the Copper Arc.[§] The light passed through the window in the side of the steel chamber, and was reflected by the mirror system (previously described), which enabled the image of the arc, which was very unsteady at high pressures, to be continually focussed upon the slit of the 21½-foot Rowland Grating Spectroscope in the Physical Laboratory of the Manchester University.

The Second Order Spectrum was employed, the dispersion being 1·3 Å.U. per 1 mm.

An increase in pressure was obtained by the admission of air into the cylinder from a gasholder, suitable valves and gauges being interposed.

The arc was fed by current from the Corporation mains, which supplied 100 volts continuous, and this was reduced to about 50 at the terminals.

3. *The Behaviour of the Silver Arc under High Pressures.*—The continuous current arc between silver poles in air at atmospheric pressure was maintained without difficulty until the poles got thoroughly hot, when the convection currents became so violent that they frequently blew it out. The striking of this arc was more easily accomplished than in the case of iron or copper, where the formation of a non-conducting oxide necessitated breaking through this layer before the current could pass.

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[*] Humphreys, 'Astrophys. Journ.,' VI., p. 169, 1897.

[†] Humphreys, 'Astrophys. Journ.,' XXVI., p. 18, 1907.

[‡] W. G. Duffield, 'Phil. Trans.,' A, vol. 208, p. 111, 1908.

[§] W. G. Duffield, 'Phil. Trans.,' A, vol. 209, p. 205, 1908.

The ease with which the arc burned at any pressure seemed dependent upon the amount of air present; when the cylinder was freshly filled the arc burned steadily for some time, though not often for longer than one minute, without requiring the poles to be brought together, but later on the arc required more attention and frequent re-striking; if, however, the gases were allowed to escape from the cylinder and fresh air introduced, steadiness was again obtained. A plentiful supply of air thus appears to be necessary for steady running, but the cooling of the poles is also a factor that makes for success. Not only did the steadiness of the arc decrease at any particular pressure as time advanced, but also the brightness, the brilliance of the image on the jaws of the slit gradually waning as the arc burned, until a fresh supply of air replaced the old.

And that the readiness with which air has access to the poles is connected with the brightness is further borne out by the increased brightness as the pressure is increased, provided that arcs newly supplied with air are compared; for instance, the arc under a pressure of 200 atmospheres, when first struck, is very much brighter than the arc under a pressure of 50 atmospheres when first struck. This indicates also that the temperature of the arc under high pressure is very much greater than it is at normal atmospheric pressure. Photometric measurements of the intensity of the light emitted under different pressures have been attempted, but the intermittent nature of the arc has not permitted accurate determinations. Distinct changes were observed in the colour of the arc as the pressure was increased; at low pressures it maintained its characteristic greenish appearance, but at the highest pressure reached, 200 atmospheres, it was, when the air was fresh, as white as a carbon arc; at lower pressures, or when the arc had been burning for some time, the greenish colour returned, and my assistant pointed out to me two distinct tints besides the pure white, namely, yellowish-green and green; sometimes as the arc flickered about the poles in an irregular manner these would appear in rapid succession, possibly dependent on the varying length of the arc gap as it moved from point to point on the electrodes.

The silver contained a trace of lead, which is characterised by the line at 4058·04, and on one or two of the photographs at atmospheric pressure the cyanogen band at 3883 is visible and is due to the silver having been melted in a carbon reducing atmosphere. As is usually the case when metallic arcs are burned in air under pressure, some nitric acid was formed within the cylinder, and the air issuing from it gave the characteristic smell of nitrogen peroxide. The appearance of some finely divided particles of iron in the window-tube after the arc had been run for some time at high pressures needs explanation, but it is considered to have either been introduced with the air, which was stored in an iron cylinder, or to have scaled from the steel rods which carried the silver electrodes, though this must have been greatly obviated by the discs of asbestos which were strung on the silver poles and were a good fit in the cylinder.

The arc was more easily maintained between 50 and 200 atmospheres pressure than between 1 and 50 atmospheres. Of all the photographs taken, that at 200 atmospheres gave least trouble, the arc burning steadily for several seconds with dazzling brightness. Extension to higher pressures would be quite possible if the difficulties attendant upon the fracture of the glass and quartz windows could be overcome. As has already been described* in connection with experiments made with the copper arc, the straining of the windows resulted in splinters of glass breaking off and ruining the surfaces, and sometimes in the complete breakdown of the window. The present pressure cylinder cannot be safely used at higher pressures, but a similar but stronger one should present no great difficulties. The running of the arc itself is a simple matter.

4. *The Photographs:* (1) *Method of Exposure.*—As in the previous work with the iron and copper arcs, the comparison spectrum under atmospheric pressure was photographed in the central strip of a plate (20 inches long by 2½ inches broad) with the spectrum under pressure above and below it. To ensure that no accidental displacements were produced the comparison spectrum was photographed before and after the one under pressure. The arc was operated by the writer and the mirrors by an assistant.

The following photographs have been obtained:—

Atmospheres.	No. of photographs.	Atmospheres.	No. of photographs.
5	1	60	1
10	1	75	1
20	2	80	1
25	1	100	1
40	1	120	1
50	1	200	1

Plates: Imperial Flashlight. Developer Imperial Pyro-Metol Standard. Exposure varied from 10 minutes at 5 atmospheres to 5 minutes at 200 atmospheres; but this is little indication of the relative intensities because the width of the slit was different in nearly every exposure.

(2) *Description of the Plates.*—Plate 1 illustrates the behaviour of the silver arc under different pressures. The plate includes the region $\lambda = 4020$ to $\lambda = 4320$. The photographs, which are full-size positive reproductions of the originals, are ranged in order of increasing pressure from the top at 1 atmosphere to the bottom at 200 atmospheres, the central strip of each being at normal atmospheric pressure.

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* W. G. DUFFIELD, "The Effect of Pressure upon Arc Spectra. No. 2.—Copper." 'Phil. Trans.,' A, vol. 209, p. 205, 1908.

To facilitate reference to the lines arbitrary letters have been assigned to them, beginning alphabetically at the more refrangible end.

The prominent features are :—

(1) The broadening of the lines;
(2) Their displacement towards the red end of the spectrum;
(3) The structure which becomes apparent in the wings of the strong lines under pressure;
(4) The gradual disappearance of the line spectrum;
(5) Its replacement by a banded spectrum;
(6) The development of the banded spectrum into an almost continuous spectrum.

The lines seen on the photographs are :—

a	4055·44	1st sub-series.
[*b*	4058·04	Lead.]
c	4212·1	1st sub-series.
d	4311·28	
e	4476·29	2nd sub-series.

(*a*) 4055·44. Silver. 1st subordinate series.

At normal atmospheric pressure it is broad and covers about 13 Å.U. It is unsymmetrically reversed, its reversed portion being slightly on the violet side of the centre of the bright line. *At* 5 *atmospheres** the line spreads over 17 Å.U. or more, and is so broad that it might almost be called a band. The reversed part is badly defined, and its centre cannot be determined. Its wings now present a marked structure, and are resolvable into a number of well-defined lines, in which there is no obvious regularity. The shadings on the two wings are different from one another. *At* 20 *atmospheres* the line has spread out over a greater range and can be distinguished on the red side as far as 24 Å.U. from its original position. The structural appearance, which extends as far as the wings are visible, is well marked, though the individual lines are broader. The broadening is much greater on the red side. *At* 25 *atmospheres* the line spectrum of silver has almost disappeared and given place to a banded spectrum. *Between* 25 *and* 200 *atmospheres*, this line is indistinguishable against this background of banded or continuous spectrum.

(*b*) 4058·04. Lead?

At normal atmospheric pressure this line is fine and sharp and apparently superposed upon the less refrangible wing of line *a* (4055·44). *From* 5 *to* 25

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* Throughout this paper, unless expressly stated to the contrary, the pressure is the excess above 1 atmosphere.

atmospheres it remains a definite line, but has broadened (about 0·5 A.U. at 25 atmospheres) and is displaced. *At* 80, 100, 120, *and* 200 *atmospheres* the photographs show no trace of its presence.

(*c*) 4212·1. Silver. 1st subordinate series.

At normal atmospheric pressure it is broad and covers 16 to 20 Å.U. (according to the amount of exposure). It is unsymmetrically reversed, its reversed portion being slightly on the red side of the centre of the bright line, thus differing from a (4055·44), the other member of the 1st subordinate series. *At* 5 *and* 20 *atmospheres* its behaviour strongly resembles that of line a; it has broadened and is distinguishable 60 Å.U. from its original position; the reversal which is just visible is displaced towards the red end of the spectrum. The wings are shaded into a number of lines, which are, however, differently spaced from those into which line a is resolved. *Between* 25 *and* 200 *atmospheres*, this line cannot be distinguished from the banded or continuous spectrum which in this region takes the place of the line spectrum of silver.

(*d*) 4311·28. Non-series line.*

At normal atmospheric pressure the line is fairly sharp, being only slightly broadened towards the red. *At* 5 *and* 20 *atmospheres* it is seen to be slightly broadened towards the red, though it is still comparatively sharp; its displacement towards the same end of the spectrum is also obvious. *At* 25 *atmospheres* the line appears to be the violet head of a band stretching some distance towards the red. *At* 60 *and* 80 *atmospheres* the line at ordinary atmospheric pressure seems to mark the violet edge of the band, which becomes less sharp and less obvious as the pressure is increased. It is now doubtful if the band to the right of the line has any causal connection with it. *Between* 100 *and* 200 *atmospheres*, this band has become submerged in the continuous spectrum that now dominates the photograph.

(*e*) 4476·29. Member of the 2nd subordinate series.

At normal atmospheric pressure it is broadened towards the red. *At* 5 *and* 20 *atmospheres* its width has increased and it has suffered displacement towards the red end of the spectrum. *At* 25 *atmospheres* it can still be distinguished, though its intensity has been greatly reduced. Its displacement, though large, is difficult to measure. *At* 60, 80, *and* 100 *atmospheres* no sign of this line appears, though, if any radiation of a period close to its original period existed, it should be visible, because the

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* There were three slits in the comparison shutter where this line occurs, so that three small pieces of the line at atmospheric pressure appeared upon the photograph. Two of them may be seen on the reproduction at 60 atmospheres. They permit the comparison line to be easily placed parallel to the double cross-wires in the measuring machine.

nebulous flutings do not occupy this particular part of the plate. *At* 200 *atmospheres* the spectrum is, as in other parts of the plate, nearly a continuous one.

5. *The Broadening of the Lines.*—From the photographs we learn the following facts within the region λ 4000 to λ 4600 :—

1. All silver lines broaden under pressure.

2. The broadening increases with the pressure, but different amounts of exposure make it difficult to determine if the increase is continuous and linear with the pressure.

3. The broadening of the two 1st sub-series lines is, at normal atmospheric pressure, unsymmetrical relatively to the superposed absorption line; increase of pressure increases the width of these lines, and their wings are then seen to consist of numbers of fine lines which merge into one another at higher pressure.

4. The broadening of the 2nd sub-series line (4476·29) at normal atmospheric pressure is unsymmetrical, being greater on the red side. Under pressure this is more pronounced, but the line remains definite though its intensity diminishes.

5. The broadening of the non-series line is distinctive because the line appears to become the violet edge of a band which stretches further towards the red as the pressure is increased, but at the highest pressure the violet edge has lost its character as the head of a band.

6. The distinction that was observed in the same region of the copper spectrum is here also apparent :—the 1st sub-series lines become hazy under pressure, resembling hazy bands, and finally leaving only a cloudy banded appearance on the plate; the 2nd sub-series lines remain definite lines without abnormal broadening, though they ultimately disappear through a gradual weakening process.

7. No relation has been found between the original intensity of a line and its width under pressure.

8. The magnitude of the broadening of the 1st sub-series lines is at 20 atmospheres as great as 120 Å.U.

6. *The Structural Character of the Wings of the Members of the* 1*st Sub-Series under Pressure.*—The photographs of lines *a* and *c* at 5 and 20 atmospheres show that the wings of those lines are of complex structure, being composed of a number of closely packed lines which are comparatively fine at 5 atmospheres, and, though broader at 20 atmospheres and somewhat merged into one another, are still recognisable as the same lines.

There is no obvious regularity in the shadings on the wings, which are dissimilar for the two lines and also for the two wings of the same line.

As the pressure increases, the wings of the lines extend outwards, and at 20 atmospheres some of the patches of light are separated from the original lines, forming what is ultimately a band spectrum.

On one photograph taken at each of the pressures 10 and 20 atmospheres the structure is not apparent, either because it is not invariably present in the arc or because the slit was too wide. Upon this photograph the reversals were rather better defined than upon the reproductions.

7. *The Displacement of the Lines:* (1) *Method of Measurement of the Photographs.*—The Kayser Measuring Machine was used, the setting being always made between parallel threads as accurately as possible upon the most intense portions of the lines under pressure, and advantage was taken of the astigmatic property of the grating of narrowing a line at its extremities. Thirty-six settings were made upon each line on each plate, 18 with the plate in one position and 18 with it in the reversed position. When there was not good agreement between the readings this number was exceeded.

(2) *Table of the Displacements.*—The first column contains the arbitrary letters assigned to the lines to facilitate reference to them. The second column gives the wave-lengths according to KAYSER and RUNGE's tables. The subsequent columns give the displacements at the corresponding pressures, the use of italic figures, *e.g.*, *0·220*, for displacements, indicates that the line is reversed. An asterisk (*) denotes that the line is reversed but that measurements could not be satisfactorily made at that pressure. In all cases the displacements are towards the side of greater wave-length. The pressures are the excess above 1 atmosphere. Figures in brackets indicate that the measurements were made with difficulty.

TABLE I.

		5.	10.	20.	25.	30.	40.	80.	100.	200.
a	4055·44	*	*0·220*	(*0·444*)	(ob	literated	on all	photogr	aphs	)
[*b*	4058·04	0·030	0·052	0·080	(0·120)	(0·145)	—	—	—	] Pb.
c	4212·1	*0·087*	*0·209*	*0·233*	(ob	literated	on all	photogr	aphs	)
d	4311·28	0·099	0·128	0·188	(0·410)	(0·433)	(0·838)	(oblit	erated	)
e	4476·29	0·141	0·220	0·332	(0·558)	(0·650)	—	(oblit	erated	)

The displacements are in Ångström Units.

[This table has been revised.—*December, 1910.*]

(3) *The Relation between the Pressure and the Displacement.*—From the information that is supplied by these measurements it is gathered that an approximately linear relationship holds between the pressure and the displacement, as it does in the case of iron and copper, but the rates of displacement with the pressure are not clearly distinguishable. The higher rate belongs to the series lines *a*, *c*, and *e*, which are displaced more than the non-series line *d*.

8. *Changes in Relative Intensity under Pressure.*—It has already been pointed out[†] that for broadened lines the "intensity" is an indefinite term. If the intensity

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[†] W. G. DUFFIELD, "The Effect of Pressure upon Arc Spectra. No. 2.—Copper." 'Phil. Trans.,' A, vol. 209, p. 205, 1908; 'Roy. Soc. Proc.,' vol. 81, p. 378, 1908.

per unit of area of the plate be considered, it seems true that the members of the 1st sub-series lines *a* and *c*, Plate 1, have diminished in intensity relatively to the other two silver lines. Though if the whole intensity of the radiation in the region of the plate occupied by the broadened lines be considered, the relative strengths of the lines are very difficult to determine.

Under pressure, all the lines in this part of the spectrum become obliterated. It may be here remarked that the complete obliteration recorded by the photographs with the large Rowland grating are not entirely confirmed by photographs with a 1 m. grating. These latter sometimes show faint indications of lines under high pressures where none are apparent in those taken by the 21½ feet instrument. This is due to the fact that the lines do appear in the spectrum under pressure at the moment of extinction of the arc, and possibly at the moment of striking it (*cf.* p. 44).

With large dispersion the duration of these lines is insignificant compared with the total length of exposure necessary to affect the plate, but when the dispersion is smaller the exposure is less, and the interval during which the lines shine out is comparable with the total exposure necessary.

The lines to vanish first are those of the 1st subordinate series (a, $\lambda = 4055 \cdot 44$ and c, $\lambda = 4212 \cdot 1$), which are of great intensity at normal pressure. In this respect, and also because they become dissipated before they are obliterated, their behaviour is very similar to the 1st subordinate series lines in the corresponding region of the copper spectrum, 4022 and 4063.

The line of the 2nd subordinate series (e, $\lambda = 4476 \cdot 29$) weakens as the pressure is increased, and is only just visible at 40 atmospheres. It has disappeared at 60 atmospheres. The manner of its disappearance allies it to the two lines in the copper spectrum, also members of the 2nd subordinate series (4480·6 and 4531·0), which also become weaker as the pressure is increased, but without abnormal widening.

The non-series line (d, $\lambda = 4311 \cdot 28$) is clearly seen at 25 atmospheres, and at 40 atmospheres it seems to be the violet head of a band, but it is very doubtful if the line and the band are in any way causally related—photographs at higher pressure suggest that the band is independent of this line, which has at 60 atmospheres ceased to exist. This non-series line differs from the non-series copper lines that have been examined; the latter have not been found to undergo complete obliteration, though the "sharp" series are weakened as the pressure is increased.

9. *Series of Lines in the Silver Spectrum.*—The classification of the lines of the silver spectrum has been attempted by the same methods that have been employed for the copper spectrum.

KAYSER and RUNGE'S* classification is based upon the relationships between the frequencies of the lines, and the series have become known as the Principal, First

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* KAYSER and RUNGE, 'Über die Spectren der Elemente,' vol. V., 1892.

and Second Subordinate Series, according to the particular formula which includes all its members.

The Zeeman effect, which has been examined by RUNGE and PASCHEN,* shows distinctive behaviour for certain lines, and should afford additional data for their classification, but unfortunately only one of the lines dealt with in this paper has been investigated by their method.

Pressure is also effective in bringing to light characteristic differences between groups of lines, and studies of their behaviour as regards displacement, broadening, changes in relative intensity, and reversal have been made with this end in view. For silver this method does not yield such definite results as were obtained for the copper spectrum, but they are nevertheless of considerable assistance in this classification.

The following table summarizes the methods of forming series in the silver spectrum :—

		Frequency relationship, K. and R.	Magnetic field. RUNGE and PASCHEN'S separation, a multiple of—	Pressure effect.			Displacements per 1 atmosphere (omitting readings at 5 atmospheres).
				Broadening under pressure.	Reversal under pressure.	†Change in intensity under pressure.	
a	4055·44	1st sub-series	—	Very broad. Structure apparent in wings. Resembles band.	Reversed	Obliterated first, though originally strongest	0·022 ?
c	4212·1	1st sub-series	—		Reversed		0·021 ?
d	4311·28	—	—	Moderate	Non-reversed	Less easily obliterated	0·009
e	4476·29	2nd sub-series	0·92	Moderate	Non-reversed		0·017

Though the above table shows great resemblances under pressure between the behaviour of *a* and *c*, they differ at 1 atmosphere in the manner in which the absorption line is superposed upon the bright line, and the photographs show that the wings of the two differ greatly in structure; this difference was to have been expected from the differences shown by them in a magnetic field. No such differences under pressure were, however, discovered for the corresponding copper lines 4022, 4063.

10. *The Band Spectrum under Pressure.*—The prominent feature of these

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* RUNGE and PASCHEN, 'Astrophys. Journ.,' vol. XVI., p. 123, 1902.

† Though *d* and *e* disappear at almost the same pressure, the 2nd sub-series line has been weakened more than the non-series line because its original intensity was greater.

experiments is the replacement of the line spectrum of silver by a banded spectrum when the pressure is large. A necessary condition for the production of this new spectrum is that the arc burns steadily, because, as has just been pointed out, at the moments of extinction some of the lines have been observed to flash out instantaneously, even at 100 atmospheres. On the negatives the bands are not always easily distinguishable, but greater contrast has been obtained by using a slow Velox paper, which enables the detail to be more carefully studied.

(1) *The Structure of the Banded Spectrum.*—The photographs show a number of bright isolated patches or bands, separated by dark intervals. The bright bands are symmetrical about their centres, and are generally very broad, fuzzy and ill-defined, but a few are as narrow as 2 or 3 Å.U.

There is no easily recognisable regularity in the spacings of these patches of light, or bands, and their intensities differ considerably and show no dependence upon their widths.

The resemblance of this spectrum to an absorption spectrum is discussed under a separate heading, p. 48. If the bands be observed visually they present a novel appearance. In place of the steady spectrum which is observed with other metals, there is a constant flickering of the spectrum and waves seem to pass across it, and the bands appear more like tongues of coloured flames which are violently disturbed by a breeze. Horizontal striæ crossing the spectrum were also frequently noticed. The whole phenomenon is thought to be due to violent convection currents in the vapour surrounding the arc, which, being of varying density, cause continually changing amounts of refraction of the rays which pass through it on their way to the window. The constant play of shadows over the inner surface of the window, which is easily visible because of the fine deposit upon it, indicates that some such action as this is in progress, and the striæ may be due to shadows falling upon the slit.

The Behaviour of the Banded Spectrum under Pressure.—The bands first appear on the photographs at 20 atmospheres, where many are resolvable into a number of very fine lines, but, as it was thought possible that longer exposure at a lower pressure might show a trace of them, the normal silver arc was photographed with an exposure ten times longer than usual, and with a very wide slit (½ mm.); but there was no sign of bands in this experiment though the slit included both poles and the centre of the arc.

(2) *Broadening.*—As the pressure increases the bands strengthen and become a more definite phenomenon; many grow broader (*cf.* 4569·7, which increases from 8 Å.U. at 25 atmospheres to 13 Å.U. at 80 atmospheres and 26 Å.U. at 100 atmospheres), and several, which are separately distinguishable at 25 atmospheres, become merged into one another at higher pressures.

At 100 atmospheres the bands have become so broad that they almost constitute a continuous spectrum, though the characteristics of the banded spectrum are not entirely lost.

A photograph of this part of the spectrum has been taken at 200 atmospheres, and here the spectrum looks still more continuous.

The breadths of the bands at different pressures are given in Table II., p. 45; the measurements are in Ångström units.

(3) *Table of Wave-Lengths and Intensities of Bands.*—This is given on pp. 45–47

(4) *The Relative Intensities of the Bands under Pressure.*—Though the intensities of the bright bands are increased by pressure, it does not produce any marked change in the relative intensities of *adjacent* bands. What is, however, noticeable is the gradual increase in the intensities of the bands that are distant from the strong lines a and c relatively to those in their immediate neighbourhood, *e.g.*, band at 4162 has increased in intensity relatively to 4199 and 4215, which are near the line c at 4212. For other examples see Table II. There is an outward extension of the luminosity from these lines as the pressure increases. A line not shown on the photographs in the red (*vide* p. 50) seems also to be concerned in the production of the spectrum.

11. *The Continuous Spectrum.*—The highest pressure available for these experiments was 200 atmospheres, and one photograph was obtained at this pressure, but no bands are discernible against the background of continuous spectrum. Too much risk would be run by pushing these experiments further with the existing apparatus, but it would be of interest to observe if this continuous spectrum persists at still higher pressures and behaves like the continuous spectrum derived from black body radiation, *i.e.*, if the maximum of intensity is displaced towards the region of short wave-lengths as the temperature increases, or if the energy remains localised in the centres of a hidden banded spectrum from which the continuous spectrum has been developed.

12. *Influence of the Electrical Conditions upon the Banded and Continuous Spectra.*—It has already been remarked that at the moment of extinction the bright lines have been seen to flash out and replace the bands. The electrical conditions accompanying the sudden breaking of the circuit occasion this change. Visual observations suggest that at such times the quantity of material taking part in the discharge is diminished; for example, when the arc is burning steadily under pressure, one of the yellowish-green lines is broad, almost resembling a band, and is strongly reversed, yet at the moment when the arc is extinguished this line narrows down to the width of the reversal and flashes out as a bright line. By varying the voltage of the discharge, interesting information regarding the electrical conditions necessary for the production of the banded spectrum should be forthcoming.

13. *The Origin of the Banded and Continuous Spectra.*—The resemblance of the banded to an absorption spectrum requires discussion; hitherto it has been treated as an emission spectrum. It is necessary to inquire into the possibility of the bands being the result of a continuous radiation from the hot poles of the silver and suffering absorption by the surrounding vapours.

Careful examination has shown that no appreciable continuous spectrum is obtained

TABLE II.

25 atmospheres.	Width in Å.U.	Intensity.	40 atmospheres.	Width in Å.U.	Intensity.	60 atmospheres.	Width in Å.U.	Intensity.	80 atmospheres.	Width in Å.U.	Intensity.	100 atmospheres.	Width in Å.U.	Intensity.	Bands in electric furnace, DUFFIELD and ROSSI.
4032·4	*13*	5	4034·0	*13*	5	4031·5	*13*	7	4031·8	*14*	7				
												4040·5	*25*	10	
4046·1	*4*	6	4047·6	*9*	6	4046·9	*6*	6	4047·3	*7*	6				
4050·7	*2*	6				*4051·6*	*2·5*	5							
4062·9	*1*	8	*4063·9*	*2*	8	4063·0	*2*	6	4063·3	*1·5*	8	(? impurity	line)		
4069·1	*18*	6	4069·4	*18*	7	*4069·7*	*7*	9	4070·3	*18*	8				
						4073·0	*12*	10				*4072·7*	*22*	9	
4081·6	*2*	4							4082·3	*5*	2				
4086·1	*3*	4	*4087·9*	*2*	5										
4092·5	*4*	4	4093·0	*4*	4	4092·2	*7*	4	4090·9	*5*	5	*4092·7*	*7*	6	
4100·8	*5*	5	4100·4	*4*	5	4100·4	*5*	5	4100·6	*5*	4	*4101·7*	*6*	6	4099·5
															4107·1
															4114·4
4120·7	*20*	4	4120·7	*16*	5	4120·2	*16*	6	4121·4	*20*	6	4123·0	*21*	7	4120·8
															4129·3
															4137·1
**4144·9*	*9*	5	4143·9	*9*	5	4144·7	*9*	5	4146·0	*12*	6	4148·0	*12*	7	4145·6
															4152·6
4162·9	*16*	6	4164·2	*16*	8	4164·2	*15*	9	†4164·1	*15*	10				4160·5
															4169·0
												4172·4	*25*	8	
4176·0	*3*	7	{*4174·0*	*3*	5	*4173·7*	*4*	6							
			{4177·1			4176·7	*2*	7	*4177·9*	*5*	9				
4180·2	*2*	7	*4180·5*	*1·5*	4	4181·4	*1·5*	6							
						4184·1	*1·5*	6	*4183·9*	*4*	8				
															4186·0
4189·7	*5*	8	4189·5	*5*	8	4190·7	*5*	7	4190·8	*5*	8				
															4194·3
4199·8	*4*	10	4201·1	*5*	7	4201·2	*5*	6	4202·2	*4*	7				

* On one plate this appears to be two bands, 4143·6 (6, 4) and 4149·2 (3, 3).

† On one plate these appear as one band, 4169·9 (25, 9).

Wave-lengths printed in italics indicate that this reading was only once obtained.

TABLE II. (continued).

25 atmospheres.	Width in Å.U.	Intensity.	40 atmospheres.	Width in Å.U.	Intensity.	60 atmospheres.	Width in Å.U.	Intensity.	80 atmospheres.	Width in Å.U.	Intensity.	100 atmospheres.	Width in Å.U.	Intensity.	Bands in electric furnace, DUFFIELD and ROSSI.
4206·1	4	10	4206·3	3	7	_4206·7_	5	6	_4206·4_	4	6				4204·4
4215·7	5	10	4215·3	5	7	4215·0	6	7	4216·1	6	6				4212·2
															4221·4
4229·8	11	8	*_4232·0_	18	7	4232·0	13	5	4231·1	13	3	_4230·2_	13	6	4229·8
_4239·8_	1·5	8				_4239·7_	6	3				4237·8	18	6	4239·5
_4243·1_	2	8	_4243·3_	3	4				4243·6	4	2				
†_4247·0_	2	8													4248·0
†_4252·0_	3·5	9	4252·7	6	6	4253·6	6	6	4254·1	7	7				
															4258·7
†_4263·7_	13	10	4265·4	14	10	4264·1	12	10	4266·0	15	9	4262·6	21	6	4266·6 (v.hd.)**
															4273·9 (v.hd.)
_4277·0_	3	8				_4276·8_	5	3							
‡_4285·7_	6	9	4287·3	3	6	4288·2	4	4	4288·1	5	7				
												4293·6	23	4	4294·9 (v.hd.)
‡4298·0	9	9	4298·2	11	8	4297·8	11	8	4296·6	12	9				
						4314·0	6	8	4317·0	10	9	4317·3	11	8	
4321·0	18	10	4321·2	16	10	§_4320·8_	14	5							4322·2 (v.hd.)
									‖_4324·9_	7	10				
									‖_4334·7_	6	5				4336·5
												4339·2	22	7	
4343·6	10	6	_4346·4_	7	3	4344·5	6	3	4344·0	8	5				4344·5
															4352·2
4360·4	11	4	4361·0	10	4	4361·5	10	3	4361·3	13	4	¶_4360·7_	13	6	4358·8
						_4364·4_	15	8							
															4368·3
4376·3	14	7	4377·1	16	6	4377·7	16	8	4377·9	16	8	¶_4378·3_	14	6	
															4387·5
4396·8	3	4				4398·2	5	4	4399·2	6	3				
_4404·0_	4	5													4403·5
						_4407·4_	6	2	4407·4	7	6				
			4410·7	11	5										4409·1
						_4415·8_	19	8							
						4420·1	14	6	_4419·9_	13	7				

4424·6	*32*	5	*4423·5*	*12*	4				*4424·1*	*35*	7	††*4425·0*	*37*	4	4423·8
			4431·6	*22*	6										4432·8
						4435·2	*12*	5	*4436·0*	*15*	5				
						4438·6	*8*	1							
															4445·9
						4453·2	*4*	3							4453·4
4457·5	*9*	3	*4455·9*	*7*	5										
															4461·5
4466·8	*8*	5	4468·4	*10*	5	‡‡4467·6	*16*	5	§§*4465·2*	*23*	5	4467·8	*23*	4	4469·1
4477·9	*2·5*	8													
4487·5	*2*	5				4488·0	*4*	4							
4495·8	*10*	6	4494·0	*18*	6	*4493·2*	*15*	6	||||*4495·3*	*17*	6				
						4499·2	*9*	5							4489·7
															4505·1
									4511·8	*7*	5				4512·7
4516·0	{*15* *5*	5}	¶¶*4514·0*	*8*	5	4515·3	*9*	5							
															4520·0
4525·3	*5*	6	¶¶*4526·7*	*8*	6	4524·0	*4*	3	*4523·7*	*4*	4				
4531·0	*6*	4				4531·4	*4*	4	4530·7	*6*	6				
												4537·4	*20*	5	4537·2
															4543·1
						4550·1	*1*	6							4550·1
						4552·6	*1*	6							
4559·1	*5*	9	4557·0	*6*	6	4558·1	*5*	6	4557·5	*8*	6				4556·6
															4564·5
4569·7	*8*	10	4567·9	*9*	6	4569·2	*10*	8	4569·8	*13*	10	4569·7	*27*	6	4570·8
						4578·0	*1·5*	4							
4584·6	*3*	7	*4581·4*	*7*	5	4583·2	*2*	4	*4583·5*	*7*	6				4583·0
						4587·3	*1*	3							4588·6
4591·3	*6*	7	4590·8	*5*	3										4594·9
4598·5	*12*	7	4497·8	*6*	7	4595·7	*11*	8	*4596·4*	*12*	9	*4601·1*	*14*	9	4600·8
															4607·8
			4610·5	*7*	2	*4610·2*	*5*	1							
															4613·6
			4620·4	*9*	6	*4620·8*	*14*	10				*4619·1*	*8*	9	4619·3

* One plate shows two bands, 4223·4 (*4*, 5) and 4231·2 (*7*, 6).

† One plate shows one large band, 4260·0 (*23*, 9).

‡ One plate shows one large band, 4293·5 (*18*, 7).

§ One plate shows two bands, 4320·8 (*4*, 9) and 4326·9 (*4*, 9).

|| One plate shows one band, 4330·8 (*12*, 7).

¶ One plate shows one band, 4368·5 (*28*, 5).

** v.hd. = violet head of band.

†† One plate shows two bands, 4411·3 (*23*, 6) and 4437·9 (*20*, 5).

‡‡ One plate shows three bands, 4461·0 (*4*, 4), 4467·5 (*6*, 5), and 4473·3 (*5*, 4).

§§ One plate shows three bands, 4455·5 (*5*, 3), 4459·6 (*5*, 4), and 4468·8 (*12*, 5).

|||| One plate shows two bands, 4491·9 (*6*, 5) and 4499·0 (*7*, 6).

¶¶ One plate shows one band, 4519·8 (*16*, 3).

At 25 atmospheres any bands occurring with wave-length greater than λ 4600 are too indistinct for measurement.

between $\lambda=4000$ and $\lambda=4600$ from the poles at ordinary pressures. But the brightness of the arc increases with the pressure, and it is not impossible that the intensity of the poles becomes sufficient to give a continuous spectrum. If this is the case, we must have, at 20 atmospheres, poles sufficiently hot to give a continuous spectrum surrounded by an absorbing layer of silver vapour, and since, as the pressure increases, the widths of the bright bands increase, this hypothesis requires that the amount of absorption decreases relatively to the brightness of the poles.

There is nothing inherently impossible in these conditions, but because the arc was frequently quite free from a background of hot poles (as for instance when the bright streams of vapour met some distance from them), and because the vapour is itself intensely luminous and must emit a spectrum of its own, it is simpler to regard the band spectrum as the true emission spectrum of silver vapour under these conditions.

It should also be remarked that large white-hot molten drops do not form on the silver poles as they do in the case of iron, but that the silver seems to be vaporised without previous melting. There is, moreover, the additional evidence that the lines a and c, which are intimately connected with the formation of these bands, remain emission lines throughout.

That the silver lines really disappear and are not hidden by the continuous spectrum is borne out by the fact that on one photograph at a high pressure an impurity line (of lead) remains visible against the continuous background.

The disappearance of the line spectrum seems due to the replacement of the old vibrating systems by new ones, which are perhaps new and complicated atomic combinations. Whether these are aggregates of silver atoms, or combinations of silver and oxygen atoms, remains to be tested—a most valuable research would be the examination of the silver spectrum under pressure in an atmosphere of hydrogen.

In HARTLEY'S opinion the oxide of silver does not play any part in producing the bands in the spectrum of the flame, whose temperature he considers too high for its formation. The writer has, however, found that the brightness of the arc is dependent upon the amount of air present in the cylinder, and since WHITTAKER* has pointed out that from theoretical considerations pressure is, in some cases, a more potent factor in causing combination than is elevated temperature in producing dissociation (and it is to be remarked that the bands under discussion do not appear below about 20 atmospheres), the question of an oxide formation is not yet decided.

The experimental evidence that a spectrum other than a line spectrum can exist at the enormously increased temperature of the arc under pressure is of considerable interest in the interpretation of sunspot spectra. The discovery of the identity of the flutings of titanium oxide, magnesium hydride, &c., in these spectra has led to the conclusion that sunspots are regions of low temperature, and, though this may be actually the case, it is not necessarily so simply because of the existence of a fluted

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* WHITTAKER, 'Report British Association,' Dublin, 1908.

spectrum. Though, for the case of silver, the pressure necessary for the formation of the band spectrum is higher than that indicated by the amount of the displacement as existing in sunspots, a lower pressure may suffice for the formation of the titanium oxide flutings.

The transition from the banded to a continuous spectrum remains for discussion. Schuster and others have suggested that increase of pressure should ultimately produce a continuous spectrum. For metalloids it is known that such is the case: if the pressure of hydrogen in a vacuum tube is gradually increased the lines broaden until the resulting spectrum is continuous. Hartley,* discussing the fluted flame spectrum of silver, puts an idea of Schuster's ('Brit. Assoc. Report,' 1880) into the following words:—"Thus we see that there is really no essential difference between the constitutions of the matter which enters into vapours of metals and metalloids; there is, in fact, something in their constitution common to both which is apparently dependent upon their vapour pressures, and probably due to the actions of the molecules upon one another when their mean path is so extended that their motions become rhythmical. Reduce the freedom of their motions and the result is a continuous spectrum."

The results of the present experiments bear out this conclusion, and the development of the banded into a continuous spectrum is regarded as the outcome of the widening of the individual bands.

It remained to be seen if this banded spectrum were identical with any known spectrum of silver. Hartley had investigated the flame spectrum and had photographed flutings, but not in the region of the spectrum under present observation, and, since other methods for flame production also showed no flutings, the writer, with the help of Mr. R. Rossi, B.Sc., undertook some experiments with a carbon-tube furnace to discover if any bands were produced by this method in this region of the silver spectrum. A great number of more or less regularly spaced lines, or flutings, were found. These were photographed with a 1 m. grating spectrograph,† and measured and compared with the bands obtained in the present experiments. In the last column of Table II. are given all the measurements made in this part of the carbon-tube spectrum. In appearance the spectra are not the same, but it must be borne in mind that the pressures of the two were very different, and how far this factor is effective in masking any resemblance it is difficult to say. There are 25 lines in the carbon-tube furnace spectrum differing by less than 1 Å.U., or 29 lines differing by less than 2 Å.U., from the measurements made under pressure, out of a total of 55 furnace flutings and 63 arc flutings. The evidence is thus not entirely favourable to the two being the same spectrum, especially as the strong violet edges of bands in the furnace spectrum (4266·6, 4294·9, 4322·2) are absent under pressure, as are also the strong flutings at 4505·1, 4564·5, 4600·8, and 4607·8. But these

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* Hartley, 'Phil. Trans.,' A, vol. 185, p. 166, 1894.

† Duffield and Rossi, 'Astrophys. Journ.,' vol. XXVIII., p. 371, 1908.

differences do not conclusively prove that the spectra are not the same, as special conditions may govern the appearance of these violet heads. Further evidence upon this point is required.

The most valuable information regarding the origin of the banded spectrum is afforded by the photographs reproduced in Plate 1 at 5 and 20 atmospheres, when an incipient band spectrum seems to originate from the strong lines *a* and *c*, and, since at higher pressures there is a gradual extension of the energy outwards from these lines until the whole of the plate is covered with bands, it seems definite that the replacement of the line by a banded spectrum is most intimately associated with the vibrating system producing the line of the 1st sub-series in this particular part of the spectrum; there is, however, a member of the 2nd sub-series just off the plate which is, perhaps, responsible for some of the bands on the red of Plate 1.

The discovery that a silver arc burning in an atmosphere of hydrogen under certain conditions gives rise to the spectrum of that gas* necessitated an inquiry into the possibility of the air spectrum being produced when the same arc is burned in air under unusual conditions; but a comparison of the band spectrum with the spectra of oxygen, nitrogen, and air gives no indication that its origin is due to these gases.

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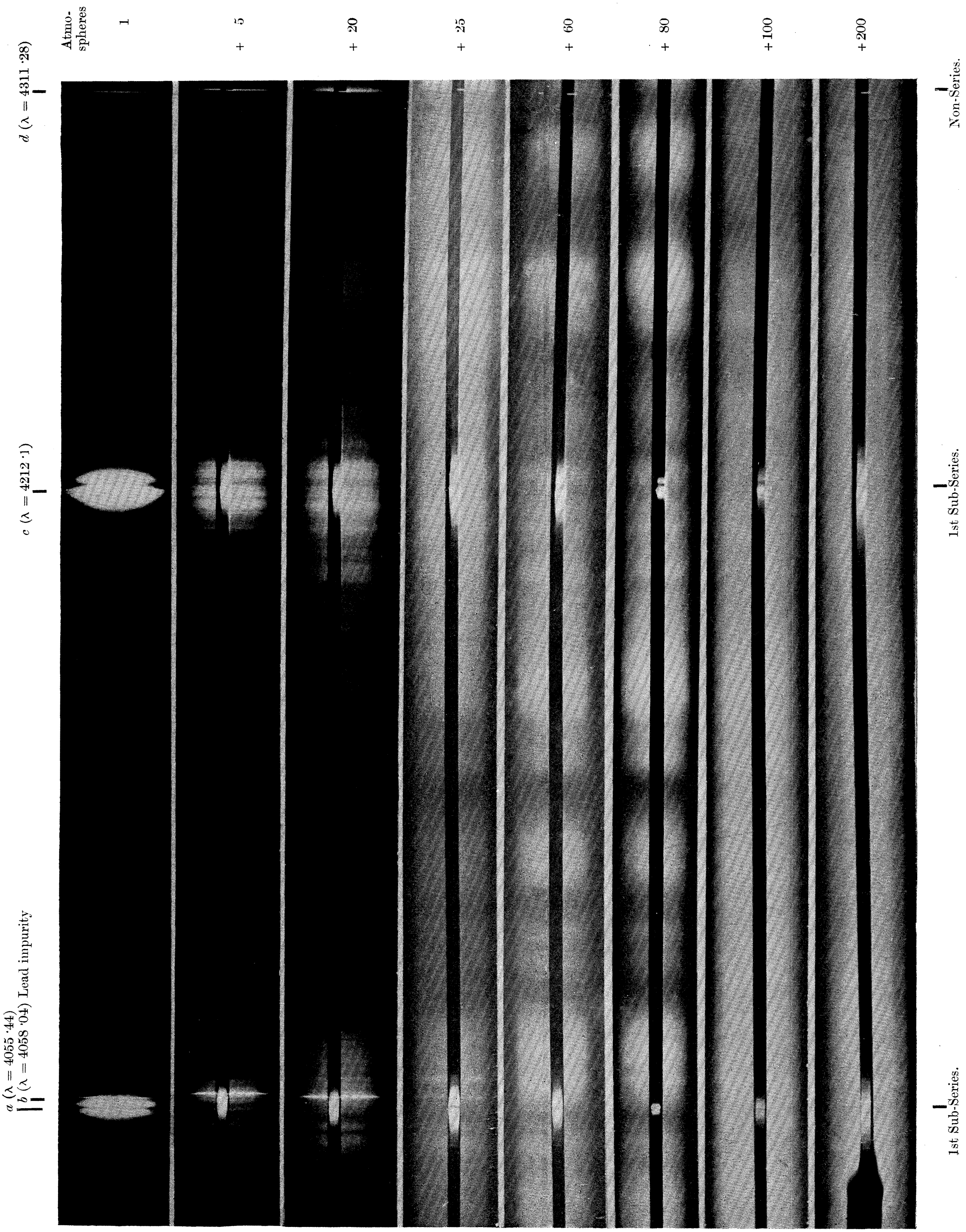
* O. H. BASQUIN, 'Astrophys. Journ.,' vol. XIV., p. 1.

SILVER.


Atmo-
spheres
1
+ 5
+ 20
+ 25
+ 60
+ 80
+100
+200
d (λ = 4311 ·28)
c (λ = 4212 ·1)
a (λ = 4055 ·44)
b (λ = 4058 ·04) Lead impurity
Non-Series.
1st Sub-Series.
1st Sub-Series.

The Effect of Pressure upon Arc Spectra.

No. 4.—*Gold.* [PLATES 2–4.]

(Received May 6,—Read June 9, 1910.)

CONTENTS.

1. *Preliminary.*—In the first part of this paper the apparatus and method of taking the photographs under pressure have been described. The investigation of the gold arc was carried out in precisely the same way, and the spectrum has now been photographed under pressures ranging from 1 to +200 atmospheres.

The photographs were taken in September, 1908, but the writer's absence in Australia necessitated a delay in measuring them and in presenting the results.

Though not exhibiting the remarkable features of the silver arc, the photographs testify to the powerful means that an increase in the pressure of the surrounding medium affords for displaying the different characters and properties of the individual lines. Moreover, an investigation over a wider range of wave-lengths than the writer has before attempted has brought nearer the solution of the problem of the relation between the displacement and the wave-length, while the extension of the pressure to +200 atmospheres enables us to investigate more thoroughly the relation between the pressure and wave-length.

In the present investigation quartz windows were discarded in favour of glass ones for use in the pressure cylinder on account of the greater tendency of the former to collapse after being subjected to the highest pressures and the attendant expense of replacing them. This, unfortunately, involved a restriction to the wave-lengths above 3550 Å.U.

The writer has not found any reference to previous work with the gold arc under pressure.

2. *The Spectrum of the Gold Arc at Atmospheric Pressure.*—In these experiments it was decided to employ the spectrum emitted by an arc passing between poles consisting of rods of the pure metal. Previous workers with the gold arc at atmospheric pressure have fed the metal into a carbon arc, but this method did not seem desirable in the present experiments, in which it has been the writer's aim to keep the element under investigation as free as possible from any sensible quantity of a different element, which might by its own vapour density introduce some disturbing effect upon the broadening or displacement of the lines.

Thanks to the courtesy of Messrs. JOHNSON and MATTHEY, of Hatton Garden, London, it was made possible to carry out these experiments with poles of metallic gold. Each pole was $\frac{5}{8}$ of an inch in diameter and $1\frac{1}{2}$ inches long, and was screwed into a copper rod of the same diameter, 6 inches long, to enable it to be properly placed in the pressure cylinder. The gold was guaranteed to be of purity 0·9995.

The current employed was supplied by the Corporation mains at 100 volts continuous, about 7·5 amperes being taken by the arc at atmospheric pressure.

The following Table I. gives a list of the lines which appear upon the photographs, together with references to the observations made by previous workers in the same part of the spectrum.

It will be noticed that in the present photographs a number of lines appear which were not described by KAYSER and RUNGE as occurring in the arc spectrum, though most of them have been recorded by EDER and VALENTA and EXNER and HASCHEK as spark lines. The difference between KAYSER and RUNGE's and the writer's lists is to be looked for in the use of metallic poles instead of a carbon arc fed with the substance, and also perhaps in the current and voltage of the supply.

The fact that the majority of the lines which appear in the arc under discussion had previously only been found in the spark spectrum points to the insufficiency of the terms "arc" and "spark" lines to distinguish lines from one another, and indicates that in the case of gold, as in that of iron*, "spark lines" [*sic*] may appear in the spectrum obtained from an arc source. The distinction implied by the terms "arc" and "spark" lines cannot, therefore, be a general and rigorous one, however useful as broad descriptive terms, but may have particular value when the current, dimensions of the poles, and voltage of the supply are known in the one case, and the induction, capacity, &c., in the other.

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* DUFFIELD, 'Astrophys. Journ.,' vol. XXVII., p. 260, 1908.

The lines in the Table were measured by comparison with the spectrum from an iron arc photographed upon the same plate, and their identification with the lines measured by KAYSER and RUNGE and EDER and VALENTA was thus rendered simple. The wave-lengths are those given in the two above-mentioned papers.

The letters in the first column of the Table, *a*1, *a*2, *b*1, *b*2, *c*1, *c*2, &c., have been added to facilitate reference to the lines to which they refer.

TABLE I.

	Wave-length.	Intensity. Max. = 10.	Previous observations in arc spectrum. Observed intensities in brackets.		Previous observations in spark spectrum.			
			K. & R. Max. = 10.	MORSE. Max. = 30.	E. & V.* Intensity. Max. = 10.	E. & H.† Intensity. Max. = 10.	Wehnelt spark. MORSE.‡ Max. = 100.	
*a*1	3553·72	0·5	K. & R. (2)§	MORSE (5)‡	6*s*	3*n*	1	
*a*2	57·70	0·5						
*b*1	86·66	4			7*s*	5*n*	4	
*b*2	3607·59	0·5			3*s*	2*n*		
*c*1	33·40	0·5			5*s*	5*s*		
*c*2	50·95	0·5				1		
*d*1	3796·15	0·5			3*n*	2*n*	2*b* ?	
*d*2	3804·22	1·5			4*s*	5		
*e*1	74·96	2·5			4*s*	3		
*e*2	80·34	1			3*s*	2		
*f*1	89·58	1			2*n*	1*n*		
*f*2	98·04	6	K. & R. (4)	MORSE (5)	10*s*	10*r*	30	
*g*1	3909·54	2·5	K. & R. (2)	MORSE (3) H. & K. (–)‖	3*s*	1*s*	1	
*g*2	14·93	1			(2*s*)	1*n*		
*h*1	27·82	1			3*s*	3		
*h*2	76·80	1			3*n*	2*n*		
*i*1	79·72	1			3*n*	2*n*		
*i*2	4016·27	2			8*s*	5*r*	1	
*j*1	41·07	3	K. & R. (2)	MORSE (5) H. & K. (–)	4*s*	3*s*	3	
*j*2	53·0	2			6*s*	7		
*k*1	57·0	2				1*b*		
*k*2	61·2	2				1*b*		
*l*1	65·22	9·5	K. & R. (6)	MORSE (10)	10*s*	15	30	L. DE B.¶
*l*2	76·52	0·5				1		
*m*1	77·83	0·5				1		
*m*2	84·26	3·5	K. & R. (2)	MORSE (5)	4*s*	2	2	
*n*1	89·95	1			2*n*	1*b*		
*n*2	4128·80				1*n*	—		

* E. & V. = EDER and VALENTA, 'Denkschr. K. Akad. Wiss. Wien,' LXVIII., 1899.

† E. & H. = EXNER and HASCHEK, 'Sitzber. K. Akad. Wiss. Wien,' CVII., 1898.

‡ H. W. MORSE, 'Astrophys. Journ.,' 21, p. 225.

§ K. & R. = KAYSER and RUNGE, 'Über die Spectren der Elemente,' V., 1892.

‖ H. & K. = HAGENBACH and KONEN, 'Atlas of Emission Spectra.'

¶ L. DE B. = LECOQ DE BOISBAUDRAN, 'Spectres Lumineux,' Paris, 1874.

TABLE I. (continued).

	Wave-length.	Intensity. Max. = 10.	Previous observations in arc spectrum. Observed intensities in brackets.		Previous observations in spark spectrum.			
			K. & R. Max. = 10.	Morse. Max. = 30.	E. & V.* Intensity. Max. = 10.	E. & H.† Intensity. Max. = 10.	Wehnelt spark. Morse.‡ Max. = 100.	
o1	4241·99	3	K. & R. (2)	Morse (5) H. & K. (–)	3n	2	2	
o2	4315·45	4·5		H. & K. (–)	8r	8s	10	L. de B.
p1	4437·44	3·5	K. & R. (4)	Morse (4) H. & K. (–)	4s	2r	5	L. de B.
p2	66·25							
q1	88·46	5	K. & R. (4)	Morse (4) H. & K. (–)	8s	4r	10	L. de B., Huggins.§
q2	4607·80	4		Morse (3) H. & K. (–)	6s	3	5	L. de B.
r1	4760·29				2s	1n		
r2	92·79	10	K. & R. (6)	Morse (30) H. & K. (–)	8b	4r	100	L. de B., Huggins, Thalén, Kirchhoff.
s1	4811·57	4·5		Morse (4) H. & K. (–)	5s		5	L. de B., Huggins.
s2	4915·57	0·5						
t1	34·37	0·5						
t2	5064·75	1	K. & R. (2)	Morse (5) H. & K. (—)	5s		3	L. de B., Huggins.

* E. & V. = Eder and Valenta, 'Denkschr. K. Akad. Wiss. Wien,' LXVIII., 1899.

† E. & H. = Exner and Haschek, 'Sitzber. K. Akad. Wiss. Wien,' CVII., 1898.

‡ H. W. Morse, 'Astrophys. Journ.,' 21, p. 225.

§ Huggins, 'Phil. Trans.,' 1864, p. 139.

A few of the above lines were first observed in comparison spectra taken in conjunction with the pressure photographs and not in the preliminary photographs—*e.g.*, 3557·70 at 30 atmospheres, 4128·80 at 5 atmospheres, 4466·25 at 5 atmospheres, 4760·29, 4915·57, and 4934·37 at 40 atmospheres.

The intensities at the violet end of the spectrum were diminished by the absorption by the glass lens and reflection from the mirrors which prevented ultra-violet light from being used. Similarly the insensibility of the plates to the green part of the spectrum affected the highest wave-lengths.

Although a large number of lines not chronicled by Kayser and Runge have been noted, one line given by them at 4364·72, intensity = 1 (maximum = 10), was not seen on any of the above photographs—it is possibly due to an impurity.

3. *The Behaviour of the Gold Arc under Pressure:* (1) *Manipulation.*—When the arc was first formed at atmospheric pressure between gold poles it burned

steadily and silently, but as the poles gradually became hotter, turbulent convection currents were produced in the vapour, the arc became noisier, and small explosions on the poles gave rise to outbursts of metallic vapour which frequently blew out the arc.

With increase of pressure the arc became more troublesome, and considerable difficulty was experienced in obtaining photographs at 5, 10, and 20 atmospheres, though at higher pressures the arc again became steadier and more easy to manipulate, behaving in this respect very differently from the copper arc.

Throughout the whole range of pressure, from 1 to 200 atmospheres, the steadiness with which the arc burned was found to depend upon two factors: (1) the coolness of the poles and (2) the freshness of the air supply. It was found expedient during an exposure, when the arc burned badly, to release a considerable quantity of the air from the pressure cylinder and to admit a fresh supply, which both cooled the poles and diluted the impure air containing the products formed by the arc burning in air. This was always effectual in improving the steadiness and brightness of the arc.

As in the case of the iron, copper, and silver arcs, with poles composed of the pure metal, the exposure consisted of a number of short-lived arcs. A difficulty that was accentuated in the manipulation of the gold arc was occasioned by the ease with which the lower pole melted, causing the arc to be frequently formed behind the upper pole in such a manner that its light was screened from the window. It required some experience with the feed-wheels to cope with this trouble.

(2) *Colour.*—At low pressures the colour of the gold arc was not very determinate, but is best described as mauve; in comparison with the copper and silver arcs it seemed soft and subdued, though it did not differ from them to any noticeable extent in actinic power, requiring about the same exposure when it burned well.

With increase of pressure it became whiter, and at 200 atmospheres was not very different from the blue-white of the silver arc under the same pressure.

(3) *Intensity.*—The brightness of the gold arc increased with the pressure of the surrounding air, but was never, as far as visual observations are reliable, as bright as the copper or silver arcs at corresponding pressures. Attempts were made as before to measure the intensities photometrically, but the fluctuations in the brightness from instant to instant were too great to enable this to be done with consistent results.

The brightness is chiefly affected by those factors upon which the easy running of the arc depends, namely, (1) the temperature of the poles, and (2) the freshness of the air supply in the cylinder, which, besides influencing the intrinsic brightness, diminished by absorption the amount of light reaching the window of the pressure cylinder.

Other difficulties which were encountered lay in (3) the variable length of the arc as it jumped about on the irregular poles (which affected the current flowing through it), and (4) the deposit of a fine material upon the window, which, though not serious for the general objects of the experiments, and not comparable with the black deposit from the iron arc at low pressures, was a serious hindrance to comparative measurements of the intensities. A (5th) difficulty is involved in the change of colour of the arc as the pressure is increased.

It has consequently not been feasible to determine whether the total intensity of the arc is strictly a linear function of the pressure, though, with the exception of the region 5 to 20 atmospheres, the brightness appeared to increase steadily as the pressure was increased.

(4) *A Change in the Physical Properties of the Gold.*—A source of great trouble was the melting of the lower pole, which was so rapid that when the pressure cylinder was opened after the first set of 12 photographs had been taken, only ½ inch of the original 1½ inches of this pole remained, the rest of the metal having trickled down the sides and solidified in ridges and lumps, exactly like the wax of a candle that has burned rapidly in a gust of wind. The other pole had remained intact.

The obvious course was to interchange the poles, first paring the drippings from what had previously been the lower one. With this re-arrangement a second set, comprising 14 photographs, was taken, and the conditions were, as far as the writer is aware, exactly the same as those under which the first set was obtained, and the pressures were extended over the same range of 1 to 200 atmospheres. Less difficulty was experienced from the irregular burning of the arc, and its image could always be easily guided by the mirror system upon the slit of the spectroscope.

At the end of these experiments it was expected that the lower pole would be found to have melted away as before; but this was not the case, it was as little affected as when it had served as the top electrode, its upper surface being but slightly pitted. Nor did a subsequent set of 8 photographs at the same pressures cause either pole to melt.

A physical change had been accomplished in the gold whereby it no longer melted, though placed under conditions under which a similar rod of gold had previously melted freely.

It is quite possible that the raising of the melting-point is due to a direct effect of pressure upon the metal, though we must also consider as possible factors the passage of a current of 10 to 15 amperes through the rod, a repeated annealing action, and perhaps some absorbent action by the hot poles of the gases within the cylinder which might affect their properties, though this last action might have equally well taken place during the original refining of the metal.

(5) *The Occurrence of the Calcium Lines* H *and* K.—In spite of the fact that the spectrum of gold did not when first examined show any impurity, either recognised or suspected, very abundant evidence of the presence of calcium is presented by the photograph taken at a pressure of 10 atmospheres in the region λ 3550 to λ 4000 (Plate 2) upon which the H and K lines appear more strongly than any other line, being very much more prominent than the gold line *f*2 at 3898·04. This is the more

remarkable because there is not the slightest trace of either of these lines in the comparison spectrum which was obtained by a divided exposure, one-half before the pressure photograph, the other half after it.

Faint traces of aluminium (3944·29 and 3961·85) and iron also occur on the same photograph, but they are feeble compared with the strong H and K lines. Except for a faint trace of the line K at 50 atmospheres (H being absent) there is no evidence of calcium on any of the other photographs taken under pressure, though they occur in the comparison spectrum at 1 atmosphere, in the next photograph at 30 atmospheres. Above 50 atmospheres there is no sign of this element in either the pressure or comparison spectra; it appears that the calcium which had by some means got on to the pole at 10 atmospheres was dissipated as time went on.

The remarkable nature of the phenomenon demanded that further photographs should be taken at low pressures, and so photographs were obtained at 5 and at 15 atmospheres. The former contained strong evidence of the presence of calcium, the H and K lines being, as on the previous photograph at 10 atmospheres, five or six times as strong as the strong line $f2$ of gold, and, again, there was only the smallest evidence of this substance in the comparison spectrum, only a faint trace of the line K being discernible, though the exposure was, as always, a divided one. Upon the photograph at 15 atmospheres there is, on the other hand, no evidence of either of these lines under pressure, though there is a faint indication of both H and K in the comparison spectrum.

An explanation that seems possible to the writer is that some calcium impurity either pre-existed in one of the gold rods and formed a tiny pocket of metal, or that some particle of dust rich in calcium (and containing aluminium) was introduced into the cylinder with the air from the gasholder, and settled upon the pole while molten. In either case, we can imagine that a small quantity of calcium becomes lodged in one particular spot upon the face of one of the poles. It is known that the arc wanders from point to point over the surface of the poles, and when it happened to spring from the spot rich in the impurities they would manifest their presence. We may suppose that the locality occupied by the calcium happened to be on an irregularity on the pole which infrequently formed the starting place of the arc. Under these circumstances, when the arc burned badly and required a very prolonged exposure, as it did most especially at 5 and 10 atmospheres, this spot would be more frequently visited by a fluctuating arc than on those occasions when the arc burned steadily and kept to one spot.

It is worth noting that the spectrum of gold at atmospheric pressure was photographed by a small 1-metre grating spectrograph before the gold was subjected to pressure, and afterwards upon the same plate after the arc had been investigated at high pressures. The two photographs show not even the slightest difference.

Another point of interest is the order of appearance of the H and K lines when only small amounts of calcium are present. When only one of them occurs either at atmospheric pressure or under 50 atmospheres pressure, it is the line K, which is to be expected as it is the stronger of the two. This is, however, not in agreement with an observation made by LIVEING, quoted by HUGGINS* in a paper entitled "The Relative Behaviour of the H and K Lines of the Spectrum of Calcium," who states that when calcium occurs as an impurity in a carbon arc the H line sometimes appears by itself.

The negatives that had previously been taken in the region λ 4000 to λ 4600 were examined for the calcium line at 4226, but only a trace of it was discovered, and then only in the comparison spectrum, on photographs at 10 and 20 atmospheres. It is unfortunate that the H, K, and g lines were not upon the same plate, as they might have contributed to our knowledge of the origin of these lines under different conditions of density. The conclusion arrived at by HUGGINS,* and later by BARNES,† that the H and K lines are produced by a rare vapour of calcium and the g lines by dense vapour is not confirmed by the fact that H and K appear far more readily at +5 atmospheres than they do at atmospheric pressure. But possibly the above results are vitiated by the localisation of an impurity, as has already been suggested.

TABLE II.

Region A. λ 3550 to λ 4000.

5 atmospheres	30 atmospheres	100 atmospheres
10 ,,	40 ,,	150 ,,
15 ,,	50 ,,	175 ,,
20 ,,	60 ,,	200 ,,
25 ,,	80 ,,	

Region B. λ 4000 to λ 4600.

5 atmospheres (2)	40 atmospheres	100 atmospheres
10 ,, (2)	60 ,,	150 ,,
20 ,,	80 ,,	200 ,, (2)

Region C. λ 4600 to λ 5100.

5 atmospheres	40 atmospheres	100 atmospheres
10 ,,	60 ,,	200 ,,
20 ,,	80 ,,	

4. *The Photographs:* (1) *Region Investigated.*—The investigation of the gold spectrum extended from $\lambda = 3550$ to $\lambda = 5100$, and to photograph these in the 20-inch camera attached to the $21\frac{1}{2}$-foot Rowland grating spectrograph it was necessary to make exposures in three different parts of the spectrum. Thanks to the

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* Sir WILLIAM and Lady HUGGINS, 'Astrophys. Journ.,' VI., 77, 1897.

† BARNES, 'Astrophys. Journ.,' vol. XXVII., p. 152, 1908.

care with which the grating had been adjusted, it was possible to move from one part of the spectrum to another and still have excellent definition, without further adjustment than that involved in making a correction for the temperature of the room, which is different in different parts of the spectrum and which had been previously found experimentally and tabulated for subsequent use.*

Making allowance for some overlap upon the neighbouring photographs each plate contributed about 600 Å.U. The photographs (Table II., p. 58) were taken in the regions indicated at the subjoined pressures.

The pressures are the excess above 1 atmosphere. In each region a photograph was also taken of the spectrum of the gold arc at atmospheric pressure in conjunction with that of an iron arc.

(2) *Description of the Plates.*—Plates 2, 3, and 4 illustrate the behaviour of the gold arc under different pressures: Plate 2 includes the region $\lambda = 3770$ to $\lambda = 4020$, Plate 3 the region $\lambda = 4010$ to $\lambda = 4280$, and Plate 4 the region $\lambda = 4300$ to $\lambda = 4620$. The photographs are full size positive reproductions of the originals, and are arranged in order of increasing pressure from the top at 1 atmosphere to the bottom at +200 atmospheres, the central strip being always at atmospheric pressure. The arbitrary letters enumerated in Table I. have been affixed to the lines to facilitate reference to them.

The prominent features of the gold arc are:—

(1) The broadening of the lines.
(2) Their displacement towards the red end of the spectrum.
(3) The changes in relative intensity.
(4) The absence of reversals.

The Nitrogen Band Spectrum.—Upon the photographs reproduced in Plates 2 and 3 occur at 10 atmospheres pressure two band spectra, one whose head is a little to the violet side of *g*2 (Plate 2) being very well marked. Measurement gives 3914·45 and 4278·28 as the wave-lengths of their chief heads, and they are evidently due to nitrogen, the former coinciding with the nitrogen band measured at 3914·60 by DESLANDRES† and the latter with that at 4278·6 measured by HASSELBERG.‡ LEWIS and KING§ have already pointed out that these bands are liable to occur in the arc spectra of some metals, especially of copper, and this is evidently an instance.

Both bands are ascribed to the negative band spectrum of nitrogen.

The silver spectrum under pressure was characterised by the production of a band spectrum of quite a different nature from the above, each band being a broad

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[*] W. G. DUFFIELD, 'Phil. Trans.,' A, vol. 208, p. 111, 1908. (Part I.—The Mounting of the Rowland Grating.)

[†] DESLANDRES, 'C. R.,' vol. 103, p. 375, 1886.

[‡] HASSELBERG, 'Mém. Acad. St. Petersburg,' 1885 (7), 32, No. 1.

[§] LEWIS and KING, 'Astrophys. Journ.,' vol. 16, p. 162, 1902.

indefinite patch of light. There is some indication of this in the gold spectrum, but the phenomenon is not nearly as fully developed. A small amount of continuous spectrum appears at the highest pressures, and is partly caused by the incandescent poles being focussed upon the slit during a portion of the exposure, and partly also by the spreading out of the wings of the strong lines as in the silver spectrum.

Individual references to the lines on these plates will be found throughout the text.

5. *Broadening of the Lines.*—From the photographs we learn the following facts:—

1. All lines broaden under pressure.

2. The broadening increases with the pressure, but different amounts of exposure necessarily make it difficult to determine if the relation between the two quantities is a linear one.

3. The broadening of the lines of the spectrum of the gold arc is of two types:—(*a*) Symmetrical. (*b*) Unsymmetrical.

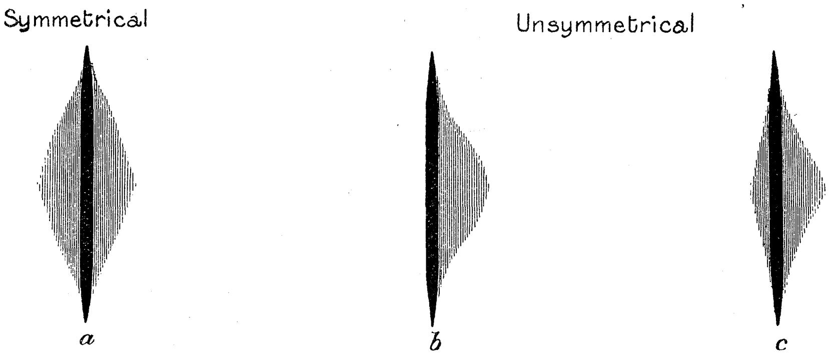
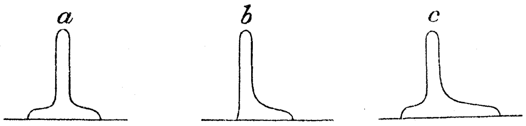


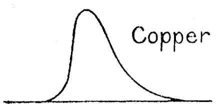
Fig. 1.

Fig. 1 is intended to illustrate these types and to draw attention to a feature which is characteristic of many of the lines of the gold spectrum under moderate pressures: this is their appearance as strong lines superposed upon hazy wings against which they are more or less sharply defined.

In this respect they afford a contrast to the lines of the copper spectrum,* in which the wings seem more intimately related to the original line. The intensity curves for the above lines of gold are of this nature

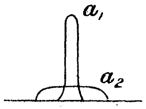


whereas those for the copper lines investigated are more of this character



Duffield, 'Phil. Trans.,' A, vol. 209, p. 205, 1908.

The shape of the curve a suggests that it may be resolved into two curves due to two different vibrating systems, of which one, a_2, may be derived from the other, a_1, by some effect of pressure such as loading or other suitable means. Similarly for the other curves.



Under higher pressures the principal part of the line (a_1) becomes broader and loses in intensity relatively to the background (which grows stronger) into which it gradually merges, until at 100 atmospheres the intensity curve is like that of the copper lines. The sharp appearance of the line is thus gradually lost and the result is a broad, diffuse and soft line.

Examples of these lines are :—

(a) *Symmetrical.*

$l1$, 4065·22 (Plate 3). This is the only very strong line that is symmetrically broadened. It preserves its character from 1 to 200 atmospheres.

(b) *Unsymmetrical—unilateral.*

$o2$, 4315·45 $p1$, 4437·44 $q1$, 4488·46 $q2$, 4607·80	The fact that at high pressures, *e.g.*, 150 and 200 atmospheres (Plate 4), these lines show some broadening on the violet side as well as the red makes it evident that this class of line cannot be rigorously separated from the following class.

(c) *Unsymmetrical—bilateral.*

$f2$, 3898·04 (Plate 2).

$r2$, 4792·79.

In this class the broadening is unequal on the two sides, and it is obviously intermediate between (a) and (b). Line $r2$ is very broad, and extends over 90 Å.U. at 40 atmospheres, the greater extension being towards the red. The inequality in the wings is not so marked as in $f2$, which approaches more closely to type a, whereas $r2$ resembles lines of type b.

4. The unsymmetrical broadening may be greater towards the red or the violet end of the spectrum.

A few lines only have been observed to broaden out more towards the violet end of the spectrum than the red, and these all occur below $\lambda = 4000$. As a rule, the lines are not strong, and become very diffuse under pressure (*e.g.*, Plate 2, line $e1$). These are the lines that appear to be displaced towards the violet, but it is not yet definite that the position of maximum intensity has been displaced in that sense; the writer's measurements of the line $b1$ point to a displacement towards the violet at two pressures, but he wishes to examine further instances of lines broadening to the violet under pressure before pronouncing definitely upon it.

5. The broadening is different for different lines.

Some lines remain comparatively fine when the pressure is increased, others are very much broadened and diffuse, and a third class become faint hazy patches. The term line is a misnomer when applied to these broadened appearances, which more closely resemble bands, but the term is retained since they are due to the same vibrating system, though perhaps modified, that produced the line spectrum at atmospheric pressure.

In the following table is stated the nature of the broadening of the lines that have been observed in this research :—

TABLE III.

*a*1	3553·72	Diffuse	Symmetrical.
*b*1	3586·66	Broad and diffuse	Broadened to violet.
*b*2	3607·59	Diffuse	
*c*1	3633·40	”	
*d*1	3796·15	Broad and nebulous at atmospheric pressure	Broadened to violet.
*d*2	3804·22	Diffuse	Broadened to red.
*e*1	3874·96	Very diffuse	Broadened to violet.
*e*2	3880·34	” ”	Broadened to violet (?)
*f*1	3889·58	” ”	Symmetrical (?)
*f*2	3898·04	Strong, very broad and diffuse	Broadened to red.
*g*1	3909·54	Remains fairly fine	Broadened slightly to red.
*g*2	3914·93	Very diffuse	
*h*1	3927·82	” ”	
*h*2	3976·80	} Very diffuse, merging into one faint hazy patch	Broadened to violet.
*i*1	3979·72		
*i*2	4016·27	Diffuse	Broadened to red.
*j*1	4041·07	Remains fairly fine	Broadened slightly to red.
*j*2	4053·0	Diffuse	
*k*1	4057·0	”	
*l*1	4065·22	Strong, very broad and diffuse	Symmetrical.
*m*2	4084·26	Diffuse	Symmetrical (?)
*n*1	4089·95	Very diffuse	Broadened to red.
*o*1	4241·99	Obliterated	
*o*2	4315·45	Strong, broad, diffuse	Broadened to red.
*p*1	4437·44	” ” ”	” ”
*q*1	4488·46	” ” ”	” ”
*q*2	4607·80	” ” ”	” ”
*r*2	4792·79	” ” ”	” ”
*s*1	4811·57	Diffuse	Symmetrical (?)
*t*2	5064·75	Fairly fine	Symmetrical (?)

6. *The Displacement of the Lines:* (1) *The Measurement of the Photographs.*—This was conducted as in the case of the silver lines (*cf.* p. 40 *supra*). Twelve settings were made upon each line upon each plate, six with the red to the right and then six with the red to the left. The whole series was then repeated, so that at least 24 readings of the displacement of each line were obtained.

(2) *Description of Table of Displacements.*—Table IV. gives in thousandths of an Ångström unit the value of the displacement of each line at the pressure stated at the top of each column. The first column contains a list of the arbitrary letters assigned to the different lines. The second column gives the wave-lengths of the lines according to the tables of KAYSER and RUNGE and EDER and VALENTA. The subsequent columns show the displacements. The pressures are the excess above one

atmosphere. Except for a very few readings which are marked with a *minus* sign, the displacements are towards the side of greater wave-length. The measurements in brackets were not considered sufficiently reliable to include in the displacement diagram.

TABLE IV.—Displacements in Thousandths of an Ångström Unit.

	λ.	5 atmospheres.	10 atmospheres.	15 atmospheres.	20 atmospheres.	30 atmospheres.	40 atmospheres.	50 atmospheres.	60 atmospheres.	80 atmospheres.	100 atmospheres.	150 atmospheres.	175 atmospheres.	200 atmospheres.
*b*1	3586·66	(+39)				(−69)				(−142)				
*d*2	3804·22		69			138		237						
*e*1	3874·96		(39)			(0)								
*f*2	3898·04	17	34	69	86	138	172	241	302	332	444	538	720	711
*g*1	3909·54					43	69	65	86	108	125	198	215	233
*h*1	3927·82		(151)											
*h*2	3976·80		(0)											
*i*1	3979·72					(−86)								
*i*2	4016·27					(116)		(181)		(224)				
*j*1	4041·07	30	34		47	60	99	112	77	125	138	142		168
*k*1	4057·0		39		86									
*l*1	4065·22	32	43		52		134		155	211	276	370		517
*m*2	4084·26		65		120		(120)			(694)				
*o*2	4315·45	28	67		134		306		336	452	573	737		961
*p*1	4437·44	45	69		160		302		380	440	633	797		975
*q*1	4488·46	37	56		125		288		392	461	633	800		983
*q*2	4607·80	50	69		138		284		388	452	660			1050
*r*2	4792·79	34	78		198		370		513	612	780			1260
*s*1	4811·57				69		(155)		228					
*t*2	5064·75						202		293					

(3) *Displacement Diagram.*—The relation between the displacement of the gold lines and the pressure of the surrounding gas is shown graphically in Diagram 1, in which the abscissæ represent excess of pressure above 1 atmosphere and the ordinates the displacements measured in thousandths of an Ångström unit.

Each line on the diagram represents the behaviour of the particular spectral line indicated by the letter attached to it.

The readings were made at those pressures which have been indicated on the base line.

(4) *The Relation between the Displacement and Wave-length.*—The investigation of the copper arc under pressure indicated that for the non-series lines (those not falling into the series described by KAYSER and RUNGE) there exists a relation between the displacements and the wave-lengths of the spectral lines, the former being proportional to some power of the latter, which in those experiments was "at least as great as the third power and possibly as high as the sixth."*

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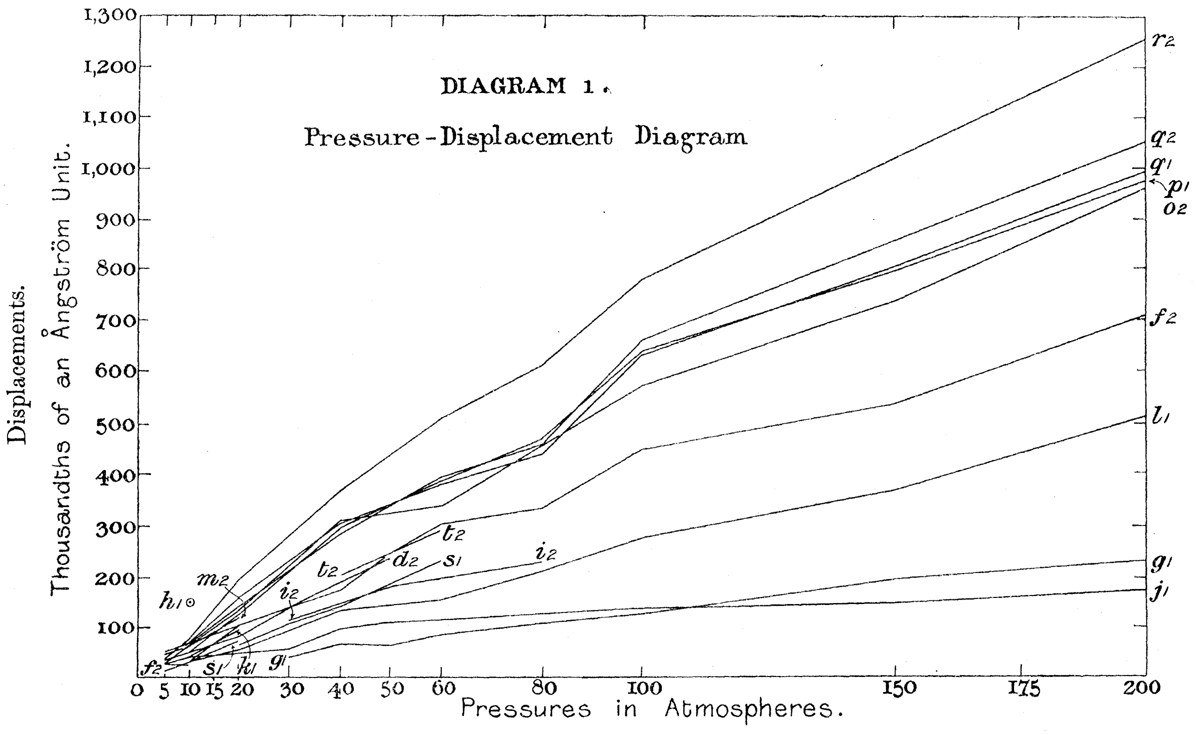
* DUFFIELD, 'Phil. Trans.,' A, vol. 209, p. 205, 1908.

Diagram 1 suggested that some relation of this sort might hold for the gold lines, since several of these are in alphabetical order in the diagram. To investigate this the rates of displacement of the lines were calculated by dividing the measured displacement by the number of atmospheres in absolute measure, and these are given in Table V. on p. 65.



In Diagram 2 the mean displacements that have been calculated for lines which

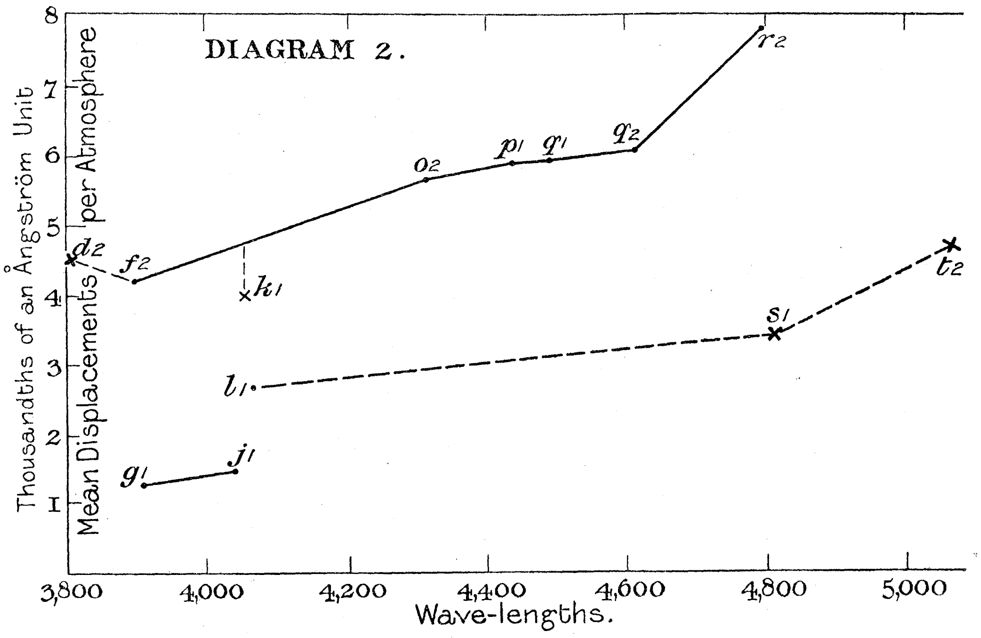


TABLE V.—Displacements per Atmosphere in Thousandths of an Ångström Unit.

	λ.	5 atmospheres.	10 atmospheres.	15 atmospheres.	20 atmospheres.	30 atmospheres.	40 atmospheres.	50 atmospheres.	60 atmospheres.	80 atmospheres.	100 atmospheres.	150 atmospheres.	175 atmospheres.	200 atmospheres.	Mean value.
*b*1	3586·66	(6·5)				(−2·2)				(−1·7)					
*d*2	3804·22		6·3			4·45		4·65							4·5*
*e*1	3874·96		(3·5)			(0)									
*f*2	3898·04	2·83	3·1	4·3	4·1	4·45	4·2	4·7	4·95	4·1	4·40	3·57	4·1	3·54	4·19
*g*1	3909·54					1·4	1·7	1·27	1·4	1·36	1·24	1·31	1·23	1·16	1·33
*h*1	3927·82		14·0												
*h*2	3976·80		(0)												
*i*1	3979·72					(−2·6)									
*i*2	4016·27					(3·7)		(3·5)		(2·76)	(1·72)				
*j*1	4041·07	5·0	3·1		2·24	1·9	2·4	2·18	1·26	1·54	1·38	0·94		0·84	1·50
*k*1	4057·0		3·55		4·1										4·0*
*l*1	4065·22	5·3	3·90		2·5		3·3		2·54	2·6	2·73	2·45		2·57	2·70
*m*2	4084·26		5·9		5·7		(2·9)			(8·5)					
*o*2	4315·45	4·6	6·1		6·4		7·5		5·5	5·6	5·67	4·9		4·78	5·66
*p*1	4437·44	7·5	6·3		7·6		7·4		6·22	5·43	6·28	5·28		4·85	5·91
*q*1	4488·46	6·16	5·1		6·0		7·0		6·42	5·7	6·28	5·30		4·90	5·93
*q*2	4607·80	8·35	6·3		6·6		6·9		6·36	5·6	6·54			5·22	6·12
*r*2	4792·79	5·7	7·1		9·4		9·0		8·4	7·55	7·73			6·26	7·79
*s*1	4811·57				3·3		(3·8)		3·7						3·5*
*t*2	5064·75						4·9		4·8						4·85*

* The means in the last column include no values below 40 atmospheres, except in those cases, marked with an asterisk, in which there were only two or three readings.

have been observed over a wide range of pressure (from 40 to 200 atmospheres inclusive) are plotted against the wave-length, and are joined together by full lines. Dotted lines join mean values (marked with a ×) which have been made from only two or three observations.

Considering the mean values for *f*2, *o*2, *p*1, *q*1, *q*2, and *r*2, the diagram suggests, in the first place, that the relation between the displacement and the wave-length may be linear, but, if this were the case, it would require that a spectral line with a wave-length of about 2600 Å.U. should not suffer displacement under pressure (a value also well in agreement with the graphs for *l*1, *s*1, *t*2 (dotted) and for *g*1, *j*1).* Measurements have not been made at such small wave-lengths, but we may be guided by our experience in dealing with the copper arc, in which it was found that displacements had been measured for lines whose wave-lengths were smaller than that of the point to which a similar graph for the copper lines tended.

If we assume that the origin is on the curve, we are led to conclude that the displacement varies with a higher power of the wave-length, and calculation demonstrates that as far as mean values are concerned the relation may be fairly well expressed by

$$d = 289 \times 10^{-9}\lambda^2 \qquad \text{or} \qquad d = 653 \times 10^{-13}\lambda^3,$$

of which the former is the more satisfactory, because the greatest deviation of any observed point from the mean value given by these formulæ is 13 per cent. in the first case and 7 per cent. in the latter. But to choose between them, it is necessary to deal with individual values at different pressures rather than with the mean value. These are given in Tables VI. and VII., in which the quantities d/λ^2 and d/λ^3 are set forth.

Graphic representation of the above tables is given in Diagrams 3 and 4.

Comparing these with Diagram 1, we see that in the later diagrams the lines *f*2 and *r*2 approach more closely to the group of lines between them, and that a criterion for selecting the most probable power of the wave-length lies in choosing that which more exactly makes *f*2 and *r*2 coincide with this group. The higher the power of the wave-length, the lower in the diagram do lines with large wave-length fall with respect to lines of lower wave-length; consequently, *r*2 tends to fall and *f*2 to rise. In the diagram for d/λ^2, it will be seen that *r*2 has not fallen sufficiently to completely mingle with the group, and that *f*2 is still too low, but in that drawn for d/λ^3, the increased power of λ has been sufficient to cause these two lines to merge completely in the group. The displacement per atmosphere is thus seen to vary more approximately with the 3rd than the 2nd power of the wave-length.

This result is quite in keeping with that previously obtained for the copper arc. It seems at least certain that the displacement varies with a higher power of the

* Had the means been taken from 60 to 200 instead of from 40 to 200 atmospheres the line joining *g*1, *j*1, would have sloped in the wrong direction.

TABLE VI.—d/λ^2.

	λ^2.	5 atmo-spheres.	10 atmo-spheres.	15 atmo-spheres.	20 atmo-spheres.	30 atmo-spheres.	40 atmo-spheres.	50 atmo-spheres.	60 atmo-spheres.	80 atmo-spheres.	100 atmo-spheres.	150 atmo-spheres.	175 atmo-spheres.	200 atmo-spheres.	Mean values.
*f*2	152×10^5	186	204	283	270	293	276	310	326	270	290	235	(270)	233	271×10^{-9}
*g*1	153					91	111	83	91	89	81	85	80	76	84
*j*1	163	307	190		137	116	147	138	77	94	85	64		57	75
*l*1	165	321	237		151		200		154	158	170	152		158	158
*o*2	186	251	328		344		403		296	301	307	264		258	285
*p*1	197	381	320		386		376		316	276	320	269		249	286
*q*1	201	307	254		299		348		320	284	314	264		244	285
*q*2	212	394	298		312		326		300	264	312			248	281
*r*2	230	248	309		408		392		365	328	339			274	327

TABLE VII.—d/λ^3.

	λ^3.	5 atmo-spheres.	10 atmo-spheres.	15 atmo-spheres.	20 atmo-spheres.	30 atmo-spheres.	40 atmo-spheres.	50 atmo-spheres.	60 atmo-spheres.	80 atmo-spheres.	100 atmo-spheres.	150 atmo-spheres.	175 atmo-spheres.	200 atmo-spheres.	Mean values.
*f*2	592×10^8	478	524	726	692	752	710	795	836	692	743	603	(693)	598	694×10^{-13}
*g*1	597					235	285	213	235	228	208	219	206	194	215
*j*1	659	758	470		340	288	364	330	161	234	209	145		127	175
*l*1	671	790	581		372		491		378	388	407	365		384	384
*o*2	804	580	758		795		932		684	696	705	610		595	660
*p*1	875	857	720		870		845		712	620	718	604		555	642
*q*1	903	682	565		664		775		710	631	695	586		542	633
*q*2	978	853	643		674		705		650	572	668			533	606
*r*2	1100	518	645		854		818		763	686	703			570	680

The means include values from 60 to 200 atmospheres inclusive.

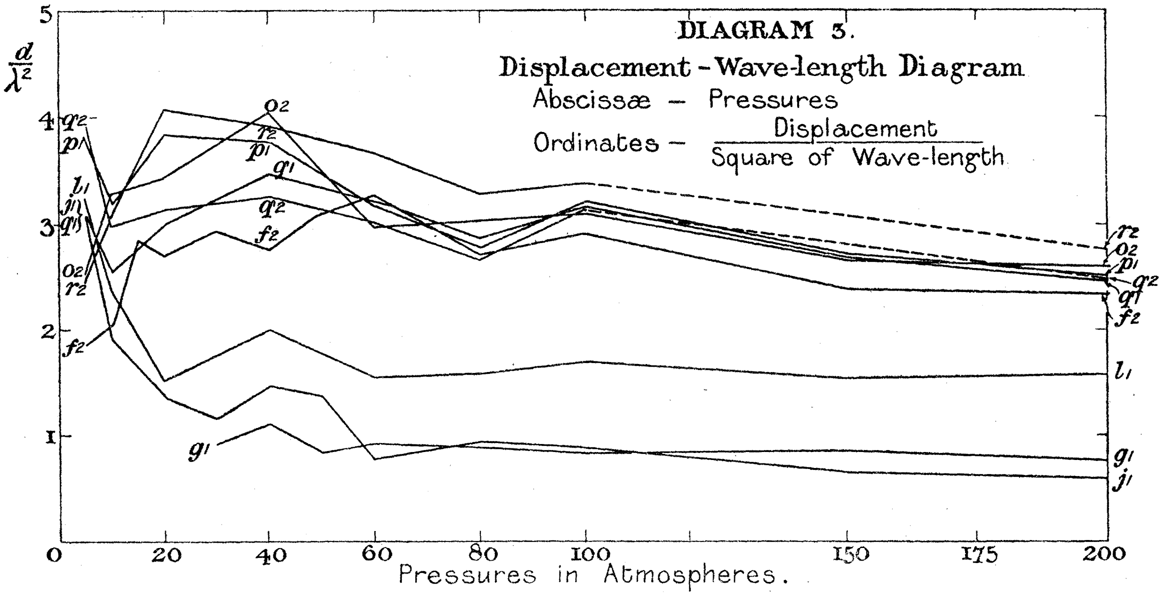


DIAGRAM 3.
Displacement-Wave-length Diagram
Abscissæ — Pressures
Ordinates — Displacement / Square of Wave-length
$\frac{d}{\lambda^2}$
5
4
3
2
1
0
20
40
60
80
100
150
175
200
Pressures in Atmospheres.
q2
p1
l1
j1
q1
o2
r2
f2
g1
o2
r2
p1
q1
q2
f2
r2
o2
p1
q2
q1
f2
l1
g1
j1

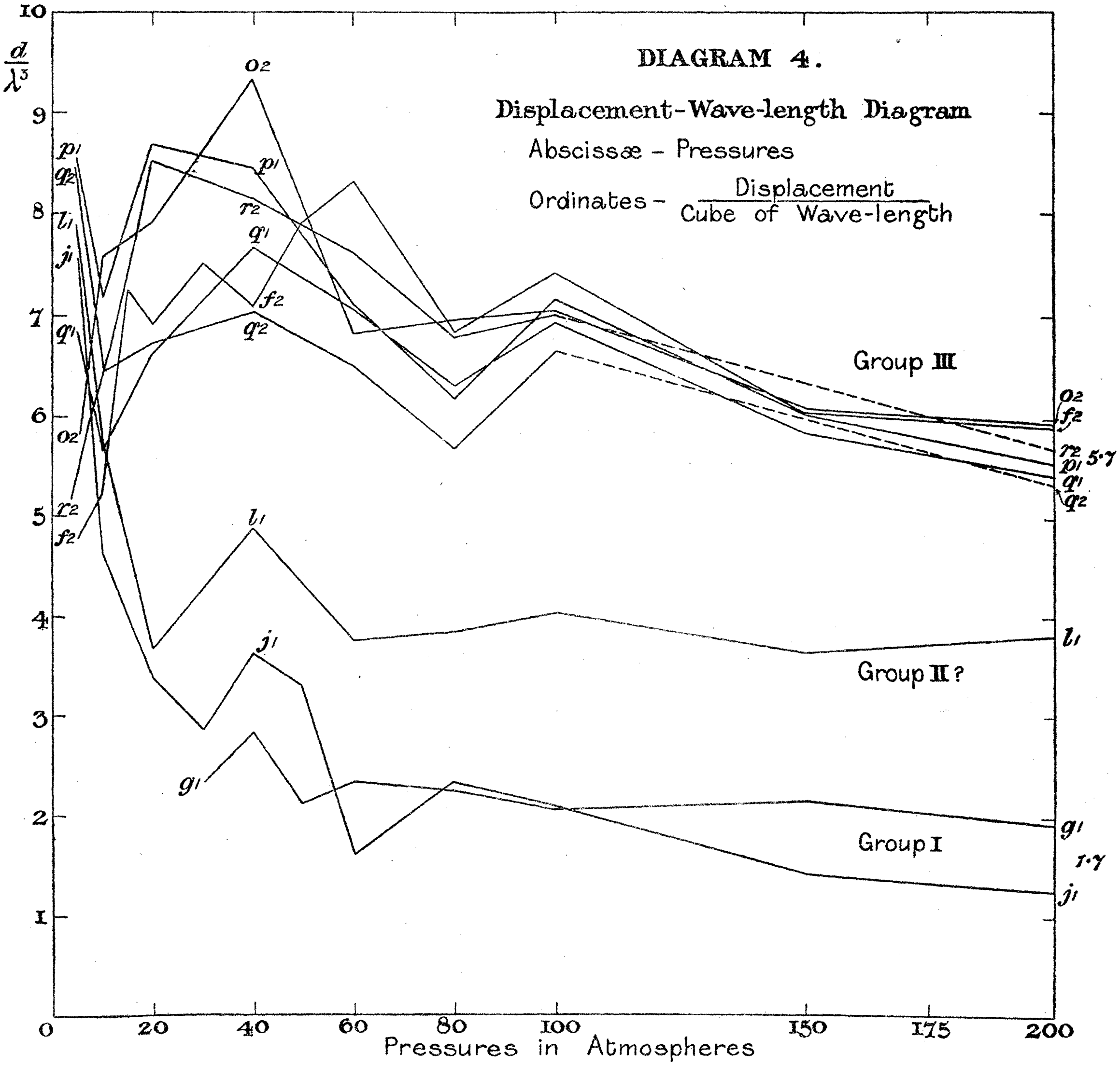


DIAGRAM 4.
Displacement-Wave-length Diagram
Abscissæ – Pressures
Ordinates – Displacement / Cube of Wave-length
$\frac{d}{\lambda^3}$
10
9
8
7
6
5
4
3
2
1
0
20
40
60
80
100
150
175
200
Pressures in Atmospheres
p1
q2
l1
j1
q1
o2
r2
f2
o2
p1
r2
q1
f2
q2
l1
j1
g1
Group III
Group II ?
Group I
o2
f2
r2
p1
q1
q2
5·7
l1
g1
1·7
j1

wave-length than the first upon which it was previously believed to depend. The results of the present investigation favour a dependence upon the 3rd power of the wave-length, and this agrees with some theoretical deductions made by Dr. O. W. RICHARDSON.*

(5) *Resolution into Groups of Lines.*—Diagram 1 afforded very little encouragement to any attempt to classify the lines according to the amounts of their displacements, but Diagram 2 provided the clue by which this might be accomplished, and indicated that *f*2 and *r*2 were to be associated with the group of lines *o*2, *p*1, *q*1, *q*2, falling between them in Diagram 1, and that the remaining lines that had been investigated over a wide range of pressures, *g*1, *j*1, and *l*1, belonged to another group or groups.

Diagram 4, which was drawn on the assumption that the displacement varies as the cube of the wave-length, further justified the separation of these three lines from the others and supplied good reason for believing that they belong to three groups with different rates of displacement; this diagram makes the scheme so much more orderly and coherent that there can be little doubt but that this method of treatment is correct.

In the iron arc it had been found possible to divide the lines into three groups according to the amounts of their displacements, and, following the nomenclature there adopted, the three groups in the gold arc are named Groups I., II., and III., in order of increasing displacement.

For gold the mean value of the displacement of Group III., divided by the cube of the wave-length, is 653×10^{-13}.

The only representative of Group II. that has been measured over the whole range of wave-lengths is *l*1, and this line was particularly difficult to measure on account of its great breadth, and because its intensity curve under pressure is very flat-topped (Plate 3). Its mean value divided by the cube of its wave-length is 384×10^{-13}. Two other lines, however, *s*1 and *t*2, which have only been observed at two or three pressures, are seen from Diagram 2 to possess displacements of the same order of magnitude as *l*1. If these lines be included in Group II., the mean value for the group is 356×10^{-13}.

Save in their mean values there is little agreement between the measurements for the lines *g*1 and *j*1, but they certainly are displaced less than any of the other lines, and it is consequently justifiable to place them in a separate group, of which the mean value divided by the cube of the wave-length is 195×10^{-13}.

The ratios of the displacements divided by the cube of the wave-lengths are:—

Group I. : Group II. : Group III. = 195 : 356 : 653. Unfortunately, only two lines belonging to Group I. and only three belonging to Group II. have been measured, so that sufficient data have not been forthcoming to decide whether this ratio may be more simply expressed as 1 : 2 : 3 or 1 : 2 : 4. The latter ratio was found to express the relationship between similar groups in the spectrum of the iron arc, and thus

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* RICHARDSON, 'Philosophical Magazine,' vol. 14, p 557, 1907.

appears to be more probable. No relationship between the displacement and wave-length was discovered in dealing with the iron arc, perhaps because a sufficiently wide range of spectrum was not examined, but the resolution of the spectrum into groups was, nevertheless, an outstanding feature. If we are correct in believing that the equations representing the behaviour of the three groups are $d = A\lambda^3$, $d = B\lambda^3$, and $d = C\lambda^3$, it is clear that when lines belonging to different groups lie close together the individual readings of their displacements will also be approximately in the ratio of A : B : C. Among those lines which have not appeared upon many of the plates are $d2$ and $k1$, and these, possessing values for the quantity d/λ^3 of 815 and 598 respectively, are to be classified as members of Group III. to whose mean 653 they more nearly approximate.

The following is a list of the lines belonging to the different groups with their mean values for the quantity d/λ^3 :—

TABLE VIII.

Group I.			Group II.			Group III.		
	Wave-length.	d/λ^3.		Wave-length.	d/λ^3.		Wave-length.	d/λ^3.
*g*1	3909·54	215	*l*1	4065·22	384	(*d*2)	(3804·22)	(815)
*j*1	4041·07	175	*s*1	4811·57	311	*f*2	3898·04	694
			*t*2	5064·75	372	(*k*1)	(4057·0)	(598)
						*o*2	4315·45	660
						*p*1	4437·44	642
						*q*1	4488·46	633
						*q*2	4607·80	606
						*r*2	4792·79	680

Values in brackets have not been used in calculating the means.

It is interesting to note that the lines that are thus grouped together have some other properties in common.

The members of Group I. are the two lines that broaden least, and that indeed remain fairly fine throughout a considerable range of the pressure. They may both be described as "hard" at low pressures, though *j*1 is more clear cut than *g*1.

Both are about equally, though very slightly, broadened to the red side under pressure.

The line *l*1, which is typical of Group II., is broadened symmetrically, and the two lines *s*1 and *t*2, though very much weaker, are believed to be similarly broadened.

Group III. is characterised by strong broadening to the red side, to which the lines *o*2, *p*1, *q*1, *q*2, bear witness. *f*2 and *r*2 only differ from these in having a bilateral broadening, but they are both more greatly extended on the red side.

In addition to these groups, we may with advantage classify in Group IV. those lines that are broadened towards the violet, and whose displacements have not been definitely determined.

Group IV. consists of the following lines :—

GROUP IV.

*b*1	3586·66
*d*1	3796·15
*e*1	3874·96
*e*2	3880·34
*h*2	3976·80

Further possibilities of finding groups of lines which are related to one another are suggested by the tables of relative intensities and broadening. (See pp. 62 and 73.) Of all the lines measured only one has been found to belong to any of the series described by KAYSER and RUNGE. This is *t*2, λ = 5064·75, which, as far as we can gauge from two measurements at different pressures, falls into Group II.

The Zeeman effect has been investigated for only five of the above lines, so that there are very meagre data for comparing the pressure and magnetic effects. The magnetic separation, however, agrees in giving a smaller value for *l*1 (Group II.) than for *d*2, *f*2, and *r*2 (Group III.).

The values given by PURVIS* are as follows :—

	Wave-length.	$\frac{\partial\lambda}{\lambda^2}$.	Pressure-groups.
*b*1	3586·66	+1·62, 0, −1·62	Group IV.
*d*2	3804·22	+2·18, 0, −2·21	Group III.
*f*2	3898·04	+2·17, 0, −2·12	Group III.
*l*1	4065·22	+1·15, 0, −1·15	Group II.
*r*2	4792·79	+1·77, 0, −1·83	Group III.

(6) *The Relation between the Pressure and the Displacement.*—In the foregoing it has been taken for granted that the relation between the pressure and the displacement is a linear one, and there is no doubt that this is approximately the case, but it is worth while examining the diagrams carefully to see if there is any indication of a departure from this relationship and, if so, in what direction.

In Diagram 1, which shows the amounts of the displacements at different pressures, the values are higher at intermediate pressures than they should be if a straight line is to describe the relationship correctly—the lines are, indeed, slightly curved, being concave towards the axis of zero displacement.

Diagram 4 puts the matter more clearly; in it each line represents the mean displacement per atmosphere at different pressures, and the fact that the displacements have been divided by a quantity which is constant for any one line need not affect our discussion. Leaving out of consideration the values at 5, 10, and even 20

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* PURVIS, 'Proc. Camb. Phil. Soc.,' 14, 217, 1907.

atmospheres, which are not very concordant, it is apparent that from 40 to 200 atmospheres there is a general downward tendency, indicating, if the figures are reliable, that there is a more rapid rate of increase of the displacement with the pressure at low than at high pressures. Group III. shows this downward tendency strongly, and so does, to a marked degree, the line *j*1 in Group I., which line, it should be mentioned, was measured both in Set A and Set B of the photographs with concordant results.

There is thus some reason for believing that there is a departure from a strict linear relationship in the direction already indicated.

A study of the negatives themselves reveals the difficulties to be encountered in measuring the displacements and in fixing upon the most intense portions of the lines, and it is at once admitted that the downward tendency of two or three of the lines should not be allowed to disturb our belief in the simpler relation; but the fact that all the gold lines, with the exception of *l*1, present the same feature, taken in conjunction with the fact that the copper lines are similarly affected (if their behaviour up to 200 atmospheres be taken into account), provides strong evidence that though the relation between the displacement and the pressure is approximately linear, there is a slightly greater increase of the displacement with the pressure at low than at high pressures.

(7) *Displacement and Reversal of Lines.*—The displacement diagrams for iron suggested a departure from the linear relationship at those pressures at which a large number of reversals appeared. No reversals have been observed in the spectrum of the gold arc, so that the slight departure from a linear relationship, discussed in the preceding section, cannot be associated with the phenomenon observed in the iron arc.

7. *Changes in Relative Intensity under Pressure.*—This is not so prominent a feature of the gold arc under pressure as it is of the copper and silver spectra; in the former, all the lines belonging (in the region investigated) to KAYSER and RUNGE'S series vanished under pressure, and well-marked changes also took place in those lines which were not members of any particular series, while in the silver arc the line spectrum vanished completely under pressure.

Of all the lines examined in the spectrum of gold, only one line, *o*1 ($\lambda = 4241 \cdot 99$), Plate 3, is obliterated at an early stage in the increase of pressure and is not observed above 25 atmospheres; the other lines usually preserve their relative intensities with but slight modifications, which can, however, be generally associated with the amount of broadening that the line undergoes. A line that remains compact and narrow under pressure is likely to have a mean intensity greater than that of a broad line covering a large area. The intensity would be best expressed by the evaluation of $\int_{\lambda_2}^{\lambda_1} i \, d\lambda$, where i is the intensity at any wave-length λ, and λ_1 and λ_2 the extreme limits of the range of wave-lengths comprised in the broadened line.

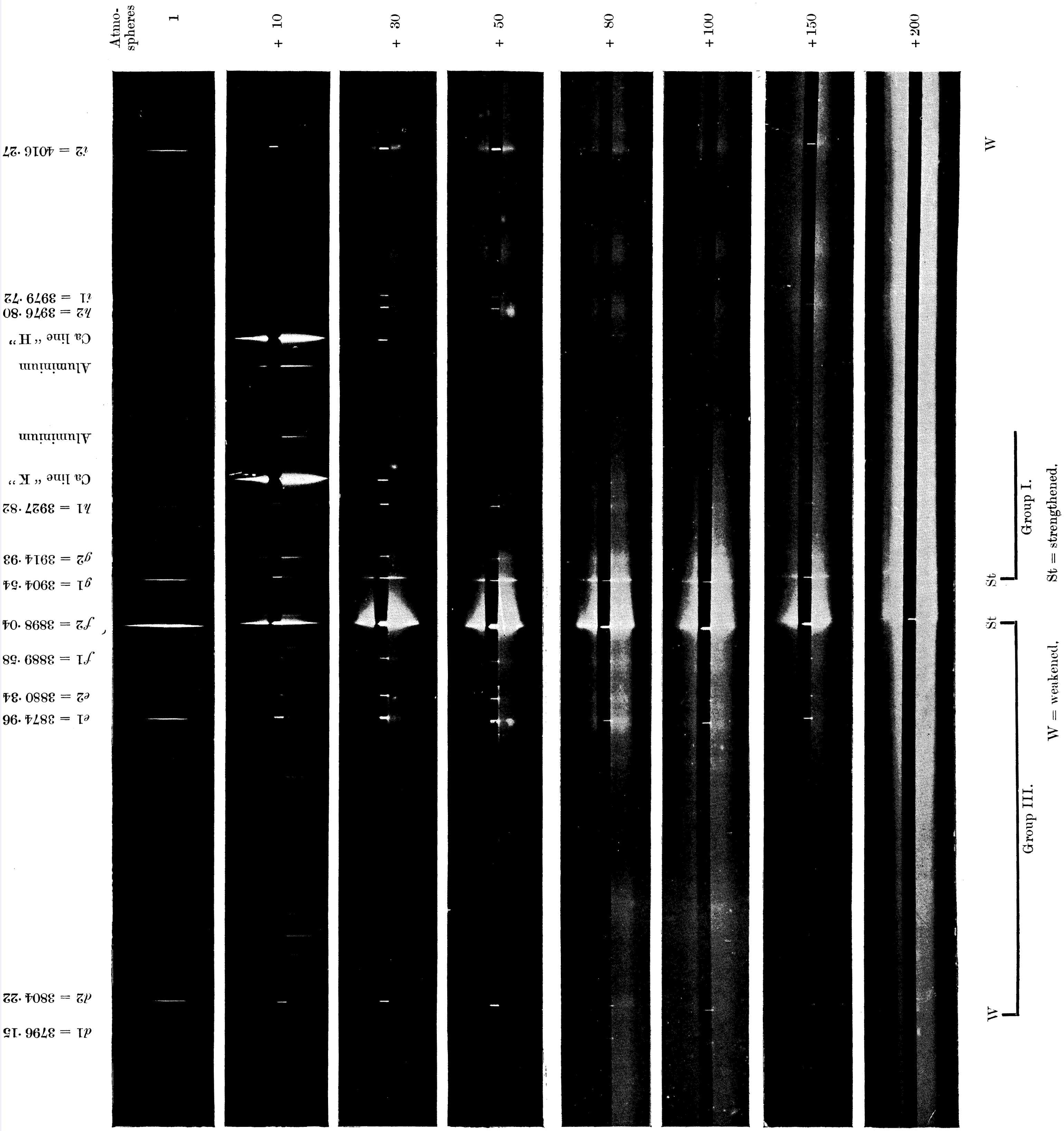
Failing any practicable means of finding the above quantity experimentally, the intensities have been gauged visually from the photographic plates by the most intense portion of each line.

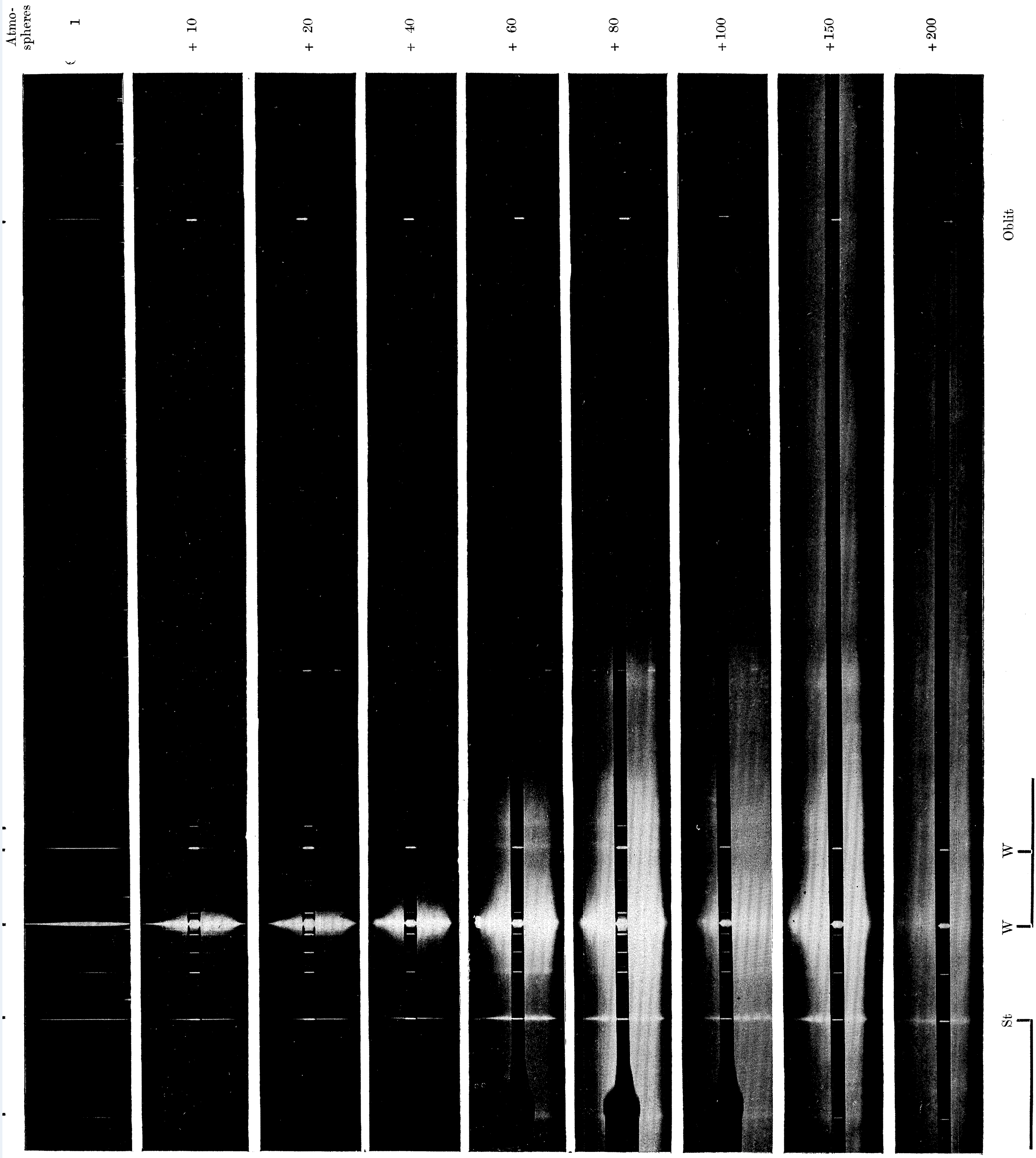
Table IX.

Weakened.		Strengthened.	
*d*2	3804·22	*f*2	3898·04
*e*1	3874·96	*g*1	3909·54
*i*2	4016·27	*j*1	4041·07
*l*1	4065·22	*o*2	4315·45
*m*2	4084·26	*p*1	4437·44
*o*1	4241·99	*q*1	4488·46
*s*1	4811·57	*q*2	4607·80
		*r*2	4792·79

Caution must be exercised in comparing the intensities of lines upon the reproduced photographs unless the lines under observation are very close together. In making the prints, a small inequality in the illumination of two parts of the same plate may cause very different photographic densities. In view of the great difficulty already mentioned of estimating the intensities of lines under pressure, it is scarcely necessary to add that the above table shows only changes in *relative* intensities. It was not found feasible to fix upon an absolute standard for their comparison.

To Prof. SCHUSTER and Prof. RUTHERFORD I express my thanks for their interest in this research, and for having placed the necessary apparatus at my disposal. I also thank Mr. R. ROSSI, B.Sc., for his help in the early stages of this research. Mr. W. C. LANTSBERRY efficiently assisted in the measurement of a large share of the photographs.

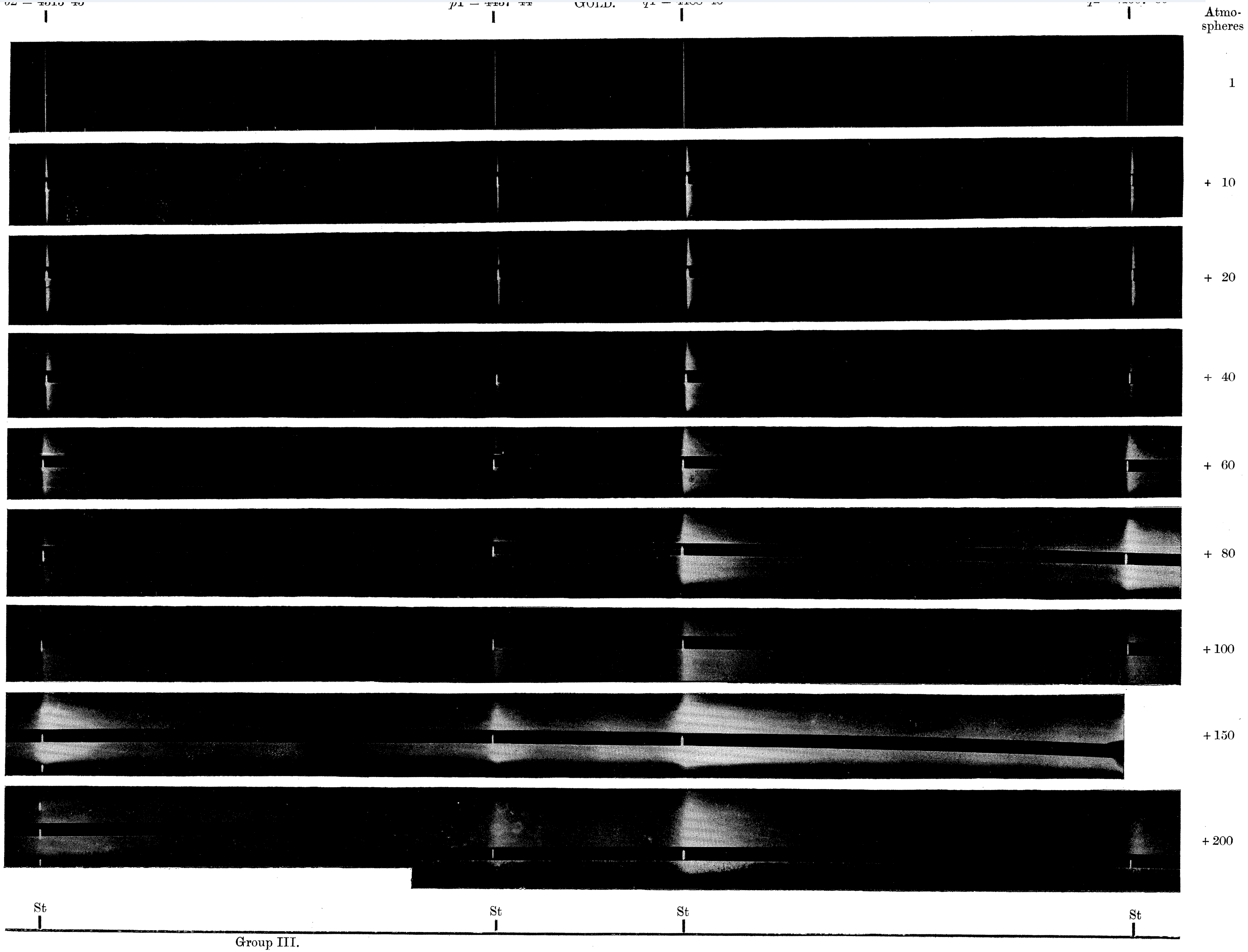

Atmo-spheres
1
+ 10
+ 30
+ 50
+ 80
+ 100
+ 150
+ 200
i2 = 4016·27
i1 = 3979·72
h2 = 3976·80
Ca line " H "
Aluminium
Aluminium
Ca line " K "
h1 = 3927·82
g2 = 3914·98
g1 = 3904·54
f2 = 3898·04
f1 = 3889·58
e2 = 3880·34
e1 = 3874·96
d2 = 3804·22
d1 = 3796·15
W
St
St
W
Group I.
Group III.
W = weakened.
St = strengthened.



W = weakened. St = strengthened. Oblit = obliterated.

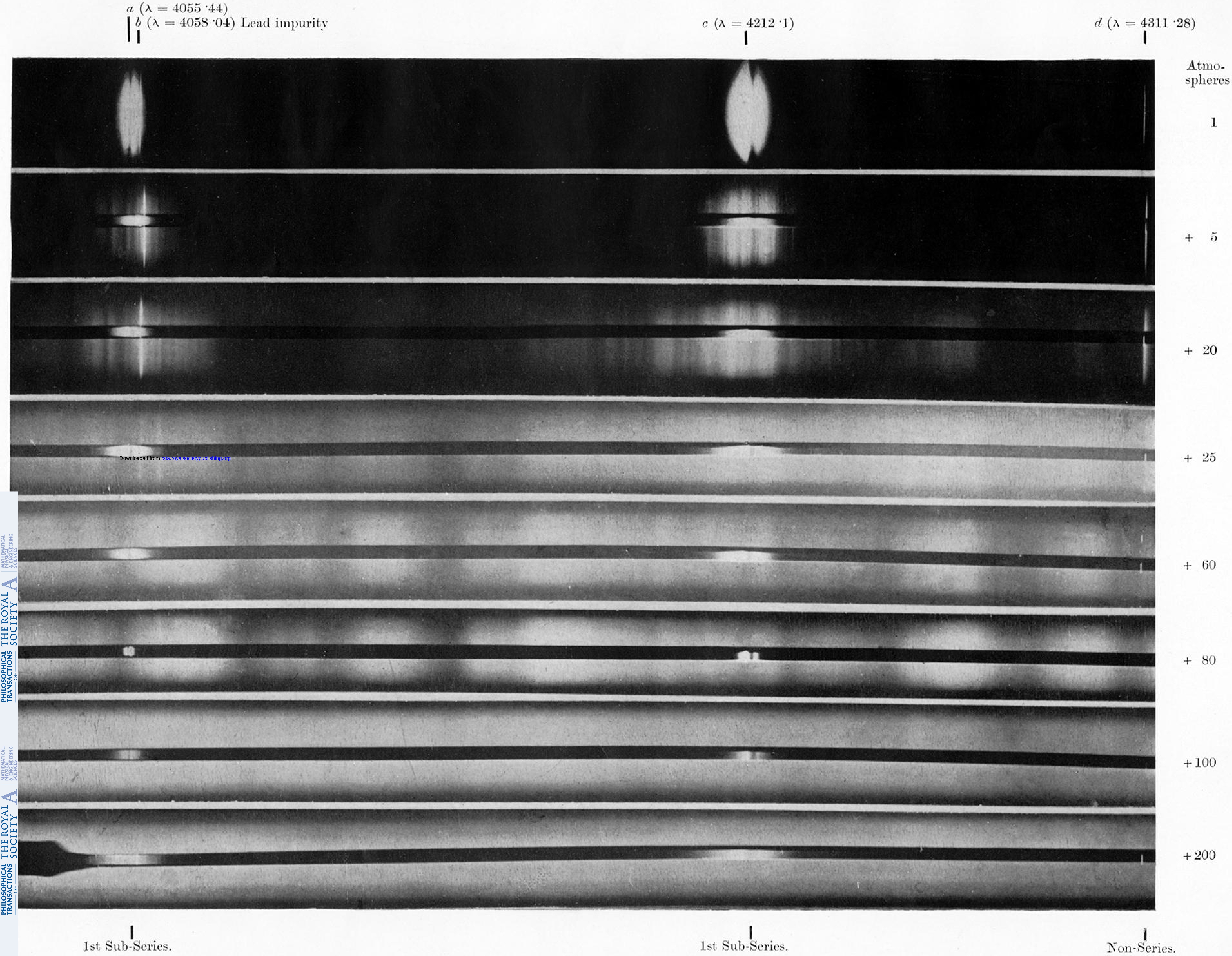
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

GOLD.

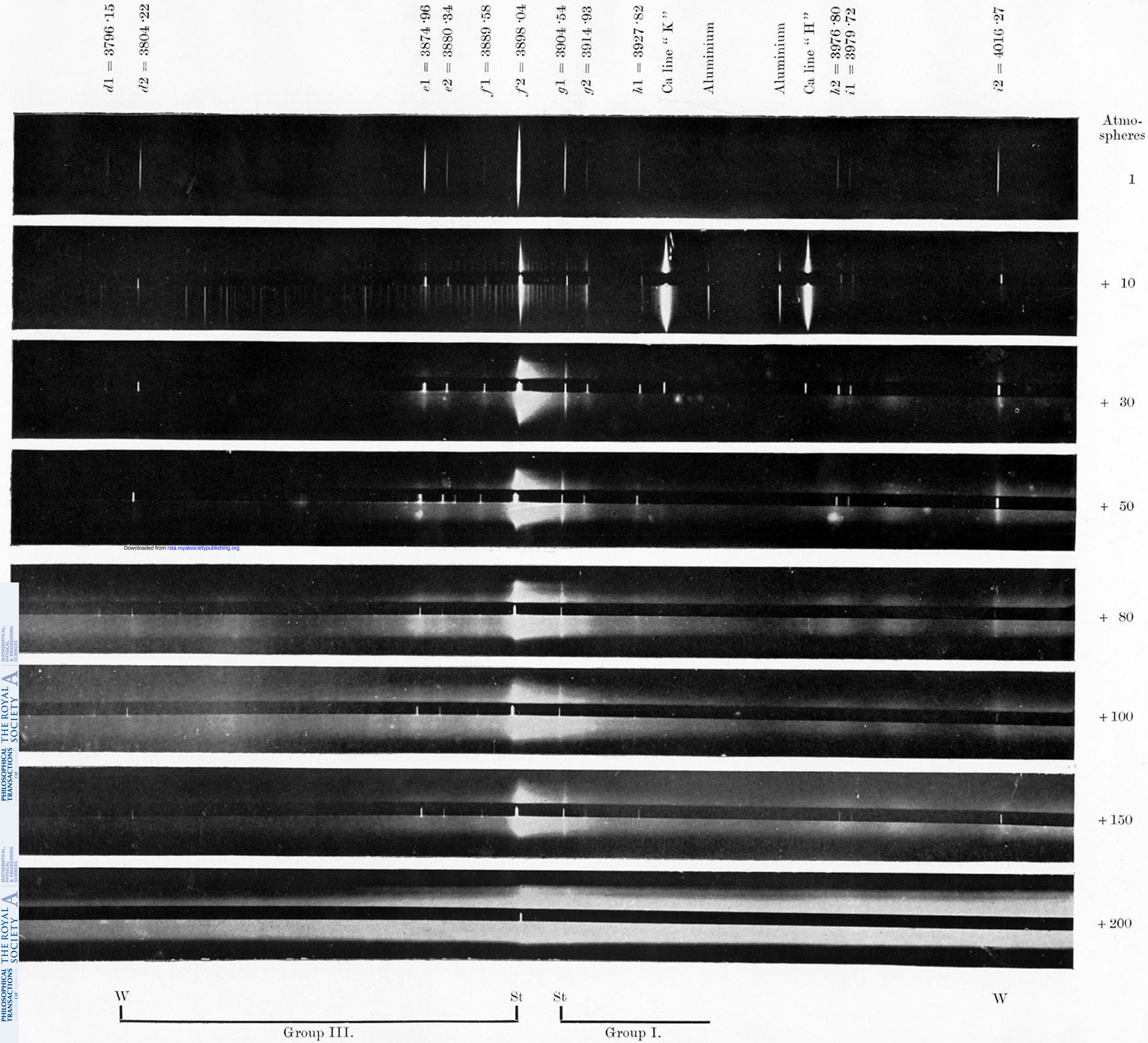


St = strengthened.

SILVER.

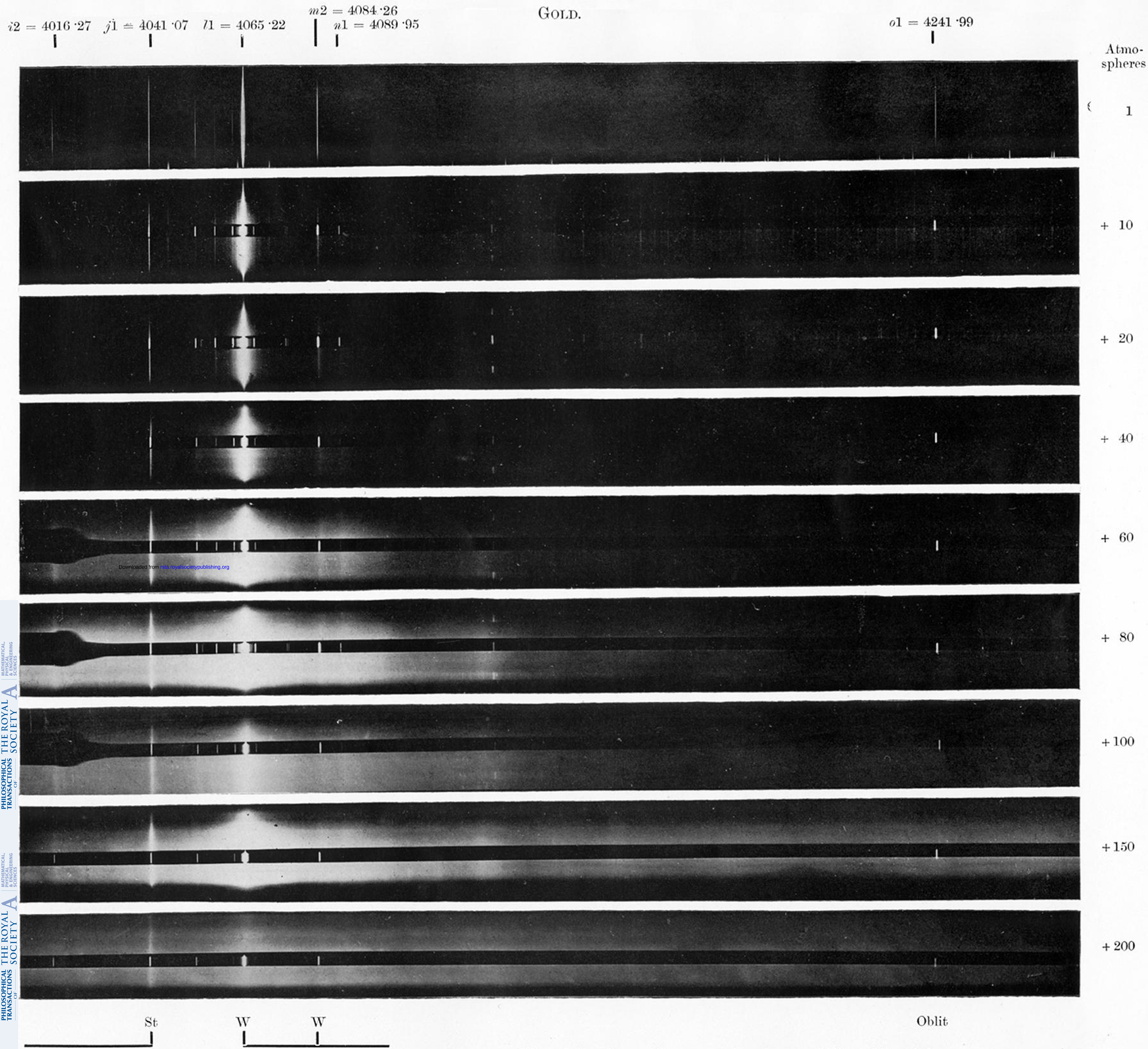

a (λ = 4055·44)
b (λ = 4058·04) Lead impurity
c (λ = 4212·1)
d (λ = 4311·28)
Atmo-spheres
1
+ 5
+ 20
+ 25
+ 60
+ 80
+ 100
+ 200
1st Sub-Series.
1st Sub-Series.
Non-Series.

GOLD.



W = weakened, St = strengthened.

GOLD.



W = weakened. St = strengthened. Oblit = obliterated.

Group III.

St = strengthened.