THE INTENSITY OF QUARTET LINES IN THE ARC SPECTRUM OF COPPER

By C. W. Allen
Commonwealth Solar Observatory, Canberra, Australia

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Abstract

Intensity measurements in the arc spectrum of copper have been made for the quartets $a^4D^1-c^4D$, a^4F-c^4D, a^4P-c^4D, by using an electric arc at atmospheric pressure, and currents ranging from 1 to 19 amperes. It has been shown that the lines of these quartets may be divided into two groups, (a) those with initial terms $c^4D_{1,4}$ (sharp lines) and (b) those with initial terms $c^4D_{2,3}$ (broad lines), such that within each group the intensity relation of the lines remains practically constant for all current strengths. In comparison with group (a), however, the lines of group (b) increase their intensity rapidly with current strength up to about 12 amperes, beyond which they remain constant. The intensities approach nearer to the sum rule predictions for currents over 12 amperes, but even then there are some deviations. Nevertheless the similarity between the observed and calculated values supports the accuracy of the line classification.

IN THE preceding paper an investigation has been made of the abnormal breadth of certain quartet lines of the copper spectrum. The same lines are characterised by unusual intensity changes, which have been measured, and are discussed in the present paper. The lines observed belong to three quartets $a^4D'-c^4D$, a^4F-c^4D, a^4P-c^4D, which occur in the region λ4000–5600, and the designations are given for convenience in Table I, where the broad lines are marked "u".

Table I. *Wave-lengths of lines measured.*

Final terms	c^4D_4	Initial terms c^4D_3	c^4D_2	c^4D_1
a^4D_4'	5292	5144_u		
a^4D_3'	5555	5391_u	5212_u	
a^4D_2'		5432_u	5250_u	5016
a^4D_1'			5355_u	5111
a^4F_5	5641			
a^4F_4	4704	4587_u		
a^4F_3	4797	4675_u	4539_u	
a^4F_2		4842_u	4697_u	4509
a^4P_3	4275	4177_u	4069_u	
a^4P_2		4378_u	4259_u	4104
a^4P_1			4416_u	4249

Experimental Method

The method of measurement employed is similar to that developed by the Physical Institute of Utrecht, but with the optical system described in the preceding paper, (see Fig. 1, p. 43). In the present case the light from the whole of the arc, including the poles, has been allowed to fall on to the spectrograph lens.

Two filters were employed (1) a photographic filter made in our own laboratory, and (2) a platinum deposit filter made by Zeiss. Both were calibrated by the method described in the previous paper, and about the same number of observations were made with each. An infrared spectrograph also was used to check the calibration of the Zeiss filter in the region λ5000–5600. The change of absorption with wave-length for the two filters was in the opposite sense, and there was no systematic difference between the results of each. The graphs should indicate the accuracy to be expected from the measurements.

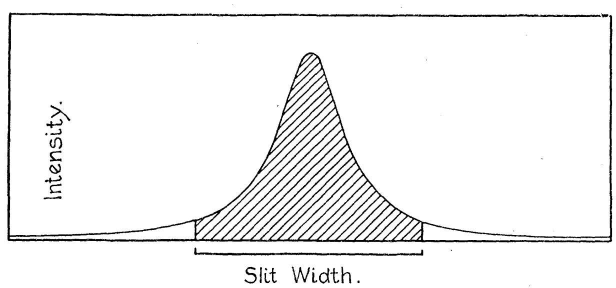

Fig. 1.

The color correction was made in the usual manner with (a) an a.c. Pointolite, and (b) a spiral filament lamp. The brightness temperature of the tungsten bead of the Pointolite was determined by means of an optical pyrometer, and from this the colour temperature was derived from the data of Hyde, Cady, and Forsythe.[1] The color temperature of the spiral lamp had been determined for a given voltage by the Nela Research Laboratory.

Most of the observations were made with a Hilger El quartz spectrograph using a slit whose width was equivalent to 27 cm^{-1} units on the plate at λ4500. Even with as wide a slit as this it was necessary to make a correction for the intensity of the broad lines relative to the sharp ones. In order to estimate the magnitude of this correction, use was made of the line contours determined in the previous paper. In making photometric observations the microphotometer deflection is determined for the center of the image only, and if the line is sharp the whole of its light energy contributes towards this central intesity. For a broad line however this is not so, since the central part of the image does not receive any of the light that lies outside the region whose wave-length distance from the center is greater than half the equivalent width of the slit. In the accompanying diagram (Fig. 1), which represents the intensity contour of the line, only the shaded part contributes towards the measured intensity, whereas it is desired to know the total intensity represented by the whole area; the values measured should therefore be increased in the ratio

[1] Hyde, Cady and Forsythe, Phys. Rev. **10**, 395 (1917).

$$\frac{\text{total area}}{\text{shaded area}}.$$

It has been shown in the preceding paper that the intensity distribution of the lines in question is of the form $a^2/[x^2+a^2]$ where for λ4587 "a" has the value 1.44 cm.$^{-1}$ Therefore for this line

$$\frac{\text{total area}}{\text{shaded area}} = \frac{\displaystyle\int_{-\infty}^{+\infty} \frac{(1\cdot 44)^2}{x^2 + (1\cdot 44)^2}\cdot dx}{\displaystyle\int_{-13\cdot 5}^{+13\cdot 5} \frac{(1\cdot 44)^2}{x^2+(1\cdot 44)^2}\cdot dx} = 1\cdot 07.$$

Consequently the intensity of λ4587 must be increased by 7 percent. Similar corrections were made for all c^4D_2 and c^4D_3 lines. It should be remarked that in adopting this procedure it is assumed that the $a^2/[x^2+a^2]$ form extends much further on either side of the line than has actually been measured. A similar assumption would have to be made whatever method was used to correct for the difference of breadth.

There was a certain amount of doubt about the intensity of some of the lines when the small resolution of the quartz spectrograph was used, on account of the proximity of other lines. In order to overcome this difficulty these lines were measured also with a large three-prism spectrograph, which gave more than sufficient resolution, but which had the disadvantage that only a small region of the spectrum could be photographed at one time; thus the intensity of lines measured with this instrument could be compared only with neighbouring lines. In order to determine the intensity of each line, the breadth was multiplied by the maximum ordinate of the intensity contour. The method of measuring line breadths has already been described.

Ilford Panchromatic plates have been employed, and developed with Rodinal in a tank similar to that described by Dobson, Griffith and Harrison.[2] Photograms of the plates were made with a Moll microphotometer, it being necessary to have a trace run off for each of the six sections of the spectrum produced by the filter steps.

The intensities were reduced graphically by the standard procedure. The background intensity, (which for the wide slit was considerable), was subtracted to give the true intensity of the line. No correction has been made for reversals, and it is believed that, if the effect is present at all, it is small because (a) in the broad lines there is no sign of reversal, which would be detected by a dip in the top of the microphotometer trace, (b) the change of relative intensity of sharp lines, (or alternatively broad lines), with current strength is small, if indeed it really exists. The small variation shown by λ4704, however, may possibly be due to a systematic diminution of the intensity of λ4651 by reversal with increased current. Reversals, then, may have modified the results slightly, but an allowance for them would not bring the results nearer the theoretical values.

[2] Dobson, Griffith, and Harrison, Photographic Photometry, p. 77.

Source of Light

An ordinary electric arc at atmospheric pressure was employed, the conditions being similar to those in the preceding work on line breadth. The distance between the poles was from 5 to 10 mm, and the current strength varied from 1 to 19 amperes.

Results

The results of the measurements are shown in the Figs. 2, 3 and 4.

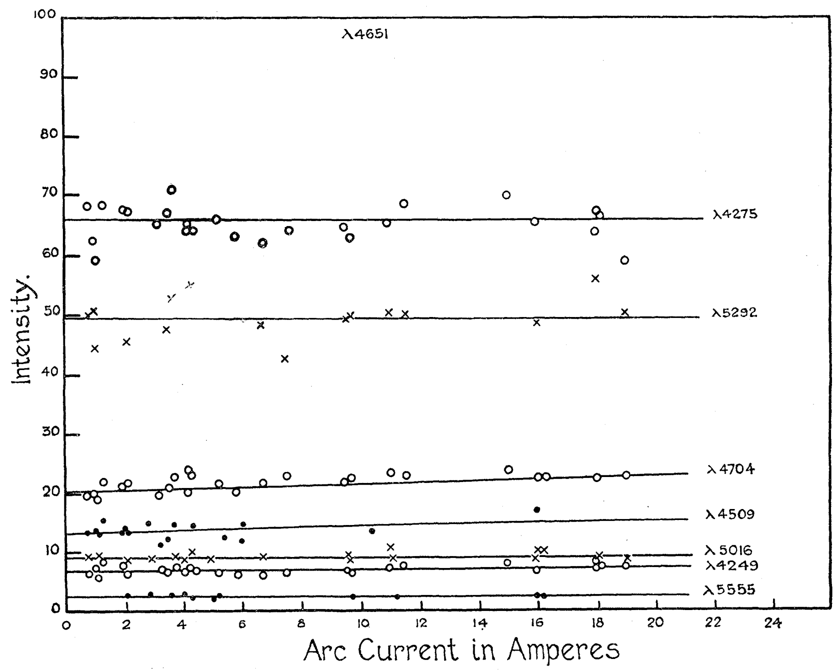

Fig. 2.

In Fig. 2 the line λ4651 ($a^4F_5 - c^4D_4$) has been taken as the standard, and for the various current strengths the relative intensities of other sharp lines, whose initial terms are either c^4D_1 or c^4D_4, are given. It will be noticed that there is practically no change of relative intensity with arc current.

In Fig. 3 the same line is taken as standard and the intensities of the broad lines, whose initial terms are either c^4D_2 or c^4D_3, are plotted. In this case a regular change of intensity is observed.

In Fig. 4 a broad line λ4587 ($a^4F_4 - c^4D_3$) is taken as standard, and the intensities of other broad lines, with initial terms c^4D_2 or c^4D_3, are compared with it. The results show no systematic change with current strength either for c^4D_2 or c^4D_3 lines. The increased irregularity of the values on the left of the diagram is due to the diminution of intensity for smaller currents.

The diagrams show that the lines of these quartets may be divided into two groups, (the $c^4D_{1,4}$ and the $c^4D_{2,3}$ groups), which are just as distinct as

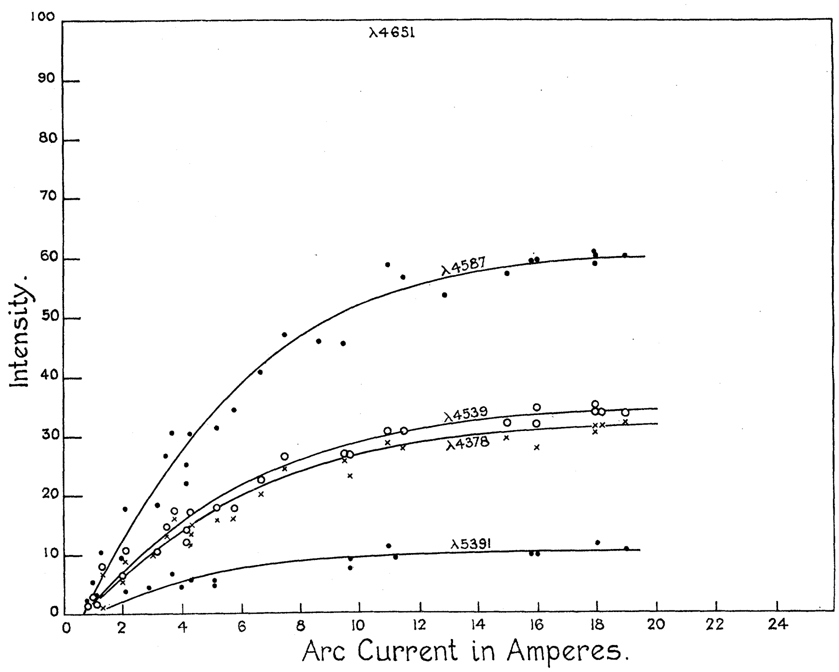
λ4651
λ4587
λ4539
λ4378
λ5391
Intensity.
Arc Current in Amperes.

Fig. 3.

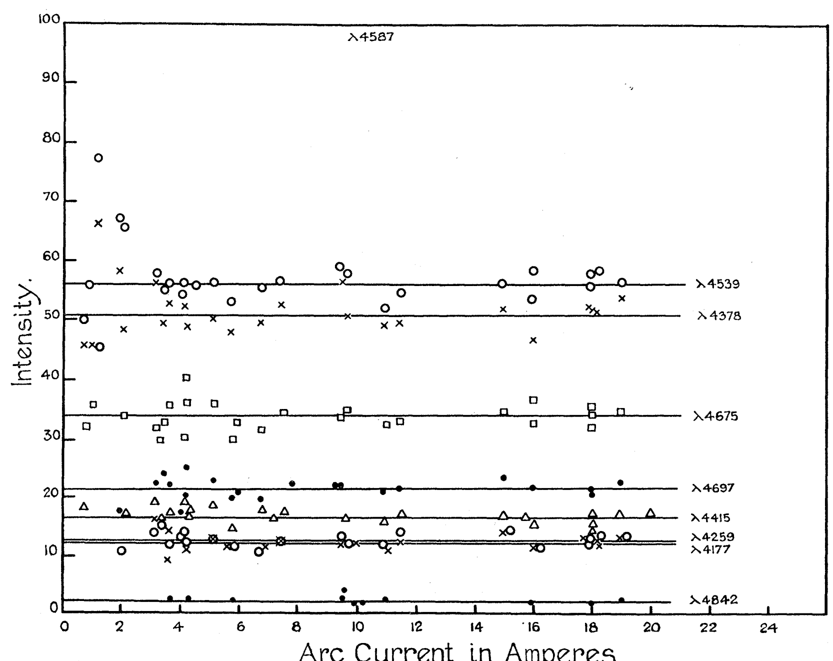
λ4587
λ4539
λ4378
λ4675
λ4697
λ4415
λ4259
λ4177
λ4842
Intensity.
Arc Current in Amperes.

Fig. 4.

regards their intensity behaviour as their breadth. Within each group the lines bear a constant intensity relation to one another, while, as a whole, the intensity of one group changes with respect to the other. In the preceding paper reasons were given for supposing that the breadth of the $c^4D_{2,3}$ lines

TABLE II.

Final terms	Initial Terms				Sums	I_m/I_c
	c^4D_4	c^4D_3	c^4D_2	c^4D_1		
a^4D_4'	82.9 68.8	(24) 11.2			106.9 80.0	1.34
a^4D_3'	4.9 11.2	19.0 34.6	5.2 14.2		29.1 60.0	0.48
a^4D_2'		11.0 14.2	17.8 15.8	12.2 10.0	41.0 40.0	1.02
a^4D_1'			9.8 10.0	8.1 10.0	17.9 20.0	0.90
Sums	87.8 80.0	54.0 60.0	32.8 40.0	20.3 20.0	194.9 200.0	0.97
a^4F_5	100.0 100.0				100.0 100.0	1.00
a^4F_4	22.0 11.6	56.7 68.4			78.7 80.0	0.98
a^4F_3	1.1 0.5	20.8 14.8	30.0 44.8		51.9 60.0	0.87
a^4F_2		1.6 0.8	12.6 11.2	11.9 28.0	26.1 40.0	0.65
Sums	123.1 112.0	79.1 84.0	42.6 56.0	11.9 28.0	256.7 280.0	0.91
a^4P_3	47.1 48.0	4.8 10.8	0.2 1.2		52.1 60.0	0.87
a^4P_3		24.0 25.2	5.3 12.8	0.7 2.0	30.0 40.0	0.75
a^4P_1			8.0 10.0	4.8 10.0	12.8 20.0	0.64
Sums	47.1 48.0	28.8 36.0	13.5 24.0	5.5 12.0	94.9 120.0	0.78
Total	258.0 240.0	161.9 180.0	88.9 120.0	37.7 60.0	546.5 600.0	
I_m/I_c	1.08	0.90	0.74	0. 3	0.91	

was an inner atomic property, i.e., was not caused by external disturbances. It is therefore, now, rather surprising to find that the intensity of these lines is very much affected by external conditions (as, for example, arc current).

It might have been expected that, since the c^4D_2 lines are broader than the c^4D_3, the former would be more affected by arc current strength than the latter. If this were so, a change of the relative intensity of λ4539: λ4378 should occur, but the results show this not to be the case (see Fig. 4).

Comparison with the Sum Rule Predictions

Since all lines with a common initial term have an intensity variation in the same sense, it is obvious that the sum rule cannot hold for all current strengths. However for currents above 12 amperes there is no great change of relative intensity, and it appears that the ratios reach a limiting value for high currents. It so happens that the intensities approach more nearly the sum rule predictions for this limiting value than for smaller currents.

In Table II the limiting intensities for high currents are divided by ν^4 and compared with the values predicted by the sum rule, as extended for individual intensities by H. N. Russell,[3]. and for intensities of triads by R. de L. Kronig.[4] The line λ4651 is given the intensity of 100 units for both measured and calculated values, and the measured value is placed above the calculated value. The ratios of the measured to the calculated sums I_m/I_c are also given. It will be noted that when the intensities are added vertically there is a gradual decrease of I_m/I_c from left to right. This may be due, to some extent, to the decrease of population of the higher initial energy levels on account of temperature equilibrium. Taking the two extremes c^4D_1 and c^4D_4, and by using the formula $\log_{10}R = 0.625(\sigma_1 - \sigma_2)/T$,[5] the derived temperature is about 5500°K. Although this is a considerably lower temperature than that found by Nottingham[6] for the electrons in the copper arc, his value being from 10,000° to 19,000°K, yet it is of interest to note that by adopting a tempera-

Table III. *Measured intensities corrected for temperature (5500°K).*

Final Terms	Initial Terms c^4D_4	c^4D_3	c^4D_2	c^4D_1	Sums	I_m/I_c
a^4D_4'	76.8	25.5			102.3	1.28
a^4D_3'	4.5	20.1	6.6		31.2	0.52
a^4D_2'		11.6	22.5	19.4	53.5	1.34
a^4D_1'			12.4	12.8	25.2	1.26
Sums	81.3	57.2	41.5	32.2		
a^4F_5	92.7				92.7	0.93
a^4F_4	20.4	60.2			80.6	1.01
a^4F_3	1.0	22.1	38.0		61.1	1.02
a^4F_2		1.7	16.0	18.9	36.6	0.92
Sums	114.1	84.0	54.0	18.9		
a^4P_3	43.6	5.1	0.3		49.0	0.82
a^4P_2		25.5	6.7	1.1	33.3	0.83
a^4P_1			10.1	7.6	17.7	0.88
Sums	43.6	30.6	17.1	8.7		
Grand sums	239.0	171.8	112.6	59.8		
I_m/I_c	1.00	0.96	0.94	1.00		

[3] Russell, Proc. Nat. Acad. **11,** 314 (1925).

[4] Kronig, Zeits. f. Physik **33,** 261 (1925). tide Harrison and Engwicht, J.O.S.A. **18,** 287 (1929).

[5] Harrison, J.O.S.A. **19,** 109 (1929).

[6] Nottingham, Bull. Amer. Phys. Soc. **3,** 11 (1928).

ture of 5500°K, and correcting the intensities to infinite temperature, there is a general improved agreement with the sum rule. The measured intensities corrected for a temperature of 5500°K are given in Table III. The vertical sums are, of course, considerably nearer the predicted values, since the temperature has been adjusted to make them so; but it will be noticed that there is an improvement in the horizontal sums also. With one exception (i.e., for a^4D_3') the values of I_m/I_c in the last column are now nearly constant within each multiplet. It cannot be assumed from this, with any certainty, that the effective emission temperature of the arc is actually 5500°K, since it is by no means certain that the line intensities approach so nearly the predicted values. There are still many wide discrepancies for the individual lines.

In view of the difference in nature of the $c^4D_{1,4}$ lines on the one hand, and the $c^4D_{2,3}$ lines on the other, one might be inclined to doubt the correctness of the term analysis, and the question arises whether the present intensity measurements support the classification that has been given. It should be remembered that the general agreement with the sum rule, described above, occurs only when high arc currents are employed, and that for low currents there is very little similarity between measured and predicted intensities. Nevertheless it is most improbable that there should be such agreement under any conditions, if the two groups of lines had no definite multiplet connection, and it is considered, therefore, that the intensities give strong support to the classification.

It has been shown that the intensity ratio of the broad $c^4D_{2,3}$ lines to the sharp $c^4D_{1,4}$ lines depends on the current flowing in the arc. This ratio depends also on other arc variables such as pressure; for it is found that at low arc pressures the $c^4D_{2,3}$ lines are very faint even for high currents. A further set of intensity observations has been made (not of great accuracy) to determine the manner in which this ratio depends on current strength when the poles of the arc are an alloy of copper and silver (10 percent copper). The result was approximately the same as for pure copper.

It is apparent that the variable factor in the arc, which controls the excitation of the $c^4D_{2,3}$ lines, increases with current strength, increases with pressure, and is not greatly affected by the composition of the poles. Nottingham's study of the copper arc[7] has shown that there is a significant increase of electron and ionic concentration with increase of arc current. Moreover these two factors would probably increase with pressure, and be independent of pole composition, and thus may be directly associated with the excitation of $c^4D_{2,3}$ lines, though there seems to be no explanation why such a connection should exist unless it is analogous to the production of forbidden lines in electric fields. A further point which is interesting, though not apparently significant, arises out of the variation of broad line intensity with pressure. Bowen[8] has shown that the intensity of lines from metastable levels (i.e., levels with long mean life) is increased at low pressures. On the other hand, the intensity of lines arising from the $c^4D_{2,3}$ levels, which I have suggested

[7] Nottingham, Jour. Frank. Inst. **207,** 299 (1929).
[8] Bowen, Astrophys. J. **67,** 1 (1928).

may be associated with a particularly short mean life (see previous paper, p. 000), is decreased at low pressure. A little consideration however shows that this decrease of intensity cannot be explained on Bowen's argument, and consequently the two phenomena are not to be ascribed to the same cause.

I have not been able to give a satisfactory explanation of the phenomena connected with the breadth and intensity of these lines, but it is hoped that the present measurements will be of some assistance in solving the problem.

Remarks on the two preceding papers by C. W. Allen on

1. Broad Lines in the Arc Spectrum of Copper.
2. Intensity of Quartet Lines in the Arc Spectrum of Copper.

The anomalous character of the Cu I quartet multiplets with which the above papers are concerned has long offered great theoretical difficulty, and I have, unsuccessfully, urged several specialists in the field of intensities to undertake quantitative measurements. Mr. Allen's papers cover the problem very effectively from the experimental standpoint but he is unable to offer any explanation for the fact that the diffuse lines still retain their great width at low pressures and that, relatively to the sharp lines, they all decrease in intensity with decreasing arc current and with pressure. The observations form the most complete confirmation of the theoretical explanation which I offered last spring (Phys. Rev. **37,** 1701A, 1931 and Phys. Rev. **38,** 873, 1931). Auto-ionization (Auger-effect) is undoubtedly responsible for these anomalies and Mr. Allen's paper offers the experimental basis for a further theoretical study of that effect. I hope to publish further observations on all of the negative terms of Cu I in the near future.

A. G. Shenstone

Princeton University,
November 20, 1931.