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BROAD LINES IN THE ARC SPECTRUM OF COPPER

BY C. W. ALLEN
COMMONWEALTH SOLAR OBSERVATORY, CANBERRA, AUSTRALIA

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ABSTRACT

Attention is called to the anomalous broadening behaviour of certain lines in the copper arc spectrum, particularly those arising from initial terms $c^4D_{2,3}$. Breadths of several lines have been measured with copper arc spectra and pressures up to eighty atmospheres. The following are the most essential conclusions drawn:—(a) broad lines with the same initial term have the same breadth, (b) all lines show a linear increase of breadth with increasing pressure, (c) lines arising from $c^4D_{2,3}$ terms have a considerable breadth at zero pressure. The intensity contours of λλ4378, 4539 and 4587 ($c^4D_{2,3}$ lines) at one atmosphere have been determined and found to have a form represented by the formula $a^2/[(\lambda-\lambda_0)^2+a^2]$. The discussion touches on the nature and cause of the breadth of some of the copper lines, it being concluded that the breadth is an inner property of the copper atom, i.e., not due to external disturbances. The effective diameter of the copper atom would need to be increased considerably by excitation if the pressure broadening is to be accounted for by the Lorentz collision effect.

1. INTRODUCTION

IT IS a fairly general result of spectral analysis that lines of a single multiplet are characterised by similar structures; but the rule is not invariable, and the classifications of Shenstone,[1] Beale,[2] and Sommer[3] for the copper spectrum all agree in ascribing lines of very different breadths to single multiplets. The copper quadruplets which exhibit this peculiarity most strikingly are associated with transitions from c^4D initial terms (Shenstone's notation[1] is adopted), and the lines are characterised by the following structure:

Initial term	Character of line
c^4D_1	sharp
c^4D_2	broad
c^4D_3	broad
c^4D_4	sharp

The object of the present work was to investigate the broadening phenomena presented by these and other multiplets in the copper spectrum. The broad lines in particular show some unusual features, and it was hoped that measurements of their breadth might lead the way to an explanation of their peculiarities.

As the breadth is generally governed by the initial term, repetition will be avoided by referring to lines by their initial terms—thus λ4509 ($a^4F_2-c^4D_1$) may be called a c^4D_1 line. The word "sharp" refers to the character of the line and not to the series.

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[1] Shenstone, Phys. Rev. **28**, 449 (1926).
[2] Beale, Proc. Royal Soc. **111**, 168 (1926).
[3] Sommer, Zeits. f. Physik **39**, 711 (1926).

2. Line Breadths in Emission Spectra

The breath of an emission line is usually defined as the whole wave-length distance between the two points where the intensity is half that of the maximum; this is often called the half-value breadth, and the definition is adopted in the present paper.

The chief objection to the use of the emission spectra for studying line breadths is that reversals are frequently present. By reversal the central part of the spectrum line is weakened more than the wings, the effect being to make the half-value breadth greater than that of the original emission line. However, the lines with whch we are particularly concerned are not reversed to any appreciable extent, and the results obtained indicate that no noticeable discrepancy has been caused in this way.

3. The Spectrum at Atmospheric Pressure

An ordinary electric arc has been employed with currents from two to ten amperes. In most cases the poles were of pure copper, but an alloy (Cu, 20 percent Ag, 80 percent) has been used for some spectra.

The spectrograms were photographed with a three-prism Hilger spectrograph of focal length 25 feet, the dispersion in the region investigated ranging from 0.8 to 2.4 mm per angstroms. Austral "Orthochromatic" and Ilford "Panchromatic" plates have been used, and were developed with "Rodinal" one-in-twenty. A good flow of developer over the plate was assured in all cases. Some plates were developed in a dish, a baffle being moved to and fro about 2 mm above the plate. Others were developed in a tank similar to that described by Dobson, Griffith and Harrison.[4]

The optical system is shown in Fig. 1.

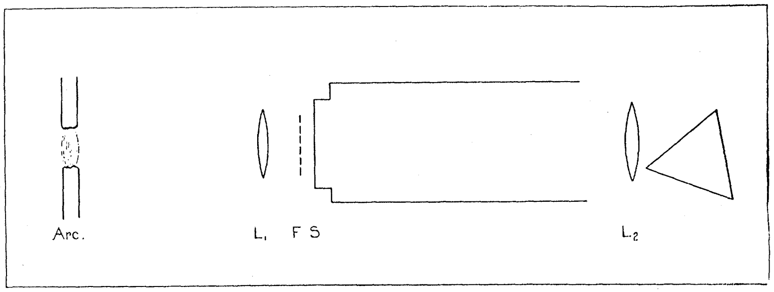

Fig. 1.

A step filter $F^{5,6}$ was mounted immediately in front of the slit S. By means of the lens L_1 the arc was focussed on to the collimating lens L_2, the image being of such size that the light from the incandescent poles could be excluded (though this made no difference). In this way it was found possible to obtain an even illumination of the slit, and the optical system was more economical

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

[5] Baly, Spectroscopy, Vol. 3, p. 157. Pannekoek and Minnaert, "Photometry of the Flash Spectrum" p. 10.

in light than that originally used by Dorgelo.[6] Times of exposure range from three minutes to two hours.

The step filter was prepared by exposing adjacent strips on a photographic plate and developing in the usual way. In order to determine the transmission coefficients for the various strips the filter was mounted as in Fig. 1, and a Pointolite spectrum photographed through it. On the same plate a series of Pointolite spectra with varying slit widths was photographed. It was assumed that the intensities of the members of this series were proportional to the slit widths; thus by measuring their densities with a Moll microphotometer at a certain point in the spectrum, it was possible to find the relation between intensity and density for that particular wave-length. In actual practice it is convenient to regard the galvanometer deflection of the microphotometer as a measure of plate density. (The plate density D is usually defined by the equation $D=\log_{10} U_0/U$, where U_0 equals deflection for clear glass, and U equals measured deflection.) The spectrum, when taken through the filter, becomes divided into a number of sections corresponding to the several filter steps. By measuring the densities of these sections, and by using the density-intensity relation just found, it is possible to derive the relative intensities for the sections, and hence the transmission coefficients of the filter steps. The calibration has been checked by comparison with a Zeiss platinum deposition filter that had been calibrated with an infrared spectrograph.

The arc spectrograms were photographed with the same optical system as shown in Fig. 1, and the microphotometer employed to trace the density curve for each section of the line. By plotting the central density for each section against intensity, as given by the filter calibrations, several points are obtained on the characteristic density-intensity curve for the wave-length region of the line being measured. From this curve one may determine the density which represents half the intensity of the line maximum, and thus the half-value breadth may be measured directly from the microphotograms. This method obviates all difficulties of uneven development and change of plate characteristic with wave-length.

The half-value breadths measured in the one atmosphere spectrum are given in Table I.

Each value in column 3 is the mean of from three to six measurements made in the different sections of the spectrum, and the variation in these values should indicate the accuracy to be expected. No instrumental correction has been applied; this will be referred to later, but it obviously cannot be greater than about ten percent for the broad lines, since λ4509 is quite sharp. Background corrections were frequently necessary; in one case the background intensity was forty percent of the intensity of the line maximum. Less reliable values are enclosed in brackets, the cause of the uncertainty being faintness of the line, or doubt about background correction.

In Table I lines with the same initial term have been grouped together, and it is apparent that within experimental error the breadth in wave-number units is the same for the lines in each group, There is, of course, a considerable change in breadth when angstrom units are employed.

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[6] Dorgelo, Zeits. f. Physik **13,** 206 (1923). Dorgelo, Phys. Zeits. **26,** 756 (1925).

TABLE I.

λ	Designation	Breadth in cm^{-1}	Mean		Remarks
			cm^{-1}	A	
5857	$a^2P_2-c^4D_3$	2.9	2.9	1.0	
5432	$a^4D_2'-c^4D_3$	(3.0), 3.0, 3.05	3.02	0.89	
5391	$a^4D_3'-c^4D_3$	2.83, 2.94, 3.00, 2.97	2.93	0.85	
5201	$a^2F_3-c^4D_3$	2.97, 2.98, 2.95	2.97	0.80	
5144	$a^4D_4'-c^4D_3$	(3.2), 2.8, 3.1, 3.1	3.0	0.79	A broad line blended
4842	$a^4F_2-c^4D_3$	(3.0), (3.3)	3.2	0.75	Faint, heavy background.
4675	$a^4F_3-c^4D_3$	2.94, 2.90, 2.87, 2.92	2.91	0.64	
4587	$a^4F_4-c^4D_3$	2.90, 2.79, 2.78, 2.86, 2.85, 2.82, 2.98, 2.91, 2.84, 2.94, 2.96, 2.98	2.87	0.60	
4378	$a^4P_2-c^4D_3$	2.71, 2.90, 2.74, 2.95, 2.92, 3.0, 2.88	2.87	0.55	
4177	$a^4P_3-c^4D_3$	2.95	2.95	0.52	
5355	$a^4D_1'-c^4D_2$	(5.0), (4.4.4), 4.7, 4.4	4.6	1.3	?? Blended line
5250	$a^4D_2'-c^4D_2$	4.75, 4.64	4.70	1.3	
5212	$a^4D_3'-c^4D_2$	(4.8)	4.8	1.3	In wings of λ5218
5034	$a^2F_3-c^4D_2$	(4.6), 4.8, 4.65	4.7	1.2	
4697	$a^4F_2-c^4D_2$	(4.7), (4.6), 4.7	4.7	1.04	
4539	$a^4F_3-c^4D_2$	5.04, 4.88, 4.94, 4.75, (5.0), 4.82, 4.78, 4.9	4.87	1.00	
4416	$a^4P_1-c^4D_2$	5.01 (5.1), 4.73, 4.88	4.87	0.95	
4259	$a^4P_2-c^4D_2$	4.95	4.95	0.90	
4069	$a^4P_3-c^4D_2$	(4.7)	4.7	0.78	In wings of λ4063
5535	$a^2D_3'-c^2D_3$	4.2	4.2	1.3	
5408	$a^2D_2'-c^2D_3$	4.2, 3.91, 4.14	4.05	1.2	
5076	$a^2F_4-c^2D_3$	3.73, 3.88, 3.95	3.85	0.99	
4776	$s^2F_3-c^2D_3$	(3.9)	3.9	0.89	Heavy background.
4253	$a^4F_4-c^2D_3$	(4.0)	4.0	0.72	Faint.
4073	$a^4P_2-c^2D_3$	3.66, 4.0	3.8	0.63	
4513	$a^2P_1-b_2$	(2.5), (2.6)	2.6	0.53	Faint.
4242	$a^4D_3'-b_2$	2.29	2.29	0.41	
4123	$a^2F_3-b_2$	2.33, 2.14, 2.16	2.21	0.38	
4866	$a^2D_3'-a_3$	9.3, 8.63	8.9	2.1	
4767	$a^2D_2'-a_3$	9.1	9.1	2.1	
4507	$a^2F_4-a_3$	9.1, (8.0), 9.06, (9.3)	9.1	1.85	
4121	$a^2D_3'-d^4S_2$	0.92, 1.04, 1.03	1.00	0.17	
4080	$a^2D_3'-d_3$	1.77, 1.82	1.80	0.30	
4075	$a^2D_3'-c^2G_4$	0.64, 0.64	0.64	0.11	
5360	$a^2P_1-c^4D_1$	0.51, 0.50, 0.56, 0.47	0.51	0.15	
4509	$a^4F_2-c^4D_1$	0.37, 0.37, 0.46, 0.39, 0.38, 0.37	0.39	0.08	
4104	$a^4P_2-c^4D_1$	0.66, 0.66, 0.67	0.66	0.11	
5352	$a^2F_3-c^4D_4$	0.98, 0.85. 0.90, 0.85	0.90	0.26	
4797	$a^4F_3-c^4D_4$	0.92, 0.93, 0.92	0.92	0.21	

From the casual inspection of the copper spectrum all c^4D_1 and c^4D_4 lines would be classified as sharp, but there is actually a considerable difference between them. In general the c^4D_1 lines are sharper than c^4D_4, but apparently exceptions to this rule exist; further refinement in measurement would be required to deal quantitatively with these lines, and for the present the chief purpose in observing them is to correct for the broader ones.

It seems obvious that there is a broadening factor present in the $c^4D_{2,3}$ and other broad lines which is definitely associated with the initial term. This will be referred to as the natural term breadth. In estimating the magnitude of this factor, which is the unusual feature of the lines in question, it is noted that all lines, broad and sharp, are influenced by instrumental breadth, pressure effect, Doppler effect, and radiation damping. I shall assume that the breadth of λ4509 (this being about the sharpest, and lying in proximity to the strongest broad lines) is entirely due to these causes. The natural term breadth can then be found by subtracting the breadth of λ4509 from the breadth of a line with the required initial term. The results of this operation are given in Table II.

TABLE II.

Term designation		Line breadth cm^{-1}	Natural term breadth cm^{-1}
Shenstone	Sommer		
c^4D_3	$^4D_3$	2.89	2.50
c^4D_2	$^4D_2$	4.87	4.48
c^2D_3	$^2D_3^1$	3.90	3.51
b_2	$^2D_2^1$	2.25	1.86
a_3	$^2D_3^2$	9.1	8.7
d^4S_2	$^2D_2^3$	1.00	0.61
d_3	$^2D_3^3$	1.80	1.41

We are justified in simply subtracting the breadth of λ4509, since the intensity contours of both broad and sharp lines are approximately of the form $a^2/[(\lambda-\lambda_0)^2+a^2]$ (see Section 6). When two primary broadening factors act independently, whether one be an instrumental effect, or whether both are spectroscopic, the resulting breadth may be obtained by combining together the two primary breadths; but not necessarily by simply adding them. The relation between Δ_1 and Δ_2 the primary breadths, and Δ the resultant breadth may be derived from the formula[7]

$$J(x) = \int_{-\infty}^{+\infty} L(u)\cdot S(x-u)du$$

where $L(x)$ and $S(x)$ represent the intensity contour of the primary factors, and $J(x)$ is that of the resulting line. x is the wave-length distance from the center of the contour. It is found that the relation between Δ_1, Δ_2 and Δ depends on the nature of the contours, and particularly on the intensity in the wings. Four types of contours are considered: (a) When there are no wings at all in the functions $L(x)$ and $S(x)$ (i.e., when they are of the form $L(x)=m$, from $x=-\Delta_1/2$ to $+\Delta_1/2$ and $L(x)=0$ for other values of x) then the relation becomes $\Delta=\Delta_1$ (supposing Δ_1 greater than Δ_2). (b) When small wings are

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[7] Ornstein and Minnaert, Zeits. f. Physik **43**, 404 (1927).

present, as in the case of the errors curve $L(x)=e^{-ax^2}$, we have the relation $\Delta=(\Delta_1^2+\Delta_2^2)^{1/2}$ and the resulting contour is also an errors curve. (c) Passing to a contour with more prominent wings, namely $a^2/[x^2+a^2]$, we find the relation $\Delta=\Delta_1+\Delta_2$, and here again the resulting contour is similar to that of the primaries. (d) At the other extreme when the wings are very prominent as for the contour $e^{-a|x|}$ no simple relation exists, but $\Delta>\Delta_1+\Delta_2$.

From the $a^2/[x^2+a^2]$ contours in the present case it is apparent that the breadths may be simply added and subtracted.

As mentioned before the current strengths ranged from two to ten amperes. All measurements have been collected in Table I regardless of arc conditions. In order to examine whether there is any appreciable change of breadth with current strength the various values under different arc conditions are shown in Table III. Neglecting λ4509 (a sharp line) it will be seen that the measurements do not show any change of breadth with current strength, and also that the Cu-Ag alloy (20 percent copper) gives the same results as pure copper; it is not unlikely that there is a slight increase of breadth with current strength of the same order as that exhibited (visually) by the sharper lines, but of course the effect is too small to detect in the broader lines. This constancy of breadth is perhaps the more significant in view of the considerable intensity changes for the same current variation. (See following paper.)

TABLE III. *Breadth in cm⁻¹.*

λ	Pure copper arc					Alloy Cu 20% Ag 80%	
	2 amps.	3 amps.	4 amps.	6 amps.	10 amps.	3 amps.	10 amps.
4674		2.94		2.90, 2.87	2.92		
4587	2.94	2.78, 2.86, 2.84	2.79	2.85, 2.82. 2.78, 2.91, 2.96	2.98	2.90	
4539	(5.0)	5.04, (4.9)	4.88	4.75, 4.78	4.82	4.94	
4416			5.01	(5.1), 4.88	4.73		
4378		2.95	2.71, 2.92	2.90, 2.74, 3.00			2.88
4509	0.38			0.37, 0.39	0.46		0.37

4. THE SPECTRUM AT HIGHER PRESSURES

The plates employed for determining the breadth of lines at higher pressures are grating spectrograms exposed some years ago by the late Dr. W. G. Duffield, and already described by him.[8] The source of light was a copper arc with a current of about thirteen amperes, and increase of pressure was obtained by forcing air into a cylinder enclosing the arc. It was not possible to deduce the characteristic curve separately for each plate, but the curve for the one-atmosphere plate was derived in a manner to be described, and it was assumed that other plates, which had been developed under similar conditions, had the same characteristics.

To find the relation between density (or galvanometer deflection of the microphotometer) and intensity for the one atmosphere plate, use was made of the two to one sum-rule intensity-ratio for the lines λ4531 and λ4480 ($2^2P_{2,1}-3^2S$). This value has been confirmed for arc spectra in this labora-

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[8] Duffield, Phil. Trans. **A209**, 205 (1908).

tory, whence it appears that reversals, if present, have not appreciably affected the intensity ratio. A small difference of breadth was observed, the ratio for λ4531:λ4480 being 1.14:1. If it be assumed that the total intensity of each of these lines is proportional to the product of the breadth and the intensity of the maximum, then the relative intensity of the line maxima for λ4531:λ4480 must be $2/1.14=1.76$. This value is required for determining the characteristic curve. The lines on the grating spectrogram are drawn out by astigmatism, and spectra of the different intensities can be measured by running the microphotometer at different sections normal to the lines. For each section the deflections for the maxima can be plotted against log intensity, as shown on the left of Fig. 2. Here the distance PQ equals the known log of the intensity ratio (i.e., log 1.76). The position of P is chosen arbitrarily. There are only two points to fix each curve, but the curves could be drawn, nevertheless, by use of the assumption that they are parallel to each other in the sense that for any pair the horizontal distance between them is constant. The final characteristic curve, AB in Fig. 2, is drawn by moving the

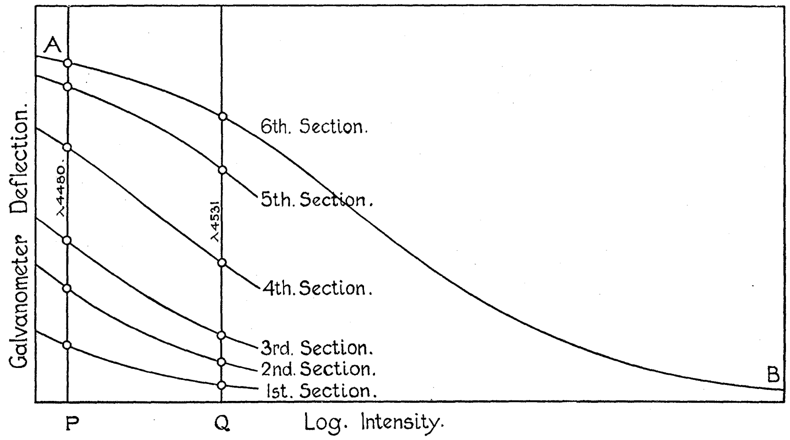

Fig. 2.

TABLE IV. *Breadth in wave-number units.*

λ	Designation	Pressure in atmospheres							Rate per atmosphere
		1	6	21	41	61	71	81	
4587	$a^4F_4-c^4D_3$	2.84	—	—	16.0	25.5	—	28.5	0.33
4539	$a^4F_3-c^4D_2$	4.4	6.9	11.4	19.2	28.6	—	36.0	0.38
4531	$2^2P_2-3^2S$	1.16	6.2	18.0	—	—	—	—	0.85
4509	$a^4F_2-c^4D_1$	0.64	2.5	6.7	—	—	—	—	
4507	$a^2F_4-a_3$	9.1*	10.6	—	—	—	—	—	
4378	$a^4P_2-c^4D_3$	2.71	4.95	9.2	15.2	19.8	26.5	30.2	0.33
4275	$a^4P_3-c^4D_4$	0.55	2.9	6.5	11.9	17.3	23.2	25.7	0.31
3530	$m^2D_2-a^4F_3$	0.6	—	2.3	4.4	6	—.	—	0.10

* Measured on prism spectrograms.

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[9] Payne and Hogg, Harvard College Observatory Circular No. 301. 1927.

shorter curves horizontally to the right until they come into contact with each other. A similar graphical method has been employed by Payne and Hogg[9] for stellar spectra. By means of the characteristic curve the galvanometer deflections may be converted into intensities. The half-value breadths may then be measured on the microphotograms. The results are shown in Table IV and Fig. 3.

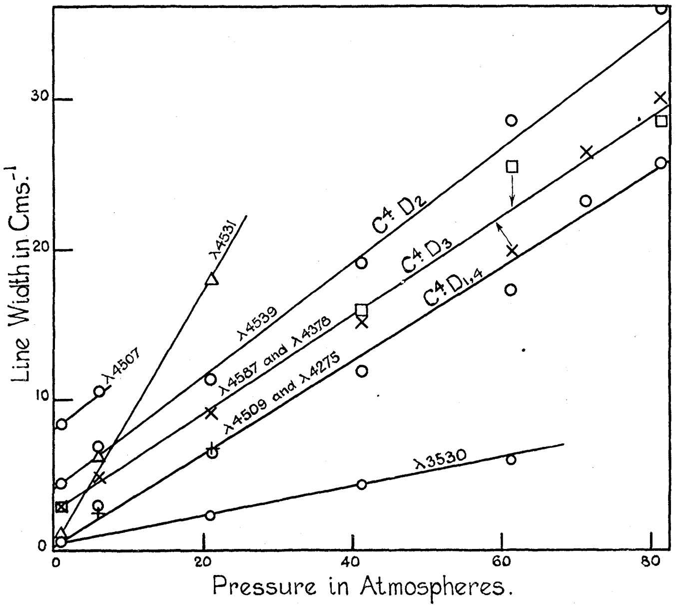

Fig. 3.

The deviations from a linear relation between breadth and pressure are probably due to the inaccuracy of the assumption that all plates have the same characteristic. It was found, in fact, that to give consistent results it was necessary to measure breadths on lines whose central density had a certain selected value. This introduces a certain amount of arbitrariness, and perhaps a considerable error into the absolute magnitude of the measurements, but it is not at all likely to affect any of the conclusions I have drawn, which are as follows:

(a) There is a linear relation between breadth and pressure for all the lines measured.

(b) For the c^4D lines the rate of increased broadening with pressure is almost the same; the variation of the rate is practically within experimental error.

(c) The line λ3530, whose initial term is at a much lower level (and therefore less likely to be disturbed by atomic collisions), is broadened much less rapidly than the other lines.

(d) The series line λ4531 is broadened much more rapidly than the nonseries lines.

(e) The rule that lines with the same initial term have equal breadths still holds as the pressure increases.
(f) Extrapolating to zero pressure it would seem that all the $c^4D_{2,3}$ lines have a considerable breadth apart from any pressure effect.
(g) The broadening of λ4507, (and presumably all lines with the initial terms a_3, b_2, c^2D_3, and perhaps some others), if of the same nature as that associated with the $c^4D_{2,3}$ lines.

5. The Vacuum Arc Spectrum

From the foregoing results it appears likely that the $c^4D_{2,3}$ lines would remain broad when produced under low arc pressures, and consequently a few vacuum arc spectra have been secured in order to ascertain whether this is actually the case. These lines, however, become particularly faint at low pressures,[10] and at a pressure of 3 cm with a current of 11 amperes they were only just visible. The breadths of the $c^4D_{2,3}$ lines, λ4587 and λ4539, at this pressure, are practically the same as at atmospheric pressure.

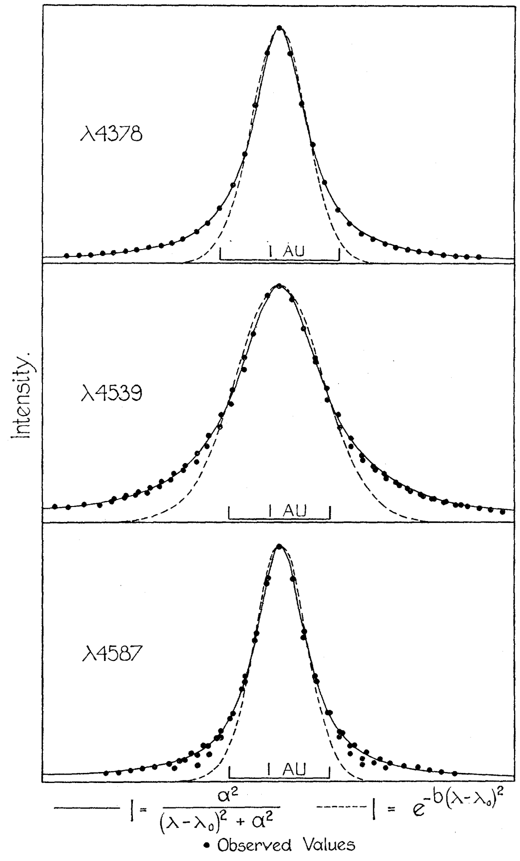

Fig. 4.

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[10] J. Barnes, Astrophys. J. **34,** 159 (1911); G. Wolfsohn, Ann. d. Physik **80,** 415 (1926).

6. Intensity Contours

Intensity contours of λ4587, λ4539 and λ4378 at one atmosphere (prism-spectra) have been derived from the microphotograms, using the intensity-density curve previously determined.

In Fig. 4 the experimental values are plotted against two empirical contours of the form $a^2/[(\lambda-\lambda_0)^2+a^2]$ and $e^{-b(\lambda-\lambda_0)^2}$ respectively, the constants a and b having been so adjusted that all the curves have the same half-value breadth. Fig. 4 shows that the lines are symmetrical and that they approximate more closely to the form $a^2/[(\lambda-\lambda_0)^2+a^2]$ then $e^{-b(\lambda-\lambda_0)^2}$. There are some differences among the contours of the sharp lines, but λ4509 approximates closely to the same form $a^2/[(\lambda-\lambda_0)^2+a^2]$.

It has not been possible as yet to plot intensity contours for lines at higher pressures. Many of them are unsymmetrical, and the shape of the contour is often different on the two sides. The ratios between the breadth of the red and the violet side $\Delta_r:\Delta_b$ are summarised briefly in Table V.

Table V.

λ	Type of line	Δ_r/Δ_v	
3530	$m^2D_2-a^4F_3$	1.0	Broadens symmetrically.
4539	$c^4D_{2,3}$ lines	1.0→2.0	1.0 at one atmosphere and approaches 2.0 as the pressure increases to about 80 atmospheres.
4275	$c^4D_{1,4}$ lines	2.0	Ratio does not change greatly with pressure.
4531	series line	2.7	Do Do

7. Discussion

The point to which it is desired to draw particular attention is that there still remains a considerable breadth to the $c^4D_{2,3}$ lines, (and probably other lines in the copper spectrum), when the arc pressure is reduced to zero. These lines therefore remain broad under conditions that in other spectra usually produce sharp lines, and one is faced with the question of the cause of their breadth. The factors usually considered to cause the broadening of lines[11] may be collected into three groups:

(a) The broadening consequent upon experimental conditions, including finite resolving power, Doppler effect, and reversals. These factors do not represent an actual range in emission frequency, and for study of atomic phenomena usually require to be eliminated.

(b) Broadening consequent upon emission conditions, including the effect of atomic collisions, coupling of atoms, electrical fields, and external disturbances of this kind.

(c) The natural breadth which remains when all external disturbances have been eliminated.

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[11] Michelson, Astrophys. J. **2,** 251 (1895); Rayleigh, Phil. Mag. **29,** 274 (1915). Holtzmark and Trumpy, Zeits. f. Physik **31,** 803 (1925); Von Kluber, Zeits. f. Physik **44,** 481 (1927).

With reference to (a), the breadth of the $c^4D_{2,3}$ lines and other broad lines cannot be attributed to incomplete resolving power, since many much sharper lines are observed; nor to Doppler broadening, since its effect, when computed, is too small. Reversals are usually stronger for the more intense lines of a multiplet; and since the breadth under discussion is in no way a function of the intensity, this cannot be the cause; moreover the contours of the lines give no indication of reversals.

Concerning (b), one would expect to find the effect of atomic collisions the same for all lines of the multiplet, and proportional to pressure. This probably plays a considerable part in the broadening of lines under higher pressures, but cannot account for such broad lines at one atmosphere. The lines have not been reported as sensitive to electrical fields[12] as is the case with the much narrower 2^2P-3^2S lines, and therefore the breadth is not a Stark effect. Moreover, the effects of any such causes as these, which depend upon total pressure, should tend to vanish as the pressure decreases to zero, whereas there is quite a considerable residual breadth at zero pressure for the $c^4D_{2,3}$ lines quoted. On the other hand, any cause which depends on concentration of copper vapour such as coupling effect[13] and broadening due to the existence of molecular copper,[14] should be sensitive to change in current strength and composition of the poles of the arc, whereas no such variations have been found.

Apparently the phenomenon comes under group (c). The fact that the breadth is influenced so little by external conditions suggests that it is an internal property of the individual copper atom, depending on some peculiarity of the orbit. It is improbable that the broadening is due to unresolved satellites of nuclear origin since the lines are so wide and have an energy distribution of the form $a^2/[(\lambda-\lambda_0)^2+a^2]$ which is so fundamental in the theory of broadened lines. No sign of composite structure can be found from the spectra.

There are two possibilities which present themselves. (a) Normal spectrum lines are known to have a small natural breadth of the order 10^8 secs.$^{-1}$ (or 10^{-2} cm^{-1}) on account of radiation damping.[15] This has been explained in quantum language[16] by taking account of the finite length of time that an atom remains in a level before spontaneously radiating a spectrum line thereby falling to a lower level. In the normal case the mean life of a state is about 10^{-8} sec., giving as before a breadth of 10^8 sec.$^{-1}$. However, metastable levels are known whose mean length of life is considerably greater than 10^{-8} sec., and the possibility arises that particularly unstable levels may also exist for which the mean life is less than 10^{-8} sec. If such were the case presumably the lines produced from the unstable levels would have natural breadths

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[12] Takamine, Astrophys. J. **50**, 23 (1919).

[13] Mensing, Zeits. f. Physik **34**, 611 (1925); Holtsmark, Zeits. f. Physik **34**, 722 (1925).

[14] Harrison and Slater, Phys. Rev. **26**, 176 (1925).

[15] Planck, Wied. Ann. **60**, 577 (1897).

[16] Van Vleck, Quantum Principles and Line Spectra, Bull. Nat. Res. Council, No. 54, p. 166, 1926.

greater than 10^8 sec.$^{-1}$, and a mean life of approximately 10^{-11} sec. would produce lines with widths of the same order as those of the $c^4D_{2,3}$ lines. Moreover, the intensity contours would be of the $a^2/[(\lambda-\lambda_0)^2+a^2]$ form as found (Section 6).

(b) On the other hand, the indefiniteness of the energy level may be due to aperiodicity of the electronic motion. A sharp quantization cannot be expected when the motion is not multiply periodic, or when the multiple Fourier series is only semi-convergent,[16] and broad lines would then be produced.

Whether due to instability or aperiodicity the breadth would be associated with the affected term, and all lines arising from one such term would have the same breadth as has been found in the present case. It is apparently rare to find wide lines of this type, but possibly the effect exists to a smaller degree in a number of sharper lines. It is however difficult to see why some lines should be affected, while others in the same multiplet are not. A study of the electron configuration has not, as yet, suggested any reason for the anomaly, nor have I been able to discover any regularity between breadth and term designation.

If the natural term breadth Δ_n is a purely inner atomic phenomenon, then the pressure broadening Δ_p of the lines concerned should be simply superimposed. In Section 3 was shown the manner in which the combination of the two broadening factors depends on their contours. In the present case the intensity contour of the natural term breadth is of the form $a^2/[(\lambda-\lambda_0)^2+a^2]$. I have not been able to determine the contour of the pressure broadening alone, (as exhibited by λ4275 ($a^4P_3-c^4D_4$) say), but the microphotograms give the impression that the wings are, if anything, more prominent than for $a^2/[(\lambda-\lambda_0)^2+a^2]$. Consequently the resultant breadth Δ should be equal to, or perhaps slightly greater than, $\Delta_n+\Delta_p$. If the pressure broadening for all the lines of the a^4F-c^4D multiplet is the same, then, as the pressure increases, we should expect the difference in the breadth to remain constant or to increase slightly. There is in fact a small increase shown in Fig. 3, though not more than could be accounted for by experimental error. The results are therefore consistent with the view that the natural term breadth and the pressure breadth act independently; that is to say, that the natural breadth is not affected by pressure.

It might be mentioned that the breadth of the pressure broadened lines is considerably greater than that produced by the Lorentz collision effect, if the ordinary gas kinetic atom radius is adopted. From the Lorentz collision theory the line breadth $2\nu'$ is given by $2\nu'=1/\pi T$ where T is the mean time between collisions.

From the kinetic theory of gases[17]

$$\begin{aligned}\frac{1}{T} &= 2\cdot N\cdot {S_{1s}}^2\cdot\left(\frac{\pi}{h}\right)\left(\frac{1}{m_1}+\frac{1}{m_s}\right)^{1/2}\\ &= \pi\cdot N\cdot {S_{1s}}^2\cdot\bar{C}\cdot\left(1+\frac{m_1}{m_s}\right)^{1/2}\end{aligned}$$

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[17] J. Jeans, The Dynamical Theory of Gases, 4th Edn., 1925, Equation 703.

and by using approximate values for the arc conditions (i.e., temperature $=3{,}000°$K; number of copper atoms in arc plasma small compared with other atoms; diameter of air molecule $=3.3\times10^{-8}$cm), and with the value of 2.7×10^{-8}cm for the diameter of the copper atom, calculation for a pressure of 61 atmospheres gives a breadth of

$$2.67 \times 10^{10}\ \text{secs.}^{-1}.$$

The measured values are:

$$\text{for}\quad \lambda 3530\ (m^2D_2 - a^4F_3)\quad 18 \times 10^{10}\ \text{secs.}^{-1}.$$

$$\text{for}\ \left\{\begin{array}{l}\lambda 4509\ \ (a^4F_2 - c^4D_1)\\ \lambda 4275\ \ (a^4P_3 - c^4D_4)\end{array}\right.\quad 57 \times 10^{10}\ \text{secs.}^{-1}.$$

If the Lorentz collision effect is the chief cause of pressure broadening, it would be necessary to assume[18] that the effective diameter of the copper atom is about 12×10^{-8} cms when emitting λ3530 and 24×10^{-8} cm for λ4509 and λ4275. However, from the asymmetry of the lines it is clear that another factor is contributing towards the line breadth,[19] and consequently these values are likely to be an overestimate of the diameter of the excited atom. It is interesting to note, nevertheless, that the lines arising from the higher energy levels, such as c^4D, lead to greater atomic diameters than for the lower a^4F levels. This would be expected since the electronic orbits are greater in the higher levels.

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[18] Stuart, Zeits. f. Physik **32,** 262 (1925).

[19] Minkowski, Zeits. f. Physik **55,** 16 (1929).