SPARK SPECTRUM OF COPPER (Cu II)

By A. G. Shenstone

Abstract

Terms in the spectrum of Cu(II.).—The spark spectrum of copper consists of (1) a low set of terms ^3D and ^1D from the structure (d^9s); (2) an intermediate set ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F (d^9p); (3) a high set ^3D, ^1D (d^9, s); (4) probably a ^1S (d^{10}), the lowest term and giving combinations outside the observed range. All of these terms except ^1S have been identified by intensities of combinations and by Zeeman effects. They are all inverted except ^3F which is only partially so; and the interval rule does not hold. The terms $^3D_3'$ and $^1F_3$ apparently share their g-sum and are otherwise not differentiable. The value of ^1S can be found from arc spectrum limits to be about 22224 wave numbers lower than $^3D_3$. The application of the combination principle makes possible the calculation of accurate wave numbers in the ultra-violet to λ1944.

Comparison with corresponding terms in Ni(I) and Pd (I).—A comparison is made with corresponding terms in Ni(I) and Pd(I) and it is shown that the limits of the component term series in all three cases apparently do not agree with Hund's predictions. It is important that the difference $^3D_3-^3D_1$ in the three spectra is constant within the series to less than 1/10%; in the case of Cu(II), being apparently absolutely constant and equal to the difference $^4D_4-^4D_1$ of the arc spectrum.

An ionization potential for Cu(II) is calculated as about 20.5 volts.

IN AGREEMENT with the theory of the production of spectra developed by Hund[1] the author has shown in a recent paper[2] that the arc spectrum of copper consists of two parts; first, an ordinary doublet spectrum due to the atom in states in which all but one of the twenty-nine electrons are in closed groups of orbits; second, a quartet-doublet spectrum due to the atom in states in which nine of the last eleven electrons are in 3_3 orbits, one is in a 4_1 orbit and the last is in either a 4_1 or some less firmly bound condition. There are indications of a less completely developed third spectrum arising from structures in which only eight electrons remain in 3_3 orbits. The lowest terms of the first two types of spectra are $1^2S(d^{10}s)$ and $m^2D(d^9s^2)$. The brackets give, symbolically, the electron configurations, the letters denoting the k-values of the orbits, and the indices the numbers of electrons. Only the last eleven electrons are given, since the others remain in closed groups.

The two types of ion on which the two branches of the arc spectrum are built are (d^{10}) and (d^9s) which spectroscopically are terms of type ^1S and ^3D, ^1D. The series of terms in the two branches of the arc

[1] Hund, Zeits. f. Physik, **33**, 841 (1925).
[2] Shenstone, Phys. Rev. **28**, 449 (1926).

spectrum will, therefore, have as limits the spark ^1S and the various components of the terms ^3D, ^1D. We can, then, find approximately the difference $^1S-{}^3D$ by calculating the limits of series of terms in the two parts of the arc spectrum. The limit of the ^2S terms is taken as zero, according to the usual convention. There are two ^4D terms (d^9s, s) available for the calculation of the limits of the second arc spectrum. The $^4D_4$ terms are the lowest and should converge to the spark $^3D_3$. This limit falls at -22224, indicating that the difference $^1S-{}^3D_3=22224$, the ^1S being the lower term. This value may be in error by perhaps 1500 units since only two series members are available for the calculation.

Combining with the low spark terms ^1S and ^3D, ^1D there should be found a triad ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F due to the electron configuration d^9p. Such terms should also combine with higher series members of the sequence ^3D, ^1D, (d^9, s). The comma between d and s is used to denote that the s-electron is in an excited level, for instance 5_1, 6_1, etc.

The spectrum of the copper arc in the ultra-violet contains many strong spark lines which can be distinguished with some difficulty by the ordinary arc-spark comparison method. If the arc is run from batteries and self-induction is avoided as far as possible, the spark lines become relatively weak and the distinction can be made more easily. The low-voltage arc[3] in Cu vapor has also been used by the author for the separation of arc and spark lines.

A number of the ultra-violet spark lines have been observed by Stücklen[4] in the under-water spark and wrongly placed as arc lines. From their appearance under the conditions of that experiment, there can be no doubt that they are among the most easily excited spark lines. They are all included in the following Table I which gives the combinations of the lowest ^3D, ^1D with the intermediate terms ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F. It will be noticed that all of the terms of Table I are inverted with the exception of the partially-inverted ^3F, in agreement with the predictions of the Hund theory. The method of determining the designations of the terms and their magnitudes is given below.

The lowest term of this set is $^3D_3$ and it has been arbitrarily assigned the value zero, the remaining terms then all assuming positive values. The assignment is provisional only, awaiting the discovery of the exact difference $^1S-{}^3D_3$ which would then be added to all of the terms.

The combinations of the intermediate set of terms of Table I with a higher ^3D, ^1D are given in Table II. These two sets include every copper spark line of the quartz region which is also emitted in the ordinary copper arc. A large number of the lines also appear in the spectrum of the low-voltage arc when the current density is large.

[3] Shenstone, Phil. Mag. **49**, 952 (1925).
[4] Stücklen, Zeits. f. Physik **34**, 562 (1925).

The lines of Table II lie, for the most part, in a spectral region in which greater accuracy of measurement is possible. The term differences have, therefore, been computed from that table. The actual values of terms above ${}^3D_3$ have then been computed by the use of the few lines of Table I which have been measured with reasonable accuracy by Mitra[5] and by Wolfsohn.[6] The wave numbers of lines calculated from Hasbach's[7] and Eder's[8] measurements diverge progressively from the values predicted by the combination principle. If these differences

TABLE I

Classification of certain ultra-violet spark lines of copper.

		a^3D_3 0.0	a^3D_2 918.5	a^3D_1 2069.7	a^1D_2 4335.7
a^3P_2	44489.9	(10) 44489.9 (W)	(5) 43571.4 (W)	(2) 42420.6	(7) 40154.3
	1497.9				
a^3P_1	45987.8		(8) 45069.3 (W)	(5) 43918.1 (WM)	(2) 41652.2
	933.4				
a^3P_0	46921.2			(5) 44852.4	
a^3F_4	46802.1	(10) 46803.6			
	−283.0				
a^3F_3	46519.1	(4) 46520.1	(10) 45601.3		(6) 42183.1
	1420.2				
a^3F_2	47939.3	(3) 47941.2	(4) 47020.7 (M)	(8) 45870.4	(0) 43603.4
a^3D_3'	48912.5	(8) 48914.8			(9) 44576.8 (WM)
	652.4				
a^3D_2'	49564.9	(1) 49568.1	(8) 48648.9	(3) 47497.2	(7) 45229.4 (W)
	1608.4				
a^3D_1'	51173.3		(2) 50258.6	(7) 49106.3	(4) 46838.0
a^1F_3	49991.3	(7) 49995.0	(6) 49075.5		(6) 45655.5 (M)
a^1D_2'	51424.3	(2) 51427.1	(2) 50509.4	(5) 49357.9	(5) 47090.2
a^1P_1	51667.1		(1) 50751.9	(1) 49600.8	(5) 47331.1 (M)

are plotted against wave-length, a curve is obtained which rises to a maximum of about $\Delta\nu = 3.8$ at $\lambda = 2000$ and thereafter falls with shorter wave-length. If the present analysis of the Cu spark spectrum is admitted as correct, then it is possible to calculate much more accurate wave-lengths than have been previously known in the region $\lambda 1944$ to $\lambda 2200$. The values given in Tables I and II are Hasbach's and Eder's; the values in the Table IV at the end of this paper are those calculated by the use of the combination principle. The frequencies given in Table IV have a probable error of about 0.4 units.

[5] Mitra, Ann. d. physique **19,** 315 (1923).
[6] Wolfsohn, Ann. d. Physik **80,** 415 (1926).
[7] Hasbach, Zeits. f. Wiss. Phot. **13,** 399 (1914).
[8] Eder, Wien. Ber. **123** II a, 616 (1914).

The intensities given in Tables I and II are the author's visual estimates of the photographic intensities of the lines. In general, the combinations which do not involve a change in multiplicity are in excellent agreement with theoretical expectation, with one striking exception, the absence of the line $a^3D_2-a^3D_3'$. Its intensity should be about 4; and, indeed, the corresponding line of Table II is present with

TABLE II

Classification of additional spark lines of copper.

		b^3D_3 86083.7	b^3D_2 86404.6	b^3D_1 88153.3	b^1D_2 88435.0
a^3P_2	44489.9	(5) 41593.8	(0) 41914.7		(0) 43945.1
	1497.9				
a^3P_1	45987.8		(5) 40416.8	(0) 42165.5	(0) 42447.3
	933.4				
a^3P_0	46921.2			(1) 41232.1	
a^3F_4	46802.1	(10) 39281.6			
	−283.0				
a^3F_3	46519.1	(4) 39564.9	(8) 39885.5		(0) 41915.5
	1420.2				
a^3F_2	47939.3	(0) 38145.2	(5) 38465.4	(6) 40213.9	(1) 40496.9
a^3D_3'	48912.5	(7) 37171.2	(3) 37492.1		(6) 39521.4
	652.4				
a^3D_2'	49564.9	(1) 36518.9	(7) 36839.7	(4) 38588.4	(0) 38870.0
	1608.4				
a^3D_1'	51173.3		(4) 35231.2	(6) 36980.2	
a^1F_3	49991.3	(6) 36092.4	(5) 36413.4		(6) 38443.7
a^1D_2'	51424.3	(1) 34659.5	(0) 34980.5	(5) 36729.0	(7) 37010.7
a^1P_1	51667.1		(5) 34737.5	(1) 36486.9	(6) 36767.9

intensity 3. The intensities of the intersystem combination lines do not obey, even approximately, the usual qualitative rules. For instance, a^1D_2 combines with a^3P_2 much more strongly than with a^3P_1. Moreover, the relative intensities of the intersystem lines of Tables I and II are entirely different. This seems quite anomalous.

ZEEMAN EFFECTS

Zeeman patterns of most of the lines included in Tables I and II have been measured. The magnet used produced a field of about 34000 gauss, and the lines were photographed in a Hilger E1 quartz spectrograph. In the region below λ2500 the dispersion is great enough to give trustworthy measurements of Zeeman separations; but, in the longer wave-lengths a rather large error may occur. The patterns, except in a few cases, are resolved only as triplets. In such cases the pattern predicted by the use of Landé's g-values has been reduced to a theoretical blend triplet by the following procedure. The intensities of the components of a complicated pattern follow a quadratic formula and in consequence the center of gravity will always be approximately 1/4 of the way from the strongest to the weakest component. For instance,

$$^3D_3-{}^3P_2\ \text{Z.E.}=(\bar{0},1,2)\bar{6},7,8,9,10\ /6\sim(0)7/6\sim(0)1.17.$$

I am indebted to Professor H. N. Russell for this useful suggestion.

The observed patterns and the calculated are both given in the wave-length Table IV at the end of this paper. The agreement is very good in the main and fixes without doubt the nature of the low ^3D, ^1D terms. In fact, all the lines of Table I show excellent agreement except those involving the terms a^3D_3' and a^1F_3. These two terms certainly have g-values which are neither 1 nor 4/3, the theoretical values. The observed patterns are, however, consistent with the sharing of the g-sum 7/3 between the two terms, the g of a^3D_3' being approximately 1.1 and of a^1F_3 approximately 1.2. From relative intensities of combinations, these two terms are also interchangeable. It is, therefore, impossible to differentiate between them and the designations given rest solely on their positions relative to the other terms a^3D_2 and a^3D_1. A parallel case occurs in the Cu arc spectrum, where a^4D_3' and a^2F_3 are apparently not differentiable.

The Zeeman patterns of the lines of Table II are satisfactory considering the smallness of the actual separations on the plates. They again show disagreement for the terms a^3D_3' and a^1F_3 discussed above. In Table IV the asterisks indicate those lines which involve the two terms in question.

There remain only comparatively weak lines of Cu(II) unclassified. A number of these are undoubtedly due to structures such as d^9d combining with d^9p. A number of individual levels have been found, but the lines are so weak and so poorly measured that in no case can the levels be classified with certainty. This material is therefore reserved for future publication.

The lowest term of the copper spark should be $^1S(d^{10})$. As has been pointed out above, it should lie about 22224 wave-numbers deeper than a^3D_3. The possible combinations are contained in $d^9p\rightarrow d^{10}$ and reduce to the following three only, because of the j-selection principle. They should lie within 1500 wave-numbers of the following positions.

$^1S-a^3P_1$	$\nu=68212$	$\lambda=1466$
$^1S-a^3D_1$	$\nu=73397$	$\lambda=1363$
$^1S-a^1P_1$	$\nu=73891$	$\lambda=1353$

Of these strong lines, the last should be the most intense.

One of the lowest states of the doubly ionized copper atom Cu III should be a ^2D term which arises from the structure d^9. The addition of an s-electron gives terms ^3D, ^1D (d^9s) which are undoubtedly the low terms of Table I and the high terms of Table II. The addition of a second s-electron yields terms ^4D, ^2D, $^2D(d^9s,\ s)$; or, when the two s-electrons both occupy 4_1 orbits (d^9s^2), a ^2D alone. Such terms are the c^4D, e^4D and m^2D of the atomic spectrum. It can be shown[9] that the series of component terms of $^4D(d^9s,\ s)$ should converge to different components of the spark ^3D term. In particular, the series $^4D_4$ should converge to $^3D_3$ and $^4D_1$ to $^3D_1$. In other words, the difference $^4D_4-{}^4D_1$ should approach, at any rate in higher series members, the difference $^3D_3-{}^3D_1$. The following table shows that in fact this difference $^4D_4-{}^4D_1$ is already in the first series member practically equal to $^3D_3-{}^3D_1$. The evidence is very strong that the same difference also persists into the spectrum Cu III where it should be $^2D_3-{}^2D_2(d^9)$.

Cu(I)	d^9s^2	$m^2D_3-m^2D_2=2042.9$	Cu(II)	d^9s	$a^3D_3-a^3D_1=2069.7$
	d^9s,s	$c^4D_4-c^4D_1=2069.0$		d^9,s	$b^3D_3-b^3D_1=2069.6$
	d^9s,s	$e^4D_4-e^4D_1=2069.6$	Cu(III)	d^9	$^2D_3-{}^2D_2=2069.6$?

The remarkable agreement of the separations in this case and of the similar terms in the spectra of Ni(I) and Pd(I) given below, is predicted by the theory recently outlined by Slater.[10]

The following approximate agreements of arc and spark separations are also significant. The arc terms belong to the group which arises from the structure $d^9s\ d$; the spark term is the lowest ^3D.

Cu(I)	$d^4G_6-d^4G_5=848.1$	$d^4G_5-d^4G_3=1220.0$
	$d^4F_5-d^4F_4=802.6$	$d^4F_4-d^4F_2=1223.4$
	$d^4D_4-d^4D_3=798.8$	
	$d^4P_3-d^4P_2=749.0$	
Cu(II)	$a^3D_3-a^3D_2=918.5$	$a^3D_2-a^3D_1=1151.2$

The ^4G term used above is the alternative given in the author's paper[2] at the foot of page 459.

In addition to the above excellent agreement of separations, there is the fact that $^4G_4-{}^4G_3$, $^4F_3-{}^4F_2$, $^4P_2-{}^4P_1$ are all small, fulfilling the theoretical prediction that each of these pairs of terms should have a single limit. For bringing to my notice all the above agreements of separation and for the prediction from them of the spark intervals I am indebted to O. Laporte.

The spectra of Ni(I) and Pd(I) should be similar to that of Cu(II). Pd(I) does in fact possess two sets of terms corresponding in detail to the high and low ^3D, ^1D sets in Cu(II). The first set is as given by

[9] Hund, Zeits. f. Physik **34**, 296 (1925).

[10] Slater, Phys. Rev. **28**, 291 (1926).

Table III

Corresponding terms in spectra of Cu(II), Ni(I) and Pd(I). Series limits and ionization potentials.

	j	Cu(II) Terms	Cu(II) $\Delta\nu$	Cu(II) $\Delta\nu$(sum)	Ni(I) Terms	Ni(I) $\Delta\nu$	Ni(I) $\Delta\nu$ (sum)	Pd(I) Terms	Pd(I) $\Delta\nu$	Pd(I) $\Delta\nu$(sum)
^3D	3	0.0	918.5		204.8	675.0		6564.0	1191.0	
(d^9s)	2	918.5	1151.2	2069.7	879.8	833.3	1508.3	7755.0	2338.9	3529.9
	1	2069.7	2266.0		1713.1	1696.8		10093.9	1627.8	
^1D	2	4335.7			3409.9			11721.7		
^3D	3	86083.7	320.9		42605.8	184.1		48804.2	215.3	
(d^9, s)	2	86404.6	1748.7	2069.6	42789.9	1322.2	1506.3	49019.5	3316.8	3532.1
	1	88153.3	281.7		44112.1	150.4		52336.3	151.4	
^1D	2	88435.0			44262.5			52487.7		
Limits of		Cu(III) (d^9)			Ni(II) (d^9)			Pd(II) (d^9)		
^3D	3	144388		$^2D_3$	62944		$^2D_3$	69106		$^2D_3$
	2	144502		2069	63017		1505	69099		3533
	1	146457		$^2D_2$	64449		$^2D_2$	72639		$^2D_2$
^1D	2	146048			64247			72452		
Ionization potentials		17.8 volts			7.8 volts			8.5 volts		

McLennan and Smith[11]; but, in the high set the $^3D_2$ and $^1D_2$ have been interchanged. In the above paper this set of levels is arranged so that ^3D is partially inverted, though the intensity relations agree equally well with the present arrangement. Moreover, it is now brought into perfect accord with the similar terms in both Cu(II) and Ni(I). The two sets of ^3D, ^1D of Ni(I) are contained in Bechert and Sommer's[12] paper. They were picked as members of a series by Hund.[1]

The corresponding terms of the three spectra are given opposite each other in Table III. The most striking similarity is found in the interval $^3D_3-{}^3D_1$. In Cu(II), this interval changes when we pass from the low ^3D to the high ^3D, by only 0.1 wave-numbers, a change which is quite within the experimental error. In Ni(I) the corresponding change is -2.0 and in Pd(I), $+2.2$ wave-numbers. The $^3D_2$ and $^1D_2$ terms are placed in relatively the same positions in all three spectra. The ^3D intervals are all reversed from the 'normal' order, i.e., $^3D_3-{}^3D_2<{}^3D_2-{}^3D_1$.

The series of component levels of ^3D and $^1D(d^9s)$ must converge to the two components of the term $^2D(d^9)$ of the next higher ion. It can be shown (Hund[9]) that the limits should be as follows: $^3D_3$ and $^1D_2$ converge to $^2D_3$; and $^3D_2$ and $^3D_1$ to $^2D_2$.

At the foot of Table III are given the series limits calculated from the two sets of levels for each of the three spectra. The ionization potentials are obtained from the $^3D_3$ limits. In the case of Cu II the potential given is for the removal of the s-electron from the structure d^9s. The ionization from d^{10} to d^9 would require approximately 20.5 volts, the difference of 2.7 volts being calculated from the term difference $^1S-{}^3D_3$.

It has been pointed out that the extreme separation of the ^3D terms ($^3D_3-{}^3D_1$) is almost constant in each of the spectra. This fact, and the behavior of the extreme terms in analogous cases in other spectra, makes possible a reasonable certainty that the separation of the calculated limits for these levels will agree closely with the actual separation. For example, the analogous ^4D terms in Cu(I) give almost exact agreement of calculated and experimental limit separations.

The calculation of limits from only two series members in such cases as $^3D_2$ and $^1D_2$ must necessarily give much less certain results, and conclusions drawn from such calculations must require confirmation. An extreme case is the series of ms^3P terms in lead.[13] Nevertheless, there is a peculiarity of the calculated limits in these three spectra which is at least noteworthy. That is, the exact agreement of the calculated limits for the component series $^3D_3$ and $^3D_2$; and the only slightly less

[11] McLennan and Smith, Roy. Soc. Proc. **112A,** 110 (1926).
[12] Bechert and Sommer, Ann. d. Physik **77,** 351 (1925).
[13] Gieseler and Grotrian, Zeits. f. Physik **39,** 377 (1926).

TABLE IV

Wave-lengths and classification of spark lines of Cu.

λ	Auth.	Int.	ν	Comb.	Z. E. (obs.)	Z. E. (calc.) Blend
2884.38	H	1	34659.5	$a^1D_2' - b^3D_3$		
2877.89	H	5	34737.5	$a^1P_1 - b^3D_2$	(0)1.19	(0)1.25
2857.9	Ex	0	34980.5	$a^1D_2' - b^3D_2$		
2837.56	H	4	35231.2	$a^3D_1' - b^3D_2$	(0)1.48	(0)1.5
2769.85	H	6	36092.4	$a^1F_3 - b^3D_3$	(0)1.22	(.84)1.16*
2745.43	H	5	36413.4	$a^1F_3 - b^3D_2$	(0)1.31	(0) .83*
2739.9	Ex	1	36486.9	$a^1P_1 - b^3D_1$		
2737.5	Ex	1	36518.9	$a^3D_2' - b^3D_3$		
2721.84	H	5	36729.0	$a^1D_2' - b^3D_1$	(0)1.31	(0)1.25
2718.96	H	6	36767.9	$a^1P_1 - b^1D_2$	(0)1.04	(0)1.00
2713.66	H	7	36839.7	$a^3D_2' - b^3D_2$	(0)1.02	(0)1.17
2703.34	H	6	36980.2	$a^3D_1' - b^3D_1$	(0) .47	(0) .50
2701.12	H	7	37010.7	$a^1D_2' - b^1D_2$	(0)1.02	(0)1.00
2689.46	H	7	37171.2	$a^3D_3' - b^3D_3$	(.57)1.17	(0)1.33*
2666.44	H	3	37492.1	$a^3D_3' - b^3D_2$	(0) .99	(0)1.50*
2620.78	Ex	0	38145.2	$a^3F_2 - b^3D_3$		
2600.43	H	6	38443.7	$a^1F_3 - b^1D_2$	(0)1.30	(0)1.00*
2598.96	H	5	38465.4	$a^3F_2 - b^3D_2$	(.82) .89	(.87) .92
2590.68	H	4	38588.4	$a^3D_2' - b^3D_1$	(0)1.40	(0)1.50
2571.91	H	0	38870.0	$a^3D_2' - b^1D_2$		
2544.96	H	10	39281.6	$a^3F_4 - b^3D_3$	(0)1.11	(0)1.13
2529.48	H	6	39521.9	$a^3D_3' - b^1D_2$	(0)1.03	(0)1.66*
2526.73	H	4	39565.0	$a^3F_3 - b^3D_3$	(.67)1.12	(.62)1.21
2506.41	H	8	39885.5	$a^3F_3 - b^3D_2$	(0) .98	(0)1.00
2489.64	H	7	40154.3	$a^1D_2 - a^3P_2$	(.86)1.21	(.75)1.25
2485.95	H	6	40213.9	$a^3F_2 - b^3D_1$	(0) .72	(0) .75
2473.47	H	5	40416.8	$a^3P_1 - b^3D_2$	(0) .83	(0)1.0
2468.58	H	1	40496.9	$a^3F_2 - b^1D_2$		
2424.56	H	1	41232.0	$a^3P_0 - b^3D_1$		
2403.47	H	4	41593.8	$a^3P_2 - b^3D_3$	(0)1.08	(0)1.17
2400.10	H	2	41652.2	$a^1D_2 - a^3P_1$	(0) .64	(0) .75
2385.06	H	0	41914.8	$a^3P_2 - b^3D_2$		
			5.5	$a^3F_3 - b^1D_2$		
2370.88	H	0	42165.5	$a^3P_1 - b^3D_1$		
2369.88	H	6	42183.3	$a^1D_2 - a^3F_3$	(0)1.12	(0)1.17
2356.65	Calc	2	42420.2	$a^3D_1 - a^3P_2$	$(\bar{0}, .9)1.45, \bar{2}.\overline{49}$	$\frac{(\bar{0}, 2)1, 3, \bar{5}}{2}$
2355.15	"	0	42447.2	$a^3P_1 - b^1D_2$		
2294.374	W	5	43571.4	$a^3D_2 - a^3P_2$	(.66)1.37	(.59)1.33
2292.68	Calc	0	43603.6	$a^1D_2 - a^3F_2$		
2276.261	W.M	5	43918.1	$a^3D_1 - a^3P_1$	(1.0).48, 1.52	$\frac{(2)1, 3}{2}$
2274.86	Calc	0	43945.1	$a^3P_2 - b^1D_2$		
2247.003	W	10	44489.9	$a^3D_3 - a^3P_2$	(0)1.15	(0)1.17
2242.621	W.M	9	44576.8	$a^1D_2 - a^3D_3'$	(0)1.16	(0)1.66*
2228.88	Calc	5	44851.5	$a^3D_1 - a^3P_0$	(0) .49	(0).50
2218.107	M	8	45069.4	$a^3D_2 - a^3P_1$	(0) .86	(0)1.00
2210.27	Calc	7	45229.2	$a^1D_2 - a^3D_2'$	(0) .96	(0)1.04
2192.27	"	10	45600.6	$a^3D_2 - a^3F_3$	(0) .96	(0)1.00
2189.631	M	6	45655.6	$a^1D_2 - a^1F_3$	(0)1.50	(0)1.00*
2179.41	Calc	8	45869.6	$a^3D_1 - a^3F_2$	(0) .80	(0) .75
2148.98	"	4	46519.1	$a^3D_3 - a^3F_3$	(.79)1.16	(.63)1.21
2135.98	"	10	46802.1	$a^3D_3 - a^3F_4$	(0)1.08	(0)1.12
2134.36	"	4	46837.6	$a^1D_2 - a^3D_1'$	(0)1.11?	(0)1.25

λ	Auth.	Int.	ν	Comb.	Z. E. (obs.)	Z. E. (calc.) Blend
2125.047	M	4	47020.8	$a^3D_2-a^3F_2$	(.82) .89	(.88) .92
2122.98	Calc	5	47088.6	$a^1D_2-a^1D_2'$	(0)1.05	(0)1.00
2112.09	"	5	47331.4	$a^1D_2-a^1P_1$	(0)1.02	(0)1.00
2104.81	"	3	47495.0	$a^3D_1-a^3D_2'$	(0)1.34	(0)1.5
2085.30	"	3	47939.3	$a^3D_3-a^3F_2$	(0)2.37†	(0)2.0
2054.99	"	8	48646.4	$a^3D_2-a^3D_2'$	(0)1.09	(0)1.17
2043.81	"	8	48912.5	$a^3D_3-a^3D_3'$	(.60)1.06	(0)1.33*
2037.13	"	6	49072.8	$a^3D_2-a^1F_3$	(0)1.22	(0) .84*
2035.85	"	7	49103.6	$a^3D_1-a^3D_1'$	(0) .48	(0) .50
2025.50	"	5	49354.6	$a^3D_1-a^1D_2'$	(0)1.29	(0)1.25
2016.90	"	1	49564.9	$a^3D_3-a^3D_2'$		
2015.58	"	1	49597.4	$a^3D_1-a^1P_1$		
λ (Vac)						
2000.348	"	7	49991.3	$a^3D_3-a^1F_3$	(0)1.08	(.84)1.16*
1989.860	"	2	50254.8	$a^3D_2-a^3D_1'$		
1979.971	"	2	50505.8	$a^3D_2-a^1D_2'$	(0)1.01	(.25)1.08
1970.497	"	0	50748.6	$a^3D_2-a^1P_1$		
1944.606	"	2	51424.3	$a^3D_3-a^1D_2'$		

† Outside of wide pattern.
* Lines involving a^3D_3' or a^1F_3.
H—Hasbach, Kayser & Konen. Vol. VII.
Ex—Exner and Haschek, " " "
M—Mitra, Ann. d. physique **19**, 315 (1923).
W—Wolfsohn, Ann. d. physik **80**, 415 (1926).

exact agreement for $^3D_1$ and $^1D_2$, contrary to the theory. The following diagram compares the theoretical prediction and the apparent result.

Theoretical limits	Apparent limits
$^3D_3, {}^1D_2 \rightarrow {}^2D_3$	$^3D_3, {}^3D_2 \rightarrow {}^2D_3$
$^3D_2, {}^3D_1 \rightarrow {}^2D_2$	$^3D_1, {}^1D_2 \rightarrow {}^2D_2$

It is remarkable that the apparent limits of $^3D_2$ and $^1D_2$ are exactly reversed from their expected positions, i.e., the deviations from the theoretical positions are closely $\mp({}^2D_3-{}^2D_2)$. In other words, there would be excellent agreement if the designations of $^3D_2$ and $^1D_2$ could be interchanged. This, however, is definitely prohibited by Zeeman effects and intensities of combinations in Cu II, and, therefore, by analogy, in the other spectra.

The same type of peculiarity of convergence is evident in the following case of the ^4D terms of Cu(I). The limits of the extreme terms agree exactly with the experimental limits. The $^4D_2$ term, however, instead of converging with $^4D_1$ to $^3D_1$ diverges apparently to $^3D_2$, as is evident from the separations given.

Limits		Δν		Δν
$^4D_4$	22224			
			$^3D_3$	
$^4D_3$	22428	899		918
			$^3D_2$	
$^4D_2$	23123			1151
		1170	$^3D_1$	
$^4D_1$	24293			

Such peculiarities may be coincidence. They would then be merely evidence of the same disturbing forces in all three spectra. This would not be surprising, since the structures involved are the same. The discovery of higher series members should remove any doubt there may be in the interpretation of these points.

The author has the greatest pleasure in thanking Dr. H. N. Russell for his very important assistance in the preparation of this paper.

Palmer Physical Laboratory,
Princeton, New Jersey.
December 10, 1926.