AN EXTENSION OF THE SPARK SPECTRUM OF COPPER, Cu II

By Gerald Kruger
Cornell University, Ithaca, N. Y.

(Received July 13, 1929)

Abstract

The ground term of Cu II is a $3d^{10}\ {}^1S_0$. The next higher terms are $3d^9\ 4s\ {}^1D\ {}^3D$ and still higher are found the terms $3d^94p\ {}^1(P^\circ D^\circ F^\circ)\ {}^3(P^\circ D^\circ F^\circ)$. These facts were already known from the work of other investigators. With a Schüler lamp of the hollow cathode type as a source, the spectrum of copper was photographed by means of a vacuum spectrograph which was so designed that the region 0A—2600A could be photographed on one plate. Two higher members of the $3d^9ns\ {}^1D\ {}^3D$ series have been found, thus giving in all four members of both series, from which the limits of the series have been calculated. The calculations show that the $3d^{10}\ {}^1S_0$ level lies 163, 634.2 cm^{-1} below the $3d^9\ {}^2D_{5/2}$ of Cu III from which the ionization potential of Cu II is computed to be 20.2 volts. This places the first members of the $3d^9ns\ {}^3D_{3,2,1}$ series at 141,709.2 cm^{-1}, 140,790.7 cm^{-1} and 139,639.5 cm^{-1} respectively. Higher members of the $3d^9np\ {}^1(P^\circ D^\circ F^\circ)\ {}^3(P^\circ D^\circ F^\circ)$ series have also been identified, thus making it possible to confirm Hund's predictions concerning the limits which the various series members approach.

Introduction

The first two terms of the $3d^9ns\ {}^1D{}^3D$ series and the first term of the $3d^9np\ {}^1(P^\circ D^\circ F^\circ){}^3(P^\circ D^\circ F^\circ)$ series of the Cu II spectrum have been reported by Shenstone.[1] From these data no accurate calculation of the series limits could be made, and therefore no absolute energy level values could be assigned.

F. Hund[2] recently predicted which levels of the terms arising from the $3d^9ns$ and the $3d^9np$ electron configurations of Cu II should approach $3d^9\ {}^2D_{2\frac{1}{2}}$ or $3d^9\ {}^2D_{1\frac{1}{2}}$ of Cu III as a limit.

Since the previous work on Cu II was also insufficient to test Hund's prediction, it was the object of the present work not only to extend the above series so that accurate limits could be established but also to determine, if possible, whether the series approached the limits predicted by Hund.

The characteristics of the Schüler Lamp[3] are such that it should produce the type of spectrum necessary for the completion of this work and it was accordingly chosen as the light source.

The Spark Spectrum of Copper (Cu II)

According to the Hund theory of the production of atomic spectra it has been shown[1] that the first spark spectrum of copper has for its ground term $3d^{10}\ {}^1S_0$. The next higher terms are $3d^94s\ {}^1D{}^3D$, and still higher are found the

[1] Shenstone, Phys. Rev. **29**, 380 (1927).
[2] F. Hund, Zeits. f. Physik **52**, 601 (1929).
[3] Schüler, Zeits. f. Physik **35**, 323 (1926).

terms $3d^94p\ ^1(P^\circ D^\circ F^\circ)\ ^3(P^\circ D^\circ F^\circ)$. The $3d^{10}\ ^1S_0$ term was reported by Lang[4] to give combinations with $3d^94p\ ^3P^\circ_1$, $^3d^94p\ ^3D^\circ_1$ and $3d^94p\ ^1P^\circ_1$. As in the case of Ni I all of the above levels are inverted except the $3d^9np\ ^3F^\circ$ which is partially inverted. When the levels are inverted it has been shown by Hund[2] that the $3d^9ns\ ^1D_2{}^3\ D_1$ series should approach $3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III as a limit. The $3d^9ns\ ^3D_{2,3}$ series should approach $3d^9\ ^2D_{2\frac{1}{2}}$ of Cu III as a limit. Moreover, Hund predicts that the $3d^9np\ ^1P^\circ_1$, $^1D^\circ_2$, $^1F^\circ_3$, $^3P^\circ_{0,1,2}$ should all approach $3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III, while all six levels of $3d^9np\ ^3D^\circ$, $^3F^\circ$ should approach $3d^9\ ^2D_{2\frac{1}{2}}$ of Cu III as a limit.

A 1500 volt d.c. potential was applied between the anode and hollow copper cathode of the Schüler lamp, and the current limited to about 300 m.a. by a suitable external resistance and the resistance of the He, (varying with pressure) in the lamp. It was found in this work that a relatively high He pressure (about 4 mm) increased the intensity of the copper lines. This is not in agreement with the phenomena observed when using certain other metals as the cathode. For in the case of Ni, Al, and Ge it has been found that a low He pressure in the lamp was most favorable for the production of the spectrum in question. It may also be remarked that successful operation of a Schüler lamp necessitates a careful cleaning of the lamp by running a discharge in oxygen so that all impurities may be oxidized and pumped out.

A vacuum spectrograph designed according to Sawyer[5] was built for use with a 1.5 meter grating which was ruled by Anderson at the Mt. Wilson Laboratory and which had approximately 15,000 lines per inch. This gave a dispersion of about 11.2A per mm which was generally adequate for the work, but was not large enough to separate all the lines. The spectrograph was about 10 inches in diameter, so that it was possible to photograph the whole region from 0A to 2600A on one plate which was bent to a radius of curvature of 75 cm.

It was found that the copper spectrum was very easy to excite. Within two hours after a copper cathode had been put into the lamp a satisfactory copper spectrum was obtained. Four exposures were taken, the time of exposure varying from 10 hr to 18 hr. During the run the He gas was constantly purified by passing it through a liquid-air-cooled carbon trap and through a hot copper oxide trap the latter to remove traces of hydrogen gas.

The notation used in this paper is in accordance with that proposed in the "Report on Spectroscopic Notation," by H. N. Russell, A. G. Shenstone Louis A. Turner.[6] For this reason it is desirable to include a short explanation of the notation. When the sum of the l values for all the electrons in a configuration is even, none of the terms is primed. Thus, terms arising from the configuration $3d^{10}$ are expressed by $3d^{10}\ ^1S_0$ and those from $3d^94s$ are expressed by $3d^94s\ ^1D_2$ and $3d^94s\ ^3D_{3,2,1}$. When the sum of the l values for all electrons in the configuration is odd, this fact is denoted by a superscript to the right. Thus, terms arising from the configuration $3d^94p$ are

[4] Lang, Phys. Rev. **31,** 773 (1928).
[5] Sawyer, J.O.S.A. & R.S.I. **15,** 305 (1927).
[6] Russell, Shenstone and Turner, Phys. Rev. **33,** 900 (1929)

expressed by $3d^94p\ ^1(P^\circ_1\ D^\circ_2\ F^\circ_3)\ ^3(P^\circ_{2,1,0}\ D^\circ_{3,2,1}\ F^\circ_{4,3,2})$. In Table II, giving the term values the designation is as follows: $3d^9(^2D_{2\frac{1}{2}})\ 4s\ ^1D_2$. This means that the $^1D_2$ term arises from the $3d^94s$ configuration and approaches $^2D_{2\frac{1}{2}}$ of Cu III as a limit.

Measurements were made on all four plates. Lines of the He and H (it was not possible to remove all traces of H) arc and He spark were used as standards in the region 600A to 1600A. Above 1600A, known lines of Cu II which had been measured by Mitra were used. The final value given to a line is the average of all measurements made. Estimated relative intensities were gotten in the same way. A part of one plate (800A to 1200A) was run through a Moll microphotometer and the relative intensities of the lines in this region were compared with the estimated intensities obtained when the plates were measured. Good agreement was found in all but a few cases and these intensities were made to agree with the values given by the microphotometer.

The first part of the analysis consisted in determining the $3d^96s\ ^1D_2$, $^3D_{3,2,1}$, $3d^97s$, $^1D_2{}^3D_{3,2,1}$ levels. Since the intervals between the terms for $3d^94s\ ^1D^3D$, $3d^95s\ ^1D^3D$ and $3d^94p\ ^1(P^\circ D^\circ F^\circ)\ ^3(P^\circ D^\circ F^\circ)$ were known from Shenstone's work, it was possible to predict from the first two members of the series where the third and fourth members would be. Sixty lines were found which resulted from possible combinations between $3d^94p\ ^1(P^\circ D^\circ F^\circ)$, $^3(P^\circ D^\circ F^\circ)$ and $3d^96s\ ^1D^3D$, $3d^97s\ ^1D^3D$ terms. The $3d^96s\ ^3D_3-3d^96s\ ^3D_1$ separa-separation equals 2069.6 cm^{-1} and the $3d^97s\ ^3D_3-3d^97s\ ^3D_1$ separation is 2071.2 cm^{-1}. At the same tine the $\Delta\nu$ separations $^3D_3-{}^3D_2$ and $^3D_1-{}^1D_2$ are getting smaller for each successive term in the series. This agrees with Shenstone's[1] data and confirms Hund's[2] recent prediction that the $3d^9ns\ ^3D_{3,2}$ levels approach $3d^9\ ^2D_{2\frac{1}{2}}$ of Cu III while $3d^9ns\ ^1D_2\ ^3D_3$ approach $3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III.

Some of the lines which were not found in the present set of data have been computed from the term values and are included in the parentheses in Table III. Line $3d^94p\ ^1P^\circ_1-3d^96s\ ^3D_1=62067.0\ cm^{-1}$ (cal) falls on a third order line $\nu=62070.9\ cm^{-1}$ of He I, $\lambda=537.12$A. Line $3d^94p\ ^1F^\circ_3-3d^97s\ ^1D_2=75014.3\ cm^{-1}$ falls together with line $3d^94p\ ^3F^\circ_2-3d^97s\ ^3D_2=75013.7\ cm^{-1}$. This line appears in the data with an intensity of 8 and is so recorded in the tables. However, it would be expected from our data that $3d^94p\ ^3F^\circ_2-3d^97s\ ^3D_2$ would have an intensity of about 4, so it would not be unreasonable to attribute the other 4 units of intensity to $3d^94p\ ^1F^\circ_3-3d^97s\ ^1D_2$. Line $3d^94p\ ^1D^\circ_2-3d^97s\ ^1D_2=73581.3\ cm^{-1}$ (cal) falls within 12.5 cm^{-1} of $3d^{10}\ ^1S_0-3d^94p\ ^1P^\circ_1=73593.8\ cm^{-1}$ (Int. 17), so it is suspected that $3d^94p\ ^1F^\circ_3-3d^94s\ ^1D_2$ is included in the line $\nu=73593.8\ cm^{-1}$ of the data.

Having once established the $3d^96s\ ^1D^3D$ and $3d^97s\ ^1D^3D$ terms, it was possible to compute the limits of the $3d^9ns\ ^1D^3D$ series and assign absolute term values to the levels, By carrying out the computation it was found that the best value for the $3d^94s\ ^3D_3$ term was 141709.2 cm^{-1}. This places the $3d^{10}\ ^1S_0$ at 163634.2 cm^{-1} from which the ionization potential of Cu II is computed to be equal to 20.2 volts.

The term values for all terms found are given in Table II. Table I gives the Rydberg denominators of characteristic terms of each series.

TABLE I. *Rydberg denominators.*

		$n=4$	5	6	7
	n^*	1.759980	2.809117	3.822282	4.828684
$3d^9ns$	$^3D_3$	141709.2	55625.5	30044.7	18825.9
	n^*	2.147390	3.047517	3.460066	
$3d^9np$	$^3F_3^\circ$	95190.1	47263.0	36664.4	
	n^*	2.174906	3.106328		
	$^3D_3^\circ$	92796.7	45490.3		
	n^*	1.774222	2.816254	3.828378	4.835444
$3d^9ns$	$^1D_2$	139443.2	55343.9	29949.1	18773.3
	n^*	2.102597	3.102147	3.710623	
$3d^9np$	$^3P_2^\circ$	99289.0	45613.0	31880.1	
	n^*	2.163386	3.136019	4.009437	
	$^1F_3^\circ$	93787.6	44633.0	27306.5	
	n^*	2.182977	3.130609	3.986427	
	$^1P_1^\circ$	92111.8	44787.4	27621.4	

The second step in the analysis was an attempt to classify two groups of lines which were found to lie between 90000 cm^{-1} and 115000 cm^{-1}. Many of the frequency differences between the terms $3d^94s\ ^1D^3D$ were found between these lines. From this it is concluded that the lines under consideration must come from combinations between $3d^9np\ ^{1,3}(P^\circ D^\circ F^\circ)$ and $3d^94s\ ^{1,3}D$. Combinations with the next most probable electron configuration ($3d^94d$) would lie to longer wave-lengths and would have to combine with terms arising from the $3d^94p$ configuration, which would not give all the above separations.

The line $3d^94s\ ^3D_3 - 3d^96p\ ^3F^\circ_4$, $\nu = 105411.8$ cm^{-1}, gives a $\Delta\nu$ separation for $^3F^\circ_4 - {}^3F^\circ_3$ which seems rather large, for the separation which one would expect by comparison with the two lower series members is approximately 250 cm^{-1}. In this case the line would fall on the hydrogen line $\lambda = 949.73$A and this H line in the data does not have sufficient intensity, so that one could safelysay that $3d^94s\ ^3D_3 - 3d^96p\ ^3F^\circ_4$ coincided with it. Since $\nu = 105411.8$ cm^{-1} was the only other strong line in this region, it was assigned to the above transition.

Line $\nu = 98754.7$ cm^{-1} has an intensity of 8 in the data. This line was used twice and theintensitysplit. Line $\nu = 122857.7$ cm^{-1} ($3d^{10}\ ^1S_0 - 3d^95p^3\ D^\circ_1$) is 12.7 cm^{-1} from the computed value but since the standards used in this part of the spectrum were poor such an error may be allowable. Line $3d^{10}\ ^1S_0 - 3d^95p\ ^1P^\circ_1$, $\nu = 138003.4$, is 79.1 cm^{-1} from its computed value and is surely a questionable classification. These last two lines are the only ones classified in this paper where the discrepancy in frequency is large enough to justify comment.

The identifications involving transitions from $3d^95$, $6p$ to $3d^94s$ and $3d^{10}$ must necessarily be regarded as somewhat tentative until they are confirmed by the finding of predictable radiation frequencies between terms involving these higher configurations and those of $3d^95$, 6, $7s$. Some of these predicted lines will lie in the infra-red and may be very difficult to observe. Radiations arising from transitions $3d^95s-3d^96p$ and $3d^95p-3d^97s$, should lie within the region $\lambda=4400$A and $\lambda=3000$A and should, therefore, be reasonably easy to observe.

Curves showing the variation in the Rydberg denominator with successive terms are given in Fig. 1.

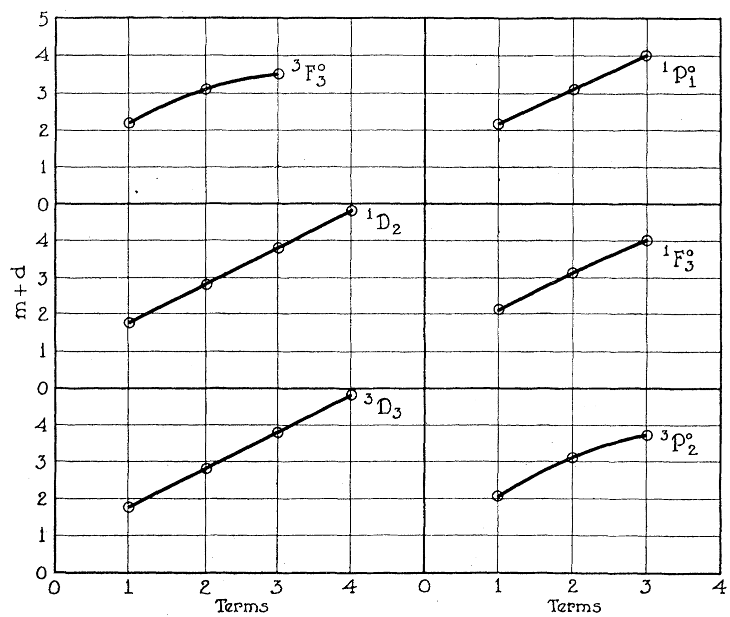

Fig. 1. Rydberg denominators for series of Cu II.

Figure 2a shows how regularly the members of the $3d^9ns\ ^3D$ series approach their respective limits.

Figure 2c shows the corresponding change in the $3d^9np\ ^3F^\circ$ series. In Figure 2b there is to be noted a peculiar spreading of the $3P^\circ$ terms in the second member of the series and a sharp contraction in the third member. The $3d^9np\ ^3D^\circ$ series members show a similar spreading in the second member, but since only two members are known a curve for the $3d^9np\ ^3D^\circ$ series was not plotted.

The $3d^94p\ ^3D^\circ$ terms are the lowest terms arising from this configuration. But the $3d^95p\ ^3D^\circ\ ^3P^\circ$ terms are interspaced and when the $3d^96p$ terms are reached the $3d^96p\ ^3P^\circ$ terms are above those of $3d^96p\ ^3D^\circ$.

This, together with the fact that the $3d^96p\ ^3P^\circ$ terms are closer together than either the $3d^94p\ ^3P^\circ$ or $3d^95p\ ^3P^\circ$ terms leads one to suspect that the $3d^9np\ ^3P^\circ$ approaches the limits $^3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III as Hund predicts.

Computations on the $3d^9np\ ^1F^\circ_3$ and $^1P^\circ_1$ show definitely that these two series approach $3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III according to the Hund prediction.

In like manner, since the $3d^9np\ ^3F^\circ$ has in the third member of the series become lowest, it might be suspected that $3d^9np\ ^3F^\circ$ approaches the $3d^9\ ^2D_{2\frac{1}{2}}$ of Cu III as a limit, which is also in accordance with Hund's prediction.

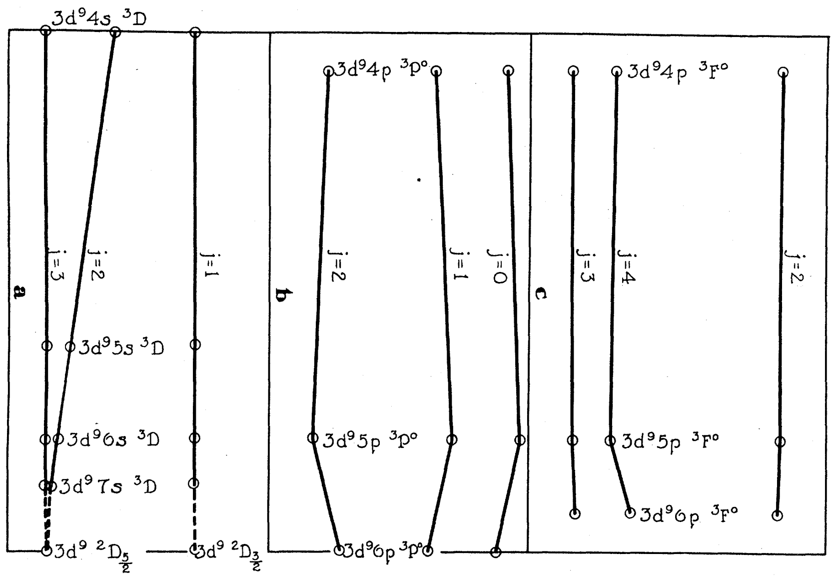

Fig. 2. Relative term separations for consecutive series members.

Table II is a complete list of all terms and term values. Column one gives the term, the electron configurations from which the term arises, and the limit which the term approaches. Column two gives the term values with respect to $3d^9\ ^2D_{2\frac{1}{2}}$ of Cu III, whether the term approaches this level as a limit or not. Column three gives only the term values with respect to $3d^9\ ^2D_{1\frac{1}{2}}$ of the term which approach $3d^9\ ^2D_{1\frac{1}{2}}$ of Cu III as a limit.

TABLE II. *Term values of singly ionized copper, Cu II.*

Term	Term values with respect to $3d^9\ ^2D_{2\frac{1}{2}}$ ν cm^{-1}	Term values with respect to their own limit $3d^9\ ^2D_{1\frac{1}{2}}$ ν cm^{-1}
$3d^{10}\ ^1S_0$	163634.2	
$3d^9(^2D_{2\frac{1}{2}})4s\ ^3D_3$	141709.2	
$3d^9(^2D_{2\frac{1}{2}})4s\ ^3D_2$	140790.7	
$3d^9(^2D_{1\frac{1}{2}})4s\ ^3D_1$	139639.5	141709.2
$3d^9(^2D_{1\frac{1}{2}})4s\ ^1D_2$	137373.5	139443.2
$3d^9(^2D_{1\frac{1}{2}})4p\ ^3P_2^\circ$	97219.3	99289.0
$3d^9(^2D_{1\frac{1}{2}})4p\ ^3P_1^\circ$	95721.4	97791.1
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3F_3^\circ$	95190.1	
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3F_4^\circ$	94907.1	
$3d^9(^2D_{1\frac{1}{2}})4p\ ^3P_0^\circ$	94788.0	96857.7
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3F_2^\circ$	93769.9	
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3D_3^\circ$	92796.7	
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3D_2^\circ$	92144.3	
$3d^9(^2D_{1\frac{1}{2}})4p\ ^1F_3^\circ$	91717.9	93787.6
$3d^9(^2D_{2\frac{1}{2}})4p\ ^3D_1^\circ$	90535.9	
$3d^9(^2D_{1\frac{1}{2}})4p\ ^1D_2^\circ$	90284.9	92354.6

TABLE II (*Continued*)

Term	Term values with respect to $3d^9\ ^2D_{2\frac{1}{2}}$ ν cm^{-1}	Term values with respect to their own limit $3d^9\ ^2D_{1\frac{1}{2}}$ ν cm^{-1}
$3d^9(^2D_{1\frac{1}{2}})4p\ ^1P_1^\circ$	90042.1	92111.8
$3d^9(^2D_{2\frac{1}{2}})5s\ ^3D_3$	55625.5	
$3d^9(^2D_{2\frac{1}{2}})5s\ ^3D_2$	55304.6	
$3d^9(^2D_{1\frac{1}{2}})5s\ ^3D_1$	53555.9	55625.6
$3d^9(^2D_{1\frac{1}{2}})5s\ ^1D_1$	53274.2	55343.9
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3F_3^\circ$	47263.0	
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3F_4^\circ$	46995.2	
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3F_2^\circ$	45844.1	
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3D_3^\circ$	45490.3	
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3D_2^\circ$	44596.8	
$3d^9(^2D_{1\frac{1}{2}})5p\ ^3P_2^\circ$	43543.3	45613.0
$3d^9(^2D_{1\frac{1}{2}})5p\ ^1P_1^\circ$	42717.7	44787.4
$3d^9)^2D_{1\frac{1}{2}})5p\ ^1F_3^\circ$	42563.3	44633.0
$3d^9(^2D_{1\frac{1}{2}})5p\ ^3P_1^\circ$	41806.0	43875.7
$3d^9(^2D_{2\frac{1}{2}})5p\ ^3D_1^\circ$	40888.6	
$3d^9(^2D_{1\frac{1}{2}})5p\ ^3P_0^\circ$	40884.8	42854.5
$3d^9(^2D_{2\frac{1}{2}})6p\ ^3F_3^\circ$	36664.4	
$3d^9(^2D_{2\frac{1}{2}})6p\ ^3F_4^\circ$	36297.4	
$3d^9(^2D_{2\frac{1}{2}})6p\ ^3F_2^\circ$	35268.7	
$3d^9(^2D_{2\frac{1}{2}})6s\ ^3D_3$	30044.7	
$3d^9(^2D_{2\frac{1}{2}})6s\ ^3D_2$	29910.8	
$3d^9(^2D_{1\frac{1}{2}})6p\ ^3P_2^\circ$	29810.4	31880.1
$3d^9(^2D_{1\frac{1}{2}})6p\ ^3P_1^\circ$	28503.4	30573.1
$3d^9(^2D_{1\frac{1}{2}})6s\ ^3D_1^\circ$	27975.1	30044.8
$3d^9(^2D_{1\frac{1}{2}})6s\ ^1D_2$	27879.4	29949.1
$3d^9(^2D_{1\frac{1}{2}})6p\ ^3P_0^\circ$	27582.1	29651.8
$3d^9(^2D_{1\frac{1}{2}})6p\ ^1P_1^\circ$	25551.7	27621.4
$3d^9(^2D_{1\frac{1}{2}})6p\ ^1F_3^\circ$	25236.8	27306.5
$3d^9(^2D_{2\frac{1}{2}})7s\ ^3D_3$	18825.9	
$3d^9(^2D_{2\frac{1}{2}})7s\ ^3D_2$	18756.3	
$3d^9(^2D_{1\frac{1}{2}})7s\ ^3D_1$	16754.7	18824.4
$3d^9(^2D_{1\frac{1}{2}})7s\ ^1D_2$	16703.6	18773.3

Table III gives all classified lines in the order of increasing frequencies and the assigned term combinations from which the line arises.

TABLE III. *Classified lines of copper II.*

Int.	λ vac.	ν cm^{-1}	Combination $3d^95p-3d^96s$
10	1663.01	60131.9	$^1P_1^\circ-{}^3D_2$
5	1660.02	60240.2	$^1D_2^\circ-{}^3D_3$
2	1656.35	60373.7	$^1D_2^\circ-{}^3D_2$
9	1649.44	60626.6	$^3D_1^\circ-{}^3D_2$
10	1621.39	61675.5	$^1F_3^\circ-{}^3D_3$
2	1617.94	61807.0	$^1F_3^\circ-{}^3D_2$
	(1611.16)	(62067.0)	$^1P_1^\circ-{}^3D_1$
1	1610.30	62100.2	$^3D_2^\circ-{}^3D_3$
4	1608.66	62163.5	$^1P_1^\circ-{}^1D_2$
9	1606.87	62232.8	$^3D_2^\circ-{}^3D_2$
3	1604.88	62310.0	$^1D_2^\circ-{}^3D_1$
9	1602.40	62406.4	$^1D_2^\circ-{}^1D_2$
9	1598.41	62562.2	$^3D_1^\circ-{}^3D_1$
	(1596.00)	(62656.5)	$^3D_1^\circ-{}^1D_2$
13	1593.56	62752.6	$^3D_3^\circ-{}^3D_3$
6	1590.19	62885.6	$^3D_3^\circ-{}^3D_2$
1	1569.21	63726.3	$^3F_2^\circ-{}^3D_3$
7	1566.45	63838.6	$^1F_3^\circ-{}^1D_2$

TABLE III (*Continued*)

Int.	λ vac.	ν cm^{-1}	Combination $3d^94p-3d^96p$
6	1565.94	63859.4	$^3F_2^\circ-{}^3D_2$
5	1558.38	64169.2	$^3D_2^\circ-{}^3D_1$
	(1556.05)	(64264.9)	$^3D_2^\circ-{}^1D_2$
15	1541.77	64860.5	$^3F_4^\circ-{}^3D_3$
5	1540.51	64913.6	$^3D_3^\circ-{}^1D_3$
8	1535.03	65145.3	$^3F_3^\circ-{}^3D_3$
15	1531.91	65278.0	$^3F_3^\circ-{}^3D_2$
6	1519.90	65793.8	$^3F_2^\circ-{}^3D_1$
6	1519.53	65809.8	$^3P_1^\circ-{}^3D_2$
1	1517.65	65891.3	$^3F_2^\circ-{}^1D_2$
6	1496.72	66812.8	$^3P_0^\circ-{}^3D_1$
12	1488.72	67171.8	$^3P_2^\circ-{}^3D_3$
1	1485.67	67309.7	$^3P_2^\circ-{}^3D_2$
1	1485.67	67309.7	$^3F_3^\circ-{}^1D_2$
2	1476.10	67746.1	$^3P_1^\circ-{}^3D_1$
2	1474.03	67841.2	$^3P_1^\circ-{}^1D_2$
	(1444.16)	(69244.2)	$^3P_2^\circ-{}^3D_1$
1	1442.11	69342.8	$^3P_2^\circ-{}^1D_2$
			$3d^94p-3d^97s$
1	1402.80	71286.0	$^1P_1^\circ-{}^3D_2$
0	1399.41	71458.7	$^1D_2^\circ-{}^3D_3$
1	1393.13	71780.8	$^3D_1^\circ-{}^3D_2$
5	1371.88	72892.7	$^1F_3^\circ-{}^3D_3$
	(1370.58)	(72961.6)	$^1F_3^\circ-{}^3D_2$
	(1364.49)	(73287.4)	$^1P_1^\circ-{}^3D_1$
	(1363.91)	(73318.4)	$^3D_2^\circ-{}^3D_3$
2	1363.54	73338.5	$^1P_1^\circ-{}^1D_2$
5	1362.61	73388.6	$^3D_2^\circ-{}^3D_2$
2	1359.94	73532.7	$^1D_2^\circ-{}^3D_1$
			$3d^{10}-3d^94p$
17	1358.81	73593.8	$^1S_0\ -{}^1P_1^\circ$
			$3d^94p-3d^97s$
	(1359.04)	(73581.3)	$^1D_2^\circ-{}^1D_2$
2	1355.35	73781.7	$^3D_1^\circ-{}^3D_1$
6	1351.88	73971.1	$^3D_3^\circ-{}^3D_3$
4	1350.61	74040.6	$^3D_3^\circ-{}^3D_2$
	(1334.33)	(74944.0)	$^3F_2^\circ-{}^3D_3$
8	1333.09	75013.7	$^3F_2^\circ-{}^3D_2$
8	1333.09	75013.7	$^1F_3^\circ-{}^1D_2$
2	1326.46	75388.6	$^3D_2^\circ-{}^3D_1$
1	1325.57	75439.2	$^3D_2^\circ-{}^1D_2$
16	1314.40	76080.3	$^3F_4^\circ-{}^3D_3$
	(1314.18)	(76093.1)	$^3D_3^\circ-{}^1D_2$
4	1309.51	76364.4	$^3F_3^\circ-{}^3D_3$
10	1308.35	76432.1	$^3F_3^\circ-{}^3D_2$
6	1299.30	76964.5	$^3P_1^\circ-{}^3D_2$
6	1298.47	77013.7	$^3F_2^\circ-{}^3D_1$
1	1297.59	77065.9	$^3F_2^\circ-{}^1D_2$
2	1281.49	78034.2	$^3P_0^\circ-{}^3D_1$
8	1275.62	78393.3	$^3P_2^\circ-{}^3D_3$
	(1274.48)	(78463.0)	$^3P_2^\circ-{}^3D_2$
0	1274.06	78489.2	$^3F_3^\circ-{}^1D_2$
2	1266.38	78965.2	$^3P_1^\circ-{}^3D_1$
3	1265.53	79018.3	$^3P_1^\circ-{}^1D_2$
	(1242.78)	(80464.6)	$^3P_2^\circ-{}^3D_1$
1	1242.01	80514.6	$^3P_2^\circ-{}^1D_2$
			$3d^94s-3d^95p$

Int.	TABLE III (*Continued*)		Combination
	λ vac.	ν cm^{-1}	$3d^94p-3d^96p$
2	1088.39	91878.8	$^1D_2-^3D_3^\circ$
5	1069.18	93529.6	$^3D_2-^3F_3^\circ$
2	1066.15	93795.4	$^3D_1-^3F_2^\circ$
6	1065.74	93831.5	$^1D_2-^3P_2^\circ$
2	1058.82	94444.8	$^3D_3-^3F_3^\circ$
6	1055.81	94714.0	$^3D_3-^3F_4^\circ$
12	1054.67	94816.4	$^1D_2-^1F_3^\circ$
4	1052.16	95042.6	$^3D_1-^3D_2^\circ$
2	1049.28	95303.4	$^3D_2-^3D_3^\circ$
5	1039.56	96194.5	$^3D_2-^3D_2^\circ$
5	1039.28	96220.5	$^3D_3-^3D_3^\circ$
10	1036.45	96483.2	$^1D_2-^3D_1^\circ$
1	1031.76	96921.8	$^3D_1-^1P_1^\circ$
1	1029.74	97111.9	$^3D_3-^3D_2^\circ$
4	1028.31	97246.9	$^3D_2-^3P_2^\circ$
1	1022.11	97836.8	$^3D_1-^3P_1^\circ$
3	1019.65	98072.9	$^3D_2-^1P_1^\circ$
11	1018.69	98165.3	$^3D_3-^3P_2^\circ$
3	1018.04	98228.0	$^3D_2-^1F_3^\circ$
8	1012.61	98754.7	$^3D_1-^3P_0^\circ$
7	1010.29	98981.5	$^3D_2-^3P_1^\circ$
7	1008.62	99145.4	$^3D_3-^1F_3^\circ$
3	1001.00	99900.1	$^3D_2-^3D_1^\circ$
			$3d^94s-3d^96p$
9	992.95	100710.0	$^1D_2-^3F_3^\circ$
1	979.41	102102.3	$^1D_2-^3F_2^\circ$
8	960.38	104125.5	$^3D_2-^3F_3^\circ$
9	958.13	104370.0	$^3D_1-^3F_2^\circ$
6	948.66	105411.8	$^3D_3-^3F_4^\circ$
1	947.68	105520.9	$^3D_2-^3F_2^\circ$
3	939.47	106443.0	$^3D_3-^3F_2^\circ$
3	910.48	109832.2	$^3D_1-^3P_2^\circ$
9	901.10	110975.5	$^3D_2-^3P_2^\circ$
9	899.77	111139.5	$^3D_1-^3P_1^\circ$
2	894.26	111824.3	$^1D_2-^1P_1^\circ$
16	893.65	111900.6	$^3D_3-^3P_2^\circ$
9	892.40	112057.4	$^3D_1-^3P_0^\circ$
12	890.60	112283.9	$^3D_2-^3P_1^\circ$
2	867.78	115236.6	$^3D_2-^1P_1^\circ$
5	865.42	115550.8	$^3D_2-^1F_3^\circ$
			$3d^{10}-3d^95p$
10	827.05	120911.7	$^1S_0-^1P_1^\circ$
9	823.98	122857.7	$^1S_0-^3D_1^\circ$
			$3d^{10}-3d^96p$
2	724.62	138003.4	$^1S_0-^1P_1^\circ$

A line $3d^94s\ ^3D_2-3d^94p\ ^3D^\circ{}_3$, $\nu=47994.0$ cm^{-1}, which Shenstone did not find has been found in the present study with intensity 2.

Values of α and μ, constants in the Ritz term formula, have been computed so that the formula which represents the $3d^9ns\ ^3D_3$ series becomes

$$T_n=\frac{4R}{[n+\mu+\alpha(T_n)]^2}$$

where n takes on integer values, and has the same value as n in the electron configurations

$$\mu=-2.1606515 \quad \alpha=-5.52\times10^{-7}.$$

The ionization potential of Cu I is known to be 7. 7 volts, and from the present data the I. P. of Cu II is found to be 20.2 volts. This means that 27.9 volts would be necessary for complete ionization of Cu II and since in the present case the energy available from the He ion is only 24.5 volts, it would be expected that complete ionization of Cu II would not occur. This is found to be true. In the present work the highest term found in Cu II is $\nu=16703.6$ cm^{-1}. The frequency difference between this value and the value of the lowest term of Cu II is 146930.6 cm^{-1} which corresponds to 18.1 volts. This means that the light source is supplying at least 25.8 volts for use in producing the spectra, and since the He ion will supply only 24.5 volts, 1.3 volts must be accounted for in some other way.

Even though the largest potential fall occurs in the region of the dark space which surrounds the negative glow, it seems probable that the potential fall across the negative glow should be at least of the order of magnitude of several volts, (i.e. 4 or 5 volts). Under these conditions some of the kinetic energy, which the He ion acquires upon being accelerated through the potential fall of the negative glow, might be transferred to the Cu atom by collision, thus increasing the amount of energy available for exciting the Cu atom to more than the 24.5 volts which the He ion supplies upon recombining with an electron. The author believes that it is at least plausible to assume that the extra 1.3 volts mentioned above comes from the transfer of mechanical kinetic energy to atomic energy of excitation.

The limit of available energy is shown very nicely in the spectrum by the distribution of the line intensities. In most cases the intensity of the lines of the spectrum falls off rapidly, and the reason that higher members of a series are not observed is that the intensity is too small. In this case, however, the intensity did not fall off rapidly, and in the case of the $3d^9np\ ^3(P^\circ F^\circ)$ to $3d^94s\ ^3D$ combinations the lines resulting from the $3d^96p\ ^3(P^\circ F^\circ)$ to $3d^94s\ ^3D$ combinations were stronger than the lines $3d^95p\ ^3(P^\circ F^\circ)$ to $3d^94s\ ^3D$. This indicates that the failure to observe the lines was not due to the usual progressive falling off in the intensities but rather to the fact that there was not enough available energy sufficiently to excite the atom so that it would radiate these lines. A similar condition exists for the series of lines

$$3d^94p\ ^1(P^oD^oF^o)^3(P^oD^oF^o)-3d^9ns\ ^1D^3D.$$

The author wishes to take this opportunity to express his appreciation and indebtedness to Professor R. C. Gibbs for his valuable advice and criticism during the period of this investigation.