The Third Spectrum of Copper (CuIII)

A. G. SHENSTONE AND L. WILETS*
Princeton University, Princeton, New Jersey
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An analysis of the second spark spectrum of copper is given. The identified levels include all those due to $3d^9$, $3d^84s$, $3d^84p$ except the ^2S and ^2P based on $3d^8\ ^1S$. The six levels $3d^8(^3F)5s\ ^4F$, ^2F have been found and allow the calculation of an I. P. of 37.08 volts. A number of levels of $3d^84d$ are present also, but $3d^74s^2$, which should be lower, has not been found.

A PARTIAL analysis of the second spark spectrum of copper (CuIII) was made by Gibbs and Vieweg in 1929. It was published in abstract only,[1] but the details were communicated to one of us in 1932. Nothing more was done until the fall of 1949, when it seemed to us that the analysis should be complated before the *Atomic Energy States*, which is being published by the Bureau of Standards, had reached that point in the periodic table.

Two other partial analyses of CuIII have been published. With the first of these, made by Rao,[2] the present analysis is in complete disagreement. The second analysis, put forward tentatively by L. and E. Bloch,[3] classified a number of lines correctly and identified several significant differences. An unfortunate error in the difference between the leading levels of the low ^4F led the authors astray, so that the analysis is, on the whole, incorrect.

TABLE I. Even levels of CuIII.

$3d^9$	$a^2D_{2\frac{1}{2}}$	0.0
$3d^9$	$a^2D_{1\frac{1}{2}}$	2071.8
$3d^8(^3F_4)4s$	$a^4F_{4\frac{1}{2}}$	60804.9
$(^3F_4)4s$	$a^4F_{3\frac{1}{2}}$	62065.0
$(^3F_3)4s$	$a^4F_{2\frac{1}{2}}$	63143.6
$(^3F_2)4s$	$a^4F_{1\frac{1}{2}}$	63886.3
$(^3F_3)4s$	$a^2F_{3\frac{1}{2}}$	67016.6
$(^3F_2)4s$	$a^2F_{2\frac{1}{2}}$	68963.6
$(^1D)4s$	$b^2D_{2\frac{1}{2}}$	77967.6
$(^1D)4s$	$b^2D_{1\frac{1}{2}}$	78779.4
$(^3P)4s$	$a^4P_{1\frac{1}{2}}$	80305.2
$(^3P)4s$	$a^4P_{\frac{1}{2}}$	80422.8
$(^3P)4s$	$a^4P_{2\frac{1}{2}}$	80551.5
$(^3P)4s$	$a^2P_{1\frac{1}{2}}$	85446.4
$(^3P)4s$	$a^2P_{\frac{1}{2}}$	86133.0
$(^1G)4s$	$a^2G_{4\frac{1}{2}}$	89017.7
$(^1G)4s$	$a^2G_{3\frac{1}{2}}$	89045.9
$(^3F_4)5s$	$e^4F_{4\frac{1}{2}}$	193369.0
$(^3F)4d$	1	193519.2
$(^3F)4d$	3	194031.6
$(^3F_4)5s$	$e^4F_{3\frac{1}{2}}$	194115.6
$(^3F)4d$	$e^4G_{5\frac{1}{2}}$	194330.8
$(^3F)4d$	4	195060.4
$(^3F)4d$	5	195342.2
$(^3F)4d$	6	195516.9
$(^3F_3)5s$	$e^4F_{2\frac{1}{2}}$	195553.2
$(^3F_3)5s$	$e^2F_{3\frac{1}{2}}$	195787.1
$(^3F_2)5s$	$e^4F_{1\frac{1}{2}}$	196444.9
$(^3F)4d$	7	196740.2?
$(^3F)4d$	8	197053.9
$(^3F)4d$	$f^2F_{3\frac{1}{2}}$	197373.9
$(^3F_2)5s$	$e^2F_{2\frac{1}{2}}$	197398.4
$(^3F)4d$	9	197898.7
$(^3F)4d$	10	198299.4
$3d^8\ ^3F_4$	(Limit)	299145

Our nearly complete analysis is based on new observations throughout the spectrum, and all of the lines of any appreciable intensity are now accounted for. The great majority of the lines fall between λ2000 and λ1500, although there is a very strong and important group extending from λ829 to λ672, comprising all the combinations of the lowest term $3d^9\ ^2D$. The spectrum photographs in the vacuum region were taken with our 2-meter 30,000-line per inch grating. The source was a condensed spark between copper electrodes about 5 mm apart in an atmosphere of pure helium at about 60-cm pressure. The gas was allowed to stream through the slit into the spectrograph where the pressure was about 4 mm. The grating is permanently adjusted with its normal at λ1500 and the source was placed so as to give a stigmatic image at about λ1000. The lines then showed, over the whole plate, sufficient stigmatism to allow a definite differentiation of the various stages of ionization. Arc lines hardly appeared at all; first spark lines were strong in the middle and tapered towards the ends; second spark lines were slightly polar and third spark lines were very polar. The times of exposure varied from 30 seconds to 45 minutes, making possible accurate measurement of all but the weakest lines. The standards of wavelength included the lines of copper,[4] nitrogen, oxygen, and carbon in various stages of ionization.[5] Although the spectrum CuII provides excellent standards when excited in the hollow cathode discharge, this is by no means true when the lines emanate from a spark. Only those lines which are due to transitions from intermediate levels to low levels maintain their positions, the others being displaced by several wave numbers towards longer wavelengths. In addition to the grating observations, a few lines of longer wavelength were measured on plates taken with a Hilger E-1 quartz instrument. The list of lines, Table IV, includes all identified and unidentified lines of reasonable intensity.

A discussion of the analysis of CuIII necessitates a

* AEC Predoctoral Fellow.
[1] R. C. Gibbs and A. M. Vieweg, Phys. Rev. **33**, 1092(A) (1929).
[2] B. V. R. Rao, Z. Physik **88**, 135 (1934).
[3] L. and E. Bloch, Compt. rend. **200**, 2017 (1935).
[4] A. G. Shenstone, Trans. Roy. Soc. (London) **235**, 195 (1936).
[5] J. C. Boyce and H. A. Robinson, J. Opt. Soc. Am. **26**, 653 (1936).

comparison with the iso-electronic spectra CoI[6] and NiII.[7] In this comparison, the following relation was used extensively. If the positions of the levels of a given configuration are plotted as ordinates, the successive ions being displaced by equal intervals on the axis of abscissas, then the points for a given level lie very nearly on a straight line. In the analysis of CuIII this relation was of very great assistance. It failed only in those cases where the additional configurations present in CoI complicate and perturb that spectrum. In such cases, the relation was indeed used to rectify a few of the assignments of configuration in CoI itself.

TABLE II. Odd levels of CuIII.

$3d^8(^3F)4p$	$z^4D_{3\frac{1}{2}}$	118864.3
$3d^8(^3F)4p$	$z^4D_{2\frac{1}{2}}$	120577.5
$3d^8(^3F)4p$	$z^4G_{4\frac{1}{2}}$	121337.2
$3d^8(^3F)4p$	$z^4G_{5\frac{1}{2}}$	121698.5
$3d^8(^3F)4p$	$z^4D_{1\frac{1}{2}}$	121863.7
$3d^8(^3F)4p$	$z^4G_{3\frac{1}{2}}$	122503.6
$3d^8(^3F)4p$	$z^4D_{\frac{1}{2}}$	122637.2
$3d^8(^3F)4p$	$z^4G_{2\frac{1}{2}}$	123440.2
$3d^8(^3F)4p$	$z^4F_{4\frac{1}{2}}$	123549.9
$3d^8(^3F)4p$	$z^2G_{4\frac{1}{2}}$	124442.5
$3d^8(^3F)4p$	$z^4F_{3\frac{1}{2}}$	124557.5
$3d^8(^3F)4p$	$z^4F_{2\frac{1}{2}}$	125381.8
$3d^8(^3F)4p$	$z^4F_{1\frac{1}{2}}$	125744.6
$3d^8(^3F)4p$	$z^2G_{3\frac{1}{2}}$	126093.8
$3d^8(^3F)4p$	$z^2F_{3\frac{1}{2}}$	126829.4
$3d^8(^3F)4p$	$z^2D_{2\frac{1}{2}}$	126891.9
$3d^8(^3F)4p$	$z^2D_{1\frac{1}{2}}$	128435.3
$3d^8(^3F)4p$	$z^2F_{2\frac{1}{2}}$	128679.4
$(^3P)4p$	$z^4P_{1\frac{1}{2}}$	136482.9
$(^3P)4p$	$z^4P_{2\frac{1}{2}}$	136607.3
$(^3P)4p$	$z^4P_{\frac{1}{2}}$	137041.0
$(^1D)4p$	$y^2F_{2\frac{1}{2}}$	138084.0
$(^1D)4p$	$y^2F_{3\frac{1}{2}}$	138982.0
$(^1D)4p$	$y^2D_{1\frac{1}{2}}$	138988.1
$(^1D)4p$	$z^2P_{\frac{1}{2}}$	139260.7
$(^1D)4p$	$y^2D_{2\frac{1}{2}}$	139756.6
$(^1D)4p$	$z^2P_{1\frac{1}{2}}$	140200.9
$(^3P)4p$	$y^4D_{2\frac{1}{2}}$	142426.3
$(^3P)4p$	$y^4D_{1\frac{1}{2}}$	142512.3
$(^3P)4p$	$y^4D_{\frac{1}{2}}$	142550.1
$(^3P)4p$	$y^4D_{3\frac{1}{2}}$	142819.7
$(^3P)4p$	$x^2D_{2\frac{1}{2}}$	144194.2
$(^3P)4p$	$x^2D_{1\frac{1}{2}}$	144875.2
$(^3P)4p$	$y^2P_{1\frac{1}{2}}$	145353.0
$(^1G)4p$	$z^2H_{4\frac{1}{2}}$	146533.6
$(^3P)4p$	$y^2P_{\frac{1}{2}}$	146675.9
$(^1G)4p$	$z^2H_{5\frac{1}{2}}$	147647.0
$(^3P)4p$	$z^2S_{\frac{1}{2}}$	147652.5
$(^1G)4p$	$x^2F_{3\frac{1}{2}}$	147805.9
$(^3P)4p$	$z^4S_{1\frac{1}{2}}$	147816.4
$(^1G)4p$	$x^2F_{2\frac{1}{2}}$	148662.9
$(^1G)4p$	$y^2G_{3\frac{1}{2}}$	153609.2
$(^1G)4p$	$y^2G_{4\frac{1}{2}}$	153808.4

The levels of CuIII are given in Tables I and II. The configurations represented in whole or part are $3d^9$, $3d^84s$, $3d^84p$, $3d^85s$, $3d^84d$, the last two being fragmentary. Those structures account for every strong line observed in the spectrum.

The multiplets due to the transition $3d^8(^3F)4s - 3d^8(^3F)4p$ were found by Vieweg, and the levels appear in our analysis with small numerical corrections. The only alteration in identification is the interchange of $^2D_{1\frac{1}{2}}$ and $^2F_{2\frac{1}{2}}$ in the odd structure. The low levels a^4F and a^2F are excellent examples of the rule given above. They plot as very nearly straight lines in the iso-electronic sequence. The terms z^4D, z^4F, z^4G also show the same behavior. In the z^4G, even a crossing of the straight lines occurs.

[6] Russell, King, and Moore, Phys. Rev. 58, 407 (1940).

[7] A. G. Shenstone, Trans. Roy. Soc. (London) 30, 255 (1927).

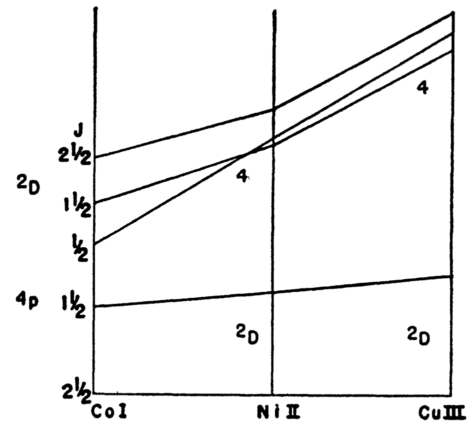

FIG. 1. ^4P and ^2D levels of $3d^84p$.

The even structure $3d^84s$ is complete except for the usual failure to find $3d^8(^1S)4s\,^2S$. A plot of this configuration in CoI, NiII, CuIII gives excellent correlation when one uses the assignment of terms in CoI given by G. Racah.[8] He shows conclusively that b^4P and not a^4P belongs to this configuration. The plot shows that a^2P in CoI is probably displaced towards lower values by its proximity to b^2P.

A difficulty arises when one tries to give names to the individual levels which comprise the group ^4P and ^2D. These five levels are shown in Fig. 1, in which the lowest has been taken as zero of ordinates in each case. In CoI there is little doubt that the lowest three levels are mainly of character ^4P and the upper two of character ^2D. In NiII which was analyzed previously to CoI, the upper three were chosen as ^4P. In point of fact, these levels share their characteristics to such an extent in both NiII and CuIII that there is very little evidence on which to make a choice. Such evidence as there is in CuIII, however, makes it more reasonable to select the higher levels as ^4P and the lower as ^2D as in NiII. Racah has done a rough calculation for us of the percentages of ^2D and ^4P character in the individual levels. His results indicate quite definitely that the

TABLE III. Reassignment of terms in CoI.

Term	Assignment: Russell	Assignment: Proposed
y^2H	$d^7s(^3H)4p$	$d^8(^1G)4p$
x^2H	$d^8(^1G)4p$	$d^7s(^3H)4p$
$y^2S_{\frac{1}{2}}$	$d^8(^3P)4p$	?
$w^2S_{\frac{1}{2}}$	?	$d^8(^3P)4p$
$y^4S_{1\frac{1}{2}}$	$d^8(^3P)4p$	$d^8(^3P)4p\,^2P_{1\frac{1}{2}}$
$x^4S_{1\frac{1}{2}}$	$d^7s(^3P)4p$	$d^8(^3P)4p$
y^4P	$d^8(^3P)4p$	$d^7s(^3P)4p$
x^4P	$d^7s(^3P)4p$	$d^8(^3P)4p$

[8] G. Racah, Phys. Rev. 61, 537 (1942).

TABLE IV. Lines of CuIII.

λ(Air)	Int.	ν	Classification
2822.05	1	35424.8	$a^2G_{4\frac12} - z^2G_{4\frac12}$
2812.96	5	35539.3	$a^2G_{4\frac12} - z^4F_{3\frac12}$
2698.46	3	37047.2	$a^2G_{3\frac12} - z^2G_{3\frac12}$
2696.39	6	37075.7	$a^2G_{4\frac12} - z^2G_{3\frac12}$
2643.92	40	37811.4	$a^2G_{4\frac12} - z^2F_{3\frac12}$
2641.54	8	37845.4	$a^2G_{3\frac12} - z^2D_{2\frac12}$
2609.31	50	38312.9	$a^4P_{2\frac12} - z^4D_{3\frac12}$
2522.36	25	39633.4	$a^2G_{3\frac12} - z^2F_{2\frac12}$
2497.58	20	40026.0	$a^4P_{2\frac12} - z^4D_{2\frac12}$
2482.34	30	40272.3	$a^4P_{1\frac12} - z^4D_{2\frac12}$
2438.47	25	40896.9	$b^2D_{2\frac12} - z^4D_{3\frac12}$
2412.32	15	41441.2	$a^4P_{\frac12} - z^4D_{1\frac12}$
2412.08	4	41445.4	$a^2P_{1\frac12} - z^2D_{2\frac12}$
2405.49	20	41558.9	$a^4P_{1\frac12} - z^4D_{1\frac12}$
2391.73	10	41798.0	$b^2D_{1\frac12} - z^4D_{2\frac12}$
2368.15	20	42214.1	$a^4P_{\frac12} - z^4D_{\frac12}$
2363.21	8	42302.3	$a^2P_{\frac12} - z^2D_{1\frac12}$
2361.56	10	42331.9	$a^4P_{1\frac12} - z^4D_{\frac12}$
2346.17	40	42609.5	$b^2D_{2\frac12} - z^4D_{2\frac12}$
2325.48	0	42988.6	$a^2P_{1\frac12} - z^2D_{1\frac12}$
2320.28	8	43084.9	$b^2D_{1\frac12} - z^4D_{1\frac12}$
2315.10	4	43181.3	
2312.31	5	43233.5	$a^2P_{1\frac12} - z^2F_{2\frac12}$
2279.45	2	43856.6	$b^2D_{1\frac12} - z^4D_{\frac12}$
2279.13	1	43862.8	
2277.43	4	43895.5	$b^2D_{2\frac12} - z^4D_{1\frac12}$
2271.69	5	44006.4	$a^4P_{2\frac12} - z^4F_{3\frac12}$
2128.59	0	46964.5	$b^2D_{1\frac12} - z^4F_{1\frac12}$
2077.81	2	48112.1	$b^2D_{1\frac12} - z^2D_{2\frac12}$
2077.07	0	48129.4	$a^4P_{1\frac12} - z^2D_{1\frac12}$
2043.37	5	48923.7	$b^2D_{2\frac12} - z^2D_{2\frac12}$
2000.78	3	49964.1	$a^2G_{4\frac12} - y^2F_{3\frac12}$

λ(Vac.)	Int.	ν	Classification
1928.715	2	51848.0	$a^2F_{3\frac12} - z^4D_{3\frac12}$
1920.653	1	52065.6	
1882.250	2	53127.9	$a^2P_{\frac12} - z^2P_{\frac12}$
1867.747	50	53540.4	$a^2F_{2\frac12} - z^4G_{3\frac12}$
1858.685	1	53801.5	$a^2G_{4\frac12} - y^4D_{3\frac12}$
1840.917	200	54320.8	$a^2F_{3\frac12} - z^4G_{4\frac12}$
1826.339	10	54754.3	$a^2P_{1\frac12} - z^2P_{1\frac12}$
1820.339	5	54934.8	
1798.761	5	55593.8	$a^2F_{2\frac12} - z^4F_{3\frac12}$
1787.902	1	55931.5	$a^4P_{2\frac12} - z^4P_{1\frac12}$
1783.935	5	56055.9	$a^4P_{2\frac12} - z^4P_{2\frac12}$
1783.799	20	56060.1	$a^4P_{\frac12} - z^4P_{1\frac12}$
1780.062	5	56177.8	$a^4P_{1\frac12} - z^4P_{1\frac12}$
1776.136	20	56302.0	$a^4P_{1\frac12} - z^4P_{2\frac12}$
1773.697	1	56379.4	$a^2P_{\frac12} - y^4D_{1\frac12}$
1772.478	2	56418.2	$a^2F_{2\frac12} - z^4F_{2\frac12}$ and $a^2P_{\frac12} - y^4D_{\frac12}$
1768.869	200	56533.3	$a^2F_{3\frac12} - z^4F_{4\frac12}$
1766.219	2	56618.1	$a^4P_{\frac12} - z^4P_{\frac12}$
1763.935	0	56691.4	$a^4F_{1\frac12} - z^4D_{2\frac12}$
1762.557	30	56735.8	$a^4P_{1\frac12} - z^4P_{\frac12}$
1761.155	20	56781.9	$a^2F_{2\frac12} - z^4F_{1\frac12}$
1760.586	10	56799.3	$a^4F_{3\frac12} - z^4D_{3\frac12}$
1755.012	20	56979.7	$a^2P_{1\frac12} - y^4D_{2\frac12}$
1750.391	500	57130.1	$a^2F_{2\frac12} - z^2G_{3\frac12}$
1741.378	500*d*?	57425.8	$a^2F_{3\frac12} - z^2G_{4\frac12}$
1741.135	30	57433.8	$a^4F_{2\frac12} - z^4D_{2\frac12}$
1739.508	300	57487.5	$a^2G_{3\frac12} - z^2H_{4\frac12}$
1738.648	10	57516.0	$a^2G_{4\frac12} - z^2H_{4\frac12}$
1738.145	30	57532.6	$a^4P_{2\frac12} - y^2F_{2\frac12}$
1737.893	30	57540.9	$a^2F_{3\frac12} - z^4F_{3\frac12}$
1732.998	5	57703.5	$b^2D_{1\frac12} - z^4P_{1\frac12}$
1728.139	200	57865.7	$a^2F_{2\frac12} - z^2F_{3\frac12}$
1726.275	5	57928.2	$a^2F_{2\frac12} - z^2D_{2\frac12}$
1724.810	10	57977.4	$a^4F_{1\frac12} - z^4D_{1\frac12}$
1722.379	1000	58059.2	$a^4F_{4\frac12} - z^4D_{3\frac12}$
1717.134	5	58236.6	
1716.400	10	58261.5	$b^2D_{1\frac12} - z^4P_{\frac12}$
1716.189	1	58268.6	
1713.346	5	58365.3	$a^2F_{3\frac12} - z^4F_{2\frac12}$
1711.437	30	58430.4	$a^4P_{2\frac12} - y^2F_{3\frac12}$
1711.257	30	58436.6	$a^4P_{2\frac12} - y^2D_{1\frac12}$
1709.036	700	58512.5	$a^4F_{3\frac12} - z^4D_{2\frac12}$
1708.958	200	58515.2	$b^2D_{2\frac12} - z^4P_{1\frac12}$
1707.500	5	58565.2	$a^4P_{\frac12} - y^2D_{1\frac12}$
1705.633	400	58629.3	$a^2G_{4\frac12} - z^2H_{5\frac12}$
1705.333	300	58639.6	$b^2D_{2\frac12} - z^4P_{2\frac12}$
1704.072	10	58683.0	$a^4P_{1\frac12} - y^2D_{1\frac12}$
1702.994	500	58720.1	$a^4F_{2\frac12} - z^4D_{1\frac12}$
1702.349	30	58742.4	$a^2P_{\frac12} - x^2D_{1\frac12}$
1702.190	300	58747.8	$a^2P_{1\frac12} - x^2D_{2\frac12}$
1702.102	400	58750.9	$a^4F_{1\frac12} - z^4D_{\frac12}$
1701.023	400	58788.2	$a^2G_{4\frac12} - x^2F_{3\frac12}$
1699.581	0	58838.0	$a^4P_{\frac12} - z^2P_{\frac12}$
1696.202	15	58955.2	$a^4P_{1\frac12} - z^2P_{\frac12}$
1692.706	300	59077.0	$a^2F_{3\frac12} - z^2G_{3\frac12}$
1689.051	200	59204.8	$a^4P_{2\frac12} - y^2D_{2\frac12}$
1688.618	100	59220.0	$a^2P_{\frac12} - y^2P_{1\frac12}$
1687.134	600	59272.1	$a^4F_{3\frac12} - z^4G_{4\frac12}$
1686.214	300	59304.5	$b^2D_{1\frac12} - y^2F_{2\frac12}$
1684.642	500	59359.8	$a^4F_{2\frac12} - z^4G_{3\frac12}$
1682.695	30	59428.5	$a^2P_{1\frac12} - x^2D_{1\frac12}$
1682.044	10	59451.5	$a^4P_{1\frac12} - y^2D_{2\frac12}$
1681.481	300	59471.4	$a^2F_{2\frac12} - z^2D_{1\frac12}$
1679.151	400	59553.9	$a^4F_{1\frac12} - z^4G_{2\frac12}$
1677.373	200	59617.0	$a^2G_{3\frac12} - x^2F_{2\frac12}$
1676.469	15	59649.2	$a^4P_{2\frac12} - z^2P_{1\frac12}$
1674.602	500	59715.7	$a^2F_{2\frac12} - z^2F_{2\frac12}$
1671.886	500	59812.7	$a^2F_{3\frac12} - z^2F_{3\frac12}$
1670.140	500	59875.2	$a^2F_{3\frac12} - z^2D_{2\frac12}$
1669.273	10	59906.3	$a^2P_{1\frac12} - y^2P_{1\frac12}$
1660.887	30	60208.8	$b^2D_{1\frac12} - y^2D_{1\frac12}$
1658.472	200	60296.5	$a^4F_{2\frac12} - z^4G_{2\frac12}$
1654.574	300	60438.5	$a^4F_{3\frac12} - z^4G_{3\frac12}$
1653.399	10	60481.5	$b^2D_{1\frac12} - z^2P_{\frac12}$
1652.010	300	60532.3	$a^4F_{4\frac12} - z^4G_{4\frac12}$
1651.758	15	60541.6	$a^2P_{\frac12} - y^2P_{\frac12}$
1642.208	2000	60893.6	$a^4F_{4\frac12} - z^4G_{5\frac12}$
1639.960	10	60977.1	$b^2D_{1\frac12} - y^2D_{2\frac12}$
1638.956	300	61014.5	$b^2D_{2\frac12} - y^2F_{3\frac12}$
1633.192	1	61229.8	$a^2P_{1\frac12} - y^2P_{\frac12}$
1629.301	1	61376.0	$a^4F_{3\frac12} - z^4G_{2\frac12}$
1628.295	300	61413.9	$a^4F_{2\frac12} - z^4F_{3\frac12}$
1628.088	50	61421.7	$b^2D_{1\frac12} - z^2P_{1\frac12}$
1626.411	200	61485.1	$a^4F_{3\frac12} - z^4F_{4\frac12}$
1626.139	200	61495.4	$a^4F_{1\frac12} - z^4F_{2\frac12}$
1625.500	1	61519.5	$a^2P_{\frac12} - z^2S_{\frac12}$
1621.723	3	61662.8	$a^2F_{3\frac12} - z^2F_{2\frac12}$
1620.776	1	61698.8	$a^4F_{4\frac12} - z^4G_{3\frac12}$
1618.408	5	61789.1	$b^2D_{2\frac12} - y^2D_{2\frac12}$
1616.607	300	61858.0	$a^4F_{1\frac12} - z^4F_{1\frac12}$
1616.160	15	61875.1	$a^4P_{2\frac12} - y^4D_{2\frac12}$
1610.571	75	62089.8	$a^4P_{\frac12} - y^4D_{1\frac12}$
1609.757	100	62121.2	$a^4P_{1\frac12} - y^4D_{2\frac12}$
1609.599	50	62127.3	$a^4P_{\frac12} - y^4D_{\frac12}$
1607.542	100	62206.8	$a^4P_{1\frac12} - y^4D_{1\frac12}$ and $a^2P_{1\frac12} - z^2S_{\frac12}$
1606.837	10	62234.1	$b^2D_{2\frac12} - z^2P_{1\frac12}$
1606.730	300	62238.2	$a^4F_{2\frac12} - z^4F_{2\frac12}$
1605.969	300	62267.7	$a^4P_{2\frac12} - y^4D_{3\frac12}$
1603.146	400	62377.4	$a^4F_{3\frac12} - z^2G_{4\frac12}$
1600.194	500	62492.4	$a^4F_{3\frac12} - z^4F_{3\frac12}$
1597.418	10	62601.0	$a^4F_{2\frac12} - 2^4F_{1\frac12}$
1593.758	1000	62744.8	$a^4F_{4\frac12} - z^4F_{4\frac12}$
1588.551	3	62950.4	$a^4F_{2\frac12} - z^2G_{3\frac12}$
1579.353	15	63317.1	$a^4F_{3\frac12} - z^4F_{2\frac12}$
1571.390	1	63637.9	$a^4F_{4\frac12} - z^2G_{4\frac12}$
1571.154	3	63647.5	$b^2D_{1\frac12} - y^4D_{2\frac12}$
1570.202	30	63686.1	$a^4F_{2\frac12} - z^2F_{3\frac12}$
1569.027	0	63733.8	$b^2D_{1\frac12} - y^4D_{1\frac12}$
1568.655	2	63748.9	$a^4F_{2\frac12} - z^2D_{2\frac12}$
1568.564	2	63752.6	$a^4F_{4\frac12} - z^4F_{3\frac12}$
1565.194	5	63889.8	$a^4P_{1\frac12} - x^2D_{2\frac12}$
1561.790	3	64029.1	$a^4F_{3\frac12} - z^2G_{3\frac12}$
1551.932	2	64435.8	

TABLE IV.—(*Continued*).

λ(Vac.)	Int.	ν	Classification
1549.203	10	64549.3	$a^4F_{1\frac{1}{2}} - z^2D_{1\frac{1}{2}}$
1548.867	300	64563.3	$a^2G_{3\frac{1}{2}} - y^2G_{3\frac{1}{2}}$
1544.110	2	64762.2	$a^2G_{3\frac{1}{2}} - y^2G_{4\frac{1}{2}}$
1544.062	2	64764.2	$a^4F_{3\frac{1}{2}} - z^2F_{3\frac{1}{2}}$
1543.438	500	64790.4	$a^2G_{4\frac{1}{2}} - y^2G_{4\frac{1}{2}}$
1543.180	2	64801.3	$a^4P_{2\frac{1}{2}} - y^2P_{1\frac{1}{2}}$
1542.562	2	64827.2	$a^4F_{3\frac{1}{2}} - z^2D_{2\frac{1}{2}}$
1541.970	40	64852.1	$b^2D_{2\frac{1}{2}} - y^4D_{3\frac{1}{2}}$
1531.588	1	65291.7	$a^4F_{2\frac{1}{2}} - z^2D_{1\frac{1}{2}}$
1502.107	1	66573.2	$b^2D_{1\frac{1}{2}} - y^2P_{1\frac{1}{2}}$
1501.173	0	66614.6	$a^4F_{3\frac{1}{2}} - z^2F_{2\frac{1}{2}}$
1487.566	0	67223.9	$z^2D_{2\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1486.904	10	67253.8	$a^4P_{2\frac{1}{2}} - x^2F_{3\frac{1}{2}}$
1486.659	25	67264.9	$a^4P_{2\frac{1}{2}} - z^4S_{1\frac{1}{2}}$
1484.010	5	67385.0	$b^2D_{2\frac{1}{2}} - y^2P_{1\frac{1}{2}}$
1483.831	15	67393.1	$a^4P_{\frac{1}{2}} - z^4S_{1\frac{1}{2}}$
1481.243	20	67511.9	$a^4P_{1\frac{1}{2}} - z^4S_{1\frac{1}{2}}$
1469.460	2	68052.2	
1469.259	0	68061.5	$z^2F_{2\frac{1}{2}} - 7$
1460.915	10	68450.3	$z^2D_{2\frac{1}{2}} - 5$
1459.568	0	68513.4	$z^2F_{3\frac{1}{2}} - 5$
1458.021	6	68586.1	
1455.200	3	68719.1	$z^2F_{2\frac{1}{2}} - e^2F_{2\frac{1}{2}}$
1451.478	1	68895.3	$z^2D_{2\frac{1}{2}} - e^2F_{3\frac{1}{2}}$
1450.165	3	68957.7	$z^2F_{3\frac{1}{2}} - e^2F_{3\frac{1}{2}}$
1448.512	2	69033.4	
1444.692	1	69218.9	$z^2F_{2\frac{1}{2}} - 9$
1441.635	3	69365.7	
1441.102	2	69391.3	
1440.446	3	69422.9	$z^2G_{3\frac{1}{2}} - 6$
1439.275	2	69479.4	
1438.983	2	69493.5	
1437.645	3	69558.2	$z^4F_{3\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1437.554	2	69562.6	
1436.994	15	69589.7	$z^2G_{4\frac{1}{2}} - 3$
1436.846	2	69596.9	
1436.376	1	69619.7	$z^2F_{2\frac{1}{2}} - 10$
1432.275	3	69819.0	$z^4F_{4\frac{1}{2}} - e^4F_{4\frac{1}{2}}$
1431.901	3	69837.2	$b^2D_{2\frac{1}{2}} - x^2F_{3\frac{1}{2}}$
1431.671	10	69848.4	$b^2D_{2\frac{1}{2}} - z^4S_{1\frac{1}{2}}$
1430.969	3	69882.7	$b^2D_{1\frac{1}{2}} - x^2F_{2\frac{1}{2}}$
1430.373	3	69911.8	$z^2F_{3\frac{1}{2}} - 7$
1429.201	5	69969.2	$z^4F_{4\frac{1}{2}} - 1$
1428.081	5*l*?	70024.0	$a^2F_{2\frac{1}{2}} - y^2D_{1\frac{1}{2}}$
1425.282	1*l*?	70161.6	$z^2D_{2\frac{1}{2}} - 8$
1425.079	2	70171.5	$z^4F_{2\frac{1}{2}} - e^4F_{2\frac{1}{2}}$
1424.020	5	70223.7	$z^2F_{3\frac{1}{2}} - 8$?
1423.504	10	70249.2	
1418.811	5	70481.6	$z^2D_{2\frac{1}{2}} - f^2F_{3\frac{1}{2}}$ and $z^4F_{4\frac{1}{2}} - 3$
1417.538	10	70544.8	$z^2F_{3\frac{1}{2}} - f^2F_{3\frac{1}{2}}$
1417.124	2	70565.5	$z^4F_{4\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1417.060	2	70568.6	$z^2F_{3\frac{1}{2}} - e^2F_{2\frac{1}{2}}$
1415.478	1	70647.5	$z^2G_{3\frac{1}{2}} - 7$
1414.431	3	70699.8	$z^4F_{1\frac{1}{2}} - e^4F_{1\frac{1}{2}}$
1414.086	2	70717.1	
1412.794	5	70781.1	$z^4F_{4\frac{1}{2}} - e^4G_{5\frac{1}{2}}$
1412.724	5	70785.2	$z^4F_{3\frac{1}{2}} - 5$
1409.248	1	70959.8	$z^4F_{3\frac{1}{2}} - 6$ and $z^2G_{3\frac{1}{2}} - 8$
1408.536	1	70995.7	$z^4F_{3\frac{1}{2}} - e^4F_{2\frac{1}{2}}$
1408.310	1	71007.1	$z^2D_{2\frac{1}{2}} - 9$
1407.196	3	71063.3	$z^4F_{2\frac{1}{2}} - e^4F_{1\frac{1}{2}}$
1407.139	5	71066.2	$a^2F_{3\frac{1}{2}} - y^2F_{2\frac{1}{2}}$?
1405.115	2	71168.6	
1403.763	1	71237.1	$a^2F_{2\frac{1}{2}} - z^2P_{1\frac{1}{2}}$
1403.181	10	71266.6	
1402.917	1	71280.1	$z^2G_{3\frac{1}{2}} - f^2F_{3\frac{1}{2}}$
1402.435	3	71304.6	$z^2G_{3\frac{1}{2}} - e^2F_{2\frac{1}{2}}$
1402.250	5	71313.9	
1401.655	5	71344.2	$z^2G_{4\frac{1}{2}} - e^2F_{3\frac{1}{2}}$
1401.602	5	71346.9	
1401.376	2	71358.4	$z^4F_{2\frac{1}{2}} - 7$
1400.539	3	71401.1	
1399.190	5	71469.9	$z^2F_{3\frac{1}{2}} - 10$
1398.397	5	71510.5	$z^4F_{4\frac{1}{2}} - 4$
1396.417	1	71611.8	$z^4G_{3\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1395.274	10	71670.5	$z^4G_{5\frac{1}{2}} - e^4F_{4\frac{1}{2}}$
1393.139	3	71780.3	
1391.667	2	71856.3	
1390.306	10	71926.6	
1389.528	5	71966.9	$a^2F_{3\frac{1}{2}} - y^2F_{3\frac{1}{2}}$ and $z^4F_{4\frac{1}{2}} - 6$
1388.276	1	72031.8	$z^4G_{4\frac{1}{2}} - e^4F_{4\frac{1}{2}}$
1386.714	1	72112.9	$z^4G_{2\frac{1}{2}} - e^4F_{2\frac{1}{2}}$
1385.921	3	72154.2	$z^4F_{1\frac{1}{2}} - 9$
1385.380	1	72182.4	$z^4G_{4\frac{1}{2}} - 1$ and $z^4F_{3\frac{1}{2}} - 7$
1384.929	3	72205.9	$z^2G_{3\frac{1}{2}} - 10$
1384.840	5	72210.5	
1384.324	5	72237.4	$z^4F_{4\frac{1}{2}} - e^2F_{3\frac{1}{2}}$
1384.276	2	72239.9	
1382.838	2	72315.1	
1382.561	5	72329.5	
1379.775	2	72475.6	
1379.379	1	72496.4	$z^4F_{3\frac{1}{2}} - 8$
1378.665	2	72533.9	
1378.238	1	72556.4	$z^4G_{3\frac{1}{2}} - 4$
1377.559	2	72592.2	
1377.504	30	72595.1	
1376.807	30	72631.8	$z^4G_{5\frac{1}{2}} - e^4G_{5\frac{1}{2}}$
1375.621	5	72694.4	$z^4G_{4\frac{1}{2}} - 3$
1374.758	3	72740.1	$a^2F_{3\frac{1}{2}} - y^2D_{2\frac{1}{2}}$
1374.298	3	72764.4	
1374.033	3	72778.2	$z^4G_{4\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1373.305	3	72817.0	
1372.965	3	72835.1	
1372.899	5	72838.6	$z^4G_{3\frac{1}{2}} - 5$
1371.144	10	72931.8	$z^2G_{4\frac{1}{2}} - f^2F_{3\frac{1}{2}}$
1369.988	1	72993.3	$z^4G_{4\frac{1}{2}} - e^4G_{5\frac{1}{2}}$
1369.612	5	73013.4	$z^4G_{3\frac{1}{2}} - 6$
1368.923	2	73050.1	$z^4G_{3\frac{1}{2}} - e^4F_{2\frac{1}{2}}$
1367.646	5	73118.3	
1366.400	3	73185.0	
1365.862	2	73213.8	
1360.922	3	73479.6	
1359.833	0	73538.4	$z^4D_{2\frac{1}{2}} - e^4F_{3\frac{1}{2}}$
1358.440	2	73613.9	$z^4G_{2\frac{1}{2}} - 8$
1358.130	2	73630.7	
1356.424	5	73723.3	$z^4G_{4\frac{1}{2}} - 4$
1353.964	2	73857.2	$z^2G_{4\frac{1}{2}} - 10$
1351.271	3	74004.4	$z^4G_{4\frac{1}{2}} - 5$
1349.441	5	74104.8	
1348.584	3	74151.9	
1348.077	1	74179.7	$z^4G_{4\frac{1}{2}} - 6$
1347.048	3*h*	74236.4	$z^4G_{3\frac{1}{2}} - 7$
1346.062	5	74290.8	
1345.506	2	74321.5	
1344.363	2	74384.7	
1343.730	5	74419.7	
1343.032	2	74458.4	$z^4G_{2\frac{1}{2}} - 9$
1342.193	3*h*	74504.9	$z^4D_{3\frac{1}{2}} - e^4F_{4\frac{1}{2}}$
1341.497	2	74543.6	
1341.178	2*h*	74561.3	
1339.497	5	74654.9	$z^4D_{3\frac{1}{2}} - 1$
1338.858	2	74690.5	
1338.386	2	74716.9	
1337.572	5*h*	74762.3	
1332.985	15	75019.6	
1330.365	2	75167.3	$z^4D_{3\frac{1}{2}} - 3$
1327.178	5	75347.8	
1326.379	3	75393.2	
1324.033	5	75526.8	
1318.582	2	75839.0	$a^4F_{2\frac{1}{2}} - y^2F_{3\frac{1}{2}}$
1316.143	5	75979.6	
1313.313	2	76143.3	
1312.400	10	76196.3	$z^4D_{3\frac{1}{2}} - 4$
1311.863	2	76227.5	
1307.595	3	76476.3	$z^4D_{2\frac{1}{2}} - 8$
1295.700	0	77178.4	$a^2F_{3\frac{1}{2}} - x^2D_{2\frac{1}{2}}$
1271.839	2	78626.3	$a^4F_{1\frac{1}{2}} - y^4D_{1\frac{1}{2}}$
1271.234	5	78663.7	$a^4F_{1\frac{1}{2}} - y^4D_{\frac{1}{2}}$
1259.937	10	79369.0	$a^4F_{2\frac{1}{2}} - y^4D_{1\frac{1}{2}}$
1254.717	3	79699.2	$a^2F_{2\frac{1}{2}} - x^2F_{2\frac{1}{2}}$

TABLE IV.—(*Continued*).

λ(Vac.)	Int.	ν	Classification
1244.377	10	80361.5	$a^4F_{3\frac{1}{2}} - y^4D_{2\frac{1}{2}}$
1238.325	1	80754.2	$a^4F_{3\frac{1}{2}} - y^4D_{3\frac{1}{2}}$
1237.776	3	80790.1	$a^2F_{3\frac{1}{2}} - x^2F_{3\frac{1}{2}}$
1219.290	5	82014.9	$a^4F_{4\frac{1}{2}} - y^4D_{3\frac{1}{2}}$
829.343	5	120577.3	$a^2D_{2\frac{1}{2}} - z^4D_{2\frac{1}{2}}$
816.313	0	122502.0	$a^2D_{2\frac{1}{2}} - z^4G_{3\frac{1}{2}}$
810.124	0	123437.9	$a^2D_{2\frac{1}{2}} - z^4G_{2\frac{1}{2}}$
808.583	20	123673.1	$a^2D_{1\frac{1}{2}} - z^4F_{1\frac{1}{2}}$
802.841	150	124557.7	$a^2D_{2\frac{1}{2}} - z^4F_{3\frac{1}{2}}$
801.154	200	124819.9	$a^2D_{1\frac{1}{2}} - z^2D_{2\frac{1}{2}}$
797.566	100	125381.5	$a^2D_{2\frac{1}{2}} - z^4F_{2\frac{1}{2}}$
795.258	2	125745.4	$a^2D_{2\frac{1}{2}} - z^4F_{1\frac{1}{2}}$
793.065	100	126093.1	$a^2D_{2\frac{1}{2}} - z^2G_{3\frac{1}{2}}$
791.371	300	126363.0	$a^2D_{1\frac{1}{2}} - z^2D_{1\frac{1}{2}}$
789.840	200	126607.9	$a^2D_{1\frac{1}{2}} - z^2F_{2\frac{1}{2}}$
788.462	300	126829.2	$a^2D_{2\frac{1}{2}} - z^2F_{3\frac{1}{2}}$
788.073	400	126891.8	$a^2D_{2\frac{1}{2}} - z^2D_{2\frac{1}{2}}$
778.603	50	128435.2	$a^2D_{2\frac{1}{2}} - z^2D_{1\frac{1}{2}}$
777.125	200	128679.4	$a^2D_{2\frac{1}{2}} - z^2F_{2\frac{1}{2}}$
743.970	30	134414.0	$a^2D_{1\frac{1}{2}} - z^4P_{1\frac{1}{2}}$
743.303	20	134534.6	$a^2D_{1\frac{1}{2}} - z^4P_{2\frac{1}{2}}$
735.224	100	136013.0	$a^2D_{1\frac{1}{2}} - y^2F_{2\frac{1}{2}}$
732.688	5	136483.7	$a^2D_{2\frac{1}{2}} - z^4P_{1\frac{1}{2}}$
732.026	100	136607.2	$a^2D_{2\frac{1}{2}} - z^4P_{2\frac{1}{2}}$
730.365	150	136917.8	$a^2D_{1\frac{1}{2}} - y^2D_{1\frac{1}{2}}$
728.906	2	137191.9	$a^2D_{1\frac{1}{2}} - z^2P_{\frac{1}{2}}$
726.295	10	137685.1	$a^2D_{1\frac{1}{2}} - y^2D_{2\frac{1}{2}}$
723.958	20	138129.6	$a^2D_{1\frac{1}{2}} - z^2P_{1\frac{1}{2}}$
719.506	150	138984.2	$a^2D_{2\frac{1}{2}} - y^2F_{3\frac{1}{2}}$
715.530	200	139756.5	$a^2D_{2\frac{1}{2}} - y^2D_{2\frac{1}{2}}$
713.262	10	140200.9	$a^2D_{2\frac{1}{2}} - z^2P_{1\frac{1}{2}}$
712.473	15	140356.2	$a^2D_{1\frac{1}{2}} - y^4D_{2\frac{1}{2}}$
712.040	5	140441.5	$a^2D_{1\frac{1}{2}} - y^4D_{1\frac{1}{2}}$
711.834	3	140482.2	$a^2D_{1\frac{1}{2}} - y^4D_{\frac{1}{2}}$
703.622	15	142121.8	$a^2D_{1\frac{1}{2}} - x^2D_{2\frac{1}{2}}$
702.112	20	142427.4	$a^2D_{2\frac{1}{2}} - y^4D_{2\frac{1}{2}}$
701.692	15	142512.7	$a^2D_{2\frac{1}{2}} - y^4D_{1\frac{1}{2}}$
700.271	150	142801.9	$a^2D_{1\frac{1}{2}} - x^2D_{1\frac{1}{2}}$
700.182	20	142820.0	$a^2D_{2\frac{1}{2}} - y^4D_{3\frac{1}{2}}$
697.930	20	143280.8	$a^2D_{1\frac{1}{2}} - y^2P_{1\frac{1}{2}}$
693.510	50	144194.0	$a^2D_{2\frac{1}{2}} - x^2D_{2\frac{1}{2}}$
691.557	100	144601.2	$a^2D_{1\frac{1}{2}} - y^2P_{\frac{1}{2}}$
690.250	75	144875.0	$a^2D_{2\frac{1}{2}} - x^2D_{1\frac{1}{2}}$
687.987	100	145351.6	$a^2D_{2\frac{1}{2}} - y^2P_{1\frac{1}{2}}$
686.903	15	145581.0	$a^2D_{1\frac{1}{2}} - z^2S_{\frac{1}{2}}$
682.171	200	146590.8	$a^2D_{1\frac{1}{2}} - x^2F_{2\frac{1}{2}}$
676.564	300	147805.6	$a^2D_{2\frac{1}{2}} - x^2F_{3\frac{1}{2}}$
672.659	50	148663.7	$a^2D_{2\frac{1}{2}} - x^2F_{2\frac{1}{2}}$

choice of names for the two levels of $J=1\frac{1}{2}$ is correct, but that the names of the two levels with $J=2\frac{1}{2}$ perhaps should be interchanged. The same result is indicated by the *g*-values in NiII, but the arrangement of the components of the terms would then be very odd, indeed.

The levels of $d^8(^1D)4p$, $d^8(^3P)4p$ and $d^8(^1G)4p$ have all been found, and they show a remarkable similarity of arrangement to their counterparts in NiII. In both spectra, the levels based on ^1D and ^3P are certainly of mixed character, and the assignment of names is consequently of doubtful validity. The one-to-one correspondence of the levels of these two groups of NiII and CuIII is so complete that it might be expected that an extrapolation back to CoI would give an unambiguous selection of the equivalent levels in that spectrum. This is not the case. In the appropriate energy range in CoI there are over 50 observed levels, of which not more than 19 can belong to this part of the d^84p configuration, the others having their origin in d^7sp. The observed levels are so mixed in character that it is perhaps meaningless even to group them into terms. There is a balance of evidence, however, which indicates that a few changes in assignment should be made. The ones we propose are given in Table III.

The lowest term of the CuIII spectrum, $3d^9\ ^2D$, was correctly identified by Vieweg. Its combinations are all below λ830 and are very intense. The ^2D difference 2071.8 is to be compared with the 2042.9 of $d^9s^2\ ^2D$, 2069.0, 2069.3, 2069.2 of $d^9s\cdot s(^4D_{2\frac{1}{2}}-^4D_{1\frac{1}{2}})$, and 2069.7, 2069.8, 2070.4, 2071.4 of $d^9s(^3D_3-^3D_1)$.

Measurements of a plate which was very much overexposed in the region of the strong multiplets yielded a number of lines of reasonable intensity in the region λ1350 to λ1450. Those lines made it possible to identify a number of high even levels; and, amongst them, were found the six levels comprising $3d^8(^3F)5s\ ^4F$ and ^2F. Since these are in series with the low levels a^4F and a^2F, it is possible to calculate an I. P. in six ways provided one knows the type of convergence and the intervals of the limit in CuIV. The latter are not known, but from a comparison with similar cases in other spectra, they cannot differ materially from the intervals of $3d^84s^2\ ^3F$ of CuII. The convergence is obviously the one which results from the non-crossing rule, i.e., $^4F_{4\frac{1}{2}}$ and $^4F_{3\frac{1}{2}}$ converge to $^3F_4$; $^4F_{2\frac{1}{2}}$ and $^2F_{3\frac{1}{2}}$ to $^3F_3$, and $^4F_{1\frac{1}{2}}$ and $^2F_{2\frac{1}{2}}$ to $^3F_2$. Using this information and assuming from a comparison with other spectra that the Ritz correction is about 1.7×10^{-7}, the length of the series from $a^4F_{4\frac{1}{2}}$ to $^3F_4$ of CuIV is 238340 cm^{-1}. Adding the $^2D_{2\frac{1}{2}}-^4F_{4\frac{1}{2}}$ difference of 60805 we obtain an ionization limit of 299145 corresponding to an I. P. of 3708 volts for the removal of a *d*-electron. In this calculation only the quartet levels were used, the doublets having very different values of the Ritz correction.

A few other high even levels have been found. They originate in the structure $3d^84d$, but the number of combinations is too small for many positive identifications to be made. Many more levels should exist in this neighborhood and an exhaustive but unsuccessful search has been made for them. It is therefore probable that the remaining levels are represented by single or double combinations only. A thorough analysis of this structure in NiII should, with the aid of the CoI analysis, lead to a more complete knowledge of the terms of CuIII.

As usual in spectra in which configurations including d^8 occur, no trace has been found of the levels based on ^1S. A more important lacuna, however, is the absence of the structure $3d^74s^2$. From all the available evidence, it appears that this structure should exist about 15,000 to 30,000ν above $3d^84p$ and should therefore produce multiplets in the easily observed part of the spectrum. No such lines have been observed, and it therefore remains an unsolved problem that the much higher levels of $3d^84d$ are observably excited but the lower ones of $3d^74s^2$ are not.

All identified and unidentified lines of CuIII, of reasonable intensity, are listed in Table IV.