THE SECOND SPARK SPECTRUM OF ZINC, Zn III

By Otto Laporte and R. J. Lang

Abstract

New accurate wave-lengths of the spectrum of the high-potential spark between zinc electrodes made it possible to identify the most important line groups of Zn III, after their position and separations had been predicted closely by means of the screening and relativistic doublet laws respectively. The *ionization potential* of the shell of ten equivalent 3_3 electrons is found to be 40 volts.

I. Introduction

THE investigation and comparison of iso-electronic spectra, i.e., of spectra emitted by atoms and ions with the same number of electrons has become one of the main problems of modern ultra-violet spectroscopy. It was found by Millikan and Bowen[1] that for families of iso-electronic spectra (such as Na, Mg^+, Al^{2+}, Si^{3+} $\cdots$) the regular and irregular doublet laws of the x-ray region furnish a powerful tool for predicting location and separations of line groups. The spectra which have thus been investigated, have however been always of the type which Heisenberg[2] designated as "normal," i.e., spectra of first or higher rank but with small level-separations.

In the following we shall show that the above-mentioned methods can also be applied to spectra with a high number of electrons and with large separations between sub-levels which are comparable with the separations between different terms. The second spark spectrum of zinc seems most suitable for an investigation as the structure of its less-ionized analogues Ni I[3] and Cu II[4] is well known. Also these two spectra follow fairly well the irregular doublet law, as Table I shows, and one may thus expect to be able to predict the location of homologous groups for the Zn III. As explanation of Table I, it may suffice that in Ni I and Cu II two ^3D terms are known which

Table I

	$^3D(3d^9, 4s)$	$^3D - ^3D'$	$^3D'(3d^9, 4p)$	$\Delta\nu^{1/2}$
Ni I	62750	29464	33290	68.0
Cu II	144200	48915	95290	71.5

are due to the configuration $(3d)^9$ $(4s)$ and $(3d)^9$ $(5s)$ respectively. By means of a simple Rydberg formula one can determine the absolute term values for $^3D(3d^9, 4s)$ which are given in the first column. Another (primed) ^3D term arising from $(3d)^9$ $(4p)$ combines most conspicuously with $^3D(3d^9, 4s)$ in a

[1] Papers in the Physical Review.

[2] W. Heisenberg, Zeits. f. Physik **32**, 841 (1925).

[3] K. Bechert and L. A. Sommer, Ann. d. Physik **77**, 351 (1925).

[4] A. G. Shenstone, Phys. Rev. **29**, 380 (1927).

multiplet whose frequency is written in the second column. In the third column the term value of $^3D(3d^9, 4p)$ is given. The differences of the square roots of the term values are approximately the same in both spectra as it should be if the two terms form an irregular doublet.

Not only the location of the group $^3D(3d^9, 4s) - ^3D(3d^9, 4p)$ can thus be computed for Zn III but also the $\Delta\nu$ of the terms may be predicted with good accuracy by means of the relativistic doublet law and of certain data on the first spark spectrum of zinc as given by v. Salis.[5] We shall show in a later paragraph, how the classified line groups agree with theoretical and empirical laws.

In the earlier stage of the investigation the identification of the line groups of Zn III was based to a large extent on such theoretical considerations. The published wave-length material on the ultra-violet spectrum of zinc, as contained in papers of R. W. Wood[6] and of R. A. Sawyer[7] was not reliable and complete enough to establish the terms and levels merely by means of constant frequency differences. Only after new photographs of the high-potential spark spectrum of zinc had been taken at Edmonton, and thus wave-length material of much higher accuracy and completeness had become available, did the classification of the lines around 1600A become entirely unambiguous and the identification of the three lines at 700A which establish the fundamental level of Zn^{++} was made possible.

2. Experimental Procedure

The vacuum-spark between electrodes of pure metallic zinc was photographed by means of a two-meter grating having 30,000 lines per inch, which has been described previously.[8] The dispersion obtained is about 4.5A per mm resulting in an error of measurement which does not exceed 0.05A at least as far as 1000A. The grating was ruled by Professor Wood of Johns Hopkins University on speculum and gives excellent results in the region 2000–1000A. It shows Rowland ghosts conspicuously about the strong lines but these because of their symmetry of position do not cause much confusion.

The standards of wave-length used were carbon lines, together with the hydrogen line 1215.68, standardized by Smith and Lang.[9] In one case the carbon line 1931.03 given by Bowen and Ingram[10] was used.

Two samples of zinc were used, one of which was purchased from the Powers-Weightman-Rosengarten Co. and the other was very generously supplied by the New Jersey Zinc Co. of America. Both these samples were found to be of high purity. In the case of the latter no known lines of impurities were found in the spectrum except those of hydrogen and carbon, the latter being introduced purposely in order to obtain standards. Fig. 1 is a reproduction of one of the photographs taken at Edmonton, showing the

[5] G. v. Salis, Ann. d. Physik **76,** 145 (1925).
[6] R. W. Wood, Phil. Mag. **46,** 741 (1923).
[7] R. A. Sawyer, Astrophys. J. **52,** 286 (1920).
[8] R. J. Lang, Jour. Opt. Soc. Amer. **12,** 523 (1926).
[9] Stanley Smith and R. J. Lang, Phys. Rev. **28,** 36 (1926).
[10] J. S. Bowen and S. B. Ingram Phys. Rev. **28,** 444 (1926).

region from 1850 to 1400A. The classified lines are marked on the upper margin.

3. The Classification of the Lines

In Table II the frequency scheme of the classified lines of Zn III is given. At the left and at the top of the table the relative term values are given

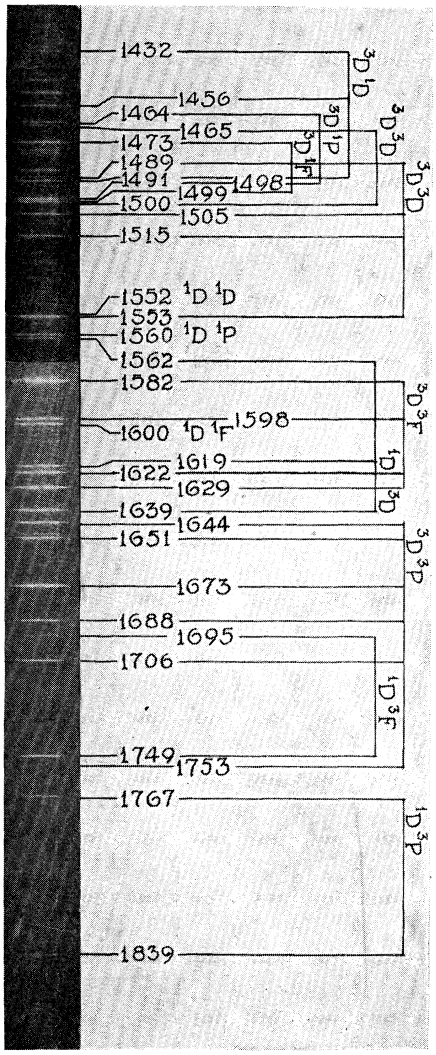

Fig. 1. Photograph of the zinc spectrum in the region from 1850 to 1400A.

taking the lowest term to be zero. The numbers in parentheses are the intensities. The satisfactory constantcy of the frequency differences (which are italicized in Table II) proves the accuracy of the wave-lengths. Except

for the $\Delta\nu$ which are linked to line ν 64391, an unresolved doublet, the differences show a fluctuation of only a few wave-number units.

TABLE II

Classification of the lines of Zn III.

		$^1S_0$	$^3D_3$		$^3D_2$		$^3D_1$		$^1D_2$
		0	78105	*1178*	79283	*1576*	80859	*2650*	83509
			(9)		(6)		(3)		(4)
$^3P_2$	137876		59771	*1178*	58593	*1577*	57016	*2650*	54366
					2204		*2205*		*2203*
		(3)			(10)		(7)		(7)
$^3P_1$	140080	140080			60797	*1576*	59221	*2652*	56569
							1321		
							(8)		
$^3P_0$	141401						60542		
			(15)						
$^3F_4$	141335		63230						
			−672						
			(8)		(10)				(9)
$^3F_3$	140664		62558	*1177*	61381				57154
			1833		*1827*				*1827*
			(x)		(10)		(10)		(3)
$^3F_2$	142491		64391	*1183*	63208	*1575*	61633	*2652*	58981
			2012						*2021*
			(8)						(10)
$^3D_3'$	144511		66403						61002
			741						*742*
			(2)		(8)		(7−x)		(8)
$^3D_2'$	145252		67144	*1175*	65969	*1578*	64391	*2647*	61744
					2253		*2255*		*2254*
		(5)			(4)		(6)		(9)
$^3D_1'$	147505	147519			68222	*1576*	66646	*2648*	63998
		72			*72*		*72*		*70*
		(5)			(5)		(5)		(7+c)
$^1P_1$	147577	147591			68294	*1576*	66718	*2650*	64068
					351		*350*		*351*
			(5)		(8)		(7)		(7)
$^1D_2'$	147928		69821	*1176*	68645	*1577*	67068	*2649*	64419
			−1952		*−1956*				*−1951*
			(8)		(6)				(9)
$^1F_3$	145974		67869	*1180*	66689				62468

There is only one possible combination in the table for which a line is not observed, namely the combination $^3D_2-{}^3D_3'$. Its theoretical intensity should be about 3. It is remarkable and certainly no accident, that the corresponding combination is also absent in the spectrum of Cu II.

The ^1S term which corresponds to the normal state of Zn^{++} lies 78100 cm^{-1} below the $^3D_2$ level; it is established by but three lines at 700A, which are the only possible combinations for a level with inner quantum number $j=0$. These three lines are, however, the only strong lines in this region of the spectrum. Additional evidence for the reality of the ^1S term will be given below.

4. DISCUSSION

a. A few words may suffice for the interpretation of these new terms, as a more complete discussion is given in Shenstone's paper on the analogous

Cu II. The whole term system of Zn III, as given in Table II, is built upon the normal state of the preceding ion Zn^{+++} which is a ^2D term arising from nine equivalent 3_3 electrons or in abreviated notation $^2D(d^9)$. The important

TABLE III

Wave-length list of doubly-ionized zinc

R. W. Wood R. A. Sawyer	this Investigation	Int.	ν	Classification
1839.21	1839.40	4	54,366	$^1D_2-{}^3P_2$
1767.79	1767.75	7	56,569	$^1D_2-{}^3P_1$
1754.04	1753.90	3	57,016	$^3D_1-{}^3P_2$
1749.87	1749.66	9	57,154	$^1D_2-{}^3F_3$
1707.18	1706.67	6	58,593	$^3D_2-{}^3P_2$
1659.49	1695.46	3	58,981	$^1D_2-{}^3F_2$
1688.72	1688.60	7	59,221	$^3D_1-{}^3P_1$
1673.21	1673.05	9	59,771	$^3D_3-{}^3P_2$
1651.94	1651.74	8	60,542	$^3D_1-{}^3P_0$
1645.05	1644.81	10	60,797	$^3D_2-{}^3P_1$
1639.54	1639.28	10	61,002	$^1D_2-{}^3D_3$
1629.43	1629.17	10	61,381	$^3D_2-{}^3F_3$
1622.87	1622.50	10	61,633	$^3D_1-{}^3F_2$
1620.01	1619.59	8	61,744	$^1D_2-{}^3D_2$
1601.15	1600.83	9	62,468	$^1D_2-{}^1F_3$
1598.1	1598.51	8	62,558	$^3D_3-{}^3F_3$
	1582.09	10	63,208	$^3D_2-{}^3F_2$
1581.4	1581.54	15	63,230	$^3D_3-{}^3F_4$
	1562.54	9	63,998	$^1D_2-{}^3D_1$
	1560.83	7+C	64,068	$^1D_2-{}^1P_1$
	1553.01	7	64,391	$^3D_3-{}^3F_2$, $^3D_1-{}^3D_2$
1552.2	1552.34	7	64,419	$^1D_2-{}^1D_2$
1515.9	1515.84	8	65,969	$^3D_2-{}^3D_2$
1505.8	1505.95	8	66,403	$^3D_3-{}^3D_3$
	1500.47	6	66,646	$^3D_1-{}^3D_1$
1499.5	1499.49	6	66,689	$^3D_2-{}^1F_3$
	1498.84	5	66,718	$^3D_1-{}^1P_1$
	1491.02	7	67,068	$^3D_1-{}^1D_2$
	1489.33	2	67,144	$^3D_3-{}^3D_2$
1473.5	1473.43	8	67,869	$^3D_3-{}^1F_3$
	1465.80	4	68,222	$^3D_2-{}^3D_1$
1464.3	1464.26	5	68,294	$^3D_2-{}^1P_1$
1456.8	1456.77	8	68,645	$^3D_2-{}^1D_2$
	1432.23	5	69,821	$^3D_3-{}^1D_2$
	713.88	3	140,080	$^1S_0-{}^3P_1$
	677.88	5	147,519	$^1S_0-{}^3D_1$
	677.55	5	147,591	$^1S_0-{}^1P_1$

configurations of Zn^{++} are therefore $(3d)^9$ $(3d)$ or $(3d)^{10}$, $(3d)^9$ $(4s)$ and $(3d)^9$ $(4p)$. They give the following terms:

(1) $(3d)^{10}$: ^1S

(2) $(3d)^9$ $(4s)$: ^3D, ^1D

(3) $(3d)^9$ $(4p)$: $^3(P\ D'\ F)$, $^1(P\ D'\ F)$

Obviously only transitions from the term group (3) to (1) and (2) are possible, whereas (1) and (2) cannot combine with each other. As a comparison with Table 2 shows all the predicted terms have indeed been found. A search is being made for levels arising from configurations with higher total quantum numbers such as $(3d)^9$ $(4d)$ or $(3d)^9$ $(5s)$, although they will produce only rather weak lines in the hot spark spectrum.

b. For a combination of the higher term triads (d^9p) and the metastable terms ^3D and ^1D, corresponding to a transition from a 4_2 to a 4_1 configuration, the irregular doublet law must hold; i.e., the frequency of the lines in question must be a linear function of the nuclear charge as we go from Ni I to Zn III. We choose, as in Table I, the line $^3D(d^9s) - {}^3D'(d^9p)$.

TABLE IV

Irregular doublet law.

Ni I	29464	
		-19451
Cu II	48915	
		-17488
Zn III	66403	

We have an approximate agreement as we found it in Table I when we compared the $\Delta\nu^{1/2}$ in Ni and Cu. If we assume (which certainly is not true) that the irregular doublet law holds *exactly* at the transition from Cu II to Zn III, i.e.,

$$[(^3D(4s))^{1/2} - (^3D(4p))^{1/2}]_{Cu} = [(^3D(4s))^{1/2} - (^3D(4p))^{1/2}]_{Zn}$$

we are able to obtain an estimate of the absolute term value of $^3D(4s)$ in Zn III. As we see from Tables I and IV the result will probably be some thousand wave-number units too low. We obtain:

$$^3D(4s) = 235,000 \text{ cm}^{-1}$$

Another way of getting an estimate of the absolute value of this term is by means of the Moseley law, which was found by Bowen and Millikan to hold also fairly accurately for iso-electronic spectra. All the $(\text{Term})^{1/2}$ curves of these optical Moseley diagrams are, however, slightly concave downwards, so that our extrapolated value will be too high. By means of the values of $^3D(d^9,4s)$ in Ni I and Cu II as given in Table I we obtain

$$^3D(4s) = 260,000 \text{ cm}^{-1}$$

As an unweighted mean of these two values we have adopted 247,000 cm^{-1} for ^3D. We then get for the lowest term

$$^1S(d^{10}) \leqq 325,000 \text{ cm}^{-1}$$

which corresponds to an ionization potential of 40 volts. This value will not be in error by more than 1 volt. For comparison the other ionization potentials of Zn may be added; for the arc spectrum: 9.35 volts and for the first spark spectrum (according to von Salis' analysis) 17.90 volts.

The Moseley diagram drawn with the above adopted term scale for Zn III and with the term values for Cu II and Ni I as given in Table I, is shown in Fig. 2. The ordinates at the left-hand side of the diagram are $\text{cm}^{-1/2}$, those at the right $(\nu/R)^{1/2}$ values. The $(\text{Term})^{1/2}$ lines are—as was to be expected— slightly curved. As the ^1S term has not yet been discovered in the spark spectrum of Cu, the point was drawn according to Shenstone's predictions from the arc spectrum. The fact that this theoretical point fits

so well into the curve may be regarded as a confirmation of Shenstone's prediction and of all his conclusions drawn from it, first of all, of the value for the ionization potential of Cu^+.

Of the four levels resulting from the configuration $(3d)^9$ $(4s)$ and of the twelve levels resulting from $(3d)^9$ $(4p)$ only the two $^3D_3$ levels were drawn for the sake of clearness. The corresponding Moseley curves run satisfactorily parallel.

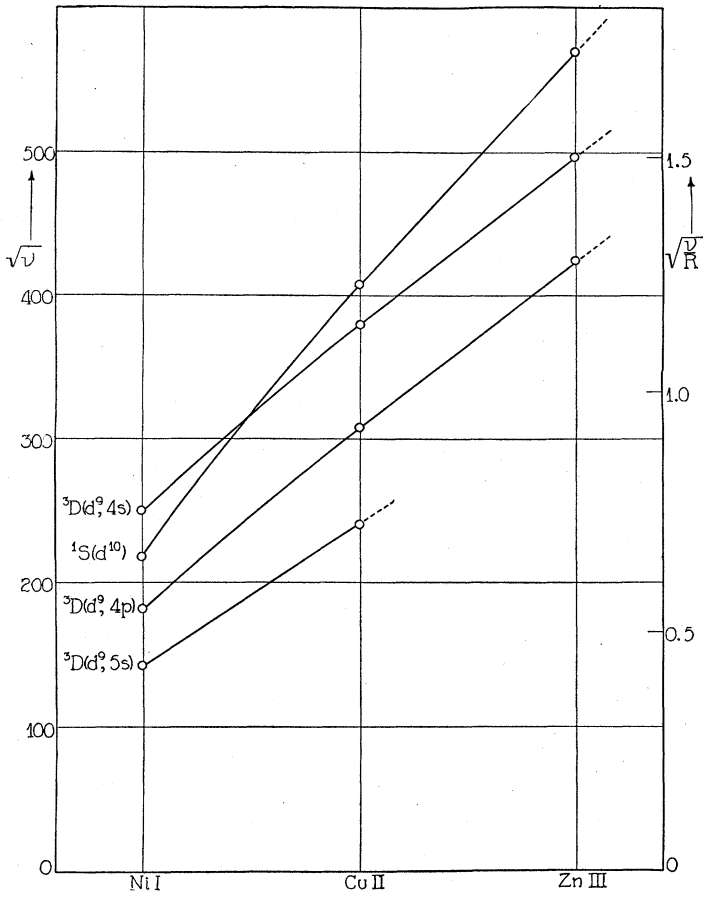

Fig. 2. Moseley diagram for Zn III.

The crossing of the $^1S(d^{10})$ and $^3D(d^9s)$ lines illustrates clearly the increase in stability of the 3_3 electrons as compared with that of the 4_1 electrons, with increasing core charge. The ten-electron configuration being at the end of the 3_3-shell ought to show a decided rare gas-energy diagram with $^1S(d^{10})$ as lowest term. In Ni I, however, the three configurations (d^8s^2), (d^9s) and (d^{10}) are about equally stable; in Cu II the configuration (d^8s^2) has become rather unstable, whereas (d^9s) and (d^{10}) have changed places; finally in Zn III (and also in the following ions) (d^{10}) is rapidly gaining in stability while (d^9s) remains a close companion of the configuration (d^9p).

c. The relativistic doublet law

$$\frac{\Delta\nu}{R}=\frac{\alpha^2(Z-s)^4}{n^3l(l+1)}$$

served as a means to predict the separation of the triplet term $^3D(d^9s)$. A further estimate of the $\Delta\nu$ of this term may be obtained from the doublet term $^2D(d^9s^2)$ which occurs in the next following ionization stage and which also

TABLE V

Separations and screening constants of D terms.

	Ni	Cu	Zn
$^2D(d^9s^2)$		arc $s=13.56$ 2043	1. spark $s=13.42$ 2719
$^3D(d^9s)$	arc $s=13.69$ 1508	1. spark $s=13.51$ 2070	2. spark $s=13.37$ 2754

follows the doublet law.[11] This term was discovered by Shenstone in the spectrum of Cu and by von Salis in that of Zn^+. In Table V the separations and screening constants of triplet or doublet D terms in the three iso-electronic

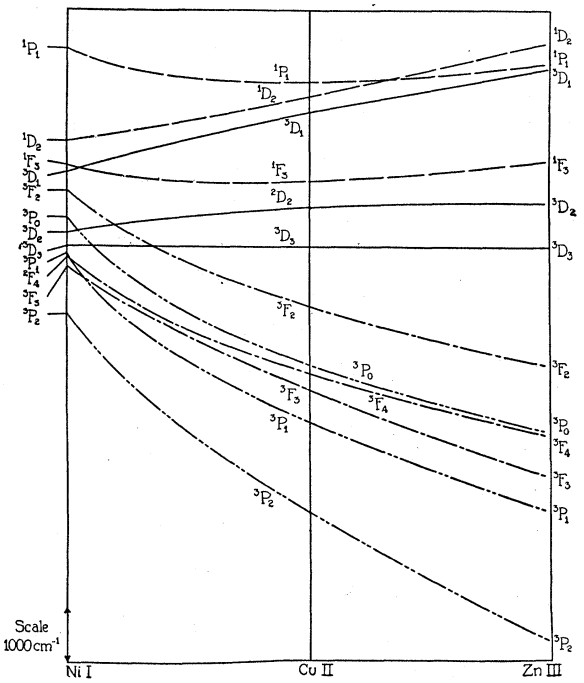

Fig. 3. Term values for Ni I, Cu II and Zn III.

[11] Compare O. Laporte, Phys. Rev. **29**, 650 (1927).

spectra are given. One can imagine that the thus *predicted* separation $\Delta(^3D_{3,1})$ was a great help in finding the combinations of Table II.

The screening constants show the familiar slow decrease as the atomic number increases, the limit being the x-ray screening constant for the doublet $M_{32}M_{33}$: $s_\infty = 13.0$

The last point which needs further discussion is the identification of the twelve high levels as $^{1,3}(P, D', F)$. These levels are not at all grouped in two term-triads each with three easily recognizable terms. The apparently irregular grouping which one notices in Table 2 is a typical feature of the spectrum of higher rank. Of course the inner quantum numbers can readily be ascribed; but there seems to be no unambiguous way to assign the l- and s-values. The crucial argument in favor of our assignment is furnished by the extrapolation from the spectra Ni I and Cu II in which Zeeman effect patterns and combinations with other terms gave additional evidence. In Table VI the separations of the P, D, and F terms are given in the three iso-electronic spectra. For further illustration the relative term values of the twelve levels with respect to $^3D_3$ are drawn in Fig. 3, and corresponding levels are connected by curves.

TABLE VI

Separations of the triplet terms arising from (d^9p)

Spectrum	ΔP		ΔD		ΔF	
	0,1	1,2	1,2	2,3	2,3	3,4
Ni I	691	931	1024	220	1298	−160
Cu II	933	1498	1608	652	1420	−283
Zn III	1321	2204	2254	741	1827	−672

All these regularities, the Moseley law, the screening and relativistic doublet laws and the above discussed increase of the $\Delta\nu$ can easily be used for an extrapolation to higher iso-electronic spectra, e.g., Ga IV, Ge V, etc. In this way the authors intend to investigate these spectra.

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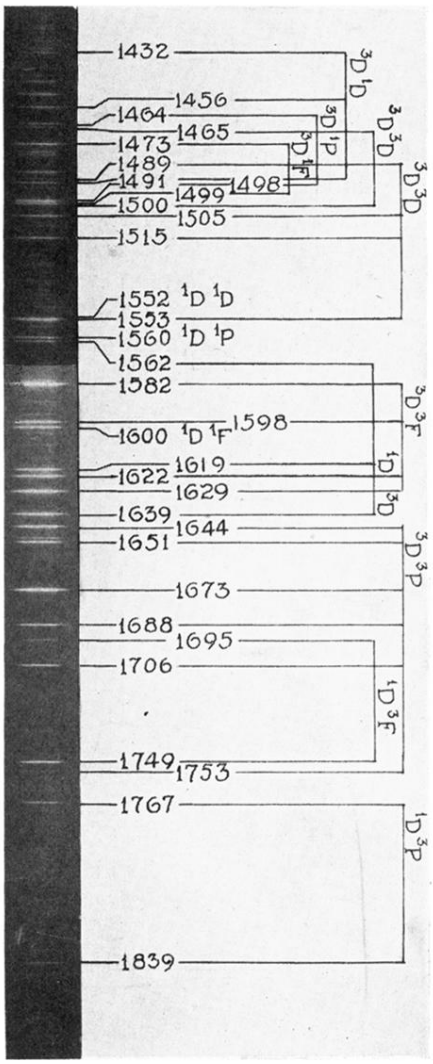

Fig. 1. Photograph of the zinc spectrum in the region from 1850 to 1400A.