The Arc Spectrum of Osmium

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Over 1050 osmium lines have been classified as transitions between 137 terms of Os I. J values have been assigned to all terms without the aid of Zeeman effect studies. If Hund theory is to apply to Os I then the J assignment is unique. The classification is consistent as regards absorption lines, persistent lines, intensities, and comparison with analogous spectra. Comparison with iron shows that nearly all the terms from d^6s^2 and d^7s found in Fe I have been found in Os I. The normal state of osmium is $5d^66s^2(^5D_4)$. The order of $J=2$ and $J=3$ is inverted in the four lowest "multiplets." Electron configurations and "multiplets" overlap to such an extent that the unambiguous assignments of L and S values and electron configurations are impossible for most terms. If the term assumed to be $5d^66s(^6D)7s\,^7D_4$ is correctly designated, then a simple series calculation gives 8.7 volts as an approximate value for the ionizing potential of osmium. New wave-length measurements to extend the analysis are to be made using a grating having a dispersion of 0.4A/mm in the second order. Evidence is presented to show that the normal electron configuration of iridium is $5d^76s^2$.

INTRODUCTION

THE first regularities found in the spectrum of osmium were noted by C. P. Snyder in 1900, long before any theory of complex spectra had been developed. His results, however, were extremely meager, consisting of a constant difference wave number array of 6 columns and 13 rows, containing 55 lines. Snyder never published his work but sent it to Professor H. A. Rowland, who gave the array to Dr. N. E. Dorsey, his assistant, who later placed it in the hands of Dr. W. F. Meggers. The author obtained the loan of the original array through the courtesy of Dr. Meggers. The present communication gives the results of an extension of the term array to 137 terms, accounting for over 1050 lines.

The arc spectrum of osmium is extremely rich in lines, the wave-length list used in this work containing over 2200. The data were taken from Meggers[1] for the region 8645–4500A, and from Kayser,[2] and Exner and Haschek[3] for the region 4500–2251A. The region from 4280–3600 is somewhat incomplete due to overlapping of cyanogen bands. Meggers and Laporte[4] photographed the underwater spark spectrum, obtaining 193 lines in absorption between 4420A and 2211A. With these data they were able to establish the energies of the levels appearing in Snyder's array.

Zeeman effect observations for 32 lines have been published by Moore,[5] but these results are of such a qualitative nature as to be of no aid in establishing quantum numbers.

PROCEDURE

The ordinary criteria used in classifying spectra, such as Zeeman effects, selection rules, interval rule, and intensities cannot be effectively applied to the elements of the third transition group. Not only is the coupling of an intermediate type, but different electron configurations of the same parity overlap to such an extent that strong perturbations enter to further distort the "multiplets."* In all but a few instances it will be quite impossible, and, in fact, quite meaningless to assign levels to electron configurations and values of L and S to the levels.

The inconvenience caused by the breakdown of the selection rules is partially compensated for

[1] Meggers, Sci. Papers Bur. Standards **20**, 35 (1924).
[2] Kayser, Astrophys. J. **7**, 181 (1898).
[3] Exner and Haschek, *Wellenlängen-Tabellen* (1904).
[4] Meggers and Laporte, Phys. Rev. **28**, 642 (1926).
[5] Moore, Astrophys. J. **28**, 1 (1908).
* Quotation marks are used to indicate that the word is not meant in the usual sense that applies when good LS coupling is present. Rather, it is used here in intermediate coupling to indicate that group of levels which appear to be most closely associated with the levels of the true multiplet that would be present if the coupling were LS. See Bacher and Goudsmit—*Atomic Energy States*, paragraphs 6, 8 and 10.

by the larger number of combinations, and hence the increased effectiveness of the combination principle as the means of establishing a term array. Because Snyder's array is so fragmentary, it was decided to make an independent start, by using the mechanical interval recorder.[6] A selected group of the 184 strongest osmium lines were run through the machine. A glance at the record showed an unusual number of coincidences occurring at an interval of 1419.9 cm^{-1}; eight pairs of lines fitting to within 0.1 cm^{-1}. Additional pairs of lines which gave intervals corresponding to intervals between different sets of the eight pairs were obtained from the record; some of which established columns that gave several combinations with the rows previously established by the eight pairs. Continuing in this manner, an array of seven columns and twenty-nine rows was established in but a few hours.[7] The new array contained all of Snyder's array except the column at 3931.0 cm^{-1}, which later proved to be false.

The mechanical interval recorder was a great aid in the combing of the complete list of wave numbers with a given interval. A record for a large number of the lines was obtained so that for a given interval 1 mm on the record was equivalent to about 200 cm^{-1}. A scale was then made so that the wave number of one of the two lines which gave the interval in question could be read directly to within 100 cm^{-1}. This aid reduced the time to comb the wave-number list with a given interval by a factor of eight or ten.

Early in the work it was obvious that the terms fell into different groups as regards combinations. In most cases there is no ambiguity as to which combination, or J group, the term belongs. Seven of these groups have been found.

The most satisfactory method of determining J values is from the number of components into which a term is split in a magnetic field. Since no quantitative Zeeman effect data are on hand for osmium, other means of assigning J values to the terms must be used. Fortunately, in this case the assignment can be done uniquely with only such criteria as the values of J and the number of each expected from the different electron configurations. Any other assignment than the present one violates theory either by resulting in larger values than allowed by the electron configurations, or by giving negative J values. Besides being uniquely assigned, the terms of given J appear in the proper number and expected positions when analogy is made with iron. Most of the intense lines, persistent lines, and strongly absorbed lines are associated with the correct type of terms as expected from theory. However, in spite of this excellent agreement a further check on the J value assignment by Zeeman effect is highly desirable.

The Term System of Os I

The complete list of terms is given in Table I. The first column gives the term symbol used in this work. The quantum numbers assigned in this column are explained below. Column two gives the J values of the term; column three, the energy of the term in cm^{-1}; column four, the number of combinations found for the term. Osmium is extremely rich in combinations, some of the leading low terms combining with more than 90 percent of the terms allowed by the J selection rule. The term 2, for example, combines with 39 out of a possible 42.

The lowest terms of osmium are expected to arise from the electron configurations $5d^6 6s^2$ and $5d^7 6s$, the normal state of the atom being either $^5D_4$ from $5d^6 6s^2$ or $^5F_5$ from $5d^7 6s$. The former is found to be the normal state of osmium; the latter occurs at a position 5144.0 cm^{-1} above the ground state.

Existing data[8] indicate that the term order of the elements in the third transition group should be more nearly similar to the corresponding elements in the first group, rather than to the ones in the second group. This is because the d electrons are more tightly bound than the s electrons in the second group in comparison with the first and third groups. For this reason the term systems of osmium and iron should show similarities. Fig. 1 shows that this is the case, especially among the very low terms. The broken lines in the figure connect iron and osmium terms which, in the opinion of the author are most nearly analogous. Electron configurations and "multi-

[6] Harrison, R.S.I. **3**, 753 (1932); **4**, 581 (1933).

[7] Albertson, Phys. Rev. **43**, 501 (1933).

[8] Bacher and Goudsmit, *Atomic Energy States*, McGraw-Hill (1932).

TABLE I. *Complete list of terms.*

Term symbol	J value	cm^{-1}	Number of combinations	Term symbol	J value	cm^{-1}	Number of combinations	Term symbol	J value	cm^{-1}	Number of combinations
1 $d^6s^2\ ^5D$	4	0.0	34	40°	2	32457.4	15	85°	5	43401.8	9
2 ^5D	2	2740.5	39	41°	4	32684.7	19	86°	2	43437.0	12
3 ^5D	3	4159.4	46	42°	3	33124.5	22	87°	3	43515.7	17
4 $d^7s\ ^5F$	5	5144.0	34	43°	3	34125.5	19	121°	4	43754.7	9
5 ^5D	1	5766.2	18	44°	5	34365.3	14	88°	4	43862.7	16
6 ^5D	0	6092.9	6	45°	4	34803.9	14	89°	5	43876.2	7
7 ^5F	4	8742.8	50	46°	2	35090.5	17	90°	2	44075.3	13
8 ^5F	2	10165.9	35	47°	3	35616.0	27	91°	2	44662.8	10
9 $d^7s\ ^3F$	4	11030.6	47	48°	1	35919.5	16	92°	4	44892.7	14
10 ^5F	3	11378.0	42	49° ?	1	36264.5	4	93°	5	44921.2	7
11 ^3F	2	12774.3	31	50°	2	36345.9	15	94°	2	45252.2	6
12 ^5F	1	13020.0	20	51°	2	36634.5	17	95°	6	45315.9	3
136	2	13364.8	23	52°	3	36806.3	19	96°	3	45561.9	9
13 ^3F	3	14091.4	36	53°	5	36818.1	16	97°	5	45758.9	7
14 ^3H	5	14339.0	27	54°	4	36826.2	18	98°	3	46169.5	10
15 ^3H	4	14848.1	39	55°	3	37808.6	24	99°	4	46263.5	12
16 ^3H	6	14852.4	13	56°	4	37908.8	16	100°	4	46328.0	9
17	2	15222.6	35	57°	2	37921.8	18	101°	3	46776.3	15
18 $d^7s\ ^5P$	3	15390.7	37	58°	4	38130.1	19	120°	3	47057.2	7
126	1	16212.4	16	59°	1	38244.2	17	102°	4	47158.4	9
19	1	17667.4	16	60°	3	38264.1	22	103 $d^6s\cdot s\ ^7D$	5	47198.8	8
137 ^3P	0	18301.4	4	61°	2	38330.8	20	104°	5	47200.2	5
20	3	18902.0	37	62°	3	38485.9	20	105°	3	47614.7	10
21	4	19108.9	35	63°	1	38613.6	11	106°	3	48302.6	10
22	2	19410.6	23	64°	2	38741.3	16	107 ^7D	4	48737.5	12
23?	4	19759.9	10	65°	2	38875 9	9	108°	2	49112.0	9
24	4	19893.1	33	66°	3	39383.0	16	133° ?	5, (4)	49534.2	4
25	1	21033.5	12	67°	5	39406.0	11	109°	3	49946.9	7
124	2	21303.3	20	68°	2	39493.8	13	132°	4	50293.9	9
128	0, (1)	22563.7	4 (6)	69°	2	39674.9	14	135°	5	50377.2	7
26° $d^6sp\ ^7D°$	4	22615.8	11	70°	3	39772.3	7	131°	4	50937.3	8
125	2	23317.6	18	71°	4	40087.1	14	110 $d^6s\cdot s\ ^5D$	4	51038.6	15
127	4	23322.7	19	72°	6	40290.6	5	111 ^7D	3	51138.2	15
27° $^7D°$	5	23463.0	9	73°	4	40361.8	13	130°	5, (4)	51152.0	8
28	5	24292.0	15	74°	1	40497.5	10	112	2	52148.7	16
29° $^7D°$	3	25013.0	9	75°	2	40888.1	11	113 ^5D	3	52401.9	21
31° $^7D°$	2	25275.4	9	76°	6	41023.2	5	134°	4, (3)	52534.6	5
30	3, (4)	25593.9	15	77°	5	41225.1	14	114	2	53594.6	17
32° $d^6sp\ ^7P°$	4	28331.8	14	78°	5	41725.6	11	115	3	54676.9	19
33°	3	28371.7	17	79° ?	6	41754.1	3	116	3	55388.9	9
34° $d^6sp\ ^7F°$	6	29099.4	4	80°	3	41875.9	18	122	5	55402.6	12
35°	3	29381.6	15	81°	5	42310.4	10	117	4	55419.0	11
36°	2	30078.3	14	82°	3	42316.8	13	123	2	56092.5	8
37°	5	30280.0	12	129°	1, (2)	42422.3	8	118	5	56222.5	15
38°	1	30524.9	10	83°	4	42746.7	14	119	4	56729.2	17
39°	4	30591.5	17	84°	3	43011.4	16				

plets" overlap to such an extent that this analogy cannot be carried too far. Since the L and S values assigned to certain terms in column one of Table I were all obtained in this manner, they should be considered only as a notation for stating that in the opinion of the author this osmium term with its L, S and J values more nearly resembles the corresponding iron term of same L, S and J value than does any other osmium term of the same J value. Such statements can be made, since particular values of L and S do dominate a given term when the coupling is intermediate; although in certain instances the domination is by such a scant margin that the choice of particular values of L and S is a matter of personal opinion.[9]

One particular feature of the lower terms is the inversion of the expected order of $J=2$ and 3 in

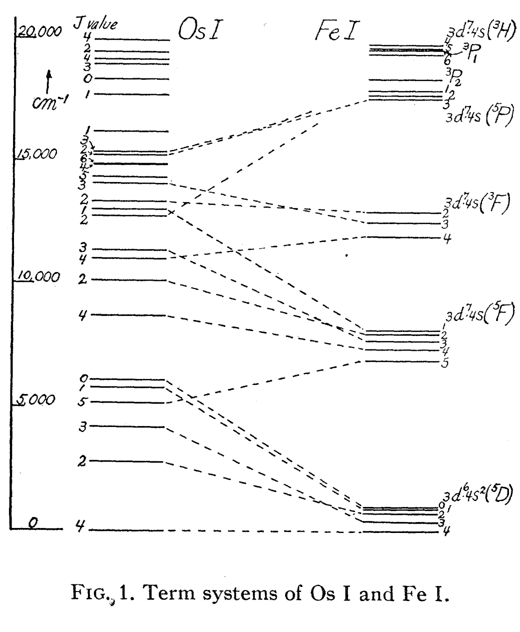

FIG. 1. Term systems of Os I and Fe I.

[9] Bacher and Goudsmit, *Atomic Energy States.* Paragraphs 6, 8 and 10.

the four "multiplets" ^5D, ^5F, ^3F, ^5P. All the other terms in these "multiplets" occur in the expected order.

The term 107 appears to be analogous to $d^6s\cdot s\ ^7D_4$ of iron. If such is the case, it can be used with the ground level to give a rough approximation of the ionization potential. The simple series calculation gives a value of about 8.7 volts.

Fig. 2 shows a plot of the wave-number separation of the lowest term of $d^{n-1}s^2$ from the lowest term of $d^{n-1}s$ for all the elements of the first long period (full line) and for those of the third period (broken line) for which data are available. The assignment given to osmium places its point in good agreement with its expected position. The two lowest terms in iridium are $J=9/2$ terms.[10] One is apparently the lowest term, $^4F_{9/2}$, from d^7s^2 and the other, the lowest term, also $^4F_{9/2}$, from d^8s. Omitting iridium from the plot for the moment, it is obvious where its point should go, and hence that d^7s^2 is the normal electron configuration of the atom.

It is of interest to note, as is shown in Table II, that all sensitive lines of osmium,[11] except one, have either $d^6s^2(^4D_4)$ or $d^7s(^5F_5)$ for their lowest level. Also, as is shown in Table III, 27 of the 37 strongest absorption lines start from these same levels, while the rest start from $^4D_3$ or $^4D_2$. Nearly all the absorption lines listed by Meggers and Laporte[4] have been connected with the low terms below 13,000 cm^{-1}.

Because of lack of space and incompleteness of the classification, it is not thought worth while to publish the complete list of classified osmium lines at this time. However, Table IV contains a list of all the stronger lines, from intensity 30 to 6 inclusive on Exner and Haschek's scale. Only one of the 52 lines remains to be classified. The intensities are arc intensities, an R indicates reversed in underwater spark; a P that the line is a persistent line. The average deviation of experimental and calculated wave-lengths for lines in the complete list is slightly less than ± 0.01A, which is well within the experimental error of Kayser and Exner and Haschek's measurements. The agreement for the lines measured by Meggers is even better, except in the infrared.

TABLE II. *Sensitive lines of osmium.*

λI.A. Int.	Combination	J Comb.
4420.46—20R	1—26°	4—4
4260.85—20	1—27°	4—5
3267.94—10R	1—39°	4—4
3262.30—8R	3—45°	3—4
3058.66—8R	1—41°	4—4
3030.70—4R	4—58°	5—4
3018.04—4R	1—42°	4—3
2909.08—8R (R.U.)	1—44°	4—5
2838.63—4R	4—73°	5—4
2637.12—3R	1—56°	4—4
2488.55—2R	4—95°	5—6

TABLE III. *Most strongly absorbed underwater spark lines of osmium.*

λI.A. I(abs.)	Comb.	λI.A. I(abs.)	Comb.	λI.A. I(abs.)	Comb.
3301.55—25	(1—37°)	3018.05—10	(1—42°)	2320.20— 7	
2909.07—25	(1—44°)	2838.64—10	(4—73°)	2289.32— 7	
		2714.64—10	(1—54°)		
3058.66—20	(1—41°)	2689.80—10	(4—81°)	2919.83— 6	
	(13—101°)	2613.08—10	(4—85°)	2844.39— 6	(4—72°)
2488.55—20	(4—95°)	2418.54—10	(2—90°)	2644.11— 6	(1—55°)
2425.00—20	(1—77°)	2387.29—10	(1—80°)	2379.40— 6	(4—102°)
2377.05—20	(4—104°)			2308.32— 6	
2270.18—20	(2—101°)	2370.69—10	(3—100°)		
2264.60—20	(3—106°)	2362.77—10	(1—81°)	3752.54— 5	(2—35°)
		2303.32—10	(1—85°)	3232.07— 5	(3—46°)
3267.94—15	(1—39°)			3030.70— 5	(4—58°)
2637.12—15	(1—56°)	2806.91— 8	(1—47°)	2912.36— 5	(3—62°)
2252.03—15	(4—133°)			2860.97— 5	(4—71°)
		2513.25— 7	(4—93°)	2796.73— 5	(2—62°)
3262.29—10	(3—45°)	2461.43— 7	(4—97°)		(9—101°)
3156.24—10	(4—53°)	2324.25— 7	(1—84°)	2786.31 —5	(4—76°)
3040.90—10	(2—47°)				

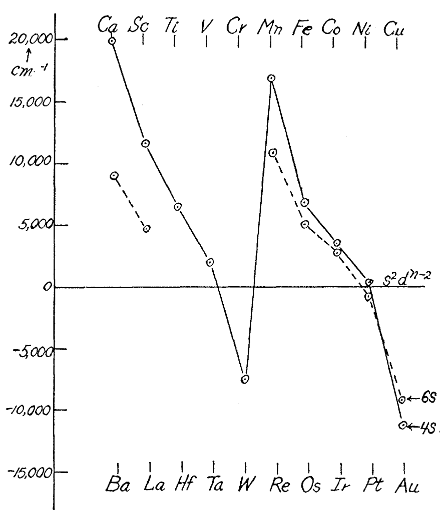

FIG. 2. Plot of the wave-number separation of the lowest term of $d^{n-1}s^2$ from the lowest term of $d^{n-1}s$ for all the elements of the first long period (full line) and for those of the third period (broken line) for which data are available.

[10] Albertson, Phys. Rev. **42**, 443 (1932).

[11] Twyman and Smith, *Wave-length Tables for Spectrum Analysis.* Adam Hilger, p. 128 (1931).

TABLE IV. *All strongest lines in Os arc from I=30 to I=6 inc.*
All intensities are from Exner and Haschek's estimates.

λI.A. Int.	Comb.	λI.A.° Int.	Comb.	λI.A. Int.	Comb.
4135.81—30	(3—32°)	3656.90—10	(2—36°)	3058.68— 8*RP***	(1—41°)
	(13—60°)	3670.90—10	(9—60°)		(13—101°)
4211.90—30*	(27°—103)	3719.49—10	(9—56°)	3156.25— 8 *R*	(4—53°)
			(15—78°)	3232.06— 8 *R*	(3—46°)
3752.54—20 *R*	(2—35°)	3720.12—10	(7—47°)	3262.30— 8 *RP*	(3—45°)
3782.19—20 *R*	(3—39°)		(16—78°)	3336.16— 8 *R*	(3—43°)
4112.04—20*	(5—36°)		(31°—112)	3370.58— 8 *R*	(4—45°)
4260.85—20 *P*	(1—27°)			3532.83— 8	(3—40°)
4420.47—20 *RP*	(1—26°)	3790.14—10	(15—77°)	3616.58— 8	(8—55°)
		3836.03—10	(7—45°)	3640.35— 8	(15—81°)
3793.93—15	(20—94°)	3840.29—10		4172.58— 8	(8—43°)
3963.65—15	(3—35°)	3849.96—10	(11—64°)	4189.91— 8	(11—51°)
3977.24—15	(4—37°)	3857.09—10	(3—36°)		
4173.24—15	(4—34°)	3876.76—10	(9—53°)	4328.69— 8	(9—43°)
		4066.70—10	(26°—103)	4394.88— 8	(10—43°)
3267.96—10 *RP*	(1—39°)	4091.84—10	(6—38°)		
3301.56—10 *R****	(1—37°)	4175.62—10	(7—41°)	3387.86— 6	(8—69°)
3528.60—10 *R*	(1—32°)	4293.98—10	(15—58°)	3401.87— 6	(7—58°)
3559.82—10	(7—54°)	4311.41—10	(4—32°)	3402.52— 6	(1—35°)
3560.88—10 *R*	(7—53°)			3504.66— 6	(3—41°)
3598.10—10	(2—38°)	2909.09— 8*RP*	(1—44°)	3865.44— 6	(31°—111)
	(13—80°)			3938.59— 6	(7—43°)

* Kayser gives 4211.90—30 and 4112.04—20 only moderate intensities.
** 3058.68—8*RP* is listed as one of the second strongest Os arc lines by Kayser.
*** 3301.56—10*R* is listed as the strongest Os arc line by Kayser.

Conclusion

It is thought advisable to obtain a new and better description of the arc spectrum of osmium before continuing with the classification. In many instances the estimated intensities as given separately by Kayser and by Exner and Haschek are not in good agreement. The region between 3800A and 3600A has never been completely photographed. Comparison between arc and spark spectra from the existing tables allows for the elimination of only a very few of the spark lines. No doubt many of the weaker unclassified lines in the arc list will later prove to be spark lines. Much is to be desired in the way of better wave-length measurements, principally because so much must be done solely by the combination principle. Surely, some of the lines will be shown to be erroneously classified when more accurate wave-lengths are at hand, and some few of the weaker ones may prove to be spark lines. Finally, Zeeman effect measurements should be obtained to check the J value assignment and for any other data that they might yield.

All the above will be undertaken in the Spectroscopy Laboratory at M. I. T. in the near future. The wave-lengths will be measured with plates taken from the large 35 ft. 180,000 line grating, having a dispersion of 0.4A mm in the second order. Preliminary measurements of the wave-lengths of iridium, with this grating, indicate that for sharp lines the accuracy of measurement is limited only by the accuracy of the iron standards.

I wish to thank Professor G. R. Harrison, in whose laboratory this work was done, and Professor H. N. Russell of Princeton for his interest and criticism during the course of the work.