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WAVE-LENGTH MEASUREMENTS IN THE ARC AND SPARK SPECTRA OF ZIRCONIUM

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ABSTRACT

The arc and spark spectra of zirconium as emitted between electrodes of pure zirconium metal were photographed with the concave grating and quartz prism spectrographs of the Bureau of Standards. The measured wave lengths in the arc spectrum cover the region from 4881 A in the blue to 9277 A in the infra-red, thus extending our knowledge of the spectrum more than 2,000 units beyond the longest Zr wave length heretofore observed. The arc spectrum in the regions investigated is superposed on a band spectrum in which the bands are shaded toward the red. The wave-length measurements of the spark spectrum extend from 2163 A in the ultra-violet to 6115 A in the red, and contain not only the lines of the singly ionized atoms but also those of doubly and trebly ionized atoms.

CONTENTS

I. INTRODUCTION

For more than a decade the spectroscopy section of the Bureau of Standards has had, as a major portion of its program, the measurement of standard wave lengths in the spectra of the chemical elements. In particular, this work has been concerned with the extension of our knowledge of spectra into those regions which have been but poorly or not at all observed, namely, the red and infra-red, as far as present-day photographic processes will permit. But the progress which recent years have seen in the analysis of complex spectra into their series relationships has demonstrated the need of a careful revision of the existing wave-length material, especially of the rarer elements. These objects have been attained for the element zirconium, atomic No. 40; and it is the purpose of this paper to present the wave-length measurements which have been made in its arc spectrum from 4881 A in the blue to 9277 A in the infra-red, and in its spark spectrum from 2163 A in the ultra-violet to 6115 A in the red.

The earlier investigations on the arc and spark spectra of Zr are described in Kayser's Handbuch, Volume VI. Since the appearance of that work in 1912 five papers dealing with measurements of Zr wave lengths have been published. These are by: (1) Eder,[1] for the limited region in the red from 6470 A to 7344 A; (2) Vahle,[2] for the entire region accessible to him photographically from 2285 A in the ultra-violet to 7203 A in the red; (3) McLennan and Lewis,[3] whose measurements extend from 1656 A to 1854 A in the Schumann region; (4) Bowen and Millikan,[4] who present seven new lines in the extreme ultra-violet, together with their series classification; (5) McDonald, Sutton, and McLay,[5] whose measurements in the arc and spark spectra extend from 1866 A to 2164 A in the ultra-violet. In 1923 announcement was made of the discovery of a new element,[6] atomic No. 72, and subsequently named hafnium, which resembles Zr in its chemical properties and is closely associated with it in nature. A full account of the occurrence and properties of hafnium has been published by G. von Hevesy,[7] codiscoverer of it with D. Coster. Its optical spectrum has been measured by Hansen and Werner.[8] Comparison of their Hf wave lengths with existing tables of Zr lines has shown that numerous faint lines ascribed to Zr are in reality the stronger Hf lines.

II. EXPERIMENTAL PROCEDURE

The spectrograms upon which the present investigation is based were secured with the concave grating and quartz prism spectrographs of the Bureau of Standards. The gratings and the method of mounting them have been described in earlier papers.[9] The quartz prism spectrograph is Hilger's type E 1.

For the region from 2100 A to 2400 A, the quartz prism spectrograph was employed, the dispersion ranging from 1.46 A per mm to 2.25 A per mm. The spectrograms were obtained on Schumann plates supplied by Hilger. For the spectral regions from 2300 A to 9300 A the grating spectrographs were used. The first order of the 20,000 lines-per-inch Rowland grating was used to photograph the regions from 2300 A to 3100 A and from 4900 A to 9100 A. From 3000 A to 5500 A the second order of this grating was used. The dispersions were 3.6 A and 1.8 A per mm, respectively, for the first and second orders. The Anderson grating with 7,500 lines per inch, giving a dispersion of 10.4 A per mm in the first order, was used to

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[1] Sitzungsberichte, K. Acad. Wiss. Wien., IIa, 123, p. 2301; 1914.
[2] Zeitschr. Wiss. Phot., 13, p. 34; 1913.
[3] Proc. Roy. Soc., London, 98, p. 109; 1920.
[4] Phys. Rev., 28, p. 924; 1926.
[5] Trans. Roy. Soc. Canada, 20, p. 318; 1926.
[6] Nature, 111, p. 79; 1923.
[7] Kgl. Danske Vid. Selskab Math-fys. Medd., 6, No 7; 1925.
[8] Kgl. Danske Vid. Selskab Math-fys. Medd., 5, No. 8; 1923.
[9] B. S. Sci. Papers Nos. 312, 441, and 499.

photograph the spectrum from 5500 A to 9300 A. The Anderson grating gives much brighter images than the Rowland grating and was used exclusively for making the longer exposures which ranged from one to four hours.

The spectrograms with the Rowland grating were photographed on Schleussner ultra-rapid plates 40 cm long by 6 cm wide. These plates were about 1 mm in thickness, and accordingly could be bent to fit the focal curve of the grating. With the Anderson grating flat plates 20.5 cm long by 6.5 cm wide were used to photograph the spectra. To render the plates sensitive to the green, yellow, red, and infra-red portions of the spectrum, they were bathed in solutions of pinaverdol, pinacyanol, dicyanin, and neocyanin,[10] respectively, by the well-known methods.[11]

The light sources were arcs or sparks maintained between Zr electrodes. The arcs were operated on 240 volts d. c., at current strengths ranging from 4 to 7 amperes. The spark discharge was supplied by a transformer which stepped-up 110 volts a. c., to 40,000 volts. A condenser 0.006 μf capacity was connected in parallel across the high-voltage terminals of the transformer. Exposures to the spark were always juxtaposed to arc exposures, and these in turn to exposures to the Fe or Cu arcs which furnished the comparison spectra. On some of the plates the neon spectrum also was photographed to serve as a comparison spectrum.

The material used in the electrodes for the earlier Zr exposures was Kahlbaum's preparation of zirconium nitrate. It was burned on cored copper rods. But for the later spectrograms, which constitute the majority of the series, the electrodes were rods or small lumps of Zr metal which was kindly supplied to us for spectrographic analysis by three different donors, namely, Prof. M. A. Hunter, of Rensselaer Polytechnic Institute; Dr. L. M. Beckett, of the Electrometallurgical Co.; and Dr. H. C. Rentschler, of the Westinghouse Research Laboratory. It is a pleasure to acknowledge here our indebtedness to these men for the interest they have taken in the work and their generosity in supplying the various samples of metallic Zr.

All the spectrograms were measured on the large measuring machine which has already been described.[12] The plates were measured in the direct and reversed position, the recorded readings of the micrometer head being the means of from 4 to 12 settings on the spectrum line. The reference lines were selected from the iron or neon spectra except in the ultra-violet where the Cu lines measured by Mitra [13] were used. For values of the Fe wave lengths the results

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[10] J. O. S. A. & R. S. I., 12, p. 397; 1926.

[11] B. S. Sci. Paper No. 422.

[12] B. S. Sci. Paper, No. 372.

[13] Annales de Physique, 19, p. 315; 1923.

of Meggers and Kiess [14] were used in the region 6750 A to 8824 A; for the region 3370 A to 6700 A the wave lengths determined by Meggers, Kiess, and Burns [15] were used; and for the regions extending from 2300 A to 3400 A the values determined by Burns [16] were adopted. The Ne wave lengths are those measured by Burns, Meggers, and Merrill.[17]

III. RESULTS

Tables 1 and 2 contain the wave lengths in international angstroms, which have been determined for the arc and spark spectra of zirconium. Following the wave lengths are numbers indicating the estimated intensities of the lines, the strongest being assigned 15, and letters which describe the character of the lines, and the accuracy of the wave-length determinations. The symbols have the following significance:

b=broad.
coin=coincident.
d=double.
g=ghost.
h=hazy.
l=shaded to red.
n=band head.
p=part of band structure.
R=reversed.
v=shaded to violet.
A=probable error of 0.000A to 0.010A.
B=probable error of 0.010A to 0.020A.
C=probable error of 0.020A to 0.030A.
D=probable error >0.030A.
E=only one determination.

The majority of the wave lengths of Table 1 represent the means of from 3 to 11 determinations. The majority of those of Table 2 are based on 2 to 4 determinations. Lines of impurities in the zirconium have been omitted in all cases where their chemical origins have been established with certainty. Although the samples of metallic zirconium represented chemical purity approximating or surpassing 99 per cent, yet all contained as impurities the elements Fe, Ti, and Cr, and in two of them were detected traces of Al, Mn, and Si. Of course, the prominent lines of the recently discovered hafnium were also present, and with a few exceptions these, too, so far as their identity has been established, have been omitted from the following wave-length lists. The comparison of the Zr wave lengths with the infra-red Hf spectrum is based on recent unpublished observations by Meggers at the Bureau of Standards.

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[14] B. S. Sci. Paper No. 479.
[15] B. S. Sci. Paper No. 478.
[16] Lick Observatory Bulletin, 8, p. 27; 1913; Comptes rendus, 160, p. 243; 1915.
[17] B. S. Sci. Paper, No. 329.

TABLE 1.—*Arc spectrum of zirconium*

λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error
9276.94	1	B	8345.99	1−	E	7723.70	4	C
9139.33	1	D	42.10	1−	E	22.48	3	C
9099.90	1−	E	32.44	5	B	21.72	1p?	E
69.40	2	B	28.54	1	E	08.38	4	B
15.13	5	B	20.12	5	B	7704.24	5	A
9011.31	1	C	16.97	1	E	7693.45	1	E
8941.74	1	C	09.50	3	B	90.81	5	A
30.10	1	E	8305.94	9	A	58.62	6	A
25.04	1	B	8299.79	4	B	54.40	1	E
10.05	1	C	96.54	2	E	50.50	1	E
8906.33	1	B	83.84	7	A	46.71	2	E
8899.52	5	B	40.36	6	A	24.48	2 Hf?	D
94.01	1−	E	12.59	9	A	21.60	2	E
44.50	1−	D	8201.73	7	A	21.16	5	A
36.09	6	B	8194.91	2 Zr?	E	15.74	2	E
8804.98	3	B	94.64	5	A	14.48	1p?	E
8786.23	2	B	88.76	5	B	12.08	5	A
78.48	1−	E	74.63	1	C	10.89	3	B
71.02	1−	E	69.72	2	C	09.69	2	C
62.93	1	C	52.59	5	A	7607.19	8	A
49.48	4	B	33.00	8	A	7562.94	1 Hf?	E
42.11	1	E	25.84	1	C	62.17	5	A
34.86	3	B	20.15	3	A	60.31	3	D
8709.24	1	C	14.29	2	E	60.04	4	C
8683.46	1 N?	C	09.23	1	E	58.47	6	A
80.30	1 N?	B	8107.50	1−	E	54.73	7	A
56.04	1− Zr?	E	8087.79	1	E	52.99	4	A
54.59	1− Mn?	E	70.12	8	A	51.50	7	A
42.76	2	B	63.10	6	A	44.62	6	A
41.01	3	B	58.14	5	A	40.65	7	A
38.51	1	D	55.73	3	C	21.03	5	B
27.71	1	C	55.32	3	C	19.34	1	E
15.66	1	E	53.08	3	A	17.97	5	A
14.16	1−	E	46.08	1	A	15.78	6	B
8610.24	2 Zr?	B	15.22	1 Zr?	C	06.56	4	B
8587.84	3	B	8005.28	3	B	7502.91	4	B
84.21	5	A	7994.75	1 Hf	E	7479.61	5	A
81.22	1	E	63.69	4	A	67.57	5	B
79.47	1	E	60.01	6	A	39.89	8	A
75.69	1	D	56.69	6	A	33.12	4	B
71.05	4	B	44.65	7	A	23.83	1 N?	E
68.54	4	B	40.46	4	A	22.77	4	A
58.64	2	C	31.76	2	E	17.91	3	A
54.42	2	C	24.17	2	E	14.24	1	E
36.22	1	C	20.76	1	E	11.42	3	A
35.13	1	C	15.17	2	E	7400.89	5	A
24.99	1	C	08.46	4	A	7399.33	3	B
15.06	3	C	7906.55	1	E	85.18	2b, n?	E
13.78	3	C	7897.98	4	A	83.64	6	A
10.38	1 Zr?	E	88.52	2	B	79.19	1p?	E
			82.15	4	A			
8502.77	2	C	76.24	4	A	77.85	1	E
8498.44	7	A	70.00	6	A	74.80	3	B
95.98	4	A	68.34	3	C	73.51	6	A
64.65	7	A	64.37	2	E	68.46	1p?	E
60.04	1 Hf?	E	49.38	7	A	67.22	3	A
57.50	4	B	45.34	2 Hf?	E	61.56	1	E
53.13	7	A	42.93	2	E	60.66	2	B
29.14	1−	E	33.36	1	E	58.60	1	B
16.91	1	E	26.75	7	A	53.34	1p?	C
14.00	7	A	22.96	6	A	52.14	1p?	E
8408.50	1−	E	19.36	8	A	43.98	7	A
8390.18	2	E	16.31	4	B	40.03	1p?	C
89.42	8	A	7800.73	3	C	36.03	7	A
86.70	3	B	7799.51	2	E	32.73	1p?	E
82.79	1	E	66.54	4	B	32.27	1p?	E
70.21	7	A	65.67	3	B	31.01	1p?	E
65.98	1 Zr?	E	55.39	2	E	27.84	5	A
61.17	2	C	45.43	2	E	23.75	3	C
60.17	1−	E	44.05	2	E	20.00	2 Hf?	D
50.45	1−	E	40.13	2 Hf?	E	18.15	8	A

TABLE 1.—*Arc spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error
7317.32	1	C	6883.27	4	B	6587.13	2p?	E
13.73	6	A	57.93	3	B	85.42	2p?	E
11.68	6	A	54.63	4	A	83.61	2p?	E
07.38	2	B	53.85	3g coin?	A	78.06	3b, p?	B
7306.24	5	A	52.59	4	A	76.57	4	B
7284.76	1	C	49.29	6	A	69.43	5	B
84.02	1	E	48.31	3p?	E	50.57	5	B
64.79	6	A	47.34	4	E	42.90	4n	B
58.23	3	B	47.03	8	A	08.15	5n	B
48.50	1	C	46.42	5	A	06.39	5	A
40.88	3 Hf	A	45.30	5	A	6503.31	5	A
37.08	3 Hf	B	43.76	2	B	6495.51	3n	C
23.87	1	D	38.69	3	A	93.12	5	A
7201.67	6	A	33.69	4	A	89.68	8	A
7193.37	2h, p?	D	32.93	7	A	84.35	2	B
79.59	2	C	28.82	7	A	80.98	2n	C
77.26	1	E	12.66	3h, p?	D	73.79	6n	B
69.14	9	A	11.32	2	E	70.25	8	A
62.12	2	C	6805.85	2p?	E	57.60	4	C
61.02	2p?	E	6796.71	3	A	51.62	4	E
57.88	2p?	C	94.66	2p?	B	45.76	7	B
46.11	2	C	90.89	6	A	39.01	5	B
44.48	4	A	87.15	3	A	34.40	4	B
43.87	2p?	C	82.09	2n	B	26.20	2p?	E
43.43	2	B	77.84	2p?	C	12.39	3n	B
40.74	3	B	77.31	3p?	D	6407.03	5	B
38.30	3	A	72.92	5	A	6390.61	2	E
32.98	4	A	69.16	9	A	86.40	2	E
31.84	3 Hf	A	62.38	9	A	78.56	4n	B
13.54	4	A	52.73	6	A	46.54	1p?	E
12.83	6	A	43.86	2p?	E	45.23	3	E
11.71	7	A	42.38	2p?	E	45.10	8n	B
03.77	8	A	41.05	1p?	E	40.39	3	B
7102.95	10	A	17.89	6	A	24.55	2b, p?	B
7097.78	10	A	09.61	5	A	21.37	5	A
95.66	7	A	6702.13		A	14.71	2	B
94.61	6	A	6698.50	1	E	13.05	8	A
92.82	3p?	C	97.94	2	B	6304.35	3	B
91.27	2p?	C	93.95	2	B	6299.72	6	A
89.50	5	A	91.46	1p?	E	92.84	3n	B
87.35	9d?	A	89.86	1p?	E	6282.66	2p?	C
60.84	3	A	88.19	6	A	79.77	1	E
57.99	4	A	78.81	3p?	B	67.09	4	A
57.38	6	A	78.03	3p?	B	61.05	4n	A
33.70	2n?	B	58.16	1p?	E	57.28	4	A
27.40	8	A	57.55	1b, p?	E	29.51	7n	B
7005.46	4	A	55.50	1p?	E	24.22	3	C
6994.38	8	A	54.98	1p?	E	14.72	6	A
90.86	9	A	50.02	2h, p?	D	13.06	6	A
75.94	3	A	47.38	1h, p?	E	04.13	4l	B
66.49	7	A	45.16	2p?	C	6200.90	2p?	B
53.87	9	A	20.62	5	B	6194.82	1p?	E
48.51	5	A	17.28	1p?	E	92.96	6	A
32.41	4	A	16.40	1p?	E	89.38	3	B
29.09	3p?	A	14.84	1p?	E	88.08	2p?	B
25.71	1p?	C	14.09	1p?	E	78.26	2	B
23.47	2 l, n?	B	13.65	1p?	E	73.56	2p?	E
22.23	2	A	06.81	1p?	E	70.49	2b, n?	D
16.90	6	A	03.27	6	A	65.44	2b, p?	C
07.40	6	A	6600.69	1p?	E	60.27	2	B
04.40	6	A	6599.89	1	D	57.75	6	A
6900.59	6	A	98.86	3p?	C	55.56	2	B
6888.30	9	A	96.75	3	C	53.86	2n	E
85.20	2	B	92.02	6	A	49.94	1p?	B
84.39	2n	B	89.00	2p?	E	47.08	1p?	E

TABLE 1.—*Arc spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error
6143.23	8	A	5659.83	1	C	5387.30	1	E
40.50	7	A	33.98	2n	C	86.65	4	A
34.58	8	A	29.58	3n	C	85.14	7	A
27.49	8	A	29.02	3p?	C	82.36	3	A
24.86	6	A	23.56	4	A	81.20	1	E
23.42	1p?	E	20.16	7	A	79.54	3	B
21.95	6	A	12.14	1	D	75.78	1n	E
6120.86	3	A	10.18	2n?	D	73.76	1p?	E
6087.07	2n	C	5604.08	3	E	72.43	2	B
82.44	2p?	E	5557.91	2	E	69.39	3	B
70.08	2n	C	56.95	2	E	63.35	2	B
62.88	6	A	56.03	2b	E	62.56	5	A
53.92	2n	B	55.38	2	E	53.30	1	E
52.84	3	A	53.17	3n	C	51.92	4	A
49.29	6	A	51.75	3n	C	50.89	3	A
6046.77	1p?	C	47.71	2b, p?	E	44.15	1p?	E
45.89	6	A	46.28	1p?	E	43.59	1p?	C
32.62	6	A	45.42	6	B	38.41	2	A
31.25	1p?	C	39.38	2n?	C	32.44	2n	E
25.41	4	A	38.77	2p?	C	31.74	2	C
21.38	2n	C	37.45	4	B	30.83	4	A
14.69	1p?	E	36.67	3	C	29.83	2p?	B
02.66	2	E	33.90	1p?	E	21.81	1p?	B
6001.03	4	B	32.30	3	B	21.27	3	A
5995.41	2	A	28.44	6	B	19.98	2	E
92.41	1p?	D	23.88	2	E	19.45	1p?	E
84.82	2	B	22.66	1p?	D	17.52	1	E
84.24	6	A	18.06	3	E	16.75	1	E
77.80	2n	B	17.12	4	B	16.32	1p?	E
69.29	1p?	E	15.37	2n	E	14.80	1p?	E
67.98	1p?	E	07.96	3	B	11.42	6	A
67.38	1p?	E	04.22	1	E	10.97	2	E
55.37	6	A	5502.16	6	A	09.64	2	E
47.11	2n	C	5488.34	3	E	08.94	2	E
35.23	6	A	87.52	3	E	08.38	2	E
25.17	6	A	86.09	4	B	07.62	2	C
08.61	3n	B	81.17	2p?	B	06.05	1	E
05.81	2p?	D	80.82	3	B	05.50	1	E
05.39	2p?	D	78.34	3	A	03.80	1	C
5901.09	4	A	77.40	2	A	03.36	1	E
5885.61	6	A	75.55	1	E	01.98	6	A
79.79	8	A	74.94	3	E	5300.11	2	B
72.62	1	E	74.39	3	E	5299.53	2d?	B
69.51	6	A	64.02	1p?	E	99.20	2	B
68.28	4	A	57.58	1p?	E	96.78	6	A
60.14	4n	B	51.20	1	E	94.82	5	A
47.33	5	A	48.55	3	A	92.52	3	B
18.48	2p?	E	47.94	3	E	81.34	1	E
09.15	2p?	B	44.52	1p?	E	80.06	5	A
5801.31	2	B	43.16	1p?	E	77.40	6	A
5797.76	7	A	40.41	3	A	72.15	2	E
91.91	1	E	37.74	3	A	63.74	2	E
91.30	2	E	37.26	2p?	E	50.33	2p?	E
87.94	2p?	E	36.91	1p?	E	48.51	2	B
78.57	2n	C	28.42	4	A	48.03	2	A
48.17	3n	B	26.36	3	A	43.46	4	A
46.59	2p?	B	23.50	2	E	42.19	1	B
35.70	7	A	21.86	4	B	41.93	1	B
18.21	5n	C	18.73	1p?	E	35.07	2	B
5708.88	3	A	13.92	4	B	33.41	1p?	E
5685.47	2	B	07.63	5	A	30.55	3	A
80.93	6	A	5405.13	4	B	24.94	5	A
74.76	2	B	5395.88	3	A	23.62	1p?	E
66.28	2	B	91.18	2	B	15.58	1p?	E
64.55	7	A	90.48	1n	E	12.26	2n	E

TABLE 1.—*Arc spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error	λ I. A.	Intensity and notes	Probable error
5209.31	5	A	5085.26	6	A	4956.90	2	C
5201.17	5	A	82.02	2	E	51.73	3	B
5187.04	3	B	80.00	4	A	50.83	2p?	B
85.06	3n	B	79.01	2	E	49.94	2p?	B
84.55	2	B	78.28	9	A	48.77	5	A
83.71	6	A	75.23	4	B	43.48	1p?	B
78.99	3	A	74.00	6	A	39.93	3	A
74.31	2p?	B	73.14	2	E	33.66	6	A
65.97	6	A	72.29	2	E	32.45	1p?	E
64.71	3	B	71.82	1	E	30.88	5	A
61.01	5	A	70.27	7	A	25.03	1p?	C
58.68	4	A	65.25	6	A	22.92	2	E
58.02	7	A	64.92	9	A	13.07	1p?	E
55.46	8	A	60.42	7	A	11.60	1p?	E
50.22	1	E	59.89	1p?	E			
						10.78	2	B
45.46	1 Ti?	B	56.10	3	B	08.10	1	B
40.42	1	E	46.61	9	A	05.09	4	A
36.78	2	B	37.43	1p?	E	4902.89	1p?	E
36.16	2	B	34.45	4	A			
35.16	1	B	32.42	2	B	4895.93	2p?	E
						94.18	4	A
34.43	1	B	26.91	2	A	93.12	6	A
33.42	7	A	11.47	4	A	87.72	2	A
32.88	3	A	02.16	2	E			
28.16	2p?	E	5000.91	3	B	86.95	1	C
26.06	3	A	4996.35	6	A	84.12	3	A
						83.61	6	A
20.44	5 Ti?	A	94.77	7	A	4881.25	6	A
19.44	2	E	92.45	1p?	E			
15.27	8	A	87.83	4	A			
13.69	1	B	80.59	2	E			
12.82	1	C	68.17	2	B			
05.56	4	A	63.74	5	A			
04.23	2	A	62.30	5	A			
5102.54	1	E	60.31	2	E			
5098.56	3	B	60.10	2	E			
89.62	2	B	59.12	2	E			

TABLE 2.—*Spark spectrum of zirconium*

λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors
6114.79	2	A	4685.18	4	A	4401.33	2	B
06.46	2	A	61.79	4	A	4388.50	2	E
6100.03	2	B	29.07	5	A	83.10	1	E
6028.63	2	A	24.86	1 ZrI?	E	82.94	1	B
5477.80	1	A	13.94	5	A	79.78	9	A
5418.01	1	E	4601.97	2	A	70.96	8	A
5350.38	5	A	4574.48	5	A	59.74	10	A
50.09	5	A	4553.96	6	A	42.23	2	A
5311.79	2	A	4496.96	7	A	39.56	3	A
5191.61	7	A	95.45	3	A	37.63	4	A
24.98	2	A	94.41	6	A	36.34	1	A
5112.29	7	A	85.44	2	A	33.28	7	A
4927.06	1	B	82.04	3	E	25.64	2	E
25.92	1	B	61.22	7	A	17.31	6	A
18.88	1	E	59.64	1 ZrI?	A	12.23	3	A
09.52	3	A	57.42	6	A	08.94	4	A
4908.33	1	E	54.80	7	A	4301.82	5	A
4894.43	1	A	45.88	1	A	4298.90	1	A
54.65	1	E	45.20	2	A	96.74	6	A
41.98	1	E	42.99	7	A	93.14	5	A
4816.46	1	B	42.49	2	A	89.18	2	A
4761.67	1	A	40.45	6	A	86.51	4	A
34.93	1	B	29.34	2	E	82.21	5	A
19.80	1	A	14.54	5	A	77.37	3	A
4703.03	4	A	03.35	6	A	73.52	4	A

TABLE 2.—*Spark spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors
4266.72	1	B	3833.87	1	E	3662.14	6	A
64.91	3	A	32.94	1	E	61.33	2	A
58.05	6	A	29.10	1	E	60.92	3	A
36.56	4	A	27.51	1	E	55.56	5	A
31.65	5	A	27.27	1	E	54.86	1	E
24.27	3	E	23.72	1	E	52.56	1	E
22.40	3	B	23.41	2	E	51.50	2	A
15.76	1	E	19.84	1	E	50.73	5	A
11.88	6	A	18.78	1	E	36.46	5	A
10.61	4	A	17.59	6	A	33.49	5	A
08.98	7	A	14.97	2	E	31.03	1b	E
4205.91	2	E	13.98	1	E	30.03	5	B
4191.50	4	E	09.69	1	E	29.12	1	E
86.70	5	A	08.22	2	A	14.91	3	E
79.81	6	A	07.41	2	E	14.79	6	A
67.39	1	E	06.06	1	E	13.08	7	A
61.20	8	A	3800.73	4	A	12.34	2	B
56.24	7	A	3796.47	6	A	11.90	7	A
50.97	6	A	90.57	2	E	3607.39	5	A
49.22	10	A	84.33	21	E	3599.91	4	A
31.31	1	A	82.72	4	A	89.77	2	A
4110.05	3	A	82.44	1	E	88.80	2	A
4096.63	4	A	82.24	4	A	88.32	4	A
90.52	6	A	72.06	4	A	87.98	5	A
77.05	3	A	71.98	2	E	82.08	2	A
52.35	2	E	67.89	3	A	79.97	1b	B
50.32	6	A	66.83	7	A	78.22	4	A
48.68	7	A	57.80	5	A	76.88	7	A
45.62	6	A	57.24	1	E	73.09	5	A
40.24	3	A	56.96	1	E	72.47	8	A
34.84	1	E	51.60	10	A	68.14	4	B
34.09	4	A	50.65	5	A	67.88	2	B
31.35	2	A	45.97	8	E	65.41	5	A
29.68	7	A	42.20	1	E	61.90	1	C
24.44	5	A	38.13	4	A	59.44	1	E
18.38	6	A	31.26	7	A	56.61	8	A
17.26	21	E	29.74	4	A	54.09	4	A
4002.95	2	E	27.72	5	A	51.94	7	A
3998.98	8	A	25.86	1	E	49.51	5	A
91.14	9	A	21.69	2	A	42.65	7	A
84.76	4	E	18.86	6	A	39.05	2	B
82.01	3	E	17.02	1	A	36.94	4	A
58.24	9	A	14.77	6	A	30.85	4	A
52.87	1	A	11.95	1	B	29.99	3	A
52.27	1	E	11.66	1	E	29.19	1	E
50.29	1	E	09.27	8	A	29.10	1	E
48.31	1	E	03.03	1	E	27.42	4	A
41.92	2	E	01.84	1	E	25.81	6	A
38.00	1	E	3701.15	1 Hf?	B	20.87	4	A
36.06	4	A	3698.17	10	A	14.64	2	A
34.80	6	A	97.49	7	A	12.67	2	A
34.14	6	A	94.48	1	A	11.55	1	A
23.90	1	B	92.60	1	A	10.46	4	A
15.94	6	A	90.75	1	A	07.66	2	A
14.36	4	E	88.93	1	E	06.04	4	A
3902.13	1	E	82.67	1	A	05.67	5	A
3895.97	1	E	80.23	1	E	05.47	5	A
81.97	4	B	79.64	1	E	3500.15	3	A
74.37	1	E	78.91	6	A	3499.58	5	A
55.43	3	A	76.02	1	E	97.90	4	A
53.07	2	E	74.74	9	A	96.18	9	A
43.03	7	A	72.88	2	A	86.34	1	B
38.28	4	A	71.28	7	A	85.31	4	A
36.76	9	A	68.46	6	A	83.54	6	A
34.04	1	E	67.06	3 ZrI?	B	81.44	2	A

TABLE 2.—*Spark spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors
3481.14	7	A	3334.62	5	A	3155.95	1	A
80.40	4	A	34.25	6	A	55.68	6	A
79.39	7	A	31.90	2	A	48.20	11	E
79.02	5	A	27.67	2	A	38.66	7	A
78.50	2	A	26.81	6	A	33.49	6	A
78.29	4	A	22.99	6	A	30.40	2	E
76.54	1	A	19.03	5	A	29.76	6	A
75.96	1b	C	18.52	4	A	29.16	6	A
74.17	1	E	14.49	6	A	28.79	1Hf?	B
72.41	1 Hf?	A	13.70	5	A	25.92	6	A
71.14	6	B	11.34	3	A	25.21	3	A
69.94	3	A	09.90	3	A	22.61	1	A
68.20	1	A	06.27	7	A	16.68	11	E
63.02	7	A	05.15	7	A	15.73	2	A
59.95	2	A	3302.66	4	A	13.92	3 b, l	B
58.93	5	A	3296.41	4	A	11.15	2	A
57.56	6	A	95.03	1	A	10.87	6	A
54.57	3	A	88.81	5	A	10.52	1	A
43.57	5	A	85.89	4	A	3106.58	8	A
38.23	9	A	85.77	3	A	3099.22	6	A
37.13	6	A	84.72	6	A	95.07	7	A
35.63	1	A	82.84	5	A	89.00	1	A
34.77	1	E	80.75	3 ZrI?	A	88.28	1	A
33.90	4	A	79.26	7	A	86.44	2	A
32.41	[illegible]	A	78.89	2	B	75.55	1	A
31.57	4	A	75.98	1	E	68.02	2	A
30.53	7	A	75.65	1	A	65.20	2	A
24.82	4	A	75.15	3	A	64.64	3	A
24.64	1	A	73.04	8	A	63.63	3b, l	B
23.82	1b	E	72.21	6	A	61.33	3	A
19.10	4	A	71.13	4	A	60.11	3	A
14.65	6	A	64.81	4	A	57.22	3	A
13.39	3	A	56.53	1	A	54.84	7	A
10.26	7	A	50.44	6	A	48.42	1	B
08.09	5	A	42.18	3	B	48.28	4	B
04.84	6	A	41.01	6	A	44.12	2	B
03.69	5	A	37.54	1	A	36.50	3	A
3402.87	5	A	36.61	3 Ti?	B	36.39	6	A
3399.36	6	A	36.17	1	A	32.00	2	A
97.65	1	A	31.69	6	A	30.91	5	A
96.66	4	A	29.73	11	B	28.05	7	A
96.34	5	A	28.81	5	A	26.18	3b, l	E
94.63	3 g coin?	B	22.48	5	A	25.70	2	B
93.12	5	A	18.68	1	A	25.16	2b	B
91.96	8	A	14.19	7	A	24.72	2b	E
88.29	6	A	12.85	4	A	23.48	1	E
87.87	6	A	10.98	1	A	21.21	2b, l	E
78.30	4	A	08.32	3	A	20.45	5	A
77.45	4	A	04.36	3	A	19.84	3	A
76.25	5	B	3200.67	1	A	18.51	2b	B
74.71	7	A	3197.08	2 Cr?	B	18.08	2b	E
73.42	6	A	96.74	11	E	15.86	1	E
69.27	3	A	91.93	6	A	15.67	1	E
67.81	5	A	82.86	7	A	13.66	1	C
63.81	5	A	81.94	5	A	13.32	3	A
62.70	4	A	81.58	5	A	10.28	1b, l	C
59.96	6	A	78.10	6	A	09.85	1	A
57.26	7	A	67.56	2	A	03.73	5	A
56.08	7	A	66.29	5	A	3000.59	2b	E
54.39	5	A	65.98	7	A	2998.49	2	A
44.80	6	A	65.45	5	A	98.34	1	A
43.81	2	A	64.32	7	A	94.05	1b	B
40.55	6	A	61.01	2	B	91.40	3	A
38.41	5	A	59.12	2	B	90.10	2	A
37.93	2	A	57.00	5	A	88.74	3b	C

TABLE 2.—*Spark spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors
2987.80	3	A	2853.66	1b	E	2742.54	6	B
84.09	1b	E	51.98	6	A	41.54	4	B
81.02	5	A	50.60	3b	B	40.49	3	B
79.18	6	A	48.17	5	B	40.33	2	B
78.07	6	A	46.16	1	E	38.40	1	E
76.61	5	A	44.57	7	A	36.96	1	E
73.69	1	E	43.53	4	B	35.79	7, ZrIII	E
69.63	5	A	39.34	5	A	34.84	7	A
68.95	6	A	38.00	3	E	32.72	6	B
64.55	3	A	36.19	6, ZrIII	E	30.73	1	E
62.69	6	A	34.38	3	A	28.58	1	E
60.57	1	E	33.90	5	A	27.54	1	E
55.77	7	A	32.81	1	E	26.99	2	B
55.37	2b	E	31.54	1	E	26.48	6	B
52.23	3	A	29.38	1	E	22.62	7	B
51.46	5	A	27.90	3, ZrIII	E	21.37	1	E
49.81	2b	E	27.52	3	A	20.36	3	A
48.94	6	A	25.54	6	A	20.08	5, ZrIII	E
45.45	4	A	24.56	1	E	15.80	6, ZrIII	E
44.19	1	E	24.08	1	E	14.25	5	A
42.26	1	E	21.09	1b	E	12.42	5	B
36.31	5	A	19.31	2 l, d?	E	11.52	5	A
34.62	5	A	18.76	7	A	09.07	6, ZrIII	E
31.89	2b	E	16.77	1b	E	04.67	1	A
31.08	5b, l	C	10.91	6	A	04.00	1	E
26.99	8	A	09.40	1	E	03.28	1	E
25.62	2	A	08.15	3	B	2700.15	6	A
24.63	5	A	07.86	2	E	2699.61	4	B
20.03	2b	E	07.13	3b	E	98.32	6, ZrIII	E
18.24	7	A	06.73	4b	C	96.52	1	E
16.63	5	A	05.71	1b	E	95.42	4	A
15.98	7	A	02.69	1Mg?	E	94.06	5	A
14.71	1b	E	02.45	1	E	93.52	5	A
10.26	5	A	2800.10	1	E	92.60	4	B
07.99	3b, d?	E	2799.16	4	A	92.01	3, ZrIII	E
07.37	4	A	98.71	1	E	90.51	7, ZrIII	E
05.22	6	A	97.78	2b	E	89.46	2	B
03.70	7d?	C	96.92	5	A	86.28	7, ZrIII	E
02.24	1	E	96.38	1b	E	82.16	7, ZrIII	E
01.81	3	B	89.47	1	E	81.75	1	E
2901.60	4	B	86.95	4b, l	C	78.64	8	B
2898.72	4	A	85.90	3b	E	75.50	1b	E
95.32	4b, l	E	83.56	3	A	70.95	4	A
91.99	1	E	82.84	1	E	69.45	4	A
91.75	1	E	81.61	1	E	67.80	5	A
89.41	3	B	79.28	1	E	66.64	1	E
88.04	4	A	77.05	1b	E	65.18	1	B
86.71	3, ZrIII	E	76.59	1b	E	64.27	8, ZrIII	E
84.57	5b, d?	C	75.26	4, ZrIII	E	62.58	1	E
83.79	3	A	74.15	6	A	58.69	2	E
82.08	3	B	72.56	1	E	56.47	7, ZrIII	E
77.56	5	A	68.76	6	A	50.37	4	A
74.22	2b	E	61.89	3	E	43.79	7, ZrIII	E
72.52	3	B	60.10	2b	E	43.40	2	B
69.80	6	A	58.80	6	A	39.09	5	A
69.06	6, ZrIII	E	54.23	2b, l	C	34.32	3, ZrIII	E
66.93	1	E	53.25	2b	E	30.91	6	A
65.93	1b	E	52.57	2	E	28.24	7, ZrIII	E
65.61	5	A	52.21	6	B	27.00	1	E
65.09	3	A	50.95	2	E	26.38	1	C
64.19	1b	E	50.44	1	E	21.28	3, ZrIII	E
59.61	4b	E	49.87	1	E	20.55	8, ZrIII	E
57.33	1b,l	E	45.86	6	B	19.20	1	E
56.05	2	A	44.49	1b	E	16.00	1	E
54.42	4	A	43.17	2	E	15.62	1	E

TABLE 2.—*Spark spectrum of zirconium*—Continued

λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors	λ I. A.	Intensity and notes	Probable errors
2609.72	2	E	2457.42	6	B	2364.63	1	E
08.73	1	E	54.60	1	E	63.88	3	C
2604.20	1	E	54.18	1	E	61.79	4	B
2593.67	7, ZrIII	E	49.83	5	B	57.47	7	C
92.80	1	E	48.84	7, ZrIII	E	54.53	1	E
91.56	1	E	45.55	1	E	53.24	2	E
89.05	5	B	44.56	6, ZrIII	E	51.70	4	C
86.88	1	E	41.96	3	B	50.94	2	E
83.40	4	B	39.26	1	E	50.26	2b	E
78.40	1	E	38.71	1	E	47.14	3	E
77.94	1	E	34.56	2	E	45.36	1	E
74.52	1	E	32.89	1	E	42.38	2b	E
71.44	8	A	32.27	1	E	41.85	1b	E
68.88	7	A	30.08	2	B	39.69	1	E
67.64	6	B	28.35	2	B	39.46	1	E
67.07	2	E	26.40	3	B	37.01	1	E
50.73	5	B	24.12	2	B	35.71	1b	E
50.04	1	E	23.32	1b	E	32.81	4	E
45.65	1h	E	22.65	1	E	31.66	3b	E
42.10	5	A	22.26	1	C	30.40	10	C
38.90	1	E	20.64	8, ZrIII	B	28.46	1	E
36.79	1	E	19.39	5	B	24.80	10	C
35.15	1	E	18.56	1b	E	24.51	5	E
34.37	1	E	17.86	1	E	21.90	5	E
34.17	1	E	17.68	1	E	20.46	1	E
33.64	1	E	16.94	1	E	19.06	1	E
32.46	5	B	16.14	1	E	17.32	10	C
29.55	1	E	14.28	1	E	16.04	2	E
26.26	1	E	10.14	1	E	10.23	1	E
25.37	1	E	06.88	4	C	08.14	8	C
22.50	1	E	06.65	2	E	07.31	1b	E
21.90	1	E	06.25	6, ZrIII	C	06.82	2b	E
13.52	1	E	05.80	7, ZrIII	C	03.01	1	E
11.75	1	E	2400.37	1	E	02.52	2b	E
09.77	1	E	2399.02	2	E	01.61	4b	E
03.96	1	E	97.62	2	E	2300.42	3b	E
2502.38	1	E	94.54	1	E	2298.30	1	E
2498.88	1	E	92.71	4	C	97.16	1	E
97.78	1	E	89.60	6	C	96.88	4	E
96.47	3	E	89.40	6	C	96.59	1	E
93.99	1	E	87.22	6	C	95.54	10	C
93.20	2	E	84.46	1	E	94.09	12	C
88.14	1	E	82.67	3	E	93.34	1	E
87.28	4	E	82.38	2	E	91.17	10	C
86.34	1	E	82.05	7	C	88.62	21	E
85.59	1	E	76.57	1b	E	88.00	1	E
82.63	1	E	72.95	6	C	86.65	15, ZrIV	C
81.35	1	E	71.38	1	E	80.34	5	E
80.18	1	E	70.54	1	E	77.17	2	E
78.58	10	B	70.19	3b	C	2251.02	3b	E
67.98	1	E	69.04	1	E	2163.62	15, ZrIV	E
66.80	1	E	67.76	1h	E			
65.34	1	E	66.61	1	E			
61.26	1	E	66.26	2	E			
58.77	1	E	64.98	1	E			

In addition to the lines of impurities contained in the electrodes, arcs and sparks operated in air excite lines characteristic of the atmospheric gases also. Such lines are prominent in spark spectra if self-inductance is omitted from the circuit. Inclusion of self-inductance suppresses the air lines, which generally are diffuse, but it also diminishes the intensity of the spark, thereby greatly increasing the exposure times. Although a bobbin of 0.00005 henry inductance was connected in series with the circuit used to excite the spark spectra, yet it was not sufficient to suppress completely the air lines. So far as these have been identified, they have been removed from the tables. Other lines which present a hazy appearance similar to that of the air lines are, no doubt, characteristic of the zirconium atom originating in the higher energy states of the atom. In the red, the most prominent air lines are the oxygen groups at 7771–7775 A and 8446 A, and the nitrogen groups at 7424–7469 A, 8185–8242 A, 8568–8656 A, and 8680–8729 A. These appear in arc as well as in spark excitation.[18] A few lines in the zirconium arc spectrum are apparently coincident with air lines, but because of their sharpness in contrast to the broader air lines, they are regarded as genuine Zr lines. It should be added that the Rowland and Lyman ghosts of all the stronger lines have been calculated and have been eliminated from the tables.

The light emitted by the arc between Zr electrodes consists of (1) band spectra originating in a molecule, perhaps of zirconium oxide; (2) line spectra originating in the neutral atom; (3) line spectra originating in the singly ionized atom. In addition to these spectral structures, the light emitted by the condensed spark discharge between Zr electrodes contains also (4) lines of the doubly ionized atom; (5) lines of the trebly ionized atom. Tables 1 and 2 attempt to designate the lines that belong to each of these classes. In Table 1 the majority of the lines belong to the spectrum of the neutral atom; the band structures are represented only by measurements of the band heads. For some lines it was difficult to decide whether they form part of the band structure or are members of the ZrI spectrum. Such are appropriately marked. All the Zr bands are shaded toward the red. In Table 2 the majority of the lines belong to the ZrII spectrum. Those which belong to ZrIII and ZrIV are so designated in the second column of the table.

The allocation of the Zr lines to the different classes of spectra is based not only on the behavior of the lines in the sources employed but also on the classification of the lines into their series relationships. Work on the classification of Zr arc and spark lines has been in progress for several years at the Bureau of Standards. Although the details of the classification have not been published, yet the main features of the structures of the ZrI, ZrII, and ZrIII have been announced.[19] Recently Gibbs and White,[20] and also Bowen and Millikan,[21] have announced the classification of lines belonging to ZrIV.

In addition to the hitherto unexplored regions, Table 1 includes the region in the red investigated by Eder,[22] and overlaps in the

[18] Publ. Amer. Astron. Soc., 4, p. 363; 1922.

[19] Popular Astronomy, 31, p. 647, 1923; Popular Astronomy, 33, p. 255, 1925; J. O. S. A. and R. S. I., 12, p. 427, 1926; J. O. S. A. and R. S. I., 14, p. 140; 1927.

[20] Proc. Nat. Acad. Sci., 12, p. 551, 1926.

[21] Phys. Rev., 28, p. 923, 1926.

[22] See footnote 1, p. 48.

orange, yellow, and green the regions measured by Eder and Valenta,[23] by Bachem,[24] and by Vahle.[25] Intercomparison of these different investigations indicates qualitative agreement among them all as far as the more intense Zr lines are concerned. But each list contains faint lines not observed by the others. These, no doubt, are to be accounted for by the differences in judgment various observers will exercise in measuring a line spectrum which is superposed on a prominent band spectrum. In Table 1 all lines suspected of being members of bands, but which, because of their intensity, stand out above the adjacent spectrum, are indicated with a letter p. In Vahle's list, however, especially between 4900 A and 5100 A appear numerous lines of intensity 2 or greater which are not to be found in the other lists. It has not been possible to establish the origin of these lines. The spark lines of Table 2 are in qualitative agreement with those of Exner and Haschek [26] from 5350 A to the ultra-violet. Their lines, which are longer than 5350 A, are nearly all members of the arc spectrum, as are many of the fainter lines throughout their table. All the prominent lines in the first spark spectrum of Zr are to be found in the tables of Bachem and of Vahle. Their values for the wave lengths of these lines are in good accord with those determined at the Bureau of Standards.

In conclusion, it should be mentioned that the wave length 9277 A is not to be regarded as the termination of the observable spectrum of Zr. Previous work in this laboratory on Fe, Ti, Cr, and other elements [27] has shown that photographic plates sensitized with dicyanin are capable of recording spectra out to wave length 10000 A and beyond, with exposures of 10 or 12 hours duration. With the rarer elements such long exposures are not feasible. The analysis of the arc spectrum of Zr, referred to above, has led to the identification of many terms belonging to the quintet, triplet, and singlet series systems. From such terms the combination principles permit the calculation of wave lengths occurring in the spectrum. Thus the lines 9015.13 A, 9276.94 A, 9531.2 A, 9822.6 A, and 10085.0 A represent the term combinations $^5F_5-^5G_6$, $^5F_4-^5G_5$, $^5F_3-^5G_4$, $^5F_2-^5G_3$, and $^5F_1-^5G_2$, respectively, and constitute the principal members of the multiplet. The last three of these lines, as well as other near infra-red lines arising from different term combinations, were sought for on our plates but could not be found, and the failure to detect them must be attributed largely to the rapid falling off in sensitivity of the bathed plates between 9000 A and 10000 A.

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[23] Sitzungsberichte, K. Acad. Wiss. Wien, IIa, **119**, p. 9; p. 519; 1910.
[24] Dissertation, Bonn 1910. *Cf.* Kayser, Handbuch, **6**.
[25] See footnote 2, p. 48.
[26] Die Spektren der Elemente bei Normalen Druck, **3**, 1912; Franz Deuticke, Leipzig und Wien.
[27] B. S. Sci. Papers, Nos. 324, 372, 411.