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CORRECTION AND EXTENSION OF THE SERIES OF THE SILVER ARC SPECTRUM, AG I.

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Abstract

Measurements, with a Schüler-tube source and helium standards, of the high series members of Ag I showed the older measurements to be rather poor. A few new lines have been added. No terms of the quartet system nor of the $d^9s^2\ {}^2D$ were found from new arc measurements. The $d^{10}5s\ {}^2S$ is at 61104.4, which gives an *ionizing potential* of 7.53 volts.

Almost no extension has been made to the classification of the silver arc spectrum as given in Fowler's Report.[1] McLennan and McLay[2] have since derived by analogy a probable $d^9s^2\ {}^2D$ difference but were not able to establish the terms. The difficulty of classification is no doubt due to the fact that the lines of this spectrum are relatively few.

Recently in this laboratory both the silver and copper arc spectra, which should be similar in structure, have been photographed and measured. In each case the excitation was brought about in arcs in which the lower electrode, the positive, consisted of a piece of the metal laid on a plate of graphite. The cathode consisted of a rod of the metal. Enough current was used, about 3 amperes on a 350 volt line, to render the lower electrode molten. In the case of silver a small amount of copper was added which provided standards and also caused the arc to run more smoothly. The spectra from this type of source are almost entirely free of air bands, a circumstance which renders it possible to obtain measurements on the faint lines. By this method only about 200 lines were obtained in silver while about four times as many were obtained in copper in the region 2,000 to 7,000A. No success attended an attempt to determine the quartet system using these silver lines. The lines belonging to this system, if present at all, must be much weaker than the corresponding ones in copper as there are few strong lines left unclassified.

While using the Schüler tube to excite the silver spark spectrum as previously described[3] it was not noticed that the high series members of the arc spectrum were being brought out. After finding they were excited quite strongly in copper, a further search in silver showed that these members were present but the newly measured wave-numbers differed from the old by 10–15 units in many cases. As the new measures were obtained from photographs with the Hilger E. 1. spectrograph using helium standards they

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[1] Report on Series in Line Spectra p. 112, 1922.

[2] McLennan and McLay, Trans. Roy. Soc. of Canada **22,** 1 (1928).

[3] Blair, Phys. Rev. **36,** 173 (1930).

are probably no more in error than 0.5 cm^{-1} in any case. For this reason and on account of there being a few new lines it was thought worth while to give the complete series.

The Data. In the tables, the older measurements for the lower members of the series have usually been retained. For higher members, where the new measurements are used, the old have not been included as they can be eliminated from lists by referring to Fowler's Report. Both the arc intensities and the Schüler tube intensites are given as they supply some indication of the results of the two types of excitation. The wave-lengths were obtained by means of tables from the wave numbers which were calculated from the measurements.

TABLE I. *Diffuse series.*

λ	Auth.	I_1	I_2	ν		Designation	$nd^2D_{2\frac{1}{2}.1\frac{1}{2}}$ observed	$nd^2D_{1\frac{1}{2}}$ calc.	R.D.
5471.52	E&H	50		18271.4		$5p^2P_{1\frac{1}{2}}^{\circ}-5d^2D_{1\frac{1}{2}}$			
					20.2				
5465.47	E&H	200		18291.6		$5p^2P_{1\frac{1}{2}}^{\circ}-5d^2D_{2\frac{1}{2}}$	12339.9		
					900.5				
5209.04	E&H	100		19192.1		$5p^2P_{\frac{1}{2}}^{\circ}-5d^2D_{1\frac{1}{2}}$	12360.0	12360.0	2.9797
4212.68	B	35	100U	23731.2		$5p^2P_{1\frac{1}{2}}^{\circ}-6d^2D_{1\frac{1}{2}}$			
					9.8				
4210.94	B	100	500U	23741.0		$5p^2P_{1\frac{1}{2}}^{\circ}-6d^2D_{2\frac{1}{2}}$	6890.5		
					911.3				
4055.27	E&H	75	200R	24652.3		$5p^2P_{\frac{1}{2}}^{\circ}-6d^2D_{1\frac{1}{2}}$	6899.8	6900.3	3.9880
3811.79*	B	5		26227.0		$5p^2P_{1\frac{1}{2}}^{\circ}-7d^2D_{1\frac{1}{2}}$			
					5.9				
3810.93	B	40	5U	26232.9		$5p^2P_{1\frac{1}{2}}^{\circ}-7d^2D_{2\frac{1}{2}}$	4398.6		
					915.1				
3682.47	B	30		27148.0		$5p^2P_{\frac{1}{2}}^{\circ}-7d^2D_{1\frac{1}{2}}$	4404.1	4404.4	4.9918
3624.71	B	20		27580.6		$5p^2P_{1\frac{1}{2}}^{\circ}-8d^2D_{2\frac{1}{2}}$	3050.9		
					916.9				
3508.08	B	20		28497.5		$5p^2P_{\frac{1}{2}}^{\circ}-8d^2D_{1\frac{1}{2}}$	3054.6	3054.1	5.9937
3521.16	B	10		28391.6		$5p^2P_{1\frac{1}{2}}^{\circ}-9d^2D_{2\frac{1}{2}}$	2239.9		
					918.8				
3410.78	B	8		29310.4		$5p^2P_{\frac{1}{2}}^{\circ}-9d^2D_{1\frac{1}{2}}$	2241.7	2242.7	6.9963
3457.10	B	5		28917.7		$5p^2P_{1\frac{1}{2}}^{\circ}-10d^2D_{2\frac{1}{2}}$	1713.8		
					919.5				
3350.56	B	3		29837.2		$5p^2P_{\frac{1}{2}}^{\circ}-10d^2D_{1\frac{1}{2}}$	1714.9	1716.5	7.9995
3414.55	B	4		29278.1		$5p^2P_{1\frac{1}{2}}^{\circ}-11d^2D_{2\frac{1}{2}}$	1353.4		
					920.1				
3310.51*	B	2		30198.2		$5p^2P_{\frac{1}{2}}^{\circ}-11d^2D_{1\frac{1}{2}}$	1353.9	1356.0	9.0030
				covered by 3382 He.?					
3282.53*	B	3		30455.6		$5p^2P_{\frac{1}{2}}^{\circ}-12d^2D_{1\frac{1}{2}}$	1100.5	1098.1	9.9868

The Diffuse Series. The $^2P_{\frac{1}{2}}-{}^2D_{1\frac{1}{2}}$ combinations were used to find a Ritz formula. After adjustment of the constants to give the best fit, the formula obtained was as follows:

$$(m+3)d^2D_{1\frac{1}{2}}=\frac{109737.1}{(m+0.9981-1.484\times10^{-6}D)^2}\,.$$

The value of the lowest term $5s^2S$ is then obtained by adding to $5d\ ^2D_{1\frac{1}{2}}$ the wave-numbers of the lines $5p\ ^2P_{\frac{1}{2}}-5d^2D_{1\frac{1}{2}}$ and $5s^2S-5p^2P_{\frac{1}{2}}$. The value obtained is 61104.4, corresponding to an ionization potential of 7.53 volts.

The column of Table I headed "^2D, observed," gives the terms as obtained from the above limit and the observed lines. The calculated terms are those derived from the formula. The Rydberg denominators are calculated from the observed terms.

The Sharp Series. The limit got from the diffuse series was assumed for the limit of the sharp series. The terms then fit the following Ritz formula with reasonable accuracy.

$$(m+4)s^2S=\frac{109737.1}{(m+0.4685-1.957\times 10^{-6}S)^2}\,.$$

The column headings of Table II have the same meanings as for the diffuse series.

TABLE II. *Sharp series.*

λ	Auth.	I_1	I_2	ν		Designation	ns^2S observed	ns^2S calc.	R.D.
8273.73	F			12083.1	920.4	$5p^2P_{1\frac{1}{2}}{}^\circ-6s^2S_{\frac{1}{2}}$	18548.4	18548.5	2.4323
7688.12	F			13003.5		$5p^2P_{\frac{1}{2}}{}^\circ-6s^2S_{\frac{1}{2}}$	18548.6		
4668.50	E&H	50	500u	21414.2	920.6	$5p^2P_{1\frac{1}{2}}{}^\circ-7s^2S_{\frac{1}{2}}$	9217.3	9217.3	3.4505
4476.06	E&H	20	500u	22334.8		$5p^2P_{\frac{1}{2}}{}^\circ-7s^2S_{\frac{1}{2}}$	9217.3		
3981.62	K	15	30u	25108.3	920 4	$5p^2P_{1\frac{1}{2}}{}^\circ-8s^2S_{\frac{1}{2}}$	5523.2	5521.7	4.4574
3840.82	K	12	20u	26028.7		$5p^2P_{\frac{1}{2}}{}^\circ-8s^2S_{\frac{1}{2}}$	5523.4		
3709.30	B	4	10U	26951.3	919.9	$5p^2P_{1\frac{1}{2}}{}^\circ-9s^2S_{\frac{1}{2}}$	3680.2	3679.3	5.4604
3586.91	B	#	6U	27871.2		$5p^2P_{\frac{1}{2}}{}^\circ-9s^2S_{\frac{1}{2}}$	3680.9		
3569.76	B	2		28005.1		$5p^2P_{1\frac{1}{2}}{}^\circ-10s^2S_{\frac{1}{2}}$	2626.4	2626.7	6.4638
3487.76	B	5		28663.5		$5p^2P_{1\frac{1}{2}}{}^\circ-11s^2S_{\frac{1}{2}}$	1968.0	1968.5	7.4674
3434.65	B	1	1	29106.7		$5p^2P_{1\frac{1}{2}}{}^\circ-12s^2S_{\frac{1}{2}}$	1524.8	1531.3	8.4836

The Principal Series. The $6p^2P$ difference, 203.4 cm^{-1}, derived from Shenstone's measurements with copper standards, is probably correct to 0.2 cm^{-1}. The $^2P-{}^2P$ combinations did not appear with the Schüler tube. The measurement of those lines in the arc can be expected to be relatively poor because of the extreme diffuseness of the lines in that source.

The $d^9\ s^2\ ^2D$. As pointed out by Shenstone[4] this ^2D may be expected to be nearly coincident with the $5p^2P$, thus its combinations with $6p^2P$ may be expected to lie about the middle of the visible spectrum. None of the lines obtained, however, appeared to represent these combinations. The conclusion to be drawn seems to be that the excited silver atom seldom emits energies allowing it to revert to this ^2D state. If the state were metastable as

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[4] A. G. Shenstone, Phys., Rev. **31**, 317 (1928).

in copper this would be unexpected. It thus appears probable that the ^2D is not metastable, but lies closer to the limit than the $5p\,^2P$. The unusual relative strengths of the resonance lines would follow as readily from this circumstance as that supposed on the alternative explanation that the ^2D and the $5p\,^2P$ are so close together that the collision processes in the arc raise the metastable atoms very quickly to the $5p\,^2P$ state.

TABLE III. *Principal series.*

λ	Author	I_1	ν		Designation	$np\,^2P_{1\frac{1}{2}.\frac{1}{2}}$
3280.66	F	150	30472.9	920.6	$5s\,^2S_{\frac{1}{2}}-5p\,^2P_{1\frac{1}{2}}{}^\circ$	30631 5
3382.86	F	150	29552.3		$5s\,^2S_{\frac{1}{2}}-5p\,^2P_{\frac{1}{2}}{}^\circ$	31552.1
2061.21	S		48499.6	203.4	$5s\,^2S_{\frac{1}{2}}-6p\,^2P_{1\frac{1}{2}}{}^\circ$	12604.8
2069.81	S		48296.2		$5s\,^2S_{\frac{1}{2}}-6p\,^2P_{\frac{1}{2}}{}^\circ$	12808.2

If the ^2D is higher than the $5p\,^2P$ its combinations with $6p\,^2P$ will be of greater wave-length than 5600. Only a very few weak lines were observed above 5600, the one of greatest wave-length being at 6450. If any of the combinations sought are represented by these lines they will probably only be the strongest.

TABLE IV. *$5p\,^2P-6p\,^2P$ combinations.*

λ	Author	I_2	ν		Designation	Calculated
5608.95*	B	4U	17823.7	202.5	$5p\,^2P_{1\frac{1}{2}}-6p\,^2P_{\frac{1}{2}}$	17823.3
5545.94	B	25U	18026.2		$5p\,^2P_{1\frac{1}{2}}-6p\,^2P_{1\frac{1}{2}}$	18026.7
5333.73	B	7U	18743.4	203.4	$5p\,^2P_{\frac{1}{2}}-6p\,^2P_{\frac{1}{2}}$	18743.9
5276.47	B	3U	18946.8		$5p\,^2P_{\frac{1}{2}}-6p\,^2P_{1\frac{1}{2}}$	18947.3

F—taken from Fowler.
E & H—Exner and Haschek.
K—Kasper.
S—Shenstone.
B—author.
I_1—Schuler tube intensity.
I_2—Arc intensity.

u—diffuse.
U—very diffuse.
#—covered by He. 3587.
*—new allocations.
complete designations are $4d^{10}ns$, np, etc.

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