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THE SPARK SPECTRUM OF SILVER (Ag II)

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ABSTRACT

The spark spectrum of silver can be based on a set of terms as follows: ${}^3D$, ${}^1D$ from the structure $4d^95s$; ${}^{3\&1}P, D', F$ from $4d^95p$; ${}^3D$, ${}^1D$ from $4d^96s$; ${}^{3\&1}S, P', D, F', G$ from $4d^95d$. The theoretically lowest term ${}^1S_0$ $(4d^{10})$ has not been found, but an estimate of its position is given. There is evidence also for the structure $4d^94f$. All terms have intervals very different from the Landé values. The g-values also are evidently very irregular.

The separate limits calculated from the ${}^3D$, ${}^1D$ series of two members show the same apparent divergence from theory as in Cu II, Ni I, Pd I. The intervals in the set $4d^95d$ also indicate divergence from theory. The calculated *ionization potential* is 17.1 volts from $5s\,{}^3D_3$.

MANY investigators have measured the spark spectrum of silver, the most recent being J. Frings.[1] It has been found in the present investigation, however, that the measures made by Exner and Haschek in 1911,[2] corrected, of course, to the international scale, give the most consistent results. Their measures have, therefore, been adopted down to λ2246. Beyond that point, it has been necessary to make new measurements using the copper standards previously given by the author.[3] Mr. C. W. Gartlein of Cornell University has kindly sent the author the measurements he has made of the stronger lines of the short wave-length region. They differ by about 0.8 wave numbers from the author's determinations, and it is not possible to determine which is the more accurate.

The identification of the lines as due to the first spark spectrum was made by photographing the spectrum of the arc as well as the spark and by photographing the spectrum of a spark sharply focussed on the spectrograph slit. (Hilger E. 1.) The Ag II lines may be divided into two classes, sharp and diffuse. As is usual in spectra of this type, it is found that the sharp lines are due entirely to transitions to the low levels, while the diffuse lines are always transitions to the middle set of terms. In addition to the lines which can be attributed to Ag II, numerous strong sharp lines occur in the spark but not in the arc. They are, undoubtedly, due to higher spark spectra. They are particularly numerous and strong in the region below

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[1] J. Frings. Zeits. Wiss. Photog. **15**, p. 165 (1915).

[2] Kayser, "Handbuch der Spectroscopie. Vol. 7."

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

λ2250 and can easily be differentiated from the Ag II lines by their polar character in the spark.

The present analysis is really an extension of that made by C. S. Beals.[4] Of his terms, only *A* and *M* have proved to be unreal, the remaining terms forming the main portion of the low ^3D, ^1D and their combining terms.

The Term Table (Table I) contains the terms identified, measured from the lowest term ($5s^3D_3$) as zero point. It will be seen from the table that they form the usual sets expected on the Hund theory, namely: (1) a low $^3D^1D$ from the structure $4d^95s$; (2) an intermediate set ^{3,1} *P*, *D′*, *F* from $4d^95p$; (3) a high $^3D^1D$ from $4d^96s$; and (4) a high set $^{3,1}S$, *P′*, *D*, *F′*, *G* from $4d^95d$. The terms have been identified from intensities only, it being evident from Beals's measures of the unresolved Zeeman patterns that the *g*-values

TABLE I

Terms, intervals and limits in Ag II.

Designation		Term	Structure	Intervals (Higher *J*'s at left)		
Beals	Sh.					
B	$5s^3D_3$	0.0				
C	$5s^3D_2$	1577.1	$4d^95s$			
	$5s^3D_1$	4574.8				
D	$5s^1D_2$	6881.3				
L	$5p^3P_2$	41008.3		$5s^3D$	1577.1	2997.7
N	$5p^3F_3$	43003.2				
O	$5p^3P_1$	44457.0		$5p^3P$	3448.7	2515.1
	$5p^3F_4$	44501.3		$5p^3D'$	−1260.0	5134.2
	$5p^3D_2'$	46032.4		$5p^3F$	−1498.0	4716.6
	$5p^3P_0$	46972.1	$4d^95p$			
P	$5p^3D_3'$	47292.4		$6s^3D$	377.5	4215.3
	$5p^3F_2$	47719.8				
Q	$5p^1F_3$	49966.4		$5d^3P'$	3.5	6304.7?
R	$5p^1P_1$	50727.1		$5d^3D$	312.0	3983.5
	$5p^3D_1'$	51166.6		$5d^3F'$	−117.3	4664.4
S	$5p^1D_2'$	51719.5		$5d^3G$	12.6	4573.2
	$6s^3D_3$	81362.7				
	$6s^3D_2$	81740.2	$4d^96s$			
	$6s^3D_1$	85955.5				
	$6s^1D_2$	86233.9				
	$5d^3S_1$	86405.0				
	$5d^3G_5$	87496.6				
	$5d^3G_4$	87509.2				
	$5d^3P_2'$	87596.3				
	$5d^3P_1'$	87599.8				
	$5d^3D_3$	88041.1				
	$5d^3F_3'$	88320.6				
	$5d^3D_2$	88353.1				
	$5d^1S_0$	88356.9?	$4d^95d$			
	$5d^3F_4'$	88437.9				
	$5d^1P_1'$	91592.1				
	$5d^3G_3$	92082.4				
	$5d^3D_1$	92336.6				
	$5d^1G_4$	92346.6				
	$5d^1D_2$	92620.0				
	$5d^3F_2'$	92985.0				
	$5d^1F_3'$	93027.9				
	$5d^3P_0'$	93904.5 ?				

Limits calculated
from 5*sD* and 6*sD*.

$^3D_3$ 138,000 $= {}^2D_3$ (Ag III)
$^3D_2$ 137,957
$^3D_1$ 142,595 $= {}^2D_2$ (Ag III)
$^1D_2$ 142,161

Ionization Potential
$^3D_3 \rightarrow {}^2D_3 = 17.1$ volts

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[4] C. S. Beals, Phil Mag. **2**, p. 770 (1926).

are mainly irregular. The terms are inverted with the exceptions that $5p^3F_4$, $5p^3D_3'$ and $5d^3F_4'$ are re-inverted. This re-inversion of the level of the middle set of highest j is the customary experience but the other two are unusual.

The term-nomenclature is designed, after the suggestion of Sommerfeld, to indicate the essentials of the atomic structure to which the term is due. This is possible in the present case since only one electron changes its quantum conditions during the process of emission of the spectrum. The term-prefixes, therefore, give the total quantum number of that electron and its azimuthal quantum number in the usual form of a letter (s, p, d etc.)

The intensities of the multiplets $4d^95p \rightarrow 4d^95s$ and $4d^96s \rightarrow 4d^95p$ are given in Table II and are in excellent agreement with theory. The intensities used are the author's visual estimates of the photographic intensities.

TABLE II

Intensities in multiplets in Ag II.

	$d^9p \rightarrow d^9s$				$d^9,s \rightarrow d^9p.$			
	$5s^3D$	$5s^3D_2$	$5s^3D_1$	$5s^1D_2$	$6s^3D_3$	$6s^3D_2$	$6s^3D_1$	$6s^1D_2$
$5p^3P_2$	100*R*	30	15	30	25*u*	—	—	—
$5p^3P_1$		80*R*	60	60		20*u*	2*u*	5*u*
$5p^3P_0$			70				8*u*	
$5p^3D'_3$	80*R*	50		80	30*u*	20*u*		5*u*
$5p^3D'_2$	10	75*R*	75	5	1*u*	30*u*	8*u*	1*u*
$5p^3D_1'$		15	60	1		1*u*	20*u*	—
$5p^3F_4$	100*R*				40*u*			
$5p^3F_3$	70*R*	90*R*		75	15*u*	35*u*		1*u*
$5p^3F_2$	—	45	70*R*	80	—	15*u*	15*u*	8*u*
$5p^1P_1$		15	10	75		3*u*	1*u*	20*u*
$5p^1D_2'$	8	20	40	60	1*u*	—	5*u*	20*u*
$5p^1F_3$	20	40		80*R*	1*u*	—		35*u*

The terms due to the structure d^9d combine with the d^9p terms to give very little except the diagonals of multiplets; but these are sufficient to fix the terms with considerable certainty. The term $5d^3G_5$ of course makes only one combination but that line is the strongest diffuse line in a wide region of the spectrum. The term $5d^3P_0'$ is doubtful because the three combinations from which it is calculated are all sharp instead of diffuse lines. The term $4d^1S_0$ is probably practically coincident with $5d^3D_2$, which makes an unexpectedly strong combination with $5p^1P_1$. In fact, this line has been observed as double by Frings and possibly the second member is $5p^1P_1 - 5d^1S_0$. $5d^1S_0$ has been calculated on that assumption.

The terms which might be expected but which have not been identified are the theoretically lowest term $^1S_0$ from the structure $5d^{10}$ and the pentad from $4d^94f$. The visible portion of the spectrum contains a considerable number of weak spark lines interspersed with a few strong ones, and the pentad referred to may produce these lines in combination with $4d^95d$. Some attempt as been made to find such terms but with insufficient success to warrant publication at present.

The position of ${}^1S_0(d^{10})$ may be very roughly estimated from analogy with Cu I and Cu II. The position of ${}^1S_0$ in Cu II was calculated from series in Cu I as being about 22,200 wave-numbers below a^3D_3. Its position is actually now found to be at 21925 below a^3D_3. This is based on the results of Mr. R. J. Lang at the University of Alberta who has used an interrupted arc in vacuo and has found the following three lines distinct in character from all others in the region: 1358.84 (12); 1368.00 (2); 1472.48 (1). Using these as the combinations of ${}^1S_0$ with a^1P_1, a^3D_1' and a^3P_1, the term ${}^1S_0$ is calculated separately as 21925, 21926, 21925 below ${}^3D_3$. These are extraordinarily accurate measures at such wave-lengths.

It should be noted here that M. Eugene Bloch wrote to the author in May 1927 suggesting these same lines from his own measurements; but the frequency differences were so far from the necessary values that the author was lothe to accept the assignation. He tenders his acknowledgment of error here.

Unfortunately, the low ${}^2D(d^9s^2)$ of Ag I, if it exists, is not yet known; but, from the general relations in the spectra of copper, silver, and gold, it is probably much higher than in Cu I. This indeed might account for the failure to observe it since in that case, its strongest combinations with 2^2P would be in the infra-red. If this is correct then the ${}^1S_0$ of Ag II will lie very far below $5s^3D_3$ and its combinations will be in the far ultra-violet. A rough estimate would place its strongest combination at about ${}^1S_0-5p^1P_1=81000$. Of the other two possible combinations, that with $5p^3D_1'$ would then be 440 wave-numbers towards the short wave-lengths and that with $5p^3P_1$ at 6270 wave-numbers towards longer wave-lengths.

{*Note added in proof.* The author's estimate of the position of ${}^1S_0(d^{10})$ proves to be too high by almost 9000 wave-numbers. The measures of Mr. H. E. White of Cornell for the three combinations are:

${}^1S_0-5p^1P_1$	1112.46 (80)
${}^1S_0-5p^3D_1'$	1107.05 (25)
${}^1S_0-5p^3P_1$	1195.87 (50)

These give the value of ${}^1S_0$ as -39163.9 on the basis used in Table I. This means that the ${}^2D$ of *Ag.* I must be nearly coincident with 2^2P.}

Since two members of the ${}^3D^1D(d^9s)$ series are known, an approximate series limit can be evaluated by using a Rydberg formula. The four separate limits so calculated are given in the Term Table. They indicate, as in Cu II, Pd I, Ni I that the ${}^3D_3$ and ${}^3D_2$ series converge to one limit which would be the ${}^2D_3(d^9)$ of Cu III; and the ${}_3D_1$ and ${}^1D_2$ series converge to another limit, the ${}^2D_2$ of Cu III. As pointed out in connection with Cu II, this differs from the theoretical prediction. This question will be discussed more fully in a later paper.

The pentad $4d^95d$ is unusual in that the triplet terms all have very small intervals between the components of higher j, and very large intervals between the components of smaller j. The latter intervals are comparable with the calculated limit separations ${}^2D_3-{}^2D_2$ of Cu III, which would indicate that the theoretical predictions may here also be in error. This is, however, in direct apposition to the evidence of the structurally similar set (d^9sd) in Cu I where the whole pentad indicates agreement with theory.

TABLE III

Classified lines of Ag II.

λ	Auth.	Int.	ν	Designation	λ	Auth.	Int.	ν	Designation
3372.51	E	1	29643.0	$5p^1D_2'-6s^3D_3$	2409.01	E	2u	41498.2	$5p^3P_1\ -6s^3D_1$
3269.81	E	1	30574.0	$5p^3D'_1-6s^3D_2$	05.00	E	8u a	41567.4	$5p^3D_2'-5d^3P_1'$
3223.50	E	3	31013.3	$5p^1P_1-6s^3D_2$	02.60	E	8u a	41608.9	$5p^1P_1-5d^3D_1$
3184.2	E	1u	31396.0	$5p^1F_3-6s^3D_3$	2392.98	E	5u a	41776.2	$5p^3P_1-6s^1D_2$
2938.55	E	15u a	34020.5	$5p^3F_2-6s^3D_2$	90.58	E	25u a	41818.1	$5p^3D_1'-5d^3F_2'$
2934.24	E	30u a	34070.4	$5p^3D_3'-6s^3D_3$	86.32	E	5u a	41892.7	$5p^1P_1-5d^1D_2$
29.37	E	30 A	34127.1	$5s^1D_2-5p^3P_2$	83.17	E	8u a	41948.1	$5p^3P_1-5d^3S_1$
20.07	E	15u a	34235.7	$5p^1D_2'-6s^3D_1$	79.7	E	1u	42009.3	$5p^3D_2'-5d^3D_3$
02.09	E	20u a.	34447.9	$5p^3D_3'-6s^3D_2$	73.71	E	8u a	42115.3	$5p^1F_3-5d^3G_3$
2896.50	E	20u a	34514.3	$5p^1D_2'-6s^1D_2$	65.69	E	10u a	42258.0	$5p^1P_1-5d^3F_2'$
82.2	E	1u	34685.6	$5p^1D_2'-5d^3S_1$	64.01	E	30u a	42288.1	$5p^3D_2'-5d^3F_3'$
73.62	E	20u a	34789.1	$5p^3D_1'-6s^3D_1$	62.20	E	20u a	42320.5	$5p^3D_2'-5d^3D_2$
37.76	E	1u	35228.7	$5p^1P_1-6s^3D_1$	58.87	E	35u a	42380.2	$5p^1F_3-5d^1G_4$
				$5p^3D_1'-5d^3S_1$	57.92	E	70 A	42397.3	$5s^3D_1-5p^3P_0$
29.2	E	1u	35335.3	$5p^3D_2'-6s^3D_3$	43.77	E	3u	42653.2	$5p^1F_3-5d^1D_2$
15.57	E	20u a	35506.3	$5p^1P_1-6s^1D_2$	39.17	E	3	42737.1	$5p^3D_1'-5d^3P_0'$?
2799.70	E	30u a	35707.6	$5p^3D_2'-6s^3D_2$	31.40	E	80R A	42879.5	$5s^3D_2-5p^3P_1$
86.50	E	2u	35876.8	$5p^1D_2'-5d^3P_2'$	25.12	E	40u a	42995.3	$5p^3F_4-5d^3G_5$
67.54	E	75 A	36122.5	$5s^1D_2-5p^3F_3$	24.68	E	70R A	43003.4	$5s^3D_3-5p^3F_3$
56.48	E	35u a	36267.5	$5p^1F_3-6s^1D_2$	24.48	S	0u	43007.2	$5p^3F_4-5d^3G_4$
43.92	E	15 A	36433.5	$5s^3D_1-5p^3P_2$	21.56	E	5u a	43061.2	$5p^1F_3-5d^1F_3'$
12.07	E	40u a	36861.3	$5p^3F_4-6s^3D_3$	20.29	E	80R A	43084.8	$5s^1D_2-5p^1F_3$
11.21	E	15u	36873.0	$5p^1P_1-5d^3P_1'$	17.05	E	70R A	43145.0	$5s^3D_1-5p^3F_2$
2688.39	E	3u	37186.0	$5p^3D_1'-5d^3D_2$	15.32	E	1	43177.3	$5p^1P_1-5d^3P_0'$
81.38	E	20u a	37283.2	$5p^3P_1-6s^3D_2$	12.4	E	1u	43231.8	$5p^3F_3-6s^1D_2$
60.49	E	60 A	37575.9	$5s^1D_2-5p^3P_1$	2296.08	E	8u a	43539.1	$5p^3F_4-5d^3D_3$
56.92	F	6u	37626.4	$5p^1P_1-5d^3D_2$	80.03	E	75 A	43845.5	$5s^1D_2-5p^1P_1$
56.65	F	4u	37630.2	$5p^1P_1-5d^1S_0$	77.43	E	10u a	43895.6	$5p^3P_1-5d^3D_2$
25.70	E	8u	38073.7	$5p^1F_3-5d^3D_3$	75.32	E	25u a	43936.3	$5p^3F_4-5d^3F_4'$
14.56	E	15u	38235.9	$5p^3F_2-6s^3D_1$	57.41	E	1	44284.8	$5s^1D_2-5p^3D_1'$
06.14	E	15u	38359.5	$5p^3F_3-6s^3D_3$	53.45	E	30u a	44362.6	$5p^3F_2-5d^3G_3$
2598.55	S	3u	38471.5	$5p^1F_3-5d^3F_4'$	48.74	E	75R A	44455.5	$5s^3D_2-5p^3D_2'$
95.67	E	8u	38514.2	$5p^3F_2-6s^1D_2$	46.43	E	100R A	44501.2	$5s^3D_3-5p^3F_4$
84.21	E	2u	38685.0	$5p^3F_2-5d^3S_1$	46.14	S	20(u?)a	44507.0	$5p^3F_3-5d^3G_4$
80.77	E	35u a	38736.5	$5p^3F_3-6s^3D_2$	41.80	S	3u	44593.1	$5p^3F_3-5d^3P_2'$
67.21	S	5u	38941.2	$5p^3D_3'-6s^1D_2$	40.39	S	10u	44621.0	$5p^3P_0-5d^1P_1'$
64.41	E	8u	38983.6	$5p^3P_0-6s^3D_1$	29.53	S	60 A	44838.4	$5s^1D_2-5p^1D_2'$
53.43	E	5	39151.3	$5s^1D_2-5p^3D_2'$	19.69	S	10u	45037.4	$5p^3F_3-5d^3D_3$
35.30	E	30 A	39431.2	$5s^3D_2-5p^3P_2$	17.87	S	2u	45054.0	$5p^3D_3'-5d^1G_4$
07.30	E	8u	39871.5	$5p^1D_2'-5d^1P_1'$	08.49	S	15u	45265.7	$5p^3F_2-5d^3F_2'$
06.63	E	60 A	39882.2	$5s^3D_1-5p^3P_1$	05.95	S	35u a	45317.7	$5p^3F_3-5d^3F_3'$
04.11	E	8u	39922.3	$5p^3D_2'-6s^3D_1$	04.38	S	10u	45350.0	$5p^3F_3-5d^3D_2$
2486.72	F	4u	40201.5	$5p^3D_2'-6s^1D_2$	03.64	S	15u	45365.3	$5p^3P_0-5d^3D_1$
85.78	E	8u	40216.7	$5p^3D_3'-5d^3G_4$	02.09	S	40u a	45397.2	$5p^3P_2-5d^3S_1$
80.41	E	20u a	40303.7	$5p^3D_3'-5d^3P_2'$	2186.76	S	50 A	45715.3	$5s^3D_2-5p^3D_3'$
79.31	E	1u	40321.6	$5p^3F_2-5d^3D_3$	71.66	S	10	46032.6	$5s^3D_3-5p^3D_2'$
77.25	E	25u a	40355.2	$5p^3P_2-6s^3D_3$	70.87	S	25u	46050.0	$5p^3D_2'-5d^3G_3$
76.74	E	4u	40363.5	$5p^1D_2'-5d^3G_3$	66.51	S	45 A	46142.6	$5s^3D_2-5p^3F_2$
76.21	E	2u	40372.1	$5p^3D_2'-5d^3S_1$	66.05	S	10	46152.4	$5s^3D_1-5p^1P_1$
73.84	E	80 A	40410.8	$5s^1D_2-5p^3D_3'$	58.95	S	1u	46304.3	$5p^3D_2'-5d^3D_1$
72.92	E	5u	40425.8	$5p^3D_1'-5d^1P_1'$	45.76	S	20u	46588.2	$5p^3P_2-5d^3P_2'$
62.26	E	20u a	40600.8	$5p^3F_2-5d^3F_3'$					$5p^3D_2'-5d^1D_2$
61.28	E	2u	40617.0	$5p^1D_2'-5d^3D_1$	45.60	S	60 A	46592.1	$5s^3D_1-5p^3D_1'$
60.32	E	20u a	40632.8	$5p^3F_2-5d^3D_2$	29.12	S	10u	46952.8	$5p^3D_2'-5d^3F_2'$
53.31	E	30u a	40748.9	$5p^3D_3'-5d^3D_3$	25.50	S	18u	47032.8	$5p^3P_2-5d^3D_3$
47.93	E	80 A	40838.5	$5s^1D_2-5p^3F_2$	20.45	S	40 A	47144.9	$5s^3D_1-5p^1D_2'$
46.34	E	10u a	40865.0	$5p^1P_1-5p^1P_1'$	13.82	S	80R A	47292.6	$5s^3D_3-5p^3D_3'$
44.22	E	25u a	40900.5	$5p^1D_2'-5d^1D_2$	11.43	S	1u	47346.1	$5p^3P_2-5d^3D_2'$
37.81	E	100R A	41008.0	$5s^3D_3-5p^3P_2$	2075.61	S	10u	48163.1	$5p^3P_1-5d^1D_2$
36.62	E	8u	41028.0	$5p^3D_3'-5d^3F_3'$	65.90	S	40 A	48389.4	$5s^3D_2-5p^1F_3$
29.65	E	35u a	41145.7	$5p^3D_3'-5d^3F_4'$	33.92	S	15 L	49150.2	$5s^3D_2-5p^1P_1$
28.21	E	5u a	41170.1	$5p^3D_1'-5d^3D_1$	21.65	S	5 L?	49448.4	$5p^3P_1-5d^3P'_0$?
22.62	E	2u a	41265.1	$5p^1D_2'-5d^3F_2'$	15.89	S	15 L	49589.7	$5s^3D_2-5p^3D_1$,
20.11	E	30u a	41307.9	$5p^1D_2'-5d^1F_3'$	00.68	S	20 L	49966.7	$5s^3D_3-5p^1F_3$
13.23	E	90 R A	41425.6	$5s^3D_2-5p^3F_3$	1993.67	S	20 L	50142.5	$5s^3D_2-5p^1D_1'$
11.41	E	75A	41456.9	$5s^3D_1-5p^3D_2'$	32.88	S	8 L	51719.1	$5s^3D_3-5p^1D_2'$

E. Exner and Hascheck Spark.
Kayser. "Handbuch der Spectroscopie. Vol. 7."
F. Frings. (as "E".)
S. Author.
A. a. Appears in arc. A—strong. a—weak.
L. Long line in focussed spark.

The list of identified lines includes practically all the spark lines which appear in the arc. One enhanced line only (λ2395.68 (15)) has not been identified and its presence seems inexplicable unless another structure altogether is assumed to be present. The list gives the authority for the wave-length measurements, the author's intensity estimates, and a note as to the line's appearance or non-appearance in the arc. The arc exposure in the region λ2500−λ2250 was most intense and it will be noticed that in that region very few of the identified lines do not appear in the arc. As a matter of technique, it may be noted that an arc run on small current between pointed electrodes and with large self-induction in the circuit is most favourable to the production of spark lines. For instance, in the present case terms which are approximately 23 volts above the lowest state of the atom are very strongly excited in the arc of this character.

It has frequently been noticed that spark lines measured in the arc yield wave-lengths shorter than in the spark. In silver, the sharp lines are apparently unshifted but all the diffuse lines show a very considerable displacement. A few cases were measured on the assumption that no shift occurs in the sharp lines and gave displacements of the diffuse lines of about 2.2 wave-numbers in the region around λ2350.

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December 17, 1927.