On the Spark Spectrum of Silver

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WITH a hollow cathode of pure silver in a neon discharge, a number of new spectral lines were observed, many of which had intensities comparable to the strongest silver arc lines, as shown on Fig. 1. Cooling the cathode with liquid air the strongest of the new lines in the visible and ultraviolet were examined with Fabry-Perot interferometers with silvered or aluminized plates, showing that the lines consisted of doublets with separations $0.05-0.06$ cm^{-1}, the components of which had nearly equal intensities. For this reason the new lines were first believed to be combinations with the $d^9s^2\,{}^2D$ term of the silver atom, since this term, because of its two s electrons, was expected to show isotope shift according to the two almost equally abundant silver isotopes. However, after the discovery of the $d^9s^2\,{}^2D$ term[1] this hypothesis was abandoned because the ${}^2D$ splitting could not be found between the lines.

In order to find constant differences between the wave numbers, exposures in the region 9000 to 2000A obtained in the first order of a 21-foot grating were measured out with an accuracy of about 0.01A. By putting together the differences so found in a quadratic scheme it was ascertained that all the strong lines and some of the weaker ones could be classified as combinations between the well-known group of twelve odd terms arising from the $4d^95p$ configuration of the silver ion,

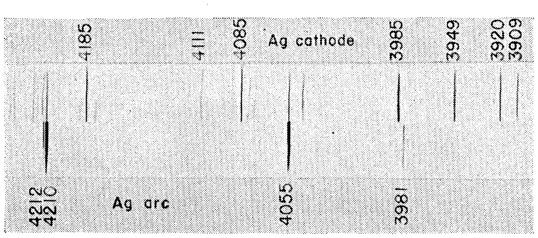

FIG. 1. Spectrum portion of the Ag spectrum showing some new lines brought out with a hollow cathode of pure silver in a neon discharge.

[1] E. Rasmussen, Phys. Rev. **57**, 243 (1940).

and five higher even terms, which do not occur either in the analysis of the silver spark spectrum by Shenstone[2] or in later supplementary papers by other investigators.[3] In fact, some of the classified lines—especially in the short wave region—have been found as weak lines in the ordinary silver spark spectrum by different observers, and are given in *Kaysers Handbook*. In Table I the intensities, wave-lengths, wave numbers and combinations of all the classified lines are given, while Table II contains the values of the new terms obtained by putting the normal state of the silver ion equal to zero.

As regards the origin of the new levels, it is very probable that the $4d^85s^2$ configuration is responsible for them, since this configuration is expected to give rise to singlet S, D, and G terms and triplet P and F terms similar to those occurring in the arc spectra of Ni, Pd and Pt from d^8s^2 configurations. This interpretation also explains the observed fine structure as an isotopic

TABLE I. *Intensities, wave-lengths, wave numbers, and classifications in the spark spectrum of silver.*

INT.	λ (AIR)	ν (VAC.)	CLASSIFICATION
20	5538.46	18050.56	$4d^95p\,{}^1D_2-4d^85s^2\,{}^3P_1$
20	5440.89	18374.26	$4d^95p\,{}^3F_2-4d^85s^2\,{}^3P_2$
15	5373.81	18603.61	$4d^95p\,{}^3D_1-4d^85s^2\,{}^3P_1$
10	5319.70	18792.84	$4d^95p\,{}^3D_1-4d^85s^2\,{}^3P_0$
20	5317.21	18801.64	$4d^95p\,{}^3D_3-4d^85s^2\,{}^3P_2$
10	5198.17	19232.20	$4d^95p\,{}^1P_1-4d^85s^2\,{}^3P_0$
80	5027.35	19885.67	$4d^95p\,{}^1D_2-4d^85s^2\,{}^1D_2$
10	4983.27	20061.56	$4d^95p\,{}^3D_2-4d^85s^2\,{}^3P_2$
5	4891.33	20438.64	$4d^95p\,{}^3D_1-4d^85s^2\,{}^1D_2$
100	4788.40	20877.98	$4d^95p\,{}^1P_1-4d^85s^2\,{}^1D_2$
50	4620.46	21636.83	$4d^95p\,{}^3P_1-4d^85s^2\,{}^3P_2$
80	4620.04	21638.79	$4d^95p\,{}^1F_3-4d^85s^2\,{}^1D_2$
10	4533.81	22050.34	$4d^95p\,{}^3F_2-4d^85s^2\,{}^3P_1$
30	4385.06	22798.32	$4d^95p\,{}^3P_0-4d^85s^2\,{}^3P_1$
20	4211.53	23737.67	$4d^95p\,{}^3D_2-4d^85s^2\,{}^3P_1$
100	4185.48	23885.41	$4d^95p\,{}^3F_2-4d^85s^2\,{}^1D_2$
30	4111.89	24312.88	$4d^95p\,{}^3D_3-4d^85s^2\,{}^1D_2$
80	4085.91	24467.47	$4d^95p\,{}^1F_3-4d^85s^2\,{}^3F_4$
70	3985.19	25085.84	$4d^95p\,{}^3P_2-4d^85s^2\,{}^3P_2$
60	3949.43	25312.97	$4d^95p\,{}^3P_1-4d^85s^2\,{}^3P_1$
70	3920.10	25502.36	$4d^95p\,{}^3P_1-4d^85s^2\,{}^3P_0$
50	3909.31	25572.75	$4d^95p\,{}^3D_2-4d^85s^2\,{}^1D_2$
80	3683.34	27141.58	$4d^95p\,{}^3D_3-4d^85s^2\,{}^3F_4$
75	3682.46	27148.06	$4d^95p\,{}^3P_1-4d^85s^2\,{}^1D_2$
80	3495.28	28601.86	$4d^95p\,{}^3F_3-4d^85s^2\,{}^1D_2$
70	3475.82	28761.99	$4d^95p\,{}^3P_2-4d^85s^2\,{}^3P_1$
10	3339.93	29932.17	$4d^95p\,{}^3F_4-4d^85s^2\,{}^3F_4$
100	3267.35	30597.05	$4d^95p\,{}^3P_2-4d^85s^2\,{}^1D_2$
90	3180.70	31430.56	$4d^95p\,{}^3F_3-4d^85s^2\,{}^3F_4$

[2] A. G. Shenstone, Phys. Rev. **31**, 317 (1928).
[3] H. A. Blair, Phys. Rev. **36**, 173 (1930); W. P. Gilbert, Phys. Rev. **47**, 847 (1935).

displacement of about 0.05 cm^{-1} caused by the two s electrons. While the assigned J values for the new terms are quite certain, the L values are of course only tentative and might possibly be altered.

The remarkable enhancement of the combinations with the new levels is explained by a resonance effect of collisions of the second kind between Ne ions and Ag atoms similar to the effect observed by Duffendack and Thomson[4] for other combinations of metals and rare gases. As seen from Table II, the values of the new terms, relative to the normal level of neutral silver, fall very close to the ionization energy of the neon atom, the energy discrepancy being less than one electron volt. As to the term $^3F_4$, which is a little higher than the normal ionization energy of neon, it must be remembered that the neon atom also has a second limit 780 cm^{-1} above the first.

TABLE II. *Values of the new terms in the spark spectrum of silver obtained by putting the normal state of the silver ion equal to zero.*

Term	Term Value	Energy Discrepancy	Number of Combinations
$4d^85s^2\ ^3P_2$	105257.9	7567.7 =0.93 volt	5
$4d^85s^2\ ^3P_1$	108934.0	3891.6 =0.48 volt	7
$4d^85s^2\ ^3P_0$	109123.3	3702.3 =0.46 volt	3
$4d^85s^2\ ^1D_2$	110769.1	2056.5 =0.25 volt	10
$4d^85s^2\ ^3F_4$	113597.8	−772.2 = −0.09 volt	4

A full account of the silver spectra will be published in the *Proceedings of the Royal Society of Denmark*. I wish to express my greatest thanks to Professor Niels Bohr for his kind interest in this work.

[4] O. S. Duffendack and K. Thomson, Phys. Rev. **43**, 106 (1933).

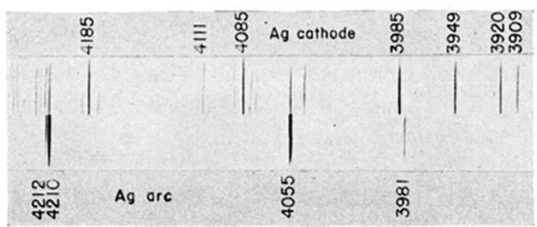

FIG. 1. Spectrum portion of the Ag spectrum showing some new lines brought out with a hollow cathode of pure silver in a neon discharge.