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THE ARC SPECTRUM OF GERMANIUM

By C. W. Gartlein

Abstract

Wave-lengths and classification of the lines of the Ge arc spectrum.—The wave-lengths of lines in the germanium arc spectrum have been measured in the region above 1870A with an accuracy of at least 0.03A. From these lines the *relative energy levels* have been determined and transitions corresponding to 73 lines have been identified. In the normal state the germanium atom contains two p valence electrons which give rise to the lower levels $^3P'_{012}$ $^1D_2$ $^1S_0$, with $^3P'_0$ lying deepest as predicted by the theory of Hund. The next higher levels arise from the configurations ps and pd. Data on the persistence of germanium lines were of great value in identification of the levels. At least two members of each of 11 series have been found and approximate limits have been calculated to be 65,300 for $^2P_2$ and 63,600 for $^2P_1$. The first *resonance potential* is 4.65 volts and the *ionization potential* determined by the limit $^2P_1$ is 7.85 volts. The similarities in the arc spectra of Si, Ge, Sn, and Pb are pointed out and the relative term values for these spectra are brought together in a single diagram.

During the past few years the arc spectra of silicon, tin, and lead have been analyzed and identified, but little has been done with the arc spectrum of either germanium or carbon. The wave-lengths of the arc lines of germanium have been measured by Rowland and Tatnall and by Exner and Haschek[1] and others to about 2200A. The only analysis attempted was the finding of several constant frequency differences by Paulson.[2]

Since there was available a generous supply of various germanium compounds and of the fused metal, prepared by the Chemistry Department of Cornell University, the author undertook the measurement and analysis of its arc spectrum. From the theory of space quantization the type of spectrum could be predicted; analogy with silicon gave the separations to be expected; and data on the persistence of germanium lines suggested the transitions into the lowest levels.

Theoretical Considerations

According to the Bohr-Stoner scheme of building up the atom the elements of the fourth group each contain two p valence electrons in the normal state and according to the theory of Pauli, Hund, and others it is these p electrons which determine the lowest levels. The levels arising from p electrons given by Hund[3] and by McLennan, Smith, and McLay[4] are $^3P'_{012}$, $^1D_2$, $^1S_0$ with $^3P_0'$ lying deepest.

In the Bohr-Stoner scheme electrons are added in the following order for elements after germanium, p electrons for As, Se, Br, and Kr, s electrons for

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[1] Kayser, Handbuch der Spectroscopie, Vol. 5, p. 470.

[2] E. Paulson, Ann. d. Physik, **45**, 419 (1914).

[3] Hund, Zeits. f. Physik **33**, 355 (1925).

[4] McLennan, Smith and McLay, Proc. Roy. Soc. **A112**, 76 (1926).

Rb and Sr and then *d* electrons from Yt to Cd. If one of the *p* valence electrons of the normal atom of germanium is excited, it seems likely that it will go into an orbit which would be occupied by the next tightest bound electron, an *s* orbit, or if excited higher, into a *d* orbit, or a higher *p* orbit. We would expect the next higher levels to be determined by these two valence electrons, one of them still in a *p* orbit but the other displaced successively into *s*, *d*, and *p* orbits. These higher levels would be ${}^3P_{012}$, ${}^1P_1$ from a *ps* configuration, ${}^3F_{234}$, ${}^3D'_{123}$, ${}^3P_{012}$, ${}^1F_3$, ${}^1D_2'$, ${}^1P_1$, from a *pd* configuration and ${}^3D_{123}$, ${}^3P'_{012}$, ${}^3S_1$, ${}^1D_2$, ${}^1P_1'$, ${}^1S_0$, from a *p-p* configuration. Thus the lowest levels of the normal state are a ${}^3P'$ and those of the lowest excited state are a ${}^3P$, so a ${}^3PP'$ multiplet of six lines should contain the strongest lines as well as the most persistent or ultimate lines.

MEASUREMENTS

Using a six foot concave grating, ruled to give high intensity in the region near 2000A and set up on a Rowland mounting, the arc spectrum produced by germanium metal or germanium dioxide in carbon or aluminum electrodes was photographed below 4700A on Eastman 33 plates and Schumann plates. The glass plates were thin enough to withstand bending to the focal curve during the exposure. The Eastman plates were sensitized with a very thin film of fluorescent oil (Liquid Veneer Furniture Polish) to photograph the region below 2200A. Exposures of 5 minutes gave lines to 1895A, including about 40 new lines below 2200A, while a 15 sec. exposure gave the lines at 2600A. The oiled plates were about one-third as sensitive as the Schumann plates which were later used, but were far superior to unoiled plates.

In measuring the plates iron arc lines were used as standards above 2300A. On the first measures below 2300A silicon lines,[5] which were the only impurity in the germanium spectrum, were used as standards along with the lines from the aluminum spark. The wave-lengths of these lines are not known with sufficient accuracy for use in final measurements. Silver spark lines were used after their wave-lengths were measured on several plates in the second order against iron standards. The wave-lengths of these silver standards will be published in a separate paper. Professor A. G. Shenstone[6] determined wave-lengths of certain copper lines by a different method. Some of these copper lines were present in the germanium spectrum as impurities from the carbons used to hold the electrodes and when measured, using silver standards, the author obtained the wave-lengths given by Professor Shenstone within 0.01 to 0.02A.

The Ge lines were very sharp and characteristic so that they could be separated from the lines due to impurities in the electrodes. The dispersion was about 4.6A per mm so that with a Gaertner comparator reading to 0.001 mm the setting errors amounted to about 0.01A and the absolute

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[5] A. Fowler, Phil. Trans. Roy. Soc. **225**, **1** (1926).

[6] Shenstone, Phys. Rev. **29**, 380–390 (1927).

wave-lengths are accurate to at least 0.03A as the variation in the frequency differences in Table II indicates.

Table I contains the wave-lengths of all the lines, with the relative intensities in the first column, the wave-lengths in I.A. (in air) in the second, the wave-numbers in vacuo in the third, the persistence in the fourth, and the transitions in the fifth. The intensities at the short wave-lengths could not be accurately related to those at longer wave-lengths because of the different sensitivities of the two kinds of plates used.

TABLE I. *Wave-lengths in the germanium arc.*

Int.	λ (air) I. A.	ν (vac)	Persistence	Transition
20	4685.86	21334.9	1.f	$4p^2\ {}^1S_0-4p5s^3P_1$
50	4226.60	23653.0	.001	$4p^2\ {}^1S_0-4p5s^1P_1$
40	3269.51	30576.8	.001f	$4p^2\ {}^1D_2-4p5s^3P_1$
20	3124.82	31992.6	.1	$4p^2\ {}^1D_2-4p5s^3P_2$
10	3067.04	32595.3	.1	$4p^2\ {}^1S_0-4p4d^3D_1'$
60	3039.07	32895.3	.0001	$4p^2\ {}^1D_2-4p5s^1P_1$
9	2829.00	35337.8	.01f	$4p^2\ {}^1S_0-4p4d^3P_1$
10	2793.93	35781.4	1.	$4p^2\ {}^1S_0-4p6s^3P_1$
50	2754.59	36292.3	.001	$4p^2\ {}^3P_2'-4p5s^3P_1$
20	2740.43	36479.9	.1	$4p^2\ {}^1S_0-4p4d^1P_1$
40	2709.63	36894.5	.001	$4p^2\ {}^3P_1'-4p5s^3P_0$
30	2691.35	37145.1	.1	$4p^2\ {}^3P_1'-4p5s^3P_1$
20	2651.57	37702.3	.0001f	$4p^2\ {}^3P_0'-4p5s^3P_1$
30	2651.19	37707.7	.0001	$4p^2\ {}^3P_2'-4p5s^3P_2$
8	2644.20	37807.4	.1	$4p^2\ {}^1S_0-4p6s^1P_1$
30	2592.54	38560.8	.001	$4p^2\ {}^3P_1'-4p5s^3P_2$
12	2589.19	38610.6	.1f	$4p^2\ {}^3P_2'-4p5s^1P_1$
10	2556.32	39107.0	1.	$4p^2\ {}^1S_0-4p5d^3D_1$
15	2533.23	39463.4	.1	$4p^2\ {}^3P_1'-4p5s^1P_1$
15	2497.97	40020.4	.1	$4p^2\ {}^3P_0'-4p5s^1P_1$
5	2436.41	41031.5	1.	$4p^2\ {}^1S_0-4p7s^3P_1$
20	2417.37	41354.7	.001f	$4p^2\ {}^1D_2-4p4d^1D_2'$
6	2397.90	41690.5	1.	$4p^2\ {}^1S_0-4p5d^1P_1$
4	2394.09	41756.8	.1f	$4p^2\ {}^1D_2-4p4d^3F_2$
5	2389.48	41837.4		$4p^2\ {}^1D_2-4p4d^3D_1$
12	2379.14	42019.2		$4p^2\ {}^1D_2-4p4d^3F_3$
4	2359.22	42373.9	.01f	$4p^2\ {}^1S_0-4p7s^1P_1$
4	2338.61	42747.3	.1f	$4p^2\ {}^1S_0-aP_1$
15	2327.92	42943.6	1.	$4p^2\ {}^1D_2-4p4d^3D_2'$
0	2316.44	43156.4		
10	2314.20	43198.2	.1f	$4p^2\ {}^1D_2-4p4d^3D_3'$
1	2305.59	43359.5		
00(?)	2262.71	44181.2		
5	2256.00	44312.5		$4p^2\ {}^1D_2-4p4d^3P_2$
00(?)	2252.76	44376.2		
1	2252.43	44382.7		
2Cu?	2247.03	44489.4		
2	2242.47	44579.8		$4p^2\ {}^1D_2-4p4d^3P_1$
0(?)	2232.27	44783.5		
2	2222.73	44975.7		
4	2220.39	45023.1		$4p^2\ {}^1D_2-4p6s^3P_1$
15R	2198.73	45466.6	.1f	$4p^2\ {}^1D_2-4p4d^1F_3$
5	2186.46	45721.7		$4p^2\ {}^1D_2-4p4d^1P_1$
1	2136.71	46786.1		$4p^2\ {}^1D_2-4p6s^3P_2$
5δ	2124.76	47049.2		$4p^2\ {}^1D_2-4p6s^1P_1$
3	2123.83	47069.8		$4p^2\ {}^3P_2'-4p4d^1D_2'$
5	2105.83	47472.1		$4p^2\ {}^3P_2'-4p4d^3F_2$
3	2102.26	47552.7		$4p^2\ {}^3P_2'-4p4d^3D_1'$
10R	2094.27	47734.1		$4p^2\ {}^3P_2'-4p4d^3F_3$
5	2086.03	47922.6		$4p^2\ {}^3P_1'-4p4dF^1D_2'$
0	2071.98	48247.6		
9R	2068.66	48325.0		$4p^2\ {}^3P_1'-4p4d^3F_2$
3	2067.63	48349.1		$4p^2\ {}^1D_2-4p5d^3D_1$
6R	2065.22	48405.5		$4p^2\ {}^3P_1'-4p4d^3D_1$
2	2058.59	48561.1		
5R	2057.25	48593.0		$4p^2\ {}^1D_2-4p5d^3F_2$
5	2054.46	48658.9		$4p^2\ {}^3P_2'-4p4d^3D_2'$
7R	2043.79	48912.9		$4p^2\ {}^3P_2'-4p4d^3D_3'$
8R	2041.72	48962.2		$4p^2\ {}^3P_0'-4p4d^3D_1$
6R	2019.08	49511.5		$4p^2\ {}^3P_1'-4p4d^3D_2'$
4R	2011.31	49702.7		$4p^2\ {}^1D_2-4p5d^1D_2'$
1	2007.55	49795.8		
0(?)	1999.65	49992.4		
7R	1998.25	50027.5		$4p^2\ {}^3P_2'-4p4d^3P_2$
2	1997.18	50054.3		
1	1988.48	50273.2		$4p^2\ {}^1D_2-4p7s^3P_1$
4R	1987.64	50294.5		$4p^2\ {}^3P_2'-4p4d^3P_1$
2	1987.22	50305.1		$4p^2\ {}^1D_2-4p5d^3D_3'$
0(?)	1972.00	50693.2		$4p^2\ {}^1D_2-4p5d^3P_2$
4δ	1970.26	50738.0		$4p^2\ {}^3P_2'-4p6s^3P_1$
2	1964.76	50880.2		$4p^2\ {}^3P_1'-4p4d^3P_2$
1	1962.76	50932.1		$4p^2\ {}^1D_2-4p5d^1P_1$
6R	1961.40	50967.4		$4p^2\ {}^1D_2-4p5d^1F_3$
4R	1954.49	51147.5		$4p^2\ {}^3P_2'-4p4d^3P_1$
0	1953.19	51181.5		$4p^2\ {}^3P_2'-4p4d^1F_3$
2R	1944.11	51423.1		$4p^2\ {}^3P_1'-4p6s^3P_0$
1	1943.50	51436.6		$4p^2\ {}^3P_2'-4p4d^1P_1$
3R	1937.68	51591.1		$4p^2\ {}^3P_1'-4p6s^3P_1$
3R	1936.87	51612.6		$4p^2\ {}^3P_1'-4p4d^3P_0$
2	1933.42	51704.7		$4p^2\ {}^3P_0'-4p4d^3P_1$
4R	1929.23	51817.0		
0δ	1922.87	51988.3		$4p^2\ {}^1D_2-aP_1$
3	1916.97	52148.3		$4p^2\ {}^3P_0'-4p6s^3P_1$
0	1911.80	52289.3		$4p^2\ {}^3P_1'-4p4d^1P_1$
1	1904.09	52500.9		$4p^2\ {}^3P_2'-4p6s^3P_2$
0(?)	1899.34	52632.4		
0	1894.61	52763.9		$4p^2\ {}^3P_2'-4p6s^1P_1$
0	1889.83	52897.3		
0	1873.62	53354.6		$4p^2\ {}^3P_1'-4p6s^3P_2$

METHOD OF ANALYSIS AND RESULTS

Hicks has shown that for elements in the same group of the periodic table the separations of similar doublets or triplets are nearly proportional to the squares of the atomic weights. In silicon[5] the separations of the lowest $^3P'$ levels are 77 and 146 wave-numbers, so that we should expect separations about 6 times as great in germanium or about 470 and 890 wave-numbers. The PP' multiplet in silicon is located near 2500A so we should expect the multiplet in Ge at a slightly greater wave-length. This alone would indicate the strong lines from 2592A to 2754A as constituting the PP' multiplet. Persistence data verify this guess.

Professor Jacob Papish, Dr. F. M. Brewer, and Mr. Donald Holt of the Chemistry Department of Cornell University have recently worked out the persistence of the germanium lines and kindly allowed the use of their data in advance of publication.[7] Working with solutions they placed small quantities of a germanium compound in the arc and photographed the spectra, noting the quantity of germanium responsible for a given spectrogram. The most persistent spectral lines are those which show when the smallest quantities of the material are present in the zone of excitation. These data are reproduced in the fourth column of Table I. The persistence is there given as the fraction of a milligram of germanium which is just sufficient to make the line appear in a spectrogram. The letter *f* after the figure indicates that the line was visible, but faint with that amount of Ge.

Arranging the most persistent lines around 2650A as a *PP'* multiplet gave separations of nearly 557 and 853 wave-numbers between the lower levels, and very close to the predicted values. This multiplet appears at the top of Table II. The work on the relative levels was begun by assigning the

Table II.

	$4p^2\ {}^3P_0'$ 0	Δ 557.1	$4p^2\ {}^3P_1'$ 557.1	Δ 852.9	$4p^2\ {}^3P_2'$ 1410.0	Δ 5715.0	$4p^2\ {}^1D_2$ 7125.0	Δ 9242.1	$4p^2\ {}^1S_0$ 16366.9
$4p5s\,{}^3P_0$ 37451.6			40 2709.63 36894.5						
$4p5s\,{}^3P_1$ 37702.1	20 2651.57 37702.3	7.2	30 2691.35 37145.1	2.8	50 2754.59 36292.3	5.5	40 3269.51 30576.8	1.9	20 4685.86 21334.9
$4p5s\,{}^3P_2$ 39117.7			30 2592.54 38560.8	3.1	30 2651.19 37707.7	5.1	20 3124.82 31992.6		
$4p5s\,{}^1P_1$ 40020.3	15 2497.97 40020.4	7.0	15 2533.23 39463.4	2.8	12 2589.19 38610.6	5.3	60 3039.07 32895.3	2.3	50 4226.60 23653.0
$4p4d\,{}^1D_2'$ 48479.7			5 2086.03 47922.6	2.8	3 2123.83 47069.8	5.1	20 2417.37 41354.7		
$4p4d\,{}^3F_2$ 48882.0			9δ*R* 2068.66 48325.0	2.9	5δ 2105.83 47472.1	5.3	4 2394.09 41756.8		
$4p4d\,{}^3D_1'$ 48962.4	8*R* 2041.72 48962.2	6.7	6*R* 2065.22 48405.5	2.8	3 2102.26 47552.7	5.3	5 2389.48 41837.4	2.1	10 3067.04 32595.3
$4p4d\,{}^3F_3$ 49144.2					10δ*R* 2094.27 47734.1	4.9	12 2379.14 42019.2		
$4p4d\,{}^3D_2'$ 50068.7			6*R* 2019.08 49511.5	2.6	5 2054.46 48658.9	5.3	15 2327.92 42943.6		

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[7] Jacob Papish, F. M. Brewer, and Donald Holt, Jour. Amer. Chem. Soc. **49,** 3028 (1927).

TABLE II. (Continued)

	$4p^2\,^3P_0'$ 0	Δ 557.1	$4p^2\,^3P_1'$ 557.1	Δ 852.9	$4p^2\,^3P_2'$ 1410.0	Δ 5715.0	$4p^2\,^1D_2$ 7125.0	Δ 9242.1	$4p^2\,^1S_0$ 16366.9
$4p4d\,^3D_3'$ 50323.1					7*R* 2043.79 48912.7	4.7	10 2314.20 43198.2		
$4p4d\,^3P_2$ 51437.4			2 1964.76 50880.2	2.7	7*R* 1998.25 50027.5	5.0	5 2256.00 44312.5		
$4p4d\,^3P_1$ 51704.7	2 1933.42 51704.7	7.2	4*R* 1954.49 51147.5	3.0	4*R* 1987.64 50294.5	4.7	2 2242.47 44579.8	2.0	9 2829.00 35337.8
$4p6s\,^3P_0$ 51980.2			2*R* 1944.11 51423.1						
$4p6s\,^3P_1$ 52148.2	3δ 1916.97 52148.3	7.2	3*R* 1937.68 51591.1	3.1	4δ 1970.26 50738.0	4.9	4 2220.39 45023.1	1.7	10 2793.93 35781.4
$4p4d\,^3P_0$ 52169.7			3*R* 1936.87 51612.6						
$4p4d\,^1F_3$ 52591.6					0 1953.19 51181.5	4.9	15*R* 2198.73 45466.6		
$4p4d\,^1P_1$ 52846.7			0 1911.80 52289.3	2.7	1 1943.50 51436.6	4.9	5 2186.46 45721.7	1.8	20 2740.43 36479.9
$4p6s\,^3P_2$ 53911.0			0 1873.62 53354.6	3.7	1 1904.09 52500.9	4.8	1 2136.71 46786.1		
$4p6s\,^1P_1$ 54174.3					0 1894.61 52763.9	4.9	5 2124.76 47049.2	1.8	8 2644.20 37807.4
$4p5d\,^3D_1'$ 55474.0							3 2067.63 48349.1	2.1	10 2556.32 39107.0
$4p5d\,^3F_3$ 55718.0							5*R* 2057.25 48593.0		
$4p5d\,^1D_2'$ 56827.7							4*R* 2011.31 49702.7		
$4p7s\,^3P_1$ 57398.3							1 1988.48 50273.2	1.7	5 2436.41 41031.5
$4p5d\,^3D_3'$ 57430.1							2 1987.22 50305.1		
$4p5d\,^3P_2$ 57818.2							0 1972.00 50693.2		

TABLE II. (Continued)

	$4p^2\ {}^3P_0'$ 0	Δ 557.1	$4p^2\ {}^3P_1'$ 557.1	Δ 852.9	$4p^2\ {}^3P_2'$ 1410.0	Δ 5715.0	$4p^2\ {}^1D_2$ 7125.0	Δ 9242.1	$4p^2\ {}^1S_0$ 16366.9
$4p5d\ {}^1P_1$ 58057.3							1 1962.76 50932.1	1.6	6 2397.90 41690.5
$4p5d\ {}^1F_3$ 58092.4							6R 1961.40 50967.4		
$4p7s\ {}^1P_1$ 58740.8									4 2359.22 42373.9
aP_1 59113.8							0δ 1922.87 51988.3	1.0	4 2338.61 42747.3

value zero to the lowest ${}^3P_0'$ level and the values of ${}^3P_1'$ and ${}^3P_2'$ were determined from two separations in the multiplet. The values of the ${}^3P$ levels were established, the ${}^3P_1$ by three lines and the ${}^3P_2$ by two lines. The great persistence of 2709.63A at once identified it as the transition ${}^3P_1'-{}^3P_0$. It should be noted that this is the only transition possible from ${}^3P_0$. The wave-numbers of all the lines in the spectrum were plotted on a large graph, and a search made for triplets with the two separations 853 and 557 wave-numbers. Five such triplets were found, as well as seven pairs of separation 853. One of the triplets, 2497.97A, 2533.23A, and 2589.19A is just below the multiplet, so it must be a transition from a level just above the ${}^3P$ levels, and seems to be from the predicted ${}^1P_1$ level. The lines of this triplet are of the same persistence but less persistent than the lines of the ${}^3PP'$ multiplet. If this upper level defined by the triplet is the ${}^1P_1$, we should also find transitions from it into the predicted ${}^1S_0$ and ${}^1D_2$ levels. These lines should be above the multiplet, perhaps several hundred Angstroms. The lines at 4226A and 3039A are among the very persistent lines in the spectrum, and might correspond to ${}^1S_0-{}^1P_1$ and ${}^1D_2-{}^1P_1$. These lines would set the values of the ${}^1S_0$ and ${}^1D_2$ as 16367 and 7125 cm^{-1}. Transitions from the ${}^3P_1$ level into these lower levels should give lines at 21334 and 30576 cm^{-1}. The lines at 4685.86 and 3269.51A are in these positions and correspond to ${}^1S_0-{}^3P_1$ and ${}^1D_2-{}^3P_1$, while the line at 3124.82A corresponds to ${}^1D_2-{}^3P_2$. Thus we have established the five levels of the normal state, ${}^3P_0'$ at 0, ${}^3P_1'$ at 557, ${}^3P_2'$ at 1410, ${}^1D_2$ at 7125, and ${}^1S_0$ at 16367 and the four levels ${}^3P_{012}$ and ${}^1P_1$ of the first excited state. The higher levels in Table II were worked out by searching for all the possible wave-number differences between the five lower levels. Since the lower levels have been identified, the upper levels can usually be identified by applying the usual selection rules, that $\Delta k=\pm 1$ or 0, (sometimes violated), and $\Delta j=\pm 1$ or 0, (except that the transition from $j=0$ to $j=0$ is barred); and by applying the intensity rule, that the most intense lines occur when changes in j and k are in the same direction. The persistence data verify these rules nicely in most cases, and also show that the transitions within the singlet system or within the triplet system are more persistent than similar transitions between the two systems. The line 2691.35, $^3P_1'-{}^3P_1$ is not as persistent as might be expected.

The final identification of terms was made more certain by comparison with the arc spectrum of tin as published by E. Back[8] and Green and Loring.[9] In cases of uncertainty, where intensity rules would permit a choice between two possible identifications, the energy level was identified by comparison with the tin spectrum. The level $4p4d\,^1D_2'$, 48479.7 was identified by the great persistence of the line 2417.37A which indicated that this line was a transition between singlet terms.

In Table II the values of the lower levels are given at the top of the table, with the differences between the levels in the columns headed Δ, while the term values of the higher levels are given at the left side of the table, with the radiations resulting from transitions into the lower levels opposite these term values. Each radiation is indicated by three numbers; the upper is the relative intensity, the second the wave-length in I.A. in air, and the third the wave-number in vacuum. The difference between the levels at the top of the table is in each case the average of the differences corresponding to transitions from a common level into two adjacent lower levels. The term values of the five lowest levels were found by successive addition of these average differences. The variations in the differences in the Δ columns indicate the accuracy of measurement and are nearly all within 1 wave-number.

It is believed that two members of each of four series of lines are represented by electron configurations $4p5s$, and $4p6s$. Series from these configurations are generally Rydbergian, so approximate limits can be calculated using a Rydberg table. The terms $4p5s\,^3P_2$, 39117.7 and $4p6s\,^3P_2$, 53911.0 give the limit 65910 cm^{-1} above $4p^2\,^3P_0$. The theory of Hund predicts that these terms as well as all singlet terms will approach the upper series limit. The levels $4p5s\,^1P_1$, 40020.3, and $4p6s\,^1P_1$, 54174.3 give the limit 65895 cm^{-1}. The level $4p7s\,^1P_1$, 58740.8 seems a possible third member of this series. The limit calculated from the second and third members is 65016 cm^{-1}. The levels $4p5s\,^3P_1$, 37702.1 and $4p6s\,^3P_1$, 52148.2 give the lower limit 64000 cm^{-1}, while the limit calculated from $4p6s\,^3P_1$, and the possible third member $4p7s\,^3P_1$, 57398.3 is 64193 cm^{-1}. Using 64100 cm^{-1} as an approximate lower limit, a prediction was made for the transition from $4p6s\,^3P_0$ into $4p^2\,^3P_1'$ and a reversed line 51423.1 cm^{-1} was found near the predicted position. It was chosen because it was the only strong unidentified line in this region. The terms $4p5s\,^3P_0$, 37451.6 and $4p6s\,^3P_0$, 51980.2, give 63867 cm^{-1} as the value of the limit.

In the spectra of silicon, tin, and lead the series limits, from the first two terms, for the levels of the *pd* configurations are several hundred wave-numbers below the limits derived from the *ps* configurations. Thus by

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[8] E. Back, Zeits. f. Physik **43**, 309 (1927).

[9] J. B. Green and R. A. Loring, Phys. Rev. **30**, 574 (1927).

choosing a lower limit than that suggested by the *ps* terms the possible series were quite easily identified and a maximum number of the stronger lines could be arranged in series. The value 65300 cm^{-1} was taken for the upper limit and 63600 cm^{-1} for the lower limit. The series thus identified are grouped with those from the *ps* configurations in Table III. The series approaching the upper limit are given in the upper half of the table. The wave-number of the level is given for the first member of the series, then its term value, obtained by subtracting the value of the level from the limit, and below this the Rydberg denominator, $(\nu/R)^{1/2}$. Below these figures the same data are given for the second and third members of the series. The limit predicted from the 1st and 2nd series members are then given and below it, in a few cases, the limit predicted from the second and third members. The lower half of Table III contains similar data for the series and terms approaching the lower limit.

TABLE III. *Series approaching the upper limit* $(^2P_2) = 65300$.

	$ps\ ^3P_2$	$ps\ ^1P_1$	$pd\ ^1D_2'$	$pd\ ^1F_3$	$pd\ ^1P_1$	$pd\ ^3D_3'$	$pd\ ^3P_2$
Levels	39118	40020	48480	52592	52846	50323	51437
Term Values	26182	25280	16820	12708	12454	14977	13863
Rydberg Den.	2.047	2.083	2.554	2.938	2.968	2.706	2.813
	53911	54174	56828	58092	58057	57430	57818
	11389	11126	8472	7208	7243	7870	7482
	3.103	3.140	3.598	3.901	3.891	3.733	3.829
		58741					
		6559					
		4.089					
Limit predicted from 1st and 2nd terms	65831	65896	65640	65068	64823	65488	65405
From 2nd and 3rd		65016					

Series approaching the lower limit $(^2P_1) = 63600$.

	$ps\ ^3P_1$	$ps\ ^3P_0$	$pd\ ^3P_1$	$pd\ ^3P_0$	$pd\ ^3D_2'$	$pd\ ^3D_1'$	$pd\ ^3F_3$	$pd\ ^3F_2$
Levels	37702	37452	51704	52169	50069	48962	49144	48882
Term Values	25898	26148	11896	11431	13531	14638	14456	14718
Rydberg Den.	2.058	2.048	3.036	3.098	2.847	2.737	2.754	2.730
	52148	51980				55474	55718	
	11452	11620				8126	7882	
	3.095	3.072				3.674	3.730	
	57398							
	6202							
	4.205							
Limit predicted from 1st and 2nd terms	63998	63866				63147	63396	
2nd and 3rd	64193							

The average of the limits obtained from the series is about 100 wave-numbers above those chosen, but the values derived from the early members of the series are valuable only as a clue to the real limit obtained from the higher terms. The ionization potential is therefore about 7.85 volts and the resonance potential is 4.65 volts.

The first two members of most of these series are believed to be correctly identified, but the selection for the third members is doubtful. The difference 1700 between the chosen limits is in fair agreement with the separation of the lowest terms in the germanium spark predicted from a comparison of the separations in silicon, tin, and lead. Assuming that these separations are proportional to the square of the atomic weights of the elements, a calculation using the values 287 for silicon and 4253 for tin gave the value 1800 for germanium. No attempt has been made to work out formulae for the series as the identifications did not warrant this.

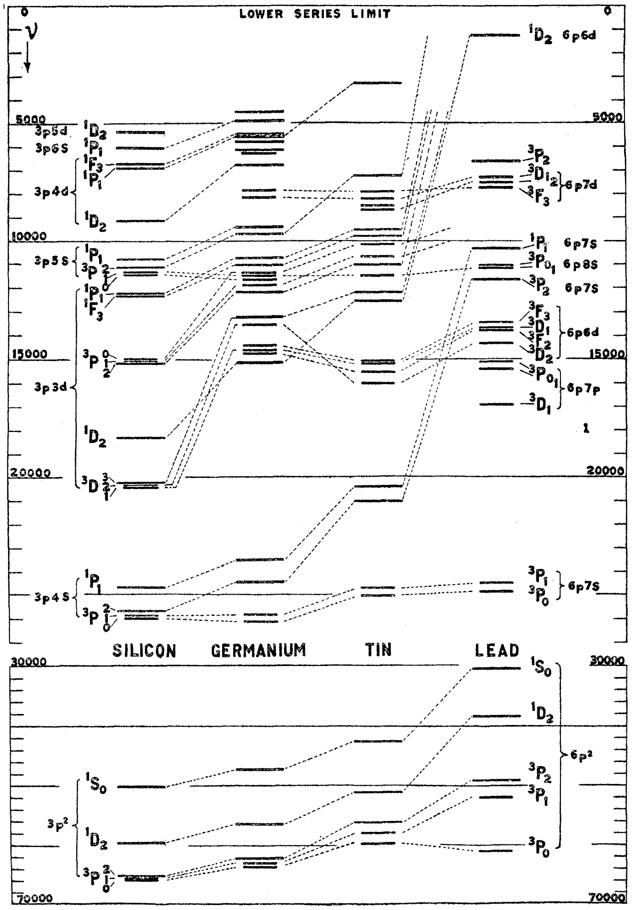

Fig. 1 Energy levels of the elements of the fourth group. The arc spectra.

A diagram of the energy levels of the arc spectra has been drawn (Fig. 1) for the elements of the fourth group. The data on silicon were obtained from Professor H. N. Russell,[10] that on germanium from the author's measurements, that on tin from Back[8] and Green and Loring[9], and the data on lead from Gieseler and Grotrian[11] and E. Back.[12] The four energy level diagrams have been combined in a larger diagram so that their lower series limits coincide at the top and they are set at $\nu=0$. The names of the elements separate the levels of the normal state from those of the excited states. The scale of frequencies above this division is 4 times as large as the scale below and 3000 wave-numbers have been omitted from the graph at the break in the scale. The configurations are indicated both on the left and the right of the diagram. The energy levels which approach the upper limit, according to the theory of Hund, are indicated by a line of slightly greater length than the lines representing the levels which approach the lower limit. The dotted lines connect similar terms in the four spectra.

The regularities of the spectra are brought out in this diagram. 1. The configurations and terms are those predicted by the recent theories and in general both are in the predicted order. 2. As the atomic number increases, the terms approaching the upper limit separate more and more from those approaching the lower limit, especially in the excited states. 3. The singlets always lie above the triplets of the same azimuthal quantum number in a given (in each) configuration, (one exception in germanium). 4. Some of the levels of the *pd* configuration invert as the atomic number increases. 5. The separations of the triplets of the p^2 and *ps* configurations are roughly proportional to the squares of the atomic number, especially the $^3P_0$ to $^3P_2$ separation for germanium and tin, as is shown in Table IV. The separations

TABLE IV. *Comparison of triplet separations.*

	Separations in Si	Ratio Ge/Si	Separations in Ge	Ratio Sn/Ge	Separations in Sn	Ratio Pb/Sn	Separations in Pb
Atomic number	14	2.29	32	1.56	50	1.64	82
Square of at. no.	196	5.22	1024	2.44	2500	2.69	6724
Term Difference							
$3p^2$ ($^3P_2'-{}^3P_0'$)	223	6.317	1410	2.43	3428	3.11	10648
$3p^2$ ($^3P_2'-{}^3P_1'$)	146	5.84	853	2.04	1736	1.63	2831
$3p4s$ ($^3P_2-{}^3P_0$)	272	6.13	1666	2.39	3988	3.32	13228
$3p4s$ ($^3P_2-{}^3P_1$)	195	7.26	1416	2.62	3714	3.47	12901
$3p3d$ ($^3P_0-{}^3P_2$)	111	6.59	732	1.11	816		
$3p3d$ ($^3P_1-{}^3P_2$)	67	6.93	465	.65	303		
$3p5s$ ($^3P_2-{}^3P_0$)	273	7.06	1931				
$3p5s$ ($^3P_2-{}^3P_1$)	218	8.09	1763	2.38	4196		

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[10] Professor H. N. Russell kindly furnished the author with his unpublished analysis of the silicon spectrum using data of Fowler[5] corrected.

[11] H. Gieseler and W. Grotrian, Zeits. f. Physik **34**, 374; (1925); **39**, 377 (1926).

[12] E. Back, Zeits. f. Physik **37**, 193 (1926).

are given in a column under the name of the element, and the ratios of the separations for adjoining elements are given in the columns marked ratios. In Table IV the ratios of the separations of the levels of the *pd* configuration for Ge and Sn do not even approximate the ratio of the squares of the atomic number. This may indicate an incorrect assignment of terms in one of these elements. A preliminary analysis of the first spark spectrum of Ge indicates that the separations of the doublet terms of Ge and of the first spark spectrum of Sn are almost exactly in the ratio of the squares of their atomic numbers.

A Schüler tube has been constructed and will be used to study the higher terms of the germanium arc and the entire first spark spectrum and possibly part of the second spark. Gratings will be used to photograph the spectra to 10000A.

Shortly after the results contained in this paper were presented before the meeting of the American Physical Society in December, 1926, a reprint of a paper by McLennan and McLay[13] containing their analysis of the germanium arc spectrum was received. Their analysis covered the lower 12 levels but the identifications are somewhat different from those given in this paper.

More recently a very short paper on the wave-lengths of the germanium arc was published by Richter[14] but only the frequency differences between the lowest 5 levels were given. They are almost identical with those given in this paper.

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Department of Physics,
Cornell University,
Ithaca, N. Y.
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Correction in proof. The $^3P_{012}$ terms of the *pd* configuration approach the upper series limit and should be represented by long lines in Fig. 1. The terms *pd* $^3P_0$ and *pd* $^3P_1$ should be placed in the upper half of Table III. The apparent anomaly in the ratio of the separations of the terms in Sn and Ge is also accounted for and the identifications are probably correct.

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[13] J. C. McLennan and A. B. McLay, Trans. of Royal Society of Canada **20,** Sec. 3, p. 355 (1926).

[14] Richter: Naturwissenschaften, p. 266 (March 18, 1927).