THE SPARK SPECTRA OF GERMANIUM

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Abstract

The first three spark spectra of germanium have been extended by the discovery of many new terms and combinations as follows: Ge II $s4p^2\ {}^2S$ and $p^3\ {}^2P$. Ge III $s4s\ {}^1S_0\ s5s\ {}^1S_0\ s4p\ {}^1P_1\ s5s\ {}^1P_1\ s4d\ {}^1D_2\ s4f\ {}^1F_3\ p4p\ {}^1D_2\ p4d\ {}^1P_1\ {}^1F_3\ {}^1D_2\ d4d\ {}^1D_2$ and possibly $s5g\ {}^3G\ {}^1G$. Ge IV $d^{10}\ 6p\ {}^2P\ d^{10}\ 5g\ {}^2G$, $d^9\ s^2\ {}^2D$.

THE first and second spark spectra of germanium were investigated for the first time by the writer[1] over a year ago and this work was followed by the work of Rao and Narayan.[2] The detailed agreement of the results of these two investigations is very gratifying and leads to a good measure of confidence in the term scheme there proposed. In these reports, however, not much more was attempted than an outline of the first two or three terms of each series from the normal configurations and in neither were the normal G terms recorded.

This report records the results of an attempt to extend these term schemes, especially for the singlet system of Ge III, but in the course of this work certain new terms were located also in Ge II and IV. These results are discussed separately for each stage of ionization throughout the body of the report. At the end of the report a complete list of all the classified lines of Ge II, III and IV is given.

The condensed spark between metallic germanium electrodes in vacuo and in an atmosphere of hydrogen with various amounts of inductance in series has been employed as a source and the spectra were resolved by means of a two-meter grating having 30000 lines per inch mounted in a vacuum spectrograph. In the case of the spark in hydrogen the spark chamber was separated from the main body of the spectrograph by means of a thin disk of fluorite which was cemented over the slit. The hydrogen was placed only in the spark chamber and usually at a pressure of one atmosphere. Ordinary commercial hydrogen was used and it was found that when the gas was placed in the spectrograph proper as well as in the spark chamber no radiation reached the photographic plate shorter than λ1600A or so on account of the absorption of the gas in the light path of 4 meters length.

For photographs of the vacuum spark between germanium electrodes in the region between λ5000A and λ2450A the writer is indebted to Professor Stanley Smith of this laboratory. Plates were taken on a two meter grating in a Rowland mounting and also on a Hilger E 178 one meter interchangeable prism spectrograph.

[1] Lang, Proc. Nat. Acad. Sci. **14**, 32 (1928).
[2] Rao and Narayan, Proc. Roy. Soc. **A119**, 607 (1928).

In the tables which follow, the wave-lengths are given in I.A. (air) above λ2000A and I.A. (vacuum) below that value while all the wave-numbers have been reduced to values in vacuum. The wave-lengths of about ten lines in the Schumann region are taken from data by Carroll.[3]

The notation used throughout this report is in accordance with the recent recommendations of the committee on notation[4] in so far as these have been understood by the writer.

THE FIRST SPARK SPECTRUM, Ge II

No extensive investigation of this spectrum has been attempted here chiefly because the available sources are not well adapted to the excitation of the first spark spectrum beyond a few low-lying terms. It appears, however, that a doublet P and a doublet S term from the $4s4p^2$ configuration have been located. The doublet D term had already been located.

TABLE I. *Predicted and empirical terms in Ge II.*

Configuration	Predicted Terms	Empirical Terms and Term Values	
	^4P		
$s4p^2$	^2D	$^2D_{1\frac{1}{2}}$	63623
		$^2D_{2\frac{1}{2}}$	63454
	^2S	$^2S_{\frac{1}{2}}$	42240
	^2P	$^2P_{\frac{1}{2}}$	37625
		$^2P_{1\frac{1}{2}}$	36518

In Table I all the terms expected from this configuration are given together with all the empirical terms which have been found. The term values are taken relative to an assumed value of $s^24f\,^2F=28320$ cm^{-1}. This value was chosen by Rao and Narayan[2] and seems to be of about the proper value. The ^2D and ^2P terms were given in the previous report of the writer,[1] with slightly different absolute values, but are repeated here for completeness

TABLE II. *New combinations in Ge II.*

$s4p^2$			$s^24p\ ^2P_{\frac{1}{2}}$ 128635		1764	$s^24p\ ^2P_{1\frac{1}{2}}$ 126871	
$^2S_{\frac{1}{2}}$	42241		86397 3	(3)		84627 −3	(3)
$^2P_{\frac{1}{2}}$	37625		91012 2	(7)		89249 3	(5)
		1107					
$^2P_{1\frac{1}{2}}$	36518		92119 2	(7)		90355 2	(8)

and also to point out that but one of the suggested P terms given by Rao and Narayan was correct. The separation of their two suggested P terms was much too great.

[3] Carroll, Trans. Roy. Soc. **A225**, 357 (1926).

[4] Russell, Shenstone and Turner, Phys. Rev. **33**, 900 (1929)

In Table II the combinations of these $s4p^2$ terms with the s^24p^2P terms are given. In this table the levels are designated at the heads of the columns and at the left side for the rows; in the body of the tables are the wave-numbers of the observed lines followed in parentheses by their intensities. Below each wave-number is the discrepancy between the observed wave-number and the wave-number calculated from the values assigned to the levels.

Ge III

Some of the important states and terms expected on the Hund theory in the spectrum of doubly-ionized germanium are given below.

Configuration	Terms		Configuration	Terms
$s4s$	^1S		$s5s$	^3S ^1S
$s4p$	^3P	^1P	$p4p$	^3P $^1S\,D$
$s4d$	^3D	^1D	$p4d$	$^3P\,D\,F$; $^1P\,D\,F$
$s4f$	^3F	^1F	$p4f$	$^3D\,F\,G$; $^1D\,F\,G$
$s5g$	^3G	^1G		

The empirical terms and term values of Ge III which have been located are given in Table III. These term values depend upon an arbitrary choice of 65500 cm^{-1} for the value of the $^3F_4$ term. There are successive members

TABLE III. *Empirical terms and term values of Ge III.*

Odd Terms: Terms	Odd Terms: Term Values	Even Terms: Terms	Even Terms: Term Values
$s4p\ ^3P_0$	214303	$s4s\ ^1S_0$	276036
$s4p\ ^3P_1$	213540	$s4d\ ^1D_2$	131064
$s4p\ ^3P_2$	211898	$p4p\ ^3P_0$	128345
$s4p\ ^1P_1$	184163	$p4p\ ^3P_1$	127392
$s5p\ ^3P_0$	94165	$p4p\ ^1D_2$	127260
$s5p\ ^3P_1$	93997	$p4p\ ^3P_2$	125663
$s5p\ ^3P_2$	93538	$s5s\ ^3S_1$	117459.8
$s5p\ ^1P_1$	91727.2	$s4d\ ^3D_1$	113185.0
$p4d\ ^1D_2$	78914	$s4d\ ^3D_2$	113114.2
$s4f\ ^3F_2$	65580.7	$s4d\ ^3D_3$	113007.7
$s4f\ ^3F_3$	65563.3	$s5s\ ^1S_0$	108586
$s4f\ ^1F_3$	65505.	$s6s\ ^3S_1$	64887
$s4f\ ^3F_4$	65500	$s5d\ ^3D_1$	62902.8
$p4d\ ^1P_1$	63677	$s5d\ ^3D_2$	62872.2
$p4d\ ^1F_3$	62457	$s5d\ ^3D_3$	62828.0
		$s5g\ ^1G_4$	41126.?
		$s5g\ ^3G$	41108
		$d4d\ ^1D_2$	40128

of series which may be used to calculate limits but in all cases these combinations fall rather far in the extreme ultra-violet and since there are but two members in any case the results of such calculations may be looked upon merely as a rough guide in making the choice for the basic term value. The comparison of term values for the isoelectronic sequence given in Table IV shows clearly that this choice has been made with reasonable accuracy. In this table the term values for Ga II have been taken from unpublished work by Dr. R. A. Sawyer and the writer and those for As IV and Se V from the results of Sawyer and Humphreys.[5] On the other hand Rao and Narayan

[5] Sawyer and Humphreys, Phys. Rev. **32**, 583 (1928).

based their term values upon an assumed value of 63000 cm^{-1} for $^3F_4$. This value is almost certainly too small by 2000 cm^{-1}. The estimate seems to have been made on the assumption that the $4F$ orbits are non-penetrating and that these term values can therefore be estimated on the basis of a Coulomb field; but while this is the case for lighter elements it does not seem to be justified for Ge III and still less for Pb III.

All of the term values given are measured from one origin; namely, the $3d^{10}4s^2S_1$ term of Ge IV, for while the $4p4p$, the $4p4d$ and the $4p4f$ terms all converge to the limit $3d^{10}4p^2P$ of Ge IV, no sequence of terms for any of these has been obtained to enable one to estimate the true term values as measured from the proper limits.

The ionization potential of Ge III as estimated by means of the 4^1S_0 term is 34.07 volts.

The comparison of term values made in Table IV will serve to show not only that the term values form a very uniform sequence for the various ions

TABLE IV. *Comparison of term values.*

	$N=$ $R/N^2=$	4 6858.56	5 4389.48	6 3048.25	7 2239.53
S_1	Zn		22094.4	10334.4	6020.5
	Ga/4		15629	8111	4991
	Ge/9		13051	7030	—
	As/16		12443	—	—
	Se/25		12094	—	—
P_2	Zn	43455.0	14519.4	7695.8	
	Ga/4	29177	11683	—	
	Ge/9	23544	10393	—	
	As/16	21232	—	—	
	Se/25	19793	—	—	
D_3	Zn	12997.6	7187.0	4553.3	
	Ga/4	12896	7069	4481	
	Ge/9	12556	6981	—	
	As/16	13018	—	—	
	Se/25	13268			
F_4	Zn	6931.3	4442.3		
	Ga/4	7031	4494		
	Ge/9	7278	—		

and thus constitute a proof of the essential correctness of the choice of the term values, which, in all cases but Zn I, rest upon an arbitrary basis, but also to show the increasing departure, not only of the D terms, but also the F terms from the value derived for a purely hydrogenic orbit. In this connection we may compare the results with those for the sequence of ions beginning with Rb I[6]. Here it was found that in the Moseley diagram the line for the $4D$ terms was no longer parallel to the line for the $4F$ terms but diverged in such a way that it crossed both the $5P$ and $5S$ lines before the second stage of ionization had been reached. Here we can see that exactly the same thing is happening. In Zn I the $4D$ terms are smaller than either

[6] Bowen and Millikan, Phys. Rev. **28**, 923 (1926).

TABLE V. *Combinations and intensities in the spectrum of Ge III.*

Even Terms \ Odd Terms		$s4p\,^3P_0$	$s4p\,^3P_1$	$s4p\,^3P_2$	$s4p\,^1P_1$	$s5p\,^3P_0$	$s5p\,^3P_1$	$s5p\,^3P_2$	$s5p\,^1P_1$	$p4d\,^1D_2$	$s4f\,^3F_2$	$s4f\,^3F_3$	$s4f\,^1F_3$	$s4f\,^3F_4$	$p4d\,^1P_1$	$p4d\,^1F_3$
		214303	213540	211898	184163	94165	93997	93538	91727.2	78914	65580.7	65563.3	65505	65500	63677	62457
$s4s\,^1S_0$	276036	0 −2	9 0		40 0				2 −113							
$s4d\,^1D_2$	131064		8 0	20* 3	6 0					00 −4	2 −2		10 0			
$p4p\,^3P_0$	128345		10 0						3? −3							
$p4p\,^3P_1$	127392	12 4	8 0	15 0						3 0					0 −1	
$p4p\,^1D_2$	127265		8 −5	3 −6							0 −1.3	0 −1.7		00 1	0 9	1 −5
$p4p\,^3P_2$	125663		10 2	8 0	00 −5					1 −5					1 −1	
$s5s\,^3S_1$	117459.8	8 −2.2	12 −0.2	12 −2.2	0 −1	150 −0.6	200 −0.1	200 −2.2	15 2.4							
$s4d\,^3D_1$	113185.0	12 −2.0	10 4.0	2 −2.0		3 −1.6	3 −0.2	0 2.2	4 −0.2		15 −1.6				2 0	
$s4d\,^3D_2$	113114.2		15 3.2	10 0.2			5 0.3	10 −0.2	10 −0.3	3 2.9	2 −0.6	15 −0.8	15 −6.5		4 −2.9	1 1
$s4d\,^3D_3$	113007.7			15 1.7				18 0.3				1 −1.1	25 0.5	25 −2.5		2 −1
$s5s\,^1S_0$	108586		2 4		4 −4					5 −2.1						
$s6s\,^3S_1$	64887	0 −2	1 −12	2 −13		20 2.5	40 1.6	40 2.3	2 1.4							
$s5d\,^3D_1$	62902.8	1 −4.2				25 2.6	25 1.5	3 0.9	1 0.8							
$s5d\,^3D_2$	62872.2		2 −12.8	00 −5.8			35 0.8	20 1.2	8 0.2							
$s5d\,^3D_3$	62828.0			3 −13				40 2.5								
$s5g\,^1G_4$	41126?									0 −2			50 0			6 3.7
$s5g\,^3G$	41108?										30 −1.8	35 −1.8		40 3.2		0 −0.2
$d4d\,^1D_2$	40128								0 −2.2		0 −0.7	2 −0.2			12 −0.8	

* Classified also as Ge II.

5*P* or 5*S* but before Ga II is reached 4*D* has exceeded 5*P* and has practically reached 5*S* at Ge III and exceeds it in As IV and Se V. This may be taken as evidence of the increasing penetration of the 5*D* orbits. The steady *increase* rather than decrease of the comparative term values for the *F* terms is found here exactly as it was in the Rb sequence.

In Table V the combinations in the spectrum of Ge III are given. The levels are designated at the heads of the columns and rows together with the term values referred to an arbitrary value $s4f\,^3F_4=65500$. In the body of the table the intensities of the observed combinations are given and below each intensity the discrepancy (observed value minus calculated value) between the observed wave-number and the wave-number calculated from the positions assigned to the levels.

Table V together with the table of classified lines at the end of the report exhibits fully all the data in connection with the spectrum of Ge III but since the singlet system and the resonance lines form such an important part of any spectrum and since only a few lines are involved it was thought wise to place these in a separate table (Table VI) for ease of reference in connection with the discussion which follows.

TABLE VI. *Singlet terms and combinations in Ge III.*

Combination	(I.A. vac)	I	ν	Term	Values
$s4s\ ^1S_0-s5p\ ^1P_1$	542.90	2	184195	$s4s\ ^1S_0$	276036
$s4p\ ^3P_1-s5sp\ ^1S_0$	952.76	2	104958	$s4p\ ^1P_1$	184163
$s4s\ ^1S_0-sp\ ^1P_1$	1088.46	20	91873	$s4d\ ^1D_2$	131064
$s4p\ ^1P_1-s5s\ ^1S_0$	1323.22	4	75573	$s5s\ ^1S_0$	108586
$s4d\ ^1D_2-s4f\ ^1F_3$	1525.38	10	65559	$s5p\ ^1P_1$	91728
$s4s\ ^1S_0-s\,p\ ^3P_1$	1600.09	9	62496	$s4f\ ^1F_3$	65505
$s4p\ ^1P_1-s4d\ ^1D_2$	1883.26	6	53099		

It is necessary of course to assume the identification of several of the singlet lines in order to make a start on the analysis of the singlet spectrum. However, since the leading triplet terms were already known and also since the singlet spectrum of Ga II has been analysed thus making the irregular doublet law data available (Table VII) it is now possible to choose these

TABLE VII. *Irregular doublet law.*

	$^1S_0-^1P_1$	Difference	$^1S_0-^3P_1$	Difference	$^1P_1-^1D_2$	Difference
Zn I	46745		32502		15713	
		23954		15316		21305
Ga II	70699		47818		37018	
		21174		14678		16081
Ge III	91873		62496		53099	

singlet lines with a fair amount of assurance. The last three lines in Table VI are prominent in the spark in hydrogen and are the only three unclassified Ge lines of any considerable intensity in this region. They occur also in the vacuum spark with about equal intensity. The resonance line seems to be almost certainly chosen correctly not only because the line itself has the proper characteristics but also because it fits so well into Table VII. The line at λ1733.8 suggested by Rao and Narayan does not appear on my plates at all and no other line appears which can possibly be used that would approximate to the requirements of Table VII. The line given in the writer's previous report also was much too long in wave-length. The choice for the singlet line D–F leads to a term value for ^1F which differs from $^3F_4$ by but 5 units of wave-number. In Ga II these terms are separated by 8 units and in Zn I they have probably not been separated. We must thus conclude that in Ge III the intercombination lines D–F are blended with two lines of the triplet spectrum $^3D_3$–$^3F_4$ and $^3D_1$–$^3F_2$ as they are in Ga II and probably in Zn I also. This blending of these lines is indicated in Table V by entering the intensities of the lines in both spaces and in the table of classified wave-lengths by writing both classifications opposite the blended line. It may be stated in connection with these and other lines in the germanium spectrum which are supposed to be blends of two or more lines, that a new vacuum spectrograph capable of accommodating a grating of three meters radius has been completed and it is hoped shortly to attempt to resolve many of such lines in the Schumann region.

The intercombination lines between triplet and singlet terms are but few in number and some of these are weak. This weakness of intercombination lines is characteristic of lighter elements. In Al II but four such lines were found[7] including the resonance line and no singlet P or triplet S terms were involved. Thus in Ge III we actually have an increase in the number and intensity of these lines. In Pb III we find a further pronounced increase in the intensity of intercombination lines[8] over those in Ge III. This increasing intensity is associated with the increasingly wide triplet intervals in these spectra.

A peculiar feature of the spectrum of Ge III is the fact that the $s5p\,^1P_1$ term gives stronger intercombinations than $s4p\,^1P_1$. This may be partially accounted for by the fact that the combinations of $s4p\,^1P_1$ term with the second triplet D terms are very far in the ultra-violet but the absence of combinations with the first triplet D terms is quite abnormal.

In Table III possible values for the $s5g\,^3G$ and ^1G terms are given. Just in the region about λ4100A where the 4^3F–5^3G combination is expected there are four very intense lines which occur in two pairs with nearly equal separations. These four lines certainly belong together for changes of inductance alter all four in the same way. Besides the photographs taken in connection with this work those shown by Lunt[9] were available. On the plates used by the author all these lines have about the same characteristics as other strong Ge III lines in the neighborhood as for example the triplet $5S$–$5P$. These lines are all fairly broad and the measurement of them is not a highly accurate

[7] Sawyer and Paschen, Ann. d. Physik **84**, 1 (1927).
[8] Smith, Phys. Rev. **34**, 393 (1929).
[9] Lunt, Roy. Astro. Soc. **85**, 38 (1924).

one so it could not be decided absolutely whether the separations involved are those of the ^3F levels or not. Certainly they are approximately so if we use the three shortest lines for the ^3F–^3G combination assuming that ^3G is unresolved. This leaves the fourth line (λ4100A) to be accounted for and if the foregoing is true this can be no other than 4^1F–5^1G. This results in a value for ^1G slightly greater than ^3G. In support of the assignment there are two further combinations, the triplet and singlet G terms each combining with $p4d^1F_3$.

Rao and Narayan have given two terms suggested as two members of the $p4p^3P$ term but while the first of these agrees with the $^3P_1$ in the table the writer is of the opinion that the other is unreal since the pair of lines on which it was based turn out upon more accurate measurement not to have the correct separation. The singlet D term expected from this configuration is thought to have been found although it is higher in this case than in most similar spectra where it usually lies below the $s4d^3D$ terms. It may have been this singlet D term which was found in Sn III at 99650 cm^{-1} but this is hard to decide since both this and the normal singlet D terms may combine with the normal $4s4p$ and $4s4f$ terms only.

The terms of the $p4d$ configuration may combine with those from $s4s$, $s4d$, $p4p$, $p4f$ whenever the inner quantum numbers permit. The three singlet terms seem clearly to be the P, D and F terms expected from this configuration. The D term is expected to lie somewhat lower than the P term. The combinations of this D term are comparatively intense and plentiful. The variations in the wave-numbers with respect to the calculated values are irregular and somewhat large, a feature which seems to be characteristic of all these terms from higher states. The question of the reality of the term given as $^1G_4$ is not clarified at all by these data since the only combination expected, if it really is a G term, is masked by a very strong arc line and one combination may be present (with $p4d\ ^1D_2$) which would be forbidden in such a case. Some traces of the triplet P term of this configuration have been found also but these were too fragmentary to place in the tables.

Some other terms have been located which come from either the $d4d$ or $p4f$ configurations. Unfortunately the terms from these two configurations may combine with exactly the same terms out of all those which have been identified thus far so that one cannot distinguish between them by means of their combinations alone. But one of these terms will be given here; it is given tentatively as arising from the $4d4d$ state.

Evidence for Change of Coupling

If the ratio of the two intervals in the triplet P terms of C III,[10] Si III,[11] Ge III, Sn III[12] and Pb III[13] be compared as in Table VIII a progressive increase is clearly evident in these interval ratios for both the first and

[10] Bowen and Millikan, Phys. Rev. **26**, 316 (1925).
[11] Fowler, Trans. Roy. Soc. **A225**, 1 (1925).
[12] Green and Loring, Phys. Rev. **30**, 574 (1927).
[13] Smith, Nat. Acad. Sci. Proc. **14**, 878 (1928).

second P terms and the effect is much more marked in the second case. When the electronic spins of all the electrons involved in the production of the spectrum (in this case two) combine to form a resultant magnetic moment s and the moments of each electron in its orbit taken separately are combined to form a resultant moment l and when these two resultants combine to give a total resultant j we have the familiar Russell-Saunders coupling which leads to the interval rule of Landé. For triplet P terms we therefore expect the intervals to have a ratio of 2:1. An increase in this ratio is taken to indicate a change from the Russell-Saunders coupling toward the (jj) coupling in which the electronic spin of each electron forms a resultant moment with the magnetic moment of its orbital motion and the resultants for each electron combine to give the final moment of the system.[14] The

TABLE VIII. *Progressive change in triplet interval ratios.*

	First P terms	Second P terms
C III	Unresolved	2.34
Si III	1.85	2.22
Ge III	2.15	2.72
Sn III	2.45	4.43
Pb III	3.66	30.12

failure of the Landé interval rule is far more pronounced for the second P terms than for the first P terms. This can only mean that the (jj) coupling tends to predominate for a $4s$ and $5p$ electron over a $4s$ and $4p$ electron. Thus when the total quantum numbers are the same for the two electrons the failure of the Russell-Saunders coupling is not so pronounced as when these numbers are different. This is borne out also by the fact that for the P terms of the $p4p$ state in Ge III the interval ratio is 1.81. One finds the same result in the arc spectra[15] of the elements mentioned at the beginning of this paragraph. Here the failure of the Landé interval is very marked for the $p5s\,^3P$ terms but not nearly so complete for the $3p^2\,^3P$ terms. It would seem that the explanation for this increasing departure from the Russell-Saunders coupling is simply that the influence of the rest of the electrons on the more loosely bound radiating electron is lessened when the latter is in the higher states. It then tends to act more as an independent unit and less in association with neighboring electrons.

Ge IV

The third spark spectrum of germanium arises from the stripped atom and is therefore the simplest of the three, the normal spectrum comprising an ordinary doublet system. This normal doublet spectrum has been studied by Carroll[3] Rào and Narayan[2] Smith[16] and the writer[17] and the lowest two or three terms of each configuration are well known.

[14] Goudsmit and Humphreys, Phys. Rev. **31**, 960 (1928).
[15] Gartlein, Phys. Rev. **31**, 782 (1928).
[16] Smith, Nature, Nov. 19 (1927).
[17] Lang, Phys. Rev. **30**, 762 (1927).

In Table IX all the known term values of Ge IV are given and in Table X the observed intensities of all lines assigned to this spectrum; below each intensity the discrepancy is also given. All of the term values rest upon an arbitrary choice of 111200 cm^{-1} made by Carroll for $d^{10}4f\,^2F_{3\frac{1}{2}}$. The comparison

TABLE IX. *Empirical terms and term values of Ge IV.*

Odd Terms Configuration	Term	Value	Even Terms Configuration	Term	Value
$d^{10}\,4p$	$^2P_{\frac{1}{2}}$	287386	$d^{10}\,4s$	$^2S_{\frac{1}{2}}$	368701
$d^{10}\,4p$	$^2P_{1\frac{1}{2}}$	284598	$d^{10}\,4d$	$^2D_{1\frac{1}{2}}$	178094
$d^{10}\,5p$	$^2P_{\frac{1}{2}}$	142242	$d^{10}\,4d$	$^2D_{2\frac{1}{2}}$	177840
$d^{10}\,5p$	$^2P_{1\frac{1}{2}}$	141304	$d^{10}\,5s$	$^2S_{\frac{1}{2}}$	169432
$d^{10}\,6p$	$^2F_{2\frac{1}{2}}$	111205	$d^9\,s^2$	$^2D_{1\frac{1}{2}}$	108759
$d^{10}\,4f$	$^2F_{3\frac{1}{2}}$	111200	$d^9\,s^2$	$^2D_{2\frac{1}{2}}$	104256
$d^{10}\,6p$	$^2P_{\frac{1}{2}}$	85080	$d^{10}\,5d$	$^2D_{1\frac{1}{2}}$	102064
$d^{10}\,6p$	$^2P_{1\frac{1}{2}}$	84938	$d^{10}\,5d$	$^2D_{2\frac{1}{2}}$	101984
			$d^{10}\,6s$	$^2S_{\frac{1}{2}}$	98643
			$d^{10}\,5g$	^2G	70322

TABLE XI. *Comparison of term values.*

	$N=$ $R/N^2=$	4 6858.56	5 4389.48	6 3048.25
S	Cu	62308.0	19171.1	9459.5
	Zn/4	36222.56	14113.60	7848.47
	Ga/9	27533	11796	6694
	Ge/16	23044	10589	6165
P	Cu	315244	12925.0	—
	Zn/4	23884.13	10820.08	6232.88
	Ga/9	20102	9612	—
	Ge/16	17787	8832	5308
D	Cu	12365.9	6917.1	4413.4
	Zn/4	11982.85	6724.55	4312.08
	Ga/9	11512	6507	
	Ge/16	11115	6374	
F	Cu	6881.6	4400.0	
	Zn/4	6907.01	4422.93	
	Ga/9	6930		
	Ge/16	6950		

of term values made in Table XI shows that this value is as nearly accurate as it can be hoped to make it at present and the results obtained by applying a Rydberg formula to the *P* or *D* terms confirm this conclusion.

The $d^9s^2\,^2D$ terms arise from a configuration characterised only by the absence of one *d* electron and we expect therefore to find them inverted as they have been found in Cu I.[18] The only normal terms with which they combine according to the combination rules are those from the $d^{10}\,np$ states. An exception occurs in the case of the combination $d^{10}5s\,^2S_{\frac{1}{2}}-d^9s^2\,^2D_{1\frac{1}{2}}$. This combination violates both rules but was found by Paschen[19] in Hg II who

[18] Shenstone, Phys. Rev. **28**, 449 (1926).
[19] Paschen, Sitzungsber Berl. Akad. Dec. (1928).

TABLE X. *Combinations and intensities in Ge IV.*

Odd Terms \ Even Terms		$d^{10}4s\ ^2S_{\frac{1}{2}}$	$d^{10}4d\ ^2D_{1\frac{1}{2}}$	$d^{10}4d\ ^2D_{2\frac{1}{2}}$	$d^{10}5s\ ^2S_{\frac{1}{2}}$	$d^9s^2\ ^2D_{2\frac{1}{2}}$	$d^9s^2\ ^2D_{1\frac{1}{2}}$	$d^{10}5d\ ^2D_{1\frac{1}{2}}$	$d^{10}5d\ ^2D_{2\frac{1}{2}}$	$d^{10}6s\ ^2S_{\frac{1}{2}}$	$d^{10}5g\ ^2G$
		368701	178094	177840	169432	108759	104256	102064	101984	98643	70325
$d^{10}4p\ ^2P_{\frac{1}{2}}$	287386	20 −2	8 −3		3 −2					1 443	
$d^{10}4p\ ^2P_{1\frac{1}{2}}$	284598	20 1	4 3	8 −1	3 1					1 423	
$d^{10}5p\ ^2P_{\frac{1}{2}}$	142242	1 −189	30 −1.4		50 1		5 −1.6	30 −1.3		2 −1.5	
$d^{10}5p\ ^2P_{1\frac{1}{2}}$	141304	1 −185	15 −1.5	30 1.7	60 −0.2	5 −0.6	3 4.4	2 0.2	20 0.5	2 −0.6	
$d^{10}4f\ ^2F_{2\frac{1}{2}}$	111205		2 6	6 5							15 1.0
$d^{10}4f\ ^2F_{3\frac{1}{2}}$	111200		2 1	6 0							15 0.5
$d^{10}6p\ ^2P_{\frac{1}{2}}$	85080		3 −3	2 2	0 1						
$d^{10}6p\ ^2P_{1\frac{1}{2}}$	84938				15* 12						

* Classified also as Ge III.

TABLE XII. *Classified lines of Ge II, Ge III and Ge IV.*

Designation	Stage	I.A.	I	ν
$s4p^2\ ^2D_{1\frac{1}{2}}-s^24p^2P_{\frac{1}{2}}$	II	7147.0		13990.9
$s4p^2\ ^2D_{2\frac{1}{2}}-s^24p^2P_{1\frac{1}{2}}$	II	7050.1		14181.0
$s4p^2\ ^2D_{1\frac{1}{2}}-s^24p^2P_{1\frac{1}{2}}$	II	6967.5		14350.4
$s^25p^2P_{\frac{1}{2}}-s^25s^2S_{\frac{1}{2}}$	II	6484.32	6	15417.5
$s^25p^2P_{\frac{1}{2}}-s^25s^2S_{\frac{1}{2}}$	II	6336.31	4	15777.7
$5s^25s^2S_{\frac{1}{2}}-5s^25p^2P_{\frac{1}{2}}$ }	II	6021.14	8	16603.6
$s4p^2\ ^2S_{\frac{1}{2}}-4p^3\,^2P_{\frac{1}{2}\ 1\frac{1}{2}}$ }				
$5s^25s^2S_{\frac{1}{2}}-5s^25p^2P_{1\frac{1}{2}}$	II	5893.46	10	16963.2
$s4d^3D_1-s5p^3P_0$	III	5256.61	3	19018.4
$s4d^3D_2-s5p^3P_1$	III	5229.37	5	19117.5
$s4d^3D_1-s5p^3P_1$	III	5210.36	3	19187.8
$s^24d^2D_{2\frac{1}{2}}-s^24f^2F$	II	5178.58	10	19304.9
$s4d^3D_3-s5p^3P_2$	III	5134.75	18	19470.0
$s^24d^2D_{1\frac{1}{2}}-s^24f^2F$	II	5131.7	10	19481.3
$s4d^3D_2-s5p^3P_2$	III	5016.88	10	19576.0
$s4d^3D_1-s5p^3P_2$	III	5087.8	0	19649.4
$s^25p^2P_{\frac{1}{2}}-s^25d^2D_{1\frac{1}{2}}$	II	4824.20	10	20723.0
$s^25p^2P_{\frac{1}{2}}-s^25d^2D_{2\frac{1}{2}}$	II	4814.80	200	20763.5
$s^25p^2P_{\frac{1}{2}}-s^25d^2D_{1\frac{1}{2}}$	II	4742.00	50	21082.3
$s4d^3D_2-s5p^1P_1$	III	4674.36	10	21387.3
$s4d^3D_1-s5p^1P_1$	III	4659.04	4	21457.6
$s5s^3S_1-s5p^3P_0$	III	4291.71	150	23294.2
$s5s^3S_1-s5p^3P_1$	III	4260.85	200	23462.9
$p4d^1P_1-d4d^1D_2$	III	4245.41	12	23548.2
$s5s^3S_1-s5p^3P_2$	III	4178.96	200	23919.6
$s4f^3F_3-d4d^1D_2$	III	3930.47	2	25435.1
$s4f^3F_2-d4d^1D_2$	III	3927.64	0	25453.4
$s5s^3S_1-s5p^1P_1$	III	3884.78	15	25734.2
$s5p^1P_1-s6s^3S_1$	III	3724.51	2	26841.6
$d^{10}5s^2S_{\frac{1}{2}}-d^{10}5p^2P_{\frac{1}{2}}$	IV	3676.65	50	27191.0*
$d^{10}5s^2S_{\frac{1}{2}}-d^{10}5p^2P_{1\frac{1}{2}}$	IV	3554.19	60	28127.8*
$s5p^3P_2-s6s^3S_1$	III	3489.09	40	28653.3
$s5p^1P_1-s5d^3D_1$	III	3468.20	1	28825.2
$s5p^1P_1-s4d^3D_2$	III	3464.59	8	28855.2
$s5p^3P_1-s6s^3S_1$	III	3434.03	40	29111.6
$s5p^3P_0-s6s^3S_1$	III	3414.27	20	29280.5
$s5s^1S_0-p4d^1D_2$	III	3369.57	5	29668.9
$s5p^3P_2-s5d^3D_1$	III	3263.18	3	30636.1
$s5p^3P_2-s5d^3D_2$	III	3259.90	20	30667.0
$s5p^3P_2-s5d^3D_3$	III	3255.05	40	30712.5
$s5p^3P_1-s5d^3D_1$	III	3214.95	25	31095.7
$s5p^3P_1-s5d^3D_2$	III	3211.86	35	31125.6
$s5p^3P_0-s5d^3D_1$	III	3197.56	25	31264.8
$d^{10}5p^2P_{1\frac{1}{2}}-d^94s^2\,^2D_{2\frac{1}{2}}$	IV	3071.84	5	32544.4
$s4d^3D_2-p4d^1D_2$	III	2922.86	3	34203.1
$s4p^2\ ^2D_{2\frac{1}{2}}-s^24f^2F$	II	2845.47	30	35133.3
$s4p^2\,^2D_{1\frac{1}{2}}-s^24f^2F$	II	2831.77	20	35303.2
$d^{10}4d^2D_{1\frac{1}{2}}-d^{10}5p^2P_{\frac{1}{2}}$	IV	2788.61	30	35850.6*
$d^{10}4d^2D_{2\frac{1}{2}}-d^{10}5p^2P_{1\frac{1}{2}}$	IV	2736.09	30	36537.7*
$d^{10}4d^2D_{1\frac{1}{2}}-d^{10}5p^2P_{1\frac{1}{2}}$	IV	2717.44	15	36788.5*
$d^{10}5p^2P_{1\frac{1}{2}}-d^9s^2\,^2D_{1\frac{1}{2}}$	IV	2698.08	3	37052.4
$d^{10}5p^2P_{\frac{1}{2}}-d^9s^2\,^2D_{1\frac{1}{2}}$	IV	2631.78	5	37985.8
$d^{10}5p^2P_{1\frac{1}{2}}-d^{10}5d^2D_{1\frac{1}{2}}$	IV	2547.64	2	39240.2†
$d^{10}5p^2P_{1\frac{1}{2}}-d^{10}5d^2D_{2\frac{1}{2}}$	IV	2542.44	20	39320.5†
$d^{10}5p^2P_{\frac{1}{2}}-d^{10}5d^2D_{1\frac{1}{2}}$	IV	2488.25	30	40176.7†
$d^{10}4f^2F_{2\frac{1}{2}}-d^{10}5g^2G$	IV	2445.71	15	40875.5
$d^{10}4f^2F_{3\frac{1}{2}}-d^{10}5g^2G$	IV	2445.38	15	40881.0
$d^{10}5p^2P_{1\frac{1}{2}}-d^{10}6s^2S_{\frac{1}{2}}$	IV	2343.37	2	42660.4†
$d^{10}5p^2P_{\frac{1}{2}}-d^{10}6s^2S_{\frac{1}{2}}$	IV	2293.0	2	43597.5†
$p4p^3P_2-p4d^1D_2$	III	2138.65	1	46743.7
$s4d^3D_3-s4f^3F_3$	III	2107.11	1	47443.3

* Classified by Smith.
† Classified by Rao

TABLE XII. (*Continued*)

Designation	Stage	I.A.	I	ν
$s4d^3D_3-s4f^3F_4$ }	III	2104.45	25	47503.2
$s4d^3D_3-s4f^1F_3$ }				
$s4d^3D_2-s4f^3F_2$	III	2103.19	2	47532.9
$s4d^3D_2-s4f^3F_3$	III	2102.42	15	47549.1
$s4d^3D_1-s4f^3F_2$ }	III	2100.05	15	47602.7
$s4d^3D_2-s4f^1F_3$ }				
$p4p^3P_1-p4d^1D_2$	III	2062.14	3	48477.7
$s4d^3D_2-p4d^1P_1$	III	2022.25	4	49434.3
$s4d^3D_1-p4d^1P_1$	III	2019.22	2	49508.0
		I.A. vac		
$s4d^3D_3-p4d^1F_3$	III	1978.22	2	50550
$s4d^3D_2-p4d^1F_3$	III	1974.02	1	50658
$s5p^1P_1-d4d^1D_2$	III	1930.10	0	51597
$s4d^1D_2-p4d^1D_2$	III	1917.69	00	52146
$s4p^1P_1-s4d^1D_2$	III	1883.26	6	53099
$s4p^1P_1-p4p^3P_2$	III	1709.55	00	58495
$d^{10}5s^2S_{\frac{1}{2}}-d^9s^2\,{}^2D_{2\frac{1}{2}}$	IV	1648.14	3	60674
$s^24p^2P_{1\frac{1}{2}}-s^25s^2S_{\frac{1}{2}}$	II	1649.26	20	60633
$p4p^1D_2-s4f^3F_2$	III	1621.19	0	61683
$p4p^1D_2-s4f^3F_3$	III	1620.74	0	61700
$s4s^1S_0-s4p^3P_0$	III	1619.92	0	61731
$p4p^1D_2-s4f^3F_4$	III	1619.01	00	61766
$p4p^3P_2-p4d^1P_1$	III	1613.30	1	61985
$s^24p^2P_{\frac{1}{2}}-s^25s^2S_{\frac{1}{2}}$	II	1602.56	20	62400
$s4s^1S_0-s4p^3P_1$	III	1600.09	9	62496
$s^24p^2P_{1\frac{1}{2}}-s4p^2\,{}^2D_{1\frac{1}{2}}$	II	1581.16	3	63245
$s^24p^2P_{1\frac{1}{2}}-s4p^2\,{}^2D_{2\frac{1}{2}}$	II	1576.93	10	63414
$p4p^1D_2-p4d^1P_1$	III	1572.40	0	63597
$p4p^3P_1-p4d^1P_1$	III	1569.52	0	63714
$p4p^1D_2-p4d^1F_3$	III	1543.14	1	64803
$s^24p^2P_{\frac{1}{2}}-s4p^2\,{}^2D_{1\frac{1}{2}}$	II	1538.20	2	65011
$s4d^1D_2-s4f^3F_2$	III	1527.15	2	65481
$s4d^1D_2-s4f^1F_3$	III	1525.32	10	65560
$d^{10}4d^2D_{2\frac{1}{2}}-d^{10}4f^2F$	IV	1500.61	6	66640‡
$s4p^1P_1-s5s^3S_1$	III	1499.2	0	66702
$d^{10}4d^2D_{1\frac{1}{2}}-d^{10}4f^2F$	IV	1494.89	2	66895‡
$s4p^1P_1-s5s^1S_0$	III	1323.24	4	75573
$s^24p^2P_{1\frac{1}{2}}-s^24d^2D_{1\frac{1}{2}}$	II	1264.68	10	79071
$s^24p^2P_{1\frac{1}{2}}-s^24d^2D_{2\frac{1}{2}}$	II	1261.87	18	79247
$s^24p^2P_{\frac{1}{2}}-s^24d^2D_{1\frac{1}{2}}$	II }			
$s4p^3P_2-s4d^1D_2$	III }	1237.05	20	80837
$d^{10}4s^2S_{\frac{1}{2}}-d^{10}4p^2P_{\frac{1}{2}}$	IV	1229.81	20	81313‡
$s4p^3P_1-s4d^1D_2$	III	1212.47	8	82476
$d^{10}4s^2S_{\frac{1}{2}}-d^{10}4p^2P_{1\frac{1}{2}}$	IV	1188.99	20	84104‡
$d^{10}5s^2S_{\frac{1}{2}}-d^{10}6p^2P_{\frac{1}{2}}$	IV	1185.50	0	84353
$d^{10}5s^2S_{\frac{1}{2}}-d^{10}6p^2P_{1\frac{1}{2}}$	IV }	1183.34	15	84506
$s4p^3P_2-p4p^3P_1$	III }			
$s^24p^2P_{1\frac{1}{2}}-s4p^2\,{}^2S_{\frac{1}{2}}$	II }	1181.65	3	84627
$s4p^3P_2-p4p^1D_2$	III }			
$s4p^3P_1-p4p^3P_0$	III	1173.78	10	85195
$s4p^3P_1-p4p^3P_1$	III	1160.79	8	86148
$s4p^3P_2-p4p^3P_2$	III	1159.62	8	86235
$s4p^3P_1-p4p^1D_2$	III	1159.15	8	86270
$s^24p^2P_{\frac{1}{2}}-s4p^2\,{}^2S_{\frac{1}{2}}$	II	1157.44	3	86397
$s4p^3P_0-p4p^3P_1$	III	1150.55	12	86915
$s4p^3P_1-p4p^3P_2$	III	1137.92	10	87879
$s^24p^2P_{1\frac{1}{2}}-s4p^2\,{}^2P_{\frac{1}{2}}$	II	1120.45	5	89249
$s^24p^2P_{1\frac{1}{2}}-p4p^2\,{}^2P_{1\frac{1}{2}}$	II	1106.74	10	90355
$s^24p^2P_{\frac{1}{2}}-s4p^2\,{}^2P_{\frac{1}{2}}$	II	1098.76	7	91012
$s4s^1S_0-s4p^1P_1$	III	1088.45	40	91873
$s^24p^2P_{\frac{1}{2}}-s4p^2\,{}^2P_{1\frac{1}{2}}$	II	1085.55	7	92119

‡ Classified by Carroll.

TABLE XII. (*Continued*)

Designation	Stage	I.A.	I	ν
$d^{10}4d^2D_{2\frac{1}{2}}-d^{10}6p^2P_{\frac{1}{2}}$	IV	1078.02	2	92762
$s^24p^2P_{1\frac{1}{2}}-s^26s^2S_{\frac{1}{2}}$	II }	1075.14	3	93011
$d^{10}4d^2D_{1\frac{1}{2}}-d^{10}6p^2P_{\frac{1}{2}}$	IV }			
$d^{10}4d^2D_{1\frac{1}{2}}-d^{10}6p^2P_{1\frac{1}{2}}$	IV	1073.44	1	93158
$s4p^3P_2-s5s^3S_1$	III	1058.91	12	94436
$s^24p^2P_{\frac{1}{2}}-s^26s^2S_{\frac{1}{2}}$	II	1055.08	1	94780
$s4p^3P_1-s5s^3S_1$	III	1040.99	12	96080
$s4p^3P_0-s5s^3S_1$	III	1032.62	8	96841
$s^24p^2P_{1\frac{1}{2}}-s^25d^2D_{1\frac{1}{2}}$	II	1017.12	2	98317
$s^24p^2P_{1\frac{1}{2}}-s^25d^2D_{2\frac{1}{2}}$	II	1016.69	8	98358
$s4p^3P_2-s4d^3D_1$	III	1013.07	2	98710
$s4p^3P_2-s4d^3D_2$	III	1012.31	10	98784
$s4p^3P_2-s4d^3D_3$	III	1011.21	15	98892
$s^24p^2P_{\frac{1}{2}}-s^25d^2D_{1\frac{1}{2}}$	II	999.14	5	100086
$s4p^3P_1-s4d^3D_1$	III	996.50	10	100351
$s4p^3P_1-s4d^3D_2$	III	995.72	15	100429
$s4p^3P_0-s4d^3D_1$	III	988.96	12	101116
$s4p^3P_1-s5s^1S_0$	III	952.76	2	104958
$d^{10}4p^2P_{1\frac{1}{2}}-d^{10}4d^2D_{1\frac{1}{2}}$	IV	938.90	4	106507‡
$d^{10}4p^2P_{1\frac{1}{2}}-d^{10}4d^2D_{2\frac{1}{2}}$	IV	936.70	8	106757‡
$d^{10}4p^2P_{\frac{1}{2}}-d^{10}4d^2D_{1\frac{1}{2}}$	IV	915.00	8	109289‡
$d^{10}4p^2P_{1\frac{1}{2}}-d^{10}5s^2S_{\frac{1}{2}}$	IV	868.30	3	115167‡
$d^{10}4p^2P_{\frac{1}{2}}-d^{10}5s^2S_{\frac{1}{2}}$	IV	847.80	3	117952‡
$s4p^3P_2-s6s^3S_1$	III	680.28	2	146998
$s4p^3P_1-s6s^3S_1$	III	672.76	1	148641
$s4p^3P_2-s5d^3D_2$	III	671.05	00	149020
$s4p^3P_2-s5d^3D_3$	III	670.88	3	149058
$s4p^3P_0-s6s^3S_1$	III	669.28	0	149414
$s4p^3P_1-s5d^3D_2$	III	663.77	2	150655
$s4p^3P_0-s5d^3D_1$	III	660.52	1	151396
$s4s^1S_0-s5p^1P_1$	III	542.90	2	184195
$d^{10}4p^2P_{1\frac{1}{2}}-d6s^2S_{\frac{1}{2}}$	IV	536.54	1	186378
$d^{10}4pP_{\frac{1}{2}}-d6s^2S_{\frac{1}{2}}$	IV	528.58	1	189186
$d^{10}4s^2S_{\frac{1}{2}}-d^{10}5p^2P_{\frac{1}{2}}$	IV	441.95	1	226270*
$d^{10}4s^2S_{\frac{1}{2}}-d^{10}5p^2P_{1\frac{1}{2}}$	IV	440.11	1	227212*

ascribes it to the very weak field in the specially designed tube used by him as source. However, it is a fact that a line occurs in the spectrum of Zn II, Cd II and Ge IV very close to the position which this line would occupy if it occurs. It seems unlikely that these lines can all be accidental and if not one is forced to conclude that Paschen's explanation is not the correct one for these lines all occur in the vacuum spark source. Shenstone found also the forbidden lines $d^9s^2\,{}^2D - d^{10}4f\,{}^2F$ in Cu I but if these occur in Ge IV they lie far in the infra-red.

At the end of the report a table has been arranged of all the classified lines of Ge II, Ge III and Ge IV. In the table the wave-lengths of all lines above 2000A are given in I.A. in air and below that value in I.A. vacuum, while all wave-numbers are reduced to vacuum values. The classification of each line is shown in column one while the stage of ionization of the atom which radiates the line is shown in column two. Lines classified by other observers are indicated in the table.

The writer was greatly assisted in the location of the $d^9s^2\,{}^2D$ terms in Ge IV by Dr. O. Laporte who sent him the results of his calculations in regard to separations and term values more than a year ago. The calculations were very close to the values obtained by experiment and the writer is greatly indebted to Dr. Laporte for the use of these results of his analysis.

In conclusion the writer wishes to thank Professor Smith for the use of his plates on the germanium spectrum and to acknowledge a grant from the Research Council of Canada.