ON THE SPECTRA OF GALLIUM, GERMANIUM AND INDIUM

By R. J. Lang

Abstract

The vacuum-spark spectra of gallium germanium and indium have been photographed in the ultra-violet by means of a two-meter vacuum spectrograph using a grating of 30,000 lines per inch. The known series lines of Ga III and Ge IV have been remeasured and certain new ones discovered. Term values have been recalculated. The series spectra of Ga II, Ge III, and In II have been worked out for the multiplets 4^3P-5^3S, 4^3P-4^3D, $4^3P-4^3P'$ and 4^1S-4^1P.

THE vacuum spark spectra of gallium, germanium and indium have been photographed in the ultra-violet using a two-meter vacuum spectrograph and a grating of 30,000 lines per inch ruled by Professor Wood of Johns Hopkins, which has been previously described.[1] In the case of gallium the metal of high purity was fused into a small hole in the end of an aluminum rod which was then used as the lower electrode in the spark. The upper was made of aluminum alone. Comparison plates were taken with pure Al electrodes also. The aluminum used was supplied by the Aluminum Company of America. It was found to be of exceptional purity and the author's appreciation of the kindness of the Aluminum Company is herein expressed. In the case of germanium and indium a small piece of the pure metal was used to tip each of the electrodes.

The notation adopted in this paper is the one now most generally employed, except that to save complexity in printing, the multiplicities are omitted unless needed to make the meaning clear. Thus in Ga III and Ge IV (Tables I and II) all of the terms are double and no difficulty arises. In Ga II, Ge III and In II (Tables VI, VII, X) there are triplets and single terms. Here the single terms have the multiplicity marked thus: (4^1S-4^1P) while the triple terms are written without the multiplicity. To avoid any difficulty, however, both are included in Table VIII and IX.

Ga III

This spectrum was investigated by Carroll[2] who found most of the first members of the ordinary series. These have now been re-investigated and remeasured with greater accuracy, with the exception of the $4F-5G$ doublet, the values for which are quoted from Carroll's paper. The error of measurement is thought to be not greater than 0.03A in wave-length to about 1000A. Beyond this point the error is greater in some cases.

Table I gives the series lines and term values for Ga III. The second doublet of the principal series is new. Its identification rests upon the fact that an ordinary Rydberg formula applied to this pair and the pair at

[1] Lang and Smith, J.O.S.A. **12**, 523 (1926).

[2] Carroll, Phil. Trans. **A225**, 357 (1925).

1534A leads to a value for the $4S$ term which is approximately 246,000. The value of 247,790 recorded is chosen as probably more nearly correct as found by the values of $(\nu/R)^{1/2}$ for Cu I to Ge IV as shown in Table III. The doublet $4S-5P$ lies so far into the ultra-violet that the limit calculated by the Rydberg formula will be only approximate.

TABLE I

Series spectrum of Ga III.

Designation	λ(I. A. vac.)	Int.	γ	Δγ	Term values	
$4F_4-5G$	4383.09*		22815	6.2	$4S$	247790
$4F_3-5G$	4381.90*		22821		$5S$	107046
$4D_3-4F_4$	2424.47	6	41246	107	$4P_2$	180905
$4D_2-4F_3$	2418.21	5	41353		$4P_1$	182623
$4S-4P_1$	1534.51	10	65167	1718	$5P_2$	89792
$4S-4P_2$	1495.10	10	66885		$5P_1$	90315
$4P_2-5S$	1353.94	8	73858	1719	$4D_3$	103595
$4P_1-5S$	1323.15	6	75577		$4D_2$	103712
$4P_2-4D_2$	1295.45	2	77193	117		
$4P_2-4D_3$	1293.50	4	77310	1720	$4F_4$	62352
$4P_1-4D_2$	1267.21	3	78913		$4F_3$	62359
$4S-5P_1$	635.02	2	157475	523		
$4S-5P_2$	632.92	2	157998		$5G$	39538

* Wave-lengths as given by Carroll reduced to vacuum.

Taking then the values $4S$ to be 247,790 we arrive at the terms listed in Table I. Rao[3] has investigated part of the secondary spectrum of Ga III and gives the term values $5s=107{,}064$, $5p_1=87{,}046$, $5p_2=86{,}507$ and $6s=60{,}245$. These are based partly on Carroll's work, however, and cannot be considered as confirming the term values quoted in Table I. The $\Delta\nu$ value for the $5p$ terms does not check very well.

No trace of the satellite which should accompany one of the $4D$–$4F$ lines could be found. It will be very close to the main line, however, as shown by the group $4P$–$4D$.

NOTE ON INDIUM

Since the author's work on doubly-ionized indium was published[4] the $4F$–$5G$ line at 4071.4A has been resolved giving $\Delta\nu$ a value of 8.2. Since the value expected is 8.6 this may be taken as confirmation of Carroll's choice of these lines.

GE IV

This spectrum also was investigated by Carroll.[2] Table II contains the results of a remeasurement of the lines chosen by him.

[3] Rao, Phys. Soc. London Proc. **39**, 150 (1927).

[4] Lang, Proc. Nat. Acad. Sci. **13**, 341 (1927).

TABLE II

Series lines of Ge IV.

Designation	(I. A. vac.)	Int.	γ	$\Delta\gamma$	Term values	
$4D_3-4F$	1500.61	5	66640	255	$4S$	368684
$4D_2-4F$	1494.89	4	66895		$5S$	169439
$4S-4P_1$	1229.90	10	81307	2792	$4P$	284586
$4S-4P_2$	1189.07	10	84099		$4P$	287376
$4P_2-4D_2$	939.05	1	106491	253		
$4P_2-4D_3$	926.82	4	106744	2790	$4D$	177840
$4P_1-4D_2$	915.07	3	109281		$4D$	178095
$4P_2-5S$	868.44	2	115149	2786		
$4P_1-5S$	847.92	2	117935		$4F$	111200

COMPARISON OF TERM VALUES

The term values for similar configurations may be compared by plotting $(\nu/R)^{1/2}$ against atomic number for the same terms throughout the sequence Cu I, Zn II, Ga III, Ge IV. Table III gives the values of the $(\nu/R)^{1/2}$ and the differences. These differences are uniform and seem to confirm the values recorded in Tables I and II.

TABLE III

Values of $(\nu/R)^{1/2}$.

Term	Cu I	Diff.	Zn II	Diff.	Ga III	Diff.	Ge IV
$4S$	.7535	.3955	1.1490	.3531	1.5021	.3279	1.8300
$4P$	.5359	.3952	.9311	.3529	1.2840	.3263	1.6103
$4D$	.3357	.3252	.6609	.3107	.9716	.3014	1.2730
$4F$	.2504	.2513	.5017	.2521	.7538	.2512	1.0050
$5S$	.4180	.2992	.7172	.2705	.9877	.2523	1.2400
$5P$	.3432	.2848	.6280	.2749	.9029		

TABLE IV

Rydberg denominators and quantum defects.

	Ga III Term value	Ga III *R. D.*	Ga III q	Ge IV Term value	Ge IV *R. D.*	Ge IV q
$4S$	247790	1.9972	2.0228	368684	2.1858	1.8142
$5S$	107046	3.0374	1.9626	169439	3.2190	1.7810
$4P_1$	182623	2.3255	1.6745	287376	2.4718	1.5282
$4P_2$	180905	2.3365	1.6635	284586	2.4798	1.5202
$5P_1$	90319	3.3069	1.6931			
$5P_2$	89792	3.3226	1.6774			
$4D_2$	103712	3.0858	.9142	178095	3.1399	.8601
$4D_3$	103595	3.0877	.9123	177840	3.1422	.8578
$4F_3$	62359	3.9795	.0205	111200	3.9801	.0199
$4F_4$	62352	3.9800	.0200			
$5G$	39538	4.9979	.0021			

Table IV gives the term values, the Rydberg denominators (*R.D.*) and the quantum defects (q) for the various terms for Ga III and Ge IV. The term values seem to be very nearly correct on this scheme. The quantum defect becomes very small for the $4F$ terms and practically vanishes for $5G$.

Ga II and Ge III

The series spectra of Ga II and Ge III would be expected to follow those of Al II and Si III and the principal separations would have about the following values: in Ga II, $P_0P_1=950$, $P_1P_2=460$ and in Ge III, $P_0P_1=1675$, $P_1P_2=675$. Upon examining these spectra for triplets involving common separations of about these values it was found that the intervals 935 and 447 in Ga and 1640 and 763 in Ge were involved in several groups. Rao[3] also has chosen the triplet at 1800A as the first sharp triplet of Ga II in which these separations occur.

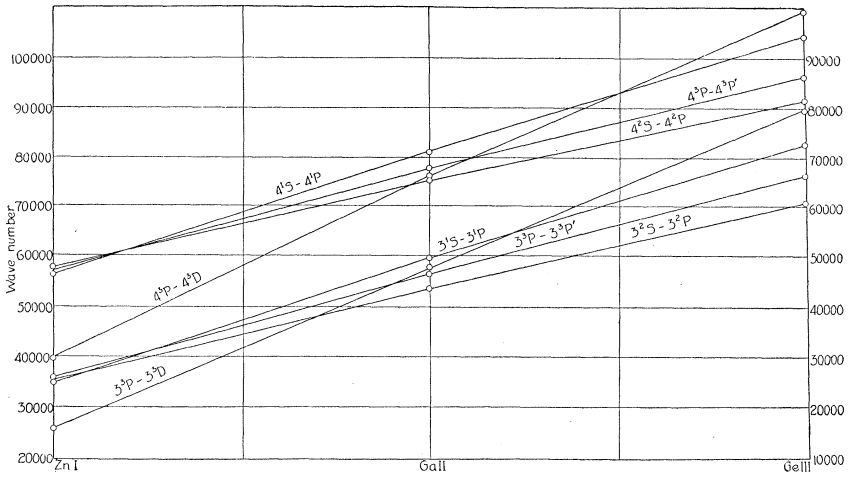

Fig. 1. Curves showing position of typical groups in Mg I—Si III and Zn I—Ge III.

Perhaps the most conspicuous, though usually not the most intense, group involving these main P intervals from a two-electron system is the PP' group. This group would be expected about 1500A in Ga II and near 1000A in Ge III. When found, these groups taken with the group found by Sawyer and Beese[5] for Zn I should obey the doublet laws. The multiplet in Ga at 1483A and that in Ge at 1160A involve the P separations chosen and obey the doublet law for position.

If one plots curves, as in Fig. 1, for these PP' groups of Mg I, Al II, Si III and also for the single lines 3^1S–3^1P as well as the doublets of the once more ionized atoms (stripped atoms) the curves so obtained are nearly straight and diverge slightly from each other fanlike as we proceed to higher atomic weight. The curve for the single lines crosses the other two between Mg I and Al II. Having plotted the PP' groups chosen for Zn I, Ga II and Ge III and also the stripped doublets, the location of the single lines

was fairly evident, since that for Zn I is already known. Very strong lines in Ga and Ge were located which satisfy the conditions for 4^1S–4^1P very well. The curves have almost exactly the same relative positions as in the Mg I–Si III sequence. In order to save space both sets of curves are placed in the same drawing. The lower curves and scale reading on left refer to the sequence Mg I–Si III, the upper curves and scale reading on right refer to sequence Zn I–Ge III.

The next group sought was $4P$–$4D$. The curve for this group in Mg I–Si III is nearly straight but has much steeper slope than those for PP' etc., and crosses these curves at Al II. The group for Zn I is known and the location of that for Ga II must be near the PP' group and the same P separations must be involved. Thus the group recorded was located in Ga II. The doublet law gives the corresponding group in Ge III. The curve so obtained crosses the other two at Ga II.

A difficulty arises, however, on account of the fact that three groups of Ga fall very close to 1500A. These are, one line of the doublets of the stripped atom (λ1494.86) the PP' group and the $4P$-$4D$ triplet. One would expect from the curves that the center of the PP' group should fall about $\nu = 67{,}000$ and that the diffuse group should be longer in wave-length, as they have been recorded, but this leaves one member of PP' unlocated unless it is blended with the doublet line above. The group is so complex and the interval $\Delta\nu = 935$ is repeated so frequently that it has been thought

TABLE V

λ (I. A. vac.)	Int.	ν	λ (I. A. vac.)	Int.	ν	λ (I. A. vac.)	Int.	ν
1537.61	1	65036	1527.41	1	65470	1483.95	5	67386
1536.91	1	65065	1515.19	3	65999	1483.52	3	67410
1536.39	3	65088	1514.57	5	66025	1483.15	0	67424
1536.09	1	65100	1514.35	0	66035	1477.83	0	67667
1535.40	7	65130	1505.01	4	66446	1473.73	2	67853
1535.53	15	65167	1504.41	4	66472	1463.65	5	68322
1533.00	1	65232	1504.12	0	66484	1454.90	1	68733
1531.46	1	65297	1494.86	15	66885			

well to record all of the lines present in the group in Table V. Undoubtedly there are other ways in which the groups may be arranged but on the whole the arrangement recorded seems the best one. Table VI shows the groups together with the separations and term values for Ga II and Table VII those for Ge III. The multiplets in Ge III are less in doubt than those of Ga II merely because they are not superimposed in any case.

The resonance line recorded at 2199A may be in doubt. It has about the correct position as shown by the value of the $4S$ term obtained and appears strongly in the spark in hydrogen becoming quite faint in the vacuum spark. The 4^1S and 4^1P terms, of course, depend on the identification of this line. The corresponding line in Ga has not been located for certain. The line at λ2500.94 (7) 39985 is approximately in the correct position but has already been classified otherwise.

TABLE VI

Series spectrum of Ga II.

Designation	λ (I. A. vac.)	Int.	γ	$\Delta\gamma$	Term values	
$4P_2-5S$	1845.30	9	54192	935	$5S$	57760
$4P_1-5S$	1813.98	8	55127			
$4P_0-5S$	1799.42	3	55574	447*	$4P_2$	111950
					$4P_1$	112885
$4P_2-4D_1$	1536.91	1	65065		$4P_0$	113332
$4P_2-4D_2$	1536.39	3	65088	934		
$4P_2-4D_3$	1535.40	7	65130		$4D_3$	46820
$4P_1-4D_1$	1515.19	3	65999	936	$4D_2$	46862
$4P_1-4D_2$	1514.57	5	66025	447	$4D_1$	46885
$4P_0-4D_1$	1505.01	4	66446			
$4P_2-4P_1'$	1504.41	4	66472			
$4P_1-4P_0'$	1494.86	?	66885	938		
$4P_2-4P_2'$	1483.95	5	67386			
$4P_1-4P_1'$	1483.52	3	67410	936		
$4P_0-4P_1'$	1473.73	2	67853	443		
$4P_1-4P_2'$	1463.65	5	68322			
4^1S-4^1P	1414.44	20	70700			

* Chosen by Rao.

TABLE VII

Series spectrum of Ge III.

Designation	λ (I. A. vac.)	Int.	ν	$\Delta\nu$	Term values	
4^1S-4^3P	2199.63	20	45462		4^1S	258962
$4P_2-4P_1'$	1183.34	10	84506		$4P_2$	211860
$4P_1-4P_0'$	1173.78	9	85195	1642	$4P_1$	213500
$4P_1-4P_1'$	1160.79	8	86148		$4P_0$	214263
$4P_2-4P_2'$	1159.62	8	86235	767		
$4P_0-4P_1'$	1150.55	9	86915	1644	4^1P	167086
$4P_1-4P_2'$	1137.92	10	87879			
					$4D_3$	112987
4^1S-4^1P	1088.42	20	91876		$4D_2$	113094
					$4D_1$	113166
$4P_2-5S$	1059.03	10	94426	1640		
$4P_1-5S$	1040.95	9	96066		$5S$	117434
$4P_0-5S$	1032.75	7	96829	763		
					$6S$	64930
$4P_2-4D_1$	1013.23	1	98694			
$4P_2-4D_2$	1012.50	4	98765	1643		
$4P_2-4D_3$	1011.49	6	98873			
$4P_1-4D_1$	996.64	4	100337	1644		
$4P_1-4D_2$	995.93	5	100409	766		
$4P_0-4D_1$	989.09	4	101103			
$4P_2-6S$	680.59	2	146931	1642		
$4P_1-6S$	673.07	1	148573			
$4P_0-6S$	669.58	0	149347	774		

TERM VALUES IN GA II AND GE III

In Ge III two members of a series are found at 1059A and 680A, and, while both lie well in the extreme ultra-violet, they have been used to deter-

mine the $4P$ terms. The other terms for Ge III then follow from the $4P$ term in the usual way. In Ga II no second members have yet been identified and it became necessary to estimate one of its terms. It was decided to get an approximate value for $4P$ by the use of the relation $(\nu/R)^{1/2}$ from the corresponding terms of the sequence Zn I to Ge III.

Table VIII gives the values of the $(\nu/R)^{1/2}$ for the various terms of the sequence Zn I to Ge III with differences, and in Table IX are recorded the term values with Rydberg denominators (*R.D.*) and quantum defects (q). The quantities enclosed in brackets are merely estimates.

TABLE VIII

Values of $(\nu/R)^{1/2}$

Term	Zn I	Diff.	Ga II	Diff.	Ge III
4^1S	.8309	.3493	(1.1802)	.3560	1.5361
4^3P	.6178	.3922	1.0100	.3795	1.3895
4^1P	.5142	———	(.8653)	———	.8183
4^3D	.3440	.3092	.6532	.3615	1.0147
5^3S	.4487	.2768	.7255	.3100	1.0355
6^3S	.2342	———	———	———	.7692

TABLE IX

Rydberg denominators and quantum defects.

Term Notation	Ga II			Ge III		
	Term value	*R. D.*	q	Term value	*R. D.*	q
4^1S	(152850)	———	———	258962	1.9529	2.0471
4^3P_2	111950	1.9802	2.0198	211860	2.1590	1.8410
4^1P	(82165)	———	———	167086	2.4312	1.5688
4^3D_3	46820	3.0620	.9380	112987	2.9565	1.0445
5^3S	57760	2.7566	2.2434	117434	2.8971	2.1028
6^3S	———	———	———	64930	3.9000	2.1000

SINGLY-IONIZED INDIUM

By the method described in the preceding pages the corresponding groups of single-ionized indium have been located also. The curves for the sequence Cd I, In II, etc., are not shown but are perfectly symmetrical with those for the Zn I–Ge III sequence. The wave-lengths and wave-numbers of the lines for In II are given in Table X.

Rao[3] has already chosen the $5P$–$6S$ triplet from wave-lengths given by Carroll. The intensity of the most refrangible member seems to be abnormally low but there is no other choice on these plates and the fact that the $5P$–$5D$ and $5P$–$5P'$ groups are found seems to confirm the choice made.

Sawyer and Beese[5] state that "in many two-valency-system spectra the frequency of the first PP' group is nearly a mean between the frequency

[5] Sawyer and Beese, Nature **116**, 936 (1925).

TABLE X

Series spectrum of In II.

Designation	λ (I. A. vac.)	Int.	γ	$\Delta\gamma$
$5P_2-6S$	2079.38	12	48091	2479
$5P_1-6S$	1977.43	10	50570	
$5P_0-6S$	1936.21	5	51647	1077*
$5P_2-5D_1$	1777.51	1	56258	
$5P_2-5D_2$	1774.79	10	56345	2479
$5P_2-5D_3$	1748.77	15	57183	
$5P_1-5D_1$	1702.51	6	58737	2478
$5P_1-5D_2$	1700.01	7	58823	1075
$5P_0-5D_1$	1671.89	5	59812	
$5P_2-5P_1'$	1741.59	5	57419	
$5P_1-5P_0'$	1716.55	6	58256	
$5P_2-5P_2'$	1674.04	10	59736	2479
$5P_1-5P_1'$	1669.51	5	59898	2477
$5P_0-5P_1'$	1640.10	5	60972	1074
$5P_1-5P_2'$	1607.38	5	62213	
5^1S-5^1P	1586.37	15	63037	

* Chosen by Rao.

of the first line of the principal series of singlets in the spectrum and the first line of the principal series of doublets of the once-more-ionized atom."

How well this rule is obeyed will be seen at once from Table XI provided we use the long wave-length member of the doublet as was done by Kichlu and Saha[6] and not the shorter line as Sawyer and Beese have done for Zn and Cd.

TABLE XI

Rule of Sawyer and Beese.

Element	$^1S-{}^1$P 2 valency	$P-P'$ 2 valency	$^2S-{}^2P$ 1 valency
Ga	70700	67398	65167
Ge	91876	86196	81307
In	63037	59817	57185

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UNIVERSITY OF ALBERTA,
EDMONTON, CANADA.
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Note added November 21: While this paper was at press Green and Loring published a report on Sn II and III (Phy. Rev. **30,** 574, 1927). The above results for In II seem to check very well with Sn III by Moseley curves and the prediction of these authors that the P separations of In II will be approximately 2420 and 1050 is very closely fulfilled and two members of the group PP' were located by them.

[6] Kichlu and Saha, Phil. Mag. **4,** 199 (1927).