THE SPECTRUM OF GALLIUM II AND THE $(4s4p^2)$ CONFIGURATION IN GALLIUM I AND INDIUM I

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Abstract

The spectrum of gallium has been excited in a hollow cathode discharge in helium and photographed in the region from $\lambda 10{,}000-\lambda 200$. About 90 lines so excited have been classified in singlet and triplet series of Ga II. Peculiarities in the run of intensities in successive members of series have been found due to the excitation by helium which is sufficient to excite only terms greater than 12,000 ν-units in this spectrum. Absolute term values are calculated and the lowest term is $(4s^2)^1S=165458$ corresponding to an ionization potential for Ga II of 20.43 volts. Tables of classified lines and of term values are given. The lines arising from combinations of $(4p^2)^4P$ and $(4p^2)^2S$ with $(4s4p)^2P$ of Ga I have been identified and values of these terms are given. Preliminary work on the excitation of the indium spectrum in helium has enabled the location of $(4p^2)^4P$ in In I and its term values and combinations with $(4s4p)^2P$ are given.

THE first classifications in the spectra of singly-ionized gallium were published by Lang[1] who from vacuum spark data in the extreme ultraviolet identified the triplet groups $(4s4p)^3P-(4s5s)^3S$, $(4s4p)^3P-(4s4d)^3D$, and $(4s4p)^3P-(4p^2)^3P$ and the singlet resonance line $(4s^2)^1S-(4s4p)^1P$. Rao[2] independently chose the same $(4s4p)^3P-(4p5s)^3S$ triplet and identified the $(4p4d)^3D-(4p4f)^3F$ group in the violet. Lang later from unpublished data chose tentatively a $(4s4p)^3P-(4s6s)^3S$ group and a $(4s4d)^3D-(4s5f)^3F$ group but as is well known the vacuum spark is poorly adapted to the excitation of higher series members. The success of the hollow cathode discharge in helium in exciting the spectrum of Al II[3] suggested the attempt to excite the spectrum of gallium by a similar method.

The use of the hollow cathode source with gallium is somewhat more difficult than with aluminum. Gallium melts at 30°C and so cannot be used directly as cathode. Paschen[4] has found that in the case of metals of low melting point or which vaporize too rapidly, good results may be obtained by placing a small quantity of the metal in a carbon hollow cathode.

Carbon neither vaporizes nor sputters in this discharge and if it is sufficiently carefully purified only the spectrum of the metal in the carbon cylinder will be obtained. In the case of gallium this purification was found to be extremely important. Gallium has a very slight vapor pressure even at red

[1] Lang, Phys. Rev. **30,** 762 (1927).

[2] Rao, Phys. Soc. London Proc. **39,** 161 (1927).

[3] Paschen, Ann. d. Physik **71,** 537 (1923); Sawyer and Paschen, Ann. d. Physik **84,** 1 (1927).

[4] Paschen, Preuss, Akad. Wiss, Berl. Ber. **29,** 207 (1927); Sawyer, Naturwiss. **16,** 765 (1927).

heat and as long as traces of the oxygen or hydrogen compounds of carbon remained in the cathode their band systems were excited while the gallium spectrum was but weakly excited.

The system for the circulation and purification of helium was similar to that previously described.[3] The helium was kept in circulation by a two stage Kurth mercury vapor pump and purified by passing over hot copper oxide to remove hydrogen and over charcoal cooled in liquid air to remove other impurities. Many hours of operation of the tube were found necessary sufficiently to remove the carbon compounds and under the best conditions faint traces of the stronger bands and of the carbon lines in the extreme ultra-violet usually persisted. The gallium itself, obtained from Messrs. Adam Hilger, proved to be very pure and the only impurities in the spectra attributed to it were the strongest lines of the indium spectrum. The only other impurities found in the spectra were the strongest lines of mercury, introduced by the circulating pump, and of neon, in the helium, which is the only gaseous impurity not removed by the purification system.

The spectrum was photographed in the extreme ultra-violet with a vacuum spectrograph similar to the one previously described[5], in the ultra-violet with a Hilger E2 and a Hilger E1 quartz spectrograph and in the visible and near infra-red with a Hilger E1 glass spectrograph. The spectra thus photographed covered the region from λ10,000 $-\lambda$200 Angstrom units. In the vacuum region the known lines of helium, carbon, neon and mercury occurring in the discharge were used as standards, while in the quartz region and in the visible supplementary copper and iron arc lines were used as comparison spectra, and in the red, neon and argon comparison spectra were used. It is of interest to note that on some plates in the ultra-violet there were observed as many as eight members of the He I series 1^1S-m^1P beginning at λ584 and four members of the He II series 1^2S-m^2P beginning at λ304 were observed. λ584 is by far the strongest line excited and appears broad and strongly reversed up to the fifth order on the vacuum spectrograms, sometimes obscuring other predicted lines. The spectra were not exceedingly rich in lines but about 300 lines were tentatively attributed to gallium. Among these were all but a few of the faint ultra-violet lines of Ga I measured by Uhler and Tanch[6] as well as a few other new lines classified below in the Ga I spectrum and about 90 lines which have been classified in the Ga II spectrum. These 300 lines extended from λ8400 to λ830 and the analysis of the singlets would have been quite impossible without so extensive a spectral region.

Inspection of the vacuum spectrograph data at once revealed higher members of the 4^3P-m^3S and 4^3P-m^3D series.[7] Visual observations with a Gaertner constant deviation spectroscope had shown the two triplets 5^3P-5^3D and 5^3S-5^3P at $\lambda\lambda$5425–5338 and $\lambda\lambda$6456–6334 respectively and these observations formed a basis for readily completing the triplet analysis.

[5] Sawyer, J.O.S.A. **15**, 305 (1927).

[6] Uhler and Tanch, Astrophys. J. **55**, 291 (1922).

[7] For convenience configurations will not be given from here on in discussion of the normal singlets and triplets.

Three members of the ^3F term sequence, four of ^3D, two ^3P and four ^3S terms were found. Absolute values were assigned to the terms by the aid of Paschen's Rydberg Term Tables[8] in such a way as to make the deviations from true Rydberg type similar to those found in Al II. An inspection of these terms, in Table I, reveals one striking fact. No terms smaller than

TABLE I. *Gallium II terms. Values of term T and Rydberg denominator n^x.*

n^x, T	$m=4$	5	6	7	8
n^x	1.629	2.732	(3.754)	4.762	5.764
$^1S_0$	165458	58802	(31150)	19445	13265
n^x	2.173	3.136	(4.125)	5.120	
$^1P_1$	94758	44918	(25800)	16626	
n^x	2.757	(3.387)	4.125	5.055	
$^1D_2$	57739	(38270)	25764	17021	
n^x	3.963	4.943	(5.940)		
$^1F_3$	28115	17966	(12440)		
n^x		2.650	3.680	4.689	5.694
$^3S_1$		62515	32446	19965	13539
n_2^x	1.940	3.065	(4.095)	(5.110)	
$^3P_0$	118088	47031	(26200)	(16840)	
$\Delta_{0,1}$	446	89			
$^3P_1$	117642	46942			
$\Delta_{1,2}$	934	210			
$^3P_2$	116708	46732			
n_3^x	2.917	3.940	4.948	5.948	
$^3D_1$	51642	28304	17942	12397	
$\Delta_{1,2}$	25	12	8		
$^3D_2$	51617	28292	17934		
$\Delta_{2,3}$	34	17	9		
$^3D_3$	51583	28275	17925		
n^x	3.957	4.941	5.936		
^3F_i	28125	17975	12458		

$(4p^2)^3P_0 = 50757$
$(4p^2)^3P_1 = 50233$
$(4p^2)^3P_2 = 49321$

12,000 ν-units appear although in the case of Al II terms as high as $n=20$ and with ν-values as small as 1100 were excited. Furthermore inspection of the classified lines and intensities in Table II shows for the extreme ultra-violet triplets a marked minimum of intensity in the 4^3P-m^3S and 4^3P-m^3D series. Thus 4^3P-6^3S is much weaker than 4^3P-7^3S and 4^3P-5^3D slightly weaker than 4^3P-6^3D. That is, terms of value about 30,000 are less strongly excited than those a few thousand smaller or larger. A similar phenomenon was noticed in the hollow cathode spectra of Al II excited in helium where in many of the series a similar minimum occurred for values of the running term about 12,000 ν-units above the limit. These two facts may be immediately explained if we assume that the lowest level of Ga II is 12,000–15,000

[8] Paschen, J.O.S.A. **16**, 231 (1928).

TABLE II. *Wave-lengths of Ga II excited in hollow cathode discharge in helium.*

I	λ(air)	ν obs.	ν cal	Combination
2	7793.0	12828	821	4^1D-5^1P
7	7198.7	13887	886	5^1S-5^1P
0	7000.0	14282	286	$6^3S-5^3P_2$
3	6456.3	15484	484	$5^3S-5^3P_0$
5	6419.4	15573	573	$5^3S-5^3P_1$
10	6334.2	15783	783	$5^3S-5^3P_2$
0	5425.6	18426	428	$5^3P_2-5^3D_1$
1	5421.6	18440	440	$5^3P_2-5^3D_2$
3	5416.8	18456	457	$5^3P_2-5^3D_3$
0	5363.5	18639	638	$5^3P_1-5^3D_1$
2	5360.6	18649	650	$5^3P_1-5^3D_2$
1	5338.3	18727	727	$5^3P_0-5^3D_1$
3	5218.21	19158	154	5^1P-6^1D
10	4261.78	23458	458	$4^3D_3-4^3F_i$
6	4255.52	23492	492	$4^3D_2-4^3F_i$
1	4253.74	23502	502	$4^3D_2-4^1F_3$
5	4250.91	23517	517	$4^3D_1-4^3F_2$
9	3924.39	25474	473	5^1P-7^1S
4	3734.85	26768	767	$5^3P_2-7^3S$
2	3705.85	26977	977	$5^3P_1-7^3S$
1	3693.93	27064	066	$5^3P_0-7^3S$
2	3583.60	27897	897	5^1P-7^1D
0	3472.52	28789	789	$5^3P_2-6^3D_1$
1	3471.46	28798	798	$5^3P_2-6^3D_2$
5	3470.34	28807	807	$5^3P_2-6^3D_3$
2	3447.26	29000	000	$5^3P_1-6^3D_1$
3	3446.46	29007	008	$5^3P_1-6^3D_2$
2	3436.66	29089	089	$5^3P_0-6^3D_1$
0	3375.95	29613	614	$4^1D-4^3F_i$
4	3374.94	29622	624	4^1D-4^1F
1	3158.18	31655	653	5^1P-8^1S
2	3011.90	33192	193	$5^3P_2-8^3S$
1	2992.84	33403	403	$5^3P_1-8^3S$
0	2884.83	33493	492	$5^3P_0-8^3S$
5	2974.77	33606	608	$4^3D_3-5^3F_i$
3	2971.60	33642	642	$4^3D_2-5^3F_i$
1	2971.01	33649	651	$4^3D_2-5^1F_3$
3	2969.41	33667	667	$4^3D_1-5^3F_2$
2	2910.77	34345	335	$5^3P_2-7^3D_i$
(a)	2893.65	34548	545	$5^3P_1-7^3D_i$
0	2886.45	34634	634	$5^3P_0-7^3D_1$
15	2780.15	35958	956	4^1P-5^1S
20	2700.47	37020	019	4^1P-4^1D
4	2555.28	39123	125	$4^3D_3-6^3F_i$
3	2552.87	39160	159	$4^3D_2-6^3F_i$
2	2551.26	39184	184	$4^3D_1-6^3F_2$
3	2514.15	39764	764	$4^1D-5^3F_i$
5	2513.55	39773	773	4^1D-5^1F

(a) Coincides with mercury line

TABLE XII. (*Continued*)

I	λ (air)	ν obs.	ν cal	Combination
5	2438.88	40990	988	4^1D-7^1P
2	2377.53	42048	051	5^1S-7^1P
20	2091.34	47816	816	$4^1S-4^3P_1$
15	1845.30 (b)	54192	193	$4^3P_0-5^3S$
10	1813.98	55127	127	$4^3P_1-5^3S$
5	1799.42	55574	570	$4^3P_2-5^3S$
5	1695.85	58969	969	$4^3P_2-4^1D$
3	1669.83	59902	903	$4^3P_1-4^1D$
1	1536.91	65066	066	$4^3P_2-4^3D_1$
5	1536.37	65088	091	$4^3P_2-4^3D_2$
8	1535.40	65125	125	$4^3P_2-4^3D_3$
3	1515.19	65997	000	$4^3P_1-4^3D_1$
5	1514.57	66025	025	$4^3P_1-4^3D_2$
3	1505.01	66446	446	$4^3P_0-4^3D_1$
3	1504.41	66472	471	$4^3P_2-(4p^2)^3P_1$
3	1495.21	66885	885	$4^3P_1-(4p^2)^3P_0$
3	1483.95	67386	387	$4^3P_2-(4p^2)^3P_2$
3	1483.52	67410	409	$4^3P_1-(4p^2)^3P_1$
3	1473.73	67853	855	$4^3P_0-(4p^2)^3P_1$
2	1463.65	68322	321	$4^3P_1-(4p^2)^3P_2$
5	1449.49	68990	994	4^1P-6^1D
20	1414.44	70700	700	4^1S-4^1P
5	1327.81	75312	313	4^1P-7^1S
5	1286.38	77738	737	4^1P-7^1D
0	1227.13	81493	493	4^1P-8^1S
3	1186.81	84259	262	$4^3P_2-6^3S$
2	1173.78	85195	196	$4^3P_1-6^3S$
1	1167.62	85644	642	$4^3P_0-6^3S$
5	1130.81	88432	433 416 404	$4^3P_2-5^3D_i$
3	1119.25	89346	350 338	$3^3P_1-5^3D_i$
1	1113.87	89777	778	$4^3P_0-5^3D_1$
8	1033.69	96741	743	$4^3P_2-7^3S$
5	1023.80	97675	677	$4^3P_1-7^3S$
3	1019.10	98126	123	$4^3P_0-7^3S$
5	1012.38	98777	783 774 766	$4^3P_2-6^3D_i$
3	1002.95	99706	708 700	$4^3P_1-6^3D_i$
2	998.52	100148	146	$4^3P_0-6^3D_1$
2	969.19	103179	169	$4^3P_2-8^3S$
0	960.57	104105	103	$4^3P_1-8^3S$
2	958.67	104311	311	$4^3P_2-7^3D_i$
2	829.60	120540	540	4^1S-5^1P

(b) From here on λ vac.

ν-units deeper than in Al II. This would also be expected from the fact that the two spectra Zn I, which is isoelectronic with Ga II, and Mg I, isoelectronic with Al II, have values of the deepest term, ^1S, of 75767 and 61672 respectively, leading to the expectation that the analogous term of Ga II will be some 14,000 ν-units deeper than in Al II.

The analysis of the singlets showed this to be the case. The clue to the singlet analysis was provided by the intercombination $4^3P_{1,2}-4^1D$, $\lambda\lambda 1695-1669$. Starting from this and the resonance line 4^1S-4^1P, it was relatively a simple matter to find the only two strong lines having as the difference of their wave-number the thus determined value of $(4^1S-4^1P)-(4^3P_1-4^1D)=(4^1S-4^3P_1)-(4^1P-4^1D)$, $\lambda\lambda 2091$ and 2700, and the argument of the preceding paragraph as to the value of 4^1S fixed the assignment of these lines as $4^1S-4^3P_1$ and 4^1P-4^1D respectively. This led to a value of 4^1S of 165458, or 13598 ν-units deeper than in the case of Al II. The further analysis of the singlets was straightforward and unequivocal but rendered more difficult than in Al II by the above mentioned failure of terms smaller than 12,000 ν-units and by the weakness of terms about 30,000 ν-units. The intercombination lines are however somewhat more numerous than in Al II, as is to be expected with increased atomic number, and substantiate the analysis. Table I gives the values of four terms of the ^1S sequence, three ^1P, and three ^1D and two ^1F terms.

All of the triplet terms based on the Ga III term $(4s)^2S$ which were to be expected in this excitation—having ν greater than 12,000—have been found except 6^3P and 7^3P. The corresponding high ^3P terms in the analogous spectra of Al II and Mg I are also weak although in the isoelectronic spectrum Zn I they are well developed. In Ga II the approximate values of these terms can be calculated—$6^3P=26{,}200$, $7^3P=16{,}840$—and careful search has failed to reveal the expected lines although other terms in the spectrum of nearly the same magnitude are excited. Among the singlet terms four are missing—6^1S, 6^1P, 5^1D, and 6^1F. Of these 6^1S can be predicted to be about 31,150 and so falls at the minimum of excitation mentioned above. 6^1P should be about 25,800 and the reason for its failure is not clear. Likewise 5^1D should be about 38,270, although the wide deviation of the ^1D terms from a Rydberg formula makes exact prediction difficult, and should be excited. 6^1F is at about the lower limit of excitation and its combination with 4^1D and 6^1D would fall at about $\lambda 2200$ and $\lambda 7500$, both weak regions in our photographic spectra.

The lowest terms to be expected in Ga II based on higher terms of Ga III are $(4p^2)^3P$, ^1S, and ^1D which should be expected about 65,000 ν-units above $(4s4p)$ ^3P from the Ga III data;[9] $(4p5s)^3P$, ^1P and $(4p4d)^3P$, ^3D, ^3F, ^1P, ^1D, ^1F, all about 80,000 ν-units above $(4p^2)$. Of these only $(4p^2)$ could be excited in our discharge. $(4p^2)^3P$ was identified by Lang. $(4p^2)^1S$ and ^1D should be above ^3P and our failure to find them leads to the belief that they may lie near our minimum of excitation.

[9] Lang, Phys. Rev. **30**, 762 (1927).

Since no more than four terms were found in any series it was impossible to calculate series limits with great accuracy. However, it may be expected that terms of the various series will depart from Rydberg terms in a manner quite parallel to Al II and the term limits have been chosen with this in mind. The values so determined can hardly be in error by more than 100 units and probably by less than 50. All the series have quantum defects which behave very closely like the analogous Al II with the exception of the ^3F. The ^3F terms in Al II shows a very great deviation from expected value,—successive Rydberg denominators being 3.929, 4.882, 5.745, 6.400, 7.152. This effect was explained by Schrödinger[10] as due to resonance between the 7^3F orbits and the atom-core.

No such effect is found in Ga II. The only anomaly found in Ga II which appeared in Al II also is the very large deviation of ^1D terms from Rydbergian. The lowest term in Ga II, $^1S=165458$ corresponds to an ionization potential of 20.43 volts

($4p^2$) Configuration in Gallium I and Indium I

The spectrographic analysis supplied by Hilger gave a list of several unassigned lines found in the gallium arc. Six of these lines appeared also strongly in our discharge and must be due to Ga I since equally strong Ga II in the same region were not found in Hilger's analysis. Five of the lines obviously are the intercombination $(4s^24p)^2P-(4s4p^2)^4P$. These lines are:

I	λ	ν	Combinations
8	2691.29	37146	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{\frac{1}{2}}$
10	2665.05	37511	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{1\frac{1}{2}}$
10	2632.66	37972	$(4s^24p)^2P_{\frac{1}{2}}-(4s4p^2)^4P_{\frac{1}{2}}$
8	2624.82	38087	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{2\frac{1}{2}}$
5	2607.47	38339	$(4s^24p)^2P_{\frac{1}{2}}-(4s4p^2)^4P_{1\frac{1}{2}}$

The $(4s^2p)$ configuration should give also ^2P, ^2S, ^2D. The term $(4s4p^2)^4P$ is however metastable and its combination with $(4s^24p)^2P$ might be expected to be strong. $(4s^24p)^2P-(4s4p^2)^2P$ is weak in the Al discharge in helium and has not been found here but two lines were found which are apparently $(s^2p)^2P-(sp^2)^2S$. These are:

I	λ	ν	Combinations
6	2534.83	39439	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^2S_{\frac{1}{2}}$
5	2482.76	40265	$(4s^24p)^2P_{\frac{1}{2}}-(4s4p^2)^2S_{\frac{1}{2}}$

Taking $(4s^24p)^2P$ as 48380 and 47553 the values of $(4s4p^2)^4P$, ^2S are as follows: $^4P_{\frac{1}{2}}=10408$; $^4P_{1\frac{1}{2}}=10042$; $^4P_{2\frac{1}{2}}=9467$; $^2S_{\frac{1}{2}}=8115$.

An investigation of the spectrum of In II excited similarly in He is now underway and will be reported later. Inspection of the data on in-

[10] Schrödinger, Ann. d. Physik **77,** 43 (1925).

dium already obtained revealed the $(4s^24p)^2P-(4s4p^2)^4P$ of In I as a group of five strong lines also given by Fowler as unclassified arc lines from Exner and Haschek's data who however apparently observed the reversed components of two of these lines (λλ3051 and 2858) as separate lines. Two more of them (λλ2957 and 2937) they also observed as reversed, only the weakest member of the group being unreversed. This reversal in the arc is of course strong evidence for our assignment of these lines. The group is

I	λ	ν	Combination
8	3051.25	32763	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{\frac{1}{2}}$
10	2957.01	33808	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{1\frac{1}{2}}$
15	2858.74	34971	$(4s^24p)^2P_{\frac{1}{2}}-(4s4p^2)^4P_{\frac{1}{2}}$
15	2836.89	35239	$(4s^24p)^2P_{1\frac{1}{2}}-(4s4p^2)^4P_{2\frac{1}{2}}$
8	2775.39	36020	$(4s^24p)^2P_{\frac{1}{2}}-(4s4p^2)^4P_{1\frac{1}{2}}$

Taking $(4s^24p)^2P$ as 46668 and 44455 the values of $(4s4p^2)^4P$ are as follows: ${}^4P_{\frac{1}{2}}=11697$; ${}^4P_{1\frac{1}{2}}=10648$; ${}^4P_{2\frac{1}{2}}=9216$.

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