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THE SPECTRA OF TIN AND THEIR ZEEMAN EFFECTS

By J. B. Green* and R. A. Loring

Abstract

Analysis of the spectra of Sn, Sn I, Sn II, Sn III.—(1) *Zeeman effects* of the lines of the tin spectrum have enabled the authors to classify the spectra of tin in the neutral state and in two stages of ionization. (2) The spectrum of neutral tin has 5 low levels, $^3P_{012}$, $^1D_2'$, $^1S_0'$, due to the configuration 5_25_2. The configuration 5_26_1 yields $^3P_{012}'$ and $^1P_1'$. The configuration 5_25_3 yields twelve terms of which the four lowest are definitely established. *Pauli's g-sum rule* is found to be valid. *The ionization potential of SnI* is calculated as $7.37 \pm .05$ volts and the *resonance potential* 4.30 volts. (3) *The spectrum of Sn II* is a doublet spectrum like In I and the *principal doublet separation* found from some results of Lang is found to be *4253* cm^{-1}. Several series are noted, including lines due to *abnormal states*, the electrons having the configuration $5_1\ 5_2\ 5_2$. *The ionization potential* is computed as approximately 14.5 volts and the *resonance potential* 6.5 volts. (4) *The spectrum of Sn III* consists of singlets and triplets, like that of Cd I. Several series are noted, and the *ionization potential* calculated as about 30 volts, and the *resonance potential* as 6.81 volts. A very strong group in the extreme ultra-violet is classified as a *pp′ group*. (5) Application of the *regular doublet law* leads to possible classifications in the spectra of In II, and Ge II.

I. Introduction

The spectrum of tin has been the subject of a number of investigations, and while regularities have been known in the spectrum of neutral tin, Sn I, for some time, very little work has been done on the spark spectrum. Lockyer[1] and others have recorded the "enhanced" lines of tin, and more recently, Kimura and Nakamura[2] have separated the lines of the spark spectrum into three classes corresponding to the spectra of tin in various stages of ionization, Sn II, Sn III, and Sn IV, by noting the position of appearance of the lines with reference to the electrodes in different types of sparks. Lang,[3] in an investigation in the extreme ultra-violet has succeeded in classifying the principal lines of Sn IV (similar to the arc spectrum of Ag), and has succeeded in showing that the energy relations involved satisfy the regular and irregular doublet laws.

The authors, while working on the Zeeman effect of the arc spectrum of tin, succeeded in getting experimental conditions just right so that the source was quite rich in spark lines, and in this way were enabled to classify several groups of lines in Sn II and Sn III. The preliminary results of the work have been reported.[4] Through the kindness of Dr. R. J. Lang of the University of Alberta, these classifications were extended to the ultra-violet, and we have

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* National Research Fellow.

[1] Lockyer, Solar Physics Committee, 1906.

[2] Kimura and Nakumura, Jap. Journ. Phys. **3**, 29 (1924); **3**, 197 (1924).

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

[4] Green and Loring, Proc. Nat. Acad. Sci. **13**, 347 (1927); **13**, 492 (1927).

since succeeded in classifying all but a very few of the strong lines in this region and in the ordinary photographic region.

II. THE SPECTRUM OF SN I

(*a*) *General remarks.* The arc spectrum of tin contains very few lines in the visible region, but is remarkably rich in lines in the ultra-violet. Kayser[5] succeeded in finding several constant-frequency differences in the spectrum. Zumstein[6] succeeded in extending these investigations into the Schumann region and classified the lines according to their absorption. McLennan, Young, and McLay[7] attempted to classify the lines into series, but, unfortunately, their conclusions were based on the assumption of six low levels in the spectrum.

(*b*) *Theoretical considerations.* The tin atom, according to the usual ideas, has four outer electrons, two in 5_1 orbits, forming a closed shell, and two in 5_2 orbits. According to Hund's[8] theory, then, the lowest levels, corresponding to the configuration 5_25_2, should be $^3P_{012}$, $^1D_2'$, $^1S_0'$. If one of the electrons remains in a 5_2 orbit, while the other goes to other orbits, we get the ordinary spectrum of neutral tin. So, the configuration 5_26_1, 5_27_1, etc. gives us $^3P_{012}'$ and $^1P_1'$ of which the levels $^3P_{01}'$ converge to the limit $^2P_1$ of Sn II and $^3P_2'$ and $^1P_1'$ converge to $^2P_2$ of Sn II. 5_25_3, 5_26_3, etc. gives us $^3F_{234}'$, $^2D_{123}$, $^3P_{012}'$, $^1F_3'$, $^1D_2$, and $^1P_1'$ of which $^3F_{23}'$ and $^3D_{12}$ converge to $^2P_1$ and all the others to $^2P_2$. Both of these configurations can combine with the normal configuration. There is another configuration which has a high energy value, namely, 5_26_2, with the levels $^3D_{123}'$, $^3P_{012}$, $^3S_1'$, $^1D_2'$, $^1P_1$, $^1S_0'$. This cannot combine with the normal configuration, but may combine with 5_26_1.

(*c*) *Regularities.* Sponer[9] and Zumstein[6] have shown conclusively that most of the arc lines of tin can be arranged as combinations between one unknown energy term and one of five other energy terms. From the arrangement of these five terms there can be little doubt but that they are in order $^3P_{012}$, $^1D_2'$ and $^1S_0'$ as predicted by Hund's theory. Of the next lower terms, if we examine Zumstein's table, we find three that are separated considerably from the others. The inner quantum numbers of these are, in order, 1, 2, and 1. We see that if there were a still lower level of inner quantum number 0, we should have just the set of levels corresponding to the configuration 5_26_1. There is a strong absorption line, $\lambda3034$, which, if given the assignment $^3P_1 - {}^3P_0'$ will fit into the scheme very nicely and thus complete the second set of low levels. This assignment is checked by Zeeman effect.

Of the next set of levels, corresponding to 5_25_3 we can be sure of only the lower levels. In Zumstein's list the four inner quantum numbers are in order, 2, 2, 1, 3. Now $^3F_{23}'$ and $^3D_{12}$ are the next set of levels required by the theory. There can be no question about $^3D_1$ and $^3F_3$, but the other two levels,

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[5] Kayser, Hand. d. Spektr., Vol. 6.

[6] Zumstein, Phys. Rev. **27**, 150 (1926).

[7] McLennan, McLay, and Young, Trans. Roy. Soc. Can. **18**, 57 (1924).

[8] Hund, Zeits. f. Physik **33**, 345 (1925); **34**, 296 (1925).

[9] Sponer, Zeits. f. Physik **32**, 19 (1925).

each with inner quantum number 2, are interchangeable as to interpretation. The Zeeman effect seems to choose the lower level as $^3D_2$ and the higher as $^3F_2'$ although this is the opposite of what we should ordinarily expect.

TABLE IA

Principal series, $3s^3P_{01}'-mp^3P_{01}$; $3s^3P_0'=25049$; $3s^3P_1'=24775$.

m	λ, ν, Int.		λ, ν, Int.	mp^3P_{01}	$(mp^3P_{01}/R)^{1/2}$
2	−3009.138 (6R) *−33222.46*	*(273.5)*	−3034.16 (6R) *−32948.96*	57998	1.375
	(1691.8)				
	−2863.320 (6R) *−34914.29*			59690	1.355
3	11457.3 (60) *8726.0*	*(272.6)*	11827.2 (40) *8453.4*	16323	2.592
	(1025.3)				
	12982.9 (50)? *7700.7*			17074	2.535
4	6068.94 (8h) *16472.8*	*(273.7)*	6171.49 (4) *16199.1*	8576	3.577
	(543.0)				
	6275.78 (2)? *15929.8*			8845	3.521

TABLE IB

Principal Series $3s^3P_{01}'-mp^3D_1'$

m	λ, ν, and Intensity			mp^3D_1'	$(mp^3D_1'/R)^{1/2}$
3	11618.0 (65) *8605.4*	*(276.4)*	11990 *8338.0*	16437	2.583
4	6203.62 (3) *16115.2*	*(273.8)*	6310.83 *15841.4*	8934	3.504

TABLE II

Sharp series $(2p^3P_{012}, 2p^1D_2', 2p^1S_0')-ms^3P_1'$

m	λ	Int.	ν	s^3P_1'	$(s^3P'_1/R)^{1/2}$
3	2863.320	(6R)	34914.29	24776	2.104
	3009.138	(6R)	33222.46		
	3175.039	(5R)	31486.51		
	3801.031	(4R)	26301.21		
	5631.69	(5)	17751.7		
4	2072.86	(6R)	48226.9	11463	3.093
	2148.44	(3R)	46530.6		
	2231.68	(4R)	44795.3		
	2523.912	(3R)	39609.13		
	3218.690	(3)	31059.60		
5	1885.8	(R)	53028	6662	4.057
	1947.6	(1R)	51329		
	2015.75	(2R)	49593.3		
	2251.12	(4R)	44408.9		
	2787.936	(4R)	35858.26		
6(?)	1808.8	(R)	55285	4405	4.990
	1865.6	(R)	53602		
	———		———		
	2141.34	(2R)	46684.9		
	2621.7		38132		

The frequency difference between the lines 3034 and 3009, namely, 273.5, occurs several times in the red and infra-red. The unknown levels involved in such a combination must have the inner quantum number 1, since they combine with the inner quantum numbers 0 and 1. We think that these are possibly the levels ${}^3P_1$ and ${}^3D_1{}'$ of the configuration $5_2 6_2$ etc., since these are the only terms of inner quantum number 1 converging toward the lower limit.

(*d*) *Possible series relations.* Four levels comprising nineteen lines, may be arranged into a series. This is a sharp series of the type $(2p^3P_{012}, 2p^1D_2{}', 2p^1S_0{}') - ms^3P_1{}'$ (see Table II). The value of the term $2p^3P_0$, the lowest level of tin, is then computed approximately as 59690 cm^{-1}. If we use this as the limit, we can also arrange the possible series of diffuse type, $(2p^3P_{012}, 2p^1D_2{}', 2p^1S_0{}') - md^3D_1$, and $(2p^3P_2, 2p^1D_2{}') - md^3F_3{}'$, (see Tables III and IV).

TABLE III

Diffuse series $(2p^3P_{012}, 2p^1D_2{}', 2p^1S_0{}') - md^3D_1$

m	λ	Int.	ν	md^3D_1	$(md^3D_1/R)^{1/2}$
	2246.02	(6R)	44509.7		
	2334.799	(5R)	42817.09		
3	2433.473	(2)	41081.01	15181	2.688
	2785.027	(3R)	35896.15		
	3655.78	(3)	27345.5		
	1941.81	(1)	51482.2		
	2007.90	(2R)	49787.2		
4	2080.51	(2R)	48049.7	8212	3.655
	———		———		
	2913.542	(2R)	34312.47		
5	———	——	———	——	——
	1778.0	(R)	56243		
	———		———		
6	———		———	3446	5.642
	2098.77	(1R)	47631.8		
	2558.056	(4r)	39080.47		
	———		———		
	———		———		
7	1860.3	(R)	53755	2507	6.615
	2058.28	(2R)	48569.0		
	2497.724	(2)	40024.39		

TABLE IV

Diffuse series $(2p^3P_2, 2p^1D_2{}') - md^3F_3{}'$

m	λ	Int.	ν	$md^3F_3{}'$	$(md^3F_3{}'/R)^{1/2}$
3	2429.490	(6R)	41148.41	15114	2.695
	2779.814	(4R)	35963.03		
4	2068.47	(4R)	48329.3	7933	3.718
	2317.21	(6R)	43142.1		
5	1951.54	(3R)	51224.8	5037	4.665
	2171.21	(3R)	46042.2		
6	1891.1	(R)	52879	3383	5.696
	2096.19	(4R)	47690.4		

The difference between the two limits to which the various terms converge, namely, $^2P_1-{}^2P_2$ of Sn II, is 4252, as will be shown later. Using this value, we can find second members of the series of the various terms in the first four configurations of Sn I. The assignments are indicated in Table V.

TABLE V

The spectrum of Sn I.

$2p^3P_0$ 59690	(1692)	$2p^3P_1$ 57998	(1735.9)	$2p^3P_2$ 56262	(5158.5)	$2p^1D_2'$ 51077	(8549.5)	$2p^1S_0'$ 42527	Term Value	Classification
		32949							25049	$3s^3P_0'$
34914		33222		31487		26301		17752	24775	$3s^3P_1'$
		36937		35201		30016			21061	$3s^3P_2'$
39257		37565		35830		30644		22095	20433	$3s^1P_1'$
		41991		40255		35069			16007	$3d^3D_2$
		42453		40717		35531			15545	$3d^3F_2'$
44510		42817		41081		35896		27346	15181	$3d^3D_1$
				41148		35963			15114	$3d^3F_3'$
		45455		43719		38533			12544	$3d^1D_2$
				44060		38875			12202	$3d^3D_3$
48227		46531		44795		39609		31060	11467	$4s^3P_1'$
				45253		40057			11009	$3d^3P_2'$?
48983		47289		45556				31819	10706	$3d^3P_1'$?
		47795							10193	$3d^3P_0'$
				46467		41281			9795	$3d^1F_3'$
50127		48435		46700		41513		32963	9562	$3d^1P_1'$
		49314		47585		42398			8677	$4d^3D_2$
		49469		47736					8527	$4d^3F_2'$
51482		49787		48050				34312	8212	$4d^3D_1$
				48329		43142			7933	$4d^3F_3'$
		50726		48991		43803			7271	$4s^3P_2'$
52713		51014				44094		35544	6984	
53028		51329		49593		44409		35858	6669	
		51945		50206					6056	
				50403		45214			5860	
				51225		46042			5037	$5d^3F_3'$
55078		53382						37911	4617	
		53444				46525		37974	4554	
55157				51734		46544			4528	
				51842				38105	4420	
55285		53602				46685		38132	4393	
		53932						38459	4065	
55688		53996		52268		47075			3994	
				52320		47127			3942	$4d^3P_2'$?
55803						47188			3890	$4d^3P_1'$?
56243						47632		39080	3446	$6d^3D_1$
				52879		47690			3383	$6d^3F_3'$
56389						47777			3300	$4d^1P_1'$?
		54852		53115		47933			3147	
				53152		47965			3110	
		55414		53674		48495			2588	
				53755		48569		40024	2507	$7d^3D_1$
		55457?		53726		48539			2536	
						48670		40121	2407	
		56167		54425					1837	
		56202				49280			1797	
		56408		54672					1590	
		56702		54966					1296	

(*e*) *The Zeeman effect.* The Zeeman patterns previously reported have been more carefully measured and corrected for a mistake in scale. Additional lines have been measured and the results are given in Table VI. It will be noted that the g-values determined from these lines are different from the theoretical values. Pauli[10] has shown that, although the g-values for individual terms are not the theoretical values, the sum of the g-values for all terms of the same inner quantum number of a particular configuration is the same as the sum of the theoretical g-values.

Goudsmit and Back[11] have calculated the g-values for the terms on the basis of three different kinds of coupling between the two outer electrons:

A $\{(s_1l_1)(s_2l_2)\}=(j_1j_2)=j$

B $[\{(s_1l_1)s_2\}l_2]=\{(j_1s_2)l_2\}=j$

C $[\{(s_1l_1)l_2\}s_2]=\{(j_1l_2)s_2\}=j$

TABLE VI

The Zeeman effect in the spectrum of SnI.

λ	Zeeman pattern	Calc. g.
2334	not resolved, but $j_1=j_2$	
2422	(0) 1.00 obs. (0) (.025) (.050) .975 1.000 1.025 1.050 1.075 calc.	1.05 1.025
2429	not measureable. Appeares as single line.	
2456	1.01 (0) 1.24 obs. 1.125 (0) 1.125 calc.	0/0 1.125
2572	(0) 1.46 shaded out from center (0) (.19) (.38) .86 1.05 1.24 1.43 1.62	1.05 1.24
2661	(.38) 1.15 1.50 (.38) 1.14 1.51	1.135 1.51
2706	(0) 1.51 (0) 1.51	1.51 1.51
2780	(0) 1.30 (0) (.12) (.23) .935 1.05 1.17 1.28 1.39	1.05 1.165
2785	(0) 1.39	
2813	(0) 1.09 (0) (.08) (.16) 1.05 1.13 1.21	1.05 1.13
2840	(0) 1.50 (.05) (.10) 1.42 1.47 1.52 1.57	1.47 1.52
2851	(.30) .94 (.19) (.38) .67 .86 1.05 1.24	1.05 .86
2863	(0) 1.38 (0) 1.38	0/0 1.38
2913	(0) .845 (0) .845	0/0 .845
3009	(.12) 1.44 outside components resolved but not measureable (.12) 1.38 1.50	1.38 1.50

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[10] Pauli, Zeits. f. Physik. **16**, p. 155, (1923).

[11] Goudsmit and Back, Zeits. f. Physik **40,** 530 (1926).

TABLE VI (continued)

The Zeeman effect in the spectrum of SnI

λ	Zeeman pattern	Calc. *g*.
3032	(0) 1.055	0/0
	(0) 1.055	1.055
3034	(0) 1.51	0/0
	(0) 1.51	1.51
3141	(0) 1.22	0/0
	(0) 1.22	1.22
3175	(0) 1.50	1.38
	(0) (.07) 1.38 1.45 1.53	1.45
3219	(0) 1.32 very unsymmetrical	0/0
	(0) 1.32	1.32
3262	(0) 1.01	1.045
	(0) (.07) .97 1.04 1.12	1.12
3331	(.44) (.89) .59 1.07 1.51 1.96	1.055
	(.45) (.90) .60 1.06 1.51 1.96	1.505
3656	(0) .64	0/0
	(0) .64	.64
3801	(0) (.34) .715 1.06 1.40	1.055
	(0) (.34) .715 1.06 1.40	1.395
4525	(0) 1.115	0/0
	(0) 1.115	1.115
5632	(0) 1.38	0/0
	(0) 1.38	1.38

TABLE VII

The g-values of SnI.

Config.	Term	Theor. *g*	Obs. *g*	A	B	C
$5_2 5_2$	$^1S_0'$	0/0	0/0	0/0	0/0	0/0
	$^1D_2'$	1	1.05	1.33	1.42	1.43
		2.50	251			
	$^3P_2$	3/2	1.46	1.17	1.08	1.07
	$^3P_1$	3/2	1.51	1.50	1.50	1.50
	$^3P_0$	0/0	0/0	0/0	0/0	0/0
	Σg	4	4.02			
$5_2 6_1$	$^1P_1'$	1	1.121	1.17	1.17	1.17
	$^3P_2'$	3/2 2.50	1.512 2.504	1.50	1.50	1.50
	$^3P_1'$	3/2	1.383	1.33	1.33	1.33
	$^3P_0'$	0/0	0/0	0/0	0/0	0/0
	Σg	4	4.016			
$5_2 5_3$	$^3D_2$	7/6	.86	.767	1.00	.755
	$^3F_2'$	2/3	1.13	1.211	1.055	1.300
	$^3D_1$	1/2	.64	.833	.833	.833
	$^3F_3'$	13/12	1.16	1.111	1.111	1.111
	$^3D_3$	4/3 3.416	1.24 3.425			
	$^1F_3$	1	1.025			
$5_2 7_1$	$^3P_1'$	3/2	1.32	1.33	1.33	1.33
$5_2 6_3$	$^3D_1$	1/2.	.845	.833	.833	.833

where the s and l are given the usual meaning of impulse quantum numbers of the electron spin and of the orbit. The theoretical g-value is obtained from the coupling

$$\{(s_1s_2)(l_1l_2)\}=(sl)=j$$

A is the Russell and Saunders[12] scheme. It may be seen from Table VII that the g-sum rule is satisfied within the limit of error of the observations, and in the two cases where second members of the series could be measured the g-values tend toward the calculated value.

(*f*) *Stark effect.* The effect of intense electric fields on the spectrum of tin was studied by means of an apparatus similar to that of Anderson,[13] and another similar to that of Fujioka,[14] and in fields up toabout 30,000 volts per cm. no effect on any of the lines was observed.

(*g*) *Conclusions.* The ionization potential of Sn I calculated from the value of the $2p^3P_0$ term is $7.37\pm.05$ volts and the resonance potential computed from the resonance line 2863 is 4.30 volts. Unfortunately, no accurate measurements have been made on the ionization and resonance potentials of the group of elements to which tin belongs.

III. The Spectrum of Sn II

(*a*) *General remarks.* According to the Kossel-Sommerfeld displacement law, the spectra of the ionized elements of this column should be doublet spectra like those of the earths, and their lowest terms should be P terms. This has been verified for the cases of C II (by Bowen),[15] Si II (by Fowler),[16] and Pb II (by Gieseler).[17]

A strong pair of lines in the spark spectrum of tin were suspected of being the first member of the principal series and this classification was later verified by the Zeeman effect. The frequency difference, 884, between these two lines was then looked for through the region of the yellow and green, but was not found. However, a weak line, 5597, found on our plates and having the Zeeman pattern $^2P_2{}^2D_2$, when taken in combination with the strong line 5333, gave us the required difference and established a complete $^2P^2D$ multiplet. No other examples of $\Delta\nu=884$ have yet been found. Starting then with the D difference as determined assearch was made in the extreme ultra-violet for the diffuse series. All the wave-lengths below 2000A listed in these tables are taken from data supplied to us by Dr. R. J. Lang.

(*b*) *The series system.* In attempting to determine the important lines of the spectrum of Sn II, it was necessary to get some idea of the magnitude of the doublet separation of the lowest ^2P levels. If we try to extrapolate from the second ^2P difference, 884, which is about three times the second difference for indium, we should expect that the first ^2P difference would be about

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[12] Russell and Saunders, Astrophys. Journ. **61,** 38 (1925).

[13] Anderson, Astrophys. Journ. **46,** 104 (1917).

[14] Fujioka, Sci. Pap. Inst. Phys. Chem. Res., Tokyo, No. 68, 1926.

[15] Bowen, Phys. Rev. **29,** 231 (1927).

[16] Fowler, Trans. Roy. Soc. Lon., **A225,** 1 (1925).

[17] Geiseler, Zeits. f. Physik **42,** 265 (1927).

TABLE VIII

Doublet system of Sn II.

Sharp series $5^2P_{12}-m^2S_1$ $5^2P_2=113451$ $5^2P_1=117704$

m	λ, ν, Int.		λ, ν, Int.	m^2S_1	$(m^2S_1/R)^{1/2}$
6	1900.05 (25) *52630*	*(4253)*	1758.00 (20) *56883*	60821	2.686
7	1243.00 (105) *80451*	*(4247)*	1180.67 (10) *84698*	33000	3.646
8	————		1073.45 (15)? *93158*	20293?	4.650?

Principal series $6^2S_1-m^2P_{12}$ $6^2S_1=60821$

m	λ, ν		λ, ν	m^2P_{12}	$(m^2P_{12}/R)^{1/2}$
6	6844.05 *14607.7*	*(883.6)*	6453.36 *15491.5*	46213 45329	3.081 3.111
7	2789.323 *35840.15*	*(357.4)*	2761.784 *36197.82*	24980 24623	4.191 4.221

First diffuse series $5^2P_{12}-m^2D_{23}$ $5^2P_2=113451$ $5^2P_1=117704$

m	λ, ν, Int.		λ, ν, Int.	m^2D_{23}	$(m^2D_{23}/R)^{1/2}$
5	1489.22 (20) *67149*	*(4254)*	1400.50 (50) *71403*	46301	3.078
	(644) 1475.08 (50) *67793*			45658	3.100
6	1162.98 (5) *85986* *85985 calc.*	*(4249)*	1108.22 (4) *90235* *90238 calc.*	27467	3.997
	(101) 1161.62 (20)* *86087* *86094 calc.*			27360	4.005

Second diffuse series $6^2P_{12}-m^2D_{23}$ $6^2P_2=45329$ $6^2P_1=46213$

m	λ, ν		λ, ν	m^2D_{23}	$(m^2D_{23}/R)^{1/2}$
6	5596.91 *17862.7*	*(883.6)*	5333.10 *18746.3*	27467	3.997
	(109.1) 5562.96 *17971.8*			27360	4.005
7	————		————	———	———
	3639.0 *27472?*			17857?	4.956?

Fundamental series $5^2D_{23}-m^2F$ $5^2D_3=45658$ $5^2D_2=46301$

m	λ, ν		λ, ν	m^2F	$(m^2F/R)^{1/2}$
4	5799.58 *17237.8* *17242 calc.*	*(648.5)*	5589.32 *17886.3* *17885 calc.*	28416	3.93
5	3624.6 *27581* *27602 calc.*	*(660)*	3540.0 *28241* *28245 calc.*	18056	4.93

* This line appears too strong for this combination, but it is used again as the combination $5^3P_0-6^3S_1$ of Sn III, which should have the wave number 86083. The average of this and the calculated value of $5^2P_2-6^2D_3$, 86094, is 86088, which agrees well with observation.

6600. This difference is much too large, however. An examination of the strong lines in the extreme ultra-violet region reveals the fact that the difference 4253 occurs a number of times. It was assumed that this was the first ^2P difference. Further evidence in support of this assumption is found in the spectrum of Sn I. If we take the difference between the average of s^3P_0' and $s\ ^3P_1'$, and the average of s^3P_2' and s^1P_1', of the configuration $5_2 6_1$, i.e. between the two terms converging toward the lower limit and the two terms converging toward the upper limit, we get 4166. If we repeat the process for the configuration $5_2 5_3$, we get about 4300. It is seen that both of these values lie close to the assumed difference 4253. A similar result was found by Gieseler[17] in the case of lead.

Table VIII gives our classification of the lines of the ordinary spectrum of Sn II. It may be seen that the ^2D terms are not inverted as in the case of Pb II.

(*c*) *Combination series.* In addition to these lines, there are several liens which cannot be assigned to the usual series. There are two well-known pairs in the ultra-violet with $\Delta\nu = 626$, and this same frequency difference occurs in the extreme ultra-violet in connection with the difference 4253. The terms involved must therefore be of ^2D type since they combine with ^2F and ^2P. They correspond to the x-terms found by Fowler[16] in Si II.

In the ordinary series of SnII, the outer electrons are supposed to have the configuration $5_1 5_1 5_2$ in the normal state, and in the excited states the 5_2 electron is in outer orbits while the two 5_1 electrons remain fixed. If, however, one of these electrons is excited, so that we have the configuration $5_1 5_2 5_2$, we should expect, according to Hund's theory, the terms $^4P_{123}'$, $^2D_{23}$, $^2S_1$, $^2P_{12}'$. The terms mentioned above are very likely those due to the $^2D_{23}$ of this configuration. Table IX shows the combinations between these terms and other known ones.

TABLE IX

	$p^2D_{23} - m^2F$		$p^2D_3 = 58243$	$p^2D_2 = 58863$		*Combination*: $5^2P_{12} - p^2D_{23}$		
m	λ, ν, Int.		λ, ν, Int.	m^2F	$(m^2F/R)^{1/2}$	λ, ν, Int.		λ, ν, Int.
4	3352.33 (20) *29821.5*	(*625.4*)	3283.46 (20) *30446.9*	28416*	3.93	1831.88 (12) *54589* (*620*)	(*4252*)	1699.50 (10) *58841*
5	2849.8 (2u) *40807*	(*627*)	2488. (1u) *40180*	18056*	4.93	1811.29 (10) *55209*		

* Used in calculation of 5^2P_{12}

Other combinations involving the difference 4253 are given in Table X. The terms involved, which combine with 5^2P_{12}, may be other terms of the configuration $5_1 5_2 5_2$.

(*d*) *Zeeman effect.* The Zeeman effects of some of the lines have already been reported. A complete list of the lines of Sn II whose Zeeman effects have been studied is given in Table XI.

(*e*) *Comparison with indium.* Table XII gives a comparison of the term values of Indium I and Sn II. The terms of Sn II have been divided by 4. The ionization potential of Sn II is found to be 14.5 volts and the resonance potential 6.5 volts.

TABLE X

Unclassified pairs. $5^2P_{12}-X$

λ, ν, Int.		λ, ν, Int.	X	Possible classification
1290.90 (20) *77465*	*(4248)*	1223.79 (10) *81713*	35991	p^2S_1
1533.00 *65234*	*(4255)*	1439.07 *69489*	48215	p^2P_2'
1687.28 *59267*	*(4245)*	1574.51 *63512*	54192	p^2P_1'
2229.1 *44847*	*(4255)*	2036.56 *49102*	68602	p^4P_2'
2386.96 *41882.3*	*(4255)*	2166.72 *46137.4*	71567	p^4P_1'
2445.4 *40880*	*(4252)*	2215.0* *45132*	72572	

* Given by Kimura and Nakamura as Sn III.

TABLE XI

Magnetic resolution of the lines of Sn II

λ	Zeeman patterns	Classification	λ	Zeeman patterns	Classification
6453	(.36) 1.01 1.66 obs. (.33) 1.00 1.67 theor.	$^2S_1{}^2P_2$	5562	(0) 1.04 (.07) (.20) 1.00 1.13 1.27 1.40	$^2P_2{}^2D_3$
5799	(0) 1.07	$^2D_3{}^2F_{34}$	5333	(0) .835 (.07) .73 .87	$^2P_1{}^2D_2$
5596	(—) (.80) .55 1.06 1.60 (.27) (.80) .53 1.07 1.60	$^2P_2{}^2D_2$	3352	(0) 1.06 compare with 5799	$p^2{}_3D^2F_{34}$
5589	(0) .90	$^2D_2{}^2F_3$	3284	(0) .91 compare with 5589	$p^2D_2{}^2F_3$

TABLE XII

Comparison of In I and Sn II

Term	Element	$m=4$	5	6	7	8
$^2S_1$	In I Sn II			22295 15205	10366 8250	6031 5074
$^2P_1$	In I Sn II		46668 29426	14811 11553	7807 6245	
$^2P_2$	In I Sn II		44455 28363	14519 11332	7696 6156	
$^2D_2$	In I Sn II		13775 11575	7620 6867	4832 ——	
$^2D_3$	In I Sn II		13752 11415	7570 6840	4806 4468	
$^2F_{34}$	In I Sn II	6960 7104	—— 4514			

IV. The Spectrum of Sn III

(*a*) *General remark.* The third spectrum of tin is formed by a system of triplets and singlets, like that of cadmium. A very strong triplet having the Zeeman effect of a ${}^3S{}^3P$ group was found on our plates, together with a ${}^3D{}^3P$ multiplet. The ${}^3P$ separations, as determined from these groups of lines were found to be 1224 and 276, while the ${}^3D$ separations were 312 and 205. These groups of lines in the ordinary photographic region are evidently lines of secondary series, and we had to resort to Lang's tables to find the first series.

(*b*) *The triplet system.* Starting with the ${}^3D$ differences found in the green region, we found a typical first member of a ${}^3P_2{}^3D$ group at 1218, 1210, 1206 with the short wave-length line the strongest, having the separations 312 and 209, which are within the limit of error in this region. The second member of this triplet is at 1161 and 1158, with a separation 202, also within the limit of error, and the third member is at 1139. These lines give us the first ${}^3P$ separations as 4033 and 1647, and the sharp triplet was next located by means afforded from this result. The lines of the triplet system of Sn III are given in Table XIII.

(*c*) *The singlet system.* The singlet system was unfolded by means of the Zeeman effect of the line 4330, which revealed the fact that it was a ${}^3S_1{}^1P_1$ combination. This led to the calculation of the term ${}^1P_1$ the second member of the ${}^1P$ sequence.

The lowest term of the Sn III spectrum should be a ${}^1S_0$ term and the combination line ${}^1S_0-{}^3P_1$ should have very marked characteristics.

The line 1811 was noted by Saunders[19] as being quite a strong line in the ordinary spark spectrum of tin, and it occurs in the combination series in Sn II. But this is not sufficient to account for its persistence. Lang's tables first revealed the fact that this line is double 1811.29(10) and 1811.90(20). If, as we have done, we use the short wave-length component for Sn II, and the long wave-length component for Sn III ${}^1S_0-{}^3P_1$ we get a value for ${}^1S_0$ which when combined with the first ${}^1P_1$ yields the line 1251.43(50), one of the strongest lines in this part of the spectrum, for the combination ${}^1S_0-{}^1P_1$. The lines of the singlet system of Sn III are given in Table XIV.

(*d*) *Intercombinations.* Several other intercombinations between the singlet and triplet systems have also been found. These are given in Table XV.

(*e*) *Combination series.* As in the case of all two-electron systems, there is a very characteristic group of lines which may be formed into a ${}^3P{}^3P'$ group, with the ${}^3P'$ separations about the same as the ${}^3P$ separations. This group of lines is shown below (Table XVI).

The position of the P P' group agrees with the rule given by Sawyer and Beese, that the wave-number of this group shall be about midway between ${}^1S_0-{}^1P_1$ of Sn III and ${}^2S-{}^2P$ of the spectrum of Sn IV (given by Carroll[18]

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

[19] Saunders, Astrophys. Journ. **43**, 234 (1916).

TABLE XIII

Triplet system of Sn III.

λ, Int.	ν	$\Delta\nu_1$	$\Delta\nu_2$	Term values
Sharp series, $5^3P_{012}-6^3S_1$; $5^3P_0=189691$; $5^3P_1=188044$; $5^3P_2=184011$				
1243.70 (20)	80405			
		(4031)		
1184.33 (20)	84436			$6^3S_1=103604$
		(1651)		
1161.62 (20)*	86087			
Diffuse series, $5^3P_{012}-5^3D_{123}$				
1218.23 (3)	82086			
		(209)		
1215.14 (15)	82295			
		(312)		
1210.55 (30)	82607			$5^3D_1=101921$
			(4033)	$5^3D_2=101716$
1161.09 (20)	86126			$5^3D_3=101404$
		(202)		
1158.37 (20)	86328			
			(1643)	
1139.35 (20)	87769			
Principal series $6^3S_1-6^3P_{012}$				
4585.62 (20u)	21801.2			$6^3P_2=81802$
		1222.8		
4858.12 (6u)	20578.4			$6^3P_1=83026$
		275.9		
4924.12 (6u)	20302.5			$6^3P_0=83302$
Fundamental series $5^3D_{123}-m^3F_{234}$				
———	———			
2665.60 (1)	37503.9			
		(98.1)		
2658.64 (10)	37602.0			
			(312.1)	$4^3F_2=63937$
2646.18 (2)	37779.1			$4^3F_3=63900$ (assumed)
		(36.9)		
2643.60 (6)	37816.0			$4^3F_4=63802$
			(205.4)	
2631.87 (4)	37984.5			
———	———			
———	———			
1650.02*	60605			
		(284)		$5^3F_4=40799$
———	———			$5^3F_3=40827$
1642.33	60889			$5^3F_2=40837$
		(195)		
1637.10	61084			
Combination $4^3F_2-5^3G$				
4056.75	24643.9			$5^3G=39158$
Combination $5^3D_{123}-6^3P_{012}$				
5369.5	18616			
		(276)		
5291	18895			
———	———			
			(205.2)	
5349.37	18689.8			
			(1223.2)	
5020.7	19913			
			(312.1)	
5100.56	19600.9			

* See note accompanying Table VIII

and by Lang[3] as 1437 and 1314). The P terms thus found, yield the following combinations with the P terms. An unclassified triplet is given also.

There should be, according to Hund's theory, a $^1D_2$ and a $^1S_0$ term belonging to the same configuration as P′, namely $5_2 5_2$. The value of the term involved in the triplet shown is about the correct order for the ^1D term required by theory, but the fact that the term combines with $^3P_0$ seems to preclude the possibility that it has the inner quantum number 2, although the line which would violate the selection principle for inner quantum num-

TABLE XIV

Singlet system of Sn III

$5^1S_0-5^1P_1$	1251.43 (50)	79908	$5^1S_0=243235$ $5^1P_1=163327$
$5^1S_0-6^1P_1$	614.6 (2) 614.56	162707 obs. 162718 calc.	$6^1P_1=80517$
$5^1P_1-5^1D_2$	1570.41 (12)	63677	$5^1D_2=99650$
$5^1D_2-6^1P_1$	5224.92 (5u)	19133.9 obs. 19133 calc.	
$5^1D_2-4^1F_3$	2618.69 (1)	38175.4	$4^1F_3=61475$
$5^1D_2-5^1F_3$	1665.45 (1δ)	60044	$5^1F_3=39611$
$4^1F_3-5^1G_4$	4474.9 (0u)	22342	$5^1G_4=39133$

TABLE XV

Intercombinations in Sn III

$5^1S_0-5^3P_1$	1811.90 (20)	55191*	$5^1\mathrm{P}_1-5^3D_2$	1623.13 (4)	61609 obs. 61611 calc.
$5^1S_0-6^3P_1$	624.0 (1) 624.18	160256 obs. 160209 calc.	$5^3\mathrm{D}_2-6^1P_1$	4715.82 (0u)	21199.1 obs. 21199 calc.
$5^1P_1-6^3S_1$	1674.47 (2)	59720 obs. 59723 calc.	$5^3\mathrm{D}_1-6^1P_1$	4670.68 (2u)	21404.1 obs. 21404 calc.
$5^1P_1-5^3D_1$	1628.51 (3)	61406 obs. 61406	$6^3\mathrm{S}_1-6^1P_1$	4330.13 (5u)	23087.5†

* Used for calculation of 5^1S_0.
† Used for calculation of 6^1P_1.

TABLE XVI

PP′ group of Sn III

		1369.76 (12) *73005*			$5^3P_0'$
		(1916)			
1410.68 (30) *70888*	*(4033)*	1334.74 (30) *74921*	*(1648)*	1306.01 (15) *76569*	$5^3P_1'$
(4447)		*(4446)*			
1327.40 (30) *75335*	*(4032)*	1259.97 (20) *79367*			$5^3P_2'$
5^3P_2		$5^3\mathrm{P}_1$		5^3P_0	
$5^3P_0'=115039$	$5^3P_1'=113123$	$5^3{}_2P'=108676$			

TABLE XVII

Other regularities in Sn III

Triplet $5^3P_{012}-X$		$(X={}^1D_2?)$			
	1294.41 (8)	77255			
			(4030)		
	1230.24 (10)	81285			$X=106759$
			(1647)		
	1205.80 (3)	82932			
$5^3P_{01}'-Y$		1346.10 (20)	74289		
				(1912)	$Y=38838$
		1312.31 (15)	76201		
$5^1P_1-5^3P'_{012}$		2070.66 (1δ)	48294 obs. 48288 calc.		
		1991.79 (1)	50206 obs. 50204 calc.		
		1829.76 (1)	54652 obs. 54651 calc.		
$5^3P_2'-6^1P_1$		3550.6 (1u)	28156 obs. 28159 calc.		
$5^3P_0'-6^1P_1$		2896.12 (3)	34519 obs. 34518 calc.		

TABLE XVIII

Magnetic resolution of the lines of Sn III

λ	Zeeman Pattern	classification
5369	(0) .48 obs. (0) .50 theor.	${}^3P_0{}^3D_1$
5349	(0) .96 (0) (.33)**.83** 1.17 1.50	${}^3P_1{}^3D_2$
5291	(.95) .47 1.41 (1.00) .50 1.50	${}^3P_1{}^3D_1$
5100	(0) 1.10 (0) (.16) (.33) **1.00** 1.17 1.33 1.50 1.67	${}^3P_2{}^3D_3$
5020	(.67) 1.29 (.33) (.67) .83 **1.17** **1.50** 1.83	${}^3P_2{}^3D_2$
4924	(0) 1.97 (0) 2.00	${}^3S_1{}^3P_0$
4858	(5.5) 1.49 2.02 (.50) 1.50 2.00	${}^3S_1{}^3P_1$
4585	(0) (.50) **1.02** 1.52 (0) (.50) **1.00** 1.50 2.00	${}^2S_1{}^3P_2$
4330	(.93) .99 2.00 (1.00) 1.00 2.00	${}^3S_1{}^1P_1$
2660	group ${}^3D{}^3F$ not measurable, but qualitatively correct.	
5225	(0) 1.04 very fuzzy (0) 1.00	${}^1D_2{}^1P_1$
4715	(0) 1.20 (0) (.16) 1.00 1.16 **1.33**	${}^3D_2{}^1P_1$
3550	(0) 1.75 very fuzzy: obscured by band lines (0) (.50) 1.00 1.50 **2.00**	${}^3P_2{}'{}^1P_1$

bers is quite weak in comparison with the others. This same violation was found by one of the authors and Dr. Petersen in an investigation on magnesium.[20] although at the time the proper assignment could not be made, the Hund theory not yet having been developed.

The difference 1912, ${}^3P_1'-{}^3P_0'$ is found between the two strong lines 1346 and 1312.

(*b*) *The Zeeman effect.* The Zeeman effect for all the lines of Sn III that appeared on our plates is given in Table XVIII. They are seen to agree quite closely with theory.

(*g*) *Comparison with cadmium I.* A comparison between the terms of Sn III and Cd I is given in Table XIX. The terms of Sn III have been divided·by 9. The ionization potential of Sn III as calculated from the term ${}^1S_0$ is about 30 volts and the resonance potential calculated from the combination ${}^1S_0-{}^3P_1$ is 6.81 volts.

TABLE XIX

Comparison of Cd I and Sn III

		$m=4$	5	6			$m=4$	5	6
${}^2S_1$	Cd I			21055	${}^3D_3$	Cd I		13023	
	Sn III			11512		Sn III		11267	
${}^3P_0$	Cd I		42425	14148	${}^3F_3$	Cd I	6957	4445	
	Sn III		21075	9256		Sn III	7100	4536	
${}^3P_1$	Cd I		41883	14077	${}^1S_0$	Cd I		72539	
	Sn III		20893	9225		Sn III		27026	
${}^3P_2$	Cd I		40712	13903	${}^1P_1$	Cd I		28847	12633
	Sn III		20446	9089		Sn III		18147	8946
${}^3D_1$	Cd I		13052		${}^1D_2$	Cd I		13319	
	Sn III		11305			Sn III		11072	
${}^3D_2$	Cd I		13041						
	Sn III		11302						

IV. CONCLUSIONS

(*a*) *The doublet separations of Sn II.* The first and second ${}^2P$ differences in the spectra of the singly-ionized elements of the fourth column of the periodic table are given in Table XX.

TABLE XX

First and second ${}^2P$ differences in the spectra of the singly-ionized elements of the fourth column of the periodic table.

Element	N	First difference $\Delta\nu$	$\Delta\nu/N^2$	Second difference $\Delta\nu$	$\Delta\nu/N^2$
C	6	65	1.81		
Si	14	287	1.47	60	0.306
Ge	32	(1900)	(1.85)	361	.353
Sn	50	4253	1.70	884	.354
Pb	82	14070	2.09	2816	.418

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[20] Green and Petersen, Astrophys. Journ. **60,** 301 (1924).

The difference 361 in the spectrum of Ge II is from the obvious principal pair 6020 and 5890. The value $\Delta\nu = 1900$ for the first ^2P difference is predicted from the arc spectrum of Ge but is probably a little too large. The spectra of Ge are now under investigation by Dr. Lang. It seems that the doublet separations are roughly proportional to the square of the atomic numbers.

(*b*) *The triplet separations of Sn III.* By means of the separations of the ^3D terms in Sn III, we were able, by means of the fourth power law, to classify a group of strong lines in the spectrum of In II.

	$\Delta\nu$	$(\Delta\nu)^{1/4}$
Cd I	18.2	2.07
Sn III	312	4.17

Interpolation for indium gives about 118 and 76 for the ^3D separations. In just the region where we should expect it, there is a group of lines which behaves like a fundamental group, having the separations

4682.00	*21352.4*	
		116.2
4656.66	*21468.6*	
		82.2
4638.90	*21550.8*	

116 and 82 which satisfy quite well the calculated value. The ultra-violet data and the red data on indium are very poor, so that little more could be done with this spectrum.

If we consider the fourth power law as holding even for triplet spectra, however, we may also interpolate for the P separations in indium II. We have

	$\Delta\nu$	$(\Delta\nu)^{1/4}$
Cd I	1171	5.85
Sn III	4033	7.96

and interpolation for Indium II gives 2420. The ratio of the ^3P separations in CdI is 2.16; for Sn III it is 2.44. Interpolation for Indium II gives the second P separation as 1050. Carroll[24] gives the following lines which may be arranged into triplets schemes. The first of these

2079.3 (4)		1977.3 (3)		1936.8 (3)
48091	*(2483)*	*50574*	*(1058)*	*51632*

is probably $5^3P_{012} - 6^3S_1$.

This difference occurs again between the lines

1700.0 (6)	*58824*	
		2480
1774.8 (4)	*56344*	

just in the neighborhood where we should expect a PP' group. Unfortunately the data on Indium in this region is not accurate enough, so that further work could not be done.

The authors wish to express their thanks to Professors Lyman and Saunders for their generosity in placing the facilities of the laboratory at their disposal, and to Dr. R. J. Lang for his list of wave-lengths.

Jefferson Physical Laboratory,
Harvard University,
August, 1927.

Note added August 15: During the progress of this work, two articles have appeared on the spectra of tin. The first by Back, Zeits. f. Physik. **43,** p. 309 (1927), is on Sn I and is almost completely in agreement with the authors' results. The second, on Sn III, by Rao appears in Proc. Phys. Soc. Lon. **39**: p. 161 (1927), and did not reach us until very recently. Rao classifies the lines 4858, 5100, and 5225 as the $6^3S_1-6^3P_{012}$ triplet. From the Zeeman effect of these lines, this classification is obviously incorrect, and the frequency differences occurring here and repeated elsewhere are fortuitous. Rao, however, comes to the same conclusions as the authors with regard to the fundamental multiplet in Sn III, and the groups in In II that are mentioned in this paper.