CERTAIN MULTIPLETS IN THE SPECTRA OF CADMIUM III AND INDIUM IV*

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Abstract

Terms and related wave-lengths and frequencies arising from the configuration d^{10}, d^9s, d^9p of Cd III and In IV.—Guided by the transitions from ^3PDF, ^1PDF, $(4d^95p)$ to ^3D, ^1D $(4d^95s)$ already determined for Pd I and Ag II the corresponding lines have been identified in the spectra of Cd III and In IV. The transitions from $^3D_1$, $^3P_1$ and $^1P_1(4d^95p)$ to $^1S_0(4d^{10})$ the latter being the lowest level in each of these spectra, have also been identified for Ag II, Cd III and In IV. These combinations account for nearly all of the strong lines in each spectrum. The term values for the four iso-electronic systems Pd I, Ag II, Cd III, and In IV, together with those for the corresponding elements in the first long period have been plotted on a Moseley diagram which brings out certain similarities and variations between these two sets of spectra. The validity of the irregular doublet law is again confirmed by the almost constant shift in the corresponding radiated frequencies $(4d^95s-4d^95p)$ on passing in succession from Pd I to Ag II, to Cd III, and to In IV.

THE spectra of cadmium III and indium IV reported in this paper were photographed in this laboratory with a new vacuum spectrograph. A concave glass grating having a radius of curvature of 160 cm ruled and etched at the Johns Hopkins University, with about 15,000 lines to the inch was used. With a Rowland setting a dispersion of 10.5A per mm was obtained at the focal surface. The photographs were made on Schumann glass plates, one by six inches, bent to the focal curve. A thin piece of fluorite, 0.5mm thick, mounted immediately behind the slit, free from sputtering by the spark source, and capable of being rotated into the path of the radiation by means of a tapered rod running to the outside, was used in the region 1300 to 2100A to cut out second order lines from the region below 1300A. By using suitably mounted pairs of electrodes, screened from each other by thin strips of aluminum, and capable of being rotated, raised, and lowered from the outside, several exposures for different elements can be made on the same plate without modifying the vacuum. Usually it is convenient to take three or four exposures on each plate, for example, (1) Cadmium electrodes with fluorite screen, 60 minutes, (2) Cadmium electrodes without screen, 30 minutes, (3) Aluminum electrodes for standards, 15 minutes. If desired a fourth exposure of 5 to 10 minutes can be made for the element being studied, from which more exact measurements of the positions of the stronger lines can be made. An interrupted spark was used so that the actual time of exposure was about 1/10 of that given above.

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[1] Data kindly furnished to the authors by A. G. Shenstone in advance of publ cation.

[2] McLennan and Smith, Trans. Roy. Soc. Canada, **20**, 1926.

Recent analysis by Shenstone[1] of Ag II, and the analysis of Pd I as reported by McLennan and Smith[2] and corrected by Shenstone,[1] made the analysis of Cd III and In IV very easy and certain. The normal state of Pd I is given by $(4d^{10})\ {}^1S_0$. Lying just above this are the ${}^3D$ and ${}^1D$ levels of $4d^9 5s$.

TABLE I. *Cadmium III triplets and singlets*

		${}^1S_0$	${}^3D_3$	(1900.1)${}^3D_2$	(3866.0) ${}^3D_1$	(2652.4) ${}^1D_2$
		000	80463.2	82363.3	86229.3	88881.7
			15			
			1707.11			
${}^3F_4$	139042		58578.5			
	2817.9		12	15		8
			1793.38	1856.64		2112.31
${}^3F_3$	136224		55760.6	53860.7		47341.4
	6541.3		1?	10	10	9
			1605.08	1655.62	1768.77	1855.84
${}^3F_2$	142765		62302.3	60400.3	56536.5	53883.9
			12	8		9
			1601.50	1651.80		1851.10
${}^3D_3'$	142905		62441.5	60540.0		54021.9
	2464.4		1?	7	12	5
			1667.38	1721.89	1844.67	1939.58
${}^3D_2'$	140441		59974.3	58075.7	54210.2	51557.5
	7196.7	8		7	10	4
		677.33		1532.03	1628.48	1702.02
${}^3D_1'$	147637	147637		65272.9	61406.9	58753.7
			15	3	1?	4
			1874.08	1943.31	2101.17	2225.13
${}^3P_2$	133823		53359.5	51458.6	47592.5	44941.1
	4942.3	8		12	5	6
		720.64		1773.01	1903.52	2004.73
${}^3P_1$	138765	138765		56401.3	52534.5	49882.0
	3358.0				8	
					1789.15	
${}^3P_0$	142123				55892.5	
			5	8		12
			1523.50	1568.92		1747.65
${}^1F_3$	146101		65638.3	63738.1		57219.7
			4	5	7	12
			1470.34	1512.62	1606.59	1678.07
${}^1D_2'$	148475		68011.5	66110.5	62243.6	59592.3
		15		3	5	10
		684.53		1569.33	1670.64	1748.10
${}^1P_1$	146085	146085		63721.5	59857.3	57205.0

Most of the stronger lines of this spectrum result when the transitions take place from ${}^3(PD'F)$ and ${}^1(PD'F)$ levels of $4d^9 5p$ into the levels of these two lower configurations. Lines for the corresponding transitions $4d^9 5p$ into $4d^9 5s$ of Ag II have been identified by Shenstone.[1] The lines

of these triads of singlets and triplets for Pd I lie in the region 3500–3900A, while for Ag II they lie between 2100 and 2600A, being shifted to higher frequencies by approximately 15,000 wave-numbers.

Assuming these multiplets follow relations similar to those for isoelectronic systems in the first long period as previously reported,[3] it was predicted that the corresponding singlets and triplets for Cd III would have wave-numbers about 15,000 larger than those of Ag II. Guided by the relative positions of the lines in Pd I and Ag II, as shown graphically in Fig. 1, the corresponding lines of Cd III, Table I, were easily identified.

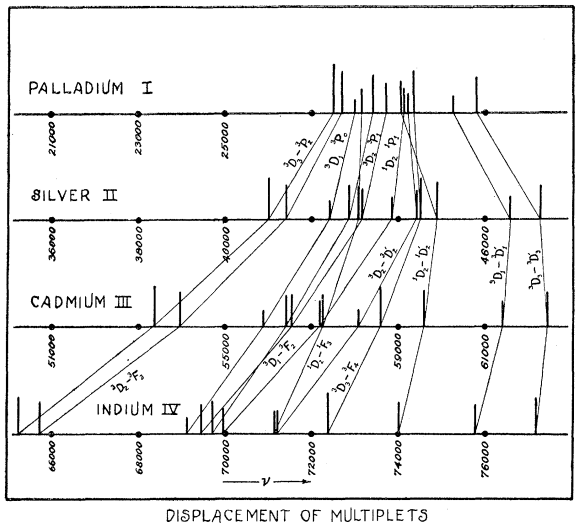


Fig. 1

Inter-combinations between triplets and singlets, as well as relative intensities make certain the assignments and relative positions of the terms arising from the two configurations d^9p and d^9s. With lines of Cd III known, it was an easy matter to indentify the lines of In IV by applying the method of extrapolation shown in Fig. 1, together with relative intensities of lines and common differences between terms.

By a direct analogy with the corresponding elements Ni I,[4] Cu II,[5] and Zn III[6] in the first long period, one would expect to find the most stable electron configuration for Cd III, $(4d^{10})^1S_0$, about 90,000 cm^{-1} lower than $(4d^95s)$. The three combinations with this single level, $^1S_0-{}^1P_1$, $^1S_0-{}^3P_1$ and $^1S_0-{}^3D_1'$ were found at 684.53A, 720.64A, and 677.33A respectively. On the cadmium plates these three lines stand out alone in this region of the spectrum and are very strong. Knowing now the relative positions of $4d^{10}$

[3] Gibbs and White, Proc. Nat. Acad. Sci. **13,** 525 (1927).
[4] Bechert and Sommer, Ann. d. Physik **77,** 367 (1925).
[5] A. G. Shenstone, Phys. Rev. **29,** 383 (1927).
[6] Laporte and Lang, Phys. Rev. **30,** 378 (1927).

and $4d^95p$ for Pd I and Cd III, the $^1S_0(4d^{10})$ level for Ag II and for In IV could be predicted with considerable accuracy from a Moseley diagram as shown in Fig. 2. The three strong lines $^1S_0-{}^1P_1$, $^1S_0-{}^3P_1$, and $^1S_0-{}^3D_1'$ of Ag II were found at 1112.46A, 1195.87A, and 1107.05A respectively, while those for In IV were found at 479.15A, 498.35A, and 472.48A respectively.

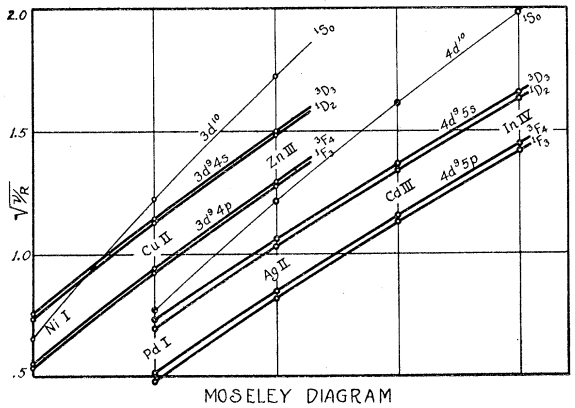
TABLE II. *Indium IV triplets and singlets*

		$^1S_0$ 000	$^3D_3$ (2196.8) 128785	$^3D_2$ (4911.7) 130981	$^3D_1$ (2871.3) 135893	$^1D_2$ 138764
			15			
			1381.73			
$^3F_4$	201158		72373.0			
	4452.1		5	10		1
			1472.30	1521.52		1725.91
$^3F_3$	196706		67920.9	65723.7		57940.4
	8651.2		1	8	6	4
			1305.99	1344.53	1439.58	1501.66
$^3F_2$	205357		76570.3	74375.4	69464.7	66593.0
			10	7		
			1295.86	1333.82		
$^3D_3'$	205953		77168.8	74972.6		
	3824.0		1	8	7	3
			1363.42	1405.52	1509.74	1578.15
$^3D_2'$	202129		73344.8	71148.0	66236.6	63365.3
	9521.5	10		3	7	3
		472.48		1239.61	1320.00	1372.00
$^3D_1'$	211650	211650.3		80670.5	75757.6	72886.3
			12	?		
			1533.37	1586.82		
$^1P_3$	194004		65215.8	63019.0		
	6658.2	10		7	2	2
		498.35		1435.19	1544.06	1615.67
$^1P_1$	200662	200662.0		69677.2	64764.3	61893.8
	4395.3				7	
					1445.93	
$^3P_0$	205057				69159.6	
			4	5		12
			1233.02	1267.36		1406.05
$^1F_3$	209886		81101.7	78904.2		71121.2
			2	2	5	10
			1190.47	1222.46	1300.54	1351.00
$^1D_2'$	212785		84000.4	81802.3	76891.1	74019.2
		15		3	5	10
		479.15		1286.66	1373.45	1429.83
$^1P_1$	208702	208702.0		77720.6	72809.3	69938.3

The term values given in Tables I and II for Cd III and In IV are taken with respect to $^1S_0$ as zero.

In order to plot a Moseley diagram, however, it was necessary to determine approximately the limits toward which the various levels converge in

series. Having only the first members of any series, extrapolations from the known term values of Ag I were made for Pd I by use of the relations previously reported for the elements in the first long period.[3] The configurations



MOSELEY DIAGRAM

Fig. 2

$4d^{10}$, $4d^9 5s$, and $4d^9 5p$ have as a limit $^2D_{2,3}(4d^9)$. The levels $^1S_0(4d^{10})$, $^3D_3$, $^1D_2(4d^9 5s)$ $^3P_2$, $^3D_3'$, $^3F_4$, $^1P_1$, $^1D_2'$, $^1F_3(4d^9 5p)$ according to Hund's rule, approach the same level $^2D_3(4d^9)$. The method of extrapolation used to determine the term values given in Table III, is essentially the same as has been explained in a previous report.[7] It will be noted in the alternate columns of this table that the differences in $(\nu/R)^{1/2}$ are remarkably constant between any two elements, except for the $^1S_0$ terms where it should not be the same.

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

Terms (Limit $4d^9$)	Pd I	Diff.	Ag II	Diff.	Cd III	Diff.	In IV
$4d^{10}\ ^1S_0$	.772	.446	1.218	.397	1.615	.366	1.981
$4d^9 5s\ ^3D_3$	.732	.330	1.062	.307	1.369	.290	1.659
$4d^9 5s\ ^1D_2$	.699	.333	1.032	.309	1.341	.290	1.631
$4d^9 5p\ ^3F_4$	.518	.332	.850	.308	1.158	.288	1.446
$4d^9 5p\ ^3D_3'$	.505	.330	.835	.308	1.143	.288	1.431
$4d^9 5p\ ^3P_2$	.534	.334	.868	.310	1.178	.290	1.468
$4d^9 5p\ ^1F_3$	.482	.338	.820	.310	1.130	.289	1.419
$4d^9 5p\ ^1D_2'$	.473	.337	.810	.310	1.120	.289	1.409
$4d^9 5p\ ^1P_1$	.473	.343	.816	.314	1.130	.293	1.423

The regularity with which the term separations increase in going from Pd I to Ag II, to Cd III, and to In IV is given in Table IV. In this sequence of elements the separations are from two to three times the corresponding separations for Ni I, Cu II and Zn III in the first long period. Here also, as in Ni I, Cu II and Zn III, the $^3F_{3,4}$ terms are inverted as may be seen from

[7] Gibbs and White, Phys. Rev., **31**, 520 (1928).

TABLE IV. *Term separations.*

	$^3D_3-{}^3D_2$	$^3D_2-{}^3D_1$	$^3D_1-{}^1D_2$	$^3F_4-{}^3F_3$	$^3F_3-{}^3F_2$	$^3D_3'-{}^3D_2'$	$^3D_2'-{}^3D_1'$	$^3P_2-{}^3P_1$	$^3P_1-{}^3P_0$	$^3D_1'-{}^1D_2'$
Pd I	1191	2339	1628	− 476	3360	− 418	3393	2112	1908	403
Ag II	1577	2998	2306	−1498	4717	−1260	5134	3449	2515	553
Cd III	1900	3866	2652	−2818	6541	−2464	7197	4942	3358	838
In IV	2197	4912	2871	−4452	8651	−3824	9521	6658	4395	1135

Table IV. By the use of extrapolations similar to those discussed above it is planned to extend these investigations to the iso-electronic spectra of Sn V, Sb VI, etc.

Note added to galley proof, March 31, 1928. Since writing this paper a report, dated December 17, 1927, on the spectra of Ag II by Shenstone[8] has been printed, and we have received a reprint of a paper by McLennan and McLay[9] dated January 3, 1928, in which they describe the structure of the spectra of Ag II and make certain corrections to the previous report by McLennan and Smith on the spectra of Pd I. More recently we have received a reprint of a paper by McLennan, McLay and Crawford[10], dated February 8, 1928, in which the transitions $4d^95p$ to $4d^95s$ for Cd III are identified in complete agreement with this report. They did not determine the $^1S_0(4d^{10})$ level.

CORNELL UNIVERSITY,
January 31, 1928.

[8] A. G. Shenstone, Phys. Rev. **31,** 317 (1928).

[9] McLennan and McLay, Trans. Roy. Soc. Canada, **22,** 1 (1928).

[10] McLennan, McLay, and Crawford, Trans. Roy. Soc. Canada, **22,** 45 (1928).