The Zeeman Effect of the Spectra of Arsenic

J. B. GREEN AND W. M. BARROWS, JR., *Mendenhall Laboratory of Physics, Ohio State University*
(Received October 26, 1934)

Zeeman Effect in Arsenic: Zeeman patterns of the spectra of As I, As II and As III have been measured. The results give g-values that are in general agreement with perturbation theory, although it appears that Goudsmit's method of adding an s-electron to parts of a configuration is not sufficiently accurate.

THE Zeeman patterns of the spectrum of arsenic from 2200 to 6500 Angstroms were photographed with the apparatus previously described.[1] One important alteration in the arrangement of the source has been made.

Above and forward of the holes, which admit the pole-pieces into the vacuum-box, are two five-eighths inch tapped holes, directly opposite one another. Into these are screwed hard rubber plugs with close-fitting threads, well covered with stopcock grease. The left-hand plug (as seen looking forward) is drilled and tapped to receive a one-quarter inch, twenty-thread screw, while the right-hand one has a blind, three-sixteenths inch smooth side hole, extending about three-quarters of its length from the inside. A brass rod about five inches long, consisting of three inches of three-sixteenths inch round rod and two inches of one-quarter inch, twenty male thread, is inserted in the right plug and screwed into the left plug, after being greased to insure air-tightness. This rod forms the axle for a horizontal lever arm of three-sixteenths inch brass rod, which is provided with a long brass bushing. A short helical spring pushes this bushing away from the right plug and a washer stops it at the beginning of the threaded part of the axle. The axle is screwed in or out of the left plug until the lever arm is in the plane of the disk. The lever arm is free to turn about the axle in this vertical plane. On the inner end of the lever arm, vertically above the center of the disk, is a brass fixture, through which is drilled a vertical hole, tapped to accommodate a No. 5–40 machine screw. On the side of the fixture opposite the lever arm (toward the back of the box) is a set-screw, which also has a No. 5–40 thread.

A one-eighth inch round brass rod, about seven inches long, is now threaded with a No. 5–40 die and screwed into the hole in this fixture until, when the arm is horizontal, the rod just touches the uppermost point of the disk, in which position it is secured by means of the set-screw. The upper end of the rod then protrudes about two inches above the top of the box, through a one-inch hole cut in the box for this purpose.

On the forward end of the lever arm (on the opposite side of the axle) is fastened a lead counterweight of sufficient mass so that only a slight pressure is exerted on the disk by the vertical rod. This pressure may be increased at will by screwing brass weights onto the top of the rod. Now if the disk is set rotating, the magnetic field is on, the vacuum-box (and therefore the disk) is connected to the negative terminal and the vertical rod (through the lever arm and axle) to the positive terminal of a source of direct current, the arc will operate. The disk becomes its negative electrode and the vertical rod its positive electrode. The magnetic field is in such a direction that as soon as a current flows through the rod it suffers a backward force. This force produces a torque about the axle which tends to lift the upper electrode, thus striking the arc. When the arc blows out, as it will in a magnetic field, the current ceases, the torque vanishes and the electrode falls back against the disk, whereupon the process is repeated indefinitely. By this means an average current of one ampere through the arc will produce a spectrum considerably brighter than was obtained by the former method with a current of three amperes.

The insertion of rubber gaskets between the pole-pieces and the vacuum box, to insulate the box from the frame of the magnet, which is grounded, necessarily widens the pole-gap slightly, so that the field intensity is reduced to some 36,000 gauss at ninety amperes actuating current.

Since arsenic cannot be successfully cast or alloyed in large proportion in air, the following method was used to introduce it into the arc:

The rod which was to become the upper electrode was provided with an axial hole one-sixteenth inch in diameter, extending inward about one and one-quarter inches from one end. This hole was filled with finely powdered arsenic, which was firmly tamped down. The rod was then placed in the arc in the usual manner with the filled end down. With this arrangement the arc would operate for about an hour before the arsenic was exhausted.

A fairly large hole was cut in the back-plate of the vacuum-box at a point slightly higher than the pole-gap. Over this hole was soldered a flanged, tapered bushing, into which fits a tapered, hollow plug with a stopcock grease seal. The longitudinal hole in this plug is covered with a plate-glass window cemented to the plug. Through this window the source may be observed in operation, either with the naked eye or through a small direct-vision spectroscope, without interfering with the beam which enters the spectrograph. If the plug be removed, a long-shanked screw-driver may be inserted into the box for adjustment of the set-screw, without removing the back-plate.

The hole in the box, through which projects the upper end of the electrode, is closed by means of the same hollow brass cap previously used.[1] By removing this cap and the tapered plug in the back-plate, the electrode may be adjusted, or removed and replaced without disturbing the back-plate.

The complete Zeeman patterns and then the p-components were exposed for forty-eight hours, with a slit-width of 0.045 mm, the source being in an atmosphere of hydrogen at a pressure of ten millimeters of mercury. In the meantime a small tank of helium became available. It was found that the arsenic spectrum was increased in intensity and the bands were less objectionable when the vacuum-box contained helium at 10 mm pressure. Accordingly, the s-components were photographed with helium replacing the hydrogen as residual gas and the exposure was reduced to sixteen hours. This exposure brought out considerably more lines in the arsenic spectrum than the others.

As I

The spectrum of As I has been partially classified by Meggers and DeBruin[2] and by Rao.[3] These classifications are in substantial agreement, that of Rao's being the more recent and more complete.

Table I summarizes the results of the present investigation of the Zeeman effect as As I.

The third column gives the classification of each line (Rao).

In the fifth column are recorded the displacements, in terms of the unit L, of the various components from the center of the pattern. In the cases of unresolved patterns these displacements are measured to the centers of intensity of the groups of s-components. The figures in parentheses refer to p-components and the others to s-components.

The last two columns give the g-values calculated for the levels; g_a is that of the level first mentioned in the classification and g_b of the other.

The $4s^24p^3$ configuration has been studied by Inglis[4] and by Inglis and Johnson[5] and the g-formulae calculated on the basis of the perturbation theory. The results calculated according to this method are compared with observations in Table II.

No very definite conclusion can be drawn from this comparison. The levels of As I are so close to LS coupling that the g-values are almost normal. A striking discrepancy is seen in the g-value of $^2P_{1/2}$, which should not change with coupling. This comes about as a result of the pattern of λ2991, which shows a marked departure from the g-value computed from λ2745. A similar disturbance in the same level of Sb I[6] has been noticed and attributed to hyperfine structure of this level. The g-value of $^2P_{3/2}$ is in quite good agreement with the present theory.

Johnson[7] and Goudsmit[8] have studied the $4s^24p^25s$ configuration from the standpoint of the addition of an s-electron to a ^3P set of levels.

TABLE I. *Zeeman patterns of As I.*

λ	ν	Classification	Pattern	g_a	g_b
2288.2	43689	$4p^2D_{5/2}-5s^2P_{3/2}$	(0) 1.090	1.208	1.327
2349.9	42542	$4p^2D_{3/2}-5s^2P_{1/2}$	(0) .830	.811	.736
2369.8	42185	$4p^2P_{3/2}-5s^2D_{3/2}$	(.73) 1.08	1.32	.84
2437.3	41017	$4p^2D_{3/2}-5s^4P_{3/2}$	(1.35) —	.81	1.71
2493.0	40101	$4p^2D_{3/2}-5s^4P_{1/2}$	0 (.901) 1.716	.815	2.617
2745.1	36418	$4p^2P_{1/2}-5s^2P_{3/2}$	(.331) .993 1.659†	.663	1.326
2780.3	35956	$4p^2P_{3/2}-5s^2P_{3/2}$	(0) 1.324	1.319	1.329
2860.6	34948	$4p^2P_{1/2}-5s^2P_{1/2}$	(0) .704	.687	.721
2898.8	34487	$4p^2P_{3/2}-5s^2P_{1/2}$	(.292) 1.040 1.597†	1.319	.743
2991.1	33424	$4p^2P_{1/2}-5s^4P_{3/2}$	(.505) 1.217 2.217†	.711	1.717
3033.0	32961	$4p^2P_{3/2}-5s^4P_{3/2}$	(.618) 1.489	1.283	1.695

† Stronger lines.

TABLE II.* $4s^24p^3$ *configuration of As I.*

	$^2P_{3/2}$	$^2P_{1/2}$	$^2D_{5/2}$	$^2D_{3/2}$	$^4S_{3/2}$
g LS	4/3	2/3	6/5	4/5	2
g obs.	1.313	.687	1.208	.813	—
g calc.	1.317	2/3	6/5	.822	1.994

* In this table, as well as Tables III, IV, VI, VII the well-resolved lines have been weighted more heavily in calculating the $g_{obs.}$ values taken from the lists of lines.

TABLE III. *The* $4s^24p^25s$ *configuration of As I.*

Level	ν	Referred to $^4P_{5/2}$ Obs.	Calc.	$g_{calc.}$	$g_{obs.}$	g_{LS}
$^4P_{1/2}$	30,000	−2204	−2098	2.620	2.617	2.667
$^4P_{3/2}$	29,084	−1288	−1368	1.722	1.706	1.733
$^4P_{5/2}$	27,796	(0)	(0)	1.600	——	1.600
$^2P_{1/2}$	27,558	238	223	.713	.736	.667
$^2P_{3/2}$	26,088	1708	1788	1.345	1.327	1.333

TABLE IV.* *The 4s4p5s configuration of As I.*

Level	ν	Referred to 23838	Calc.	$g_{calc.}$	$g_{obs.}$	g_{LS}
$^4P_{1/2}$	30,000	−6162	−6242	2.572	2.617	2.667
$^4P_{3/2}$	29,084	−5246	−5234	1.718	1.706	1.733
$^4P_{5/2}$	27,796	−3958	−3958	1.591	——	1.600
$^2P_{1/2}$	27,558	−3720	−3824	.761	.736	.667
$^2P_{3/2}$	26,088	−2250	−2284	1.329	1.327	1.333
$^2D_{5/2}$	19,879	+3958	+3958	1.209	——	1.200
$^2D_{3/2}$	19,859	+3978	+4000	.819	.84	.800
$^2S_{1/2}$	15,882	+7956	+8140	2.000	——	2.000

* This same configuration has been studied by Schlapp (Proc. Roy. Soc. Edin. **54**, 109 (1934)), a reprint of which has just been received (Nov. 16, 1934).

Using the matrices calculated by Johnson we find the following results, which are compared with the observations in Table III.

From this table it is seen that $^2P_{3/2}$ shows a great discrepancy, in that the observed g-value is lower than the LS-value, while that calculated on the basis of Johnson's matrix is higher. This can only mean that even so close to $L–S$ coupling as this configuration is, the perturbing effect of the $(^1D_2+s)$ must be taken into account.

More recently, Johnson[9] has studied the p^2s configuration, taking this into account, and the above-mentioned discrepancy then disappears. Table IV gives the comparison.

As II

The spectrum of As II has been partially classified by Rao.[10] A number of levels have not been completely identified and are designated by letters.

Following is Table V, showing the data relative to the observed patterns of As II. Data followed by ♯ were supplied by the authors upon the basis of the present observations.

Two levels tentatively identified as $5d^3D_2$ and $5d^3F_2$ have been included and several transitions involving them have been classified. It is certain that each of the levels has a j-value of two and their apparent g-values are consistent with these classifications. Two additional transitions between known levels, apparently not observed by Rao, have been classified and included in Table II.

While, in general, Rao's classifications appear to be correct, the configuration $4s^24p4d$ still seems to be in doubt, especially $4d^1D_2$ and $4d^1P_1$, the Zeeman patterns of whose combinations are inconsistent. In addition to these levels, the

TABLE V. *Zeeman patterns of As II.*

λ	ν	Classification	Pattern	g_a	g_b
2830.5	35319	$4d^3F_3-F$	(0) 0.914		
2831.3	35310	$4d^3F_2-D$	(0) 1.279	0.58	0.93
2884.5	34657	$4d^3F_3-E$	(0) 1.276		
2890.2	34589	$4d^3F_3-D$	(.30) 1.01	1.07	0.95
3053.5	32740	$4d^3F_2-4f^3F_3$	(0) 1.607	0.58	1.09
3058.1	32691	$4d^3F_2-A$	(0) 1.289		
3116.7	32076	$4d^3F_3-B$	(0) 1.165		
3843.1	26013	$sp^3\,^3D_3-5p^3P_2$	(0) 1.256	1.345	1.433
3931.3	25430	$sp^3\,^3D_1-5p^3P_1$	0.529 (.877) 1.376	0.519	1.386
3945.9	25336	$sp^3\,^3D_2-5p^3D_3$	(0) 1.485	1.183	1.334
3948.7	25318	$sp^3\,^3D_2-5p^3P_1$	(0) 1.031	1.159	1.406
4006.3	24954	$sp^3\,^3D_3-5p^3D_3$	(0) 1.327	1.320	1.334
4065.5	24590	$4d^3D_2-D$	.302† .607 .888*	1.217	0.912
4157.6	24045	$5p^3P_1-6s^3P_2$	(0) .988	1.389	1.121
4197.6	23816	$4d^3D_3-E$	(0) .83		
4208.0	23758	$4d^1P_1-G$	(0) 1.226		
4225.9	23657	$5p^3D_2-d$	(0) .97		
4243.3	23560	$5p^1P_1-5d^3F_2$#	(0) .640	0.812	0.698
4297.5	23263	$5s^3P_1-5p^1D_2$	.643† 1.05 —*	1.43	1.05
4299.5	23252	$sp^3\,^3D_2-5p^3D_2$	(0) 1.174	1.179	1.170
4315.9	23164	$sp^3\,^3D_1-5p^3D_1$¶	(0) 1.002		
4324.1	23120	$5p^3P_0-e$	(0) .730	$\frac{0}{0}$	0.730
4336.9	23052	$sp^3\,^3D_2-5p^3D_1$	(0)† (.280) .894† 1.183 1.463	1.183	0.897
4352.3	22970	$5s^1P_1-5p^1S_0$	(0) 1.078	1.078	$\frac{0}{0}$
4353.1	22966	$5p^3P_2-6s^3P_2$¶	(0) 1.206		
4359.9	22930	$5p^3P_2-5d^3D_2$#	.777 1.110† 1.433† 1.744*	1.433	1.110
4371.4	22870	$sp^3\,^3D_3-5p^3D_2$	(0) 1.509	1.341	1.174
4404.6	22692	$5p^3S_1-f$	.410† 1.131 —*	1.874	1.143
4413.7	22651	$4d^1P_1-D$¶	.743† 1.071 1.439		
4427.4	22581	$4d^1P_1-C$	(0) .983		
4431.8	22558	$4d^3D_1-4f^3F_2$	(0) .946	0.895	0.93
4466.6	22382	$4d^1D_2-F$	(0) .985		
4507.9	22177	$5p^3P_1-e$	0.723 1.389*	1.389	0.723
4516.1	22137	$5p^3S_1-6s^3P_2$	.440† 1.152 1.893*	1.893	1.165
4528.6	22076	$4d^3D_2-4f^3F_2$	.423 .842† 1.285† 1.685*	1.285	0.842
4539.9	22021	$4d^3D_2-4f^3F_3$	(0) .77	1.29	1.03
4549.2	21976	$5p^3D_1-5d^3F_2$#	(0) .55	0.90	0.67
4552.4	21960	$5s^3P_1-5p^3S_1$	1.419 1.895*	1.419	1.895
4591.0	21776	$5p^3D_2-5d^3F_2$#	.220 .698† 1.174† 1.654*	1.174	0.698
4602.7	21720	$4d^1D_2-E$	(0) 1.440		
4617.3	21652	$4d^1D_2-D$	(0) .917	0.94	0.93
4630.1	21592	$5p^3P_1-d$	(0) 1.494		
4632.6	21580	$sp^3\,^3D_1-5p^1P_1$# [Rao $4d^1D_2-C$]	(.325) .497 .808	0.497	0.808
4672.7	21395	$5p^1D_2-f$	(0) 1.087	1.046	1.128
4707.8	21235	$4d^3D_3-B$	(0) .593		
4730.9	21132	$5s^3P_1-5p^3P_2$	(0) 1.440	1.423	1.434
4787.3	20883	$5s^3P_2-5p^1D_2$	(–) .585 (.959) 1.040† 1.491† 1.943	1.491	1.045
4799.7	20829	$5p^3D_1-b$	(.232) .921 1.086	0.906	1.104
4888.8	20450	$5s^3P_0-5p^3P_1$	(0) 1.390	$\frac{0}{0}$	1.390
4985.6	20052	$5s^3P_1-5p^3P_1$	(0) 1.413	1.430	1.395
5105.7	19580	$5s^3P_2-5p^3S_1$	(0) (.439) 1.085† 1.492 1.902	1.492	1.902
5107.8	19572	$5s^1P_1-5p^1D_2$	(0) 1.025	1.075	1.050
5231.5	19110	$5s^3P_1-5p^3P_0$	(0) 1.428	1.428	$\frac{0}{0}$
5331.5	18751	$5s^3P_2-5p^3P_2$	(0) 1.464	1.492	1.436
5385.5	18563	$5p^3P_1-b$	(.263) 1.10 1.37	1.38	1.12
5472.0	18270	$5s^1P_1-5p^3S_1$	(.853) — 1.91	1.06	1.91
5498.0	18183	$5s^3P_0-5p^3D_1$	(0) .887	$\frac{0}{0}$	0.887
5558.3	17986	$5s^3P_1-5p^3D_2$	(0) (.289) .903† 1.150 —	1.439	1.171
5651.6	17689	$5s^3P_2-5p^3D_3$	(0) 1.13	1.49	1.31
5657.2	17672	$5s^3P_2-5p^3P_1$	(0) 1.558	1.502	1.389
6022.6	16599	$5s^3P_0-5p^1P_1$	(0) .810	$\frac{0}{0}$	0.810
6110.7	16360	$5s^1P_1-5p^3P_1$	1.073 1.386*	1.073	1.386
6170.3	16202	$5s^3P_1-5p^1P_1$	(.606) .819 1.423	1.423	0.819

* Measured only in perpendicular polarization.
† Stronger lines.
¶ Apparently incorrect classifications.

levels C, E and d give inconsistent patterns, while those levels called D, b, e, f have definitely j-values of 3, 1, 1, 2, respectively.

The g-values of the $4s^24p5s$ configuration have been calculated according to Houston's method[11] and are compared with the experimental values in Table VI. The agreement is excellent.

TABLE VI. *$4s^24p5s$ configuration of As II.*

Level		Referred to C. of G.	ϵ	$g_{calc.}$	$g_{obs.}$	g_{LS}
$^1P_1$	79972	+2225	2.402	1.073	1.075	1
$^3P_2$	81281	+ 926	1	1.500	1.492	1.500
$^3P_1$	83662	−1455	−1.571	1.427	1.424	1.500
$^3P_0$	84059	−1852	−2	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{0}{0}$

The calculation of the g-values of the $4s^24p5p$ configuration is much more complicated, since six parameters must be adjusted to fit three linear equations and give the roots of a quadratic ($j=0$), a cubic ($j=2$), and a quartic ($j=1$) within a reasonable degree of accuracy. By using Johnson's[7] matrices and the following values of the parameters

$$\alpha=3900,\quad \gamma=-1560,\quad a_1=1840,$$
$$\beta=1600,\quad \delta=7360,\quad a_2=380,$$

the g-values were calculated, with Marvin's[12] suggestion of replacing the diagonal term of the energy W by $W_0-g_1\omega+g\omega$ and neglecting terms in ω^2. The comparison of theory and experiment is given in Table VII.

TABLE VII. *The $4s^24p5p$ configuration of As II.*

Level	ν	Referred to $^3D_3$ Obs.	Calc.	$g_{calc.}$	$g_{obs.}$	g_{LS}
$^1P_1$	67460	−3869	−3845	0.800	0.812	1.000
$^3D_1$	65872	−2281	−2200	0.905	0.895	0.500
$^3D_2$	65675	−2084	−2035	1.180	1.174	1.167
$^3P_0$	64552	− 961	− 960	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{0}{0}$
$^3P_1$	63610	− 19	12	1.405	1.389	1.500
$^3D_3$	63591	(0)	(0)	1.333	1.325	1.333
$^3P_2$	62530	1061	1030	1.435	1.433	1.500
$^3S_1$	61702	1889	1753	1.890	1.896	2.000
$^1D_2$	60399	3192	3175	1.052	1.046	1.000
$^1S_0$	57002	6589	6590	$\frac{0}{0}$	$\frac{0}{0}$	$\frac{0}{0}$

The g-sums are 4.992 instead of 5.00 for $j=1$, and 3.655 instead of 3.667 for $j=2$, quite within experimental error, and the general agreement of each level is quite satisfactory.

Several other lines attributed to As II by Rao[10] were also measured and are listed in Table VIII, together with other pertinent infor-

Table VIII. *Unclassified lines of As II.*

	Pattern		j_a	j_b	g_a	g_b	Suggested combinations
2603.0	38406	(0) 0.704					
2959.7	33777	(0) 1.090					
3004.0	33280	(.300) 1.198	1 ?	1 ?	1.05	1.35	
4119.8	24266	(0) 1.258					
4228.4	23643	(0) 1.302					
4302.3	23237	(0) 1.529					
4412.3	22658	(0) .497	0	1	0.497		$^3D_1$, $j=0$
4421.1	22612	.498 1.415*	1	1	0.498	1.415	$^3D_1$, $^3P_1$
4447.7	22478	.821 1.179*	1	1	0.821	1.179	
4456.9	22431	(0) 1.903					
4458.8	22421	(0) 1.025					
4474.6	22342	(0) .943					
4532.4	22057	.54† 1.00 1.47	2	1	1.47	1.00	$^3P_2$, $^1P_1$
4543.7	22003	(0) 1.042					
4580.9	21824	0 .44† .97† 1.48*	2	2	0.45	0.98	$^3F_2$, $^1D_2$
4619.6	21641	(0) 1.188					
4627.8	21602	1.05† 1.50 —*	2	1	1.50	1.95	$^3S_1$, $^3P_2$
5043.4	19822	(0) .853					
5161.3	19370	(.565) .867 1.462	1	1	1.454	0.875	$^3P_1$, $^1P_1$
5497.1	18186	(0) 1.044					
5685.7	17583	(0) .917					
5838.2	17124	(.07) 1.468	1	1	1.43	1.50	$^3P_1$, $^3P_1$

* Measured only in perpendicular polarization.
† Stronger lines.

mation gleaned from their Zeeman patterns.

As III

Of the spectrum of As III only two lines were found to be resolved, the principal doublet of this spectrum[13]

3922.6	25486	$5s^2S_{1/2}-5p^2P_{3/2}$	(0.347)	1.005†	1.666
4037.2	24763	$5s^2S_{1/2}-5p^2P_{1/2}$	(0.669)	1.327	

† Stronger lines.

yielding g-values

$^2S_{1/2}$	1.996
$^2P_{1/2}$	1.333
$^2P_{3/2}$	0.658

which are, within experimental error, the LS-values, 2, 4/3, 2/3.

In conclusion, the authors wish to express their gratitude to Dr. R. A. Loring for his many suggestions and valuable assistance during the progress of this work.

Bibliography

1. Green and Loring, Phys. Rev. **30**, 574 (1927); **43**, 457 (1933).
2. Meggers and De Bruin, Bur. Standards J. Research **3**, 765 (1929).
3. Rao, Proc. Roy. Soc. **A125**, 244 (1929); Proc. Phys. Soc. London **44**, 594 (1932).
4. Inglis, Phys. Rev. **38**, 377 (1931).
5. Inglis and Johnson, Phys. Rev. **38**, 1642 (1931).
6. Löwenthal, Zeits. f. Physik **57**, 828 (1929); Green and Loring, Phys. Rev. **31**, 707 (1928).
7. Johnson, Phys. Rev. **38**, 1628 (1931).
8. Goudsmit, Phys. Rev. **35**, 1325 (1930).
9. Johnson, Phys. Rev. **39**, 197 (1932).
10. Rao, Proc. Phys. Soc. (London) **44**, 343 (1932); Ind. J. Phys. **7**, 561 (1933).
11. Houston, Phys. Rev. **33**, 297 (1929).
12. Marvin, Phys. Rev. **44**, 818 (1933).
13. Rao and Narayan, Zeits. f. Physik **57**, 867 (1929).