

by the proximity of  $sp^2\ ^4P_{2\frac{1}{2}}$ . These perturbation effects explain very satisfactorily the inversion of the  $6d\ ^2D$  and the abnormally large separations of the  $7d$  and  $8d$  doublets as observed.

The effect of the perturbations on the  $sp^2$  levels is not so readily discussed, since the unperturbed arrangement is not so well known. Referring to Fig. 4, however, the larger separation of the  $^4P_{1\frac{1}{2}}-^4P_{2\frac{1}{2}}$  levels in Pb II may well be due to the presence of the  $6d\ ^2D$  terms, both of which would tend to increase the separation. In Bi III<sup>19</sup> the

<sup>19</sup> McLay and Crawford, Proc. Roy. Soc. A143, 540 (1934).

effect does not occur, since the  $6d$  doublet lies above the  $^4P$  group. The difference in location of the  $sp^2\ ^2D_{2\frac{1}{2}}$  levels in the two spectra may be explained by the downward effect of the  $7d\ ^2D_{2\frac{1}{2}}$  term in Pb II and the upward effect of  $6d\ ^2D_{2\frac{1}{2}}$  in Bi III. The perturbations existing in the  $sp^2$  levels with  $J=\frac{1}{2}$  and  $1\frac{1}{2}$  appear too complicated to admit of present interpretation on a qualitative basis.

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## Hyperfine Structure of Singly Ionized Lead

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Some one hundred and thirty lines of Pb II were observed with Lummer-Gehrcke plates and Fabry-Perot interferometers from 2300 to 10,000Å. The isotope shifts between Pb<sup>208</sup> and Pb<sup>206</sup>, and the h.f.s. splitting of Pb<sup>207</sup> were computed from the h.f.s. measurements of these lines

for all of the levels of Pb II, classified by Earls and Sawyer, with the exception of  $6s^26p^2P_{1/2, 3/2}$  and  $6s6p^2\ ^2P_{1/2}$ . Parameters were obtained for equations derived by Breit and Wills for finding the h.f.s. constants,  $a'$ ,  $a''$ ,  $a'''$ , and  $a(s)$ , of the  $6s6p^2$  configuration in intermediate coupling.

NUCLEAR spins for the three more abundant isotopes, Pb<sup>208</sup>, Pb<sup>206</sup> and Pb<sup>207</sup>, of ordinary lead were found from h.f.s. measurements of spectral lines by several investigators<sup>1, 2, 3</sup> to be  $I=0$  for Pb<sup>208</sup> and Pb<sup>206</sup>, and  $I=\frac{1}{2}$  for Pb<sup>207</sup>. Most of the lines observed were those of Pb I. The h.f.s. of a few of the more intense lines of Pb II was measured from which the isotope shift and Pb<sup>207</sup> splitting was found for several levels. In the present work an attempt was made to increase the intensity of the Pb II radiation from a hollow cathode tube in order to observe the h.f.s. of the weaker lines. The Paschen-Schüler type tube with a hollow iron cathode (2.5 cm diameter  $\times$  7.5 cm), supported in the center of a brass tube (10 cm diameter  $\times$  25 cm) serving as the anode, and the conditions of excitation, with the exception of the He pressure were similar to

those used in the investigation of the h.f.s. of Pb I<sup>3</sup>. It was found that a He pressure of about 1.0 cm of Hg and currents from 50 to 500 ma would produce a Pb II spectrum much more intense than that of Pb I. With these currents and no cooling of the cathode all of the h.f.s. components of Pb II were very sharp and it was possible to operate the tube with a current as high as 500 ma for several weeks continuously before a few grams of lead, previously placed in the cathode, were completely carried over as a fine powder to the anode. Any increase of current above 500 ma caused very little increase in the intensity of the Pb II spectrum, but a very small increase of current at this point showed a large gain in the radiation due to Pb I. At about 600 ma the more intense lines of both spectra seemed to be of about the same intensity and with larger currents the arc lines were decidedly the stronger. A large number of new lines always appeared with the above He pressure which had

<sup>1</sup> H. Kopfermann, Zeits. f. Physik 75, 363 (1932).

<sup>2</sup> H. Schüler and E. G. Jones, Zeits. f. Physik 75, 563 (1932).

<sup>3</sup> J. L. Rose and L. P. Granath, Phys. Rev. 40, 760 (1932).

TABLE I. Measured separation of h. f. s. components in Pb II lines.†  
( $\Delta\nu 10^{-3} \text{ cm}^{-1}$ .)

$\lambda$	Classification	Pb <sup>208</sup>	Pb <sup>206</sup>	Pb <sup>207</sup>	Pb <sup>207</sup>	Pb <sup>207</sup>	$\lambda$	Classification	Pb <sup>208</sup>	Pb <sup>206</sup>	Pb <sup>207</sup>	Pb <sup>207</sup>	Pb <sup>207</sup>
8545.0	$7P_{3/2} - p^2 2D_{5/2}$	0	+338	+673	-438	X	3451.7	$p^2 4P_{5/2} - 6F_{7/2}$	0	-286	-572	+374	
6229.7	$p^2 2D_{5/2} - 9P_{3/2}$	0	-345	-681	+443		2887.3	$p^2 4P_{5/2} - 7F_{7/2}$			(Same as $\lambda 5372.1$ )		
4788.1	$p^2 2D_{5/2} - 10P_{3/2}$	0	-350	-694	+443		5367.3	$p^2 4P_{5/2} - 5F_{5/2}$			( " " " )		
4195.5	$p^2 2D_{5/2} - 11F_{3/2}$	0	-341	-692	+438		3450.0	$p^2 4P_{5/2} - 6F_{5/2}$			( " " " )		
8395.6	$7P_{3/2} - 8S_{1/2}$	0	~0	X	~-60	X	2886	$p^2 4P_{5/2} - 7F_{5/2}$			( " " " )		
4152.8	$7P_{3/2} - 9S_{1/2}$	0	very small	X	~-165	X	5308.2	$8P_{1/2} - 12S_{1/2}$			(Single)		
3261.0*	$7P_{3/2} - 10S_{1/2}$			(Single)			5109.6	$p^2 2D_{5/2} - 7F_{5/2}$			(Same as $\lambda 7193.6$ )		
2914.5*	$7P_{3/2} - 11S_{1/2}$			(Single)			5049.3	$p^2 2D_{3/2} - 6F_{5/2}$	0	-351	-80	-430	
8335.0	$p^2 2D_{3/2} - 8P_{1/2}$			(Same as $\lambda 5049$ )			3927.3	$p^2 2D_{3/2} - 7F_{5/2}$	0	-360	-84	-432	
7558.7	$7D_{5/2} - 7F_{7/2}$	0	-70	-133	+88		3463.6	$p^2 2D_{3/2} - 8F_{5/2}$	0	-348	-79	-422	
6009.7	$7D_{5/2} - 8F_{7/2}$			(Same as $\lambda 7558.7$ )			3217.9	$p^2 2D_{3/2} - 9F_{5/2}$			(Same as $\lambda 5049.3$ )		
5306.8	$7D_{5/2} - 9F_{7/2}$			( " " " )			3068.5?	$p^2 2D_{3/2} - 10F_{5/2}$			( " " " )		
4912.7	$7D_{5/2} - 10F_{7/2}$			( " " " )			5042.5*	$7P_{1/2} - 7D_{3/2}$			(Single)		
7193.6	$p^2 2D_{5/2} - 6F_{7/2}$	0	-348	-692	+436		3455.0	$7P_{1/2} - 8D_{3/2}$	0	+168	X	+317	X
5111.9	$p^2 2D_{5/2} - 7F_{7/2}$	0	-354	-680	+434		2873.0*	$7P_{1/2} - 9D_{3/2}$			(Single)		
4352.7	$p^2 2D_{5/2} - 8F_{7/2}$	0	-353	-698	+440		2634.3*	$7P_{1/2} - 10D_{3/2}$			( " )		
3971.3	$p^2 2D_{5/2} - 9F_{7/2}$			(Same as $\lambda 7193.6$ )			2498.9*	$7P_{1/2} - 11D_{3/2}$			( " )		
3746.9	$p^2 2D_{5/2} - 10F_{7/2}$			( " " " )			4684.9	$p^2 2D_{3/2} - 9P_{1/2}$			(Same as $\lambda 5049.3$ )		
3601.8	$p^2 2D_{5/2} - 11F_{7/2}$			( " " " )			3784.0	$p^2 2D_{3/2} - 10P_{1/2}$			(Pattern masked by $\lambda 3785.9$ )		
3501.9	$p^2 2D_{5/2} - 12F_{7/2}$			( " " " )			3389.4	$p^2 2D_{3/2} - 11P_{1/2}$	0	-353	-76	-421	
7013.2	$7D_{3/2} - 7F_{5/2}$			(Single)			4476.3	$p^2 4P_{5/2} - 8P_{3/2}$			(Same as $\lambda 5372.1$ )		
6790.8	$7P_{1/2} - 8S_{1/2}$	0	~0	X	(-100)	(+100)	4386.4	$6D_{5/2} - 5F_{5/2}$	0	-86	**		
3718.2	$7P_{1/2} - 9S_{1/2}$	0	very small	X	~-168	X	3016.4	$6D_{3/2} - 6F_{5/2}$			(Same as $\lambda 4386.4$ )		
2986.9*	$7P_{1/2} - 10S_{1/2}$			(Single)			2576.6	$6D_{3/2} - 7F_{5/2}$			( " " " )		
6660.0	$7S_{1/2} - 7P_{1/2}$	0	+53	X	+322	-105	4245.1	$6D_{5/2} - 5F_{7/2}$	0	-202	-425	+288	
6518.2	$8P_{3/2} - 11S_{1/2}$			(Single)			2948.5	$6D_{5/2} - 6F_{7/2}$			(Same as $\lambda 4245.1$ )		
6181.9	$8P_{3/2} - 10D_{3/2}$			( " )			2526.7	$6D_{5/2} - 7F_{7/2}$			( " " " )		
6041.4	$p^2 4P_{1/2} - 7F_{1/2}$	0	-413	-657	+956	X	2326.2	$6D_{5/2} - 8F_{7/2}$			( " " " )		
5163.8	$p^2 4P_{1/2} - 7P_{3/2}$	0	-412	-659	+916	X	4242.5	$6D_{5/2} - 5F_{5/2}$			( " " " )		
5876.7*	$7P_{3/2} - 7D_{3/2}$			(Single)			2947.5	$6D_{5/2} - 6F_{5/2}$			( " " " )		
3827.2	$7P_{3/2} - 8D_{3/2}$	0	+168	X	~+305	XX	2526	$6D_{5/2} - 7F_{5/2}$			( " " " )		
3125.6*	$7P_{3/2} - 9D_{3/2}$			(Single)			3785.9	$p^2 4P_{3/2} - 5F_{5/2}$	0	-428	-629	+328	
2845.2*	$7P_{3/2} - 10D_{3/2}$			( " )			2719.8	$p^2 4P_{3/2} - 6F_{5/2}$			(Same as $\lambda 3785.9$ )		
5608.8	$7S_{1/2} - 7P_{3/2}$	0	+50	-54	+275	~-80	2356.9	$p^2 4P_{3/2} - 7F_{5/2}$			( " " " )		
2717.5	$7S_{1/2} - 8P_{3/2}$	0	(+50)	X	~+274		3699.2	$7P_{3/2} - p^2 2S_{1/2}$	0	+383	+689	¶	X
5544.6	$7P_{3/2} - 7D_{5/2}$	0	+65	+124	-77	X	3665.6	$6D_{5/2} - 8P_{3/2}$	0	-205	-421	+282	
3714.0*	$7P_{3/2} - 8D_{5/2}$			(Single)			2772.7	$6D_{5/2} - 9P_{3/2}$	0	-206	-412	+295	
3117.7*	$7P_{3/2} - 9D_{5/2}$			( " )			3649.0	$7P_{3/2} - p^2 2P_{3/2}$	0	+225	X	+423	XX
2840.6*	$7P_{3/2} - 10D_{5/2}$			( " )			3309.2	$7P_{1/2} - p^2 2P_{3/2}$	0	+227	X	(+455)	X
2684.9*	$7P_{3/2} - 11D_{5/2}$			( " )			5857	?	0	~0	-131		
2587.2*	$7P_{3/2} - 12D_{5/2}$			( " )			4182.(5)	?	0	-361	-760	(?)	
2521.1*	$7P_{3/2} - 13D_{5/2}$			( " )			3352	?	0	(-305)†	+187	(?)	
5372.1	$p^2 4P_{5/2} - 5F_{7/2}$	0	-283	-570	+387		3284.(2)	?	0	small	-350		

† The following lines were observed and found to be single:  $\lambda 9063.7$ ,  $6081.5$ ,  $5074.6$ ,  $4582.3$ ,  $4296.6$ ,  $4113.4$ ,  $3987.6$ ,  $5F_{5/2} - mG$  ( $m=5, \dots, 11$ );  $\lambda 9050.7$ ,  $6075.8$ ,  $5070.7$ ,  $4579.1$ ,  $4293.8$ ,  $4110.8$ ,  $3985.2$ ,  $5F_{7/2} - mG$  ( $m=5, \dots, 11$ );  $\lambda 8719.7$ ,  $7739.8$ ,  $7165.1$ ,  $6791.7$ ,  $6533.1$ ,  $6345.0$ ,  $6203.7$ ,  $6094.0$ ,  $6F_{5/2} - mG$  ( $m=8, \dots, 15$ );  $\lambda 8710.1$ ,  $7732.3$ ,  $7158.7$ ,  $6785.9$ ,  $6527.8$ ,  $6339.8$ ,  $6198.8$ ,  $6089.4$ ,  $6F_{7/2} - mG$  ( $m=8, \dots, 15$ );  $\lambda 7050.7$ ,  $5767.9$ ,  $5155.8$ ,  $4804.5$ ,  $4581.3$ ,  $4428.7$ ,  $4319.2$ ,  $4237.6$ ,  $8P_{1/2} - mD_{3/2}$  ( $m=9, \dots, 16$ );  $\lambda 7632.2$ ,  $6160.2$ ,  $5472.4$ ,  $5081.2$ ,  $4833.7$ ,  $4665.5$ ,  $4544.8$ ,  $4454.9$ ,  $8P_{3/2} - mD_{5/2}$  ( $m=9, \dots, 16$ ).

X This expected Pb<sup>207</sup> component was not observed. It is either too near to a stronger component to be resolved or of insufficient intensity to be photographed.

not been observed when working at much lower pressures.<sup>3</sup> The entire spectrum from 2200 to 11,000Å was photographed in the first order of a 21-ft. concave grating<sup>4</sup> and it was found on

<sup>4</sup> The Anderson grating used at present in this mounting is the property of Townsend Harris Hall, College of the City of New York.

XX Two very weak Pb<sup>207</sup> components were not observed.

\* The several components expected for this line are too close to each other to be resolved.

\*\* The two Pb<sup>207</sup> components are masked by Pb<sup>208</sup> and Pb<sup>206</sup>.

¶ The spectral range of the Lummer-Gehrcke plate used in observing  $\lambda 3699.2$  was a little more than 1.10 cm<sup>-1</sup>. It is very probable that this component nearly coincided with the Pb<sup>208</sup> component in the next order of the interference pattern.

†  $\lambda 3352$  was not observed for uranium-lead and it is not certain that this apparent component is due to Pb<sup>208</sup>. This may be a weak line very near to  $\lambda 3352$ .

measuring their wavelengths that very few of the new lines had been previously reported. A comparison of the h.f.s. patterns of ordinary lead with those of uranium-lead, which contained more than 90 percent of Pb<sup>206</sup>, proved the unknown lines, which showed h.f.s., to be

definitely those of Pb. This is a very effective method of identifying Pb lines, especially those with observable isotope shifts. The strongest apparent component which is due to Pb<sup>206</sup> of uranium-lead always coincides with the next to the strongest apparent component of ordinary lead which is also due to Pb<sup>206</sup>, the second abundant isotope of ordinary lead. Dr. L. T. Earls and Professor R. A. Sawyer, of the University of Michigan, who used a much smaller cathode and lower pressures of He, have observed these new lines. Practically all of them have been included in the new classification of Pb II lines which they have reported in the article immediately preceding this one.

#### HYPERFINE STRUCTURE MEASUREMENTS

The h.f.s. patterns were investigated by the use of fused quartz and glass Fabry-Perot interferometers with silica-aluminum and silvered surfaces, and two Lummer-Gehrcke plates, one of crystal quartz (200×30×3.518 mm), the other of glass (130×15×4.991 mm). Interferometer spacers ranging from 1.78 mm to 25 mm in thickness were used. The h.f.s. data for the Pb II lines which could be observed and measured are tabulated in Table I. These measured separations of the apparent components of ordinary lead are considered accurate to  $\pm 5.0 \times 10^{-3} \text{ cm}^{-1}$  except those indicated in the table as approximate values.

The isotopes, Pb<sup>208</sup> and Pb<sup>206</sup>, with  $I=0$  always give single lines but several components

TABLE II. Theoretically expected relative intensities for Pb<sup>207</sup> components.

For $I=1/2$															
$F \rightarrow$	0	0	1	1	1	2	2	2	3	3	3	4	4	4	4
	0	1	0	1	2	1	2	3	2	3	4	3	4	5	5
$J$															
1/2→1/2	0	1	1	2	.	.	.	.	.	.	.	.	.	.	.
1/2→3/2		2	1	5	.	.	.	.	.	.	.	.	.	.	.
3/2→1/2			2	1	5	.	.	.	.	.	.	.	.	.	.
3/2→3/2				5	1	1	9	.	.	.	.	.	.	.	.
3/2→5/2					9	1	14	.	.	.	.	.	.	.	.
5/2→3/2						9	1	14	.	.	.	.	.	.	.
5/2→5/2							14	1	1	20	.	.	.	.	.
5/2→7/2								20	1	27	.	.	.	.	.
7/2→5/2									20	1	27	.	.	.	.
7/2→7/2										27	1	1	35	.	.
7/2→9/2											35			1	44

TABLE III. Isotope shift and splitting of Pb II terms ( $\Delta\nu 10^{-3} \text{ cm}^{-1}$ ).

Term	Term splitting for Pb <sup>207</sup> , $I=1/2$	Isotope shift of Pb <sup>206</sup> with respect to Pb <sup>208</sup>
6s <sup>2</sup> 7s <sup>2</sup> S <sub>1/2</sub>	+ 350	- 53
8s <sup>2</sup> S <sub>1/2</sub>	+1(00)	~ 0
9s <sup>2</sup> S <sub>1/2</sub>	+2(00)	~ 0
m s <sup>2</sup> S <sub>1/2</sub> , $m \geq 10$	0	0
6p <sup>2</sup> P <sub>1/2</sub>	No data	
7p <sup>2</sup> P <sub>1/2</sub>	~ + 80	~ 0
m <sup>2</sup> P <sub>1/2</sub> , $m \geq 8$	0	0
6p <sup>2</sup> P <sub>3/2</sub>	No data	
7p <sup>2</sup> P <sub>3/2</sub>	~ + 20	~ 0
m p <sup>2</sup> P <sub>3/2</sub> , $m \geq 8$	0	0
6d <sup>2</sup> D <sub>3/2</sub>	~ + 90	+ 86
7d <sup>2</sup> D <sub>3/2</sub>	0	0
8d <sup>2</sup> D <sub>3/2</sub>	- 250	+168
md <sup>2</sup> D <sub>3/2</sub> , $m \geq 9$	0	0
6d <sup>2</sup> D <sub>5/2</sub>	+ 713	+202
7d <sup>2</sup> D <sub>5/2</sub>	+ 221	+ 70
md <sup>2</sup> D <sub>5/2</sub> , $m \geq 8$	0	0
m f <sup>2</sup> F <sub>5/2</sub> , $m \geq 5$	0	0
m f <sup>2</sup> F <sub>7/2</sub> , $m \geq 5$	0	0
m g <sup>2</sup> G <sub>7/2, 9/2</sub> , $m \geq 5$	0	0
6s 6p <sup>2</sup> <sup>4</sup> P <sub>1/2</sub>	+159(4)	+413
<sup>4</sup> P <sub>3/2</sub>	+ 957	+428
<sup>4</sup> P <sub>5/2</sub>	+ 957	+283
<sup>2</sup> D <sub>3/2</sub>	- 348	+360
<sup>2</sup> D <sub>5/2</sub>	+1120	+348
<sup>2</sup> P <sub>1/2</sub>	No data	
<sup>2</sup> P <sub>3/2</sub>	-36(2)	+227
<sup>2</sup> S <sub>1/2</sub>	+18(08)	+383

may be expected for Pb<sup>207</sup> with  $I=\frac{1}{2}$ . In lines of ordinary lead where there is an observable isotope displacement the strongest apparent component is always due to the most abundant isotope, Pb<sup>208</sup>, and the next to the strongest apparent component to the next abundant isotope, Pb<sup>206</sup>. The relative intensities and the number of weaker components, due to Pb<sup>207</sup> in the h.f.s. patterns, vary with the  $J$ -values of the terms for the lines. Table II shows for various  $J$ -values the theoretical relative intensities of the components expected for Pb<sup>207</sup>. In Table I all of the components are given from left to right in the order of their expected relative intensities.

#### Pb<sup>207</sup> TERM SPLITTING

The classification, kindly furnished by Dr. Earls and Professor Sawyer, for the lines whose h.f.s. had been observed made it possible to find the Pb<sup>207</sup> splitting and isotope shift for all the terms of Pb II with the exception of 6s<sup>2</sup>6p<sup>2</sup>P<sub>1/2, 3/2</sub> and 6s6p<sup>2</sup><sup>2</sup>P<sub>1/2</sub>. The lines to the former terms have wavelengths too short for the h.f.s. to be

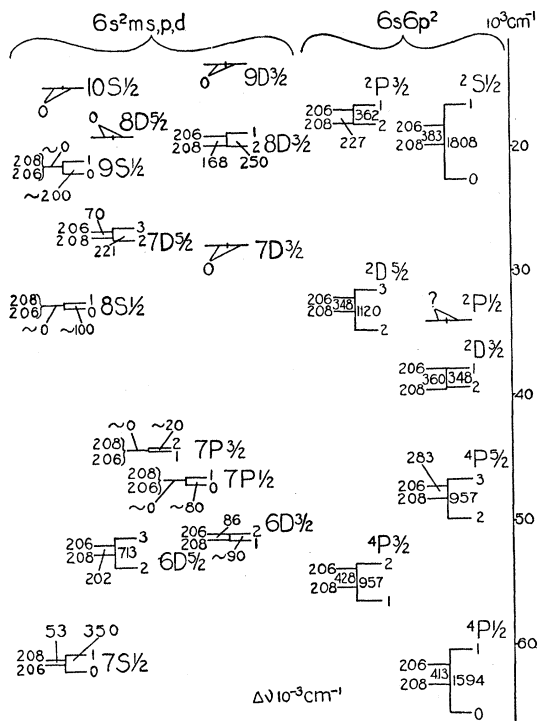


FIG. 1. Isotope shift between  $Pb^{208}$  and  $Pb^{206}$ , and  $Pb^{207}$  splitting of  $Pb$  II terms. Higher terms for  $6s^2ms, p, d$  and all  $6s^2mf, g$  terms, which are not included in the diagram, are single. No data for  $6s^26p^2P_{1/2, 3/2}$  and  $6s6p^2^2P_{1/2}$ .

easily resolved and no line to the latter term was found with sufficient intensity to photograph its interference pattern. The calculated  $Pb^{207}$  term separations are shown in the second column of Table III. A negative sign indicates that the h.f.s. levels for the term are inverted. All of the terms in which splitting was found are included in the energy level diagram in Fig. 1. The  $Pb^{207}$  levels with the  $F$ -values and calculated separation are indicated on the right side of the h.f.s. diagram for each term. Many of the  $Pb^{207}$  term separations listed represent an average of several values. These values could be found independently by using the h.f.s. data for different lines or groups of lines which have a common term. The largest errors are expected in the values of the splitting for  $8s^2S_{1/2}$ ,  $9s^2S_{1/2}$ , and  $p^2^2S_{1/2}$ . The separation for  $8s^2S_{1/2}$  was determined from the patterns of two lines  $\lambda\lambda 8395.6$  and  $6790.8$ . Only one  $Pb^{207}$  component could be observed for the former line and the measurements for the latter are not very accurate. In each of the lines

to  $9s^2S_{1/2}$  the position of the  $Pb^{207}$  component had to be determined with respect to a very broad apparent component which actually consisted of three unresolved components. The value of the splitting for  $p^2^2S_{1/2}$  was calculated indirectly from the observed structure of  $\lambda 3699.2$ . This is a very weak line which required more than ten hours to photograph its pattern and its proximity to other lines made it very difficult to measure. The best photographs showed only one component which could be due to  $Pb^{207}$ . In making a calculation for the position of other possible components it was assumed that the observed component was the most intense one expected for  $Pb^{207}$ , and that the center of gravity of the  $Pb^{207}$  term was between the  $Pb^{208}$  and  $Pb^{206}$  terms and displaced with respect to  $Pb^{208}$  by a little more than 60 percent of the displacement for  $Pb^{206}$  with respect to  $Pb^{208}$ . The latter assumption was used on the basis that this type of isotope displacement has been observed for all terms of both  $Pb$  I and  $Pb$  II where the shift could be measured. The calculations showed that the next to the strongest  $Pb^{207}$  component, in the interference pattern for the Lummer-Gehrcke plate used, would nearly coincide with the  $Pb^{208}$  component in an adjacent order and would not be resolved. If this is the case the separation for the  $^2S_{1/2}$  level is approximately  $1.808 \text{ cm}^{-1}$ . A very large separation for this term is in agreement with the equations discussed below. The error expected in the above result will be several times that in the individual measured separations of the components of  $\lambda 3699.2$ .

ISOTOPE SHIFT

According to the data for several series of lines from  $m^2F$  levels ending on a common level, the isotope shift between  $Pb^{208}$  and  $Pb^{206}$  is practically the same for all lines ending on the same level. It appears that the displacements must be attributed to the lower levels rather than the  $^2F$  terms. In the last column of Table III the shifts are based on the assumption that the isotope separation for  $^2F$  terms is zero. Isotope shifts for lead have been discussed by Rosenthal and Breit<sup>5, 6</sup> and the shifts listed are in general

<sup>5</sup> J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).  
<sup>6</sup> G. Breit, Phys. Rev. **42**, 348 (1932).

agreement with theory. The shifts observed in  $\lambda\lambda 6660.0$  and  $5608.8$  and contributed to 7P terms by Kallman and Schüler<sup>7</sup> were not in accordance with the theory which predicted the shift to be the result of a displacement in the 7S term and opposite in direction to the shifts for terms of the  $6s6p^2$  configuration. Additional data for other lines, recently classified by Earls and Sawyer, definitely prove that the above shifts are the result of a displacement between the  $Pb^{208}$  and  $Pb^{206}$  levels for the 7S term and in the direction suggested by theory. For the 6D terms where a negligible shift is expected, it was pointed out<sup>5</sup> that the shifts observed in these terms were the results of perturbations and could be contributed to certain terms with the same  $J$ -values of the  $6s6p^2$  configuration. (In the above paper  $p^2\ ^2D_{3/2, 5/2}$  are now classified as  $p^2\ ^4P_{3/2, 5/2}$ .) In the same way shifts for  $7D_{5/2}$  and  $8D_{3/2}$  can be explained as the result of  $6s6p^2$  terms in the proximity of these  $D$  terms. No doubt some of the  $ms^2S_{1/2}$  terms are perturbed to some extent by  $6s6p^2$  terms with  $J=\frac{1}{2}$  but the isotope displacement was too small to be observed for the higher terms and for  $7S_{1/2}$  it was opposite in direction to the displacements for  $6s6p^2$  terms. When the isotope shifts for the  $mD$  terms are added to the observed shifts for the proper  $6s6p^2$  terms the displacements due to this configuration are nearly the same for all terms. This is what one would expect for terms with the same electron configuration, as a result of nuclear field perturbations.

A very weak component, attributed to a lesser abundant isotope,  $Pb^{204}$ , was observed by Schüler and Jones<sup>2</sup> for  $\lambda\lambda 7228$ , 5201 and 5005 of Pb I and  $\lambda 5609$  of Pb II. These lines were photographed with long exposures during the course of the present work but a faint ghost appeared in each order of the interference pattern and the position of the ghost in orders nearest the center, where the dispersion is large, was too near the position of the reported  $Pb^{204}$  component to be certain of the existence of the latter. The relative position of the ghost in any one order varied with the order of interference and in the fourth order from the center, the ghost was in a position which would not interfere with the observance of

a  $Pb^{204}$  isotope. The failure to observe any  $Pb^{204}$  component in this order and other orders farther from the center may have been due to the small dispersion in these orders. Another set of interferometer plates, which do not produce the same type of ghost, are now available and will be used in re-photographing the above lines, and also  $\lambda\lambda 6660$  and  $4386$ , whose patterns should show a  $Pb^{204}$  component.

#### INTERMEDIATE COUPLING FOR $6s6p^2$ CONFIGURATION

With the above  $Pb^{207}$  term separations it is possible to make a comparison with theory for the h.f.s. constants of the  $6s6p^2$  configuration. In order to do this it is first necessary to consider the gross structure of the  $6s6p^2$  terms. The position of levels in intermediate coupling can be obtained as the solution of certain algebraic equations (secular equations) which involve the interaction integrals  $G^1$ ,  $X$  and  $a$ .<sup>8, 9, 10</sup> By using the  $^3P_{0, 1, 2}$  and  $^1P_1$  levels of the  $6s6p$  configuration in Pb III,  $G^1$  was found to be  $3.6 \times 10^4$   $cm^{-1}$  and  $a = 1.24 \times 10^4$   $cm^{-1}$ . Then, by using the levels  $^3P_{0, 2}$ ,  $^1D_2$ ,  $^1S_0$  of the  $6s^26p^2$  configuration of Bi II, the values  $X = 3.36 \times 10^3$   $cm^{-1}$  and  $a = 1.22 \times 10^4$   $cm^{-1}$  were obtained. Since the  $a$ 's as calculated from these two configurations agree very well it is reasonable to suppose that the values of the parameters so obtained are valid for the  $6s6p^2$  of Pb II.

The energy matrix was calculated in  $ls$  coupling with the values  $G^1$ ,  $X$  and  $a$ .<sup>9</sup> From this one readily obtains the energies and expressions for wave functions in intermediate coupling in terms of wave functions corresponding to  $ls$  or  $jj$  coupling. The calculated energies, referred to the midpoint between  $^4P_{5/2}$  and  $^2D_{5/2}$ , are shown in comparison with the experimental values of Earls and Sawyer in Fig. 2. (In this figure slightly different scales are used in plotting the two sets of data.) The levels  $W = 27.4 \times 10^3$   $cm^{-1}$  and  $W = 9.7 \times 10^3$   $cm^{-1}$  are undoubtedly  $^2S_{1/2}$  and  $^2P_{1/2}$ , respectively. The assignments for all the other levels could be made without difficulty.

<sup>8</sup>  $G^1$  is Slater's radial exchange integral between the  $s$  and  $p$  electrons,  $X = 3/25 F^2$  is the interaction integral between the two  $p$  electrons, and  $a$  is the magnetic interaction of the  $p$  electrons.

<sup>9</sup> M. H. Johnson, Jr., Phys. Rev. **39**, 197 (1932).

<sup>10</sup> G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).

<sup>7</sup> H. Kallman and H. Schüler, Ergebnisse der Exakten Naturwissenschaften **11**, 134-175 (1932).

Experimental	Calculated
${}^2P_{3/2} = 16575 \text{ cm}^{-1}$	${}^2P_{3/2} = +30800 \text{ cm}^{-1}$
${}^2S_{1/2} = 16947$	$J=1/2 = +27400$
${}^2D_{3/2} = 32272$	${}^2D_{3/2} = +10600$
${}^2P_{1/2} = 32999$	$J=1/2 = +9700$
${}^2D_{5/2} = 38161$	${}^2D_{3/2} = +4000$
	$= 0$
${}^4P_{3/2} = 47336$	${}^4P_{3/2} = -10600$
${}^4P_{1/2} = 55116$	${}^4P_{3/2} = -17300$
${}^4P_{1/2} = 63333$	${}^4P_{1/2} = -28000$

FIG. 2. Pb II  $6s6p^2$  term values. The calculated energies are referred to the midpoint between  ${}^4P_{5/2}$  and  ${}^2D_{5/2}$ .

The calculated results, neglecting perturbations due to even terms of other configurations, are in as good agreement as could be expected with the experimental values. This indicates that the assignment of these levels to the  $6s6p^2$  configuration is essentially correct. At the same time deviations of levels from calculated positions are connected with decreased isotope shifts, showing that the isotope shift is due to the  $6s$  electron. The wave functions determined are given by the following transformation matrices:

$J=5/2$	${}^2D'_{5/2}$	${}^2D_{5/2}$	${}^2P_{5/2}$
	${}^2P'_{5/2}$	0.89	-0.463
		.463	.89
$J=3/2$	${}^2D'_{3/2}$	${}^2D_{3/2}$	${}^4P_{3/2}$
	${}^4P'_{3/2}$	0.943	0.0873
	${}^2P'_{3/2}$	-.119	.99
		.319	.114
			.943
$J=1/2$	${}^4P'_{1/2}$	${}^4P_{1/2}$	${}^2S_{1/2}$
	${}^2P'_{1/2}$	0.935	-0.138
	${}^2S'_{1/2}$	.305	.775
		-.184	.605
			.775

where the unprimed states are for  $ls$  coupling and the primed for intermediate coupling. The trans-

formation from  $jj$  into intermediate coupling can now be obtained by multiplying the above matrices by the transformation from  $ls$  to  $jj$  coupling given in Table VIII of Breit and Wills.<sup>10</sup> The coefficients of the  $jj$  to intermediate coupling transformation are just the  $c$ 's of the above reference, so that the separation factors,  $A$ , in intermediate coupling can be immediately obtained from their formulae:

$$A({}^2D_{5/2}) = 0.763a' + 0.042a'' - 0.461a''' + 0.200a(s) \quad (1)$$

$$A({}^4P_{5/2}) = .646a' + .160a'' + .461a''' + .200a(s) \quad (2)$$

$$A({}^2D_{3/2}) = .871a' + .302a'' - .463a''' - .176a(s) \quad (3)$$

$$A({}^4P_{3/2}) = .926a' - .192a'' + .236a''' + .268a(s) \quad (4)$$

$$A({}^2P_{3/2}) = 1.137a' + .019a'' + .226a''' - .159a(s) \quad (5)$$

$$A({}^4P_{1/2}) = .306a' - .061a'' + 2.033a''' + .759a(s) \quad (6)$$

$$A({}^2P_{1/2}) = 1.110a' - .221a'' - .956a''' + .088a(s) \quad (7)$$

$$A({}^2S_{1/2}) = .252a' - .050a'' - 1.100a''' + .805a(s). \quad (8)$$

In these equations the h.f.s. coupling constants,  $a'$ ,  $a''$ ,  $a(s)$ , denote the values of  $A$  for the  $p_{3/2}$ ,  $p_{1/2}$ , and  $6s$  electrons respectively;  $a'''$  is an analogous constant which owes its existence to the fact that there are non diagonal matrix elements of the nuclear magnetic field between  $p_{1/2}$  and  $p_{3/2}$  states. The sum rule equations<sup>11, 12</sup> require a knowledge of  $A$  for all of the levels of the  $6s6p^2$  configuration in order to be solved for  $a'$ ,  $a''$ , and  $a(s)$ , but with the above equations these constants together with  $a'''$  can be obtained when  $A$  is accurately known for any four of the eight possible levels. When various values of  $A$ , calculated directly from the observed  $\text{Pb}^{207}$  splittings for  $6s6p^2$  terms in Table II, were substituted in the equations it was impossible to find reasonable values for the constants. This result was not surprising since one would expect the perturbations between these terms and even terms of other configurations with the same  $J$ -values to have an effect on the  $\text{Pb}^{207}$  splitting for

<sup>11</sup> S. Goudsmit, Phys. Rev. **37**, 663 (1931).

<sup>12</sup> R. A. Fisher and S. Goudsmit, Phys. Rev. **37**, 1057 (1931).

terms in which an effect for the isotope displacements was observed. For the  ${}^2D$  terms of the  $6s^2md$  configuration the  $\text{Pb}^{207}$  splitting would be expected to be very little different from the splitting for  $6s^2mf$  terms which was found to be zero. The fact that large splittings were found in  ${}^2D$  terms only where isotope shifts were observed and that a large inverted splitting was observed for  $8D_{3/2}$ , in the proximity of  $p^2 {}^2P_{3/2}$  with inverted levels, and between two single terms  $7D_{3/2}$  and  $9D_{3/2}$ , indicate that the splitting in  ${}^2D$  terms must be attributed to perturbations by  $6s6p^2$  terms.

More reasonable values for the constants were found when the splitting for the perturbed  $6s^2md$  terms was taken into account. The sum of the  $A$ 's for the perturbed and perturbing term was used in the calculations with Eqs. (1)–(8) because the sum rule applies to  $A$  values in such perturbations. Consistent results could not be found when Eq. (8) was used. This is no doubt due to the error in the calculated value for the separation of the levels of  ${}^2S_{1/2}$  and because of some perturbation effect between this term and  $9S_{1/2}$ , which could not be readily observed. The best results were obtained by using the sum of Eqs. (1) and (2) with a value of  $A$  from  $6D_{5/2}$ ,  $7D_{5/2}$ ,  ${}^2D_{5/2}$ ,  ${}^4P_{5/2}$ ; Eq. (3) with  $A$  from  ${}^2D_{3/2}$ ; Eq. (4) with  $A$  from  ${}^4P_{3/2}$  and  $6D_{3/2}$ ; and Eq. (6) with  $A$  from  ${}^4P_{1/2}$ . From the above four equations

$a(s) = 1.89$ ,  $a'' = 0.402$ ,  $a' = 0.078$ , and  $a''' = 0.07$  were determined. The result for  $a'$  is higher than expected and a plus value for  $a'''$  is meaningless. The expected values for these constants,  $a' = a''/17$  and  $a''' = -5a'/16$ , are very small and are quite sensitive to experimental error. Even in cases where there are no perturbations, it is almost impossible, experimentally to determine with sufficient accuracy  $A$  values which will give good results for  $a'$  and  $a'''$ . The value of  $a''$  is in good agreement with the following experimental values found from other spectra,  $\text{Pb I}$ ,<sup>3</sup> 0.370;  $\text{Bi I}$ ,<sup>11, 12</sup> 0.375 and 0.390;  $\text{Bi II}$ ,<sup>12</sup> 0.340. The value of  $a(s)$  for  $\text{Pb II}$  also compares favorably with other experimental values,  $\text{Bi II}$ ,<sup>12</sup> 1.60;  $\text{Bi III}$ ,<sup>12</sup> 1.80;  $\text{Bi IV}$ ,<sup>13</sup> 2.34;  $\text{Bi V}$ ,<sup>12</sup> 2.6.

In conclusion the writer wishes to express his appreciation to Dr. Earls and Professor Sawyer for their cooperation in sending unpublished data on the classification of  $\text{Pb II}$  which they have corrected and extended, to Professor G. Breit for his interest and many suggestions throughout the progress of this investigation, and to the National Research Council for a grant-in-aid, a part of which was used to obtain apparatus for this research.

<sup>13</sup> A. B. McLay and M. F. Crawford, Phys. Rev. **44**, 986 (1933).