

The Hyperfine Structure of Lead

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The hyperfine structure of several lines of Pb I and Pb II in the violet and ultra-violet regions has been determined. $\lambda\lambda 4168, 4062, 4058, 4019, 3739, 3683, 3671, 3639, 3572, 2873, 2833, 2823, 2802$ of Pb I, and $\lambda\lambda 4386, 4245, 3786, 3016, 2948$ of Pb II were found to have structure. $\lambda\lambda 2663, 2614, 2613, \text{ and } 2577$ of Pb I were observed and found to be simple. Exposures with uranium-lead showed that all of the above lines are single for Pb²⁰⁶. It was also found from the line patterns that there is a larger abundance of Pb²⁰⁷ than Pb²⁰⁸ in uranium-lead (Belgian Congo). The hyperfine splittings of $s^3P_{0,1}$ and $p^3P_{0,1,2}$ of Pb²⁰⁷ I were calculated. The center of gravity of the Pb²⁰⁷ terms and the single Pb²⁰⁶ and Pb²⁰⁸ terms for these levels were found to fall in the order of their masses. Much larger isotope displacements were observed for Pb II than for Pb I.

Variations in the relative intensities of certain lines of Pb I with excitation conditions made it appear that there may be something wrong in the classification of some of the lines with initial levels, $d^3D_{1,2}$ and $d^3F_{2,3}$. A change of several of the line patterns was observed with a variation of voltage and temperature.

INTRODUCTION

WITH a Paschen-Schüler tube¹ as a source, the hyperfine structure of Pb I and Pb II for ordinary and uranium-leads has been investigated from $\lambda 4386$ to $\lambda 2393$ by the use of two quartz Lummer-Gehrcke plates² ($197 \times 30 \times 6.55$ mm and $130 \times 15 \times 4.40$ mm). The lines, $\lambda\lambda 4168, 4062, \text{ and } 4019$, reported single by Janicki,³ Luneland,⁴ Wali Mohammed,⁵ and Wali Mohammed and Sharma,⁶ and $\lambda\lambda 3740, 3683, 3671, 3572, 2873, 2823, \text{ and } 2802$, found simple by the latter, have been observed to have structure. The line, $\lambda 4058$, found by all of the above investigators to have three components and by Murakawa⁷ to have five, appeared with four components which is in agreement with Kopfermann;⁸ $\lambda\lambda 2833$ and 3639 , observed by Wali Mohammed and Sharma with three components, were found to have four and five components, respectively. They have also reported two components for $\lambda 2614$ which we have found to be single. In addition to the above lines of Pb I, $\lambda\lambda 4386, 4245, 3786, 3016, \text{ and } 2948$ of Pb II, which appeared on the photographic plates when the pressure of He in the tube was high, were found to have structure. The measurements for $\lambda 4245$ agree with those made by Janicki, Wali Mohammed, and Murakawa. The separation of the two com-

¹ Schüler, Zeits. f. Physik **35**, 323 (1926).

² Kindly loaned by R. W. Wood.

³ Janicki, Ann. d. Physik **29**, 833 (1909).

⁴ Luneland, Ann. d. Physik **34**, 505 (1911).

⁵ Wali Mohammed, Astroph. J. **39**, 185 (1914).

⁶ Wali Mohammed and Sharma, Phil. Mag. **12**, 1106 (1931).

⁷ Murakawa, Zeits. f. Physik **72**, 793 (1931).

⁸ Kopfermann, Naturw. **19**, 400 (1931); **19**, 675 (1931).

ponents of $\lambda 4386$ agrees qualitatively with that found by Murakawa for this line.

APPARATUS

Two tubes, one for ordinary lead and the other for uranium-lead, were mounted at right angles to each other. No auxiliary heater was required to vaporize the lead in the hollow cathode since the discharge developed sufficient heat for this purpose. With large currents it was possible to bring the iron cathode to a red heat. The tubes were connected in series with a vacuum system in which He could be admitted and purified. The He with pressures from 2 mm. to 0.01 mm of Hg was continuously circulated through the two tubes and a trap filled with chabazite at liquid air temperature. The chabazite was very effective in cleaning up the nitrogen in the He and the gases given off by the metal parts of the discharge tube.

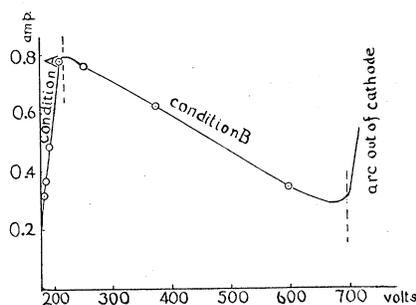


Fig. 1. Curve showing the variation of current with increasing voltage across the Paschen-Schüler lamp.

The source of excitation was a d.c. 3 k.w. motor-generator capable of producing voltages up to 1500 volts. A 450 ohm resistance was kept in series with the lamp which was being operated.

The Lummer-Gehrcke plates were used with a Hilger E2 quartz spectrograph. The light from the source, which was rendered slightly convergent by a large crystal quartz lens, entered the prism of the Lummer-Gehrcke plate after passing through a Wollaston prism. The fringes due to the extraordinary ray were brought to a focus by a quartz-fluorite lens² on the slit of the spectrograph. A brass slide was arranged in front of the wide slit which allowed the line patterns for two exposures to be photographed side by side on the same photographic plate. Since very long exposures were required for some of the lines, the Lummer-Gehrcke plates were mounted in a large, electrically heated, double wall, Beaver-board box whose temperature was kept constant to within 0.01° C by an ether thermostat.

VARIATION OF RELATIVE INTENSITIES OF LINES WITH EXCITATION CONDITIONS

A study of the general appearance of the spectra of Pb and He as the voltage of the generator was increased led to rather interesting results. Start-

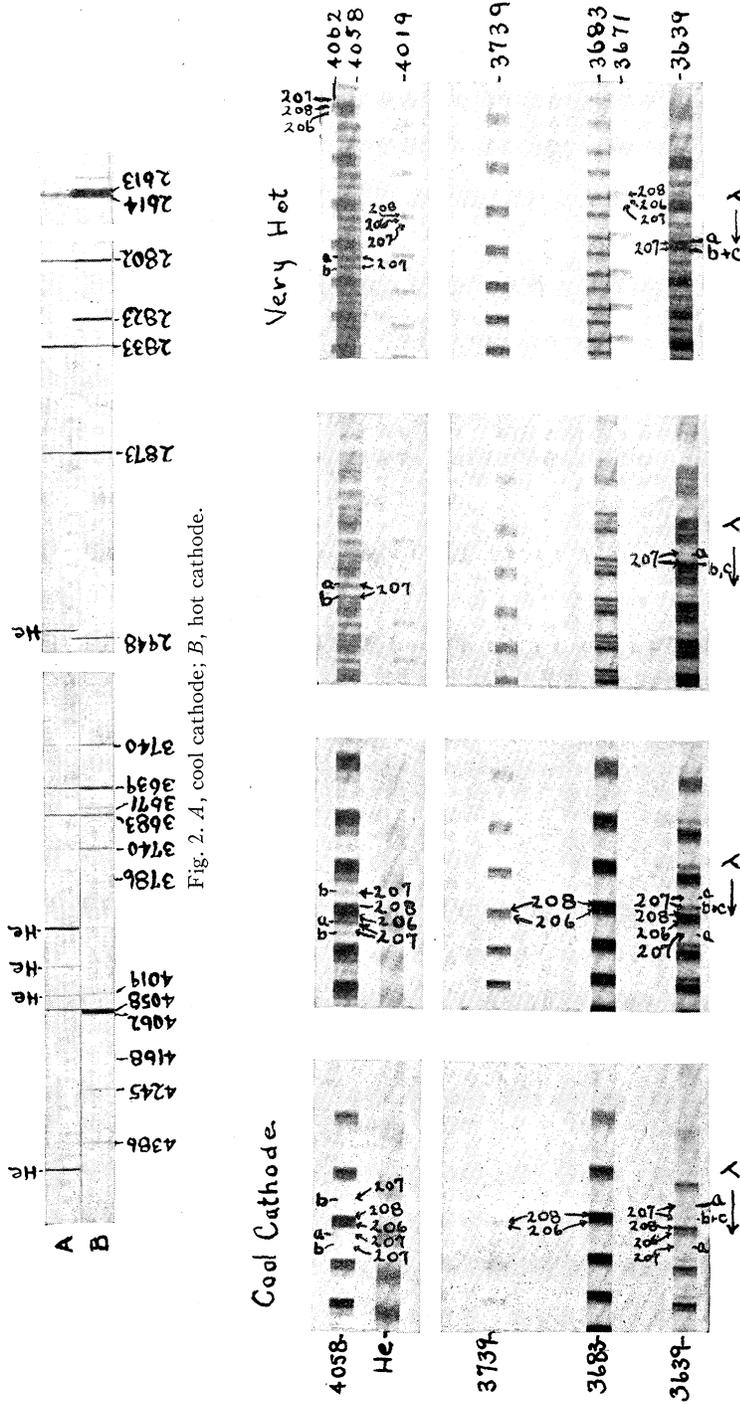
ing with 180 volts across the tube as measured directly by an electrostatic voltmeter and a current of 0.2 amp., an increase of the generator voltage caused a considerable increase of current through the tube with a very small increase of voltage across it. The voltage of the generator was steadily increased until the current was 0.8 amp. while the voltage on the tube went up to 210 volts. A further increase of generator voltage caused a decrease in the current with a large increase in the voltage across the tube. As shown in Fig. 1, it was possible to increase the generator potential until the current dropped to 0.3 amp. and the voltage of the tube increased to 700 volts before the discharge jumped out of the inside of the cathode and arched from the outside of the cathode to the walls of the tube.

For convenience the condition with increasing current and cool cathode will be called condition *A*, and with decreasing current and very hot cathode will be called condition *B*. The He spectrum was more intense than that of the lead in condition *A* with a small vapor pressure of lead while the lead spectrum was relatively stronger than the He in condition *B* with larger pressures of lead vapor. See Fig. 2. In *A* the lines, $\lambda\lambda 2873, 2833, 2802,$ and 2614 , were quite strong and of nearly equal intensities while $\lambda\lambda 2823$ and 2613 were several times less intense. The relative intensities of these lines varied on changing to condition *B* in such a manner that $\lambda\lambda 2613$ and 2823 appeared as intense as $\lambda\lambda 2873, 2802$ and 2614 , and at the same time $\lambda 2833$, which was the strongest in condition *A*, became the least intense of this group.

The variation of the relative intensities of these lines together with the fact that $\lambda 2657$ ($p^3P_1-d^3D_2$) was very faint in both conditions makes it appear that there may be something incorrect in the classification⁹ of some of the lines. This line would be expected to appear with intensity comparable to that of $\lambda 2873$ ($p^3P_2-d^3D_2$), provided there are no strong perturbations due to other terms.* The classification does not explain why $\lambda 2613$ ($p^3P_1-d^3D_1$) and 2823 ($p^3P_2-d^3F_2$) should be so much weaker than $\lambda\lambda 2802$ ($p^3P_2-d^3F_3$), 2873 ($p^3P_2-d^3D_2$), and 2614 ($p^3P_1-d^3F_2$) in condition *A* and finally approach the same intensities in condition *B*. If the final levels for all of these lines are members of the triplet $p^3P_{0,1,2}$ there should be no variations in the relative intensities of the above lines which have been classified with common initial levels. Furthermore, since $\lambda 4019$ ($p^1D_2-d^3F_3$) appeared, there should be expected a line, $\lambda 4063.4$ ($p^1D_2-d^3F_2$) which has never been reported for Pb I. Also since $\lambda\lambda 2613$ ($p^3P_1-d^3D_1$) and 2170 ($p^3P_0-d^3D_1$) appeared, the third member of this triplet, $\lambda 2822.6$ ($p^3P_2-d^3D_1$), is certainly expected. This line has also never been reported, nor observed by us. It is also difficult to see how $\lambda 2393$, a very strong line in both conditions, should be omitted from the classification. The way in which the more intense components of $\lambda\lambda 4058, 3683, 3639,$ and 2833 reversed with an increase of lead vapor pressure shows, however, that these lines are associated with the lower states of Pb I. This is in agreement with the classification. In Fig. 3 the series of photographs made with an increasing temperature of the cathode shows

⁹ Gieseler and Grotrian, *Zeits. f. Physik* **39**, 377 (1926).

* The possibility of such a perturbation has been indicated to us by Professor A. G. Shennstone.



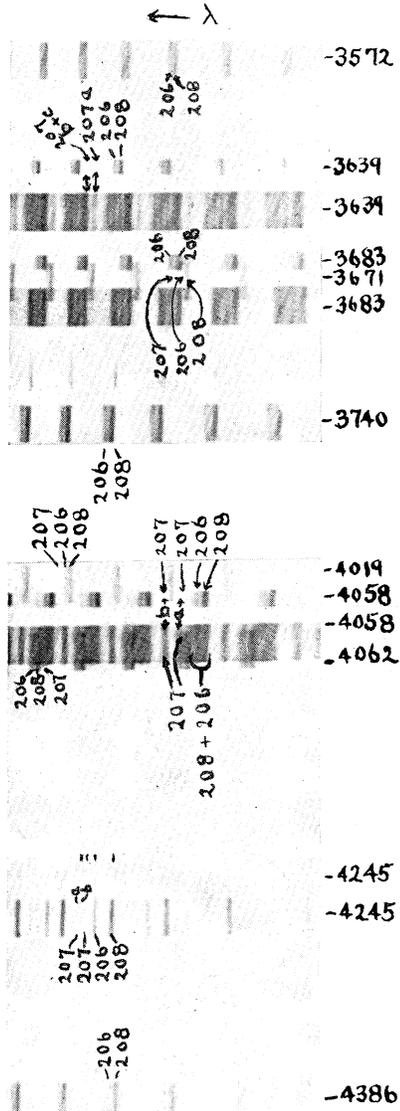


Fig. 4. Juxtaposed Lummer-Gehrcke plate patterns for conditions *A* and *B*. Condition *A* (narrow slit) is on the right of condition *B* (wide slit). Several weak lines appear only in condition *B*.

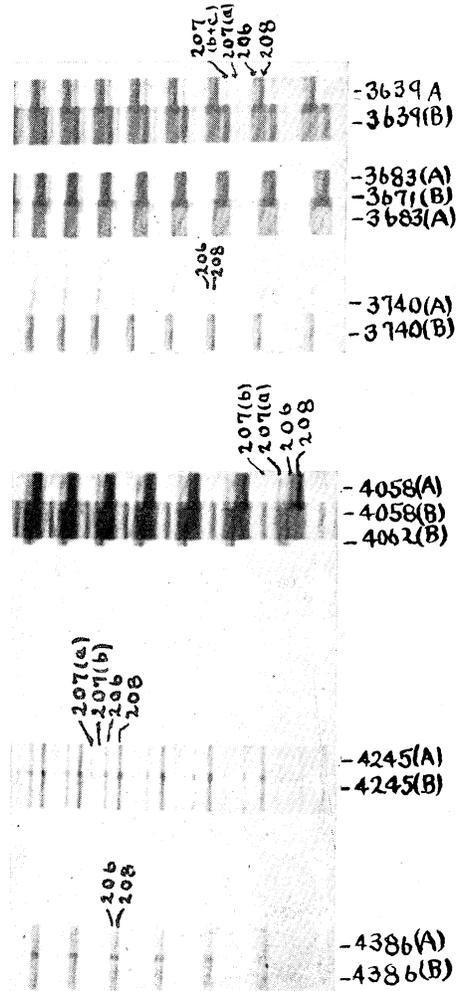


Fig. 5. Condition *A* (right) and condition *B* (left) photographed with equal slit widths.

the changes due to self reversal of the line patterns of $\lambda\lambda 4058, 3683$ and 3639 .

Because of the complexity of the line patterns and the apparent change of the relative intensities of the components of certain lines in condition *B*, it is difficult to interpret the patterns in Fig. 3, which were photographed with a very hot cathode. Schüler and Keyston¹⁰ have observed that a variation of the excitation conditions of the same hollow cathode discharge tube produced large changes in the relative intensities of the hyperfine structure lines of Cd, Tl, and Hg. These changes of intensity were not thought by them to be due to self reversal and have not as yet been explained. Although intensity measurements have not been made on our photographs obtained with different conditions of excitation, it appears that there may be a variation in the relative intensities of the components of some of the Pb I lines, exclusive of the absorption observed for the stronger components of several lines. In order to be more certain of the interpretations of the complicated patterns with a very hot cathode, the line structures with high and low temperatures were photographed side by side on the same photographic plate. This was done by allowing the Lummer fringes for one condition to enter a vertical portion of the wide slit of the spectrograph; another vertical portion of the slit was used for the second condition. The juxtaposed patterns in Figs. 4 and 5 with different slit widths show the relative positions of the components for conditions *A* and *B*.

URANIUM-LEAD

An exposure in condition *A* with uranium-lead (atomic weight 206), derived from ore of the Belgian Congo, showed that the Pb²⁰⁶ lines are single. See Fig. 6A. By juxtaposing the patterns of ordinary and uranium-leads in condition *A* it was found that the single Pb²⁰⁶ line corresponded to the next to the strongest component of ordinary lead for all of the Pb I and Pb II lines above $\lambda 2802$, with the exception of $\lambda\lambda 2873, 2823$ and 2802 of Pb I. See Fig. 7. The single line of Pb²⁰⁶ for the above three lines appeared very close the strongest component of ordinary lead. It has been previously shown by Kopfermann⁸ that the strongest and the next to the strongest components of $\lambda\lambda 4058, 4242, 4245,$ and 5373 were due to isotopes Pb²⁰⁸ and Pb²⁰⁶ respectively, with nuclear spin, $i=0$, while the other components belong to Pb²⁰⁷ which has a nuclear spin, $i=\frac{1}{2}$.

In condition *B* when uranium-lead was used, the lines of Pb²⁰⁶ with low term values were found reversed. See Fig. 6B. In this condition faint components of Pb²⁰⁷ were also observed for some of the more intense lines. Because of the large isotope displacements and the small amount of reversal for $\lambda 4245$, it was very easy to compare the relative intensities of the components of this line for ordinary lead with the components for uranium-lead. The two patterns of this line, side by side on the same photographic plate, have been reproduced in Fig. 8. These photographs show a larger abundance of Pb²⁰⁷ than Pb²⁰⁸ in uranium-lead.¹¹ This observation is in agreement with

¹⁰ Schüler and Keyston, *Zeits. f. Physik* **71**, 413 (1931).

¹¹ Rose and Granath, *Phy. Rev.* **39**, 1017 (1932).

Aston's¹² mass-spectragraph determination of the relative abundance of isotopes of uranium-lead derived from uranium bearing Norwegian bröggerite. Rutherford¹³ in commenting upon Aston's results, suggests that Pb^{207} is the end product of protactinium which in turn may be due to the disintegration of an isotope of uranium of atomic weight 235.

MEASUREMENTS OF THE LINE PATTERNS OF Pb I

Practically all of the measurements of the separations of the hyperfine structure components were made from the photographed line patterns which

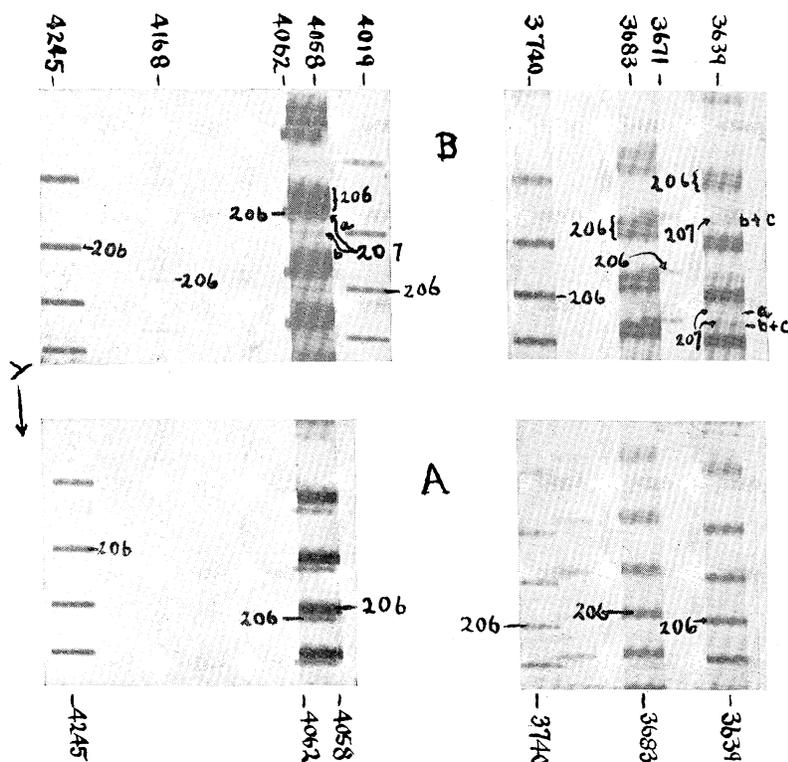


Fig. 6. Line patterns for uranium-lead (Belgian Congo). A, only single lines of Pb^{206} appear with cool cathode. B, in addition to the self reversed Pb^{206} line, components of Pb^{207} appear for some of the lines when the cathode is very hot.

were obtained by using the Lummer-Gehrcke plate of thickness, $t = 6.55$ mm. The lines were measured by a Fuess comparator which could be read to 0.001 mm, and the calculated separations of the components are considered accurate to at least ± 0.005 cm^{-1} . Table I gives the measurements on the line patterns of Pb I in terms of both frequency and wave-length differences. The line of the pattern from which the differences are measured is the most intense one, which in general is due to Pb^{208} . The isotopes to which the

¹² Aston, *Nature* **123**, 313 (1929).

¹³ Rutherford, *Nature* **123**, 313 (1929).

TABLE I. Hyperfine structure of Pb I lines.

| λ | Classification | Com- ponents | $\Delta\nu$ cm ⁻¹ | $\Delta\lambda A$ | Order of inten- sities | (Theoretical) Expected relative intensities for Pb ²⁰⁷ components |
|-----------|-----------------|-----------------|------------------------------|-------------------|---------------------------------|---|
| 4168.045 | $p^1D_2-d^3D_2$ | 208 | 0.000 | 0.000 | 1 | (9, 1, 1, 14) |
| | | 206 | -0.065 | +0.011 | 2 | |
| | | 207 | -0.157 | +0.027 | 3 | |
| 4062.149 | $p^1D_2-d^3D_1$ | 207 | +0.090 | -0.015 | 3 | (5, 1, 9) |
| | | 208 | 0.000 | 0.000 | 2 | |
| | | 206 | -0.075 | +0.012 | 1 | |
| 4058.826 | $p^3P_2-s^3P_1$ | 207(b) | +0.213 | -0.035 | 4 | (5, 1, 9) |
| | | 208 | 0.000 | 0.000 | 1 | |
| | | 206 | -0.093 | +0.015 | 2 | |
| | | 207(a) | -0.217 | +0.036 | 3 | |
| 4019.644 | $p^1D_2-d^3F_3$ | 208 | 0.000 | 0.000 | 1 | (14, 1, 20) |
| | | 206 | -0.069 | +0.011 | 2 | |
| | | 207 | -0.153 | +0.025 | 3 | |
| 3739.947 | $p^1D_2-s^3P_2$ | 208 | 0.000 | 0.0000 | 1 | (9, 1, 1, 14) |
| | | 206 | -0.089 | +0.0125 | 2 | |
| 3683.471 | $p^3P_1-s^3P_0$ | 208 | 0.000 | 0.000 | 1 | (1, 2) |
| | | 206 | -0.085 | +0.012 | 2 | |
| | | 207 | -0.12(?) | +0.02(?) | 3 | |
| 3671.506 | $p^1D_2-s^3P_1$ | 208 | 0.000 | 0.000 | 1 | (5, 1, 9) |
| | | 206 | -0.092 | +0.012 | 2 | |
| | | 207 | -0.230 | +0.031 | 3 | |
| 3639.583 | $p^3P_1-s^3P_1$ | 207(b) | +0.135 | -0.018 | 3 | (2, 1, 1, 5) |
| | | 208 | 0.000 | 0.000 | 1 | |
| | | 206 | -0.088 | +0.012 | 2 | |
| | | 207(a) | -0.304 | +0.040 | 5 | |
| | | 207(c) | -0.429 | +0.057 | 4 | |
| 3572.737 | $p^1D_2-s^3P_1$ | 208 | 0.000 | 0.0000 | 1 | (5, 1, 9) |
| | | 206 | -0.069 | +0.0088 | 2 | |
| 2873.324 | $p^3P_2-d^3D_2$ | 207(b) | +0.218 | -0.018 | 2(?) | (9, 1, 1, 14) |
| | | 208\} | 0.000 | 0.000 | 1 | |
| | | 206\} | | | | |
| | | 207(a) | -0.248 | +0.020 | 2(?) | |
| 2833.071 | $p^3P_0-s^3P_1$ | 207(b) | +0.097 | -0.0078 | 3 | (1, 2) |
| | | 208 | 0.000 | 0.0000 | 1 | |
| | | 206 | -0.079 | +0.0063 | 2 | |
| | | 207(a) | -0.337 | +0.027 | 4 | |
| 2823.199 | $p^3P_2-d^3F_2$ | 207(b) | +0.195 | -0.0155 | 3 | (9, 1, 1, 14) |
| | | 208\} | 0.000 | 0.0000 | 1 | |
| | | 206\} | | | | |
| | | 207(a) | -0.166 | +0.013 | 2 | |
| 2802.009 | $p^3P_2-d^3F_3$ | 208\} | 0.000 | 0.000 | 1 | (14, 1, 20) |
| | | 206\} | | | | |
| | | 207 | -0.231 | +0.018 | 2 | |
| 2614.200 | $p^3P_1-d^3F_2$ | | single | | | (5, 1, 9) |
| 2613.678 | $p^3P_1-d^3D_1$ | | single | | | (2, 1, 1, 5) |

components belong are listed in the third column of the table. Where more than one component due to Pb^{207} was observed, small letters, a, b, c , etc., are used in describing the Pb^{207} components. No quantitative estimate of the relative intensities of the components has been made. In the next to the last column of the tables, however, the order of the intensities is given, the number 1 being assigned to the strongest component. The theoretical relative intensities for the components of Pb^{207} with nuclear spin, $i = \frac{1}{2}$, which would be expected from the classification by Gieseler and Grotrian⁹ are given in the last column. These intensities were found by use of the Kronig-Sommerfeld-Höul intensity formulas as first applied to hyperfine structure by Hill.¹⁴

$\lambda\lambda$ 4168, 4062, 4019, and 3671

The strongest line of this group is λ 4062. Since its pattern almost completely overlaps with the pattern of the very intense line, λ 4058, it was very difficult to measure. In condition *A* the two strong components due to Pb^{208} and Pb^{206} appeared with very long exposures for all of these lines, while in condition *B* with a hot cathode the third component, presumably due to Pb^{207} , appeared on the plate intense enough to measure. No self reversal was noted for the stronger components with condition *B*. For this group at least two relatively strong Pb^{207} components are expected for each line, but only one was observed. It may be that the other Pb^{207} component is too close to one of the stronger components to be resolved. If both of the stronger Pb^{207} components were masked by Pb^{206} and Pb^{208} in these lines, the weak component may be the least intense one expected for Pb^{207} , or perhaps belong to another isotope of lead. Schüler and Jones¹⁵ working in the red and green regions have recently reported evidence of Pb^{204} .

$\lambda\lambda$ 3739 and 3572

These lines appeared with the same patterns with either a cool or a very hot cathode. With high temperatures there seems to be a slight tendency for the two components of λ 3572 to fuse together. No trace of a third component could be found.

λ 4058

This line with high lead vapor pressure could be photographed in one to five minutes, but the two strongest components were usually reversed. It required an exposure of one and one half hours with a low lead vapor pressure to photograph the unreversed line pattern, which consisted of four components. Components of Pb^{208} and Pb^{206} were seen as three in the former condition with component Pb^{207} (a) appearing the most intense in the pattern. The component due to Pb^{208} was the first to reverse with increasing temperature. This component was not as easily reversed as the corresponding component of $\lambda\lambda$ 2833, 3683, and 3639.

¹⁴ Hill, Proc. Nat. Acad. Sci. **15**, 779 (1929).

¹⁵ Schüler and Jones, Naturw. **20**, 171 (1932).

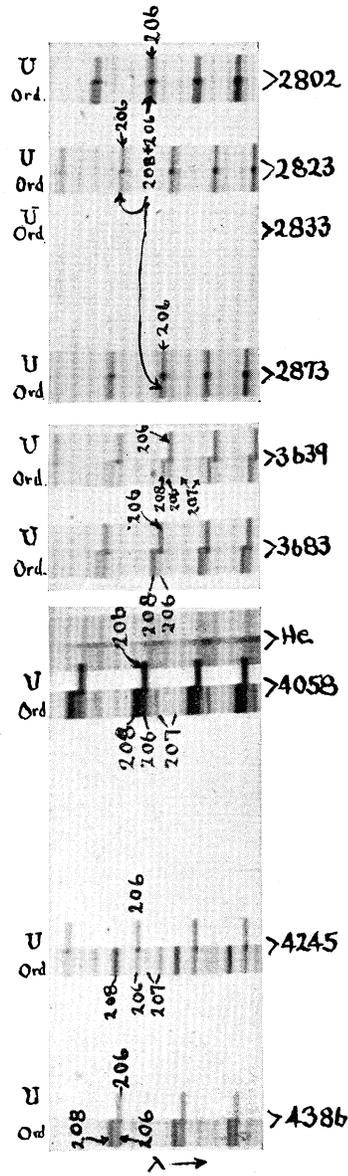


Fig. 7. Juxtaposed Lummer-Gehrcke plate patterns with cool cathode for uranium-lead (right) and ordinary lead (left). The exposure for $\lambda\lambda 2873, 2823,$ and 2802 with ordinary lead was too short to show the Pb^{207} components. The reproductions for the lines above and below $\lambda 3639$ were made from different photographic plates.

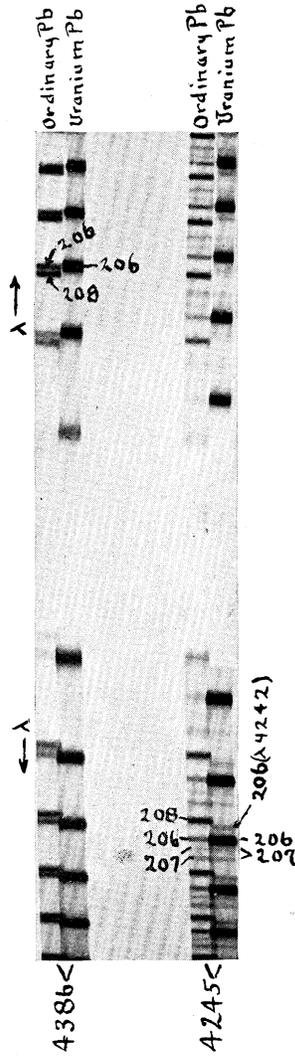


Fig. 8. A moderate exposure of ordinary lead (left) with cool cathode and a very long exposure of uranium-lead (right) with very hot cathode. The pattern of $\lambda 4245$ for uranium-lead consists of the very intense Pb^{208} line and two components of Pb^{207} ; no trace of Pb^{206} can be detected. The line which appears displaced slightly to the right of $\lambda 4245$ is $\lambda 4242$ (Pb^{206} for uranium-lead). No components of $\lambda 4242$ for ordinary lead can be seen in this reproduction.

λ 3683

A very faint component appeared near the Pb^{206} line with a very long exposure and with low currents in condition *A*. It was impossible to measure this component, but it was estimated to be not over 0.12 cm^{-1} from Pb^{208} . A small increase of current in condition *A* was sufficient to cause the two main lines to fuse together and to appear as one very broad line. A further increase of current made this very broad line appear as three sharp equally spaced lines; with a very hot cathode the center one of the triplet nearly vanished and the outside ones were separated still farther and quite intense. See Fig. 3. A much cooler cathode must be used for this line than for $\lambda\lambda 4058$ or 3639 .

 λ 3639

The patterns for $\lambda 3639$, reproduced in Figs. 3, 4, 5, and Fig. 7, were obtained by the Lummer-Gehrcke plate of thickness, $t=6.55 \text{ mm}$. The orders for (b) and (c) of Pb^{207} overlapped with this plate and these two components appeared as one. The fourth component of Pb^{207} was too close to a strong component to be observed with either plate.

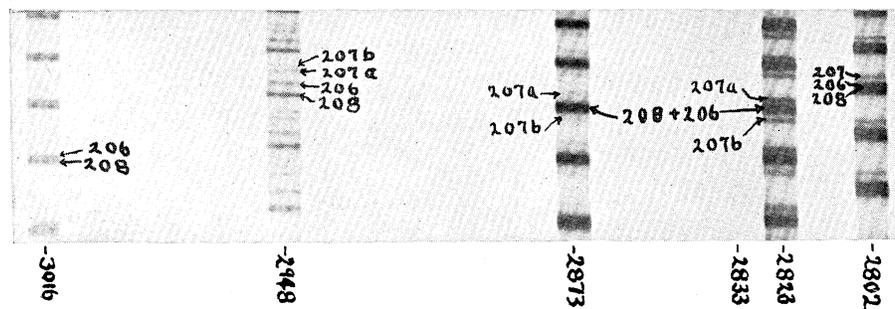


Fig. 9. These patterns were obtained by a long exposure with a hot cathode. The strong component of $\lambda 2802$ appears to be slightly reversed. A very faint trace of $\lambda 2833$ can be seen.

 $\lambda\lambda$ 2873 and 2802

One very weak component for $\lambda 2802$ and two very weak components of about equal intensity for $\lambda 2873$ could be photographed with a twelve hour exposure in condition *A* and a one hour exposure in condition *B*. The principal component for each of these lines was very broad and intense. It appeared on the photographic plates with a short exposure in either condition. The patterns of these lines did not seem to change with the temperature of the cathode, although in some photographs there is evidence that $\lambda 2802$ is subject to reversal before $\lambda 2873$. See Fig. 9. The single Pb^{206} line of uranium-lead was thought to fall on the long wave wide of the center of the broad ordinary lead component. The above separations are from the center of the very heavy principal component.

 λ 2833

This resonance line, the most difficult to obtain without reversal, has four components. With currents as low as 0.1 amp. and exposures up to fifteen

hours it was possible to obtain the pattern of this line without reversal. Its pattern changed with larger currents in such a way that it could not be recognized as the same line; with still larger currents, on the border of condition *B*, it practically disappeared. See Figs. 7 and 9.

λ 2823

This line is too weak to obtain its Lummer pattern when conditions are the best for getting good photographs of λ 2833. In condition *B* exactly the reverse is true. On one plate the conditions were such that the patterns of both lines were of equal intensity. In conditions *A* and *B*, when its pattern appeared, it has three components. See Fig. 9. Its main component is broad but not as broad as λ 2873 and 2802, although its two weaker components are relatively much stronger than the weak components of λ 2873 and 2802. No marked reversal was observed even though the lead vapor pressure was very high. The uranium-lead line coincided with the main component; so it should be expected that this apparent component is unresolved and due to both Pb^{206} and Pb^{208} as in the case of λ 2873 and 2802. The intensities of Pb^{207} (a) and Pb^{207} (b) are sufficient to account for the two stronger components of Pb^{207} predicted by theory; this does not seem to be the case with the other two lines. Although components Pb^{207} (a) and Pb^{207} (b) of λ 2823 were fairly intense, it was possible for them not to appear on a photographic plate even though the main component appeared quite dense. See Fig. 7.

λ 2614

It was difficult to measure this line since it and λ 2613 almost completely overlapped each other. Measurements made on plates which were taken when the tube was being run with considerable power showed two components of nearly equal intensities with separation of 0.190 cm^{-1} . One heavy broad component was observed with smaller currents in condition *A* with long exposures. The previously observed separation must have been due to self reversal.

λ 2613

This line, which was many times weaker than λ 2614 in condition *A*, became nearly as strong as λ 2614 in condition *B*. It did not seem to be subject to any great reversal and appeared single and broad on all plates.

λ 2663, 2577, and all other strong lines down to λ 2393 have appeared on a few plates in one condition or the other with fair intensity. All of them have a very broad single component with no suggestion of any weaker components. The strong lines below 2600A were less intense than those above and it was more difficult to use a Lummer plate in this region; so it might be that the principle component is a combination of the single components of Pb^{206} , Pb^{208} , and the strongest one of Pb^{207} , while other components due to Pb^{207} were too weak to appear with the exposures which have been used.

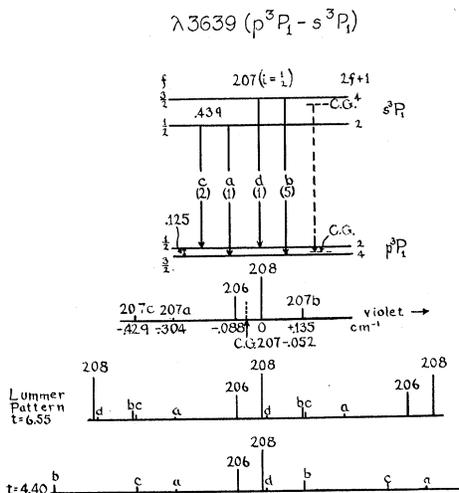
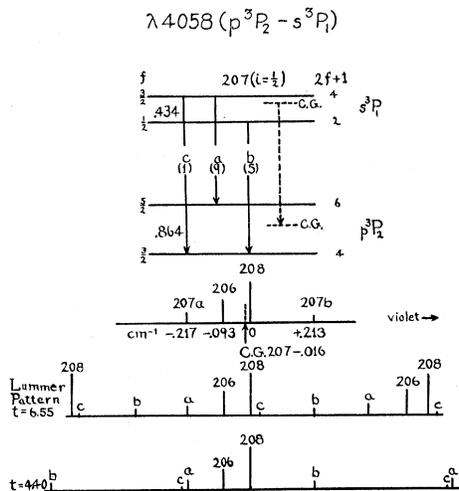
MEASUREMENTS OF THE LINE PATTERNS OF Pb II

λ 4386 and 3016

These lines, members of the same series, showed only two components. The Pb^{207} components must be very close together and nearer to Pb^{206} than

$\lambda\lambda$ 4245 and 2948

These members of another series have also nearly identical patterns. The line structure of $\lambda 4245$ reproduced in Figs. 4, 5, 7, and 8 was obtained by use of the large Lummer-Gehrcke plate while that of $\lambda 2948$ in Fig. 9 was obtained with the small plate, which has a larger spectral range.



λ 3786

Only two photographs of $\lambda 3786$, one with each Lummer-Gehrcke plate, were sufficiently good for measuring the separations of the components. The above values for the displacements of the Pb^{207} components are not as accurate as that for Pb^{206} with respect to Pb^{208} .

λ 5372

The measurements of this line by Janicki³ have been included in order to compare the isotope displacement of Pb^{206} with respect to Pb^{208} with the displacements found in other lines.

ASSIGNMENTS OF LEVELS TO Pb^{207} I LINES

In the Figs. 10, 11, and 12 the theoretically determined values of the relative intensities of the components of Pb^{207} for $i = \frac{1}{2}$ and the possible transitions are indicated for $\lambda\lambda 4058, 3639,$ and 2833 . The line patterns of the two quartz Lummer-Gehrcke plates ($t = 6.55$ mm and 4.40 mm) are also shown. With these data it is possible to find the hyperfine splitting of the $p^3P_{0,1,2}$ and $s^3P_{0,1}$ levels of Pb^{207} I.

The above measurements for the pattern of $\lambda 2833$ give the separation of s^3P_1 to be 0.434 cm^{-1} since the final level of this line has no splitting. Although the weakest component, Pb^{207} (c) of $\lambda 4058$ can not be seen with either Lummer plate, the separation of the final level can be found, however, by using the above value of the initial level, determined from $\lambda 2833$, and the separation of components, Pb^{207} (a) and Pb^{207} (b) of $\lambda 4058$. A separation of 0.864 cm^{-1} for p^3P_2 , the final level for $\lambda 4058$, agrees with the patterns and in addition explains why Pb^{207} (c) was not observed. This weak component in the case of each Lummer pattern would appear too close to a very strong component to be seen. From $\lambda 3639$ the splitting of s^3P_1 is found to be 0.439 cm^{-1} ; the levels of p^3P_1 are inverted and separated 0.125 cm^{-1} . This shows that component Pb^{207} (d) of $\lambda 3639$ practically coincides with a very strong component and would not be expected to appear. The splitting of p^3P_1 could also be determined from $\lambda 3683$ if the two predicted components of Pb^{207} had been seen, in as much as the initial level for this line has no splitting. It was observed, however, in the pattern of this line that the maximum separations of the components could not be more than 0.12 cm^{-1} , which in turn should be the maximum separation of the final level. This observation qualitatively agrees with the result for p^3P_1 obtained from $\lambda 3639$.

TABLE III. Separation of the hyperfine levels of Pb^{207} I.

| Term | Separation | Nature of term |
|----------|-------------------------|----------------|
| s^3P_0 | 0.000 cm^{-1} | — |
| s^3P_1 | 0.436 " | regular |
| p^3P_0 | 0.000 " | — |
| p^3P_1 | 0.125 " | inverted |
| p^3P_2 | 0.864 " | regular |

The separation for s^3P_1 is in agreement with 0.430 cm^{-1} found by Schüler and Jones¹⁵ from the pattern of $\lambda 7228 p^1D_2 - s^3P_1$. The above separations and the patterns of $\lambda\lambda 2873, 2823, 2802, 2614, 2613, 4168, 4062,$ and 4019 should enable one to find the nature of $d^3D_{1,2}, d^3F_{2,3},$ and p^1D_2 . Two independent calculations for d^3F_2 and three for p^1D_2 were made. Very poor agreement for the several possible values for these levels was obtained. This appears to be further evidence of something incorrect in the classification of some of the lines discussed above.

ISOTOPE DISPLACEMENT

Measurements showed that the displacement of Pb^{206} with respect to Pb^{208} did not vary directly with the wave-length, although the separation was much larger for Pb I above 3500A than below with the exception of $\lambda 2833$. The displacements above 3500A varied from 0.065 cm^{-1} to 0.092 cm^{-1} for the different lines with the Pb^{206} component always on the long wave side of Pb^{208} . Even though these displacements are much larger than that expected from the Bohr mass correction to the Rydberg constant, it has been found in the spark spectrum that the displacements for $\lambda\lambda 5372, 4245, 3786,$ and 2948 are several times the maximum displacement found in the arc lines.

With the line patterns and the splitting of the levels known for $\lambda\lambda 3639, 4058, 2833,$ and 3683 , the Pb^{207} displacements with respect to Pb^{208} and Pb^{206} can be calculated. This was done by considering the center of gravity of the initial and final term levels of each line, and the displacement as the result of the splitting of the terms was calculated for one of the components of Pb^{207} . By the center of gravity of a split term is meant the weighted mean of the terms values of the sublevels, each sublevel being given the relative weight $2f+1$ (its statistical weight). The center of gravity of the hyperfine levels of Pb^{207} coincides with the position which the term would have were it not split. The broken line in Figs. 10, 11, and 12 represents the Pb^{207} line for

TABLE IV. *Isotope displacement of Pb^{206} and Pb^{207} with respect to Pb^{208} .*

| λ | Pb^{206} $\Delta\nu \text{ cm}^{-1}$ | C.G. of Pb^{207} $\Delta\nu \text{ cm}^{-1}$ |
|-----------|---|---|
| Pb I | | |
| 7228* | -0.088 | -0.055 |
| 4168 | -0.065 | |
| 4062 | -0.075 | |
| 4058 | -0.093 | -0.016 |
| 4019 | -0.069 | |
| 3739 | -0.089 | |
| 3683 | -0.085 | -0.04‡ |
| 3671 | -0.092 | |
| 3639 | -0.088 | -0.052 |
| 3572 | -0.069 | |
| 2873 | Very small | |
| 2833 | -0.079 | -0.048 |
| 2823 | Very small | |
| 2802 | " " | |
| 2663 | " " | |
| 2614 | " " | |
| 2613 | " " | |
| 2577 | " " | |
| Pb II | | |
| 5372† | -0.275 | |
| 4386 | -0.086 | |
| 4245 | -0.199 | |
| 3786 | -0.415 | |
| 3016 | -0.078 | |
| 2948 | -0.199 | |

* The measurements for this line were made by Schüler and Jones.

† The measurements for this line were made by Janicki.

‡ This result is only an estimate since the positions of the Pb^{207} components for $\lambda 3683$ could not be measured. The uncertainty is estimated to be $\pm 0.01 \text{ cm}^{-1}$.

TABLE V. Term displacement with respect to Pb^{208} .

| Term | C.G. Pb^{207} $\Delta\nu$ cm^{-1} | Pb^{206} $\Delta\nu$ cm^{-1} |
|----------|--|-------------------------------------|
| s^3P_0 | -0.01* | -0.003 |
| s^3P_1 | 0.000 | 0.000 |
| p^3P_0 | -0.048 | -0.079 |
| p^3P_1 | -0.052 | -0.088 |
| p^3P_2 | -0.016 | -0.093 |

* The uncertainty of this result is ± 0.01 cm^{-1} since the displacement for the center of gravity of Pb^{207} for $\lambda 3683$ was used; cf. isotope displacement of $\lambda 3683$ in Table IV.

no splitting of the terms. The results for the displacements of Pb^{207} and Pb^{206} with respect to Pb^{208} are given in Table IV.

The above isotopes displacements for $\lambda\lambda 4058$, 3683, 3639, and 2833 are in very good agreement with the displacements of Pb^{206} , Pb^{207} , and Pb^{208} found by Schüler and Jones¹⁵ from the pattern of $\lambda 7228$.

The relative displacements of the terms, $s^3P_{0,1}$ and $p^3P_{0,1,2}$, for Pb^{206} , Pb^{207} , and Pb^{208} can be determined from the isotope displacements in the line patterns of $\lambda\lambda 4058$, 3683, 3639, and 2833. The term displacements given in Table V were found by arbitrarily considering no displacements for s^3P_1 . The way in which the terms, with the exception of Pb^{207} for s^3P_0 , fall in the order of their masses is in agreement with the results of Schüler and Keyston¹⁶ for Hg. Since the uncertainty for Pb^{207} of s^3P_0 is much greater than the given displacement for Pb^{206} , the order of this term can not be definitely determined. The results for s^3P_0 do show, however, that the displacements for this term are approximately the same as those for s^3P_1 . With the exception of Pb^{207} for p^3P_2 , the relative isotope separations for the triplet term, $p^3P_{0,1,2}$, are found to be of the same order of magnitude.

In conclusion the authors wish to express their appreciation to Professor G. Breit, who suggested this problem, for his generous interest and advice throughout the progress of the investigation. We are also indebted to Professor R. W. Wood of Johns Hopkins University for the loan of the two Lummer-Gehrcke Plates and a quartz fluorite lens, to Professor J. P. Simmons of the Chemistry Department for the use of chemical equipment, to Dr. E. W. Riblett for the purification and reduction of the uranium-lead, and to all who have assisted us in obtaining samples of uranium-lead. Thanks are also due to Mr. Herman Beck for the construction of the discharge tubes.

Note added in Proof: May 14, 1932

After the manuscript for this article was sent to the editor, an article on the hyperfine structure of lead by Kopfermann¹⁷ was received. Practically all of his measurements of the line patterns agree with those reported by us. He was able apparently, to resolve and measure the separations of Pb^{208} and Pb^{206} for several lines which we reported to be very small. Two components of Pb^{207} for $\lambda 4062$ were observed by him in which case we had seen only one,

¹⁶ Schüler and Keyston, *Zeits. f. Physik* **72**, 433 (1931).

¹⁷ Kopfermann, *Zeits. f. Physik* **75**, 363 (1932).

while the Pb^{207} components for $\lambda\lambda 4168$ and 4019 measured by us were not included in his measurements. The principal difference in the results of the two articles is in the value for the regular splitting of p^3P_2 given by him to be approximately 0.220 cm^{-1} . Our value, 0.864 cm^{-1} , was found by considering the two visible Pb^{207} components of $\lambda 4058$ to be those with relative intensities 9 and 5. Kopfermann considered them to be the components, predicted by theory, with relative intensities 5 and 1. He was able to see the strongest component with intensity 9 in the position of Pb^{208} when uranium-lead was used. This was possible since uranium-lead contains a smaller abundance of Pb^{208} than Pb^{207} .

With a sample of uranium-lead we have tried to see this component of Pb^{207} . Several high resolving power instruments and different types of photographic plates have been used. Due to the large difference in the relative abundance of Pb^{207} and Pb^{206} , the Pb^{206} line had to be very much overexposed in order to see this component of Pb^{207} . Since the component is very close to Pb^{206} it could be easily masked by the photographic broadening of the intense Pb^{206} line caused by overexposure. From over twenty five photographic exposures of $\lambda 4058$ with uranium-lead, only two or three plates seemed to indicate the presence of the Pb^{207} component which was observed by Kopfermann. One of these plates is better than any of the others as judged by the sharpness of other lines, and makes us believe that Kopfermann's interpretation is correct. The patterns of this line for ordinary lead were again observed. With a very cool cathode it is possible that the relative intensities of Pb^{207} (a) and Pb^{207} (b) may be 5 and 1, but on plates taken with a slightly higher temperature of the cathode the ratio of the relative intensities of these components is certainly less than 5 to 1. Using the interpretation of the line pattern of $\lambda 4058$ given by Kopfermann, the regular splittings of s^3P_1 and p^3P_2 from our measurements of $\lambda 4058$ are 0.430 cm^{-1} and approximately 0.213 cm^{-1} , respectively. With this value for p^3P_2 the isotope displacement of Pb^{207} with respect to Pb^{208} becomes -0.058 cm^{-1} instead of -0.016 cm^{-1} as given above. This result fits in better with the displacements of Tables IV and V.

The splittings of d^3D_2 , d^3F_3 and d^3F_2 were found by Kopfermann to be 0.255 cm^{-1} (regular), 0.250 cm^{-1} (regular), and 0.130 cm^{-1} (inverted), respectively. Considering the splittings of p^3P_2 to be 0.213 cm^{-1} , our measurements for the line patterns of $\lambda\lambda 2873$ and 2823 give splittings for d^3D_2 and d^3F_2 to be of the same order as that above. The relative intensities of the components of $\lambda 2802$ on our plates are such that a regular splitting of 0.250 cm^{-1} for d^3F_3 does not appear to be correct. For $\lambda 2802$ three components of Pb^{207} with relative intensities 20, 14, and 1 are predicted by theory. With a splitting of 0.250 cm^{-1} for d^3F_3 the two stronger components of Pb^{207} would nearly coincide in the line pattern of $\lambda 2802$. Only one apparent component of Pb^{207} was observed by us, and its intensity with a cool cathode is much too small to account for both of the stronger components of Pb^{207} . A hotter cathode, which does not seem to give the correct relative intensities for the components of $\lambda 4058$, shows an increase in the intensity of the apparent Pb^{207} component. A comparison of the relative intensities of the components of

$\lambda\lambda 2823$ and 2802 in Fig. 9, a reproduction of a plate obtained by using a very hot cathode, shows that the apparent Pb^{207} component of $\lambda 2802$ can not account for both of the stronger components of Pb^{207} . If it should be due to the stronger components, the center of gravity of Pb^{207} would not fall between Pb^{208} and Pb^{206} as it does for other lines.

Kopfermann's results for d^3D_2 and d^3F_3 could be verified however, by observing another Pb^{207} component for each of the lines $\lambda\lambda 4168$ and 4019 since Schüler and Jones¹⁵ have found a regular splitting for p^1D_2 , the final level for these lines, to be 0.049 cm^{-1} . The second Pb^{207} component for these lines would fall near Pb^{208} and should be observed by a long exposure with uranium-lead.

With the above data it is possible to make a comparison with theory. Defining with Goudsmit¹⁸ the interaction constant A by

$$W(j) = [A(j)/2] [f(f+1) - i(i+1) - j(j+1)]$$

letting a' , a'' be respectively the values of A for $ap_{3/2}$, $p_{1/2}$ electron moving in the same central field as each of the two equivalent p electrons, $(6p)^2$, responsible for the normal set of levels of Pb , the following relations hold:

$$3a' = A(^3P_1) + A(^3P_2) + A(^1D_2)$$

$$3a'' = 5A(^3P_2) + 5A(^1D_2) - 7A(^3P_1).$$

We obtain using $\Delta W(^3P_1) = -0.125 \text{ cm}^{-1}$, $\Delta W(^3P_2) = 0.215 \text{ cm}^{-1}$, $\Delta W(^1D_2) = 0.049 \text{ cm}^{-1}$ for $a'' = 0.370 \text{ cm}^{-1}$, $a' = 0.007(4) \text{ cm}^{-1}$. It is very curious that the values obtained by Goudsmit¹⁸ for the $(6p)^3$ configuration of Bi are $a'' = 0.375 \text{ cm}^{-1}$, $a' = 0.007 \text{ cm}^{-1}$. The value of a' is very sensitive not only to experimental errors but also to corrections which must be applied to the above simple theory on account of the energy differences of the three terms involved. On the other hand a'' is much less sensitive to such corrections. Thus even though a''/a' is greater than the possible theoretical value,¹⁹ $5 \times 3.4 = 17$, it may be that these values are not real indications of disagreement with the theory. The agreement of a'' for Pb^{207} and Bi indicates on the other hand that the ratio of the magnetic to the mechanical moment is nearly the same for the two nuclei. It is also of interest that a'' for Tl is 0.71 cm^{-1} , a value nearly twice as large as the above.

¹⁸ S. Goudsmit, Phys. Rev. **37**, 663 (1931); See table p. 675 and theory of pp. 668-669. Note that on account of intermediate coupling only sum rules are applicable without calculating complex parameters. See also G. Breit and F. W. Doermann, Phys. Rev. **36**, 1732 (1930); Discussion on p. 1750 and G. Racah, Zeits. f. Physik **71**, 431 (1931), the latter for discussion of intermediate coupling.

¹⁹ G. Breit, Phys. Rev. **38**, 463 (1931); **37**, 1182 (1931); G. Racah, Cim. **8**, 178 (1931).

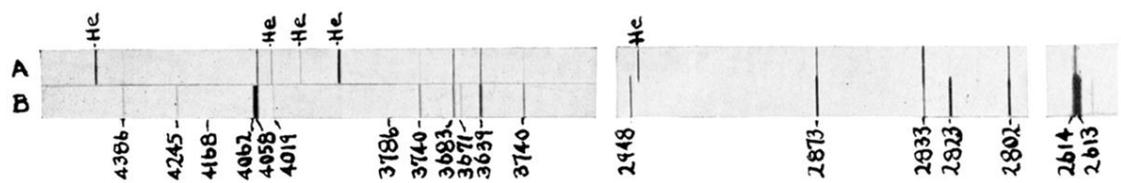


Fig. 2. *A*, cool cathode; *B*, hot cathode.

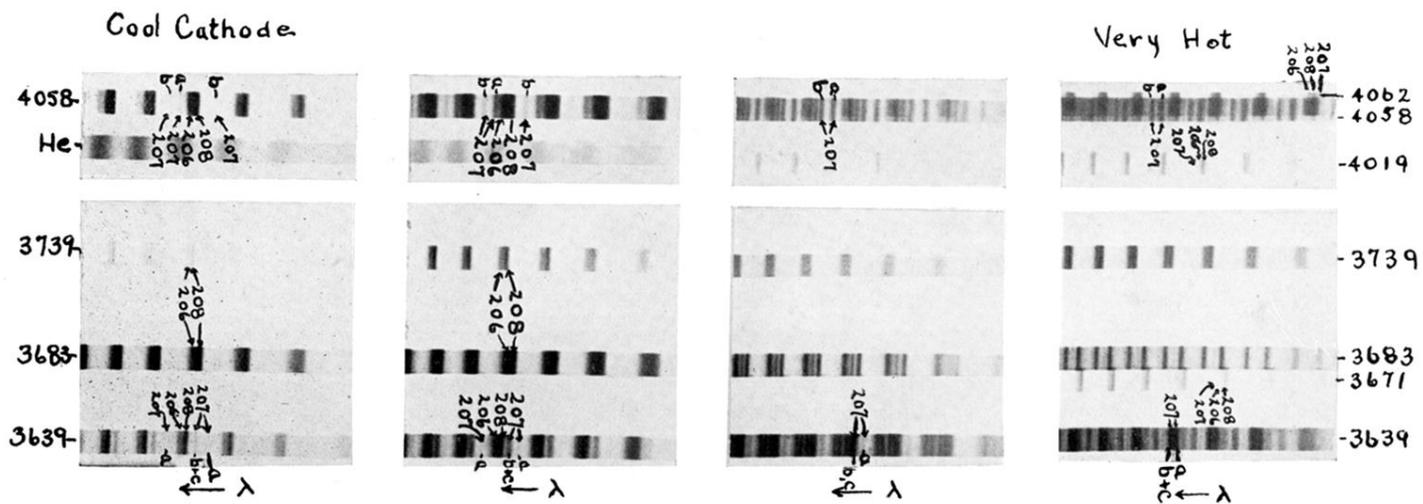


Fig. 3. Variations of Lummer-Gehrcke plate patterns with increasing temperature of the cathode.

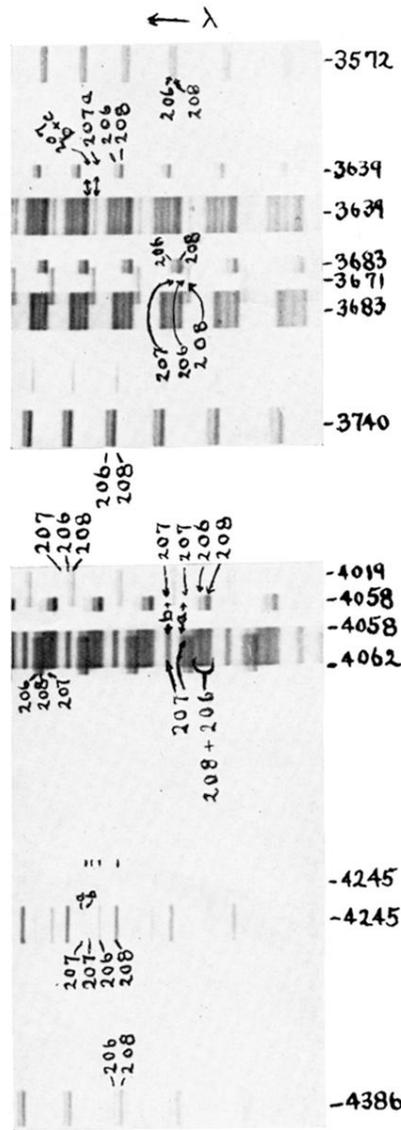


Fig. 4. Juxtaposed Lummer-Gehrcke plate patterns for conditions *A* and *B*. Condition *A* (narrow slit) is on the right of condition *B* (wide slit). Several weak lines appear only in condition *B*.

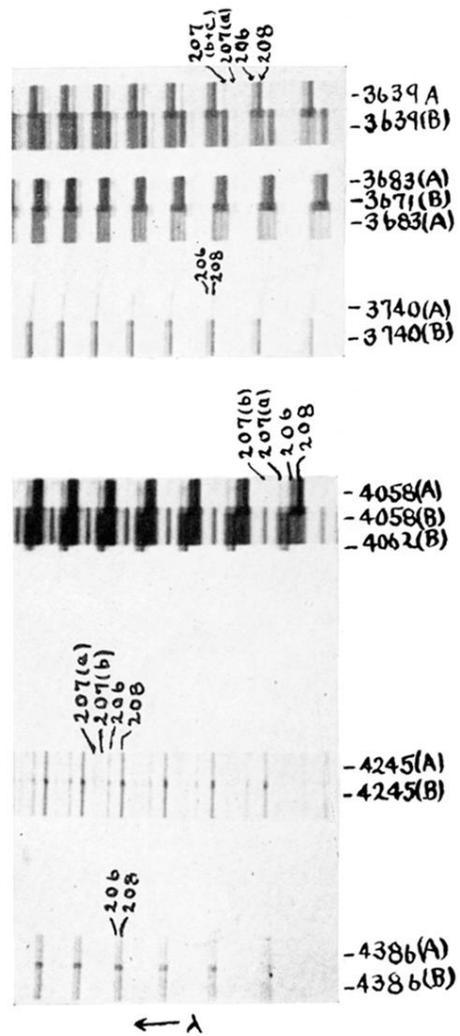


Fig. 5. Condition *A* (right) and condition *B* (left) photographed with equal slit widths.

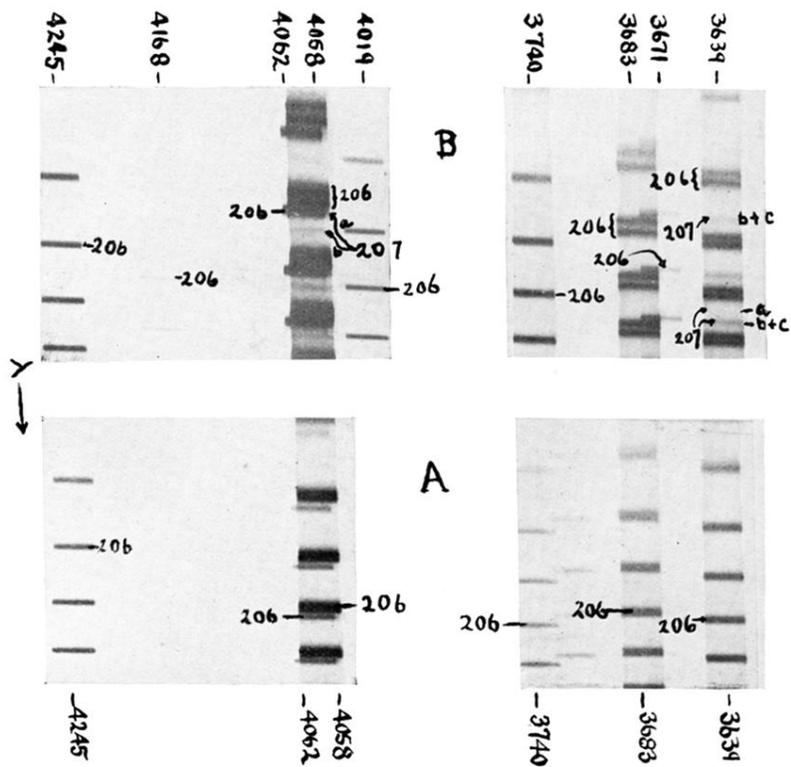


Fig. 6. Line patterns for uranium-lead (Belgian Congo). A, only single lines of Pb^{206} appear with cool cathode. B, in addition to the self reversed Pb^{206} line, components of Pb^{207} appear for some of the lines when the cathode is very hot.

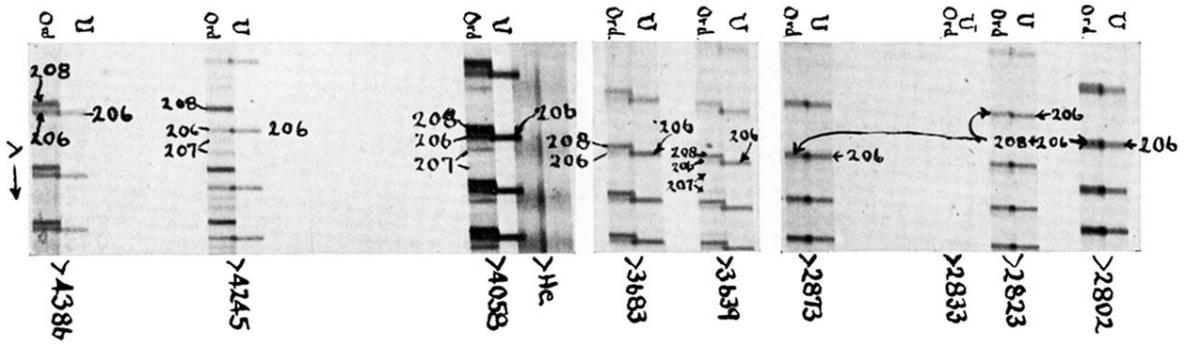


Fig. 7. Juxtaposed Lummer-Gehrcke plate patterns with cool cathode for uranium-lead (right) and ordinary lead (left). The exposure for $\lambda\lambda 2873, 2823,$ and 2802 with ordinary lead was too short to show the Pb^{207} components. The reproductions for the lines above and below $\lambda 3639$ were made from different photographic plates.

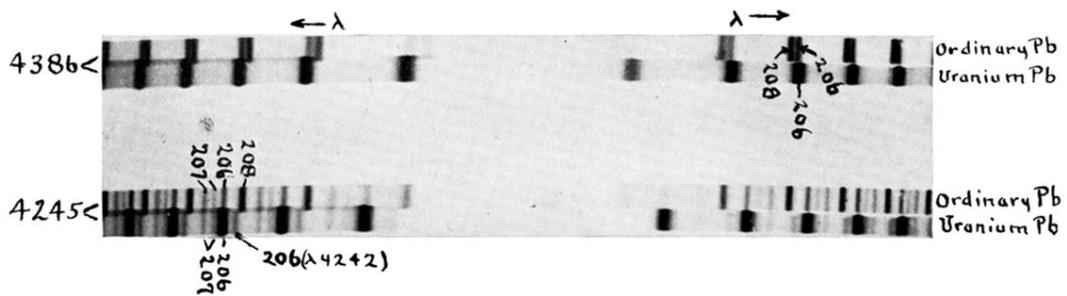


Fig. 8. A moderate exposure of ordinary lead (left) with cool cathode and a very long exposure of uranium-lead (right) with very hot cathode. The pattern of $\lambda 4245$ for uranium-lead consists of the very intense Pb^{206} line and two components of Pb^{207} ; no trace of Pb^{208} can be detected. The line which appears displaced slightly to the right of $\lambda 4245$ is $\lambda 4242$ (Pb^{206} for uranium-lead). No components of $\lambda 4242$ for ordinary lead can be seen in this reproduction.

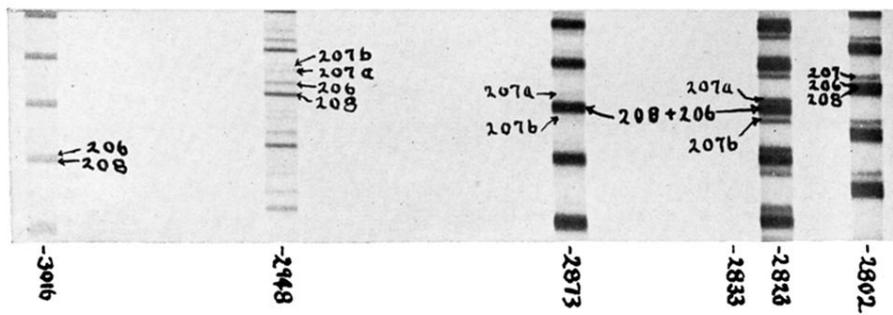


Fig. 9. These patterns were obtained by a long exposure with a hot cathode. The strong component of $\lambda 2802$ appears to be slightly reversed. A very faint trace of $\lambda 2833$ can be seen.