Hyperfine Structure and Intensities of the Forbidden Lines of Pb I

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The hyperfine structure of the forbidden lines of lead is studied in order to establish the intensity rules in the hyperfine structure of such lines. Those here investigated arise from transitions between the levels of the $6p^2$ configuration, and show hyperfine structure because of the presence of a nuclear spin and magnetic moment in the isotope 207. They are excited very intensely by 3-meter standing waves in helium at about 5 mm pressure, containing saturated Pb vapor at 800°C. The type of discharge and its dependence on several factors are studied. Intensities are quantitatively determined from calibrated plates. For the quadrupole line λ5313, the intensity ratio (3 : 2), and the ratio of the distances from the center of gravity, are found to agree with the Rubinowicz formulas transcribed for hyperfine structure by Opechowski (selection rule $\Delta F=0, \pm 1, \pm 2$). For the magnetic dipole line λ4618, these ratios agree with the well-known rules for electric dipole transitions (2 : 1). In the case of λ7330, which is of mixed type, the intensities are approximately those for ordinary electric dipole transitions, showing that this line is mostly magnetic dipole radiation and that for such radiation the selection rule $\Delta F=0, \pm 1$ holds. An upper limit of the admixture of electric quadrupole can be evaluated from these measurements. The measurements also show that the total transition probabilities for electric quadrupole and magnetic dipole are independent of the existence of a magnetic moment of the nucleus since they are the same for the various isotopes. Finally, the relative intensities of these three lines and of two others, λ4659 and a newly found line at $\lambda 9250(^3P_2-{}^1D_2)$, have been measured for comparison with theory. The results are $I_{4618} : I_{5313} = 5.0 \pm 0.3$ and $I_{4659} : I_{7330} : I_{9250} = 0.023 \pm 0.006 : 1 : 0.84 \pm 0.07$. These ratios are independent of the furnace temperature. The ratio $I_{5313} : I_{4659}$ varies somewhat with temperature, changing from about 15 to 12 in going from the lower to the higher temperatures.

THE selection rules and intensity formulas have been accurately checked in the hyperfine structure of ordinary electric dipole lines. Very little is known about the case of forbidden lines, probably because of the relatively greater experimental difficulties in investigating them. Of the four known types of forbidden lines three present certain features of interest for further investigation. (1) Quadrupole lines. For only one line of this type has the hyperfine structure been observed (λ2815 in Hg II[1]). Formulas for the relative intensities in the hyperfine structure of such lines have been obtained by Opechowski[1] from the Rubinowicz formulas for multiplet structure, using the same process as that used in getting the hyperfine structure formulas of Hill from the Hönl and Kronig multiplet formulas, namely by substitution of the quantum numbers F, J and I in place of J, L and S. The selection rule $\Delta F=0, \pm 1, \pm 2$ and the intensity formulas of Opechowski have been checked by the excellent agreement of the predicted and observed structures of the Hg II line mentioned above, but no exact photometric measurements were made. For this line, the proof would not have been completely satisfactory anyway, in view of the partial overlapping of components belonging to the two odd isotopes of Hg. It therefore seemed worth while to make an accurate test of the applicability of the formulas for this case. (2) Magnetic dipole lines. No hyperfine structure has been observed and no theoretical predictions made about the intensities in the hyperfine components of lines of this type. Furthermore, the problem of lines of mixed character (magnetic dipole+electric quadrupole) appeared to be of considerable interest.[1] (3) Forbidden lines caused by inner hyperfine structure perturbations. These have been the most extensively investigated. Not only has the case of perturbations by nearby levels been studied, as in Al[2] and Hg,[3] but also one[4] where an extremely small perturbation induces the emission of a line forbidden for all types of spontaneous radiation, namely λ2656 in Hg I, $^3P_0 \rightarrow {}^1S_0$. Although the intensities of the components in this line were found to agree roughly with theory,[5] the two components belong

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[1] S. Mrozowski, Phys. Rev. **57**, 207 (1940).
[2] F. Paschen, Sitz. Preuss. Akad. Wiss. **32**, 502 (1932).
[3] S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933).
[4] S. Mrozowski, Zeits. f. Physik **108**, 204 (1938).
[5] W. Opechowski, Zeits. f. Physik **109**, 485 (1938).

to different Hg isotopes. Hence it would be interesting to check the perturbation theory in a case where the intensities of different components emitted by the same isotope could be compared. For this purpose, the investigation of $\lambda 2270(^3P_2 \rightarrow {}^1S_0)$ of Hg I[6] offers an opportunity for comparison with the calculations of Einaudi.[7] (4) The fourth type of forbidden transitions is caused by external fields, but these present no interest for hyperfine structure investigations because of the strong broadening of the lines.[1]

Some years ago Niewodniczanski[8] showed that the forbidden lines of Pb I are emitted very strongly in a discharge through a mixture of lead vapor and a rare gas excited by high frequency current. The intensity of these lines was great enough so that he not only found two new lines, λ5313 and λ4659, in addition to the two previously known ones, λ4618 and λ7330, but also was able to study the Zeeman effect in λ4618.[9] This was the first and, up to the present, the only proof of the existence of radiation of magnetic dipole character. A more detailed investigation of these forbidden transitions seemed to promise results of considerable interest. Having at my disposal an excellent oscillator built kindly by Messrs. W. W. Salisbury and L. W. Wouters for my investigations of the spectra of radioactive substances, I was able to get extremely high intensities of these forbidden lines of lead and to study their hyperfine structure. An investigation of their Zeeman effect, in collaboration with Professor F. A. Jenkins, has given successful results, and will be reported in the near future.

Experimental

In preparing the discharge tube, a small portion of chemically pure lead was inserted in a quartz tube 12 cm long and 2 cm in diameter, having a plane window fused on the end. During the experiments the tube was permanently connected to the vacuum system by a side tube of quartz with a constriction close to the discharge tube. The latter, and part of the connecting tube, were surrounded by an electric furnace. The tube could be used for a month or more of daily operation without refilling with fresh lead, because the distillation of lead was retarded by the constriction, and by the presence of helium at a pressure of several mm. One of the difficulties encountered was cracking of the tube at the places where the quartz came in contact with metallic lead. At high temperatures lead attacks the inner surface of the quartz, roughens it, and adheres to it very strongly. Cooling of the tube below the temperature of solidification of lead produces strains which cause the cracks. Therefore the furnace was always kept hot, the temperature being kept at about 400°C when the discharge was not running. The furnace was designed to give a slightly lower temperature at the end containing the lead near the constriction, thus preventing the distillation of lead onto the window at the other end, through which the discharge was observed end-on. This precaution is essential, because formation of a few drops of metallic lead on the surface of the window at high temperature (above 700°C) soon leads to roughness of a large part of the window, the drops acting as centers of the disturbance, which can spread a distance of some mm. A tube thus attacked can be renovated by a procedure devised more than ten years ago by Dr. W. Kessel in Warsaw, consisting of treatment with warm hydrofluoric acid and subsequent heating close to the melting point in an oxygen flame. Naturally the planeness of the window is destroyed in this process.

A liquid-air trap was used between the tube and the vacuum system to avoid the vapors of the diffusion pump oil and of stopcock grease. These vapors decompose in the discharge giving an absorbing layer of carbon, which can only be removed from the window by allowing the tube to cool and burning off the carbon in air. Cooling the trap merely during operation of the discharge does not avoid this difficulty completely. The carbon deposits chiefly in the neighborhood of the electrodes, that is on the ends of the tube. Another type of opaque deposit forms at the ends of the tube during operation, the presence of which is probably due to the presence of PbO molecules, since its formation seemed to be

[6] T. Takamine and M. Fukuda, Phys. Rev. **25**, 23 (1925).
[7] F. R. Einaudi, Rend. R. Accad. dei Lincei **17**, 552 (1933).
[8] H. Niewodniczanski, Acta Phys. Polonica **2**, 375 (1934).
[9] H. Niewodniczanski, Acta Phys. Polonica **3**, 285 (1934); see also his more general article on forbidden lines, *ibid.* **5**, 111 (1936).

correlated with the existence of PbO bands in the spectrum. This deposit evaporates rapidly if the discharge is discontinued, and hence the discharge was interrupted every 15 minutes for about 5 minutes. If the formation of a considerable thickness of this deposit is not prevented, the deposit grows more stable, and this again can only be removed by cooling the tube and heating the window in air to the softening point of quartz.

The electrical apparatus for exciting the discharge consisted of a self-excited half-wave resonant line oscillator using two 500-watt tubes, one at each end of the line. The plate voltage was furnished by a transformer with rectifiers, and the voltage in the primary could be changed in small steps. The electrodes of the discharge tube were two rings of platinum wire around the ends of the tube, and were connected to the oscillator by leads attached on both sides of, and close to the center of, the oscillating line. The best distance was 5–10 cm from the center. At greater distances, too much energy goes into the discharge and suppresses the forbidden lines (see below), at the same time spoiling the balance in the oscillator. At smaller distances the intensity of the discharge is insufficient. Protective condensers and a choke grounded at the middle were inserted in the lines leading to the tube. This was necessary to avoid burning the asbestos in the furnace around the platinum wires.

A careful study was made of the various factors influencing the type of discharge, and the intensity of the allowed and forbidden lines. The wave-length used was about 3 m and could only be varied within small limits (± 0.5 m). No effect of such small changes of frequency on the type and intensity of discharge was found. The most important factor was the temperature of the furnace, that is, the density of the lead vapor. With increase of temperature we first have a pure helium spectrum, but above 500°C the helium lines gradually become weaker and the spectra of both Pb II and Pb I appear, the lines first growing in intensity and then decreasing. The intensity maximum appears at higher temperatures for lines of lower excitation energy. The helium lines disappear completely a little earlier than the Pb II lines. A complete spectrum of Pb I (in the region 2500–11,000A) appears at relatively low temperatures, while the Pb II spectrum behaves quite differently. Of the ^2P levels in Pb II only those below 25,000 cm^{-1} are excited.[10] Lines were observed that originate from ^2D levels lying a little higher (17,000 cm^{-1}), from ^2F levels lying considerably higher (9300 cm^{-1}), and from ^2G levels very much higher (about 5400 cm^{-1}). This preferential excitation of the ^2G levels is probably connected with the mechanism of the discharge. The energy of an ionized He atom ($\sim$198,000 cm^{-1}) is just a little higher than the energy required to doubly ionize a Pb atom ($\sim$181,000 cm^{-1}). As long as there is a small concentration of Pb atoms there are many highly excited atoms and free ions of helium. The latter, because of their longer lifetime, have a chance to collide with Pb atoms and to transfer their energy, taking on an electron and expelling another in the process. The spectrum of Pb II at low temperatures looks like a typical recombination spectrum, in which the free electrons have a much greater probability of being bound into states with high L values, and thus high statistical weights, from which by successive jumps they reach levels with lower and lower L values. Probably a different mechanism of excitation must be assumed in the case of the levels 8^2S and 9^2S of Pb II. These are quite strongly excited, although no trace of the lines from 11^2S and 10^2P could be detected, and the levels 8^2P and 9^2P are excited rather weakly. Nothing can be said about the line from 10^2S as it is covered by strong Pb I line λ3262. The excitation in this case is probably produced by collisions with metastable He atoms ($\sim$160,000 cm^{-1}), whose energy is just about sufficient to excite the higher level 9^2S ($\sim$161,000 cm^{-1}). That in such collisions, accompanied by expulsion of an electron, a preferential excitation of ^2S levels occurs is perhaps connected with the operation of some selection rule. A somewhat similar intensity distribution in the spectrum of Pb II was observed by Earls and Sawyer.[10] No doubt this was also due to the admixture of helium.

An increase of the density of Pb vapor results in a decrease of the average energy of the free electrons, thus resulting in direct excitation of

[10] See the classification of L. T. Earls and R. A. Sawyer, Phys. Rev. **47**, 115 (1935).

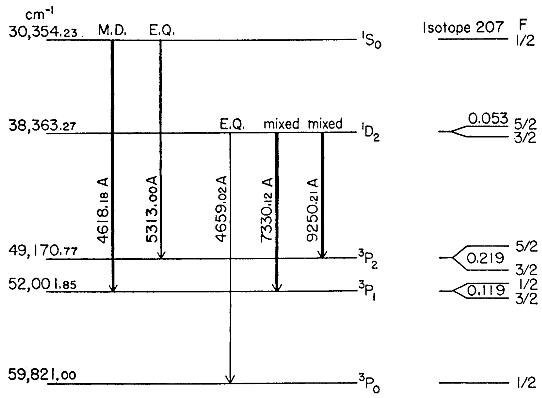

FIG. 1. The lowest levels of Pb I, all belonging to the $6s^26p^2$ configuration. Arrows show the transitions giving the forbidden lines investigated. On the right, the hyperfine splitting of levels of the isotope 207 is shown, but not to scale. M.D. = magnetic dipole, E.Q. = electric quadrupole.

lower and lower energy levels. At high temperatures, above 800°C, only a few lines, originating principally from low Pb I levels, are observed. Increase of the power of the oscillations produces an increase of the intensity of all lines, but the type of the spectrum is very little affected. The change apparently corresponds to a small lowering of the temperature of the furnace. Addition of helium enhances the whole spectrum, but the magnitude of the He pressure above 1 mm has little effect on the intensity. The intensity of most lines increases slowly in the range 1–10 mm of He.

The five lowest levels of Pb I arising from the normal $6p^2$ configuration are represented in Fig. 1. All transitions between these levels are forbidden for electric dipole radiation by Laporte's rule. The wave numbers of the levels were calculated using the very exact wavelengths of the Pb I lines contained in *M. I. T. Wavelength Tables*.[11] The separations of the levels were determined from different pairs of allowed transitions involving a common upper level. The disagreement between independent determinations did not exceed 0.3 cm^{-1}. Average values were used in finding the terms and the wavelengths of the forbidden lines studied. The five lines shown in Fig. 1 comprise all the forbidden lines found thus far. The remaining forbidden transitions which may occur for magnetic dipole or electric quadrupole radiation, namely ${}^1S_0 \rightarrow {}^1D_2$ and the transitions between the ${}^3P$ levels, lie far in infra-red region, and would be very difficult to identify or investigate. The two groups of observed lines are emitted from the two metastable states ${}^1S_0$ and ${}^1D_2$. Corresponding to the observations on the allowed lines described above is the fact that the maximum of intensity for the second group lies at higher temperatures (~850°C) than for the first (~800°C). But the forbidden lines differ markedly from the allowed ones in other respects. Their intensity first rises and then diminishes quite rapidly with increasing power and voltage of the oscillations. This is due to the destruction of metastable atoms by multiple excitation into higher levels. The influence of helium is very pronounced. The intensity of the forbidden lines is very small in a discharge through pure Pb vapor, but increases at first rapidly and then more slowly, tending to saturation as the He pressure is increased. All experiments were carried out with He at 5–6 mm. This is well above the range of the first rapid increase, and not far from saturation.

The forbidden lines are very sensitive to the slightest traces of impurities. Amounts which are small enough so that they do not affect the intensity of other lead lines at all, and which cannot be detected by visual observations of the spectrum, reduce the intensity of these lines very considerably. This does not refer to PbO molecules, which have comparatively small quenching effect. If the lead is slightly oxidized, PbO bands appear in the spectrum, but they are very weak in the temperature range used. Their intensity increases quite rapidly at the cost of the whole Pb spectrum above 850°C. The chief sources of impurities are the vapors of stopcock grease and the impurities coming out of the metallic lead. The latter source gives a constant supply of impurities, even though when starting with fresh lead it was always heated to well above 1000°C for at least ½ hour in order to outgas it. Therefore every few hours, at the start of a series of runs, the tube was pumped out and fresh helium introduced. In this way an exceptionally high intensity of the forbidden lines was achieved. Not only could the weak line λ4659 be easily seen in the spectrograph, but

[11] G. R. Harrison, *M.I.T. Wavelength Tables* (Wiley and Sons, New York, 1939).

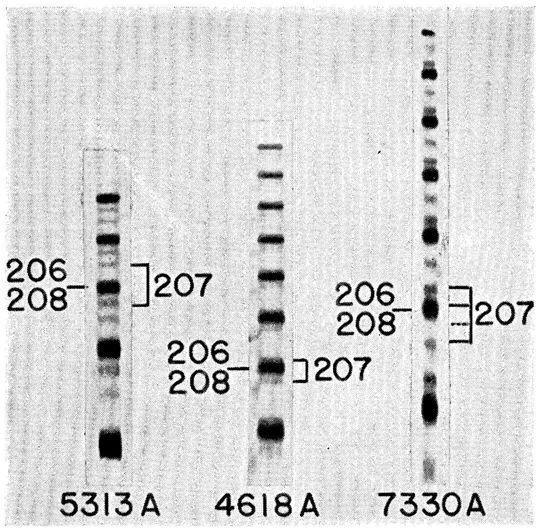

FIG. 2. Hyperfine structure of λ5313 (separator 17 mm); λ4618 (separator 15 mm); λ7330 (separator 19 mm).

also the line λ7330 appeared as a faint companion of the strong allowed line λ7229. After insertion of a Fabry-Perot etalon, the hyperfine structure of the lines 4618 and 5313 was visible. Since many attempts to increase further the intensity of these lines failed, it was concluded that in these experiments the concentration of metastable atoms had practically reached its saturation value, and was limited by the dimensions of the tube and the diffusion of metastable atoms to the walls.

The spectroscopic apparatus consisted of a one-prism glass spectrograph with lenses of 1-m focus, aperture 1 : 12, and a Fabry-Perot etalon, which was used between the prism and the collimator lens. The image of the source was projected on the slit by a short focus quartz lens. The Fabry-Perot plates were silvered, with the kind assistance of Mr. B. G. Saunders, the thickness of deposit being rather light, but still giving sufficient resolving power. (A very high resolving power was not necessary in view of the strong Doppler broadening of the lines.) Intensity marks were recorded on each plate above and below the interferometer pattern. This was done with a step-slit, removing the Fabry-Perot etalon and putting a sheet of white paper in front of the slit. The paper was illuminated from the side toward the slit by an ordinary frosted bulb, placed at such a distance as to make the time of exposure of the steps and of the Pb lines approximately the same. Photographic densities were measured with a Zeiss recording microphotometer and the intensity distribution was then evaluated by a method used by the author on the spectrum of boron and described in a previous paper.[12]

RESULTS

The hyperfine structure of the forbidden lines studied consisted of a strong main component belonging to the even isotopes of Pb (204, 206 and 208, comprising about 79 percent) and much weaker components belonging to the isotope 207 (20.2 percent), which has a nuclear spin of $\frac{1}{2}$. As all Pb levels involved belong to the same configuration, $6p^2$, practically no isotope shift in the lines is to be expected because whatever isotope shift occurs in the levels should be the same for all levels of one configuration. The hyperfine structure of the ordinary lead lines has been investigated by several different authors, and all find nearly equal shifts in all levels of the $6p^2$ configuration. The values given by them[13] of the hyperfine structure splitting of these levels for Pb^{207} are in excellent agreement with the values here measured, and shown in Fig. 1.

The quadrupole line λ5313[14]

In Fig. 2 is an enlargement of a 10-minute exposure of this line taken with a 17-mm Fabry-Perot separator. Eastman Super Panchro Press plates were used here. Two weaker components, on opposite sides of the main component, are observed. They obviously arise from the two transitions for the quantum number F $\frac{1}{2}\rightarrow\frac{5}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2}$, for the isotope 207. The distances from the main component are, in units of 10^{-3} cm^{-1}, 87.5 and 131.5, that is, exactly in the proportion 2 : 3. The possible error does not exceed a few percent. The relative intensities of these components were rather easy to evaluate, because, since the half-widths for all components are the same and much smaller than their separations, a direct measurement of peak intensities could

[12] S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).
[13] See, for instance, H. Kopfermann, Zeits. f. Physik **75**, 363 (1932).
[14] The type of forbidden transitions in Pb I has been discussed by J. Blaton and H. Niewodniczanski, Phys. Rev. **45**, 64 (1934), and by J. Blaton, Zeits. f. Physik **89**, 155 (1934).

be used. A fairly large correction for the background had to be made because, besides the ordinary background due to the etalon,[12] a strong additional background is produced by the PbO bands in this region. The intensity of the first component was found to be 1.55 ± 0.06 times that of the weaker, so that they are within the limits of error in the proportion 3 : 2. This is clear *proof of the applicability of the Rubinowicz-Opechowski formulas to the intensities in the hyperfine structure of quadrupole lines*. The doublet here observed corresponds exactly to the forbidden (S, D) fine structure doublet first observed by Datta[15] in the spectrum of potassium.

The magnetic dipole line, λ4618

In Fig. 2 is shown an enlargement of a 40-second exposure of this line, taken with a 15-mm separator. Here Eastman 40 plates were satisfactory. This pattern shows one component well separated, and another on the opposite side, merging with the main line. They come from the two transitions of $F\ \frac{1}{2}\rightarrow\frac{1}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2}$, showing that the hyperfine structure in the level $^3P_1$ is inverted. This agrees with the results of other investigators.[13] The curve of the intensity distribution has been treated in the manner described before,[12] which consists essentially of reflection of the side of the main component not overlapped, and adjustment of its position so as to get from the remainder a component of the same Doppler width. The distances of the components and their relative intensities may then be found. A correction of 7.5 percent for the background was made.[12] The distances are 79.4 and 39.7, these being the mean values from the two best plates. Their ratio is 2.00 ± 0.06. The relative intensities are $1 : 2.05\pm0.08$. This shows that *for a magnetic dipole line the same intensity rules apply in the hyperfine structure as for electric dipole lines*. This result finds further confirmation in the structure of λ7330. Although not unexpected, it is also not quite evident, since in fine structure there is no such similarity of the two cases. This point needs some clarification on the theoretical side.

[15] S. Datta, Proc. Roy. Soc. **A101**, 539 (1922); see also W. Prokofjew, Zeits. f. Physik **57**, 387 (1929) for this and other alkalis.

The mixed line, λ7330

The greatest experimental difficulties were encountered in the study of this line. In Fig. 2 is an enlargement of a 15-min. exposure taken with a 19-mm separator. Eastman I–U plates were used. In the lower part of Fig. 3 the predicted components for the isotope 207, and their intensities, are given for the two extreme cases of pure magnetic dipole and pure electric quadrupole radiation. A careful search for the extra component ($\Delta F=-2$; $\frac{5}{2}\rightarrow\frac{1}{2}$), which arises only from quadrupole radiation, was made. For this purpose excessive background had to be carefully avoided. Therefore the plates were not hypersensitized, although this would have considerably reduced the time of exposure. The presence of a very strong line at λ7229 gave a great deal of trouble, because it lies very close to the line investigated. An adjustable razor-blade edge was mounted in the plateholder to prevent this line from blackening the plate. Special care was taken to avoid scattered light in the spectrograph. A strong continuous background is also produced by the temperature radiation of the furnace; its influence was reduced by narrowing the spectrograph slit. Corrections of 8–15 percent for the furnace radiation alone had to be made on different plates (in addition to the normal correction), the variations depending on the furnace temperature and on the slit width. No trace of the extra component could be found. The distances from

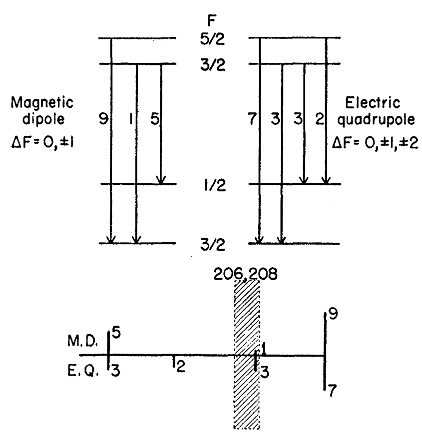

FIG. 3. Hyperfine structure level scheme for the isotope 207 and relative intensities of the components of λ7330 for the two extreme cases, pure magnetic dipole and pure electric quadrupole radiation. Below, the expected hyperfine structure of this line for both cases, in juxtaposition.

the main line of the two components visible in Fig. 2 were measured, and found to be 112 and 60, from which the splitting of the $^1D_2$ level given in Fig. 1 was calculated. The ratio of intensities of the two components is 1.87 ± 0.08, or about 9 : 5.[16] This shows *that the line λ7330 is chiefly of a magnetic dipole character, and that for magnetic dipole radiation the selection rule* $\Delta F=0, \pm 1$ *holds.*

An upper limit to the percentage of quadrupole radiation can be roughly evaluated in the following way. We make the assumption, which as Dr. L. I. Schiff pointed out is not perfectly obvious and requires proof, that the intensities of the components are proportional to the sums of intensities of the two kinds of radiation. If we denote the percentage of quadrupole radiation by x, then the relative intensities of the two observed components will be $[9(100-x)+7x]/[5(100-x)+3x]$. This cannot be set equal to the observed value 1.87, as this ratio was obtained with the assumption of a certain correction for the background. If there is an extra component in the gap between the main line and the weaker component, the background correction must be taken as smaller, and the value for the relative intensity will also be a little smaller. We must adjust the background correction so as to have a consistent value of x from the three components (the last one being fictitious) in the ratio $[9(100-x)+7x] : [5(100-x)+3x] : 2x$. After thus adjusting the background, we find $x\sim 9$ percent, instead of 20 percent which we would obtain directly from the value 1.87. Naturally this estimate is very rough and only gives the order of magnitude. The method is only really sensitive around $x\sim 50$ percent.

In all three forbidden lines the ratio of the total intensity of the components belonging to the isotope 207 to that for the even isotopes is found to be in very good agreement with the known concentration of the isotopes. The ratio is 21 : 79 in λ5313, 21 : 79 in λ4618, and 21.5 : 78.5 in λ7330. This means that, in contradistinction to forbidden transitions caused by inner perturbations, *for spontaneous quadrupole and magnetic dipole radiation the transition probabilities are the same for all kinds of isotopes*, as is to be expected. The small deviation in the direction of too high an intensity for the isotope 207 probably arises from the underestimation of the peak value of the plate blackening resulting from the finite slit width of the microphotometer. This underestimation is especially important in the case of a high peak value, that is, for the main component. In the case of λ7330, where the slit width of the spectrograph was small, the slit had to be taken especially wide in order to get reasonable deflections on the microphotometer. Also connected with this microphotometer slit width are some inconsistencies in the results on the half-widths of the lines. The most reliable of these widths was the value 0.042 cm^{-1}, obtained for λ4618 from the lowest orders, with a separator of 28 mm. It probably differs very little from the true value. The Doppler half-width for a temperature of 830°C is computed to be 0.035 cm^{-1}. The temperature in the discharge is no doubt a little higher than that in the surrounding oven. At lower temperatures a gradual change of the spectrum was observed during the first few minutes of running, the change being of the sort to be expected from a heating up of the tube by the discharge. The difference of the measured and calculated half-widths may indicate the presence of a small isotope shift, much smaller however than the shift expected on the basis of Kopfermann's[13] data. For λ5313, the measured half-width was 0.040 cm^{-1}, and for λ7330, it was 0.038 cm^{-1}. These are to be compared with 0.030 and 0.022 cm^{-1}, calculated for 830°C. That this result is really a consequence of the finite slit width of the microphotometer is shown by the fact that the half-widths slowly increased with the order of interference, and were slightly greater for the main component than for the others. But it is possible that for λ5313 the isotope shift also plays a considerable role. According to Kopfermann[13] it should be greatest for this line, about 0.018 cm^{-1}, but this figure is certainly too high. For λ7330 which, according to Kopfermann,[13] should have practically no isotope shift, the whole discrepancy can be accounted for by the very wide microphotometer slit.

The hyperfine structure of the two remaining

[16] The weak line visible on Fig. 2 (7330A) close to the weakest component (below to right) is probably λ7346.0 of Cd. This line is much weaker at higher temperatures and therefore did not disturb the photometric measurements. The small hump in the curve may easily be seen, and was eliminated in the calculations.

lines, λ4659 and λ9250, was not investigated. A one-hour exposure of λ4659 showed that a pattern with sufficient blackening could be obtained in 3–4 hours for this line, but in view of the smallness of the $^1D_2$ level splitting, the attempt was not made. In any case, the component would not be clearly resolved from the main line. Furthermore, this line does not present anything new, as it is completely analogous to λ5313. The new line λ9250 occurs in an inconvenient spectral region and is similar in some respects to λ7330.

To complete the investigation of these forbidden transitions within the p^2 configuration, the relative intensities of all five lines were determined. After removal of the Fabry-Perot etalon, photographs of the spectrum of the discharge at different temperatures were taken. Two sets of intensity marks were photographed on each plate, using the step-slit and a Kipp and Zonen calibrated band-filament lamp in quartz. The lamp was placed as close to the discharge tube as possible to prevent errors due to lack of achromatism in the optical system. The blackening of the plates was measured on the microphotometer and the relative intensities determined by the usual method, including corrections for the background. The relative intensity of λ4618 and λ5313 was determined using the Super Panchro Press plates. The mean result, $I_{4618} : I_{5313} = 5.0 \pm 0.3$, was found to be independent of the temperature. The relative intensity of 5313 and 4659 was determined using the same kind of plates but longer exposures, to keep the blackenings in a suitable range. A large background correction had to be made for λ4659, due to the exact superposition of this line on the head of one of the PbO bands. The result was found to depend on the temperature $I_{5313} : I_{4659}$ being 15 for lower temperatures, and decreasing to 12 for the higher ones. The relative intensities of the three lines λ4659, λ7330 and λ9250 were measured, using hypersensitized Eastman I–M plates. Large background corrections were made for the first and last lines, amounting to about 35 percent. In the last case the background was produced by the very strong continuous furnace radiation. The average result was $I_{4659} : I_{7330} : I_{9250} = 0.023 \pm 0.006 : 1 : 0.84 \pm 0.07$, and was independent of temperature.

A comparison of these relative intensities with the theoretical formulas of Stevenson[17] cannot be made, because his formulas are derived for small deviations from Russell-Saunders coupling only, namely, when the intensities of the above triplet differ only slightly from 0 : 1 : 3. Since in this spectrum the coupling is very nearly j, j, the more general formulas of Condon[18] should be used. Unfortunately Condon does not give formulas for all the transitions here investigated. More complete, and independent, calculations have been carried out recently by Mr. E. Gerjuoy and will be published soon. The comparison of the experimental results with theory will be made in his paper, and at the same time other problems mentioned above will be discussed.

Finally, an attempt has been made to detect a possible forbidden line $^1S_0 \rightarrow {}^3P_0$, at λ3392.7, corresponding to the well-known Hg I line λ2655.8. This line would only be emitted by the isotope 207, as a result of the coupling of the electronic shell with the nuclear spin. A careful search, made with a small spectrograph, led to a negative result, and it was concluded that this line, if present, has an intensity smaller than 1/20 of the intensity of λ4659. This upper limit is high, because the presence of PbO bands in this region made it impossible to greatly increase the time of exposure. A very faint line was found quite close to the expected position, but it turned out to be λ3397.2 of Bi I. That the lead used contained not only Cd, but also traces of Bi was proved by the appearance of some of the other strong lines of the Bi I spectrum. It seems probable that the forbidden line λ3392.7 is not emitted at all, because of the operation of the Laporte's rule.

In conclusion, I wish to express my sincere thanks to Professor E. O. Lawrence for making possible my stay in Berkeley, and for extending to me the facilities of his laboratory. I also wish to thank Professor F. A. Jenkins for his many suggestions and his great kindness during the whole time of my stay. I am also much indebted to Dr. L. I. Schiff, to Mr. W. Opechowski (Leiden), and Mr. E. Gerjuoy for stimulating discussions.

[17] A. F. Stevenson, Proc. Roy. Soc. **137**, 298 (1932). See also J. Blaton, reference 14.

[18] E. U. Condon, Astrophys J. **79**, 217 (1934).

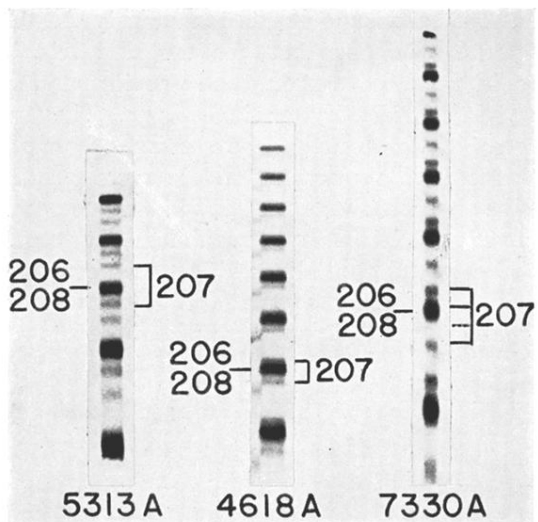

FIG. 2. Hyperfine structure of λ5313 (separator 17 mm); λ4618 (separator 15 mm); λ7330 (separator 19 mm).