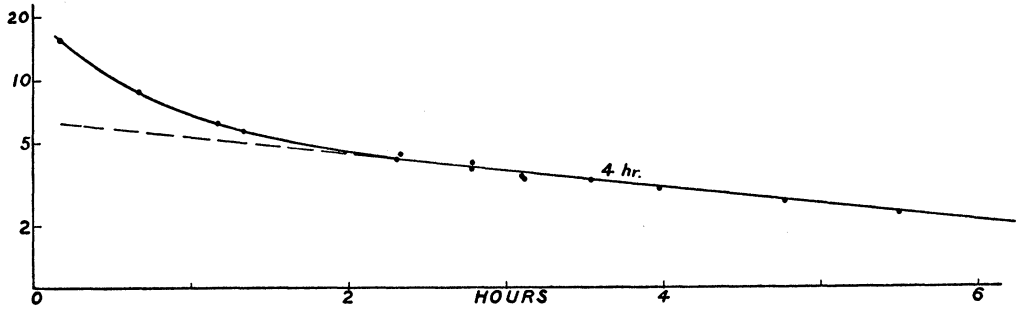

FIG. 2. The decay of the negative electron emission of In bombarded by protons.

by an inelastic collision similar to an inelastic collision of a neutron or through the action of the electric field of the proton.[4]

The authors gratefully acknowledge their indebtedness to Dr. L. Szilard and Dr. M. Goldhaber for suggestions which prompted this study and for valued suggestions made by them and Professor L. A. DuBridge during the course of the work. They wish to thank Professor Line for microanalytical work, Mr. R. Grabenstetter for chemical separations and particularly Mr. T. Enns for much help in connection with cyclotron operation.*

[4] V. F. Weisskopf, Phys. Rev. 53, 1018 (1938).

* *Note added in proof.*—Indium has been bombarded with 0.01 μa of 8.5-Mev alpha-particles. No 4.1-hr. activity was observed. According to this result the cross section for excitation of In^{115} with 8.5-Mev alpha-particles cannot be more than twice the cross section for the excitation of In^{115} by 6.5-Mev protons.

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The Quadratic Zeeman Effect

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The Zeeman effects of the principal series lines of sodium and potassium in the range $n=10$ to 35 are observed in absorption, using the new 60-inch cyclotron magnet. With a field of 27,000 gauss, the lines having n in the neighborhood of ten show a normal triplet representing the complete Paschen-Back effect of the narrow ^2P doublet. From about $n=12$ to 20 all components show an increasing displacement toward short wave-lengths proportional to (n^*),[4] the shift of the π components being half that of the center of the two σ components. This is the quadratic Zeeman effect, varying as H^2, and is here measured and compared quantitatively with theory for the first time. The agreement with the simple theory is excellent as far as $n=20$. Beyond this the lines show an additional displacement in the same direction, increasing as a higher power of n. At the same time the lines are broadened toward the red, with indications of an unresolved component whose intensity increases rapidly with n. The displacement is interpreted as a perturbation by the F states, whose separation from the P states in this region becomes comparable with the magnetic energy. The additional lines causing the broadening represent forbidden transitions $^2S\rightarrow{}^2F$. Beyond $n=28$ the broadening increases suddenly and becomes symmetrical, until the lines are no longer distinguishable at $n=35$. All of these perturbation effects are compared with the theoretical results given in the accompanying paper by Schiff and Snyder. Some features are accounted for quantitatively, while the others are satisfactorily explained qualitatively.

THE quadratic Zeeman effect is a displacement toward short wave-lengths of the Zeeman components of a spectral line, proportional to the square of the magnetic field. It is directly related to the diamagnetic term in the theory of magnetism, which contains the square of the "radius" of the atom. In both classical and quantum mechanical theories of the Zeeman

effect this quadratic term is usually neglected, because it is unobservable under most circumstances. The existence of the quadratic shift was first shown experimentally by Segrè[1] in a study of the Zeeman effect of the last observable members of the principal series of sodium. The shift could only be detected qualitatively, and no accurate measurements could be made for comparison with theory. Hence we have repeated these experiments under improved conditions, and have extended them, for reasons mentioned below, to potassium. In our work the Zeeman patterns are completely resolved, and the shifts are measured rather accurately. For the last members of the series, a new perturbation effect is found, which in sodium appears as an unsymmetrical broadening of all Zeeman components, eventually becoming symmetrical and smearing the lines into an apparent continuum considerably before they reach the series limit. The theory of these effects is discussed in the accompanying paper by Schiff and Snyder.

The simple theory of the quadratic effect[2] gives displacements proportional to the fourth power of n^*, the effective quantum number, and since the coefficient is of the order of magnitude of 10^{-15} cm^{-1}, the shifts become detectable only for rather large values of n^*, exceeding about 12. The Zeeman effects usually studied involve small n, and hence the quadratic term is negligible in these cases. In the study of lines of large n, one is practically restricted to absorption lines, since for emission it is not possible to put a sufficient number of atoms in the initial states to obtain the required intensity. The principal series of the alkalis afford the most favorable case, the sodium series having been observed in absorption[3] as far as $n=59$. To obtain these lines without undue pressure broadening, the length of the absorbing column of vapor cannot be made too small, and therefore a magnetic field of considerable dimensions is required. We were fortunate in having available the new cyclotron magnet of the Crocker Radiation Laboratory, the poles of which have a diameter of 152 cm.

[1] E. Segrè, Nuovo Cimento **11**, 304 (1934).
[2] See for example J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, p. 178.
[3] R. W. Wood and R. Fortrat, Astrophys. J. **43**, 73 (1916).

Experimental

The original pole separation of the magnet was 56 cm. This was reduced to 4.4 cm by inserting large iron blocks, the final pole faces being 15×63 cm. In the remaining space a magnetic field of 27,000 gauss was obtained, as measured by a fluxmeter. By inserting suitable shims, the field was made constant to ±100 gauss over the region to be occupied by the absorbing vapor.

The absorption tube was of Pyrex tubing 3.5 cm in diameter and 110 cm long. The ends were closed by plane fused quartz windows, and the central portion, 30 cm long, heated by a Nichrome winding. A few lumps of the alkali metal were placed along the heated part, and after the tube had been evacuated and heated until the metal fused, fresh hydrogen was introduced at about ten cm pressure to prevent diffusion to the windows. The temperature required to bring out the high series members of sodium was 500°C. A sensitive criterion for the proper pressure is a characteristic azure blue color of the transmitted light. For potassium it is a light green.

As a source for the continuous spectrum, we used a hydrogen lamp of the conventional design, carrying a current of 180 ma at 7000 volts. With this source, the exposures for the sodium series, which converges at λ2412, varied from 15 to 30 min. For potassium, with a convergence at λ2856, 5 to 10 min. were sufficient. The light was rendered parallel by a quartz-fluorite achromat, and, after traversing the absorption tube, focused on the slit of the spectrograph by a lens of fused quartz. Between this lens and the slit was placed a calcite crystal of such a thickness that the two images of the source, polarized perpendicular and parallel to the magnetic field, almost touched. A diaphragm was used which in one position exposed the two adjacent halves of the images (for the spectra of the π and σ polarizations with field) and in another the two outer halves (for the spectrum without field). A slight artificial shift of about 0.04 mm was introduced between the spectra with and without field, as a result of small mechanical displacements arising from the magnetization of the spectrograph. In the measurements this could be easily determined and corrected for, thanks to the presence of emis-

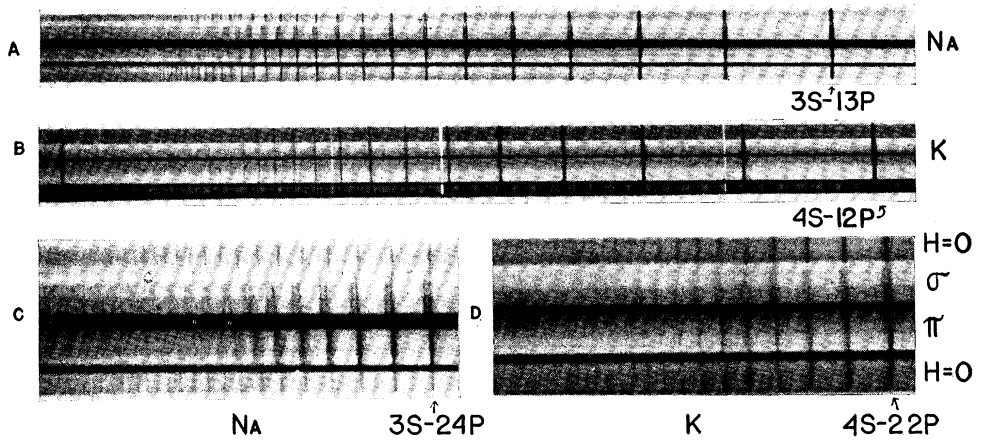

FIG. 1. Zeeman effect of the absorption lines of sodium and potassium. $H=27{,}000$ gauss. (a) Na, low density, (b) K, low density, (c) Detail of the end of the series, Na, higher density, (d) Same for K, higher density.

sion lines coming from a contamination of mercury in the hydrogen lamp.

The spectrograph was a 3-meter Littrow instrument, with a combination of 60° and 30° quartz prisms automatically adjusted for minimum deviation.[4] It gave a dispersion of 0.75A/mm at λ2412, and 1.36A/mm at λ2856. Our best plates of the series without field resolved the sodium lines as far as $n = 51$, and the potassium lines as far as $n=43$.

Several exposures were taken for both sodium and potassium, with different densities of the absorbing vapor. Fig. 1 shows enlargements from two of our plates of each. The fact that the lines with field have a false shift toward the red will be seen from the emission lines on the plates. In the case of potassium, the lines are broader when the vapor is dense enough to produce the high members with any intensity, and only at the lowest densities used were the σ components well resolved. This, combined with the lower dispersion of the spectrograph, made the results for potassium less accurate than those for sodium.

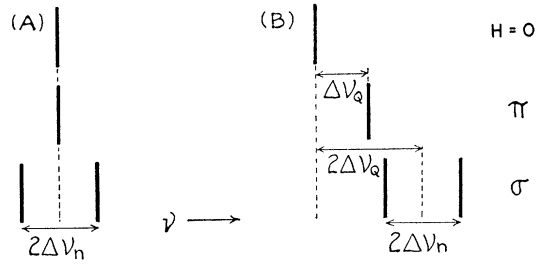

FIG. 2. Zeeman patterns (a) without and (b) with the quadratic effect. The pattern shown in (b) is that predicted for the line $3S-27P$ of Na, with $H=27{,}000$ gauss.

[4] H. E. White, J. Opt. Soc. Am. **25**, 241 (1935).

DATA AND RESULTS

The simple theory of the quadratic effect, outlined in the following section, predicts the Zeeman pattern shown in Fig. 2(b). Both π and σ components are displaced toward higher frequencies, the quadratic shift $\Delta\nu_Q$ of the π component being half of the shift of the center of gravity of the σ components. For comparison, Fig. 2(a) shows the normal pattern to be expected for the lines of fairly low n, i.e., in the neighborhood of $n=10$. This is really a complete Paschen-Back effect of the very narrow doublet ${}^2S_{\frac{1}{2}}-n\,{}^2P_{\frac{1}{2},\frac{3}{2}}$.

The lines were measured with a Geneva Society comparator, and a curve of the dispersion in cm^{-1}/mm drawn, by using the known wavelengths of the lines without field. Two different plates were measured for both Na and K. The splitting $\Delta\nu_n$ of the σ components was first used to check the value of the magnetic field by the relation

$$\Delta\nu_n = 4.67\times10^{-5}\,H\ \text{cm}^{-1}.$$

The more accurate measurements for sodium gave values of H varying from 26,700 to 27,300, and therefore we adopt the figure 27,000 obtained with the fluxmeter.

The displacements of the Zeeman components from their no-field positions were then evaluated. The plotted points in Figs. 3 and 4 represent the average displacements obtained from the measurements of lines up to $n=28$. The theory on which the curves are based will be considered in the following section.

As will be seen, especially by inspection of Fig. 1(c), the lines beyond $n=28$ become rapidly broader. In Na this broadening is at first definitely unsymmetrical, shading off toward the longer wave-lengths, and is greater for π than for σ. Fig. 5 shows microphotometer curves of the last few members of these series taken with the Zeiss recording microphotometer. The K lines

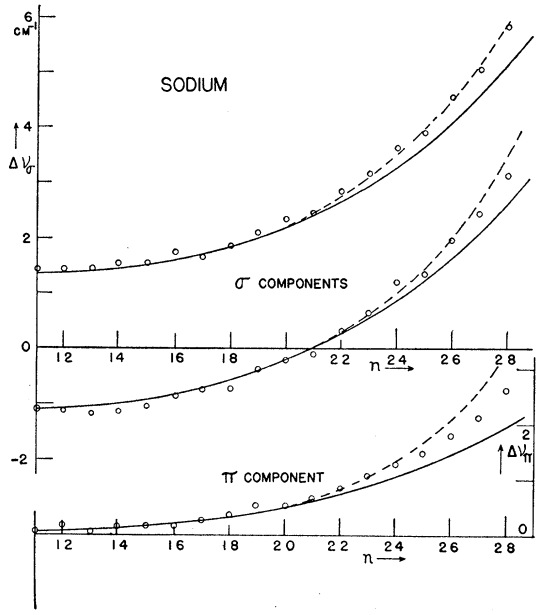

FIG. 3. Displacements of the Zeeman components for sodium. The continuous curves give the theoretical displacements by the simple theory (Eq. (2)), while the broken curves include the perturbation effect (Eq. (9) of Schiff and Snyder).

photometered in Fig. 5(b) were necessarily much weaker than the Na lines, for if the vapor density was further increased to render them stronger, all lines, including those with no field, became rapidly broader.

The microphotometer curves for Na show that the unsymmetrical broadening of the π components is already appreciable for the line $3S-23P$. That it also exists for the σ components is shown by fact that the long wave-length component is

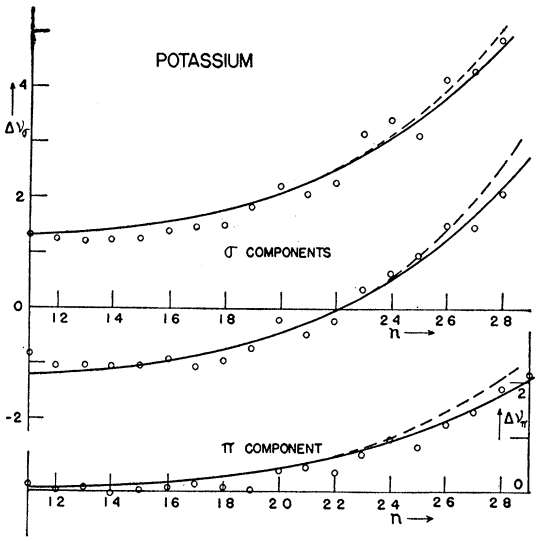

FIG. 4. Displacements of the Zeeman components for potassium. Similar to Fig. 3 for sodium.

consistently stronger, being enhanced by the wing of the adjacent line. Furthermore, there seems to be a definite indication in the curve for the π components that the wing is actually a faint, nearly resolved line that increases in intensity until it is practically equal to the original line at $n=30$. In K the lines are too faint to show such a component even if it existed. It was the anticipation that the broadening effects should be different in K that caused us to try this element. The fact that the unsymmetrical broadening does not appear is in agreement with theoretical expectation, as explained below. One can also conclude that the large difference in broadening between the π and σ components observed for Na is either nonexistent or much less pronounced for K.

We have measured the positions of the intensity maxima of the broadened lines beyond $n=28$. They could be followed as far as $n=35$ in Na and $n=33$ in K. In the case of the π components of Na it is obvious that these maxima do not follow the simple theory of the quadratic effect even approximately. Instead of continuing to increase in proportion to n^4, the displacements reach a maximum at $n=30$, and then decrease rapidly toward zero again. This may be easily seen in Fig. 5(a). Table I gives the results of these measurements. It will be noticed that in K only the last measured π maximum deviates significantly from the simple theory. As pointed out

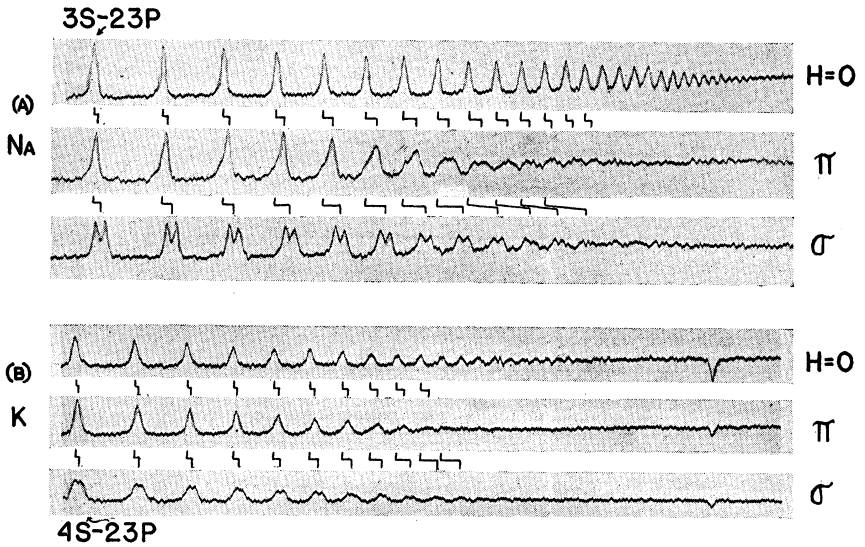

FIG. 5. Microphotometer curves (a) for Na, (b) for K. For the σ components, the displacements of the centers of gravity from the no-field lines are indicated.

below, the first few lines of this table are not expected to agree with the simple theory, but with a more extended theory. (See broken lines in Figs. 3 and 4.)

The displacements of the σ components, on the other hand, go on increasing more or less as expected. In Fig. 1(c) they may be seen to catch up with the no-field lines of next higher n, and on the original plate may be observed to "lap" the no-field lines three times before fading out. This behavior of the π and σ maxima has been verified on microphotometer curves like those of Fig. 5, but taken with a considerably wider slit.

As regards the widths of the lines, it is only possible to obtain qualitative results from our plates. We have measured the widths of the microphotometer peaks at half-maximum for the broadened π and σ components of Na. The curves for the σ doublets can easily be analysed into two identical unsymmetrically broadened curves separated by $\Delta\nu_n$. Table II shows the measured widths of these component peaks, for comparison with those of the π and no-field lines. It must be remembered that the width of these peaks is partly true line width and partly caused by the finite resolution of the spectrograph. The effect of finite resolving power would be to make the observed ratio of the widths of the π to the σ components less than the true ratio, so that it is legitimate to regard the ratio from Table II as a lower limit to the true ratio. The microphotometer curves give a reasonably true picture of the intensity contours of the lines on our plates, because the blackening in this region is on the linear part of the plate characteristic. Furthermore, all lines are faint enough so that there is no question of spurious differences in breadth because of saturation effects.

DISCUSSION

The Zeeman effect of the first few lines of the principal series of the alkalis is the well-known anomalous effect of a $^2S-{}^2P$ doublet, and, according to Preston's rule, is the same for all lines of the series. However, this holds only as long as the magnetic splitting is small compared to the doublet separation of the ^2P term. For the field we used (27,000 gauss) the first serious departures begin at about $n=6$ in Na. Since the ^2P separation decreases approximately as $1/n^3$, the magnetic splitting rapidly approaches a normal triplet (Paschen-Back effect) because of the uncoupling of the spin and orbit. For $n=10$ the ^2P separation is already small compared to the Larmor frequency $\Delta\nu_n=1.262$ cm^{-1} for the field we used. Therefore, since the lines we studied all have $n>10$, the spin does not need to be considered, and, but for the quadratic effect, we should obtain a normal triplet.

The quadratic Zeeman effect is due to a term in the magnetic energy of the form

$$E=\frac{e^2H^2}{8mc^2}\langle x^2+y^2\rangle_{Av}, \quad (1)$$

in which x and y are the coordinates of the electron, the z direction being that of the magnetic field. From this it is easily seen that the effect is proportional to n^4. We substitute for $\langle x^2+y^2\rangle_{Av}$ its value for hydrogen, and replace n by n^*, as a better measure of the size of the orbit. Neglecting terms in lower powers of n, Eq. (1) then becomes

$$\Delta\nu_Q=\frac{e^2H^2}{8mc^3h}a_0n^{*4}(1+m_l^2)$$
$$=4.98\times10^{-15}n^{*4}H^2(1+m_l^2). \quad (2)$$

Here $a_0=h^2/(4\pi^2e^2m)$ is the radius of the first Bohr orbit, while m_l is the orbital magnetic quantum number in the upper state. Adding the displacement (2) to the normal Zeeman displacement of the P terms, one finds that the two levels with $m_l=\pm1$ preserve their separation $2\Delta\nu_n$, but that their center of gravity is displaced toward the series limit by an amount $H^2e^2a_0n^{*4}/(4mhc^3)$, whereas the level with $m_l=0$ moves in the same direction by half as much. This causes corresponding shifts of the Zeeman components, and gives the pattern which was illustrated in Fig. 2(b).

The continuous curves in Figs. 3 and 4, as well as the calculated values in Table I, were computed from Eq. (2). It is seen that the agreement with experiment is good for $11<n<20$. It is particularly satisfactory that the long wavelength σ component crosses the π component at just the predicted place, $n=26$. However, in Na above $n=20$ there appears an increasing discrepancy in the sense that the observed shift is too large. This deviation is much too large to be caused by an error in the measurement of the field. The qualitative reason for this effect is as follows. The elementary theory considers the P terms alone, and neglects the fact that the magnetic perturbation causes a "mixing" of these states with states of different L, which lie very close to the P terms in this region. Here only the states differing in L by 2 units are to be considered in the first approximation. Thus Eq. (1) is valid only as long as the total magnetic energy is small compared to the energy differences between the P and F terms. When this condition is no longer satisfied, perturbations occur which can be qualitatively described as follows: The eigenfunctions of the F states become mixed with those of the P states of about the same energy, and, in a higher approximation, the same occurs for the H, K, $\cdots$ eigenfunctions. This causes transitions $S\rightarrow F$, $S\rightarrow H$, etc., which are normally forbidden, and at the same time the P and F levels as well as H, K, $\cdots$ are displaced because of a mutual repulsion.

The first of these effects, the occurrence of forbidden lines, is rather clearly seen in the microphotometer curve for the π components of Na in

TABLE II. *Widths of microphotometer peaks for sodium in cm^{-1}.*

	$n=25$	26	27	28	29	30	31
$H=0$	1.6	1.6	1.6	1.6	1.6	1.5	1.6
π	2.3	2.4	2.8	3.9	4.3	4.9	5.7
σ	2.1	2.0	2.0	2.2	2.5	2.7	2.5

TABLE I. *Displacements of broadened components. Measurements represent displacements of maxima in cm^{-1} except where specified. The calculated values are from Eq. (2).*

	Sodium						Potassium			
	π		σ_-		σ_+		π		σ (center of gravity)	
n	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
28	2.63	1.97	3.12	2.68	5.84	5.18	1.85	1.73	3.68	3.47
29	3.04	2.28	3.52	3.29	6.44	5.82	2.10	2.01	3.28	4.02
30	3.58	2.62	4.59	4.00	7.19	6.49	2.28	2.33	3.78	4.65
31	3.63	3.00	5.67	4.73	7.91	7.26	2.48	2.67	4.87	5.34
32	1.80	3.41	6.75	5.58	9.06	8.07	1.59	3.06	6.55	6.11
33	0.96	3.88	7.59	6.49	10.08	9.01			6.81	6.96
34	0.83	4.38	8.09	7.51	10.72	10.02				
35	1.00	4.93								

Fig. 5. The nearly resolved wing on the red side of the lines $n=24$ to 30 evidently represents these forbidden lines. This broadening is therefore not a true broadening of the lines, but merely represents the occurrence of new lines not clearly resolved by our spectrograph.

The second effect, namely the displacement of the P terms, is qualitatively in the right direction, as may be seen by reference to Fig. 6, in which a few of the high levels of Na and K are plotted to scale for zero field. In both cases repulsion of the P by the F levels will displace them upward, shifting the line to the violet, but the effect should be much larger in Na because P and F lie closer together. The exact separations of these levels are best seen from the values of the quantum defects, given in Table III. In this table is also included a quantity Δ, the difference between the effective quantum number n^* and the nearest whole number. It is Δ which determines the magnitude of the perturbations. Since the quantum defects $n-n^*$ of the F levels are practically zero for all the alkalis, Δ gives the distance from a P level to the nearest F level, expressed as a fraction of the separation of successive P levels. That the perturbation effect should be smaller in K than in Na is clear from these figures.[5] Furthermore, the intensities of the forbidden lines should be smaller in K, and this accounts for the greater symmetry of the π components in this case (Fig. 5).

The quantitative treatment of these perturbations is given in the accompanying paper by Schiff and Snyder. There it is shown that the displacement of the P states is proportional to n^{11}, and inversely proportional to the separation of the P state and the nearest F state. The broken

TABLE III. *Quantum defects of P states.*

	Li	Na	K	Rb	Cs
$n-n^*$	0.04	0.85	1.71	2.66	3.59
Δ	−0.04	0.15	0.29	0.34	0.41

[5] A similar situation arises in the Stark effect; cf. E. Segrè, Rend. Lincei **19**, 395 (1934).

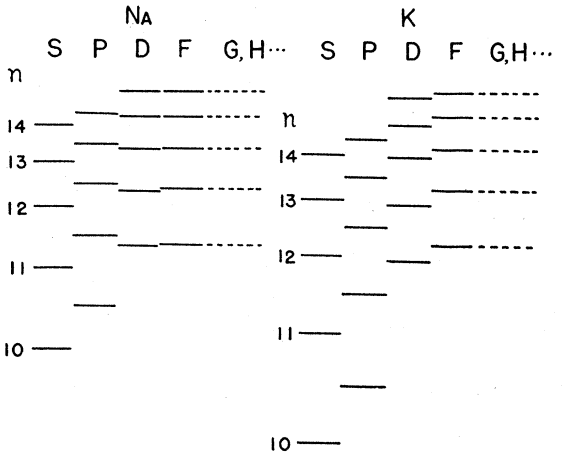

FIG. 6. High terms of Na and K.

curves in Figs. 3 and 4 are plotted from their Eq. (9), and are seen to agree very well up to the point where the lines cease to be relatively sharp, i.e., up to $n=28$ in Na.

For the diffuse maxima above $n=28$ the perturbation by the states of different L is inadequate to account for the observations. In this region the magnetic energy becomes comparable with the separation of states of successive total quantum number n, and thus there occurs a mixing of states differing not only in azimuthal quantum number, but also in total quantum number. This effect is responsible for the large symmetrical broadening of the last observable lines, and also probably for the premature death of the series, which becomes unobservable because of the excessive broadening of its members. The total intensity in this region will, however, remain constant because of the sum rules. For a more quantitative discussion of the effects in this region, and comparison of our measured widths with theory, we again refer to the following paper.

In conclusion, we wish to thank Professor E. O. Lawrence for his cooperation in making the large magnet available. We are also much indebted to Dr. Luis Alvarez, who assisted with the design of apparatus, and to Professor W. F. C. Ferguson, for help with the spectroscopic work.

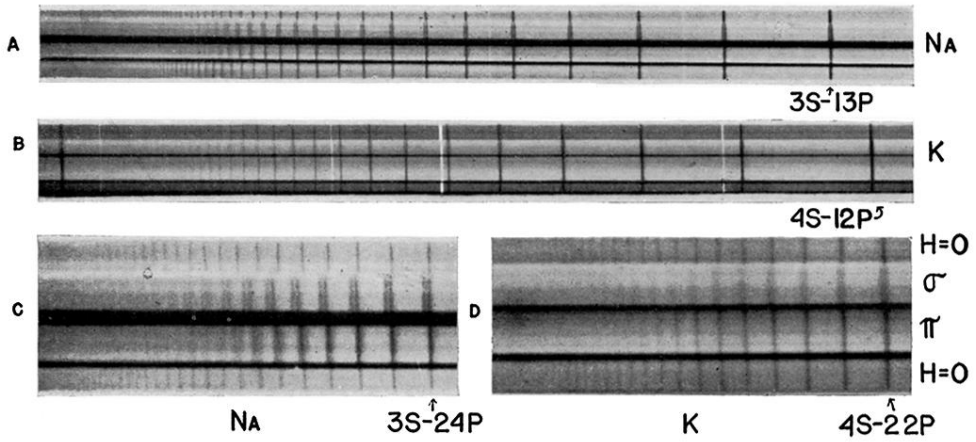

FIG. 1. Zeeman effect of the absorption lines of sodium and potassium. $H = 27{,}000$ gauss. (a) Na, low density, (b) K, low density, (c) Detail of the end of the series, Na, higher density, (d) Same for K, higher density.

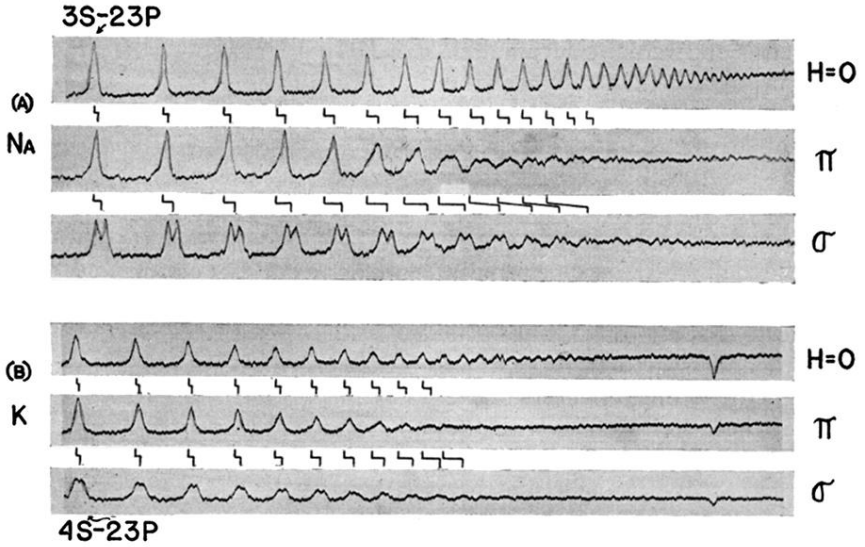

FIG. 5. Microphotometer curves (a) for Na, (b) for K. For the σ components, the displacements of the centers of gravity from the no-field lines are indicated.