Paschen-Back Effect of Hyperfine Structure and Polarization of Resonance Radiation. Cadmium ($6^1P_1 - 5^1S_0$)

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Because of the Paschen-Back effect of the hyperfine structure of the odd isotopes, the polarization of cadmium λ2288A resonance radiation excited by plane polarized incident light changes from 76.7 percent in zero field to 100 percent in a strong field parallel to the electric vector of the exciting light. The experimental results agree very closely with computations based on Goudsmit's modification of Darwin's theory of the Paschen-Back effect and give for the separation of the two levels into which the 6^1P_1 level of Cd (odd-isotopes) is split a value of 12.6×10^{-3} cm^{-1}. From this result and Schüler's measurements of the hyperfine separations of the triplet lines $6^3P_{0,1,2} - 6^3S_1$ the constants a and b giving the interactions of the p and s electrons, respectively, from Goudsmit's equation

$$A(J) = a(2-g) - a\frac{6\Gamma(2-g) - 2(g-1)L(L+1)}{(2L-1)(2L+3)} + b(g-1)$$

are found to be $a = 8.4 \times 10^{-3}$ and $b = 225.7 \times 10^{-3}$.

THE polarization of the cadmium resonance lines λλ2288A and 3261A has been discussed by Ellett and Larrick[1] on the basis of Schüler's[2,3] explanation for the hyperfine splitting of the Cd energy levels. It will be recalled that Schüler has assigned nuclear moments of 0 and $\frac{1}{2}$ (in units $h/2\pi$) to the even and odd isotopes of Cd, respectively. For the λ2288A line, using nonpolarized exciting light, Ellett and Larrick found for the polarization in zero field

$$P = (3+9\gamma)/(11+9\gamma)100,$$

where γ is the ratio of the abundance of the even and odd isotopes which they found from experimental data to have the value 2.53. From observations of Schrammen[4] and the narrowness of the Cd red line λ6438.47A ($7^1D_2 - 6^1P_1$), it is known that the line λ2288A is very narrow therefore the splitting of the upper level caused by the interaction of the nucleus with the valence electrons must be small. Hence it is reasonable to suppose that a Paschen-Back effect should occur for these levels in rather small fields.

Up to the present time the components of the λ2288A line have not been resolved by spectroscopic methods. However measurements of the polarization for different fields should lead to information on the separation of these components, for it will be shown later that the theoretical equation of the polarization as a function of the field strength depends on a parameter β which determines the separation of the hyperfine levels. In order to derive the expression for the polarization as a function of the field strength it is necessary to obtain the various Zeeman transition probabilities as functions of the field. As the Zeeman pattern of the λ2288A line for the even isotopes with $I = 0$ is a normal pattern excitation with either perpendicular or parallel components alone will give complete polarization for all field strengths. Therefore these components need no further consideration. The Zeeman pattern for the odd isotopes with $I = \frac{1}{2}$ given in Fig. 1 is similar to that of the sodium D lines. Darwin[5] and also Heisenberg and Jordan[6] have published theoretical discussions of the Zeeman effect in intermediate fields for ordinary multiplets. The latter authors have worked out the explicit intensity formulas for the sodium D type doublets. However, these formulas must be altered somewhat for our case as we are dealing with the interaction of the nuclear spin and the angular momentum of the valence electrons so that different

[1] Ellett and Larrick, Phys. Rev. **39**, 294 (1932).
[2] Schüler and Brück, Zeits. f. Physik **56**, 291 (1929).
[3] Schüler and Keyston, Zeits. f. Physik **67**, 433 (1931).
[4] Schrammen, Ann. d. Physik **83**, 1161 (1927).
[5] Darwin, Proc. Roy. Soc. **A115**, 1 (1927).
[6] Heisenberg and Jordan. Zeits. f. Physik **37**, 263 (1926).

g values will be involved. Goudsmit[7] has pointed out that we can use the formulas derived for ordinary multiplets by Darwin after replacing m_s and m_l by $g_i m_i$ and $g_j m_j$, respectively. After making these changes and associating with a given Zeeman level the quantum numbers m_i and m_j appropriate to strong fields we find the intensities to be given by the following formulas:

$$|z'|^2(1, \tfrac{1}{2}, -\tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) = 2\{1+[\beta-\omega(g-g_i)]/\Delta_-\},$$

$$|z'|^2(1, -\tfrac{1}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) = 2\{1+[\beta+\omega(g-g_i)]/\Delta_+\},$$

$$|z'|^2(1, \tfrac{1}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) = 2\{1-[\beta-\omega(g-g_i)]/\Delta_-\},$$

$$|z'|^2(1, -\tfrac{1}{2}, \tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) = 2\{1-[\beta+\omega(g-g_i)]/\Delta_+\},$$

$$|x'-iy'|^2(1, \tfrac{3}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) = 2,$$

$$|x'-iy'|^2(1, \tfrac{1}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) = \{1-[\beta-\omega(g-g_i)]/\Delta_-\},$$

$$|x'+iy'|^2(1, -\tfrac{1}{2}, -\tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) = \{1-[\beta+\omega(g-g_i)]/\Delta_+\},$$

$$|x'+iy'|^2(1, -\tfrac{3}{2}, -\tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) = 2,$$

$$|x'-iy'|^2(1, \tfrac{1}{2}, \tfrac{1}{2}; 0, -\tfrac{1}{2}, -\tfrac{1}{2}) = \{1+[\beta-\omega(g-g_i)]/\Delta_-\},$$

$$|x'+iy'|^2(1, -\tfrac{1}{2}, \tfrac{1}{2}; 0, \tfrac{1}{2}, \tfrac{1}{2}) = \{1+[\beta+\omega(g-g_i)]/\Delta_+\},$$

where $\Delta_- = \{(\beta-\omega(g-g_i))^2+8\beta^2\}^{\frac{1}{2}}$; $\Delta_+ = \{(\beta+\omega(g-g_i))^2+8\beta^2\}^{\frac{1}{2}}$

and β is the separation constant of the hyperfine levels. The brackets on the left give the quantum numbers of the upper and lower levels involved in the transitions in the order $(f, m_f, m_i; f', m_f', m_i')$.

In calculating the polarization of the resonance radiation two additional factors must be taken into consideration, the intensity distribution in the source and the separation of the hyperfine levels in zero field. In order to obtain an approximate value of the separation of these levels the polarization will first be calculated for a source with uniform intensity distribution across the absorption region. It seems reasonable to suppose that this will give nearly correct values of the polarization as the source was operated at a fairly high temperature but very low Cd vapor pressure insuring a broad line free from self-reversal. The polarization is then obtained by the usual method of finding the population in resonance of the upper levels, then the intensity in resonance of each component, the polarization being given by $P = (I_\perp - I_{||})/(I_\perp + I_{||})$, where $I_\perp$ and $I_{||}$ are the sums of the intensities of all the perpendicular and parallel components, re-

spectively. Completing these computations we find for the case where the incident light is plane polarized with its electric vector parallel to the field H

$$P_{||} = \frac{16x^4+32x^2+27}{16x^4+48x^2+63} \, 100, \qquad (1)$$

where $x = g\omega/2\beta = gehH/8\pi mc\beta$. In plotting $P_{||}$ against H we obtain a family of curves, a curve for each value of the parameter β.
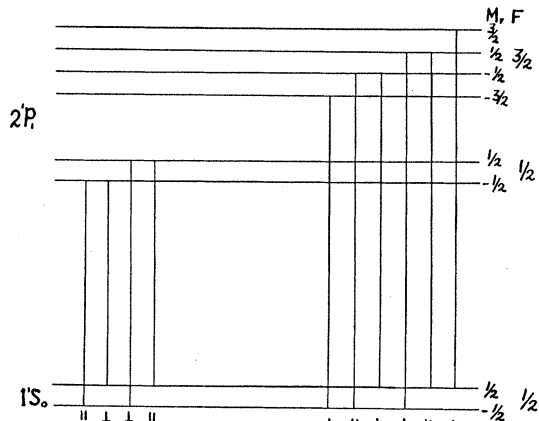
The value of β, giving that curve which most

[7] Pauling and Goudsmit, *Structure of Line Spectra*, p. 219

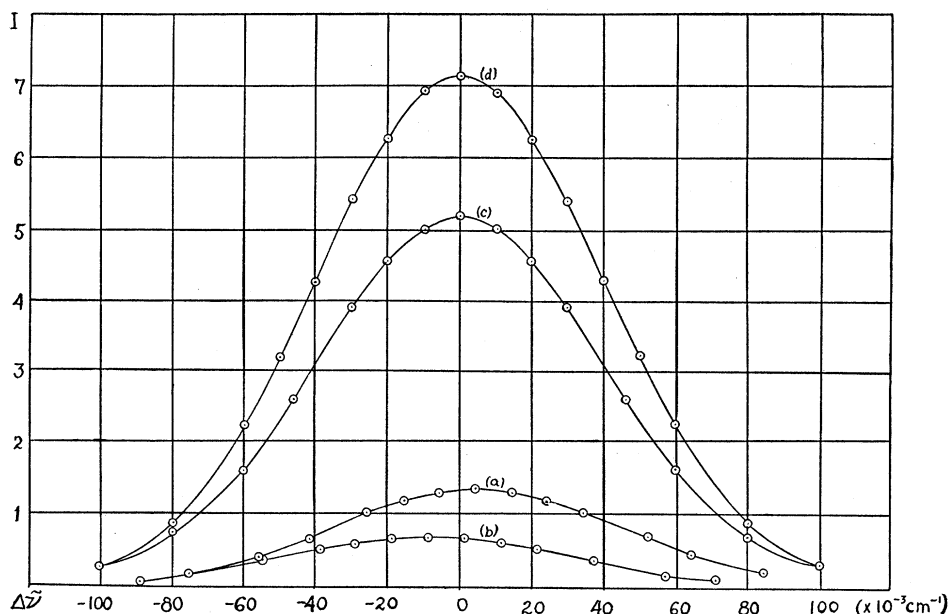FIG. 1. Zeeman pattern for the odd isotopes with $I = \tfrac{1}{2}$.

FIG. 2. Intensity curves for the three components in the source.

nearly coincides with the experimental curve, can then be used in calculating the polarization when the theoretical distribution of intensity in the source is taken into account. This intensity distribution can be computed from the known formula for the Doppler broadening of spectral lines,

$$I = I_0(c/\nu_0) \exp\left[-a^2 c^2 (\nu/\nu_0 - 1)^2\right], \qquad (2)$$

where $a^2 = M/2RT$, M being the molecular weight, R the molecular gas constant and c the velocity of light. In Fig. 2 are plotted the intensity curves of the three components in the source taking its temperature to be 727°C. Curve (c) is the component due to the even isotopes. Curves (a) and (b) represent the two hyperfine components of the odd isotopes when the value of β is taken to be 4.2×10^{-3} cm^{-1} which was obtained by comparing the theoretical curves using Eq. (1) and the experimental curve of $P_{||}$ against H (Fig. 5). These add to give the resultant curve (d). As this curve has very nearly the same half value breadth as curve (c) it may be represented without appreciable error by Eq. (2) without changing the value of the temperature. Thus the energy radiated from the source at a given frequency range ν to $\nu + d\nu$ is given by

$$dI = I_1(c/\nu_1) \exp\left[-a_1^2 c^2 (\nu/\nu_1 - 1)^2\right] d\nu. \qquad (3)$$

The energy absorbed in the resonance bulb by a component of frequency ν_2 for this same frequency range is

$$dI' = \{I_2(c/\nu_2) \exp\left[-a_2^2 c^2 (\nu/\nu_2 - 1)^2\right]\}$$
$$\{I_1(c/\nu_1) \exp\left[-a_1^2 c^2 (\nu/\nu_1 - 1)^2\right]\} d\nu. \qquad (4)$$

Integrating this value over all frequencies we obtain for the total energy absorbed

$$I' = \frac{B}{\nu_1 \nu_2} \exp\left[-\frac{a_1^2 a_2^2 c^2 (\nu_2 - \nu_1)^2}{a_1^2 \nu_2^2 - a_2^2 \nu_1^2}\right], \qquad (5)$$

where B is a constant depending upon the relative intensity of the absorbing line. The frequency shift of the Zeeman components with changing field strengths is readily obtained from the equations for the energy of the Zeeman levels. The relative population in resonance of the upper levels can be calculated from Eq. (5), then the polarization is obtained as before.

After comparing the curve obtained by plotting these new values of the polarization against the field strength with the experimental curve, it may be necessary to change the value of the separation constant β to give better agreement. This

new value assigned to β must then be used to re-calculate the polarization. Hence it is seen that by a series of approximations we may approach very closely the theoretical polarization based on the theoretical intensity distribution in the source.

EXPERIMENTAL

The experimental set-up was the same as that described by Ellett and Larrick.[1] A monochromator was used to eliminate the $\lambda 3261$A resonance line. The vapor pressure of Cd in the source was maintained sufficiently low so that the red line of Cd was faint compared to the hydrogen $H\alpha$ line. Under these conditions no appreciable self-reversal of the $\lambda 2288$A line should have occurred. The resonance bulb was operated at temperatures between 100° and 105°C well below the temperature at which depolarization due to secondary radiation occurs. A calibrated Helmholtz coil wound with copper tubing through which water flowed for cooling was used to obtain the magnetic field at the resonance bulb, its axis being parallel to the direction of the incident beam.

Polarization measurements were made photographically by the Cornu method with Wollaston prisms as in the work of Olson.[8] In this method one of the Wollastons is rotated about their common axis until two of the images on the photographic plate are of equal intensity. The polarization is then given by the cosine of twice the angle of rotation measured from the position of the fixed prism. In the actual determination of this angle three or four photographs were taken at various angles within the region of the probable match position. A microphotometer curve of the cross section of each image was taken. The area under these curves as measured by a planimeter was taken to be a measure of the intensity of the image. This is justified in the present case as the images compared were nearly of the same intensity and were exposed and developed together. The function $x = (C-D)/(C+D)$, where C and D are the intensities of the two images on a plate, was then plotted against the angle made by the Wollaston prism. Fig. 3 shows a typical curve obtained in this manner. The angle at which the line crosses the axis is taken as the
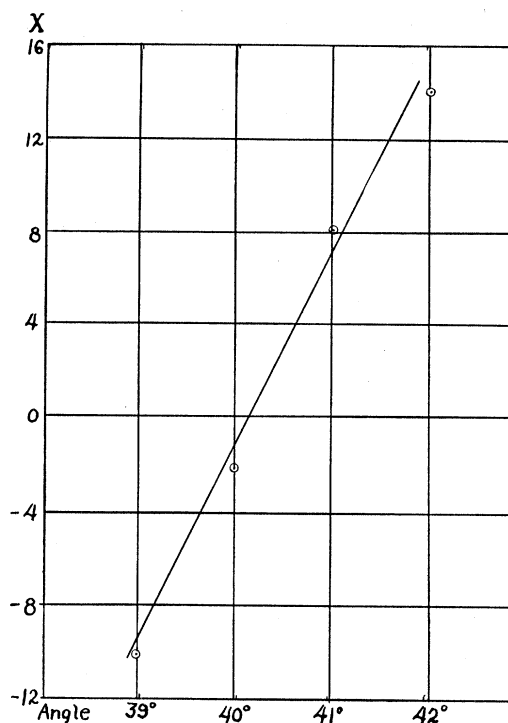
[8] Olson, Phys. Rev. **32**, 443 (1928).

FIG. 3.

angle where the two images would have exactly the same intensity.

For the Cd line $\lambda 2288$A an exposure time of $2\frac{1}{2}$ to 3 hours was necessary to obtain photographs of sufficient intensity for measuring purposes hence after the general outline of the experimental curve of polarization against field strength was obtained, the other points were found by estimating the angle at which the images should be matched, then a photograph was taken at a small angle either side of this position and the actual match position determined from these. All of the points on the experimental curve with the exception of one were obtained before the form of the theoretical curve had been determined. Several photographs were taken throughout the course of the experimental work with the heat removed from the resonance bulb and as no images could be detected on these films it was certain that stray light had been eliminated.

It is necessary to correct the experimental values of the polarization for the depolarization caused by the slight convergence of the incident beam after passing through the lens system. The

depolarization due to the divergence of the beam which passed through the Wollaston prisms is negligible as the angle of maximum divergence of the rays was less than 3°. Gaviola[9] discussed this depolarization effect for the case of plane polarized incident light. A similar correction for the case of nonpolarized light is easily calculated. Fig. 4 illustrates how the incident intensity is
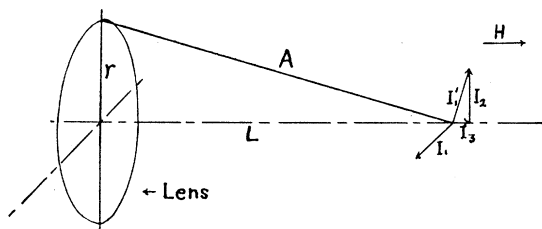

FIG. 4.

split up into components parallel and perpendicular to the field. The intensity of a ray A may be represented by two mutually perpendicular equal components I_1 and I_1' one of which is chosen perpendicular to the field H. The other can then be split into components I_2 perpendicular to the field and I_3 parallel to the field. Integrating over the aperture of the lens we obtain for the intensity of the perpendicular component

$$I_{\perp} = \int^{\text{over lens}} (I_1 + I_2) ds = I_0 \pi \int_0^R \left(\frac{r^2 + 2L^2}{r^2 + L^2} \right) r dr$$

and for the parallel component

$$I_{||} = \int^{\text{over lens}} I_3 ds = I_0 \pi \int_0^R \frac{r^3 dr}{r^2 + L^2},$$

where I_0 is the intensity of the radiation passing through a unit area of the lens. When the aperture is small compared to the focal length of the lens, I_0 may be considered as constant over the lens aperture. The amount of depolarization resulting from the presence of the parallel component can be readily calculated for each field strength by determining the difference between the theoretical value of the polarization with and without this added parallel component. For zero field this correction becomes

[9] Gaviola and P. Pringsheim, Zeits. f. Physik **34**, 1 (1925).

$$Y = \left\{ \frac{3 + 9\gamma}{11 + 9\gamma} - \frac{105(2 - x)}{274 - 8x} \right\},$$

where $x = R^2/L^2$ while for very large fields it reduces to

$$Y = 4x/(4 + x).$$

The value of x for the experimental set-up used was 0.010.

DISCUSSION

Obviously we cannot compare the measured polarization values directly with those given by Eq. (1) as the measurements are for the case of excitation by perpendicular components and are the resultant polarizations from components of both even and odd isotopes. It can easily be proved that the polarization $P_{\perp}$ of the components from the odd isotopes alone in terms of the polarization P_0 of the components from both even and odd isotopes is given by the following formula

$$P_{\perp} = (3\gamma - 3\gamma P_0 - 4P_0)/(-\gamma + \gamma P_0 - 4). \quad (6)$$

Then from the equation

$$P_{||} = 2P_{\perp}/(1 - P_{\perp}) \quad (7)$$

relating the polarization $P_{\perp}$ for excitation with perpendicular components to the polarization $P_{||}$ for excitation with parallel components we obtain values which can be compared with those given by Eq. (1).

In the first four columns of Table I are given respectively, the experimental values as measured, the values corrected for the depolarization caused by the convergence of the incident beam, the values $P_{\perp}$ obtained from Eq. (6), and the values $P_{||}$ obtained from Eq. (7). It will be noticed that the experimental value P_0 for zero

TABLE I. *Experimental values of the polarization for different magnetic fields.*

P observed	P_0 corrected	$P_{\perp}$ odd isotopes	$P_{||}$ odd isotopes	H (gauss)
76.3%	76.7%	27.3%	42.7%	0
76.8	77.3	28.8	44.7	75
79.3	79.9	36.0	53.0	144
81.9	82.5	43.4	60.5	200
85.5	86.2	54.4	70.5	255
88.3	89.1	63.4	77.6	315
91.3	92.1	73.0	83.7	375
94.0	95.0	82.6	90.5	563

field differs slightly from that obtained previously by Ellett and Larrick,[1] their value not having been corrected for the convergence of the incident beam. This gives 2.6 as the value of the constant γ instead of 2.53.

In Table II are recorded the theoretical values of the polarization for different field strengths.

TABLE II. *Theoretical values of the polarization as a function of field strength.*

$P_{||}$ (calc. from 1)	$P_{||}$ (calc.)	H (gauss)
42.7%	42.7%	0
48.6	48.9	100
54.5	54.8	150
62.0	62.4	200
69.1	69.6	250
75.0	75.6	300
79.8	80.5	350
83.3	84.0	400
88.8	89.2	500
91.8	92.1	600

In the first column are the values computed from Eq. (1) by using $\beta = 4.2 \times 10^{-3}$ cm^{-1}, and in the second column are the values obtained on taking into account the theoretical intensity distribution in the source. These differ very little from those in the first column.

In Fig. 5 the theoretical values of the polarization calculated from Eq. (1) are plotted against the field H and compared with the extrapolated experimental values givin in column 4 of Table I. Fig. 6 gives a comparison of the theoretical curve by using the values of the polarization given in column 2 of Table II with the experimental curve. As the general agreement of the curves in Fig. 6 has not changed appreciably from that in Fig. 5 it may be said that the consideration of the intensity distribution in the source has not effected a noticeable correction to the value of β previously assigned.

Fig. 7 gives a comparison of the experimental curve with two theoretical curves having values of β relatively 10 percent larger and smaller than that in Fig. 6. These curves lie outside the range of experimental error hence we may safely say that the value $\beta = 4.2 \times 10^{-3}$ cm^{-1} is correct to within 10 percent error. The separation of the two hyperfine levels of the odd isotopes is then $3\beta = 12.6 \times 10^{-3}$ cm^{-1}. The accuracy of this determination represents a resolving power of 3.5×10^{7}.

As a resolving power of this magnitude is not available by use of present spectroscopic methods this is the only means of determining the separation of these levels at present.

In order to resolve spectroscopically the hyperfine components of the line $\lambda 6438.47$A ($7'D_2 - 6'P_1$) resulting from the separation of the $6'P_1$ level a resolving power of 1.2×10^6 would be required if the components had zero breadth. Since the line breadth cannot be entirely eliminated and the much stronger component due to the even isotopes is superimposed on the hyperfine pattern, it is not feasible at present to detect any variation from the intensity distribution given by a single line.

Goudsmit[10] has derived the following equation for the hyperfine splitting constant A, where A is just twice the constant β used above,

$$A(J) = a(2-g)$$

$$-a \frac{6\Gamma(2-g) - 2(g-1)L(L+1)}{(2L-1)(2L+3)} + b(g-1) \quad (8)$$

as usual $\Gamma = [J(J+1) - L(L+1) - S(S+1)]/2$, while a and b determine the absolute value of the splitting due to the p and s electrons, respectively. The A's for the triplet levels $^3P_{1, 2}$, $^3S_1$ and the singlet level $^1P_1$ have been calculated using Eq. (8) giving

$$A(^3P_1) = 3a/2 + b/2, \quad = 148.6 \times 10^{-3} \text{ cm}^{-1}, \quad (9)$$

$$A(^3P_2) = 3a/10 + b/2, \quad = 120.0 \times 10^{-3} \text{ cm}^{-1}, \quad (10)$$

$$A(^3S_1) = b, \quad = 264.0 \times 10^{-3} \text{ cm}^{-1}, \quad (11)$$

$$A(^1P_1) = a, \quad = 8.4 \times 10^{-3} \text{ cm}^{-1}. \quad (12)$$

The numerical values given for the triplet levels were obtained from Schüler's data[2,3] on the separation of the hyperfine components of the triplet lines $6^3P_{0, 1, 2} - 6^3S_1$ ($\lambda\lambda 4678, 4800, 5086$A). The value of $A(^1P_1)$ is that found by the author. Schüler's results provide a unique solution as well as a check for the values of a and b. It will be noticed however that his results are not sufficiently accurate for a determination of the smaller constant a, for if the value of b from Eq. (11) is substituted into Eqs. (9) and (10) positive and negative values for a are obtained respectively.

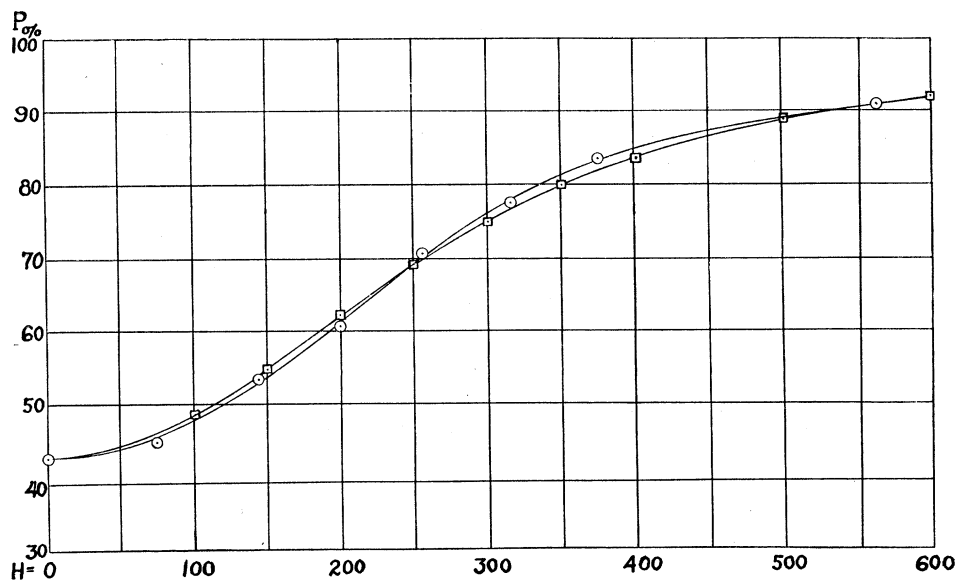
[10] Goudsmit, Phys. Rev. **37**, 663 (1931).

FIG. 5. Theoretical values of polarization from Eq. (1) and experimental values (column 4, Table I) plotted against magnetic field. Circle with dot, experimental curve; square with dot, theoretical curve. $\beta = 4.2 \times 10^{-3}$ cm^{-1}.
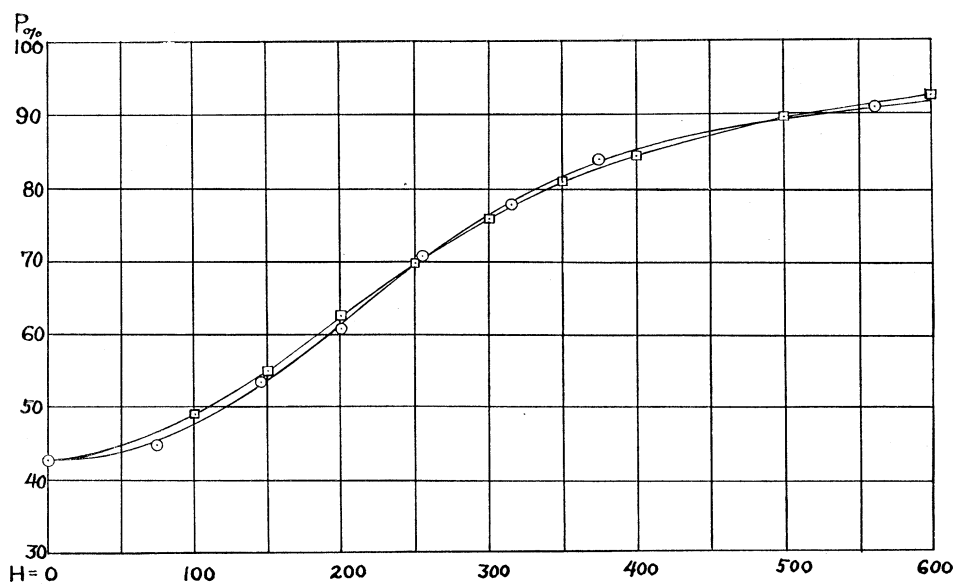

FIG. 6. Plot of theoretical values of polarization (column 2, Table II) with the experimental values. Circle with dot, experimental curve; square with dot, theoretical curve.
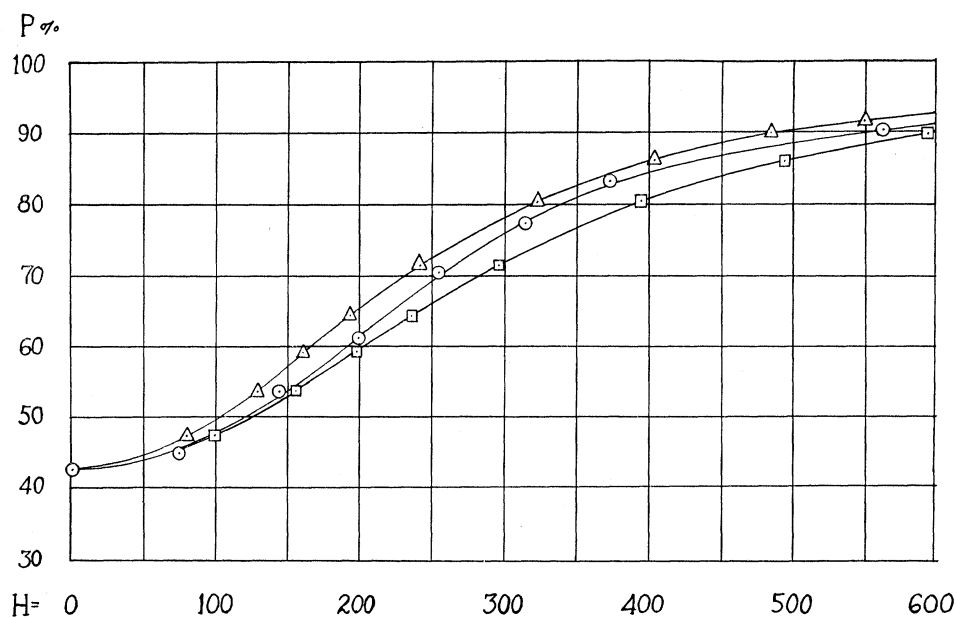
FIG. 7. Comparison of experimental curve for polarization with two theoretical curves. Circle with dot, experimental curve; square with dot, $A = 9.25 \times 10^{-3}$ cm^{-1}; triangle with dot, $A = 7.57 \times 10^{-3}$ cm^{-1}.

If we substitute the mean value of b from Schüler's results and the value from a of Eq. (12) into Eqs. (9) and (10) we obtain

$$A\,(^3P_1) = 135.0 \times 10^{-3} \text{ cm}^{-1},$$
$$A\,(^3P_2) = 124.9 \times 10^{-3} \text{ cm}^{-1}.$$

As these values differ by less than 10 percent from those obtained directly from Schüler's results they are probably within the range of his experimental error.

In conclusion I wish to express my thanks to Dr. Ellett for his many helpful suggestions throughout the progress of the work.