Hyperfine Structure and the Polarization of Resonance Radiation. II. Magnetic Depolarization and the Determination of Mean Lives

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Breit has derived formulae giving the polarization $P(H)$ and the angle of maximum polarization θ of a resonance line showing hyperfine structure, as a function of a weak magnetic field applied in the direction of observation of the resonance radiation. The formulae give a means of estimating the effect of hyperfine structure on the calculation of the mean life τ of an excited atom from experiments on the magnetic depolarization and rotation of the plane of polarization of resonance radiation. The calculation has been carried through for the case of the resonance line of Cd(λ3261) and that of Hg(λ2537), and it is found that the differences between the value of τ calculated from hyperfine structure data and that calculated from tan 2θ by the usual non-hyperfine structure method lie well within the experimental error. $P(H)/P_0$ is found to be practically the same whether hyperfine structure is taken into account or neglected. This is due to the fact that the greatest contribution of the polarization in these cases comes from the isotopes having no nuclear spin and the g-value for the upper state of these isotopes is larger than any other upper hyperfine structure state involved. The mean lives of the 7^3S_1 state of mercury have been recalculated from Richter's data on the polarization of stepwise radiation. The values of τ obtained by this method of calculation are 7.2×10^{-9} for λ4047, 1.69×10^{-8} for λ4358 and 1.53×10^{-8} for λ5461. A discussion of Richter's results is given.

INTRODUCTION

RECENTLY, the writer[1] has given a general method for the calculation of the polarization to be expected for any resonance or fluorescence line showing *hfs*[2] if the *hfs* of the line in question is known. Breit[3] has derived expressions for the polarization, $P(H)$, in weak magnetic fields, oriented along the direction of observation, as a function of the field, and also for the angle of maximum polarization θ. It is the purpose of this paper to carry through the calculation for certain resonance and fluorescence lines and to compare the results with the observed experimental data. Since the expressions for $P(H)$ and θ contain the mean life, τ, of the excited state giving rise to the radiation as a parameter, this quantity may be calculated.

In making the calculation for a line showing *hfs* one must make use of quantities related to the polarization of the line in zero magnetic field discussed in I. Consider an element consisting of various isotopes α, of nuclear spin i_α and relative abundance N_α. Let the lowest gross state of such an isotope be denoted by a, having a quantum number j_a and various hyperfine levels f. By absorption of radiation of a suitable frequency from an exciting arc, atoms are raised to various hyperfine levels φ of an upper state b having a quantum number j_b. Atoms may return to a by the emission of resonance radiation ab or to another state $c(h, j_c)$ by the emission of line fluorescence (bc). (See Fig. 1 of I.)

Suppose that the resonance tube, containing the gas to be investigated, is situated at the origin of a rectangular coordinate system in which the exciting light is progressing along the Y-axis and the direction of observation is along the Z-axis. Let a magnetic field of strength H be placed anywhere in the XY plane such that the angle between the electric vector of the exciting light and the field is Θ. The chance of reaching a magnetic sublevel μ of φ by the absorption of a suitable *hfs* component of the line ab is therefore

$$\frac{CN_\alpha I_\nu}{(2j_a+1)(2i_\alpha+1)}\left[A_\pi^{\varphi\mu\alpha}(a)\cos^2\Theta+\tfrac{1}{2}A_\sigma^{\varphi\mu\alpha}(a)\sin^2\Theta\right], \tag{1}$$

[1] A. C. G. Mitchell, Phys. Rev. **40**, 964 (1932). Hereafter referred to as I. See this paper for references to calculations by other authors.

[2] The term hyperfine structure will be designated by *hfs*.

[3] G. Breit, Rev. Mod. Phys. **5**, 91 (1933).

where $A_\pi{}^{\varphi\mu\alpha}(a)$ is the transition probability for a π component between the magnetic sublevels $\mu(\varphi, j_b)$ and $m'(f, j_a)$ of the lower state (equivalent to γ of I); and $A_\sigma{}^{\varphi\mu\alpha}(a)$ is the sum of σ transition probabilities from $\mu(\varphi, j_b)$ to $j_a(\Gamma$ of I). The quantity $(2j_a+1)$, being the same for all *hfs* components of a given line, may be absorbed into the constant C as may also I_ν if we limit our considerations to exciting sources in which all *hfs* components have equal intensity (broad line source). If $X(\varphi\alpha)$ and $Y(\varphi\alpha)$ are the contributions to the intensity of the line bc, from the level φ, which are polarized along and perpendicular to the field, respectively, we have

$$\left.\begin{aligned} X(\varphi\alpha) &= \frac{CN_\alpha}{(2i_\alpha+1)}\sum_\mu \frac{A_\pi{}^{\varphi\mu\alpha}(c)}{A_\pi{}^{\varphi\mu\alpha}(c)+A_\sigma{}^{\varphi\mu\alpha}(c)}\left[A_\pi{}^{\varphi\mu\alpha}(a)\cos^2\Theta+\tfrac{1}{2}A_\sigma{}^{\varphi\mu\alpha}(a)\sin^2\Theta\right], \\ Y(\varphi\alpha) &= \frac{1}{2}\cdot\frac{CN_\alpha}{(2i_\alpha+1)}\sum_\mu \frac{A_\sigma{}^{\varphi\mu\alpha}(c)}{A_\pi{}^{\varphi\mu\alpha}(c)+A_\sigma{}^{\varphi\mu\alpha}(c)}\left[A_\pi{}^{\varphi\mu\alpha}(a)\cos^2\Theta+\tfrac{1}{2}A_\sigma{}^{\varphi\mu\alpha}(a)\sin^2\Theta\right], \end{aligned}\right\} \quad (2)$$

where $A_\pi{}^{\varphi\mu\alpha}(c)$, $A_\sigma{}^{\varphi\mu\alpha}(c)$ are the sums of the transition probabilities from the magnetic sublevel $\mu(\varphi, j_b)$ to all $m'''(h, j_c)$ for π and σ components, respectively.

Let us denote the contribution to the polarization of the line bc from the hyperfine level φ by $P(\varphi, \alpha)$ defined by the relation

$$P(\varphi\alpha) = \frac{X(\varphi\alpha)-Y(\varphi\alpha)}{\sum_\alpha\sum_\varphi(X(\varphi\alpha)+Y(\varphi\alpha))}. \quad (3)$$

The total polarization of the line will then be given by

$$P = \sum_\alpha\sum_\varphi P(\varphi\alpha). \quad (4)$$

The expressions for $P(\varphi\alpha)$ may be brought into the form

$$P(\varphi\alpha) = \frac{[N_\alpha/(2i_\alpha+1)]\{3\sum_\mu A_\pi{}^{\varphi\mu\alpha}(a)A_\pi{}^{\varphi\mu\alpha}(c)-[(2\varphi+1)/3]A^{ab}A^{bc}\}(3\cos^2\Theta-1)}{\sum_\alpha[N_\alpha/(2i_\alpha+1)]\{\sum_\varphi\sum_\mu A_\pi{}^{\varphi\mu\alpha}(a)A_\pi{}^{\varphi\mu\alpha}(c)(3\cos^2\Theta-1)+[(2j_b+1)(2i_\alpha+1)/3]A^{ab}A^{bc}(3-\cos^2\Theta)\}} \quad (5)$$

by using the relations

$$A_\pi{}^{\varphi\mu\alpha}(a)+A_\sigma{}^{\varphi\mu\alpha}(a)=A^{ba}, \qquad \sum_\mu A^{ab}=(2\varphi+1)A^{ba}, \qquad \sum_\mu A_\pi{}^{\varphi\mu\alpha}(a)-\tfrac{1}{2}\sum_\mu A_\sigma{}^{\varphi\mu\alpha}(a)=0, \quad (6)$$

which express respectively the fact that: The total chance of leaving the sublevel μ of φ is A^{ba}; there are $(2\varphi+1)$ magnetic sublevels of φ; and all *hfs* components coming from φ are unpolarized if the level is isotropically excited. Similar relations hold for the fluorescence line bc.

In making the calculation for resonance lines the same procedure is adopted as in I, namely that the transition probabilities are so chosen that the chance of leaving any magnetic sublevel of any upper hyperfine state is the same for all such states. This makes A^{ba} directly calculable. In the case of fluorescence lines the transition probabilities for the line ab are left unchanged and the total transition probability from $\mu(\varphi)$ to all levels h_1, h_2, $\cdots$ etc., is called A^{bc}. The relative transition probabilities from $\mu(\varphi)$ to h_1, h_2, $\cdots$ etc., must be adjusted to be in accord with the sum rule for intensities. If the line ab is resolved spectroscopically from bc it is convenient to choose A^{ab} equal to A^{bc}.

If the resonance tube is in a zero magnetic field and the exciting light is polarized with its electric vector parallel to X, then from spectroscopic stability we may place $\Theta=0$ in Eq. (5). Throughout the article we shall use the notation $P_0(\varphi\alpha)$ for the value of the expression at $\Theta=0$. If we are dealing with resonance rather than fluorescent light it is, of course, to be understood that one takes $c=a$ in (5). Furthermore, if $P_{||}$ and $P_\perp$ be the polarizations observed with the electric parallel or perpendicular to the magnetic field, it follows from (5) that $P_\perp=P_{||}/(P_{||}-2)$.

MAGNETIC DEPOLARIZATION

1. Theory

It is well known that if a small magnetic field is directed along the Z-axis (direction of observation) the degree of polarization decreases as the field increases and the plane of maximum polarization is rotated through an angle θ with respect to its original direction. If the polarization $P(H)$ is measured by observing the intensity of light polarized parallel to X and Y respectively, then according to Breit,[3] $P(H)$ is given by

$$P(H)=\sum_\alpha\sum_\varphi\frac{P_0(\varphi\alpha)}{1+[(eH/mc)g_\varphi(\alpha)\tau]^2}, \quad (7)$$

where $g_\varphi(\alpha)$ is the *hfs* Lande g-factor for the state φ. In making the calculation it is assumed that τ is the same for all hyperfine states of the gross state b. Similarly the angle θ is given by

$$\tan 2\theta=\frac{\sum_\alpha\sum_\varphi P_0(\varphi\alpha)\sin(2\theta)_{\varphi\alpha}\cos(2\theta)_{\varphi\alpha}}{\sum_\alpha\sum_\varphi P_0(\varphi\alpha)\cos^2(2\theta)_{\varphi\alpha}}, \quad (8)$$

where the angle $(2\theta)_{\varphi\alpha}$ is given by

$$\tan(2\theta)_{\varphi\alpha}=(eH/mc)g_\varphi(\alpha)\tau. \quad (9)$$

2. Comparison with experiment

(*a*) *Mercury resonance radiation* $\lambda 2537$. With the methods outlined above the values of $P(H)$ for mercury resonance radiation ($\lambda 2537$) were calculated for different values of the magnetic field H, by using for the mean life[4, 5] $\tau=1.08\times10^{-7}$ sec. The values of $P_0(\varphi\alpha)$ and $g_\varphi(\alpha)$ for the various upper *hfs* states of the line are given in Table I for reference. The results of

TABLE I.

State (isotope, i, φ)	$P_0(\varphi\alpha)$	$g_\varphi(\alpha)$
(even, 0, 1)	0.754	3/2
(199, 1/2, 1/2)	0.000	...
(199, 1/2, 3/2)	0.058	1
(201, 3/2, 1/2)	0.000	...
(201, 3/2, 3/2)	0.016	2/5
(201, 3/2, 5/2)	0.020	3/5
$P_0=$	0.848	

the calculation are shown by the full curve in Fig. 1, in which $P(H)$ is plotted as ordinate and

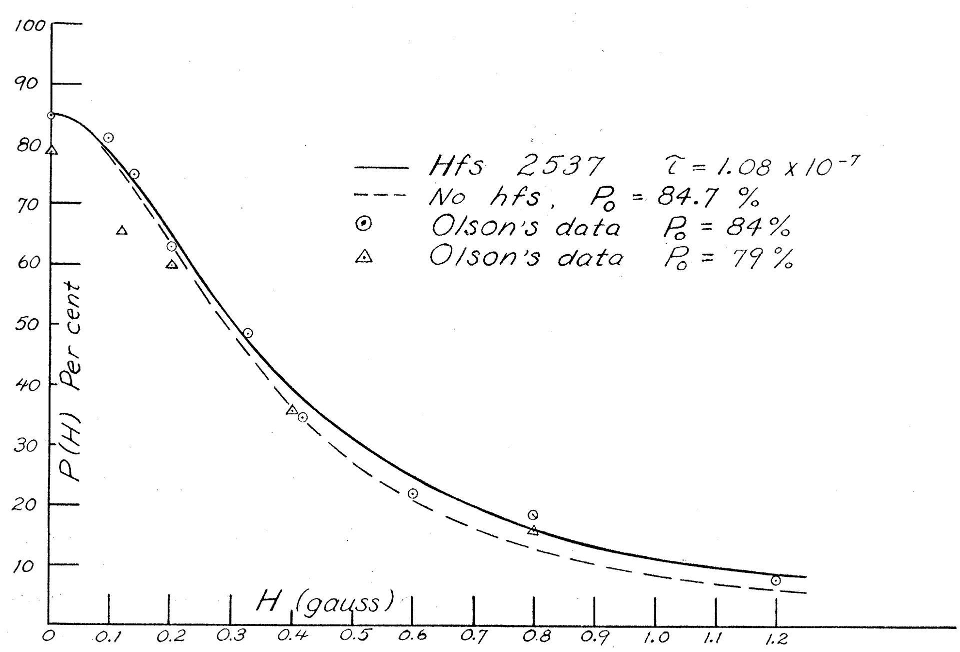

FIG. 1.

[4] W. Zehden and M. W. Zemansky, Zeits. f. Physik **72**, 442 (1931).

[5] P. H. Garrett and H. W. Webb, Phys. Rev. **37**, 1686 (1931).

H as abscissa. The broken curve is a hypothetical curve obtained on the assumption that the λ2537 line is due to isotopes having no nuclear spin with a g-value for the 6^3P_1 state of 3/2, but that for some unknown reason the degree of polarization in zero field is 84.7 percent instead of 100 percent, as would be expected in such a case, i.e., calculated by

$$P(H)=P_0/(1+[(eH/mc)g\tau]^2)$$

with $P_0=84.7$ percent. Some experimenters have made exactly this assumption in calculating τ for mercury from a curve showing $P(H)$ as a function of H. Comparison of the two curves shows that the error in such a procedure is within the limits of experimental measurement. The reason for this is two-fold. In the first place the greatest contribution to the polarization comes from the non-spin isotopes (70 percent of the mixture), and secondly these isotopes have the largest g-values for the upper excited state, so that they contribute relatively more to the depolarization in weak magnetic fields than do the other isotopes. A similar situation arises in the case of the resonance line of cadmium λ3261.

Olson's[6] experimental points are also plotted on Fig. 1. He made two sets of experiments. In the series represented by the circles in the figure, the exciting mercury arc lamp was run at low current density, and it was found that the degree of polarization in zero field attained the theoretically predicted value of 84 percent. In the other set of experiments represented by the triangles, the exciting source was operated at higher current density and the degree of polarization obtained in zero magnetic field was found to be 79.5 percent, considerably lower than that predicted from the theory. It will be seen from Fig. 1 that the observed points from the first group of experiments fit the theoretical curves admirably. The data from the second set of experiments deviate from the theoretical curve, especially in the region of low fields. The cause of the deviation in the second case is not exactly clear but it is possible that at the high current densities used the vapor pressure in the exciting source was high enough to cause a relatively greater self-reversal in the strong (non-spin) components than in the weaker components. The distribution of intensity over the various *hfs* components in the exciting source probably did not correspond to the assumption of a "broad line" exciting source on which the calculation is based. It is interesting to note that Olson, without introducing considerations of *hfs*, calculated a value for the mean life τ of the 6^3P_1 state of 0.98×10^{-7} sec., whereas when one takes into account *hfs*, his data appear to be in good accord with the value $\tau=1.08\times10^{-7}$ sec.

The result of the calculation of the angle of maximum polarization, θ, as a function of the magnetic field in the case of mercury resonance radiation is given in Fig. 2, in which tan 2θ is

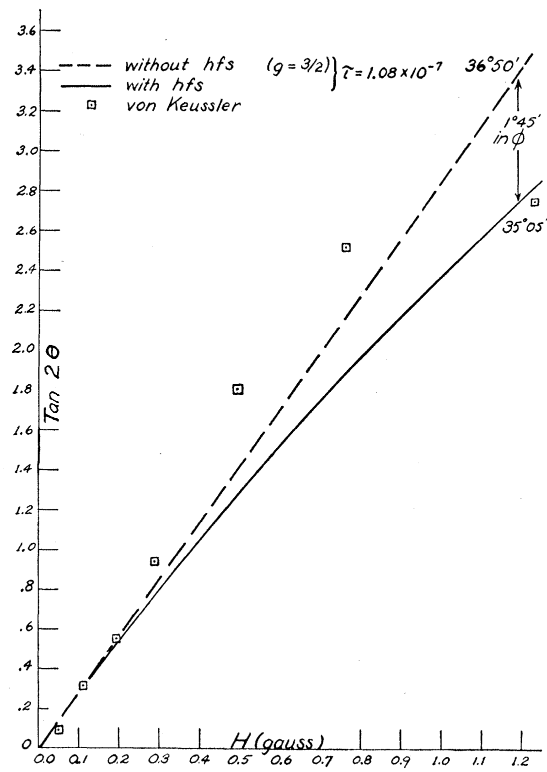

FIG. 2.

plotted as a function of the magnetic field. The full curve gives the result of the present calculation whereas the broken curve represents the results to be expected if mercury resonance radiation consisted of lines from the non-spin isotopes alone. Here again the difference between the two curves is probably within the limit of experimental error of present experiments. The

[6] Olson, Phys. Rev. **32**, 443 (1928).

observations of von Keussler[7] are represented by the squares on the diagram and it will be seen that the agreement is, in general, not good. The reason for the discrepancy is at present not clear. It should be pointed out that the value of τ obtained by von Keussler from these measurements was 1.13×10^{-7} sec.

Recently Mrozowski[8] has been able to excite individual *hfs* components of the mercury resonance line as resonance radiation, and to measure the angle of maximum polarization of this resonance radiation as a function of weak fields in the direction of observation. Two sets of experiments are of interest to us in these calculations. He was able to excite as resonance radiation either (a) the 0.0 and +11.5 mA components together, or (b) the −25.4 mA component separately. The first two components are due to the non-spin isotopes (see Fig. 3) the

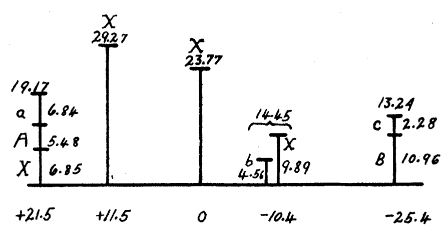

FIG. 3.

upper state of which shows $g=3/2$. The −25.4 mA component, on the other hand, is made up from components B and c from the isotopes of mass 199 and 201, respectively. The component c is, however, unpolarized under all circumstances and hence contributes nothing to the angle of maximum polarization. The upper state of the component B shows $g=1$. From Eq. (8), therefore, a plot of tan 2θ against H should yield straight lines for the case a and b, respectively. Furthermore, if the mean life τ is the same for the two upper *hfs* states of the two isotopes, the ratio of the slopes of the straight lines obtained in the two cases should be that of their respective g-values of the upper states; namely, 3/2 : 1. A plot of Mrozowski's data does indeed yield straight lines for tan 2θ plotted against H and the ratio of the slopes of the two lines is 1.5 as expected. This would appear to be evidence in favor of the usual view that the mean life of any *hfs* state of any gross level j is the same for all such *hfs* states.[9]

(*b*) *Cadmium resonance radiation* (λ*3261*). A calculation similar to that for mercury resonance radiation has been made for the case of cadmium resonance radiation (λ3261). The polarization of this line has already been calculated by Mitchell[10] and Ellett and Larrick[11] on the assumption that the line is made up of contributions from isotopes of even atomic weight (having no spin) and isotopes of odd atomic weight with a spin of 1/2. Table II gives the values of $P_0(\varphi\alpha)$ and $g_\varphi(\alpha)$

TABLE II.

State (isotope, i, φ)	$P_0(\varphi\alpha)$	$g_\varphi(\alpha)$
(even, 0, 1)	0.765	3/2
(odd, 1/2, 1/2)	0.000	...
(odd, 1/2, 3/2)	0.102	1
$P_0=$	0.867	

necessary for carrying out the calculations for the polarization $P(H)$ in weak magnetic fields parallel to the direction of observation. The values are computed for broad line excitation using the value of $\gamma=2.53$ (the ratio of even to odd isotopes) given by Ellett and Larrick. By using the value $\tau=2.5\times10^{-6}$ sec., as determined by Koenig and Ellett,[12] the value of $P(H)$ was computed as a function of the magnetic field H. The results of the calculation are given by the full curve of Fig. 4. The circles in the figure represent experimental points obtained by Solleillet[13] who used, however, unpolarized exciting light. Strictly speaking, experiments ob-

[7] V. von Keussler, Ann. d. Physik **82**, 793 (1927).

[8] S. Mrozowski, Bull. Acad. Pol. p. 491 (1930).

[9] The value of the mean life of the 6^3P_1 state obtained from these curves is 1.67×10^{-7} sec., not in agreement with other values. Such a discrepancy might arise if the value of the applied magnetic field was calculated from the current flowing in a coil of given dimensions. The actual field in the resonance tube might thus differ from that calculated by a constant multiplier. This would leave the ratio of the slopes of the two curves a and b the same but might account for the abnormally large calculated value of τ. This point should certainly be tested.

[10] A. C. G. Mitchell, Phys. Rev. **38**, 473 (1931).

[11] A. Ellett and L. Larrick, Phys. Rev. **39**, 294 (1932).

[12] Koenig and Ellett, Phys. Rev. **39**, 576 (1931).

[13] P. Solleillet, Comptes Rendus **185**, 198 (1927); **187**, 212 (1928).

tained using unpolarized exciting light are not comparable with a theoretical curve based on the assumption of polarized exciting light. Unfortunately, no data are available for the case in which polarized exciting light is used.

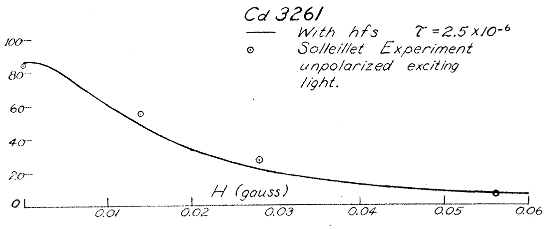

FIG. 4.

THE MEAN LIFE OF THE 7^3S_1 STATE OF MERCURY

If a mixture of nitrogen and mercury vapor is irradiated by the full spectrum of the mercury arc, the visible triplet (λ4047, 4358, 5461) and diffuse triplet (λ2967, 3131, 3663) of mercury, together with other mercury lines, are found to be emitted as fluorescence. A discussion of this effect and the method of calculating the degree of polarization of the lines for various orientations of electric vector of the exciting light and applied magnetic field are given in I. Because of the fact that the sum rule for intensities of the various *hfs* components was not correctly applied, the values of the polarization for the lines λ4358, 5461, 3131 and 3663, given in I are in error. When the sum rule is correctly applied, in order to obtain correct values of $A_\pi^{\varphi\mu\alpha}(c)$, as explained in the introduction, the values of P_0 given in Table III are obtained by the use of (4) and (5). These values are arrived at on the assumption that the incident light shows "broad line" characteristics and that it is polarized in a direction at right angles to the observation direction. The degree of polarization to be expected for other orientations of electric vector and magnetic field may be calculated from (5).

TABLE III.

	Polarization			*Mean Life*	
Line	Obs.	Calc.	θ (Obs.)	τ (Richter)	τ (Calc.)
4047	72 ± 6	84.7	17°	4.8×10^{-8}	7.2×10^{-9}
4358	-49 ± 6	-67.0	29°	4.6×10^{-8}	1.69×10^{-8}
5461	13 ± 1	8.6	29.5°	1.7×10^{-7}	1.53×10^{-8}
2967	67 ± 7	84.7			
3131	-29 ± 7	-67.0			
3663	42 ± 4	8.6			

The minus sign (−) indicates that the line is polarized with its electric vector at right angles to the electric vector of the incident light

Richter[14] has made observations on the angle of maximum polarization θ for the various lines of the visible triplet for several different values of a magnetic field parallel to the direction of observation. From these values of θ he attempted to calculate the value of the mean life of the 7^3S_1 state giving rise to the three lines in question. With an applied magnetic field of 2.81 gauss and at a nitrogen pressure of 1.75 mm, he found the values of θ given in column 4 of Table III for the three lines in question. In making the calculation of the mean life of the upper state from the observed angle, he did not consider the effect of hyperfine structure. Furthermore, the formulae he used relating tan 2θ and τ are incorrect. Moreover, there appears to be a mistake of a factor of 2π in the calculation since his formulae contain the quantity $eH/2\pi mc$ instead of eH/mc usually occurring in such formulae. The values obtained by Richter are given in column 5 of Table III.

With the angles θ given by Richter for the three lines λ4047, 4358 and 5461, the value of τ for the 7^3S_1 state has been computed from Eqs. (8) and (9) by using the hyperfine structure data for the lines in question. The results of the calculation are given in column 6 of Table III. As might be expected, they do not agree with those calculated by Richter.

One should point out here that Richter believed his results to be a confirmation of the results of Randall[15] obtained by an entirely different method. Randall found that the mean life of the 7^3S_1 state of mercury appears to depend on the line which is used to measure it. Richter's calculation seemed to show that the value of the mean life of this state obtained from measurements on the line λ5461 was four times as long as that obtained from measurements on λ4047, and λ4358 in agreement with Randall. The present calculation shows, however, that the values of τ, calculated by the present method, are no longer in agreement with those of Randall. Indeed, it appears, from the values given in the

[14] E. F. Richter, Ann. d. Physik **7**, 293 (1930).

[15] R. H. Randall, Phys. Rev. **35**, 1161 (1930).

table, that Richter's measurements on the two lines λ4358 and 5461 give equal mean lives for the 7^3S_1 state, while the measurement on the line λ4047 leads to a value of the mean life about half as large as that obtained by measurements on the other two.

At the present writing it seems futile to speculate on the meaning of the results obtained for the mean life of the 7^3S_1 state of mercury. In the first place the values of the polarization obtained by Richter in zero magnetic field do not agree with the theoretical values; and in the second, the effect of the nitrogen is a disturbing factor. The writer is repeating Richter's experiments with an improved apparatus, and preliminary results on the polarization of the λ4358 line in zero magnetic field yield a value more nearly in agreement with the theoretical value than that obtained by Richter. It is to be hoped that these new experiments will help to clear up the perplexing difficulty of the mean life of the 7^3S_1 state of mercury.