# Interactions in the Tungsten Atom, W I, in a Magnetic Field

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General theoretical expressions are given for the magnetic field dependence of the energies and intensities belonging to neighboring levels (regardless of coupling) of an atom. The energy dependence is tested experimentally for the levels $21{,}448_2$ and $21{,}453_1$ of W I in fields up to 4.5 $cm^{-1}$ ($=9.7\times10^4$ c.g.s.), where the pattern of levels extends more than 30 $cm^{-1}$. The values found for the constants are $\Delta\nu_0=5.154$ $cm^{-1}$, $g(214_2)=1.4787$, $g(214_1)=2.5113$, $k^2(214_1, 214_2)=0.0447$. The deviations $\nu_{obs}-\nu_{calc}$, obtained from individual determinations at different field strengths, are in some instances as great as 0.05 $cm^{-1}$, which is somewhat greater than the estimated error in the observations; they may be attributed in part to slight repulsive effects from other levels and similar disturbances of the reference lines, which have not yet been calculated in detail.

## INTRODUCTION

IN a magnetic field, each level of an atom splits into $2J+1$ nondegenerate sublevels with magnetic quantum numbers ranging from $+J$ to $-J$. When the Larmor precession frequency $c\eta(=eH/4\pi mc)$ is small compared with the no-field frequency separations $c\Delta\nu_0$ between the level under consideration and neighboring levels with the same parity that differ by not more than 1 in $J$ value, the sublevels are equally spaced, symmetric about the field-free level, and linear in the field (linear or ordinary "anomalous" Zeeman effect), if we neglect a certain small effect[1] (diamagnetic quadratic Zeeman effect). When $\eta$ is not small compared with the $\Delta\nu_0$'s, the dependence upon the field is more complicated: the approximate equidistance, symmetry, and linearity are lost through an interaction that may be described as a mutual repulsion of sublevels with the same $M$. Thorough studies have been made of the interactions among the levels of an $LS$-coupling multiplet (Paschen-Back effect, called "incipient" when the asymmetries are slight), but hardly any attention has been paid to the more general case, presumably because levels other than members of the same "good" multiplet rarely lie close enough together to give rise to noticeable interactions in the fields commonly used.[2-8]

The work reported here is a detailed study of the mutual influence of any two levels of an atom in a magnetic field, with the experimental behavior of the levels $214_1$ and $214_2$ of W I as an

[1] Shown in references 12 and 23 to be negligible in the cases considered here.

[2] For the interesting case of Hg I $6s6d\ ^3D_1$, "$1$" $D_2$, which lie only 3.2 $cm^{-1}$ apart, see P. Zeeman, Proc. Amst. Acad. Sci. **10**, 351 (1907); Physik. Zeits. **10**, 217 (1909); P. Gmelin, Physik. Zeits. **9**, 212 (1908); Ann. d. Physik **28**, 1079 (1909); Physik. Zeits. **11**, 1193 (1910); M. M. Risco, Physik. Zeits. **13**, 137 (1912); J. B. Green and R. A. Loring, Phys. Rev. **46**, 888 (1934); E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 294. The interaction of these levels is complicated by their relatively great hyperfine structure; cf. S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933).

[3] Asymmetric Zeeman effect patterns were reported for several Mo I and W I lines by R. Jack, diss. Göttingen (1908); Ann. d. Physik **28**, 1032 (1909); Proc. Roy. Soc. Edinburgh **29**, 75 (1908).

[4] Incipient Paschen-Back effect in certain configurations $2p^5nl$ of Ne I, where the coupling is intermediate, has been studied by K. Murakawa and T. Iwama, Tokyo Inst. Phys. Chem. Research **13**, 283 (1930); J. B. Green and J. A. Peoples, Phys. Rev. **56**, 54 (1939).

[5] The qualitative explanation of certain of the asymmetries[3] in W I, and preliminary reports on the present quantitative study, were given by J. E. Mack and O. Laporte, Phys. Rev. **51**, 291 (1937); J. H. Roberson and J. E. Mack, Phys. Rev. **55**, 1126 (1939); **57**, 1074 (1940).

[6] A surprising intensity anomaly in the Zeeman effect of Ni I is attributed to interaction between levels 28 $cm^{-1}$ apart labeled $3d^84s5s\ ^5F_1$ and $3d^94d\ ^3D_1$, but unfortunately without data on the positions of the sublevels, by H. Dijkstra, Physica **4**, 81 (1937).

[7] J. B. Green and J. F. Eichelberger, Phys. Rev. **56**, 51 (1939) discuss the theory of the Paschen-Back effect for intermediate coupling.

[8] The general considerations in this paper apply to hyperfine structure levels if $J$ is replaced by $F$ throughout.

example. These levels are particularly suitable because, while their nearest neighbor with the same parity is almost 1400 $cm^{-1}$ away, they are only 5 $cm^{-1}$ apart, and, moreover, one of them has an exceptionally large $g$ value. All the levels specifically referred to in this paper are listed in Table I;[9] of course, it is understood that except for parity and $J$, the designations of quantum numbers in this complex spectrum are only crude approximations. In a prospective paper[10] a study will be made of several smaller interactions in W I and the dependence of the interaction constants $k$ upon the structure of the atom.

TABLE I. *Levels of* W I *referred to in this paper. The designation "PF" for* $13_2$ *indicates an approximately equal mixture of two L values.*

| NAME | DESIGNATION | ENERGY | $g$* |
|---|---|---|---|
| $D_0$ | $5d^46s^2\ {}^5D_0$ | 0.00 | 0/0 |
| $S_3$ | $5d^56s\ {}^7S_3$ | 2951.27 | 1.9751 |
| $13_2$ | $5d^46s^2\ {}^3PF_2$ | 13777.71 | — |
| $18_1$ | $5d^46s^2\ {}^3D_1$ | 18082.84 | — |
| $214_2°$ | $5d^46s6p\ {}^7F_2$ | 21448.65 | 1.4787 |
| $214_1°$ | $5d^46s6p\ {}^7D_1$ | 21453.80 | 2.5113 |
| $261_3°$ | $5d^46s6p\ {}^7D_3$ | 26189.11 | 1.7408 |
| $353_2°$ | — | 35311.46 | — |
| $415_2°$ | — | 41583.16 | — |
| $44_2$ | $5d^46s7s\ {}^7D_2$ | 44919.74 | 1.9470 |

* The $g$'s given here were determined in this study. In the cases indicated by dashes, it was unnecessary to know the $g$'s.

## THEORY[11]

In considering the interaction of levels in a magnetic field, we shall assume that it is sufficient to take into account the mutual influence of only two levels at a time; and[12] that

$$\eta \ll h/\pi mc\Sigma[x^2+y^2]_{Av}.$$

The energy of an atom in a magnetic field differs from the no-field energy by an amount proportional to $\Sigma j_z+\Sigma s_z$, where $j_z$ and $s_z$ are the projections, respectively, of the total angular momentum and the spin angular momentum in the direction of the field, and the summation takes place over all electrons. In consequence of a general theorem regarding the matrix elements of a component of a vector,[13] the matrix elements of the contribution of the magnetic field to the Hamiltonian of the atom can be written:

$$(aJ_aM_a|H_{mag}|bJ_bM_b)=hck_{ab}f\eta\cdot\delta(M_a,M_b), \quad (1)$$

$$\text{where } f=\begin{cases} M, & \text{if } J_a=J_b. \\ (J^2-M^2)^{\frac{1}{2}}, & \text{if } |J_a-J_b|=1. \\ 0, & \text{if } |J_a-J_b|>1. \end{cases}$$

Here $J$ stands for the greater of the two values $J_a$, $J_b$; and $M$, for the common value $M_a=M_b$ where $M$ is used. The coefficient $k_{ab}$ is the same for all the sublevels, characterized by different $M$ values, of the two levels. The indices $a$ and $b$, which are used simply to distinguish different states with the same parity, may be interchanged throughout any expression, here and in the discussion below. It will be observed that for a diagonal element the coefficient $k_{aa}$ is the ordinary weak-field $g$ factor of the Zeeman effect.

The simplicity of the general discussion in the previous paragraph arises from the fact that one may start with exact wave functions in no field; even though these functions are not explicitly known, they are known to have the above-mentioned properties.

For the special case of $LS$ coupling, all the $k$'s are zero[14] except in the case of two states within the same multiplet, and in that case[15]

[9] O. Laporte and J. E. Mack, J. Research Nat. Bur. Stand., in preparation.

[10] J. H. Roberson, in preparation.

[11] We are indebted to Professor Breit for essential help in the preparation of this section.

[12] The term on the right is the value of $\eta$ at which the diamagnetic quadratic effect would equal the normal effect ($\doteq 5\times10^3$ $cm^{-1}$ for the lowest, and $5\times10^2$ $cm^{-1}$ for the highest level listed in Table I; cf. reference 23).

[13] Cf. M. Born and P. Jordan, *Elementare Quantenmechanik* (Julius Springer, Berlin, 1930), Section 29.

[14] Here we assume $n$ to be a good quantum number. In a better approximation there is an interaction closely related to the famous sharing of intensity among members of a series; E. Fermi, Zeits. f. Physik **59**, 680 (1929). For a heavy atom like W the radial functions are not strictly the same for the orbits $nl_{l+\frac{1}{2}}$ and $nl_{l-\frac{1}{2}}$, and not strictly orthogonal for $nl_j$ and $n'l_j(n'\neq n)$ to such a good approximation as in the lightest elements. For this reason, on the one hand there may be incipient "Paschen-Back" interactions between different series members (although a rough calculation shows that these effects are negligible in practical cases), and on the other hand the exact validity of Eq. (2) is subject to doubt because the calculation of this formula presupposes that the radial functions are strictly the same for $nl_{l+\frac{1}{2}}$ and $nl_{l-\frac{1}{2}}$. While this departure from simplicity, associated with large $ls$ interaction energy, may be properly described as a breakdown of $LS$ coupling, it is not always recognized as such because it cannot be read directly from the elementary vector model; for instance, it occurs even in one-electron spectra.

[15] P. Güttinger and W. Pauli, Zeits. f. Physik **67**, 743 (1931); cf. E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, Eqs. $10^32a$, $10^32b$. Güttinger and Pauli's derivation does not cover the case of more than one multiplet with the same $L$ and the same $S$ in a configuration, but Professor Breit informs us that $k=0$ between different multiplets even in this case as a consequence of

$$k(J,J)=1+[J(J+1)+S(S+1)-L(L+1)]/2J(J+1), \quad (2a)$$

$$k(J,J-1)=k(J-1,J)=[(J+L-S)(J-L+S)(L+S+1+J)\times(L+S+1-J)/4J^2(4J^2-1)]^{\frac{1}{2}}, \quad (2b)$$

where it will be noticed that $k(J,J)$ is the well-known $LS$ coupling weak-field $g$ value and $k(J,J-1)$ is the coefficient leading to the well-known expression for the Paschen-Back effect. The sign of $k$ depends, in general, upon a convention in the choice of phases for the wave functions, but we may, without loss of generality, use the positive sign throughout this paper.

In any case where the values of the coefficients for the transformation between the actual case and the ideal $LS$ coupling case are known, $k_{ab}$ may be determined. The interpretation of $k_{ab}$ for particular cases, and the discussion of the inverse problem of interpreting actual levels from experimental values of $k_{ab}$ is postponed.[10]

This paper is concerned especially with the nondiagonal coefficients $k_{ab}$, $a\neq b$. Reference hereafter to $k_{ab}$ (or for brevity, $k$) implies a nondiagonal coefficient unless the contrary is specified.

The secular equation from Eq. (1) for the two sublevels with the same $M$, of the interacting levels $a$ and $b$, has the solutions

$$\nu=\nu_0'+Mg'\eta\pm[(\nu_0''+Mg''\eta)^2+k^2f^2\eta^2]^{\frac{1}{2}}, \quad (3)$$

where $\nu_0'$ and $\nu_0''$ are half the sum and half the difference, respectively, of the no-field wave numbers $\nu_{0a}$ and $\nu_{0b}$, and $g'$ and $g''$ are half the sum and half the difference, respectively, of the weak-field $g$ factors, $g_a$ and $g_b$.

Equation (3) is the equation of a hyperbola with its center at

$$\eta_{\text{cent}}=-\nu_0''Mg''/(M^2g''^2+k^2f^2), \quad (4a)$$

$$\nu_{\text{cent}}=\nu_0'-\nu_0''M^2g'g''/(M^2g''^2+k^2f^2) \quad (4b)$$

and asymptotic slopes

$$(d\nu/d\eta)_\infty=Mg'\pm(M^2g''^2+k^2f^2)^{\frac{1}{2}}. \quad (4c)$$

The wave numbers at $\eta_{\text{cent}}$, which is the point of minimum energy separation of the branches, are

$$\nu_{\text{min sep}}=\nu_{\text{cent}}\pm\nu_0''kf(M^2g''^2+k^2f^2)^{-\frac{1}{2}}. \quad (4d)$$

The intensity of a line component is

$$I_a=(I_{0a}^{\frac{1}{2}}x\pm I_{0b}^{\frac{1}{2}})^2/(1+x^2), \quad (5)$$

where $I_{0a}$, $I_{0b}$ are the intensity contributions of the two sublevels with the same $M$ to the no-field lines, and

$$x\equiv kf\eta/(\nu-\nu_{0a}-Mg_a\eta).$$

It will be noticed that $x=1$ when $\eta$ has the value $-\nu_0''/Mg''$ at which the linear approximation would predict the crossing of the sublevels. At this field the intensities of two Zeeman effect sublines are equal in the important case where $I_{0a}$ or $I_{0b}$ is zero, for instance on account of a selection rule. When $I_{0a}$ and $I_{0b}$ are both different from zero, the general expression for the intensity, Eq. (5), contains an ambiguity in sign that can be removed in any special case.

Figure 1$A$ shows the results of the calculations for a representative case. The values used for the seven constants $J_a$, $J_b$, $g_a$, $g_b$, $\nu_{0a}$, $\nu_{0b}$, and $k$ are those found experimentally for the levels $214_1$ and $214_2$ of W I. Although negative values of $\eta$ have no physical meaning, it is convenient to draw the curves for the two values of $M$ that differ only in sign, on opposite sides of the $\eta=0$ axis, for then they form a single complete hyperbola. This simple property arises from the fact that all the results depend, not upon the signs of $M$ and $\eta$ separately, but only upon the sign of the product $M\eta$. Thus Fig. 1$A$ shows the complete hyperbola representing the $M=\pm1$ sublevels, and in addition the reflection in the $\eta=0$ axis of the (dotted) portion representing $M=+1$.

An approximate solution, valid for incipient asymmetry, $\eta\ll|\Delta\nu_0|$, in agreement with second-order perturbation theory, is

$$\nu_a\doteq\nu_{0a}+Mg_a\eta\pm k^2f^2\eta^2/(\Delta\nu_0+M\eta\Delta g), \quad (7)$$

where in any particular case only the "repulsive" sign is to be chosen in front of the last term. Neglecting this $k^2f^2\eta^2$ term leads, of course, to the linear Zeeman effect.

## Apparatus and Exposures

The study in fields $\eta<2$ cm$^{-1}$ was made at Wisconsin. The magnet, containing $\frac{3}{4}$ ton of iron,

the orthogonality of the space components of the wave functions, following the general treatment of spectroscopic terms given in E. Wigner, *Gruppentheorie* (F. Vieweg, Braunschweig, 1931).

was built in the shape of a Θ. The current was supplied by means of 48 pancake coils of copper tubing in parallel. The tubes were cooled by distilled water, pumped through a closed circulating system and cooled by city water at an interchanger. The resistance of the coils was about 1 ohm. The field became sufficiently steady for Zeeman effect work after about 30 minutes of running. The current, which was about 10 amperes for $\eta=1$ cm$^{-1}$ and 160 amperes for $\eta=1.9$ cm$^{-1}$, was supplied by a 200-volt, 200-ampere motor generator. The pole pieces consisted mainly of Armco iron rods 12 cm in diameter; but each was furnished with a tip of Permendur[16] carefully threaded into the pole piece with a minimum of clearance, and ending in a cone with a half-angle of 56°, truncated at a diameter of 6 mm. During the exposures the tips were from 3.0 to 4.5 mm apart.

The source was an arc, enclosed in a Back chamber that has already been described[17] and was made over for this use. The pole tips were protected by quartz plates about 0.5 mm thick, each mounted upon a brass ring machined to fit the conical tip and to allow the quartz to rest almost in contact with the Permendur face; but for the strongest fields, requiring the greatest crowding, the quartz was omitted from the tip next to the grounded electrode. The arc was produced across a gap, longitudinal to the field, between electrodes made of pure tungsten rods[18] or 50-mil tungsten wires placed in pairs, filed to form plates about 1 mm thick. One electrode was placed on a pivoted rod and agitated by a motor-driven eccentric shaft to make about 5 contacts per second, and an inductance was introduced into the arc circuit to help maintain a fairly steady current.

The exposures at Wisconsin were made with the Physics Department's 21-foot Rowland mounting and 5.6-inch, 15,000 lines/inch Rowland grating. The exposures were made in the second order, with a dispersion of about 1.33A/mm. Eastman 33 and 40 plates were used; the greatest exposure time required, with the strongest fields, was about 2 hours.

The study in fields $\eta>2$ cm$^{-1}$ was made at Massachusetts Institute of Technology. The apparatus and the technique of exposure have been described.[19] Gratings $F$ and $G$ were used in the first order. In exposures[20] 2.4, 3.5, and 4.2, and in no others, the $\pi$ and $\sigma$ components were separated with the aid of a Rochon prism.

## Measurements and Reduction of Data

The lines studied were $\nu$21,453 ($=D_0-214_1$), and $\nu\nu$23,465, 23,471 ($=214_{1,2}-44_2$). The former was studied principally for $\eta<2$ cm$^{-1}$ and the latter, only for $\eta>2$ cm$^{-1}$. The former was carefully examined for self-reversal, with negative results.

Each of the readings recorded on our data sheets, of the position of a spectrum line on a plate, is the result of several settings to 1 micron (0.004 to 0.006 cm$^{-1}$) made on the large Société Génevoise comparator at Wisconsin. After each group of settings the plate was moved, so that the next group would be shifted to a different point along the length of the line, i.e., to different grains of the emulsion.

A serious difficulty arose in our attempt to provide reference lines. If we had attempted to use field-free lines of any element as standards, it would have been necessary to try to avoid the possibilities of error inherent in any attempt to superimpose the radiation diffracted by the grating from two sources separated in time or in space. Instead, we used as actual reference points for each line the centers of the patterns of two neighboring lines (or only one, as discussed in the next paragraph). For $D_0-214_1$ the reference lines were $\nu$21,533 ($=13_2-353_2$) and $\nu$21,359 ($=D_3-261_3$), and for $214_{1,2}-44_2$, $\nu$23,500 ($18_1-415_2$) and $\nu$23,237 ($=S_3-261_3$). Our method has the serious defect that any departure of the center of the pattern of any reference line from the no-field wave number introduces an error into the result. For that reason, these pairs of reference line patterns were selected in each case only after a careful study had shown both patterns to be symmetric and their centers to have the same separation as the no-field lines, within 0.02 cm$^{-1}$. Yet, even for lines thus chosen, we have been forced to tolerate the undesirable

[16] Kindly furnished by the Bell Telephone Laboratories.
[17] A. E. Whitford, Phys. Rev. **39**, 898 (1932).
[18] Kindly furnished by the General Electric Company.
[19] F. C. Bitter and G. R. Harrison, Phys. Rev. **56**, 15 (1940).
[20] Each exposure is designated by the first two digits in $\eta$.

possibility of bodily shifts away from their no-field positions as a possible source of error in our final result.

Since every sufficiently intense and well-resolved line between $\nu 23{,}471$ and $\nu 23{,}237$ was found to wander with respect to $\nu 23{,}500$ and $\nu 23{,}237$, and experience showed that $\nu\nu 23{,}471$, 23,465 could be measured as accurately with reference to $\nu 23{,}500$ alone as by interpolation between $\nu 23{,}500$ and $\nu 23{,}237$, some of the measurements upon $\nu\nu 23{,}471$, 23,465 were made with reference to $\nu 23{,}500$ alone. These measurements required the independent determination of the dispersion curve of each plate involved, for different plates from the same grating were found to differ as much as 0.1 percent in dispersion.

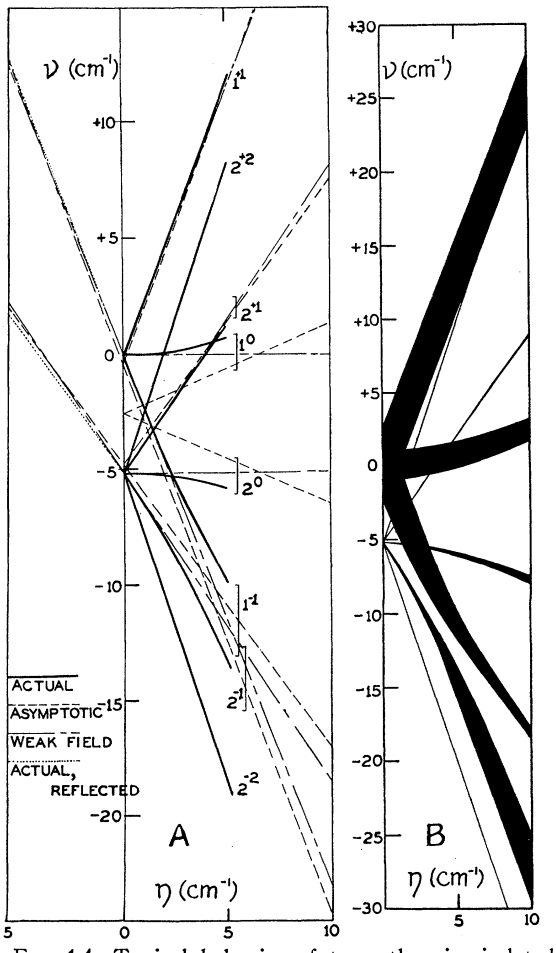


FIG. 1*A*. Typical behavior of two otherwise isolated atomic energy levels in a magnetic field, predicted by Eq. (3) and found for the W I levels $21{,}453.80_1$, $g=2.511$, and $21{,}448.65_2$, $g=1.479$. *B*, Sharing of properties between the levels shown in Fig. 1*A*, as predicted by Eq. (5) and qualitatively found. The thickness of each line (above that of the thinnest) is proportional to the intensity of a transition to a $J=0$ level, permitted for $J=1$ but forbidden for $J=2$.

In order to eliminate false relative shifts of the differently polarized components arising from possible imperfections of adjustment in the cases of the exposures taken with the Rochon prism, all measurements of any line component in these exposures were made with respect to reference line components similarly polarized.

Although the wave-length dispersion $d\lambda/dx$ is sensibly constant over any one line pattern, the approximation involved in considering the wave number dispersion $d\nu/dx$ to be constant over a pattern would have introduced errors (almost 0.002 $cm^{-1}$ for our widest patterns, 17 $cm^{-1}$ wide) in our calculations. Of course the words "symmetry," "center," etc., in our discussion of the patterns, refer to the patterns reduced to a wave number scale, rather than to the photographic plates themselves. The equations used in our routine reductions were as follows, where $\lambda_0$ refers to the wave-length in air of the no-field line (or of the no-field line involving the level $214_1$ in the case of patterns arising from $214_1$ and $214_2$, which were always considered as single patterns); $\delta\lambda$, $\delta\nu$, and $\delta x$ to deviations from the no-field line; and $\delta\nu'$ to an approximation to the vacuum wave number deviation, $\delta\nu$, obtained in an intermediate step:

$$\left.\begin{aligned} \delta\lambda &= \delta x\, d\lambda/dx \\ \delta\nu' &= -\delta\lambda/\lambda_0{}^2 \\ \delta\nu &= \delta\nu'/n_{\text{air}} + \lambda_0(\delta\nu')^2. \end{aligned}\right\} \quad (8)$$

## FIELD DETERMINATIONS

Because no quantitative determinations have been made heretofore of magnetic fields as great as those used in this work, it was necessary to give careful consideration to the question of field determination. The procedure finally selected was: first, to determine as our principal field standard[21] the field $\eta=(4.093\pm0.006)$ $cm^{-1}$ found for an auxiliary exposure, calculated as discussed below from certain patterns chosen for theoretical reasons from among the lines of several

[21] $\pm$ here refers to probable error.

TABLE II. *Individual determinations of sublevels of $214_{1,2}$ from exposure 3.5($\eta=3.552$ cm$^{-1}$). Superscripts in the body of the table give M for the even sublevel of the transition. A = shift of $D_0^0$ with respect to the center of (supposedly symmetric) $44_2$, determined to be $-0.036$ cm$^{-1}$ by adjustment to best agreement with the other line ($214_{1,2}-44_2$). Dashes indicate lines too faint to measure, or missing.*

| LINE | GRATING | $\nu_1^{+1}$ | $\nu_1^0$ | $\nu_1^{-1}$ | $\nu_2^{+2}$ | $\nu_2^{+1}$ | $\nu_2^0$ | $\nu_2^{-1}$ | $\nu_2^{-2}$ |
|---|---|---|---|---|---|---|---|---|---|
| $214_{1,2}-44_2$ | $G$ | $+9.089^{+2}$ | $+0.400^{+1}$ | $-8.158^0$ | | — | $-5.572^{+1}$ | $-11.186^0$ | $-15.662^{-1}$ |
| | | $.092^{+1}$ | $.408^0$ | $.171^{-1}$ | $+5.351^{+2}$ | $-0.082^{+1}$ | — | — | $.673^{-2}$ |
| | | — | — | — | $.371^{+1}$ | $.072^0$ | $.545^{-1}$ | $.173^{-2}$ | |
| $214_{1,2}-44_2$ | $F$ | $.124^{+2}$ | $.428^{+1}$ | $.107^0$ | | — | — | $.149^0$ | $.634^{-1}$ |
| | | $.115^{+1}$ | $.407^0$ | $.155^{-1}$ | $.351^{+2}$ | $.081^{+1}$ | — | — | $.654^{-2}$ |
| | | — | — | $.139^{-2}$ | $.368^{+1}$ | $.077^0$ | $.550^{-1}$ | $.166^{-2}$ | |
| $D_0-214_1$ | $F$ | $.139^0+A$ | $.456^0+A$ | $.079^0+A$ | | $.046^0+A$ | $.526^0+A$ | $.119^0+A$ | |
| mean | | +9.105 | +0.413 | −8.141 | +5.360 | −0.079 | −5.557 | −11.165 | −15.656 |

TABLE III. *Observed sublevels of $214_1$ and $214_2$ referred to $\nu_0(214_1)$. All quantities are expressed in cm$^{-1}$; uncertainty $\sim\pm0.010$ cm$^{-1}$. B—Impossible to determine value on account of line blends. b—Value with unusually large uncertainty on account of partly resolved blends. Exposures listed in brackets are plotted together in Fig. 2.*

| $\eta$ | $\nu_1^{+1}$ | $\nu_1^0$ | $\nu_1^{-1}$ | $\nu_2^{+2}$ | $\nu_2^{+1}$ | $\nu_2^0$ | $\nu_2^{-1}$ | $\nu_2^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| 1.586 | +4.068 | +0.117 | −3.835 | | | | | |
| 1.586 | +4.080 | +0.098 | −3.835 | | | | | |
| 1.588 | +4.093 | +0.098 | −3.878 | | | | | |
| 1.646 | +4.222 | +0.123 | −4.013 | | | | | |
| 1.664 | +4.258 | +0.123 | −4.062 | | | | | |
| 1.666 | +4.277 | +0.117 | −4.050 | | | | | |
| 1.667 | +4.277 | +0.129 | −4.050 | | | | | |
| 1.679 | +4.295 | +0.123 | −4.074 | | | | | |
| 1.693 | +4.338 | +0.110 | −4.099 | | | | | |
| 1.698 | +4.350 | +0.110 | −4.154 | | | | | |
| 1.915 | +4.897 | +0.153 | −4.627 | | | | | |
| 2.252 | +5.727 | +0.179 | −5.420 | *B* | −1.885 | −5.330 | −8.696 | *B* |
| 2.426 | +6.208 | +0.234 | −5.821 | +2.035 | −1.649 | −5.326 | −9.015 | −12.276 |
| 3.552 | +9.105 | +0.413 | −8.141 | +5.360 | −0.079 | −5.557 | −11.165 | −15.656 |
| 4.285 | +11.016 | +0.602 | *B* | +7.540 | +0.966 | −5.688 | −12.721 | −17.802 |
| 4.533 | +11.677 | +0.674 | −9.947*b* | +8.272 | +1.320 | −5.795 | −13.307 | −18.584*b* |

elements introduced as impurities; and second, to determine the field for each exposure from the separations, assumed to be linear in the field, within the W I line $\nu 23{,}237$ ($=S_3-261_3$), which was especially selected as the reference line from theoretical and experimental considerations discussed below. The necessity of considering the value of a transformation factor between field and energy separation is automatically eliminated by the use of the Lorentz unit ($\eta=1$ cm$^{-1}$, or about $2.142\times10^4$ c.g.s.) instead of the c.g.s. unit of magnetic field, because the unit is dimensionally the same as that in which we measure the separation of the levels.

The impurity lines used to determine our principal standard of field were the resonance doublets of Ca II, Sr II, and Ba II. The concentration of each impurity was sufficiently low to produce sharp lines without self-reversal. The exposure was gauged to bring out the impurity lines and the W I reference lines with optimum blackening for measurement. The two directions of polarization were not separated. The field was calculated by making use only of the five intervals in each doublet that would have been, for weak fields, symmetric about no-field lines. This method compensates for all nonlinear effects that do not influence the interval within any pair of sublevels of a level that differ only in the sign of $M$, i.e., to a good approximation, for the diamagnetic quadratic Zeeman effect and for incipient mutual repulsion effects such as the Paschen-Back effect (cf. the last subsection of this paper). The error introduced in the calculations by the approximate treatment of the Paschen-Back effect can be seen from Eq. (7) to be, to the next approximation,

$$2M\Delta g\cdot k^2f^2\eta^3/(\Delta\nu_0)^2.$$

This error, which we have neglected, amounts to no more than $1.3\times10^{-3}$ cm$^{-1}$ in line separation, or $2.0\times10^{-3}$ cm$^{-1}$ in $\eta$, in any case. Earlier tenta-

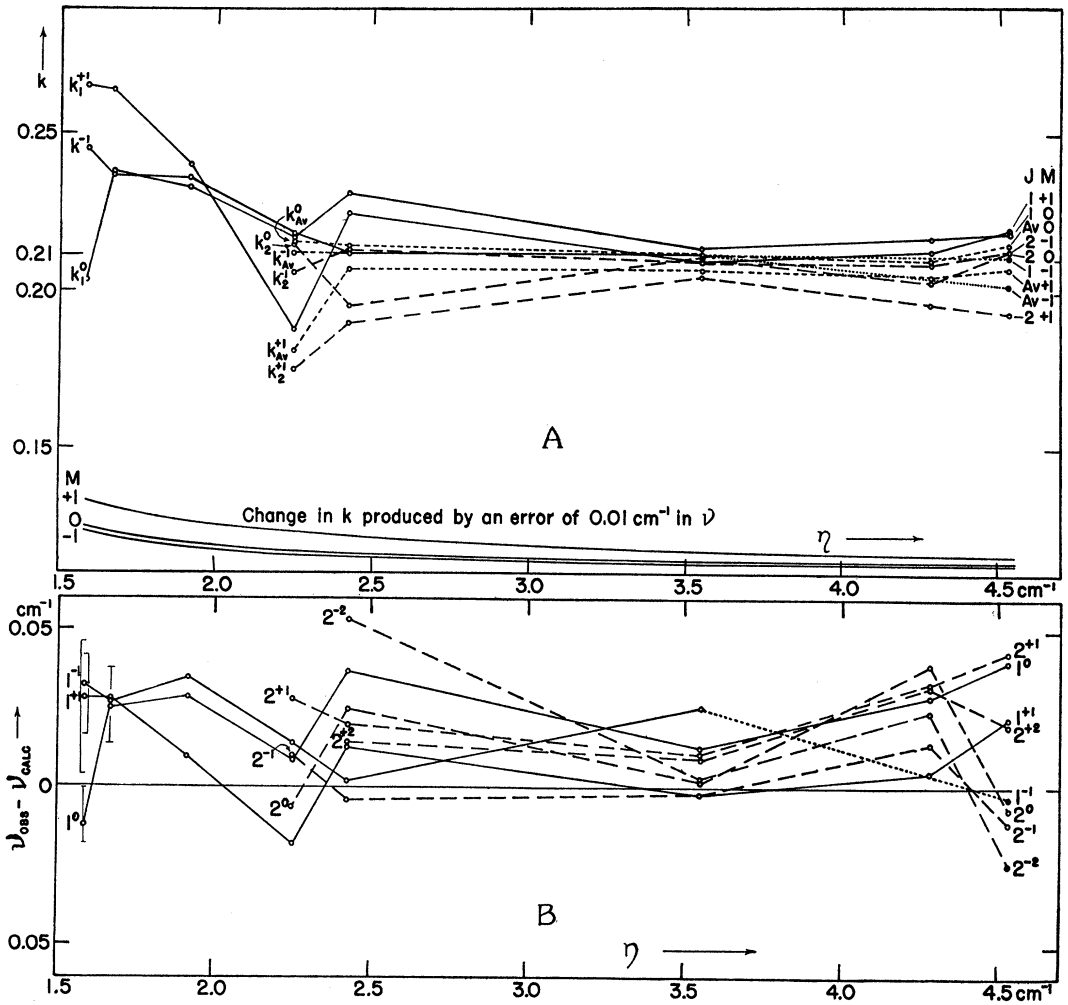


FIG. 2A, Values of $k(214_1, 214_2)$ observed for each sublevel in each of a number of fields. Full lines, $J=1$; dashes, $J=2$; filled circles, relatively unreliable values obtained from line blends. The ordinate labeled "0.21" should be labeled "0.211." B, Discrepancies, $\nu_{obs}-\nu_{calc}$, between the energy levels observed and those calculated from Eq. (1) with the best values of the constants. The scale of ordinates (discrepancy) is spread out tenfold compared with that of abscissas (field).

tive field values calculated from Al, Ca, and Sr impurities in two of the exposures listed in Table III, were $\eta=3.543$ and 4.267 $cm^{-1}$, lower by 0.3 and 0.5 percent, respectively, than the accepted values; but these values were abandoned on account of the relatively poor observational quality of the impurity lines, some of which were self-reversed.

The W I reference line $\nu 23{,}237$ was chosen primarily for experimental reasons: its great width ($\doteq 5\eta$), the relative slightness of its observed asymmetry, its stable distance from certain other relatively symmetric patterns, and its general favorable appearance on the plates. A secondary reason for the choice was the fact that the theoretically estimated[10] nonlinearities for both levels are small (although, as in all other levels in the spectrum, there are enough levels near to each level to make one expect some asymmetry). The observed pattern in the largest field (expressed as $\Delta\nu/\eta$, where $\eta=4.533$ $cm^{-1}$) was

2.445 2.209 *1.976* *1.741* 1.502 1.272 (*0.710* 0.466 0.237 $\bar{0}$ $\dot{0}$.236 0.466 *0.710*) 1.272 1.505 *1.743* *1.975* 2.212 2.447
236 233 235 239 230 244 229 473 230 244 233 238 232 237 235

The greatest discrepancy between this pattern and the weak-field one calculated from the accepted $g$ values, $g(S_3)=1.9751$ and $g(261_3)=1.7408$, is 0.022 $cm^{-1}$ ($\sim$5 microns).

## Results and Comparison with Theory

Although only the energies and not the intensities were measured, it may be remarked that the intensities were found, by visual estimation, to be qualitatively in agreement with Eq. (5) and Fig. 1*B*.

By means of an auxiliary study, the level $44_2$ was found to be very nearly symmetric, with $g(44_2)=1.9470$. In the calculation, levels $D_0$ and $44_2$ were assumed to follow the weak-field formula.

Table II shows the results of all the readings recorded for levels $214_{1,2}$ from exposure 3.5. It is typical except that the discrepancies (average deviation from accepted means, 0.011 $cm^{-1}$) are rather larger than in most exposures and that it is derived from both the line pair $\nu\nu$23,471, 23,465 and the line $\nu$21,453, the former having been photographed simultaneously with two gratings, while usually the data for one field were determined from one line or pair photographed on one plate. In Table II and throughout the paper, a subscript (except 0, *a*, *b*) stands for $J$ and a superscript stands for $M$. Table III is a summary, showing the final values of the sublevels observed in each field. The no-field interval between the levels was found to be

$$2\nu_0''\equiv\Delta\nu_0=(5.154\pm0.002)\ cm^{-1}.$$

In the calculations discussed below, all line components were given equal weight, except for partly resolved blends (marked *b*), which were recorded but given no weight when other readings were available for the same quantity, and unresolved blends (marked *B*), which were not recorded. Each interval was weighted by a factor proportional to its magnitude. In averaging the $k$'s, each value was weighted by a factor inversely proportional to the change that would result in $k$ from an arbitrary small alteration of a single reading (Fig. 2*A*, bottom).

The calculations and the comparison of the observed with the calculated sublevels proceeded as follows: $g_2$ and $g_1$ were determined in that order, and then $k$ (called $k_J{}^M$), independently for each sublevel, for all the exposures with $\eta>2$ $cm^{-1}$; and finally the wave number difference $\nu_{obs}-\nu_{calc}$ between the observed and the calculated value was determined for each sublevel in each field. Each calculation for one constant used the best (the weighted mean) value for each one previously listed; e.g., all the calculations for $g_1$ used $g_2=1.4787$. From the linear theory

$$g_2=(\nu_2{}^{+2}-\nu_2{}^{-2})/4\eta. \tag{9}$$

From the linear theory, modified by an interaction with spur invariance:

$$g_1=(\nu_1{}^{+1}+\nu_2{}^{+1}-\nu_1{}^{-1}-\nu_2{}^{-1})/2\eta-g_2. \tag{10}$$

The results for the $g$'s are as follows:

| $\eta(cm^{-1})$ | $g_2$ | $g'$ |
|---|---|---|
| 2.252 | *B* | 1.9936 |
| 2.426 | 1.4754 | 1.9986 |
| 3.552 | 1.4792 | 1.9940 |
| 4.285 | 1.4785 | *B* |
| 4.533 | 1.4811*b* | 1.9993*b* |
| weighted mean | 1.4787 | 1.9950 |

An independent determination of $k_J{}^M$ was made for each sublevel in each field, where $k_J{}^M$ was available, by solving Eq. (3) for $k$:

$$k_J{}^M=[(\nu_J{}^M-\nu_0'-Mg'\eta)^2-(\nu_0''+Mg''\eta)^2]^{\frac{1}{2}}/f\eta \quad \begin{cases} M=+1,\ 0,\ -1 \\ J=1,\ 2. \end{cases} \tag{11}$$

In addition to these six $k_J{}^M$ there were calculated for each field the following weighted means: three $k^M$ from $k_1{}^M$ and $k_2{}^M$; two $k_J$, from $k_J{}^{+1}$, $k_J{}^0$, and $k_J{}^{-1}$; and one $k$ from all six $k_J{}^M$. Finally the grand average $k$ was computed from all the fields with complete (six) $k_J{}^M$ data, i.e., from fields 2.2, 2.4, 3.5, and 4.5. The values are shown in Fig. 2*A*. The grand average $k$ is

$$k(214_1,\ 214_2)=0.211.$$

The best value of $k$ squared (formerly[5] called $K$ and given a tentative value of 0.06) is 0.0447.

The $k_J{}^M$ show small systematic trends, and it should be noted that the values of $k_1{}^M$ are consistently larger than those of $k_2{}^M$.

The values of $\nu_{calc}$ were obtained from Eq. (3) with the best values of the constants. The resulting curves are shown in Fig. 1*A*. The constants of the hyperbolas, calculated from Eq. (4),

are:

| $M$ | $\eta$(center) | $\nu$(center) | $(d\nu/d\eta)_\infty$ |
|---|---|---|---|
| $\pm1$ | $-3.312M$ cm$^{-1}$ | $-9.195$ cm$^{-1}$ | $\begin{cases}2.632M\\1.364M\end{cases}$ |
| 0 | 0.000 | $-2.577$ cm$^{-1}$ | $\pm0.424$ |

The values of $\nu_{\text{obs}}-\nu_{\text{calc}}$ are shown in Fig. 2*B*. The discrepancies are somewhat greater than our estimated experimental uncertainty, and are almost all positive.

In interpreting Fig. 2*B*, two distinct types of discrepancy ought to be considered: (1) *Experimental error.* Of all the factors possibly contributing to the accumulated experimental errors in our results, two deserve special mention here: First, the wandering of the reference levels. Each energy determination for $214_{1,2}$ depends upon the assumption that each of five reference levels exhibits in certain respects the weak-field behavior described in the second sentence of this paper.[22] The fact is that most of the discussion in the next paragraph is applicable to the reference levels as well as to levels $214_{1,2}$. Second, the repeated application of the same measurements in the determination of several constants: For instance, the same readings upon $\nu_1{}^{+1}$ and $\nu_1{}^{-1}$ were used successively in determining $g(44_2)$, $g_1$ and $k$, each of which depends upon its predecessors, as shown above. Thus, although we estimate our probable error in setting upon the line components to be not more than 0.010 cm$^{-1}$ ($\sim$2.5 microns), the total error in $\nu_{\text{obs}}-\nu_{\text{calc}}$ may be considerably larger than if independent data had been used for each constant with a consequent statistical canceling of errors.

(2) *Inadequacy of the calculation.* The calculation took explicitly into account only the interaction between the two levels under special consideration. Each sublevel is subject to other disturbances that we have not tried to evaluate, such as the diamagnetic quadratic Zeeman effect and incipient interactions with many other levels in the neighborhood. The disturbances specified can be expressed as a series in ascending powers of $\eta$. The first and most important member of the series is the $\eta^2$ one, which includes the incipient interactions with more distant levels, insofar as they can be described by Eq. (7), as well as the diamagnetic quadratic Zeeman effect[23] term:

$$\Delta\nu_{\text{diamagnetic quadratic}}\doteq\tfrac{1}{4}\pi mc\hbar^{-1}\eta^2 \times\sum[(r^2)_{\text{Av}}\cdot 2(l^2+l-1+m_l{}^2)/(2l-1)(2l+3)]. \tag{12}$$

Thus the $\eta^2$ member is, to a close approximation, an even function of $M$. Advantage was taken of this property in the determination of the constants, as follows: Eqs. (9) and (10) depend not upon individual $\nu$'s, but only upon differences $\nu_J{}^{+M}-\nu_J{}^{-M}$; and in the determination of the grand average $k$, Eq. (11) was used in effect only to determine the values of $k_J$, from pairs $\nu_J{}^{+M}$ and $\nu_J{}^{-M}$. Consequently the constants $g_1$, $g_2$, and $k$ used in the calculations are independent of all disturbances that are even functions of $M$ and $\eta$.

No such immunity can be claimed, however, for the individual determinations shown in Fig. 2. Parabolic terms are not evidently predominant in the discrepancies shown in Fig. 2*B*. Nevertheless, it is hoped that the outstanding discrepancies between the observations and the calculations can be improved, especially with respect to the general upward trend in Fig. 2*B* and the associated fact that the values of $k_1{}^M$ are on the whole higher than those of $k_2{}^M$, after a more detailed study[10] of the influence of more distant levels.

[22] Since the energies were measured with respect to $44_2$ (assuming the field-independence of the zero point interpolated from $18_1-415_2$ and $S_3-261_3$) in fields $\eta>2$ cm$^{-1}$, and with respect to $^5D_0$ (assuming the field-independence of the zero point interpolated from $13_2-353_2$ and $D_3-261_3$) in fields $\eta<2$ cm$^{-1}$, a false discontinuity might be expected to appear at the junction of the two regions in Fig. 2*B* (as well as in Table III). On the assumption that the effect is proportional to $\eta^2$, the value found for the quantity $A$ (Table II, caption) at $\eta=3.5$ cm$^{-1}$ leads one to expect the magnitude of the discontinuity to be about 0.01 cm$^{-1}$, the ordinate for strong fields being less than that for weak fields. Indeed such a discontinuity, probably from this cause, may be recognized in Fig. 2*B*.

[23] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, Clarendon Press, 1932), Chapter 6, Eqs. 105, 106. The summation, which is to be carried out over all electrons, is simplified by the fact that the contribution of any closed subshell is just $\Sigma 2(r^2)_{\text{Av}}/3$. From certain equations and susceptibility data (especially for $Au^+$) in Chapter 8 the value of $\Delta\nu$ (diamagnetic quadratic) for W I may be roughly estimated to range from about $+0.003$ cm$^{-1}$ to about $+0.005$ cm$^{-1}$ for the levels listed in our Table I, leading to absolute changes not greater than about 0.002 cm$^{-1}$ for any line with which we are concerned. Thus the shifts of the lines under study relative to the reference lines are too small to detect.