Hyperfine Structure of the 3^2P and 4^2P States of Lithium and Lifetime of the 3^2P State*

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The technique of level crossing spectroscopy has been used to study the hyperfine structure of the 3^2P and 4^2P states of Li^7 and the 3^2P state of Li^6. Both low-field (< 2 G) and high-field (≈ 915 G) level crossings were observed for the 3^2P state of Li^7. With the assumption that the ordinary magnetic-dipole coupling constants are related by $a_{d1/2}=5a_{d3/2}$, values have been obtained for $a_{d3/2}$ and the core-polarization constant a_c. In the 4^2P state of Li^7 and the 3^2P state of Li^6 we have inferred from our measurements individual values for $a_{d3/2}$ and a_c which are consistent with the assumptions that both constants scale as the ratio of nuclear g factors among different isotopes and that they scale as $1/n^3$ among all the n^2P states. The lifetime of the 3^2P state has also been obtained from the high-field level crossing data. The results for the hyperfine constants in MHz are the following: 3^2P Li^7: $a_{d3/2}=2.11(3)$, $a_c=-3.08(3)$, 4^2P Li^7: $a_{d3/2}=0.89(2)$, $a_c=-1.30(2)$, 3^2P Li^6: $a_{d3/2}=0.80(2)$, $a_c=-1.20(2)$. The lifetime of the 3^2P state is τ (3^2P Li^7) = 182(6) nsec.

I. INTRODUCTION

Level crossing spectroscopy has proved to be a valuable technique for measuring the lifetimes and hyperfine structures of excited atomic states.[1-6] This method exploits the interference signal that arises in reradiation from two states that are coherently excited by absorption of a photon. In order for the excitation to be coherent, the two levels must be degenerate. The degree of degeneracy or overlap is determined by both the widths of the states and separation of their centers. Variation of the overlap caused by changing electric or magnetic fields produces definite interference line shapes which are describable by the Breit formula,[7,8]

$$R \approx \sum_{mm',\mu\mu'} \frac{f_{\mu m} f_{m\mu'} g_{\mu' m'} g_{m'\mu}}{\Gamma + i(E_\mu - E_{\mu'})/\hbar} , \qquad (1)$$

where $f_{\mu m} = (\mu | \vec{f} \cdot \vec{r} | m)$, and $g_{\mu m} = (\mu | \vec{g} \cdot \vec{r} | m)$. The polarization vectors of the exciting and reradiated light are denoted, respectively, by $\vec{f}$ and $\vec{g}$; m and m' refer to the ground-state sublevels, and μ and μ' refer to the excited-state sublevels. The difference in energy between the excited states is $(E_\mu - E_{\mu'})$. Equation (1) shows that the signal is dependent upon Γ, the average width of the two excited levels, and thus reflects the lifetime of the state directly. The excited-state lifetimes obtained from such experiments are usually accurate to about 3%.

In the present work we show the results and analyses of high-field (500 – 1000 G) and low-field (< 2 G) level crossing experiments in Li^7 and of a high-field level crossing experiment in Li^6. High-field $\delta m_J = 2$ level crossings in the ^2P states of lithium occur when the $P_{3/2}{}^{-3/2}$ level is made degenerate with the $P_{1/2}{}^{1/2}$ level by application of an external magnetic field. A typical energy-level diagram is shown in Fig. 1 for Li^6 (I=1) near the field at which crossings occur. Each m_J level is split into three hyperfine components. Strong level crossing signals appear in the regions indicated by the solid black circles.

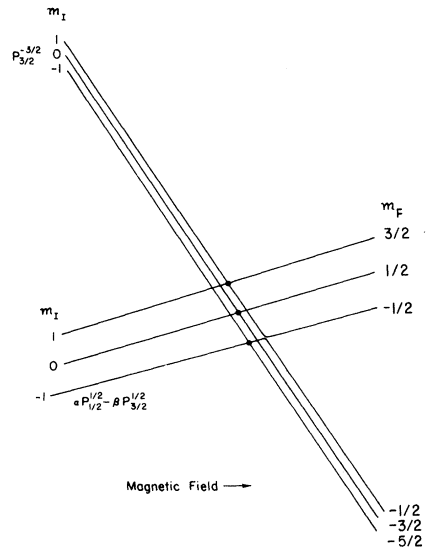

FIG. 1. Level crossing diagram for Li^6 at approximately 915 G. The lower electronic state is labeled to indicate that the $^2P_{3/2}{}^{1/2}$ and $^2P_{1/2}{}^{1/2}$ states are strongly mixed.

Hyperfine components with the same value of m_F cannot cross in a magnetic field,[9] and an anticrossing appears in the complex of levels in Fig. 1 for $m_F = -\frac{1}{2}$. In Li^7, each m_J level is split into four hyperfine levels, and two anticrossings take place. The interaction which mixes the levels and prevents the crossing in all these cases arises only from the nuclear-electric-quadrupole and second-order magnetic-dipole coupling. Numerical calculations indicate that no measurable shift in the center of the level crossing signal is caused by these anticrossings when the natural width of the levels is much larger than the matrix elements responsible for mixing the states of the same m_F. This criterion is satisfied in lithium for the $\delta m_J = 2$ crossings, where shifts are less than one part in 10^6 and can, therefore, be neglected.

In addition to the high-field level crossings which take place between two states of different J, moderately well-resolved low-field level crossings are also predicted in the 3^2P state of Li^7. These crossings occur between hyperfine intervals in the $J = \frac{3}{2}$ state only. The calculated behavior of these hyperfine levels in a magnetic field is shown in Fig. 2. Three $\delta m_J = 2$ level crossings occur at fields less than 2 G and can be directly related to the hyperfine splitting in zero magnetic field through Eq. (1) and a theory for the Zeeman effect.

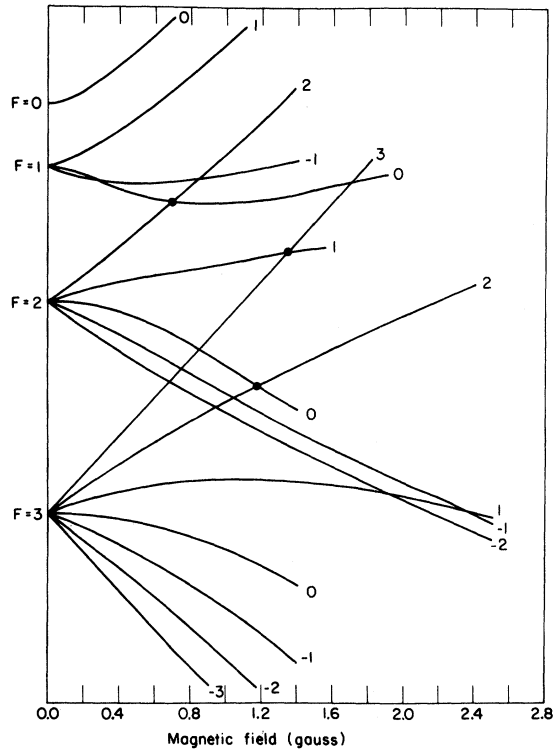

FIG. 2. Level crossing diagram for Li^7 at fields less than 3 G.

The hyperfine constants obtained from the analysis are required for an accurate evaluation of the fine-structure interval in the 3^2P state of Li^7.[10] It is also hoped that the lifetime and hyperfine constants may serve for testing various computational approaches for the calculations of the structures of simple atoms.

II. EXPERIMENTAL TECHNIQUE

The experimental techniques and apparatus are described in detail in the preceding paper, and only a brief outline is presented here. The light source is a flow lamp of the type described by Budick, Novick, and Lurio[11] in which a lithium beam is generated in an argon atmosphere and excited with a 30-MHz rf oscillator. Unpolarized resonance lines from the lamp (3233 Å for $2^2S \rightarrow 3^2P$ and 2742 Å for $2^2S \rightarrow 4^2P$) are used to optically excite the upper levels of absorbing lithium atoms. The absorbing atoms are inside a cell which is contained in an evacuated enclosure between the pole pieces of the magnet. Reradiated light is observed at a 90° angle to the incident beam, and Eq. (1) predicts that $\delta m_J = 2$ level crossing signals have Lorentzian shapes with this experimental arrangement. If the observation angle deviates slightly from 90°, the signals have a small admixture of a dispersion curve.

In order to enhance the signal-to-noise ratio, the magnetic field is modulated at 30 Hz while being swept through the crossing region. A phase-sensitive lock-in amplifier is used for the detection, and, to a first-order approximation, the signals actually recorded are the derivatives, with respect to the magnetic fields, of the signals predicted by Eq. (1).

The magnetic fields are measured with a proton NMR probe in the high-field experiments and a rotating coil in the low-field experiments.

III. EXPERIMENTAL RESULTS

Data from the three high-field experiments are illustrated in Fig. 3; the markers refer to the resonance frequency of the proton NMR probe used to measure the magnetic field. These curves are compounded from three or four level crossing signals, depending upon whether they are obtained from Li^6 or Li^7.

The intervals between the successive signals can be related directly to the hyperfine constants (Sec. IV). Precise measurements have been attempted only in the 3^2P state of Li^7 in which the curves are very well resolved. The center of each crossing is measured as the position where the derivative curve is zero. Several sets of data have been taken using different sweep rates for the magnetic field and, in some cases, using misaligned optics so that some fraction of the derivative of disper-

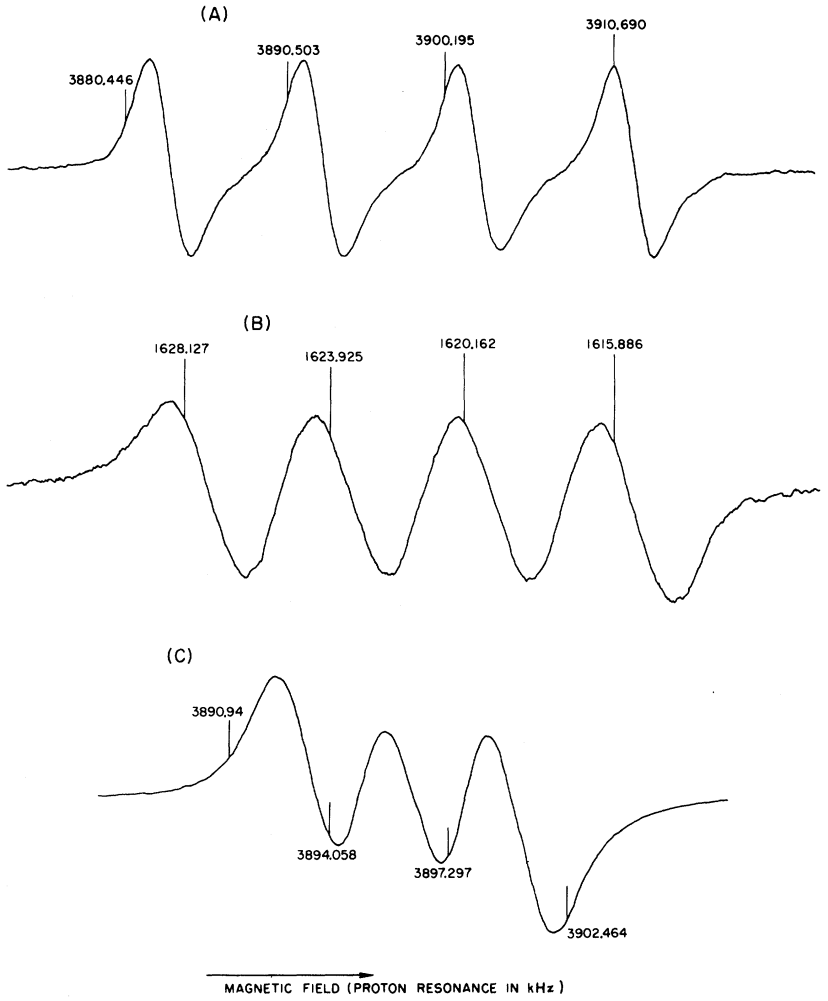

FIG. 3. Signals from level crossings between $^2P_{3/2}{}^{-3/2}$ and $^2P_{1/2}{}^{1/2}$ states, (A) Li^7 (3^2P), (B) Li^7 (4^2P), (C) Li^6 (3^2P).

sion line shapes were mixed with the derivatives of Lorentz curves. Results are consistent for all sets of data as shown in Table I. All of the listed uncertainties are three times the standard error.[12] The various sets refer to the following experimental conditions:

Set I – Several sweeps were made back and forth over a single crossing. The central magnetic field was changed and the procedure repeated for a different crossing.

Set II – Magnetic field sweeps were made over the entire set of four crossings at one time.

Set III – The same procedure was followed as for Set II, but the optics was misaligned to produce asymmetries of about 30% in the derivative peaks. The first and third intervals are the same for all sets of measurements within the experimental uncertainty, but the second interval measured in Set III disagrees slightly with the value measured from the other two sets. This disagreement is smaller than other uncertainties which affect the accuracy of the hyperfine constants. In general, the measured intervals are almost entirely unaffected by rapid sweeps and optical misalignment, experimental procedures that can seriously alter an absolute measurement of the crossing field. The three spacings would be uniform except for the presence of electric quadrupole and second-order magnetic-dipole and Zeeman-effect corrections. The second-order effects can be calculated accurately, however, and a value for the quadrupole moment of Li^7 can then be obtained from the differences in the splittings.

The resolution of the four individual signals is not as good in the 4^2P state of Li^7 as in the 3^2P state; although the lifetime of the former is longer and leads to a correspondingly narrower linewidth, the hyperfine intervals are smaller by an even greater amount. The net result is that the overlap of the signals is more pronounced than in the 3^2P crossings. The scatter in the data is too great to permit a meaningful separate tabulation of the three intervals, and the number in Table I is an average value for all three.

TABLE I. Measured intervals between zeros of level crossing signals (proton resonance frequencies in kHz).

Number of measurements	$\frac{3}{2} \longleftrightarrow \frac{1}{2}$	$\frac{1}{2} \longleftrightarrow -\frac{1}{2}$	$-\frac{1}{2} \longleftrightarrow -\frac{3}{2}$
		Li^7 3^2P state	
		Hyperfine intervals $(m_I \longleftrightarrow m_I')$	
17 (Set I)	9.518(14)	9.589(12)	9.689(10)
10 (Set II)	9.513(28)	9.596(14)	9.682(30)
6 (Set III)	9.509(28)	9.641(24)	9.676(26)
		Li^7 4^2P state	
18		Average interval = 4.044(24)	
		Li^6 3^2P state	
		Hyperfine intervals $(m_I \longleftrightarrow m_I')$	
		$1 \longleftrightarrow 0$ $\quad$ $0 \longleftrightarrow -1$	
15		3.483(20) $\quad$ 3.490(12)	

The data for Li^6 show very strong overlapping of the lines as expected for an isotope with such a small nuclear moment. The intervals between the zeros of the signal cannot be related in a simple way to the hyperfine constants. An analysis of overlapping lines is necessary to relate the spacing of the levels and linewidth to a three-component line shape such as the one shown in Fig. 3(c). Nevertheless, the observed intervals for Li^6 are presented in Table I along with the Li^7 data in order to exhibit the accuracy of the measurements.

The experimental results of Fig. 4 show that the interference signals from the low-field crossings in Li^7 are clearly observable, although not as well resolved as the high-field data. The first peak on either side of zero magnetic field arises from the Hanle effect (zero-field level crossing); the second peak results from the crossing between the states which in an $|F, M_F\rangle$ representation are designated as $|1,0\rangle$ and $|2,2\rangle$; and the third peak is from two unresolved crossings of the states $|2,0\rangle$ with $|3,2\rangle$ and $|2,1\rangle$ with $|3,3\rangle$. It is important to realize that these experimental peaks do not represent the positions of the crossings. They are, instead, the points where the slope of the level crossing signal goes through a local maximum. Again, as in the case of Li^6, the hyperfine constants can be extracted only after a complete analysis of the line shape which includes radiation from all the overlapping components.

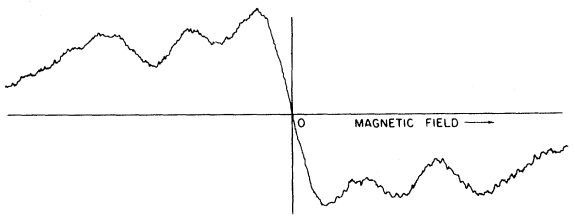

FIG. 4. Experimental level crossing signals in Li^7 at fields less than 3 G.

IV. ANALYSIS

A. Lifetime of the 3^2P State

In principle, either the high-field or low-field data may be used to obtain the lifetime of the state. A more accurate value is obtained from the high-field results, however, because of the larger signal-to-noise ratio and the difficulties caused by interference of overlapping components in the low-field curves. The analysis has been performed using one of the interior curves from the Li^7 data [Fig. 3 (a)]. If only the nearest-neighboring signals cause distortion of the line shape, the lifetime τ is calculated for a Lorentzian curve as

$$\tau = 1/\sqrt{3}\pi\Delta\nu - 64/3\sqrt{3}\pi\left[\Delta\nu^3/(\Delta\nu + 2\nu_1)^4 + \Delta\nu^3/(\Delta\nu - 2\nu_2)^4\right], \quad (2)$$

where $\Delta\nu$ is the peak-to-peak separation of the derivative line shape. The second term on the right-hand side is a correction for the influence of the neighboring lines with ν_1 and ν_2 representing the absolute spacing from the center of the derivative signal to the centers of the nearby lines. These spacings are about seven linewidths in the present experiment and produce corrections that are negligible compared to the experimental uncertainties. The actual measurement, of course, is the increment ΔH of the magnetic field between the peaks in the curve and is converted to $\Delta\nu$ in terms of energy from a theoretical calculation of the Zeeman effect near the crossing field; i.e.,

$$\tau = \left[\sqrt{3}\pi(d\nu/dH)\Delta H\right]^{-1}. \quad (3)$$

The magnetic field modulation employed in the detection scheme can influence the linewidths quite strongly, causing a broadening which, for small modulation, increases approximately as the square of the amplitude of the modulation. Figure 5 shows the variation in the peak-to-peak separation of the

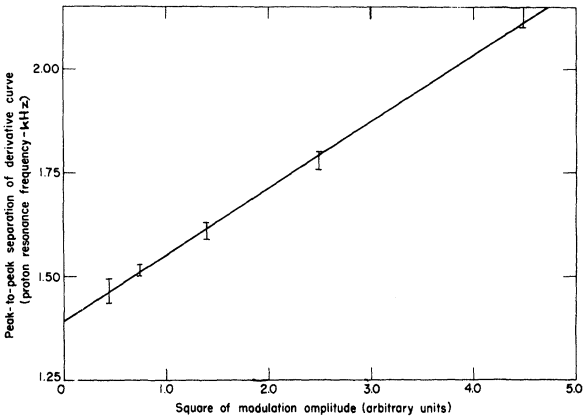

FIG. 5. Peak-to-peak separation of a level crossing signal in the 3^2P state of Li^7 as a function of modulation amplitude.

derivative of the level crossing signal plotted as a function of the square of the modulation amplitude in arbitrary units. The value for the separation extrapolated to zero amplitude is 1.39(2) kHz in terms of the proton magnetic resonance frequency. A value of $\tau = 182(6)$ nsec for the lifetime is provided by Eq. (2).

Analysis of the low-field data does not lead to as accurate a result for τ, although the results are consistent with the number obtained from the high-field crossings. The overlap of the hyperfine level crossing signals and the Hanle effect obscures the individual line shapes. A calculation of the complete theoretical signal without approximations is required in order to obtain the lifetime and the hyperfine constants from a curve such as Fig. 4. The theoretical results for different assumed lifetimes have the rather remarkable behavior seen in Fig. 6. The Hanle-effect peak would not be at all distinct if the lifetime were as short as 120 nsec; for $\tau = 160$ nsec, this peak would appear distinctly but would be lower in amplitude than the other two maxima. The curves for the longer lifetimes show the Hanle-effect peak to be somewhat larger than the other two. The experimental curves do not exactly match the calculated ones because the modulation broadening tends to degrade the resolution, but the qualitative similarity is enough to establish the lifetime as being in the neighborhood of 180 nsec, which is in good agreement with the result from the high-field level crossing data.

The 3^2P state in lithium can radiatively decay to either the 2^2S or 3^2S state. The lifetime of the 3^2P state is related to the transition probabilities to the lower levels by $\tau(3^2P) = 1/(A_{3P \to 2S} + A_{3P \to 3S})$. In order to discuss the correlation of our measurement of $\tau(3^2P)$ with experimental and theoretical results obtained by other workers for the transition probabilities, we have listed a summary of recent results in Table II. Results have also been included for the $2^2P \to 2^2S$ transition, because the measurements by Hinnov and Kohn[13] and by Filipov[14] yield only the relative transition probabilities for the first and second resonance lines, and the absolute values quoted for the $3^2P \to 2^2S$ transition are, therefore, dependent upon an assumed value for $A_{2P \to 2S}$.

The most reliable experimental value for the transition probability of the first resonance line has been obtained by Brog, Wieder, and Eck[15] from a high-field level crossing experiment in the 2^2P state similar to the present work. However, there is only a single branch in the decay of this state, and the transition probability to the ground state is simply given by the inverse of the lifetime. The agreement is excellent with both the Coulomb approximation[16] and the self-consistent (SCF) calculations of Weiss.[17]

Filipov's measurement of relative transition probabilities, together with Brog's value for $A_{2P \to 2S}$, yields $A_{3P \to 2S} = 1.16 \times 10^6$ sec^{-1}. Hinnov and Kohn's result obtained from a flame spectroscopy experiment is about 15% lower, but they used a value for $A_{2P \to 2S}$ which was about 6% lower than that of Brog *et al.* in their analysis. The Coulomb approximation again demonstrates good agreement with experiment for the second resonance line, but the SCF calculation disagrees by a factor of 2 as a result of the large uncertainties introduced by cancellations in the computed transition integrals.

Only theoretical values are available for

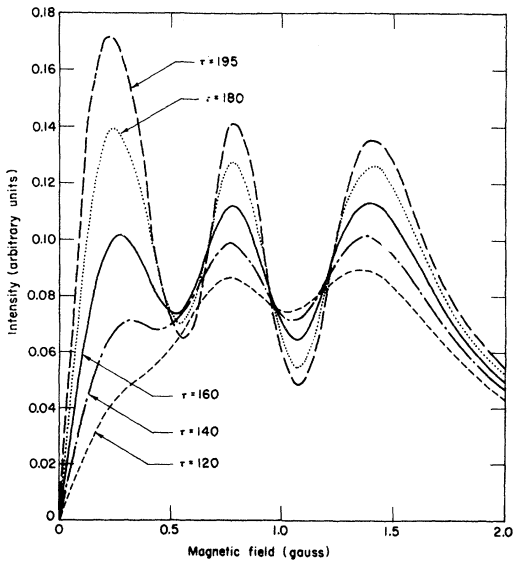

FIG. 6. Theoretical level crossing signals in Li^7 at fields less than 2 G. Values of the lifetime τ are given in nsec.

TABLE II. Theoretical (T) and experimental (E) results pertaining to the lifetime of the 2^2P and 3^2P states of lithium.

Transition probabilities (sec^{-1})				
$2P \rightarrow 2S$	$3P \rightarrow 2S$	$3P \rightarrow 3S$	Lifetime of 3^2P (nsec)	Source and method
3.68×10^7 (T) (assumed)	1.16×10^6 (E)	3.77×10^6 (assumed)	202	Filipov, relative f values by hook method[a]
3.68×10^7 (E)				Brog, Wieder, Eck level crossing[b]
3.51×10^7 (assumed)	1.02×10^6 (E)			Hinnov and Kohn, relative f values from flame spectroscopy[c]
3.68×10^7 (T)	1.09×10^6 (T)	3.70×10^6 (T)	209	Heavens, Coulomb approximation[d]
3.72×10^7 (T)	0.54×10^6 (T)	3.77×10^6 (T)	232	Weiss, Hartree-Fock SCF calculation[e]
			182(6)	Present work

[a]Reference 14.
[b]Reference 15.
[c]Reference 13.
[d]Reference 16.
[e]Reference 17.

$A_{3P \rightarrow 3S}(2.69\mu)$; the Coulomb approximation is in good agreement with the SCF result. The lifetime of the $3P$ state computed using $A_{3P \rightarrow 3S} = 3.77 \times 10^6$ sec^{-1} and $A_{3P \rightarrow 2S} = 1.16 \times 10^6$ sec^{-1} is $\tau = 202$ nsec, a value larger than that obtained from the present level crossing experiment.

B. Magnetic Hyperfine Interactions in Li^7

The important magnetic-dipole hyperfine interactions in the excited n^2P states of lithium can be considered as arising from two sources: (1) the ordinary dipole interaction of the nucleus in the magnetic field created by the valence p electron, and (2) the core-polarization interaction which comes from the coupling of the nominal $1s^2np$ configuration with other configurations such as $1s2snp$ that have unpaired s electrons and can produce a net Fermi contact interaction.

In zero magnetic field the total hyperfine-interaction constants for the $J = \frac{3}{2}$ and $J = \frac{1}{2}$ states can be written[18]

$$a_{3/2} = a_{d3/2} + a_c ,$$

and $$a_{1/2} = a_{d1/2} - a_c ,$$

where $a_{d3/2}$ and $a_{d1/2}$ are the ordinary magnetic-dipole constants and a_c is the core-polarization constant.

The low-field level crossing yields a value of $a_{3/2}$ directly. The position of the second peak in Fig. 6 is very insensitive to the natural width of the level crossing signal so that the influence of modulation broadening on the position of the peak should also be negligible. In addition, numerical computations for a reasonable range of magnetic-dipole and electric-quadrupole coupling constants show that the quadrupole interaction has little influence upon the peak, and that it is possible to determine $a_{3/2}$ to about 1% by matching the experimental curves to the theoretical ones. The result of such a fitting gives

$$a_{3/2} = a_{d3/2} + a_c = -0.965(20) \text{ MHz}. \qquad (4)$$

A second set of relationships for the dipole-coupling constants and a_c is obtained from the high-field crossing data. In this case, all crossings are well resolved and the intervals between centers have been measured quite precisely as shown in Table I. First- and second-order perturbation calculations have been employed to obtain theoretical relationships between the hyperfine constants and the separations of the level crossing signals. Nonrelativistic formulas for evaluating the perturbations are found in the Appendix of the preceding paper which deals with the evaluation of the fine-structure intervals of lithium. The results of the computations are shown in Table III for the three intervals. The coefficients of the second-order terms have been computed with the assumption that the radial wave functions for the $^2P_{3/2}$ and $^2P_{1/2}$ states are the same, so that $a_{d1/2}$ and $a_{d3/2}$ can

TABLE III. Theoretical relationships for intervals between hyperfine level crossings of the $^2P_{1/2}{}^{1/2}$ and $^2P_{3/2}{}^{-3/2}$ states of Li^7. The ΔH_i's are the differences between the fields at which each hyperfine crossing occurs and the field at which a single crossing would occur in the absence of any hyperfine structure. The fine-structure interval of the multiplet is denoted by ΔW.

Interval $(M_I \leftrightarrow M_I')$	
$\frac{3}{2} \leftrightarrow \frac{1}{2}$	$-E_H + \frac{3}{11} b - 2.182\mu_0(\Delta H_1 - \Delta H_2) + (3/2\Delta W)[38.73a_{d3/2}{}^2 + 0.84a_c{}^2 + 0.081\mu_0{}^2(\Delta H_1{}^2 - \Delta H_2{}^2) - 11.38a_{d3/2}a_c + \mu_0 a_{d3/2}(0.046\Delta H_1 - 0.015\Delta H_2) + \mu_0 a_c(0.73\Delta H_1 - 0.26\Delta H_2)] = 0$
$\frac{1}{2} \leftrightarrow \frac{1}{2}$	$-E_H - 2.182\mu_0(\Delta H_2 - \Delta H_3) + (3/2\Delta W)[13.08a_{d3/2}{}^2 + 1.83a_c{}^2 + 0.081\mu_0{}^2(\Delta H_2{}^2 - \Delta H_3{}^2) - 9.67a_{d3/2}a_c + 0.015\mu_0 a_{d3/2}(\Delta H_2 + \Delta H_3) + 0.26\mu_0 a_c(\Delta H_2 + \Delta H_3)] = 0$
$-\frac{1}{2} \leftrightarrow -\frac{3}{2}$	$-E_H - \frac{3}{11} b - 2.182\mu_0(\Delta H_3 - \Delta H_4) + (3/2\Delta W)[-12.59a_{d3/2}{}^2 + 2.84a_c{}^2 + 0.081\mu_0{}^2(\Delta H_3{}^2 - \Delta H_4{}^2) - 7.94a_{d3/2}a_c + \mu_0 a_{d3/2}(0.046\Delta H_4 - 0.015\Delta H_3) + \mu_0 a_c(0.73\Delta H_4 - 0.26\Delta H_3)] = 0,$
where $E_H = \frac{1}{11}[20a_{d3/2} + 5a_{d1/2} + 6a_c]$	

be related by angular momentum quantum numbers alone with the result that

$$a_{d1/2} = 5a_{d3/2}. \tag{5}$$

Deviations as large as 13% from similar simple relationships between hyperfine constants within the same multiplet have been observed in oxygen and fluorine.[19] Although the 5:1 ratio may not be exact for lithium,[20] comparison of our experiments with those done on the 2^2P state of Li^7 indicates that the ratio probably holds within 2%. If Eq. (5) is assumed valid, the theoretical expression for E_H from Table III, the measured interval, $(\Delta H_2 - \Delta H_3)$, and Eq. (4) can be combined to yield separate values for $a_{d3/2}$ and a_C. The central interval is chosen because it contains no dependence upon the quadrupole coupling constant b. Second-order corrections to the interval can then be computed from the preliminary values of $a_{d3/2}$ and a_C, and the expressions can be reevaluated to give final results

$$a_{d3/2} = 2.11(3) \text{ MHz} \quad \text{and} \quad a_c = -3.08(3) \text{ MHz}$$

for the 3^2P state of Li^7. Relativistic calculations which use the formalism developed by Schwartz[21] have also been performed. These calculations indicate that relativistic effects are negligible within the accuracy of the present experiments.

The justification for assuming that Eq. (5) is valid within the accuracy of the measurements originates in the comparison of the level crossing intervals for the 2^2P, 3^2P, and 4^2P states. The present results and those of Brog, Eck, and Wieder[15] reveal that the intervals between level crossing signals scale as $1/n^3$ within the accuracy of the measurements, about 5 parts in 10^3, for these three states. In addition, the double-resonance experiments of Ritter[22] in the 2^2P state yield $a_{1/2} = 46.17(35)$ MHz, from which Brog *et al.* deduce $a_{d3/2} = 7.14$ MHz and $a_C = -10.5$ MHz; they have employed the results of their own level crossing measurements and the assumption of a 5:1 ratio for the dipole constants in order to obtain these results. It is seen that the ratio $a_{d3/2}(3^2P)/a_{d3/2}(2^2P) = \frac{8}{27}$ to an accuracy greater than 1% although Ritter's primary measurement involves the hyperfine dipole constant for the $J = \frac{1}{2}$ state, whereas our low-field crossing result depends upon the dipole constant for the $J = \frac{3}{2}$ state. In view of the accuracy of the scaling for the high-field level crossing intervals, and the apparent consistency when Eq. (5) is used for applying the same scaling factor to individual hyperfine coupling constants, it would appear that Eq. (5) is valid to within 1 or 2% for the lowest three ^2P states of lithium. Any uncertainty in this regard could be removed either by measuring $a_{1/2}$ in the 3^2P state or $a_{3/2}$ in the 2^2P state. However, our own attempts at double-resonance experiments in the 3^2P state have not been successful owing to insufficient signal strength to provide an accurate

measurement. A low-field level crossing experiment in the 2^2P state does not appear feasible because the natural linewidth is wide enough to make individual hyperfine crossing signals indistinct.

Although only high-field level crossing data are available for the 4^2P state of Li^7, it is possible to infer individual values for $a_{3/2}$ and a_C in this state by assuming that $a_{d3/2}$ and a_C can each be scaled to the values in the 3^2P state by the ratio $(\frac{3}{4})^3$. The results are

$$a_{d3/2} = 0.89(2) \text{ MHz} \quad \text{and} \quad a_C = -1.30(2) \text{ MHz}$$

for the 4^2P state.

C. Magnetic-Dipole Constants in Li^6

The overlap of successive level crossing signals in the Li^6 data adds only a slight complexity to the analysis. The best fit to a series of computed curves shows that the average of centers of the successive hyperfine crossings are separated by 2.57(6) MHz. The major contribution to the uncertainty arises from the inability to evaluate the effects of modulation broadening to better than 0.04 MHz.

To first order, then, the Li^6 hyperfine constants are related to the measured interval by

$$\tfrac{135}{33}\, a_{d3/2} + \tfrac{6}{11} a_C = 2.57(6) \text{ MHz}.$$

There is no independent measurement available to provide a second relationship for $a_{d3/2}$ and a_C as there is in Li^7. However, the $a_{d3/2}$ values should scale as

$$a_{d3/2}(\mathrm{Li}^6)/a_{d3/2}(\mathrm{Li}^7) = g_I(\mathrm{Li}^6)/g_I(\mathrm{Li}^7) ,$$

so that $a_{d3/2}(\mathrm{Li}^6) = 0.80(2)$ MHz.

The core-polarization constant a_C is then computed to be $-1.20(2)$ MHz and when compared to the value obtained for Li^7, it is also seen to scale as the ratio of the nuclear g factors to the accuracy of the measurement.

D. Quadrupole Moment of Li^7

It is seen from Table III that two of the intervals between level crossings exhibit a dependence upon b, the electric-quadrupole coupling constant. The term in E_H, which is known to only a few percent, can be eliminated by subtracting these expressions, giving

$$\begin{aligned}
&\tfrac{6}{11} b - 2.182\mu_0(\Delta H_1 - \Delta H_2 + \Delta H_4 - \Delta H_3) \\
&+ (3/2\Delta W)[51.32\, a_{d3/2}^2 - 2.00 a_C^2 - 3.44 a_{d3/2} a_C \\
&+ 0.081\mu_0^2(\Delta H_1^2 - \Delta H_2^2 + \Delta H_4^2 - \Delta H_3^2) \\
&- \mu_0 a_{d3/2}(0.046\,\Delta H_1 - 0.046\,\Delta H_4 \\
&- 0.015\,\Delta H_2 + 0.015\Delta H_3) + \mu_0 a_C(0.73\Delta H_1 \\
&- 0.73\Delta H_4 - 0.26\Delta H_2 + 0.26\Delta H_3)] = 0 . \qquad (6)
\end{aligned}$$

The second term is just the measured difference between the first and third intervals shown in Table I. The second-order corrections can be estimated sufficiently accurately using values of $a_{3/2}$, a_C, and the ΔH's which are accurate to a few percent. The most reliable set of measurements to use in evaluating the second term are those from Set I in Table I. These data were obtained with very slow sweeps over single crossings so that the centers of the curves could be determined more accurately than was possible using the other two sets in which the entire signal was obtained during one sweep. Nevertheless, the difference between the outer two intervals is the same within 2% for each set of data, and the uncertainty of all the results taken together is about the same as for Set I alone. Unfortunately, there is a large cancellation between the second-order corrections and the first-order Zeeman term which prevents an accurate evaluation of b. The result from Eq. (6) is

$$b = -0.019(22) \text{ MHz}. \qquad (7)$$

The quadrupole moment of Li^7 is computed by using the measured values of both $a_{d3/2}$ and b from the expression[23]

$$Q = \frac{b}{a_{d3/2}} \frac{4L(L+1)}{J(2J-1)} \frac{\mu_B^2}{e^2} \frac{\mu_I}{\mu_N} \frac{m}{m_p} \frac{1}{I} , \qquad (8)$$

where L and J are the orbital and total angular momentum of the state, μ_B is the Bohr magneton, μ_I/μ_N is the nuclear magnetic moment in terms of nuclear magnetons, m/m_p is the electron-proton mass ratio, and I is the nuclear spin. The Sternheimer[24] correction for distortion of the electron core in lithium increases Q by about 11% over the value obtained directly from Eq. (8). The final result is

$$Q = -1.17 \pm 1.23 \times 10^{-26} \text{ cm}^2. \qquad (9)$$

As a measurement of the quadrupole moment, this result is not very satisfying because of the large uncertainty. It does overlap with the quadrupole moment obtained by Brog, Wieder, and Eck from level crossing experiments in the 2^2P state, $Q = -3 \pm 2 \times 10^{-26}$ cm^2, indicating that the actual value of Q probably lies between -1.0×10^{-26} cm^2 and -2.4×10^{-26} cm^2.

Measurements of the quadrupole moment of lithium from electric resonance experiments on mole-

cules yield values larger in magnitude than would be indicated by the two level crossing experiments considered together. Wharton, Gold, and Klemperer[25] deduce $Q = -4.5 \pm 0.45 \times 10^{-26}$ cm^2 from observations in LiH coupled with the result of a calculation by Kahalas and Nesbet[26] for the gradient of internal electric fields at the nuclei of the molecule.

The level crossing data from the 2^2P state are consistent with the results from molecular studies, but the present results on the 3^2P state do not appear to be compatible. All of the present sets of measurements of differences between the two outer intervals in the level crossing pattern are self-consistent to a much higher degree than the uncertainties would indicate, even for the highly distorted signals. It appears that even though the influence of the quadrupole interaction in the 3^2P state is quite small and cannot be measured with high accuracy, the derived value of Q is in disagreement with the results from studies on molecules.

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