Eq. (9), is

$$-2K_0\int_0^a f_0^2(K_0;r)\,dr = i\exp(-2iK_0a) - \frac{2iK_0}{f_0(-K_0)}\left(\frac{\partial f_0}{\partial k}\right)_{K_0}, \qquad (10)$$

and this in conjunction with Eq. (7) establishes the original perturbation formula (1).

We see that the heuristic calculation of the text, based upon the δ-function potential (4), has correctly obtained the form of the general result. The derivation given in this appendix only assumes that $v(r)+\lambda u(r)$ obey the usual analytic conditions required for Poincare's theorem.[1]

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*Research supported by the National Aeronautics and Space Administration, under Grant No. NSG-416.

[1] M. Goldberger and K. Watson, *Collision Theory* (Wiley, New York, 1963).

PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Hyperfine Structure of the Ground State of Mn^{55}†

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(Received 6 November 1970)

The five hyperfine transition frequencies of the $S_{5/2}$ ground state of Mn^{55} have been measured in a spin-exchange optical pumping experiment. The optical pumping flasks contained a neon buffer gas, and the measurements were made as a function of buffer-gas pressure. The measurements were carried out at a temperature of 700 °C. The linewidth of the Mn signal was typically 300 Hz. The hyperfine interaction constants were found to be $A=-72\,420\,836\,(15)$ Hz, $B=-19\,031\,(17)$ Hz, $C=-0.7\pm1.1$ Hz, $|D|<0.25$ Hz, and $|E|<0.02$ Hz. The fractional pressure shift in A was found to be $(1/A)\,(\partial A/\partial P)=(2.6\pm0.2)\times10^{-8}$ Torr^{-1}. No pressure dependence of the other interaction constants was observed.

I. INTRODUCTION

The hyperfine structure of the $S_{5/2}$ ground state ($I=\frac{5}{2}$, $J=\frac{5}{2}$) of Mn^{55} has previously been investigated by atomic-beam methods.[1,2] There are five hyperfine transition frequencies from which one can determine five interaction constants in the Hamiltonian. First-order perturbation theory relates these constants to electric and magnetic multipole interactions for atoms where LS coupling is a good approximation. In many cases, however, relativistic effects, configuration mixing, and higher-order perturbation terms contribute significantly to the interaction constants. In this case, measurement of the interaction constants can lead to a refinement of theoretical wave functions.

In the most recent atomic-beam experiment,[2] three hyperfine frequencies were measured to determine the magnetic dipole and electric quadrupole interaction constants A and B. The three remaining constants were set equal to zero. The value of B was attributed entirely to relativistic corrections.

We report here a more precise spin-exchange optical pumping experiment in which all five hyperfine frequencies were measured, eliminating the need to set any of the interaction constants equal to zero.

The Mn atoms were polarized in a weak magnetic field by spin-exchange collisions with optically pumped Rb atoms. When an rf field induces hyperfine transitions in the Mn atoms, they are depolarized and the spin-exchange collisions depolarize the Rb atoms. This results in a change in the intensity of the pumping light transmitted by the sample flask. Due to the low vapor pressure of Mn, the measurements were performed at temperatures near 700 °C. The density of the Rb atoms in the flask was controlled independently of the flask temperature in a manner described in a previous publication.[3]

II. APPARATUS

A block diagram of the apparatus is shown in Fig. 1. The magnetic field was produced by Helmholtz coils situated inside two concentric cylindrical magnetic shields. The sample flasks were 300-ml quartz spheres. They were heated to 700 °C in a firebrick oven located in the center of the shields. The oven was heated with electrical heating rods. The Mn vapor pressure at this temperature is approximately 1×10^{-6} Torr. The Rb density in the flask was adjusted for optimum signal strength in the following way. A reservoir of Rb metal was contained in a small sidearm attached to the flask

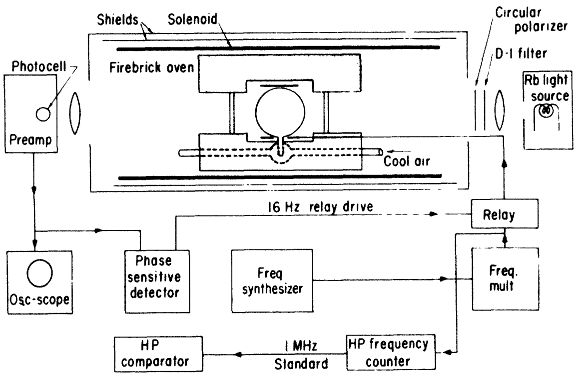

FIG. 1. A block diagram of the optical-pumping apparatus.

which fitted into a cooling tube in the bottom of the oven. The sidearm was cooled by a flow of air through the cooling tube. The amount of air flowing through the tube determined the temperature of the sidearm and thus the density of Rb atoms in the flask. The temperature of the oven was measured by a thermocouple.

The rf which induced the transitions was chopped at a rate of 16 Hz by a coaxial relay. At resonance, the transmitted pumping light intensity was amplitude modulated at this frequency. This signal was detected by a photocell, amplified, and displayed on a phase-sensitive detector.

The rf frequencies of approximately 72, 145, 217, 290, and 362 MHz were generated by frequency multiplication. The source was a General Radio 1164-A frequency synthesizer, the output of which was amplified by a linear amplifier. This was then fed into a multiplier circuit utilizing a varactor diode. The waveform of the rf applied to the sample was monitored on a sampling oscilloscope. The frequencies were measured by a frequency counter which was continuously compared with the 60-kHz standard frequency broadcast by WWVB. The time base of the counter was in agreement with WWVB to better than 2 parts in 10^9 for all measurements. The time base was atomic time in which the Cs^{133} hyperfine splitting is 9 192 631 770 Hz.

III. SAMPLE PREPARATION

The quartz flasks were prepared on a vacuum-gas handling system. Mn powder was placed in a small reservoir in the side of the flask before it was attached to the vacuum system. The flask was evacuated, and Rb was then distilled into its reservoir at the bottom of the flask. The flask was baked out at 800 °C for a short time (2 min), allowed to cool slowly and was filled with Ne gas. The pressure of the Ne was measured with a Hg manometer at a filling temperature of 297 °K. The flask was then removed and the Mn was spilled out into the flask. This could not be done earlier because the bakeout would have coated the walls of the flask with Mn, forming an opaque film. This was also the reason for the short bakeout time.

The coating of the walls of the flask by the Mn during a measurement run severely limited the lifetime of a sample. Also, the amplitude of the Mn signals we obtained varied in an unpredictable manner from sample to sample. Many flasks were prepared which had uselessly weak Mn signals.

Because the gas in the system was heated when sealing off the quartz sample from the vacuum system, corrections of the pressure had to be made by reading the manometer before and after seal off. This was a major source of error in the determination of A and in the pressure shift.

IV. MEASUREMENTS

There are six hyperfine levels in the ground state of Mn^{55} which result from the coupling of the nuclear spin $I=\frac{5}{2}$ to the electronic angular momentum $J=\frac{5}{2}$. They are characterized by total angular momenta $F=5,\ 4,\ 3,\ 2,\ 1,\ 0$. The $F=5$ level is the lowest level.[4] A weak magnetic field splits each hyperfine level into Zeeman sublevels characterized by magnetic quantum number M. The measurements were carried out in a field of approximately 4 mG. This field is so weak that all of the Zeeman splittings (~ 6 kHz) were essentially equal. The applied rf field induced $\Delta M=\pm 1$ transitions between adjacent hyperfine levels so that one observed two resonance signals associated with each hyperfine transition, separated in frequency by twice the Zeeman splitting. These two frequencies were averaged to obtain the zero-field hyperfine frequency.

The hyperfine transition frequencies are related to the multipole interaction constants through the equations[5]

$$\nu(F=5 \leftrightarrow F=4)=5A+\tfrac{3}{5}B+\tfrac{24}{5}C+8D+12E\ ,$$

$$\nu(F=4 \leftrightarrow F=3)=4A-\tfrac{3}{50}B-\tfrac{174}{25}C-26D-66E\ ,$$

$$\nu(F=3 \leftrightarrow F=2)=3A-\tfrac{9}{25}B-\tfrac{8}{25}C+40D+220E\ .$$

$$\nu(F=2 \leftrightarrow F=1)=2A-\tfrac{39}{100}B+\tfrac{153}{25}C-15D-495E\ ,$$

$$\nu(F=1 \leftrightarrow F=0)=A-\tfrac{6}{25}B+\tfrac{144}{25}C-48D+792E\ ,$$

where A, B, C, D, and E are the 2^1-, 2^2-, 2^3-, 2^4-, and 2^5-pole interaction constants, respectively.

The observed signals were weak by usual optical pumping standards because the polarization was spread over so many energy levels. As a result, the resonances were rf power broadened. The linewidth of the signals was typically 300 Hz. The contribution to the width due to gradients in the magnetic field was 150 Hz.

The signals were strongest for the three highest frequency transitions and the 145- and 72-MHz signals

TABLE I. Results for individual runs in which the 362, 290, and 217 MHz hyperfine frequencies were measured. The constants D and E are set equal to zero. This table includes data from runs in which other transitions were measured well.

Neon pressure (Torr)	A (Hz)	B (Hz)	C (Hz)
38.8	−72 420 921	−190 48	+0.02
	−72 420 922	−190 39	+0.9
	−72 420 963	−190 28	−1.4
71.3	−72 420 960	−190 19	−1.25
101.3	−72 421 026	−190 23	−1.55
	−72 421 068	−189 88	−1.87
120.6	−72 421 066	−190 34	−3.02
	−72 421 062	−190 54	+0.73
	−72 421 064	−190 27	−0.33
	−72 421 063	−190 35	−0.51
	−72 421 091	−190 07	−0.78
	−72 421 090	−190 46	−1.64
138.4	−72 421 082	−190 25	−1.25
163.7	−72 421 163	−190 54	+2.26

TABLE III. Average values of B and of C obtained from Tables I and II. The standard deviations give the spread in the values of B and C from run to run.

Transitions measured	B (Hz)	Std. dev. (Hz)	C (Hz)	Std. dev. (Hz)
3	−190 31	17	−0.69	1.3
4	−190 32	16	−0.75	1.1

were significantly weaker. At first, only the 362-, 290-, and 217-MHz transitions were measurable. As our luck improved, we obtained samples with which the 145-MHz signal could also be measured. Finally, in one flask, we obtained reliable measurements on all five transitions.

For the flasks in which three or four hyperfine frequencies could be measured, all of the observable hyperfine frequencies were measured in each run. In a single run each hyperfine frequency was determined 12 times. Each determination was made by measuring the two associated transition frequencies three times each and averaging them together. The oven was heated to 725 °C, the heaters switched off, and the measuring begun. In the time it took to make a single hyperfine-frequency determination the oven temperature dropped approximately 30 °C and the Mn signals disappeared. The oven was heated again and the process repeated to obtain another determination of the hyperfine frequency.

Half of the measurements on each hyperfine frequency were made with left circularly polarized light and then the polarization was reversed. The direction of the magnetic field was also reversed occasionally. Neither operation had a discernible effect on the results.

V. RESULTS

The results of the measurements are summarized in Tables I–IV. The sign of A is negative as determined in another experiment.[4] We find that A, B, and C all have the same sign. Table I contains values of A, B, and C calculated from measurements of the three highest frequency transitions in various flasks assuming D and E are negligibly small. This table makes use of data from every run that was made. Table II contains the results obtained from runs where four transitions were measured, assuming E is negligible.

A plot of A vs pressure of neon is shown in Fig. 2. The data for this plot were taken from Table I, since it was found that the value of A obtained at a given pressure of neon was independent of whether or not three, four, or five transition frequencies were used in its determination. The probable error in A at a given pressure is 3 Hz, and the dominant source of error in this graph is the pressure measurements.

A study of Tables I and II does not reveal any

TABLE II. Results for individual runs in which the 362-, 290-, 217-, and 145-MHz hyperfine frequencies were measured. The constant E is assumed to be zero.

Neon pressure (Torr)	A (Hz)	B (Hz)	C (Hz)	D (Hz)
38.8	−72 420 922	−190 30	+0.14	+0.11
71.3	−72 420 959	−190 35	+0.11	−0.19
	−72 421 068	−189 96	−1.13	−0.10
120.6	−72 421 066	−190 30	−3.4	+0.05
	−72 421 063	−190 39	−0.58	+0.19
	−72 421 064	−190 24	−0.67	+0.05
	−72 421 063	−190 41	+0.01	−0.07
138.4	−72 421 089	−190 59	−0.49	−0.16

TABLE IV. Results for the sample in which all five hyperfine transition frequencies were measured. The Ne pressure was 120.6 Torr. For the sake of comparison, we have calculated the interaction constants from the averages of the three highest frequencies, the four highest frequencies, and from all five frequencies as measured in this sample. The total amount of data taken on all five transitions in this sample is equivalent to five complete runs. The average transition frequencies measured in this sample were 362 116 744, 289 683 110, 217 256 343, 144 834 717, and 72 416 491 Hz.

Transitions used	A (Hz)	B (Hz)	C (Hz)	D (Hz)	E (Hz)
3	−72 421 065	−190 28	−0.91	set = 0	set = 0
4	−72 421 065	−190 26	−1.16	+0.03	set = 0
5	−72 421 065	−190 29	−0.79	−0.06	+0.01

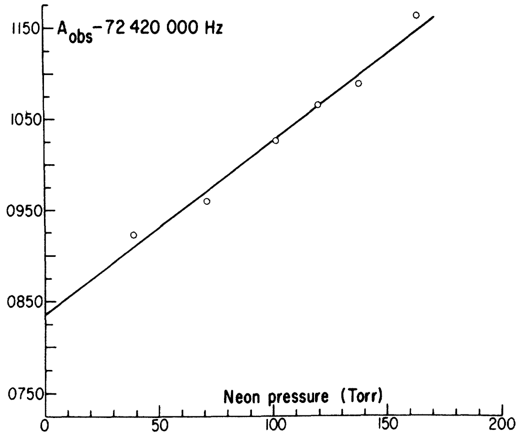

FIG. 2. A plot of A vs pressure of neon at a filling temperature of 297 °K. The estimated error in frequency at a given pressure is 3 Hz.

pressure dependence of B or C within the experimental error. In Table III, the values of B and of C in Table I are averaged and compared with the averages of B and C obtained from Table II. The standard deviations representing the spread in the results for B and C from run to run are also given.

In Table IV we present the results of our data from the sample in which all five hyperfine transitions were measured. In this case, not all the hyperfine frequencies were measured in each run. Most of the 72-MHz data were taken in runs in which the other transitions were not measured. The interaction constants were computed from the average values for the hyperfine frequencies obtained from all of the runs with this flask. The total amount of data taken was equivalent to five of the usual runs. The values of A, B, and C are computed on the basis of three, four, and five transitions and compared in Table IV.

Figure 2 contains a straight line which is a least-squares fit to the data. The slope of the line is used to determine the fractional pressure shift in A which is

$$\frac{1}{A}\frac{\partial A}{\partial P}=(2.6\pm 0.2)\times 10^{-8}\,\mathrm{Torr}^{-1}\ .$$

The zero-pressure intercept gives $A=-72\,420\,836$ (15) Hz, which is in excellent agreement with the most recent atomic-beam value[2] of $A=-72\,420\,830$ (70) Hz. Our quoted errors for the pressure shift and for A are the standard deviation of the slope and intercept of the least-squares fit.

A brief examination of Tables III and IV shows that, within the precision of this experiment, D and E are negligibly small. The values for A, B, and C are essentially the same whether they are obtained from measurements of three, four, or five transition frequencies.

We quote for our values of B and C

$$B=-1903\,1(17)\ \mathrm{Hz},\quad C=-0.7\pm 1.1\ \mathrm{Hz}.$$

The value of B is in agreement with the atomic-beam value[2] of $B=-18\,300\,(800)$ and the theoretical value[2] of $B=-19\,000$ Hz, and our small value for C clearly justifies the setting of $C=0$ in the less precise beam experiments.

The errors we quote for B and C are the standard deviations in the values obtained for B and for C from run to run. This is equivalent to a probable error of 15 Hz ($\frac{1}{20}$th of the linewidth) in the determination of the hyperfine frequencies. Upper limits to the magnitudes of D and E consistent with this error assignment are

$$|D|<0.25\ \mathrm{Hz},\quad |E|<0.02\ \mathrm{Hz}.$$

VI. CONCLUSION

The purpose of this experiment was to refine previous hyperfine measurements on the ground state of Mn^{55} and to eliminate the necessity for assuming that any of the hyperfine interaction constants were zero. Our results are in complete agreement with previous atomic-beam measurements.

The pressure shift of A in a Ne buffer gas is the first such information obtained for a group-IV element. Indeed, Mn is the first of the group-IV elements to be studied by spin-exchange optical pumping.

ACKNOWLEDGMENT

The authors are indebted to R. H. Lambert for numerous helpful discussions and for encouragement during the course of the experiment.

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†Work supported by the National Science Foundation.

[1] G. K. Woodgate and J. S. Martin, Proc. Phys. Soc. (London) 70, 485 (1957).

[2] L. Evans, P. G. H. Sandars, and G. K. Woodgate, Proc. Roy. Soc. (London) 289A, 108 (1965).

[3] L. C. Balling, R. H. Lambert, J. J. Wright, and R. E. Weiss, Phys. Rev. Letters 22, 161 (1969).

[4] L. Goodman, G. Nöldeke, and H. Walther, Z. Physik 167, 26 (1962).

[5] C. Schwartz, Phys. Rev. 97, 380 (1955).

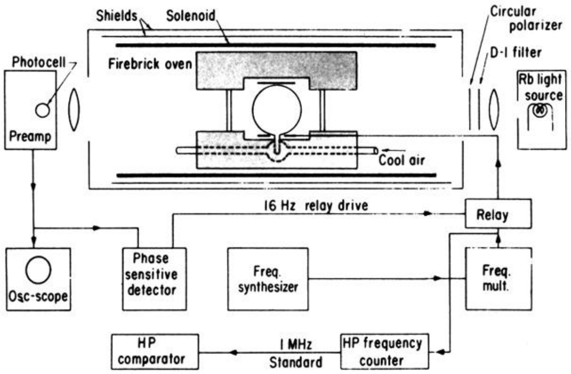

FIG. 1. A block diagram of the optical-pumping apparatus.