

Nuclear Moments of Pm¹⁴⁷

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The nuclear magnetic dipole and electric quadrupole moments of Pm¹⁴⁷ have been derived from an analysis of the optical hyperfine structure of singly ionized Pm¹⁴⁷. The hyperfine constants for the $[4f^5 \ ^6H_{5/2}, 6s]_2$ ground state are $A = -10.24 \pm 0.20$ mK; $B = -10.6 \pm 2.6$ mK. By using the known atomic-beam data for the $[4f^5 6s^2 \ ^6H_{7/2}]$ state of neutral Pm to determine the contribution of the $[4f^5 \ ^6H_{5/2}]$ core to the observed magnetic-splitting factor, the splitting factor of the 6s electron was found to be $a_{6s} = +214.2 \pm 4.9$ mK. The nuclear moments deduced from the hyperfine constants are $\mu_I(\text{Pm}^{147}) = +2.58 \pm 0.07$ nm and $Q(\text{Pm}^{147}) = +0.74 \pm 0.20$ b.

I. INTRODUCTION

A PREVIOUS paper reporting on a high resolution study of the hyperfine structure in the ground state of singly ionized Pm¹⁴⁷ by Reader and Davis¹ raised some puzzling questions regarding the interpretation of this hfs. It was found that the splittings in the $[4f^5 \ ^6H_{5/2}, 6s]_2$ ground state, which contains a single unpaired s electron, were much smaller than the splittings in the states of an upper configuration, which is presumably $4f^5 6p$ and contains no unpaired s electrons. This represented a discrepancy with the analysis of Klinkenberg and Tomkins,² who had neglected the hfs in the upper state in calculating the nuclear magnetic moment from their observations.

In a subsequent brief communication,³ we showed that these questions could be satisfactorily resolved by taking into account the contribution of the $4f^5$ core to the observed hfs. In the present paper we present these considerations in detail and derive values of the nuclear magnetic dipole and electric quadrupole moments from the optical data.

II. EXPERIMENTAL

Our information about the hfs in the ground state of Pm II comes from a detailed study of the two Pm II lines at 4075.85 and 4086.10 Å. These lines are both strong transitions to the $[4f^5 \ ^6H_{5/2}, 6s]_2$ ground state from $J=3$ upper levels at 24 527.87 and 24 466.30 cm⁻¹, respectively.⁴ Analogy with similar rare-earth ions shows that the upper configuration is probably $4f^5 6p$.

The two lines in question were excited in a liquid-nitrogen-cooled hollow cathode and photographed with a Fabry-Perot interferometer crossed with a plane grating spectrograph. All of the quantitative results were taken from exposures made with a 20-mm spacer, which was the largest spacer used. The effective line

width of the Pm lines was observed to be about 0.030 cm⁻¹. A more complete description of the light source and experimental arrangement is given in Ref. 1.

The observed hfs patterns of $\lambda 4075$ and $\lambda 4086$ are complicated and almost identical in appearance. The structures of these two lines are shown schematically in Fig. 1. In the figure, the heights of the lines representing the individual components are proportional to the estimated relative intensities. The splittings are given in mK (1 mK = 0.001 cm⁻¹).

The interpretation of these structures in terms of hfs in the energy levels is given in Fig. 2. Here the upper state, having $J=3$, is split into seven hyperfine levels. The nuclear spin I is $\frac{7}{2}$. The lower state, having $J=2$, has five hyperfine levels. The $J=3$ level has a normal ordering of the levels, whereas the $J=2$ level has an inverted order. The ratio of the magnitude of the splittings in the upper and lower states has been chosen to make the resulting theoretical hfs pattern shown below resemble the observed structures. It can be seen that the splittings measured at the beginning of the observed patterns have a clear correspondence to the level splittings. The observed components near the tail of the pattern are actually blends and cannot be used to obtain level splittings.

The hfs intervals in the $[4f^5 \ ^6H_{5/2}, 6s]_2$ state obtained from the measurements are given in Table I. The results for each line are given separately. The uncertainties listed are our estimates of the maximum possible uncertainty based on the scatter in the results from different interference rings and our ability to repeat individual measurements. The very good agreement

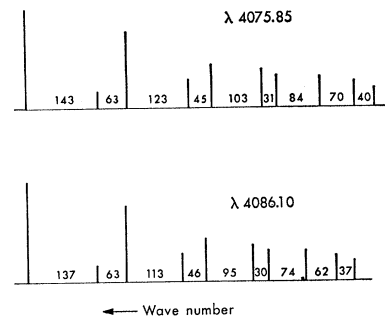


FIG. 1. Measured hyperfine intervals in mK.

¹ J. Reader and S. P. Davis, *J. Opt. Soc. Am.* **53**, 431 (1963).

² P. F. A. Klinkenberg and F. S. Tomkins, *Physica* **26**, 103 (1960).

³ J. Reader, *J. Opt. Soc. Am.* **53**, 1348 (1963).

⁴ The original conclusion of Klinkenberg and Tomkins that these two lines are transitions to the ground state of Pm II has been completely confirmed by subsequent Zeeman data. The values of the upper levels given here have been taken from the energy-level analysis of Reader and Davis, now in progress.

TABLE I. Measured hyperfine splittings in the $[4f^5 {}^6H_{5/2}, 6s]_2$ state of Pm II. The splittings are given in mK. The minus signs indicate that the hfs has an inverted order. N is the number of separate determinations of each quantity.

Hyperfine levels	$\lambda 4075$	N	$\lambda 4086$	N	Average
$F = \frac{1}{2}, \frac{3}{2}$	-62.6 ± 1.0	7	-62.6 ± 1.0	6	-62.6 ± 1.0
$\frac{3}{2}, \frac{7}{2}$	-45.2 ± 1.0	8	-45.9 ± 1.0	5	-45.5 ± 1.0
$\frac{7}{2}, \frac{5}{2}$	-30.9 ± 2.0	5	-30.4 ± 2.0	5	-30.6 ± 2.0

between the results for $\lambda 4075$ and $\lambda 4086$ indicates that the limits of error have not been underestimated.

In the process of making the measurements, it was noticed that the splittings which correspond to the first two intervals of $[4f^5 {}^6H_{5/2}, 6s]_2$ derived from overexposed patterns were systematically higher by about 2 mK than those obtained from properly exposed patterns. This is just the opposite of what one would expect, since overexposure generally causes two close lines to be "drawn together." The effect observed here is probably due to the inherent asymmetry in the Fabry-Perot fringes. This asymmetry causes the measured position of a fringe to shift toward the center of the pattern (to lower wave numbers) when the fringe is overexposed. For the intervals of interest here we measure the splitting between a strong component and a weaker component on the high wave number side. Thus, if the strong component becomes overexposed the measured splitting will be slightly too high. This assumes that the two components are well resolved, which is the case here. The results given in Table I have been taken from fairly light exposures in which no such shifts are present.

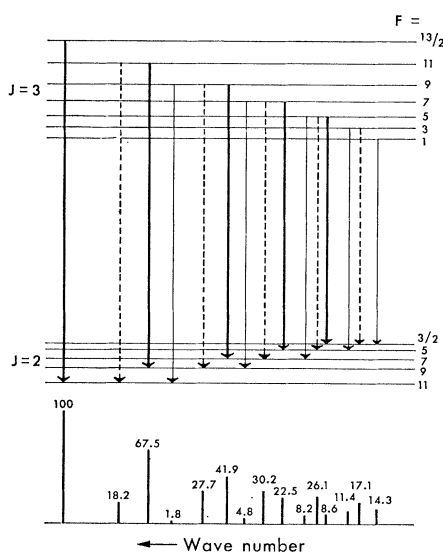


FIG. 2. Transition diagram for a $J=3$ to $J=2$ transition, $I=\frac{7}{2}$. Theoretical intensities are entered above hyperfine components. Bold lines represent $\Delta F = -1$; dashed $\Delta F = 0$; light $\Delta F = +1$.

The splitting of an energy level due to an interaction of the orbital electrons with nuclear magnetic dipole and electric quadrupole moments in terms of the magnetic splitting factor A and the quadrupole coupling constant B is given by⁵

$$W_F = W_J + \frac{1}{2}AK + B \frac{\frac{3}{4}K(K+1) - I(I+1)J(J+1)}{2IJ(2I-1)(2J-1)}, \quad (1)$$

where $K = F(F+1) - I(I+1) - J(J+1)$. Inserting the appropriate quantum numbers in Eq. (1), we find for the first three intervals of $[4f^5 {}^6H_{5/2}, 6s]_2$

$$\Delta(F = \frac{1}{2}, \frac{3}{2}) = (\frac{1}{2})A + (198/336)B, \quad (2)$$

$$\Delta(F = \frac{3}{2}, \frac{7}{2}) = (\frac{3}{2})A - (18/336)B, \quad (3)$$

$$\Delta(F = \frac{7}{2}, \frac{5}{2}) = (\frac{7}{2})A - (126/336)B. \quad (4)$$

Since the measurements of $\Delta(F = \frac{1}{2}, \frac{3}{2})$ and $\Delta(F = \frac{3}{2}, \frac{7}{2})$ were considered to be much more reliable than $\Delta(F = \frac{7}{2}, \frac{5}{2})$, the first two measured intervals were used to solve Eqs. (2) and (3) for A and B . The solutions are

$$A[4f^5 {}^6H_{5/2}, 6s]_2 = -10.24 \pm 0.20 \text{ mK},$$

$$B[4f^5 {}^6H_{5/2}, 6s]_2 = -10.6 \pm 2.6 \text{ mK}.$$

The uncertainties given here were obtained by carrying along the original uncertainties in the calculations according to the usual rules for combining errors. When these values of A and B are used in Eq. (4) to predict the third interval, we find $\Delta(F = \frac{7}{2}, \frac{5}{2}) = -31.8 \pm 1.5 \text{ mK}$, which is in good agreement with the measured value of $-30.6 \pm 2.0 \text{ mK}$.

III. MAGNETIC DIPOLE MOMENT

1. Splitting Factor of the 6s Electron

The lowest group of levels in Pm II is formed by adding a 6s electron to the $4f^5 {}^6H$ parent term. The coupling between the 6s electron and the $4f^5 {}^6H$ parent will be neither pure LS nor pure J_1j , but rather some intermediate scheme. However, since the $[4f^5 {}^6H_{5/2}, 6s]_2$ ground state is the only $J=2$ level in this group, any scheme may be used to relate the measured value of the magnetic splitting factor $A[4f^5 {}^6H_{5/2}, 6s]_2$ to the splitting factor of the core $A[4f^5 {}^6H_{5/2}]$ and the splitting factor of the 6s electron a_{6s} . The relation⁵

$$A(J) = A(J_1) \frac{J(J+1) + J_1(J_1+1) - s(s+1)}{2J(J+1)} + a_{6s} \frac{J(J+1) - J_1(J_1+1) + s(s+1)}{2J(J+1)},$$

expressed in terms of J_1j notation, will hold exactly for

⁵ H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).

the ground state, independently of the nature of the coupling. J_1 is the total angular momentum of the core. Using the appropriate quantum numbers, we have

$$A[4f^5 {}^6H_{5/2}, 6s]_2 = (7/6)A[4f^5 {}^6H_{5/2}] - (1/6)a_{6s}. \quad (5)$$

We have thus far assumed that $[4f^5 {}^6H_{5/2}, 6s]_2$ is not mixed with other $J=2$ levels based on higher parent terms of the same configuration. Conway and Wybourne⁶ have shown that in Pm I the only levels which can be expected to mix appreciably with ${}^6H_{5/2}$ are the four levels of the type $4f^5 6s^2 {}^4G_{5/2}$. Their calculations indicate that the ${}^6H_{5/2}$ level has about 96% of 6H character and about 4% of 4G character. The remaining $4f^5 6s^2$ levels with $J=5/2$ together contribute less than 0.2% to the composition of ${}^6H_{5/2}$. Since the splittings caused by the addition of a $6s$ electron (in this case we are actually considering the removal of one of the $6s$ electrons) are small compared with the separations between the parent terms of the $4f^5$ core, the $[4f^5 {}^6H_{5/2}, 6s]_2$ level of Pm II will have an appreciable mixture only with the four levels of the type $[4f^5 {}^4G_{5/2}, 6s]_2$.

Within each group of levels based on a 4G parent term, the $J=2$ level is unique. Therefore, in the approximation that states based on different parents do not mix, we have for each of the $[4f^5 {}^4G_{5/2}, 6s]_2$ states,

$$A[4f^5 {}^4G_{5/2}, 6s]_2 = (7/6)A[4f^5 {}^4G_{5/2}] - (1/6)a_{6s}.$$

That is, the relative contributions of the $6s$ electron and the $4f^5 {}^4G_{5/2}$ core to the splitting factor of $[4f^5 {}^4G_{5/2}, 6s]_2$ have the same proportions as the contributions of the $6s$ electron and the $4f^5 {}^6H_{5/2}$ core to the splitting factor of $[4f^5 {}^6H_{5/2}, 6s]_2$. If we now consider the effect of a small admixture of $[4f^5 {}^4G_{5/2}, 6s]_2$ into $[4f^5 {}^6H_{5/2}, 6s]_2$, we find that Eq. (5) will not be changed in general form. Furthermore, if we let $A[4f^5 {}^6H_{5/2}]$ refer to the splitting factor of the state which represents the appropriate mixture of ${}^6H_{5/2}$ and ${}^4G_{5/2}$ states, Eq. (2) need not be modified at all and can be considered exact for the present application.

A value for the splitting factor of the core can be derived from the atomic-beam measurement of the hfs in the $4f^5 6s^2 {}^6H_{7/2}$ level of Pm I. For this level Budick and Marrus⁷ have measured the hyperfine constants: $|A| = 447.1 \pm 9.3$ Mc/sec and $|B| = 267.5 \pm 70.8$ Mc/sec. Although the individual signs of A and B could not be determined, it was found that A and B have opposite signs. In the section below on the quadrupole moment we prove that the sign of A is actually positive, and we assume this result here.

The theoretical values of $A[4f^5 6s^2 {}^6H_{5/2}]$ and $A[4f^5 6s^2 {}^6H_{7/2}]$ in units of a_{4f} for pure LS coupling within the $4f^5$ core and the ratio of these two quantities are given in the second column of Table II. To examine the effect which the breakdown in pure LS coupling

TABLE II. Calculated magnetic hyperfine constants for Pm I in terms of a_{4f} , the splitting factor of an individual $4f$ electron.

	LS coupling	Intermediate coupling	% Change
$A[4f^5 6s^2 {}^6H_{5/2}]$	1.5492 a_{4f}	1.5444 a_{4f}	-0.31
$A[4f^5 6s^2 {}^6H_{7/2}]$	1.0700 a_{4f}	1.0661 a_{4f}	-0.36
$A[{}^6H_{5/2}]/A[{}^6H_{7/2}]$	1.4479	1.4486	-0.06

has on these quantities, we have calculated them in the intermediate coupling scheme indicated by the eigenvectors for Pm I given by Conway and Wybourne.⁶ In these calculations only components belonging to 6H and 4G terms were considered. As already noted, the remainder of the admixed states have a negligible contribution. The matrix of the tensor operator V^{12} for the 6H and 4G states of f^5 was constructed according to the method of Judd,⁸ whereby the matrix elements are related to those of the matrix U^2 for the analogous states of f^4 . The elements of U^2 have been given by Nielson and Koster.⁹ The hfs matrix elements were calculated by using the formulas given by Wybourne.¹⁰

The results for A and the percent change from the case of pure coupling are given in the last two columns of Table II. One can see that the individual values of A are changed by only about -0.3% and that the change in the ratio is practically negligible.

It has been stated by other authors^{7,11} that the change in the A factor of $4f^5 6s^2 {}^6H_{7/2}$ caused by the breakdown of pure LS coupling is approximately +2%. This is at variance with the result given in Table II, where the change is -0.36%. The source of this discrepancy has been traced to several computational errors in the original calculation of Budick.¹² Thus, for all practical purposes, no corrections for deviations from pure LS coupling in Pm I need to be taken into account.

Using the results given in Table II, we then have

$$A[4f^5 6s^2 {}^6H_{5/2}] = 1.4486A[4f^5 6s^2 {}^6H_{7/2}] = +21.60 \pm 0.45 \text{ mK.}$$

With this result and the measured value given in Sec. II of

$$A[4f^5 {}^6H_{5/2}, 6s]_2,$$

we find from Eq. (5),

$$a_{6s} = +212.6 \pm 3.4 \text{ mK.}$$

In obtaining this result we have implicitly assumed that the magnetic splitting factor of $4f^5 6s^2 {}^6H_{5/2}$ deter-

⁸ B. R. Judd, *J. Math. Phys.* **3**, 557 (1962).

⁹ C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (The MIT Press, Cambridge, Massachusetts, 1963).

¹⁰ B. G. Wybourne, *J. Chem. Phys.* **37**, 1807 (1962); **39**, 240 (1963).

¹¹ D. Ali, I. Maleh, and R. Marrus, *Phys. Rev.* **138**, B1356 (1965).

¹² B. Budick, Lawrence Radiation Laboratory Report UCRL-10245, 1962 (unpublished).

⁶ J. Conway and B. G. Wybourne, *Phys. Rev.* **130**, 2325 (1963).

⁷ B. Budick and R. Marrus, *Phys. Rev.* **132**, 723 (1963).

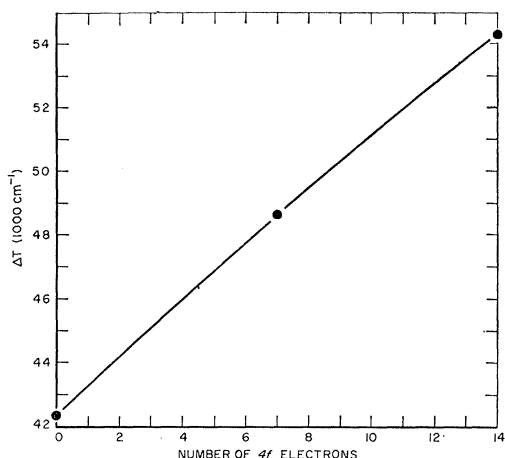


FIG. 3. Energy difference ΔT between the centers of gravity of the $4f^N 6s$ and $4f^{N+1} 7s$ configurations of the singly ionized rare earths. References: Ba II—E. Rasmussen, *Z. Physik* **83**, 404 (1933); Eu II—H. N. Russell, W. Albertson, and D. N. Davis, *Phys. Rev.* **60**, 641 (1941); Yb II—W. F. Meggers and B. F. Scribner, *J. Res. Natl. Bur. Std.* **19**, 651 (1937).

mined from Pm I, where two $6s$ electrons are present, is applicable in Pm II, where one of the $6s$ electrons has been removed. Since the splitting factor $A[4f^5 6s^2 {}^6H_{5/2}]$ results only from the interaction of the $4f$ electrons with the nuclear magnetic moment, it is proportional to the quantity $\langle 1/r^3 \rangle_{4f}$. Our assumption that the splitting factor of the core is not affected by the removal of one of the $6s$ electrons is therefore equivalent to the assumption that the value of $\langle 1/r^3 \rangle_{4f}$ for Pm II will be equal to $\langle 1/r^3 \rangle_{4f}$ for Pm I. This assumption can be justified in large measure by the comparisons made by Bleaney^{13,14} between hyperfine constants and spin-orbit parameters measured in the neutral and doubly ionized lanthanides. On the basis of data for Sm, Ho, and Tm, Bleaney¹⁴ concludes that "the rather small increases in the values of the hyperfine structure and spin-orbit constants between the atoms and divalent ions show that the $6s$ electrons have little effect on the distance of the $4f$ electrons from the nucleus," and that "the differences in $\langle 1/r^3 \rangle$ and ζ_{4f} between the divalent ions and the atoms may be taken to be in the region of 1 to 2% throughout the major part of the lanthanide series." These results are supported by the calculations of Freeman and Watson,¹⁵ which show that the $6s$ wave functions lie almost wholly outside the $4f$ wave functions.

Since Bleaney's conclusions apply to the removal of both $6s$ electrons, whereas in the present instance we are considering the removal of only one of the $6s$ electrons, Bleaney's comparison suggests that the A factor from Pm I should be increased by about 1% for use in

¹³ B. Bleaney, in *Quantum Electronics, Proceedings of the Third International Congress, Paris* (Columbia University Press, New York, 1964), Vol. 1, p. 595.

¹⁴ B. Bleaney, *Proc. Roy. Soc. (London)* **A277**, 289 (1964).

¹⁵ A. J. Freeman and R. E. Watson, *Phys. Rev.* **127**, 2058 (1962).

Pm II. If we make this correction and allow for an additional uncertainty of about the magnitude of the correction we obtain

$$a_{6s} = +214.2 \pm 4.9 \text{ mK.}$$

2. Determination of $(dn_a/dn)/n_a^3$

In order to complete the derivation of the dipole moment we must determine the strength of the magnetic field at the nucleus produced by the $6s$ electron. This field is proportional to $\psi^2(0)$, the probability density of the $6s$ electron at the nucleus. In the non-relativistic limit, the probability density of an s electron at the nucleus is given by

$$\psi^2(0) = ZZ_a^2 (dn_a/dn) / \pi a_0^3 n_a^3,$$

where n is the principal quantum number and n_a is the effective quantum number.⁵ The factor Z_a is the charge seen by the $6s$ electron while outside of the atomic core; for singly ionized atoms $Z_a = 2$. If the spectrum analysis of Pm II were sufficiently complete, we would be able to determine the factors n_a and dn_a/dn from a Rydberg-Ritz series of terms of the type $T = RZ_a^2/n_a^2$ for the $4f^5 ns$ ($n = 6, 7, 8, \dots$) series, as described in Ref. 5. However, such a series is not presently available in Pm II, so an alternative procedure must be used.

A method for obtaining reliable estimates of n_a and dn_a/dn has recently been described by Reader and Sugar.¹⁶ This method is based on the apparent constancy throughout the rare earths of the quantity $\Delta n_a = n_a(7s) - n_a(6s)$ and on interpolated values of $\Delta T = T(6s) - T(7s)$, the difference between the centers of gravity of the $4f^N 6s$ and $4f^{N+1} 7s$ configurations. A compilation of values of Δn_a derived from ns series in the region of the rare earths has been given by Sugar and Reader.¹⁷ This compilation is reproduced in Table III. It can be seen that Δn_a is practically constant throughout the rare-earth period. For Pm II we have

TABLE III. Values of Δn_a derived from ns series in the region of the rare earths.

Z	Atom	Configurations	Δn_a	Ref.
55	Cs I	($5p^6$) $6s-7s$	1.051	a
56	Ba II	($5p^6$) $6s-7s$	1.052	b
57	La III	($5p^6$) $6s-7s$	1.050	c
58	Ce IV	($5p^6$) $6s-7s$	1.052	d
58	Ce III	($5p^6 4f$) $6s-7s$	1.050	e
63	Eu II	($5p^6 4f^7$) $6s-7s$	1.049	f
70	Yb II	($5p^6 4f^{14}$) $6s-7s$	1.049	g

^a H. Kleiman, *J. Opt. Soc. Am.* **52**, 441 (1962).

^b E. Rasmussen, *Z. Physik* **83**, 404 (1933).

^c J. Sugar and V. Kaufman, *J. Opt. Soc. Am.* **55**, 1283 (1965).

^d R. J. Lang, *Can. J. Res.* **14A**, 127 (1936).

^e J. Sugar, *J. Opt. Soc. Am.* **55**, 33 (1965).

^f H. N. Russell, W. Albertson, and D. N. Davis, *Phys. Rev.* **60**, 641 (1941).

^g W. F. Meggers (to be published). This value is based on the assignment of a new high $J = \frac{1}{2}$ level of Yb II as the $8s {}^2S_{1/2}$ level.

¹⁶ J. Reader and J. Sugar, *Phys. Rev.* **137**, B784 (1965).

¹⁷ J. Sugar and J. Reader, *J. Opt. Soc. Am.* **55**, 1286 (1965).

used $\Delta n_a = 1.050$ with an estimated uncertainty of ± 0.005 .

For singly ionized atoms experimental values of ΔT are known for the configurations with $N=0$ (Ba II), $N=7$ (Eu II), and $N=14$ (Yb II). They have been plotted against N in Fig. 3. The value of ΔT for Pm II obtained from the curve drawn through the experimental points is $\Delta T = 46\,900\text{ cm}^{-1}$. This value is probably reliable to about $\pm 300\text{ cm}^{-1}$.

Using these values of ΔT and Δn_a , we solve the equation

$$\Delta T = \frac{4R}{[n_a(6s)]^2} - \frac{4R}{[n_a(6s) + \Delta n_a]^2}$$

for n_a by an iterative procedure with the result that $n_a = 2.241$. The corresponding value of T is $87\,400\text{ cm}^{-1}$.

The value of $(dn_a/dn)/n_a^3$ is then found by means of the relation

$$\frac{1}{n_a^3} \frac{dn_a}{dn} = \frac{1}{n_a^3} \frac{n_a/2T}{n_a/2T - d\sigma/dT},$$

where $\sigma = n - n_a$. For the type of series we are considering here σ is approximately a linear function of T , so that $d\sigma/dT$ can be assumed to be close to $\Delta\sigma/\Delta T$, where $\Delta\sigma$ and ΔT refer to the first two series members. It was shown in Ref. 16 that a slight improvement to the linear approximation may be made by using

$$d\sigma/dT = 1.09\Delta\sigma/\Delta T.$$

This modification makes a change of only about 1% in the magnitude of $(dn_a/dn)/n_a^3$. With the above results for n_a , T , Δn_a , and ΔT , we find $(dn_a/dn)/n_a^3 = 0.0977$. If we use all combinations of the extreme values of Δn_a and ΔT , we obtain values of $(dn_a/dn)/n_a^3$ which range from 0.0965 to 0.0989. Therefore,

$$(dn_a/dn)/n_a^3 = 0.0977 \pm 0.0012.$$

3. Magnetic Moment

The nuclear magnetic moment was evaluated by means of the Goudsmit-Fermi-Segré formula,

$$\mu_I = 117.8 a_{6s} I \frac{n_a^3}{ZZ_a^2 (dn_a/dn) F_r (1-\delta)(1-\epsilon)},$$

where F_r is the relativistic correction factor, δ the Crawford-Schawlow correction for the distribution of the nuclear charge over a finite radius, and ϵ the Bohr-Weisskopf correction for the volume distribution of the nuclear magnetism. With $F_r = 1.5176$, $\delta = 0.040$, and $\epsilon = 0.014$, we obtain

$$\mu_I(\text{Pm}^{147}) = +2.58 \pm 0.07\text{ nm}.$$

The uncertainty given here is the square root of the sum of the squares of the uncertainties in a_{6s} and $(dn_a/dn)/n_a^3$. The values used for F_r and ϵ were ob-

tained from the tables and formulas given in Ref. 5. The value of δ was calculated from the original formula of Crawford and Schawlow.¹⁸

IV. ELECTRIC QUADRUPOLE MOMENT

The quadrupole coupling constant $B[4f^5\ ^6H_{5/2}, 6s]_2$ results only from the quadrupole interaction of the $4f^5$ electrons with the nucleus, since the $6s$ electron has no quadrupole interaction. However because of the coupling between the $4f^5$ electrons and the $6s$ electron, the quadrupole interaction of the $4f^5$ electrons is different from what it would be if no $6s$ electron were present. The measured value of the coupling constant is related to the coupling constant of the $4f^5$ core according to¹⁹

$$B[4f^5\ ^6H_{5/2}, 6s]_2 = B[4f^5\ ^6H_{5/2}]_2 \frac{3C_1(C_1-1) - 4J_1(J_1+1)J(J+1)}{J_1(2J_1-1)(2J+2)(2J+3)},$$

where $C_1 = J(J+1) + J_1(J_1+1) - s(s+1)$. We find

$$B[4f^5\ ^6H_{5/2}, 6s]_2 = \frac{4}{5} B[4f^5\ ^6H_{5/2}].$$

With the value for $B[4f^5\ ^6H_{5/2}, 6s]_2$ given in Sec. II, we obtain

$$B[4f^5\ ^6H_{5/2}] = -13.3 \pm 3.3\text{ mK}.$$

This coupling constant can be related to the nuclear quadrupole moment Q using the relations for the quadrupole interaction given in Ref. 10. Neglecting the effects of intermediate coupling we find

$$B[4f^5\ ^6H_{5/2}] = -(26/63)e^2Q\langle 1/r^3 \rangle_{4f},$$

so that

$$e^2Q\langle 1/r^3 \rangle_{4f} = +32.2 \pm 8.1\text{ mK}.$$

For the present purpose, the slight decrease in shielding due to the removal of one of the $6s$ electrons from the $4f^5 6s^2$ configuration may be neglected. Therefore this result is to be compared with the result $|e^2Q\langle 1/r^3 \rangle_{4f}| = 25.7 \pm 6.8\text{ mK}$ obtained by Budick and Marrus⁷ in Pm I. The difference between these two results is less than their combined uncertainties.

Since we know that

$$B[4f^5\ ^6H_{7/2}] = -(26/75)e^2Q\langle 1/r^3 \rangle_{4f},$$

and since the result from Pm II indicates that the sign of $e^2Q\langle 1/r^3 \rangle_{4f}$ is definitely positive, we deduce that the B factor of $4f^5 6s^2\ ^6H_{7/2}$ is negative. Since $(B/A) < 0$ for this state, $A[4f^5 6s^2\ ^6H_{7/2}]$ is definitely positive. This justifies our assumption in Sec. III.

Bleaney¹³ has obtained a set of effective values of $\langle 1/r^3 \rangle$ for the lanthanides by starting with the empirical values of $\langle 1/r^3 \rangle$ for those elements for which direct

¹⁸ M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

¹⁹ R. Marrus and W. A. Nierenberg, in *Proceedings of the International School of Physics, Enrico Fermi Course XVII* (Academic Press Inc., New York, 1962), pp. 118-156.

TABLE IV. Comparison of values of μ_I and Q for Pm^{147} obtained by different methods.

Method	μ_I (nm)	Q (b)
Optical hfs—present work (Pm II)	$+2.58 \pm 0.07$	$+0.74 \pm 0.20$
Atomic beams (Pm I)	2.77 ± 0.08	0.59 ± 0.16
Paramagnetic resonance (Pm IV)	2.55 ± 0.06	

determinations of nuclear moments exist, and then interpolating for the remainder of the rare earths. For Pm I, Bleaney obtains an interpolated value of $\langle 1/r^3 \rangle = 5.56a_0^{-3}$. If we allow for a possible error of 5% in this value, we obtain for the nuclear electric quadrupole moment

$$Q(\text{Pm}^{147}) = +0.74 \pm 0.20 \text{ b.}$$

V. DISCUSSION

Our results for the nuclear moments may be compared with those obtained by other methods. Values of μ_I have been reported by Budick and Marrus⁷ based on the atomic-beam technique and by Stapleton, Jeffries, and Shirley²⁰ based on paramagnetic resonance. Bleaney¹³ has recalculated these values of μ_I using his effective values of $\langle 1/r^3 \rangle$. The recalculated values are compared with our present value in the second column of Table IV.

It can be seen that although the results are in fairly good agreement, there remain some noticeable differences. For the most part these differences are almost certainly the result of systematic errors in calculating the strength of the magnetic field at the nucleus in the different degrees of ionization. Although the result from optical hfs is in good agreement with that from paramagnetic resonance, there is no physical reason to prefer any one of the three values given in Table IV over the other two. Indeed, since we have made explicit use of the atomic-beam data in the present work, the optical hfs result is not completely independent of the atomic-beam experiment. However, inasmuch as we have used only their raw measurements only their experimental uncertainties enter into our calculations.

A lesser factor contributing to the differences is the uncertainty regarding the corrections for core polarization. This correction is intended to take into account the effect on the observed hfs of configuration interaction with configurations having unpaired s electrons. These corrections have been discussed extensively by

Bleaney.¹³ Although core polarization corrections can play an important role in the interpretation of the hfs of atoms with configurations of the type $3d^N 4s^2$, they are practically negligible in the neutral rare-earth atoms. By way of comparison, for trivalent Pm, Bleaney estimates a correction to the A factor of about 3%. In our use of the A factor from Pm I in Pm II, we have assumed that any corrections applicable to Pm I would also apply to Pm II. Although this may not be completely correct, we do not believe that a deviation from this assumption would influence our result significantly.

To compare the results for the quadrupole moment, we have recalculated the result from atomic beams using Bleaney's value of $\langle 1/r^3 \rangle$. The results are given in the last column of Table IV. The quadrupole moment was not measured in the paramagnetic-resonance experiment.

It is interesting to note that our value of a_{6s} of $+214.2$ mK is apparently in very good agreement with the value of $+216$ mK given by Klinkenberg and Tomkins. In their observations, the lines at 4075 and 4086 Å appeared as five component flag patterns. Their value of a_{6s} was derived by deducing an interval factor from the observed patterns and considering this interval factor to represent the interaction of the $6s$ electron with the nuclear magnetic moment. They thus neglected the contributions of the $4f^5$ core and the hfs in the upper levels to the observed patterns. In view of our present knowledge concerning the relative magnitudes of the hfs splittings in the upper levels and the ground state, it is surprising that these two values of a_{6s} should be so close. If one assumes that the upper levels associated with $\lambda 4075$ and $\lambda 4086$ are of the type $4f^5(^6H)6p$, and tries to predict the hyperfine splittings in the upper levels, one can show that it is possible for the sum of the contributions of the core and the $6p$ electron in the upper states to equal approximately the contribution of the core to the ground-state hfs. Therefore if one considers only the strongest hfs transitions and neglects everything except the $6s$ electron interaction in the calculations, an approximately correct value of a_{6s} would be obtained. Whether this actually occurs or not will depend on the nature of the coupling in the upper states. Since this coupling is as yet undetermined, the good agreement in the values of a_{6s} may be coincidental.

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²⁰ H. J. Stapleton, C. D. Jeffries, and D. A. Shirley, Phys. Rev. **124**, 1455 (1961).