

Ho¹⁶⁶. In order to give possible interpretations of these data it was necessary to develop a mathematical model. For this purpose the model of Bohr, Mottelson,⁹ Nilsson,⁷ and Kerman¹⁰ has been extended to describe explicitly two nucleons outside a spheroidal core. By neglecting certain terms in the Hamiltonian, it was possible to separate the problem and obtain a direct product basis with which to construct the Hamiltonian matrix. For purposes of comparing our data with theory, moments of inertia and those parts of the matrix elements which depend on the proton-neutron interaction are taken as free parameters. These parameters were allowed to vary over reasonable ranges, and for each parameter set the Hamiltonian matrix was diagonalized. With the resulting energies and wave functions, a level diagram was constructed and using a distorted-wave Born approximation,⁸ a theoretical (d, p) spectrum predicted. From the parameterized wave functions which gave the best fit, it has been possible to draw some conclusions about the nuclear structure. The validity of these conclusions is somewhat hard to assess because of the many

physical approximations incorporated in the mathematical model. Nevertheless, the agreement between theory and experiment has been encouraging.

The most obvious theoretical extension of this work is to study the effects of H_{INT} using both central and tensor components for the residual interaction. This is currently being done. Then the most important step to be taken is to correlate our data with the results of precision (n, γ) experiments. When complete and unambiguous agreement is found between the two experiments, it should be possible to have a great deal of confidence about the exact nature of the levels and to put various structure models to some severe tests.

ACKNOWLEDGMENTS

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Nuclear Magnetic Moment of Pr¹⁴¹ from the Hyperfine Structure of Doubly Ionized Praseodymium

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The hyperfine structure in the spectrum of doubly ionized Pr¹⁴¹ was observed by means of a sliding spark discharge and a concave-grating spectrograph. Measurements of the hyperfine patterns resulted in a value for the splitting factor of the 6s electron of $a_{6s} = +0.639 \pm 0.007$ cm⁻¹. The probability density of the 6s electron at the nucleus was calculated by using interpolated values of the energy difference and quantum defect difference for the 4f²6s and 4f²7s configurations. Application of the Goudsmit-Fermi-Segrè formula yields a value for the nuclear magnetic moment $\mu_I = +4.09 \pm 0.06$ nm. The various contributions to the stated uncertainties are discussed in detail.

I. INTRODUCTION

THERE has been considerable uncertainty regarding the nuclear moment of Pr¹⁴¹. Measurements made by various workers on the hyperfine structure of *neutral, singly ionized, and triply ionized* Pr have yielded values of μ_I ranging from 3.8 to 5.1 nm. No direct measurement of the Pr¹⁴¹ nuclear moment has yet been made.

The uncertainties and discrepancies in the results arise mainly from an inability to calculate reliably the strength of the magnetic field at the nucleus produced by orbital electrons in unfilled shells. In the case of an s electron, this field is proportional to $\psi^2(0)$; for an electron with $l > 0$, the field is proportional to the average value of $1/r^3$. Because of the lack of complete analyses of the spectra of neutral Pr and its ionic species, these electronic quantities cannot be determined

from the known Pr energy levels. This situation is common to many of the rare earths.

Recently an extensive analysis of the spectrum of *doubly ionized* Pr was reported.¹ As a result of this analysis and subsequent work, 22 of the 24 theoretically possible levels of the 4f²6s configuration are known. Also, 81 higher levels belonging to 4f²6p and 4f5d² are known. These levels combine strongly with the 4f²6s levels to give a large number of lines showing wide hyperfine splittings. We have measured the hyperfine structure (hfs) of these lines and have obtained a value for the splitting factor a_{6s} . We have also derived an accurate value for $\psi^2(0)$ based on the behavior of the 4f^Nns series ($n = 6, 7, 8$) of several rare-earth ions. With these results a new experimental value for $\mu_I(\text{Pr}^{141})$ could be obtained.

¹ J. Sugar, J. Opt. Soc. Am. **53**, 831 (1963).

II. REVIEW OF PREVIOUS WORK ON Pr¹⁴¹

The large hyperfine splittings produced by the Pr¹⁴¹ nuclear magnetic moment were first measured by White,² who reported the flag pattern intervals of 173 lines of Pr II and deduced a nuclear spin $I = \frac{5}{2}$. Making use of the classification of 100 of these lines by Rosen, Harrison, and McNally,³ Brix⁴ applied the Goudsmit-Fermi-Segrè (GFS) formula to the data of White and obtained a value $\mu_I = +3.9 \pm 0.3$ nm for the nuclear magnetic moment. In this calculation the field at the nucleus was estimated by plotting the known values of $\psi^2(0)$ against the difference between the centers of gravity of the 6s and 6p configurations for a number of elements in the sixth period.

The various values of $\mu_I(\text{Pr}^{141})$ which have subsequently appeared in the literature are compared with Brix's result in Table I. Lew,⁵ in addition to obtaining a

TABLE I. Summary of published values of $\mu_I(\text{Pr}^{141})$ in nm.

| | |
|---|----------|
| (1) Pr ⁺ —GFS formula applied to White's data (Brix) ^a | +3.9±0.3 |
| (2) Pr—atomic beams; $\langle 1/r^3 \rangle$ from hydrogenic wave functions (Lew) ^b | +3.8±0.4 |
| (3) Pr ⁺ —interferometric determination of a_{6s} (Murakawa) ^c | +4.0±0.2 |
| (4) Pr ³⁺ —paramagnetic resonance; $\langle 1/r^3 \rangle$ from an empirical formula (Baker and Bleaney) ^{d,e} | +3.9±0.2 |
| (5) Pr ³⁺ —paramagnetic resonance; $\langle 1/r^3 \rangle$ from an empirical formula (Hutchison and Wong) ^{f,g} | +4.6 |
| (6) Pr, Pr ³⁺ —recalculation of results in (2) and (4) using modified hydrogenic wave functions (Lindgren) ^h | +5.1 |
| (7) Pr, Pr ³⁺ —modification of result in (6) to include intermediate coupling (Wybourne) ⁱ | +5.0 |
| (8) Pr ³⁺ —recalculation of result in (4) using Hartree-Fock wave functions (Freeman and Watson) ^j | +3.9 |

^a See Ref. 4.

^b See Ref. 5.

^c See Ref. 6.

^d J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 936 (1955).

^e B. Bleaney, Proc. Phys. Soc. (London), **A68**, 937 (1955).

^f C. A. Hutchison, Jr. and E. Wong, J. Chem. Phys. **29**, 754 (1958).

^g R. J. Elliot and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

^h I. Lindgren, Nucl. Phys. **32**, 151 (1962).

ⁱ See Ref. 8.

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

value for μ_I , observed a nuclear quadrupole moment of approximately -0.054 b. Murakawa's result⁶ was obtained by measuring the hfs of several lines of Pr II very accurately with a Fabry-Perot interferometer. In the description of his work Murakawa does not state the considerations used to establish the limits of error in μ_I . Although his value of a_{6s} is probably more accurate than that of Brix, no uncertainty is given for this quantity. There is also no indication of how the field at the nucleus was obtained.

The recalculation of μ_I by Lindgren was based on the

² H. E. White, Phys. Rev. **34**, 1397 (1929).

³ N. Rosen, G. R. Harrison, and J. R. McNally, Jr., Phys. Rev. **60**, 722 (1941).

⁴ P. Brix, Phys. Rev. **89**, 1245 (1953).

⁵ H. Lew, Phys. Rev. **91**, 619 (1953).

⁶ K. Murakawa, J. Phys. Soc. Japan **15**, 2306 (1960).

Judd and Lindgren⁷ theoretical calculation of values of $\langle 1/r^3 \rangle$ for the rare earths using modified hydrogenic eigenfunctions for the $4f^N$ configurations. These eigenfunctions, when fitted to the observed spin-orbit coupling constants, produced atomic g factors in excellent agreement with experimental data. Nevertheless, in taking account of the intermediate coupling in the $4f^8$ configuration, Wybourne⁸ noted the disturbing fact that the resulting value for μ_I was outside of the Schmidt limit of 4.74 nm for Pr¹⁴¹, and that some revision of $\langle 1/r^3 \rangle$ might therefore be required.

In view of the existing discrepancies between the values listed in Table I, it seemed that an independent optical determination of μ_I by means of the third spectrum would be desirable.

III. EXPERIMENTAL PROCEDURE

The spectrum of Pr²⁺ was produced in a sliding spark light source. The details of this source have already been discussed in Ref. 1. The spark takes place between solid metallic Pr electrodes separated by a ceramic spacer which provides a path for the spark. To obtain the sharper lines needed for the present experiment, the circuit was modified to give a peak current of 6 A. (A complete development of the spectrum requires about 50 A.) The discharge chamber contained He at a pressure of 30 mm Hg, and the spark repetition rate was 20/sec.

In Pr III the lines having appreciable splittings occur almost entirely in the region of 2800–3600 Å. This region was photographed in the second order of a 21-ft, 30 000-line-per-inch concave grating in a Wadsworth mounting. The plate factor was 1.05 Å/mm. With this light source and optical arrangement, the linewidth was observed to be 0.150 cm⁻¹. Comparison with other spectrograms taken on the same instrument showed that the major part of the width was due to broadening within the source.

Nearly all of the hfs patterns obtained were flag patterns with varying numbers of resolved components. Several lines were resolved into the full six components expected for transitions involving a level with a spin-limited number of hyperfine components. A few fully resolved lines with less than six main components involving levels with $J < \frac{5}{2}$ were also observed. Although satellite components could be seen in some patterns, the satellites were not well enough resolved to be measured.

The relative positions of the components in the observed patterns were measured on a scanning comparator with repeated readings agreeing to within $\pm 5 \times 10^{-4}$ mm. This corresponds to a probable error of 0.007 cm⁻¹ in the wave number intervals. The correctness of this error estimate was borne out by the degree to

⁷ B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

⁸ B. G. Wybourne, J. Chem. Phys. **37**, 1807 (1962); **39**, 240 (1963).

TABLE II. Hfs of lines of Pr III used in determining a_{6s} . Classification gives parent and J value of $4f^26s$ level, followed by position and J value of upper level. Structures degraded to higher wave numbers are designated with a plus sign preceding the total width; those degraded to lower wave numbers are designated with a minus sign. The lines at 2942.427 and 2976.860 Å were partially obscured by other lines; their total widths could not be measured.

| λ (Å) | Classification | Intervals (10^{-3} cm $^{-1}$) | Total width (cm $^{-1}$) |
|------------------|------------------------------------|---------------------------------------|---------------------------------|
| 2841.939 | (3H_4) $7/2^-(63576)$ $5/2$ | 434, 354 | -1.36 |
| 2914.489 | (3H_5) $9/2^-(65295)$ $7/2$ | 339, 313 | -1.02 |
| 2942.427 | (3H_6) $13/2^-(66735)$ $13/2$ | 465 | + ... |
| 2952.248 | (3H_5) $9/2^-(64857)$ $9/2$ | 393 | -1.28 |
| 2953.584 | (3F_4) $9/2^-(69138)$ $9/2$ | 465, 410 | +1.66 |
| 2976.860 | (3H_6) $11/2^-(67049)$ $9/2$ | 335 | - ... |
| 2981.527 | (1G_4) $9/2^-(71978)$ $7/2$ | 510, 450 | +1.84 |
| 3004.897 | (3H_6) $11/2^-(66735)$ $13/2$ | 321 | -1.14 |
| 3006.469 | (1G_4) $7/2^-(71978)$ $7/2$ | 377 | -1.16 |
| 3014.605 | (3H_6) $13/2^-(65922)$ $11/2$ | 446, 413, 351, 315 | +1.70 |
| 3016.259 | (1G_4) $9/2^-(71592)$ $9/2$ | 479, 399, 373 | +1.67 |
| 3041.781 | (1G_4) $7/2^-(71592)$ $9/2$ | 425, 368 | -1.34 |
| 3045.812 | (3H_5) $9/2^-(63816)$ $11/2$ | 369, 303 | -1.26 |
| 3050.303 | (3H_5) $9/2^-(63768)$ $7/2$ | 342 | -1.08 |
| 3066.710 | (3H_5) $9/2^-(63593)$ $9/2$ | 311 | -1.03 |
| 3080.203 | (3H_6) $11/2^-(65922)$ $11/2$ | 346 | -1.21 |
| 3147.878 | (3F_4) $9/2^-(67049)$ $9/2$ | 488, 425, 366 | +1.73 |
| 3218.979 | (3H_6) $13/2^-(63816)$ $11/2$ | 404, 369 | +1.53 |
| 3226.691 | (1G_4) $9/2^-(69431)$ $7/2$ | 556, 448, 407 | +1.94 |
| 3255.920 | (1G_4) $7/2^-(69431)$ $7/2$ | 359 | -1.10 |
| 3257.455 | (1G_4) $9/2^-(69138)$ $9/2$ | 477, 394 | +1.65 |
| 3263.675 | (3F_4) $9/2^-(65922)$ $11/2$ | 480, 407, 352 | +1.66 |
| 3265.847 | (3H_5) $9/2^-(61605)$ $7/2$ | 373 | -1.19 |
| 3287.246 | (1G_4) $7/2^-(69138)$ $9/2$ | 437, 342 | -1.39 |
| 3293.884 | (3H_6) $11/2^-(63816)$ $11/2$ | 396, 350 | -1.47 |
| 3320.336 | (3F_2) $5/2^-(63768)$ $7/2$ | 478, 377 | +1.27 |
| 3327.489 | (1G_4) $9/2^-(68492)$ $7/2$ | 532, 473, 393 | +1.89 |
| 3331.823 | (3F_4) $9/2^-(65295)$ $7/2$ | 464, 399 | +1.70 |
| 3340.582 | (1G_4) $9/2^-(68374)$ $9/2$ | 443, 375 | +1.50 |
| 3341.434 | (3H_6) $13/2^-(62678)$ $13/2$ | 356, 323 | +1.39 |
| 3341.682 | (3F_2) $5/2^-(63576)$ $5/2$ | 432 | +1.16 |
| 3354.914 | (3H_6) $13/2^-(62558)$ $11/2$ | 463, 414, 365, 311 | +1.77 |
| 3358.583 | (1G_4) $7/2^-(68492)$ $7/2$ | 367 | -1.12 |
| 3371.924 | (1G_4) $7/2^-(68374)$ $9/2$ | 478, 382, 321 | -1.47 |
| 3381.259 | (3F_4) $9/2^-(64857)$ $9/2$ | 406, 348, 291, 224 | +1.39 |
| 3391.077 | (3H_6) $13/2^-(62240)$ $11/2$ | 421, 363, 334 | +1.60 |
| 3422.222 | (3H_6) $11/2^-(62678)$ $13/2$ | 438, 383 | -1.65 |
| 3436.358 | (3H_6) $11/2^-(62558)$ $11/2$ | 327, 309, 253 | -1.19 |
| 3474.311 | (3H_6) $11/2^-(62240)$ $11/2$ | 388, 354, 277 | -1.43 |
| 3529.728 | (1G_4) $7/2^-(67049)$ $9/2$ | 420, 365 | -1.33 |
| 3532.264 | (3F_4) $9/2^-(63593)$ $9/2$ | 454, 407 | +1.65 |
| 3577.336 | (3F_2) $5/2^-(61605)$ $7/2$ | 474 | +1.17 |

which the measured splittings followed the hfs interval rule.

The measured splittings of the lines involved in our determination of a_{6s} are given in Table II.

IV. SPLITTING FACTOR OF THE $6s$ ELECTRON

The splitting of an energy level by the interaction of the orbital electrons with a nuclear magnetic dipole moment is given by

$$W_F = W_J + \frac{1}{2}A[F(F+1) - J(J+1) - I(I+1)].$$

The level splitting factor A may be written as a linear combination of the individual electron splitting factors a_{nl} . For a $4f^26s$ level,

$$A = \theta_1 a_{4f} + \theta_2 a_{6s},$$

where θ_1 and θ_2 are angular factors which depend on the nature of the electronic coupling.

The eigenvectors of the $4f^26s$ configuration have been calculated by Spector⁹ using a pure $((L_1S_1)J_{1s}, J)$ coupling scheme as a basis. These eigenvectors show that, although the pure $((L_1S_1)J_{1s}, J)$ scheme represents a good first approximation, the deviations from pure coupling should be taken into account in calculating θ_1 and θ_2 . We have calculated θ_1 and θ_2 for the $4f^26s$ levels in intermediate coupling following the method outlined by Wybourne.⁸ In this calculation, matrix elements of the operator¹⁰

$$H_M = a_{4f} \sum_{i=1}^N \mathbf{I} \cdot [\mathbf{1}_i - 10^{1/2}(\mathbf{s}_i \mathbf{C}_i^{(2)})^{(1)}] + a_{6s} \mathbf{I} \cdot \mathbf{s}$$

between all eigenvector components having amplitudes of at least 0.1 were included. The results are given in Table III, along with the corresponding factors obtained in pure coupling for comparison.

TABLE III. Calculated values of θ_1 and θ_2 appearing in the expression $A = \theta_1 a_{4f} + \theta_2 a_{6s}$.

| Level | Parent J | θ_1 | | θ_2 | |
|---------|------------|---------------|-----------------------|---------------|-----------------------|
| | | Pure coupling | Intermediate coupling | Pure coupling | Intermediate coupling |
| 3H_4 | 7/2 | 1.46 | 1.50 | -0.1111 | -0.1111 |
| | 9/2 | 1.17 | 1.12 | +0.1111 | +0.1009 |
| 3H_5 | 11/2 | 0.91 | 0.90 | +0.0909 | +0.0869 |
| | 9/2 | 1.09 | 1.08 | -0.0909 | -0.0812 |
| 3H_6 | 13/2 | 0.72 | 0.72 | +0.0769 | +0.0769 |
| | 11/2 | 0.84 | 0.84 | -0.0769 | -0.0728 |
| 3F_2 | 3/2 | 1.49 | 1.56 | -0.2000 | -0.2000 |
| | 5/2 | 1.00 | 1.09 | +0.2000 | +0.1674 |
| 3F_3 | 7/2 | 0.76 | 0.75 | +0.1429 | +0.1215 |
| | 5/2 | 1.02 | 0.96 | -0.1429 | -0.1106 |
| 3F_4 | 9/2 | 0.69 | 0.82 | +0.1111 | +0.1111 |
| | 7/2 | 0.86 | 0.84 | -0.1111 | -0.0905 |
| 1G_4 | 9/2 | 0.89 | 0.80 | +0.1111 | +0.1111 |
| | 7/2 | 1.11 | 1.10 | -0.1111 | -0.1111 |
| 1D_2 | 3/2 | 1.20 | 1.14 | -0.2000 | -0.2000 |
| | 5/2 | 0.80 | 0.75 | +0.2000 | +0.2000 |
| 3P_0 | 1/2 | 0.00 | -0.33 | +1.0000 | +0.7972 |
| 3P_1 | 1/2 | 0.00 | 0.33 | -0.3333 | -0.1381 |
| | 3/2 | 0.00 | 0.09 | +0.3333 | +0.3172 |
| 1I_6 | 11/2 | 1.08 | 1.08 | -0.0769 | -0.0769 |
| | 13/2 | 0.92 | 0.92 | +0.0769 | +0.0769 |
| 3P_2 | 5/2 | 0.48 | 0.48 | +0.2000 | +0.2000 |
| | 3/2 | 0.72 | 0.75 | -0.2000 | -0.1827 |
| 1S_0 | 1/2 | 0.00 | 0.00 | +1.0000 | +1.0000 |

The influence of the small nuclear quadrupole moment on the observed hfs was considered in detail. Because the $6s$ electron has no quadrupole interaction, any effect would be due entirely to the $4f$ electrons. Based on the value of $e^2Q(1/r^3) = -60.1$ Mc/sec obtained by Lew⁵ for neutral Pr, the largest calculated change in the hfs intervals of the $4f^26s$ levels of Pr²⁺ caused by the quadrupole interaction was approxi-

⁹ N. Spector, J. Opt. Soc. Am. 54, 1359 (1964).

¹⁰ The magnetic hyperfine structure operator given by Wybourne should be multiplied by \mathbf{I} (scalar product) to correspond to the usual form of the interaction energy.

mately 0.0003 cm^{-1} . Since this small perturbation is negligible compared to the linewidth of 0.150 cm^{-1} and the probable error in the intervals of 0.007 cm^{-1} , we did not include a quadrupole term in the interpretation of the data.

The splitting factor of the $6s$ electron was deduced from the data in the following way. Pairs of lines originating from common upper levels were selected. The two equations representing the observed hfs of the two lines of a pair were subtracted so as to eliminate the A factor of the upper level (see example below). Only those pairs were considered for which the patterns of the two lines were oppositely degraded. This makes the resulting equation relatively insensitive to the contribution of the $4f$ electrons. As an example of the method, we consider the pair of lines at 3436.358 and 3354.914 \AA , which originate from the $[f^2(^3H_6)p_{1/2}]_{11/2}$ level and which terminate on the $[f^2(^3H_6)s]_{11/2}$ and $[f^2(^3H_6)s]_{13/2}$ levels, respectively. The observed hfs is represented by the equations

$$\begin{aligned} A[f^2(^3H_6)s]_{11/2} - A[f^2(^3H_6)p_{1/2}]_{11/2} &= -0.0423 \text{ cm}^{-1}, \\ (15/13)A[f^2(^3H_6)s]_{13/2} - A[f^2(^3H_6)p_{1/2}]_{11/2} &= +0.0597 \text{ cm}^{-1}. \end{aligned}$$

Subtracting and inserting the angular factors from Table III, one obtains

$$-0.084a_{4f} + a_{6s} = +0.631 \text{ cm}^{-1}. \quad (1)$$

Similar equations were constructed for all possible pairs of lines involving the $4f^26s$ configuration. In order to avoid complex patterns, levels with $J < \frac{5}{2}$ were not used. We also omitted the levels $[f^2(^3H_4)s]_{9/2}$, $[f^2(^3H_5)s]_{11/2}$ and $[f^2(^3F_3)s]_{7/2}$, which are perturbed by nearby levels belonging to the $4f^25d$ configuration. These three levels yielded equations which were inconsistent with those obtained from levels of $4f^26s$ far removed from any possible perturbing $4f^25d$ levels. The $[f^2(^1I_6)s]_{11/2,13/2}$ levels, which are separated by only 11 cm^{-1} , also could not be used, because of a mutual interaction between the hfs states of these two levels. Observed lines associated with these two levels all show large departures from the interval rule, the successive intervals yielding progressively larger splitting factors with decreasing values of F . The observed departures from the interval rule are in good quantitative agreement with predictions of the theory for this type of perturbation.

A set of 23 equations similar to (1) was obtained. The least-squares solution of these equations gives values for the splitting factors and their standard deviations of $a_{6s} = 0.639 \pm 0.002 \text{ cm}^{-1}$ and $a_{4f} = 0.029 \pm 0.003 \text{ cm}^{-1}$. The low standard deviation in a_{6s} indicated by the least-squares solution demonstrates the excellent over-all consistency of the data. Nevertheless, when the solutions for a_{6s} and a_{4f} are used to predict the right side of each of the 23 equations, small systematic shifts can be detected between equations asso-

ciated with different pairs of lower levels. Although the origin of these small shifts is unknown, it is likely that they are due to uncertainties in the eigenvectors. We have taken account of these apparent shifts by enlarging our estimated uncertainty in a_{6s} to include nearly all of our data in the stated result:

$$a_{6s} = 0.639 \pm 0.007 \text{ cm}^{-1}.$$

It is of interest to compare this result with that which would be obtained by assuming pure $((L_1S_1)J_{1,s},J)$ coupling. A recalculation of a_{6s} assuming pure coupling gives a result which is 1.6% lower than the above value. The standard deviation derived from the least-squares solution is five times greater than that obtained in intermediate coupling.

V. DETERMINATION OF $(dn_a/dn)/n_a^3$

The nonrelativistic probability density of an s electron at the nucleus is given by

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

where n is the principal quantum number and n_a is the effective quantum number.¹¹ Z_a is the charge seen by the $6s$ electron while outside of the atomic core; for the third spectrum $Z_a = 3$. The factors n_a and dn_a/dn may be derived from a Rydberg-Ritz series of terms of the type $T = -RZ_a^2/n_a^2$ for the $4f^2ns$ ($n = 6, 7, 8, \dots$) configurations, as described in Ref. 11. For Pr^{2+} , only the $n = 6$ member of this series is known, so that it is not possible to deduce these factors directly from the known Pr levels. However, they can be reliably calculated from values of $\Delta n_a = n_a(7s) - n_a(6s)$ and $\Delta T = T(7s) - T(6s)$ interpolated from the known structure in similar ions. The symbols $T(6s)$ and $T(7s)$ refer to the centers of gravity of the $4f^26s$ and $4f^27s$ configurations, respectively. The procedure adopted here for obtaining Δn_a and ΔT and for carrying out the calculation will now be described.

The s electron in the $4f^Nns$ rare-earth configurations is in an environment of a nuclear charge Z screened by inner closed shells and inner $4f$ electrons.¹² Therefore, the addition of a unit of nuclear charge and a $4f$ electron to form successive rare-earth atoms does not greatly affect the relative properties of the $6s$ and $7s$ orbits. The slow variation of the relative positions of the centers of the low configurations in the doubly and triply ionized rare earths has been pointed out by Dieke, Crosswhite, and Dunn.¹³

In Fig. 1, the known values of ΔT for the doubly ionized rare earths (La^{2+} , Ce^{2+} , Yb^{2+})¹⁴⁻¹⁶ are plotted. The

¹¹ H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).

¹² The contraction of the $4f$ shell in the rare earths is well illustrated by the results of Freeman and Watson (see Ref. j of Table I), which show that the probability of finding the $6s$ electron inside the $4f$ shell is very small.

¹³ C. H. Dieke, H. M. Crosswhite, and R. Dunn, *J. Opt. Soc. Am.* **51**, 820 (1961).

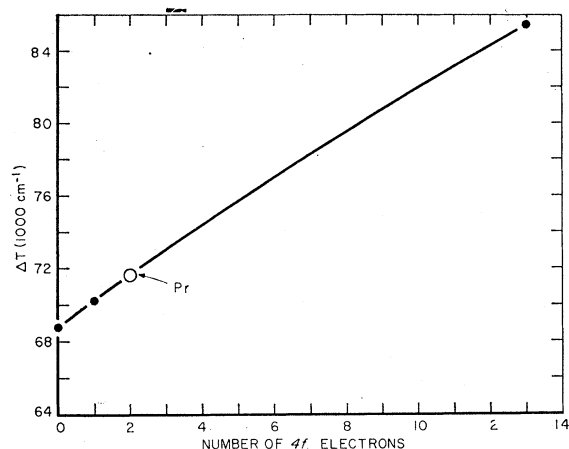


FIG. 1. Energy difference ΔT between the centers of gravity of the $4f^N 6s$ and $4f^N 7s$ configurations of doubly ionized rare-earth atoms.

ionized rare earths (La,¹⁴ Ce,¹⁵ Yb,¹⁶) are plotted. The value obtained for Pr²⁺ from the curve is $\Delta T = 71\,700\text{ cm}^{-1}$ with an estimated uncertainty of $\pm 300\text{ cm}^{-1}$. Although the uncertainty might be much greater for a point in the middle of the period, the good definition of the left-hand side of the curve justifies the uncertainty which we have assigned to the value for Pr. A similar plot for the configurations of singly ionized Ba,¹⁷ Eu,¹⁸ and Yb¹⁹ also indicates a smooth variation of ΔT throughout the rare-earth period.

Table IV gives experimental values of Δn_a for the first two members of ns series for alkali-like atoms in different periods. It shows that within each period Δn_a is relatively insensitive to Z and to the degree of ionization. The configurations $4f^N ns$ of the singly ionized lanthanides are similar to these isoelectronic sequences, because they consist of a single electron outside of a closed core and inner $4f$ electrons. The constancy of the known values of Δn_a for the lanthanides given in Table IV confirms the similarity of their structure to the other sequences in the table. For Pr²⁺ we assumed the value $\Delta n_a = 1.050$ with an estimated uncertainty of ± 0.005 .

These values of ΔT and Δn_a were used to solve the equation

$$\Delta T = \frac{9R}{[n_a(6s)]^2} - \frac{9R}{[n_a(6s) + \Delta n_a]^2},$$

yielding $n_a(6s) = 2.604$. This gives $T(6s) = -145\,700\text{ cm}^{-1}$ and an ionization energy of $174\,400\text{ cm}^{-1}$. An inde-

¹⁴ H. N. Russell and W. F. Meggers, J. Res. Natl. Bur. Std. **9**, 625 (1932).

¹⁵ J. Sugar, J. Opt. Soc. Am. **55**, 33 (1965).

¹⁶ B. Bryant, Johns Hopkins Spectroscopic Report No. 21, 1961 (unpublished).

¹⁷ E. Rasmussen, Z. Physik **83**, 404 (1933).

¹⁸ H. N. Russell, W. Albertson, and D. N. Davis, Phys. Rev. **60**, 641 (1941).

¹⁹ W. F. Meggers and B. F. Scribner, J. Res. Natl. Bur. Std. **19**, 651 (1937).

TABLE IV. Values of Δn_a and $(d\sigma/dT)/(\Delta\sigma/\Delta T)$ for the first two members of ns -series of alkali-like atoms in different periods. The numbers given were derived by us from the data in the listed references.

| Z | Spectrum | Δn_a | $(d\sigma/dT)/(\Delta\sigma/\Delta T)$ | Ref. |
|-----|----------|--------------|--|------|
| 11 | Na I | 1.016 | 1.04 | a |
| 12 | Mg II | 1.018 | 1.04 | b |
| 13 | Al III | 1.018 | 1.04 | c,d |
| 14 | Si IV | 1.017 | 1.05 | e |
| 19 | K I | 1.031 | 1.03 | a |
| 20 | Ca II | 1.032 | 1.03 | f |
| 21 | Sc III | 1.031 | | c |
| 37 | Rb I | 1.040 | 1.08 | g |
| 38 | Sr II | 1.042 | 1.08 | g |
| 39 | Y III | 1.041 | | h |
| 55 | Cs I | 1.051 | 1.09 | i |
| 56 | Ba II | 1.052 | 1.09 | j |
| 58 | Ce III | 1.050 | | k |
| 58 | Ce IV | 1.052 | | l |
| 63 | Eu II | 1.049 | | m |

a P. Risberg, Arkiv Fysik **10**, 583 (1956).

b P. Risberg, Arkiv Fysik **9**, 483 (1955).

c C. E. Moore, Natl. Bur. Std. (U. S.) Circ 467, Vol. I (1949).

d B. Edlén (private communication to C. E. Moore, 1960).

e Y. G. Toresson, Arkiv Fysik **17**, 179 (1960).

f B. Edlén and P. Risberg, Arkiv Fysik **10**, 533 (1956).

g C. E. Moore, Natl. Bur. Std. (U. S.) Circ. 467, Vol. II (1952).

h M. A. Catalán and F. R. Rico, Anales Real Soc. Espan Fis. Quím. **53A**, 85 (1957).

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

j See Ref. 17.

k See Ref. 15.

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

m See Ref. 18.

pendent check of this calculation was made by deriving the ionization energy from the $4f^2 nd$ series of Pr²⁺, for which terms with $n=5$ and 6 are known. Taking $n_a(6d) - n_a(5d) = 1.18$ from Ce²⁺,¹⁵ we obtain a limit of $174\,500\text{ cm}^{-1}$, in good agreement with the value derived from the $4f^2 ns$ data.

The value of dn_a/dn was found from

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

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. To test this assumption, we have examined the curves of the variation of σ with T for the ns series in a number of alkali-like atoms. These curves are all very regular and closely resemble the curve given by Edlén and Risberg for Ca II. From these curves the value of $d\sigma/dT$ at the position of the first member of the series can be determined. In Table IV we have listed the ratio of $d\sigma/dT$ to $\Delta\sigma/\Delta T$ for the various elements considered. It can be seen that this ratio is approximately constant in each period. We have used this regularity to improve upon the linear approximation for Pr²⁺ by estimating

$$d\sigma/dT = (1.09 \pm 0.01)\Delta\sigma/\Delta T.$$

With the above results for n_a , T , Δn_a , and ΔT , we find

$(dn_a/dn)/n_a^3=0.0619$. To obtain an estimate of the uncertainty we evaluated $(dn_a/dn)/n_a^3$ by using all combinations of the extreme values of ΔT and Δn_a . The results ranged from 0.0614 to 0.0624. Therefore

$$(dn_a/dn)/n_a^3=0.0619\pm 0.0005.$$

VI. NUCLEAR MOMENT

The nuclear moment was evaluated by use of the Goudsmit-Fermi-Segrè (GFS) formula:

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

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 $F_r=1.4716$, $\delta=0.043$, $\epsilon=0.006$, we obtain

$$\mu_I(\text{Pr}^{141}) = +4.09 \pm 0.06 \text{ nm}.$$

The correction factors used here were obtained from the tables and formulas given in Ref. 11. The uncertainty given here is the square root of the sum of the squares of the uncertainties in a_{6s} and $(dn_a/dn)/n_a^3$.

VII. DISCUSSION

In obtaining the limits of error assigned to our result for $\mu_I(\text{Pr}^{141})$ we have assumed that the GFS formula is valid. A comparison between the results of recent direct determinations of several rare-earth nuclear moments and corresponding values obtained by applying the GFS formula to optical hfs measurements is given in Table V. The direct determinations for Nd, Eu, and Tm quoted here were obtained by atomic beams triple resonance experiments. The direct determination for Yb was made by nuclear magnetic resonance (nmr) measurements on divalent Yb. From the good agreement between these two sets of data, we conclude that the use of the GFS formula does not introduce any significant error in our results.

To compare the result from Pr^{2+} with that obtained from Pr^+ , we have derived $(dn_a/dn)/n_a^3$ for Pr^+ using the method given in Sec. V. (As previously noted, values of ΔT are known for Ba^+ , Eu^+ , and Yb^+ .) The

TABLE V. Rare-earth magnetic moments obtained from the GFS formula and from direct measurements.

| Isotope | μ_I (GFS) | μ_I (Direct) ^a | Ref.— μ_I (GFS) |
|-------------------|---------------|-------------------------------|---------------------|
| Nd ¹⁴³ | -1.1 ± 0.1 | -1.064 ± 0.004 | b |
| Nd ¹⁴⁵ | -0.69 ± 0.10 | -0.653 ± 0.004 | b |
| Eu ¹⁵¹ | +3.39 ± 0.03 | +3.419 ± 0.004 | c |
| Eu ¹⁵³ | +1.50 ± 0.02 | +1.507 ± 0.003 | c |
| Tm ¹⁶⁹ | -0.21 ± 0.02 | -0.229 ± 0.003 | d |
| Yb ¹⁷¹ | +0.49 ± 0.06 | +0.4926 ± 0.0004 | e |
| Yb ¹⁷³ | -0.67 ± 0.01 | -0.677 ± 0.003 | e |

^a Results in this column are taken from Ref. 20.

^b K. Murakawa, Phys. Rev. **96**, 1543 (1954).

^c K. Krebs and R. Winkler, Z. Physik **160**, 320 (1960).

^d K. H. Lindenberger, Z. Physik **141**, 476 (1955).

^e K. Krebs and H. Nelkowski, Z. Physik **141**, 254 (1955).

calculation was made with $\Delta T=45\ 100\ \text{cm}^{-1}$ and $\Delta n_a=1.05$. Using Murakawa's value of $a_{6s}=0.426\ \text{cm}^{-1}$ for Pr^+ , we find $\mu_I=+4.08\ \text{nm}$, in very good agreement with the result from Pr^{2+} .

It is difficult to compare the optical results with the atomic beams and nmr measurements, because of the ambiguities in the values used for $\langle 1/r^3 \rangle$. Several authors (see for example Bleaney²⁰ and Judd²¹) have recently noted that the wave functions of Judd and Lindgren do not yield accurate values of $\langle 1/r^3 \rangle$. Bleaney²⁰ 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 determinations of the nuclear moments exist, and then interpolating for the remainder of the rare earths. With this technique, Bleaney estimates a magnetic moment of $+4.28 \pm 0.08\ \text{nm}$ based on the atomic beams data for neutral Pr, and $4.24 \pm 0.10\ \text{nm}$ based on the nmr data for Pr^{3+} .

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²⁰ B. Bleaney, in Quantum Electronics, *Proceedings of the Third International Congress, Paris* (Columbia University Press, New York, 1964), Vol. I, p. 595.

²¹ B. R. Judd, Proc. Phys. Soc. (London) **A82**, 874 (1963).