New Determination of the Nuclear Magnetic Moment of ^{141}Pr

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A new value for the nuclear magnetic moment of ^{141}Pr has been obtained: μ_{nucl} (^{141}Pr) $= 4.2754(5)\mu_N$. This is two orders of magnitude more precise than the best previous (atomic beam) measurement. Major limitations of previous measurements were circumvented by a direct measurement of the moment in an *electronically excited state* ($^1D_2$ of the Pr^{3+} ion in CaF$_2$), where electronic contributions to the nuclear moment are only 3 parts in 10^4.

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The nuclear magnetic moment of atoms or ions with partly filled electron shells can be substantially modified by the admixture of small amounts of electronic states via hyperfine coupling.[1] These contributions have to be allowed for in a model-dependent way in order to extract the bare moments. This is particularly true for lanthanide ions, which have closely spaced electronic levels and large hyperfine interactions. Until now, the magnetic moment of ^{141}Pr was one of the least well known of the rare-earth nuclear moments, largely because of sizable electronic contributions. The current best value for the moment comes from an atomic beam measurement[2] of the hyperfine structure of the four J levels of the ground ^4I multiplet of atomic ^{141}Pr. The original data[2] gave a J-dependent nuclear moment, but corrections for hyperfine-induced J mixing have been made by Bleaney,[3,4] giving a value of 4.25(5) nuclear magnetons (μ_N).

We have made a new measurement of the nuclear moment of ^{141}Pr, $\mu_{\mathrm{nucl}} = 4.2754(5)\mu_N$, with an improvement in accuracy of two orders of magnitude. The technique used was rf-optical double resonance in CaF$_2$:Pr^{3+}, which differs from all previous determinations[5-10] in that the nuclear moment was measured in an *excited electronic state.* This allowed the increased precision because the excited state ($^1D_2$) and the site symmetry (C_{4v}) were chosen such that the electronic contributions to the nuclear moment for magnetic fields parallel to C_4 were only 3 parts in 10^4. Since the measurement is *direct* in the sense that rf is absorbed between the Zeeman components of the nuclear sublevels $M_I = \pm\frac{1}{2}$ with essentially no electronic character, it does not depend on a knowledge of the value of $\langle r^{-3}\rangle$, in contrast to a determination from measurements of the hyperfine constant by optical,[5,9,10] ESR,[7,8] or atomic beam[6] techniques. Since the external field was calibrated by ^{19}F optically detected NMR in the same crystal, strictly what we measured was the ratio of the moment of ^{141}Pr to ^{19}F.

Measurements were made as follows. A single crystal of CaF$_2$ doped with 0.01% Pr^{3+} was placed in a broadband traveling-wave rf coil inside a superconducting solenoid. The liquid-helium-bath temperature was 1.8 K and the external magnetic field $H_0 = 22.1$ kG was parallel to [001]. A single-frequency cw dye laser (jitter width ~ 1 MHz) was tuned to resonance with one of the six resolved hyperfine components of the 5940.97-Å line. This line is assigned to transitions from the hyperfine components of the lowest crystal-field component of the $^3H_4$ ground state, which is an electronic doublet, to the lowest crystal-field component of $^1D_2$ for Pr^{3+} ions of a tetragonal (C_{4v}) site, charge compensated by a F$^-$ ion in a [100] direction.[11,12] Hole burning occurs as the result of a redistribution of population in the ground-state superhyperfine[11] and hyperfine levels by optical pumping. This leads to a reduction of more than 95% in the fluorescence emitted by the sample ($^1D_2 \rightarrow {}^3H_{6,5,4}$). Most of this hole depth is attributed to the superhyperfine mechanism[12] which dominates since the Pr nuclear spin is a good quantum number for this axial site with $H_0 \parallel C_4$. A small amount of additional hole burning can be induced by flipping the Pr nuclear spin in the nondegenerate excited electronic state (see Fig. 1). This is the same mechanism for optical detection of excited-state nuclear resonance that was demonstrated by Sharma and Erickson[13] in YLiF$_4$:Pr^{3+} but in that case superhyperfine hole burning did not occur because the ground state is an electronic singlet. The laser was tuned to either of the inner two hyperfine components of the six-line pattern so that the $M_I = \pm\frac{1}{2} \rightarrow \mp\frac{1}{2}$ nuclear transitions of ^{141}Pr could be observed (Fig. 1). Of course the $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$ transitions also appear,

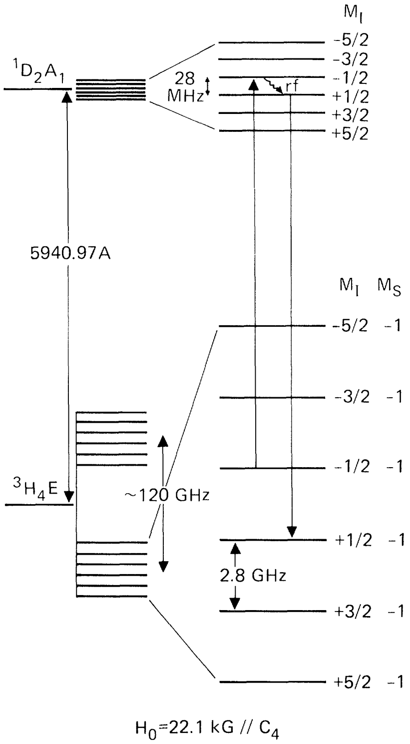

FIG. 1. Energy-level diagram for the 5940.97-Å transition of CaF_2:Pr^{+3}. The rf transition in the excited state measures the nuclear moment of ^{141}Pr and is detected by its contribution to optical hole burning since it results in population transfer in the ground state.

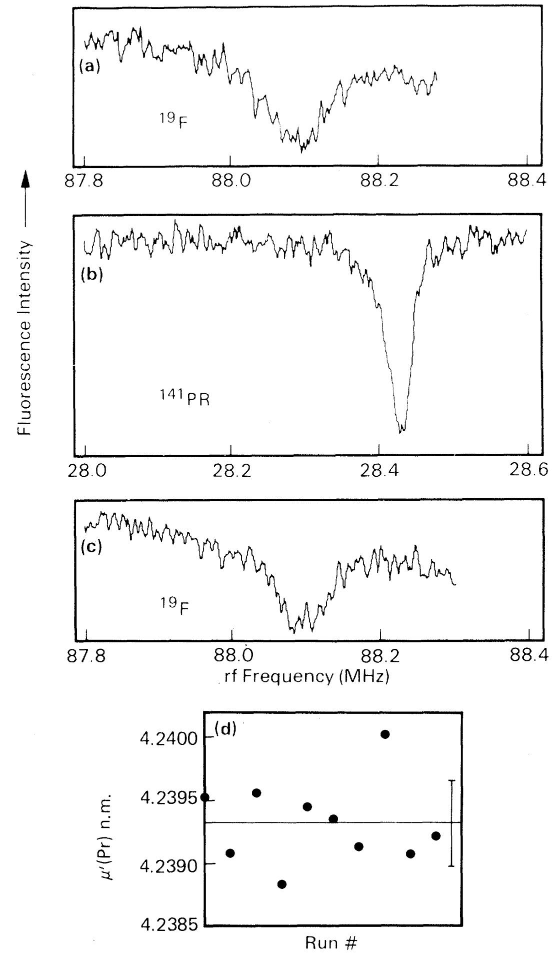

FIG. 2. Optically detected nuclear resonance signals. (a) and (c), ^{19}F resonances used to calibrate the external magnetic field before and after measurement of the ^{141}Pr resonances. (b) The ^{141}Pr resonance and (d) the scatter in the measured value of $\mu'(Pr)$ before correction for sample orientation and electronic contribution.

and from these the nuclear quadrupole coupling constant in the $^1D_2$ state was measured ($D = 0.44$ MHz). The rf source was square-wave modulated at 5 Hz and the fluorescence was phase-sensitively detected as the rf frequency was swept. When H_0 was aligned exactly (within 0.1°) along [001] the spin-lattice relaxation time controlling the hole recovery became several seconds, requiring unreasonably slow modulation rates. The sample was therefore intentionally misaligned by 0.7° to decrease the spin-lattice relaxation time and allow the 5-Hz modulation rate. We have previously shown[12] that a narrow ^{19}F resonance can be detected by inducing ^{19}F spin flips while the Pr^{3+} ion is optically excited. Since Pr-F superhyperfine coupling in the excited state is negligible, this resonance occurs at the bulk ^{19}F frequency and it was used to calibrate the applied magnetic field. Measurements of the field were made before and after each scan of the ^{141}Pr nuclear resonance (see Fig. 2). Since the ^{19}F resonance was also detected in the laser-excited volume (0.7 mm^3) the field calibration was made in exactly the same spatial location so that field homogeneity requirements were relaxed. In each run the ratio $\nu(^{141}Pr)/\nu(^{19}F)$ was recorded and

$$\mu_{nucl}'(Pr) = \frac{I(Pr)\nu(Pr)}{I(F)\nu(F)}\,\mu_{nucl}'(F)$$

determined, where μ_{nucl}' is the nuclear moment as measured in CaF_2 and I is the nuclear spin. Ten runs were made yielding an average value of $\mu_{nucl}'(Pr) = 1.6134(1)\mu_{nucl}'(F)$. These constitute the "raw data." Several corrections and calibrations were made in order to arrive at the final value of the nuclear moment. These are listed below:

(i) *Field calibration.*—The chemical shift of ^{19}F in CaF_2 relative to C_6F_6 is -56.6 ppm,[14] the shift of C_6F_6 relative to CCl_3F is +162.3 ppm,[15] and the absolute chemical shift of CCl_3F is 195.6 ppm.[16] From these measurements we obtain an absolute chemical shift of ^{19}F in CaF_2 of $+301 \pm 5$ ppm. This is subtracted from the bare nuclear moment of ^{19}F which was obtained from the following expression:

$$(1-\sigma_F)\mu_{\text{nucl}}(^{19}\text{F}) = (1-\sigma_H)\mu_{\text{nucl}}(^{1}\text{H})R\,,$$

where R is the ratio of the ^{1}H and ^{19}F NMR frequencies in HF,[17] the screening constants $\sigma_F = 410.0$ ppm and $\sigma_H = 29.2$ ppm are calculated values,[16] and $\mu_{\text{nucl}}(^1\text{H}) = 2.792\,743\mu_N$.[18] This gave $\mu_{\text{nucl}}'(^{19}\text{F}) = 2.627\,57\mu_N$.

(ii) *Sample orientation.*—This could be measured to ± 0.1°, from the optical Zeeman splitting of the set of Pr^{3+} ions for which H_0 is perpendicular to C_4 in the maximum available field of 45 kG. The sensitivity comes from the narrow inhomogeneous linewidth (<1 GHz) and the anisotropic electron moment, $g_\parallel \mu_B/h = 5.44$ MHz/G and $g_\perp = 0$. As mentioned above, a deliberate misalignment of 0.7° was made in order to decrease the spin-lattice relaxation time. To correct for this, the nuclear splitting factor for $H_0 \perp C_4$ (in the $^1D_2$ state) was required and was obtained from hole-burning measurements ($\gamma_\perp/2\pi = 2.12$ kHz/G). The magnitude of the correction for misalignment was $-0.000\,546\mu_N$ and the error in this correction was ± 0.0001.

(iii) *Electronic contribution.*—Since the excited state in which the resonance was detected is an electronic singlet, electronic contributions to the nuclear splitting occur in second order. This state has A_1 symmetry[19] and will be coupled to A_2 levels by the z component of the electronic Zeeman interaction $\mathcal{H}_z{}^{Z} = H_z(L_z + 2S_z)$ and the hyperfine interaction $\mathcal{H}_z{}^{\text{HF}} = 2\mu_B\mu_{\text{nucl}}\gamma\hbar\langle r^{-3}\rangle N_z I_z$ leading to an electronic shielding factor

$$\alpha = \sum_i \frac{-4\mu_B{}^2\langle r^{-3}\rangle\langle{}^1D_2(A_1)|L_z+2S_z|A_2{}^i\rangle\langle A_2{}^i|N_z|{}^1D_2(A_1)\rangle}{E(A_2{}^i) - E({}^1D_2(A_1))}\,.$$

Since there are no A_2 levels in the $^1D_2$ manifold, only perturbations from other terms make α nonzero. The most important are (a) intermediate-coupling corrections due to spin-orbit admixture of other $J = 2$ levels (principally $^3P_2$ and $^3F_2$) into $^1D_2$ which results in nonzero matrix elements of $\mathcal{H}^{\text{HF}}$ and $\mathcal{H}^{Z}$ between $^1D_2$ and the A_2 components of $^3P_1$ or $^3F_3$. (b) Crystal-field-induced J mixing will mix other A_1 levels into $^1D_2(A_1)$. The largest contribution to α comes from $^1I_6$, an estimate of which shows it to be 1–2 orders of magnitude smaller than the intermediate-coupling contribution. (c) Deviations from axial site symmetry relax the selection rules on hyperfine matrix elements. These deviations can be estimated from their effect on the ground-state hyperfine splittings, and can be shown to give a negligible contribution to α.

Thus, the only significant correction is that due to intermediate coupling. The admixture of $^3P_2$ and $^3F_2$ can be calculated from the known spin-orbit constant for Pr^{3+} ($\zeta = 749\ \text{cm}^{-1}$).[20] By diagonalizing the spin-orbit interaction for $J = 2$, one obtains admixtures of 10.2% $^3P_2$ and 2.1% $^3F_2$. The shielding factor α is then given by[21,22]

$$\alpha = -4\mu_B{}^2\langle r^{-3}\rangle\left[\frac{b^2\langle{}^3P_2\|L+2S\|{}^3P_1\rangle\langle{}^3P_1\|N\|{}^3P_2\rangle}{E({}^3P_1)-E({}^1D_2)} + \frac{c^2\langle{}^3F_2\|L+2S\|{}^3F_3\rangle\langle{}^3F_3\|N\|{}^3F_2\rangle}{E({}^3F_3)-E({}^1D_2)}\right]$$
$$= -[3.6\times10^{-4} - 0.6\times10^{-4}]\,,$$

where b is the admixture of $^3P_2$ into $^1D_2$, and c the admixture of $^3F_2$. The values of $\langle r^{-3}\rangle = 32.1\ \text{Å}^{-3}$ and the reduced matrix elements of $L + 2S$ and N are obtained from Ref. 4.

The ^{141}Pr moment of $4.2754(5)\mu_N$ is obtained from the above together with the diamagnetic correction for the Pr atom:

$$\mu_{\text{nucl}}(^{141}\text{Pr}) = 4.2393(3) - 0.0005(1) + 0.001\,373(1) + 0.035\,36,$$

where the first term on the right-hand side is the measured value, the second is the correction due to sample orientation, the third is the correction due to the electronic contribution, and the last is the diamagnetic correction. Random errors arose mainly from the following sources: (a) magnetic field homogeneity and stability, i.e., the measurement of the ^{19}F resonance frequency; (b) measurement of the ^{141}Pr resonance frequency itself which had a linewidth of 50 kHz; and (c) measurement of the crystal alignment. These were all in the range of 1 in 10^5 to 1 in 10^4 and from the distribution of the ten measured values [Fig. 2(d)] we set an experimental error of ± 0.0004 or ± 100 ppm on the moment. In addition the uncertainty in the calculation of the electronic contribution adds another ± 0.0001.

In conclusion, we have obtained a new value for the nuclear magnetic moment of ^{141}Pr which is two orders of magnitude more accurate than previous (atomic beam) measurements. This was done by a low-temperature, solid-state, rf-optical double-resonance measurement, where the nuclear moment was measured in the electronically excited state. This removed a major source of error in earlier measurements, which was the large, poorly known electronic contribution to the nuclear moment. Our measurement involved direct rf absorption between nuclear Zeeman levels which have a very small admixture of electronic states. For this reason the radial distribution of the electrons, expressed by $\langle r^{-3}\rangle$, is only required to calculate the small correction term, rather than the entire moment value as in determinations of μ_{nucl}(Pr) from hyperfine splittings. The greatly improved value of the nuclear moment of ^{141}Pr is of interest not only for models of the nucleus, but for allowing an accurate determination of small electronic contributions to the moment of ^{141}Pr in solids.

By increasing the magnetic field stability and homogeneity, and using line-narrowing techniques, it should be possible to improve the accuracy of this measurement even more. To justify this, a more detailed calculation of the residual electronic contributions to the nuclear moment should be made. As we have shown, there can be significant advantages in making measurements in excited electronic states which can either replace or supplement those in thermally occupied electronic states.

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