Mössbauer Isomer Shifts and Hyperfine Splitting of the 145.4 keV γ-rays of ^{141}Pr

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Dedicated to Prof. Dr. H. Maier-Leibnitz on the occasion of his 60th birthday

The Mössbauer scattering of the 145.4 keV γ-rays of ^{141}Pr was observed in a number of praseodymium compounds. From the isomer shifts between trivalent and tetravalent fluorine compounds the value $\Delta\langle r^2\rangle = +12 \cdot 10^{-3}$ fm^2 was derived for the change of the nuclear charge radius. The magnetic moment of the 145.4 keV state, $\mu_{7/2} = (2.8 \pm 0.2)\ \mu_N$, was deduced from the magnetic hyperfine pattern observed with scatterers of antiferromagnetic PrO_2.

1. Introduction

The filling of the $2d_{5/2}$ and $1g_{7/2}$ proton orbits results in a number of odd-Z nuclei with $5/2^+$ and $7/2^+$ states as their lowest energy levels. Several of the isomeric transitions between such states have been studied by the Mössbauer method. In ^{121}Sb, $^{127, 129}$I, ^{133}Cs and ^{151}Eu these measurements yielded information on the magnetic moment of the first excited states and on the change of the nuclear charge radius accompanying the isomeric transition [1–6]. Recently the magnetic moment of the 91 keV $5/2^+$ state of β^--instable ^{147}Pm ($T_{1/2} = 2.6\,y$) was determined by the Mössbauer method [7]. All these experiments were performed in the standard transmission geometry. The $2d_{5/2} - 1g_{7/2}$ transitions in ^{141}Pr and ^{139}La, however, are better suited for scattering experiments because of their high transition energies of 145.4 keV and 165.8 keV, respectively, and because no higher states than the Mössbauer levels are populated in the decay of the ^{141}Ce and ^{139}Ce parent isotopes. An early observation of the Mössbauer effect of the 145 keV γ-rays of ^{141}Pr [8, 9] in a backscattering geometry demonstrated the feasibility of such experiments but did not yield information on nuclear parameters.

In the present work a low-temperature Mössbauer spectrometer permitting the observation of the γ-rays scattered through an angle of 120° will briefly be described, and results on the 145.4 keV transition of ^{141}Pr will be reported. A preliminary account of some of these experiments has been given elsewhere [10]. From the observed isomer shifts and magnetic hyperfine structure the change $\Delta\langle r^2\rangle$ of the nuclear charge radius and the magnetic moment of the $7/2^+$ first excited state of ^{141}Pr could be determined. The discussion of the present data includes a comparison with the results of other Mössbauer experiments on ^{141}Pr, which recently became known [11–14].

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2. The Scattering Spectrometer

Since the high energy of the studied γ-radiation renders the use of low temperatures imperative, the scattering arrangement shown in Fig. 1 is attached to the lower end of a stainless-steel liquid-He cryostat resembling the one described by KAINDL et al. [15]. Both the source and the scatterer are cooled to 4.2 K in the central tube protruding from the bottom of the dewar, the thermal contact with the liquid-He bath being established by a few torr of He gas in the central tube.

By means of a stainless-steel tube the source, the tungsten collimator surrounding it, and the scatterer are rigidly connected with the velocity-drive system mounted on top of the cryostat. Together with the velocity-drive they can easily be removed for changing the source or scatterer. A drive tube transfers the sinusoidal motion of the loudspeaker-type electromechanical velocity drive to the source, which is centered by a concentric flexure plate.

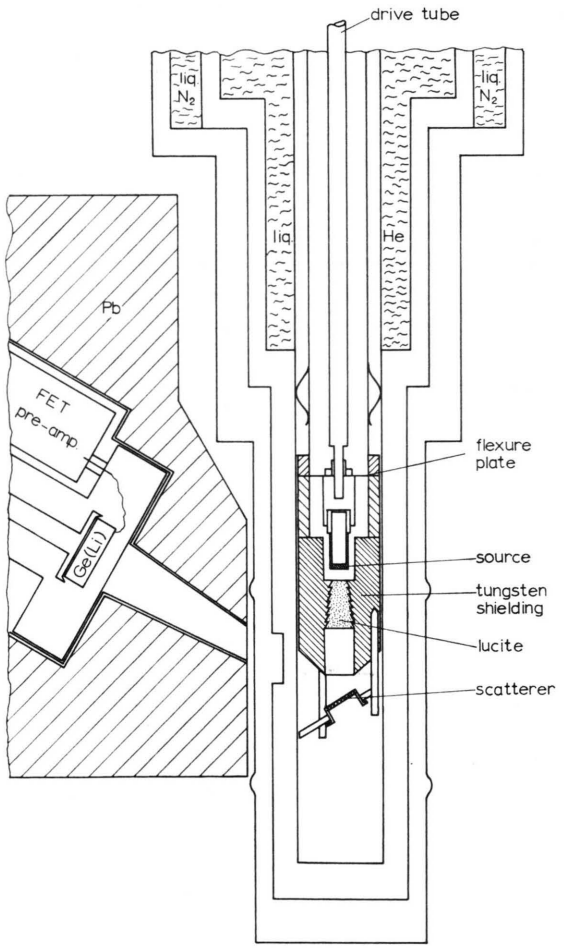

Fig. 1. Schematic drawing of the lower part of the scattering spectrometer. The upper part of the cryostat and the velocity drive resemble those described in Ref. [15].

The temperature of the source and the scatterer can be lowered below 4.2 K by pumping at the liquid-He bath. Furthermore after removal of the heat-exchange gas from the central tube the scatterer can be heated to temperatures above 4.2 K, while the source is kept at about 4.2 K by the heat conduction through the flexure plate and thermal-contact springs.

Direct radiation from the source is shielded from the detector by the tungsten collimator inside and by a lead collimator outside the cryostat. A lucite absorber between the source and the scatterer stops electrons which otherwise might produce bremsstrahlung in the scatterer. The collimators are shaped in such a way that the radiation emitted by the source does not hit any parts of the apparatus which are directly viewed by the detector, except the scatterer in its thin-walled lucite or aluminum holder.

The detector used during the ^{141}Pr experiments was a Ge(Li) diode of 30 mm diameter and 10 mm thickness with 2.8 keV resolution at 145 keV. Thus the 145.4 keV peak in the spectrum of the scattered radiation could easily be separated from the Compton-scattered γ-rays, which have an energy of 102 keV at a scattering angle of 120°.

The 145.4 keV γ-rays are but little attenuated in the 0.3 mm stainless-steel walls of the central tube and of the vacuum jacket. The copper heat radiation shield cooled by liquid N_2 has an aluminum-coated mylar window at the appropriate place.

The solid angle under which the source sees the scatterer is $6.5 \cdot 10^{-3}$ of 4π, and the detector subtends a solid angle of $2.5 \cdot 10^{-3}$ of 4π to the scattered γ-quanta. The resulting product solid angle of $1.6 \cdot 10^{-5}$ is inferiour by about a factor of 100 to that of a typical axially symmetric back-scattering geometry [8, 9]. In the case of ^{141}Pr this can to some extent be compensated by the use of strong sources. The present geometry has, however, the advantage of avoiding the smearing of the relative velocity between the source and the scatterer usually encountered in geometries were the mean angle between the direction of the source motion and of the emission of the γ-rays is non-zero [8, 9, 13].

3. Experiments and Results

a) Source preparation and properties

The 145.4 keV transition of ^{141}Pr is nearly pure M1 with only 0.4% E2 admixture [16]. The $7/2^+$ excited state is populated in about 70% of the β^--decays of ^{141}Ce, the remainder going directly to the groundstate with a maximum β-ray energy of 581 keV [16].

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The ^{141}Ce source activity ($T_{1/2} = 33$d) was produced by neutron irradiation of CeO_2 containing 99.7% ^{140}Ce. Due to the low ^{142}Ce content of 0.26% only negligible amounts of ^{143}Ce ($T_{1/2} = 33$h) and its ^{143}Pr ($T_{1/2} = 14$d) daughter are produced. The latter in particular should be avoided because of its high-energy β^--rays ($E_{max} = 993$ keV) [16]. By irradiating 600 mg CeO_2 in a neutron flux of $1 \cdot 10^{14}$ n/cm^2 s for four weeks sources of about 2 C were produced. After the irradiation the samples were annealed in air at 1100 K for several hours. Only after this heat treatment would they emit the narrow lines expected for the cubic, diamagnetic CeO_2 host. The narrowest lines observed with such sources exhibit (Table 1) no more than about 1.4 times the natural width $W = 2\hbar/\tau = 1.00$ mm/s following from the lifetime [16] $\tau = 1.9$ ns of the 145.4 keV state.

For PrO_2 as the scattering material virtually no isomer shift is observed with respect to the emission line of annealed CeO_2 sources, whereas trivalent Pr compounds exhibit shifts of about -0.8 mm/s. CeO_2 sources used without heat treatment after the neutron irradiation behave quite differently: The isomer shift then observed with a PrO_2 scatterer was $S = +(0.56 \pm 0.04)$ mm/s and the shift measured with a PrF_3 scatterer was $S = -(0.25 \pm 0.02)$ mm/s. Moreover, the emission line of such sources is considerably broadened, a typical result being $W = (2.10 \pm 0.06)$ mm/s obtained with a PrF_3 scatterer. The isomer shift results for annealed and unannealed sources show that in the former tetravalent Pr is formed after the β^--decay of ^{141}Ce, whereas in unannealed sources the majority of the praseodymium atoms are in their trivalent state when the γ-rays are emitted, obviously due to radiation damage incurred during the neutron irradiation. It is conceivable that during the neutron capture process in CeO_2 oxygen vacancies are formed in the vicinity of the hot atoms, and that these lattice defects stabilize the trivalent oxidation state of the Pr atoms originating in the β-decay of ^{141}Ce unless they are healed out at elevated temperatures.

The annealed sources gave reproducible isomer shift results: The shifts observed with eight different sources prepared in this way and with PrF_3 scatterers were found to agree within their individual limits of statistical error of about 0.02 mm/s.

b) Isomer shift results

The isomer shift results compiled in Tab. 1 and the Mössbauer spectra reproduced in Fig. 2 – 6 were

Table 1. Mössbauer isomer shifts S and full linewidth W at half maximum observed for the 145.4 keV γ-rays of ^{141}Pr with sources of CeO_2 annealed at 1100 K after the neutron activation and with various scatterers. References pertaining the preparation of the scatterers are given in the last column. Unless otherwise stated both the source and the scatterer were at 4.2 K. The results given were obtained by fitting single Lorentzian lines to the data.

Scatterer	S mm/s	W mm/s	Ref
PrO_2 at 24 K	-0.05 ± 0.01	1.76 ± 0.04	c
PrO_2 at 4.2 K [a]	-0.06 ± 0.02	2.76 ± 0.08	c
PrO_2 at 1.8 K [a, b]	-0.06 ± 0.05	2.80 ± 0.20	c
PrO_2 at 77 K [b]	-0.04 ± 0.04	1.62 ± 0.15	c
PrF_3	-0.94 ± 0.01	1.36 ± 0.02	d
$PrCl_3$	-0.78 ± 0.05	1.78 ± 0.18	e
$PrBr_3$	-0.63 ± 0.16	1.62 ± 0.54	f
K_3PrF_6	-0.88 ± 0.03	1.34 ± 0.10	g
$Pr_2(SO_4)_3 \cdot 8\,H_2O$	-0.86 ± 0.04	1.68 ± 0.16	d
$Pr(C_2O_4)_3 \cdot 10\,H_2O$	-0.77 ± 0.03	1.82 ± 0.12	d, h
$Pr(OH)_3$	-0.74 ± 0.02	1.36 ± 0.08	d, i
Pr_2O_3, cubic	-0.80 ± 0.03	1.72 ± 0.10	i, j
$PrFeO_3$	-0.78 ± 0.08	5.86 ± 0.30	k
Pr_6O_{11}	-0.14 ± 0.02	2.72 ± 0.08	l
PrC_2	-0.40 ± 0.09	9.26 ± 0.32	m
Pr metal [a]	-0.83 ± 0.06	1.24 ± 0.26	n
$CsPrF_5$	$+0.47 \pm 0.09$	6.74 ± 0.13	o
Cs_2PrF_6	$+0.54 \pm 0.08$	3.68 ± 0.30	o

[a] The results given were obtained by fitting magnetic hyperfine patterns to the data as desribed in the text.
[b] Source and scatterer were at the same temperature.
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[m] The sample was kindly supplied by Dr. M. Atoji.
[n] The sample was commercially obtained from Atomergic Chemetals Co., Carle Place, Long Island, New York 11514.
[o] The samples were kindly prepared as described in Refs. [40, 41] by Dr. R. H. Odenthal, Justus-Liebig-Universität, Gießen.

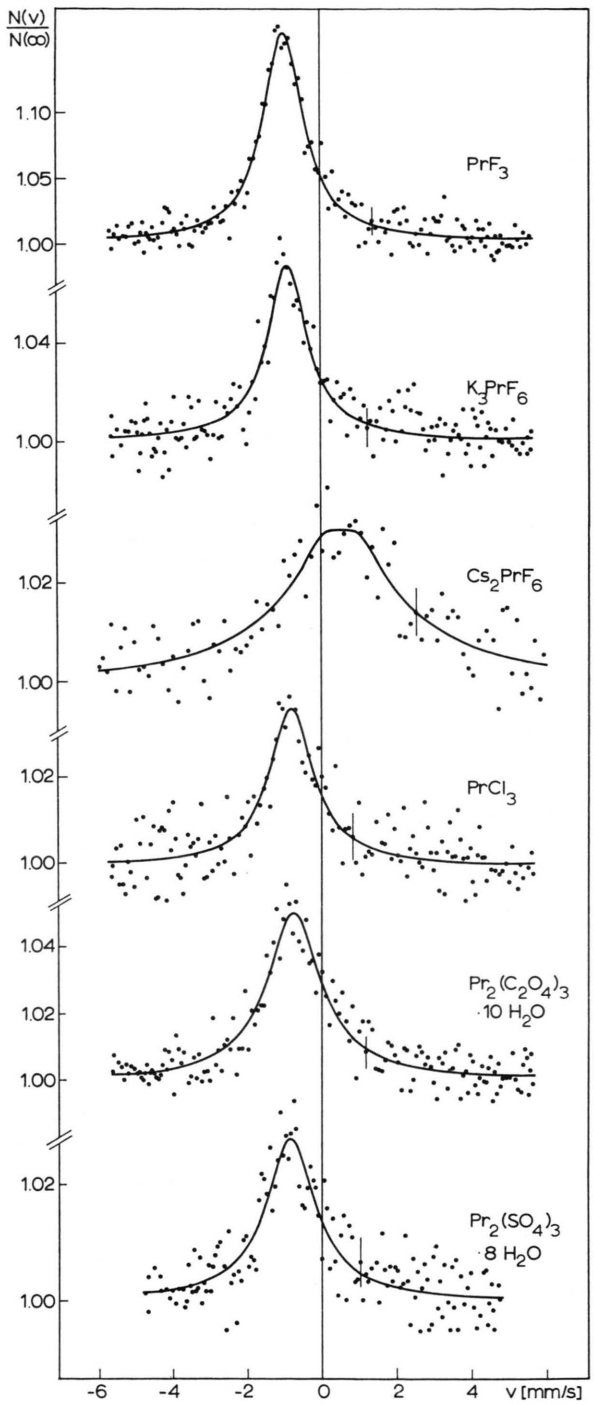

Fig. 2. Relative scattered intensity $N(v)/N(\infty)$ of the 145.4 keV-γ-rays of ^{141}Pr versus the velocity v of the CeO_2 source. The curves drawn to the data points are the results of least-squares fits of single Lorentzian lines for all scatterers except Cs_2PrF_6, in which paramagnetic relaxations have been allowed for as described in the text. $N(v)/N(\infty)$ is not corrected for the background in the pulse height spectra. Source and scatterers were at 4.2 K.

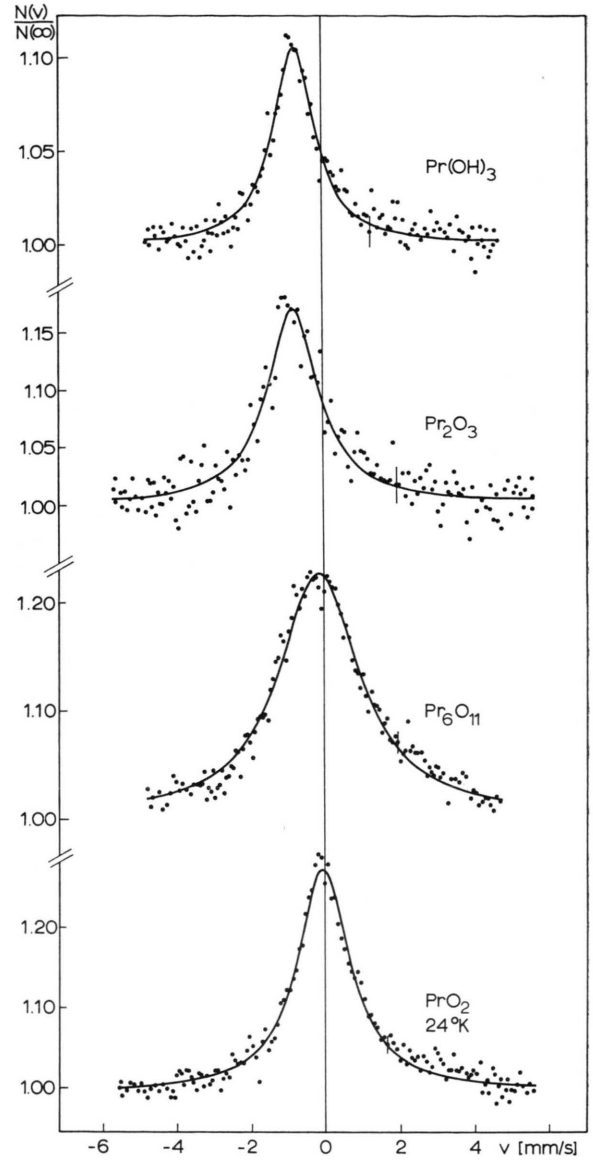

Fig. 3. Mössbauer scattering spectra obtained with both the CeO_2 source and the scatterers at 4.2 K except for the PrO_2 spectrum, which was taken with the scatterer at 24 K. The curves are single Lorentzian lines fitted to the data.

all obtained with annealed sources. The shifts and linewidths given in Tab. 1 are the results of least squares fits of a single Lorentzian line to each of the spectra except in the cases of PrO_2 below the Néel temperature and of Pr metal, both of which will be discussed in some detail later.

Fitting the spectra with Lorentzian lines implies that interference effects, which would lead to a dispersion term in the lineshape, are negligible in the

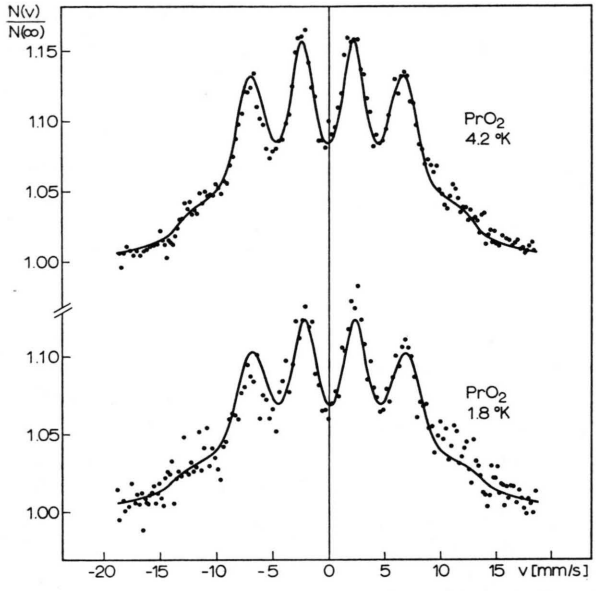

Fig. 4. Mössbauer scattering spectra of PrO_2 at 4.2 K and 1.8 K measured with a CeO_2 source. The curves fitted to the data correspond to a distribution of hyperfine fields as discussed in the text.

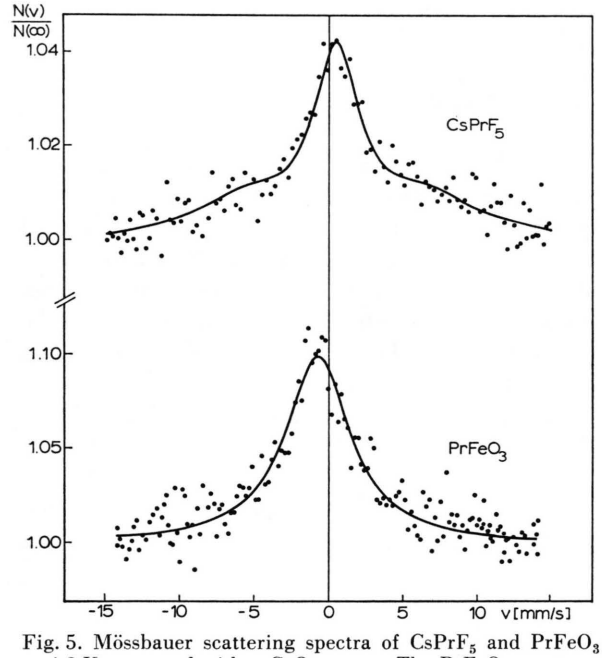

Fig. 5. Mössbauer scattering spectra of $CsPrF_5$ and $PrFeO_3$ at 4.2 K measured with a CeO_2 source. The $PrFeO_3$ spectrum was fitted with a single Lorentzian line. For $CsPrF_5$ intermediate paramagnetic relaxations were tentatively assumed as described in the text.

Pr case. Otherwise disregarding them might lead to erroneous isomer shift results. In view of the high γ-ray energy and the large scattering angle only

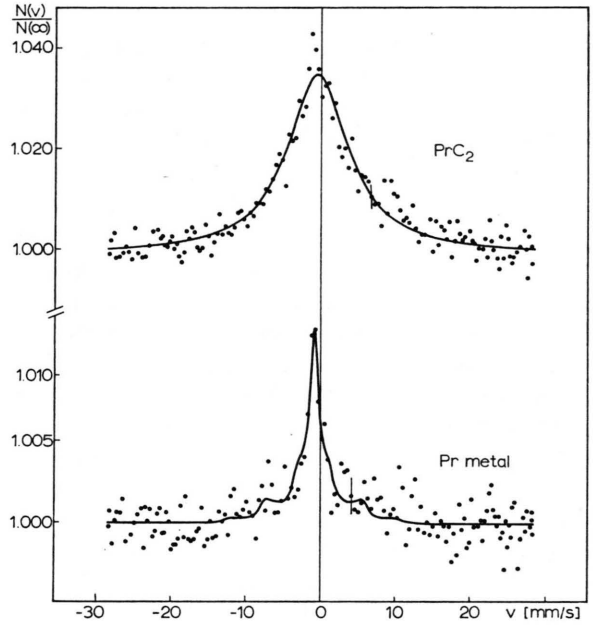

Fig. 6. Mössbauer scattering spectra of PrC_2 and Pr metal, both at 4.2 K. A single Lorentzian line was fitted to the PrC_2 spectrum; for Pr metal a superposition of a single line and a split pattern as discussed in the text has been assumed.

scattering processes occuring on the same atom will contribute to the interference term. In estimating the magnitude of the dispersion terms we may neglect those appearing even in the absorption cross-section [17] as a consequence of the phase shift which the electromagnetic waves experience due to induced electronic currents [18, 19]. These dispersion terms have been found to be of importance for E1 transitions [17, 20, 21] but are, within the accuracy of the present measurements, negligible for M1 and E2 radiation.

As has recently been pointed out [22, 23], waves scattered by different sublevels of the excited nuclear

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state may interfer, but the resulting interference terms can be neglected in the present context since, being symmetric, they do not lead to apparent isomer shifts even when their magnitude becomes appreciable in cases of unresolved hyperfine splittings [23].

Finally we have to consider the well-known interference between nuclear and Rayleigh scattering [24, 25]. This effect is, however, small for the very reason why scattering experiments are favourable at high energies, namely because the Rayleigh scattering cross-section [26] is much smaller than that for nuclear resonance scattering [9]. Moreover, the angular dependence of the interference term additionally reduces its magnitude for M1 radiation and a scattering angle of 120° [24, 27]. Explicit calculations [28] showed, that in all cases the apparent isomer shift due to interference effects remains considerably smaller than the statistical errors of the isomer shift results given in Tab. 1. Tentative fits of lineshapes including a dispersion term to our single-line spectra support these estimates by yielding zero amplitudes for the dispersion terms within the limits of statistical error.

c) Electric quadrupole interaction

In all cases the scatterers were too thin for line broadening due to finite scatterer thickness to be of any importance. Hence the slight broadening observed in most of the trivalent compounds is attributed to unresolved electric quadrupole interactions. In no case, however, was a resolved quadrupole splitting observed. The groundstate quadrupole moment of ^{141}Pr is $Q_{5/2} = +(0.0589 \pm 0.0042)$ b [29] and the moment of the excited state is also expected to be small, the theoretical prediction of KISSLINGER and SØRENSEN [30] being 0.28 b. Thus for electric field gradients V_{zz} of a few times 10^{18} V/cm^2 typical for rare earth ions, even the quadrupole splitting of the excited state is expected to be no larger than about $eQV_{zz}/4 \approx 0.5$ mm/s. Hence the broad lines observed in $PrFeO_3$, PrC_2, $CsPrF_5$ and Cs_2PrF_6 must rather be attributed to unresolved magnetic hyperfine interactions.

d) Magnetic hyperfine interactions

Magnetic order is known to exist in PrC_2 and $PrFeO_3$ below $T_N = 15$ K [31, 32] and $T_N = 707$ K [33], respectively, but in $PrFeO_3$ only the Fe^{+3} spins were found to be ordered at 4.2 K [34]. The paramagnetic Pr^{+3} ions may, however, be polarized due to the weak ferromagnetism [33, 34] of the iron sublattice. A hyperfine field of about 200 kOe induced at the sites of the praseodymium nuclei would be sufficient to explain the considerable line broadening observed in $PrFeO_3$.

According to neutron diffraction studies [31, 32] the ordered magnetic moment in PrC_2 is 44% of the free-ion Pr^{+3} moment of $\mu_{z,\,\mathrm{free}} = 3.20\,\mu_B$. Using the tabulation of ELLIOT and STEVENS [35] and $\langle r^{-3}\rangle_{\mathrm{eff}} = 5.0$ a. u. [36] one calculates $H_{i,\,\mathrm{free}} = 3370$ kOe for the hyperfine field of the $^3H_4$ groundstate of the $4f^2$ configuration of free Pr^{+3}. A 70 kOe contribution from core polarization included in this value was estimated according to the formula given by BLEANEY [37]. The validity of BLEANEY's formula has been questioned [38, 39], but since the core polarization field is small, an erroneous estimate of its magnitude is of little importance. Neglecting contributions from the conduction electrons and assuming H_i to be proportional to the μ_z value of the crystal-field groundstate as derived from the neutron diffraction data, one expects a saturation hyperfine field of $H_i \approx 1500$ kOe in PrC_2, which should result in a

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well-resolved hyperfine pattern. The PrC_2 sample used to take the spectrum of Fig. 6 was an uncrushed ingot of 99% purity handled with care to avoid deterioration by moist air. Nevertheless no resolved hyperfine splitting was observed. Actually the very broad line cannot be explained by any well-defined hyperfine field.

In the tetravalent complex fluorides $CsPrF_5$ and Cs_2PrF_6 the Pr^{+4} ions are expected to have a $4f^1$ configuration and hence Kramers-degenerate crystal field levels. X-ray powder patterns showed that the lattice parameters of our samples were identical with those reported previously [40, 41] for these compounds. Magnetic susceptibility measurements [28] in magnetic fields up to 50 kOe, however, yielded smaller magnetic moments at 4.2 K than the ones [40] reported for temperatures above 77 K. The compounds turned out to stay paramagnetic down to 2.45 K. At 4.2 K the magnetic moments per Pr^{+4} ion were found to be $\mu_z = (0.88 \pm 0.05)\,\mu_B$ for $CsPrF_5$ and $\mu_z = (0.61 \pm 0.05)\,\mu_B$ for Cs_2PrF_6. Both these values are considerably smaller than the free-ion moment $\mu_z = 2.14\,\mu_B$ [35] of the $^2F_{5/2}$ groundstate of free Pr^{+4}, which indicates strong crystalline field effects. Approximating $\langle r^{-3}\rangle_{eff}$ for Pr^{+4} by the Pr^{+3} value [36] of $\langle r^{-3}\rangle_{eff} = 5.0$ a. u. one expects [35] $H_{i,\,free} = 2180$ kOe for free Pr^{+4}, where the core polarization contribution has again been estimated from BLEANEY's [37] formula. Hence, in spite of the crystalline field effects, rather large magnetic hyperfine splittings would be expected in both compounds, if the relaxations of the Pr^{+4} spins were sufficiently slow.

The broad, unresolved spectra, however, rather indicate intermediate relaxation times. So far neither theoretical nor experimental studies of the influence of spin fluctuations on the line shapes of Mössbauer scattering spectra have become known. Moreover, without a full knowledge of the magnetic hyperfine tensor [42] an unambiguous interpretation of the present spectra would hardly be possible even if a reliable theoretical concept were available. However, tentative fits of the $CsPrF_5$ and Cs_2PrF_6 spectra with the formula of WICKMAN et al. [43] implying the effective field approximation, gave reasonable agreement with the data. In these fits only the spin relaxation time τ was varied, while the effective hyperfine field was kept constant at $H_i = H_{i,\,free} \cdot (\mu_z/\mu_{z,\,free})$, the linewidth at $W = 1.40$ mm/s and the ratio of the g-factors at $g_{7/2}/g_{5/2} = 0.48$, the value derived from the PrO_2 spectra which will be discussed in some detail later. The best fits to the data were obtained (Figs. 2 and 5) with $\tau = (0.20 \pm 0.03)$ ns for $CsPrF_5$ and $\tau = (0.07 \pm 0.04)$ ns for Cs_2PrF_6. While the physical significance of these results should not be overestimated, it is important to note that unambiguous isomer shift values can be derived from the spectra. Actually the shifts obtained from the fits with WICKMAN's formula, $S = +0.41 \pm 0.08$ mm/s for $CsPrF_5$ and $S = +0.53 \pm 0.09$ mm/s for $CsPrF_6$ are in good agreement with those obtained by fitting a single line to these spectra (Tab. 1).

In PrO_2 at 4.2 K and 1.8 K fairly well resolved magnetic hyperfine patterns were observed (Fig. 4). This compound has the cubic CaF_2-type crystal structure with a lattice constant of $a = 5.392$ Å [44, 45], which is very close to the CeO_2 value of $a = 5.411$ Å (l. c. [46]). Susceptibility measurements [45, 47] indicate, that PrO_2 becomes antiferromagnetic at 14 K [45], which has recently been confirmed by the Mössbauer measurements of BENT et al. [13]. We have studied several different PrO_2 samples prepared by leaching commercially available Pr_6O_{11} of 99.9% purity with glacial acetic acid [48, 49] as well as by firing Pr_6O_{11} at 650 K under an oxygen pressure of 100 at. for several hours [50]. The lattice parameter of all samples agreed with the known [44, 45] value for PrO_2 and the Mössbauer spectra disclosed no significant differences between the different samples. Particularly, impurities of praseodymium acetate, which have been reported [48, 49] to be adsorbed on PrO_2 prepared by leaching with acetic acid, did not noticeably con-

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tribute to the Mössbauer spectra, perhaps due to their small Debye-Waller factors.

For ^{141}Pr, like in the ^{151}Eu case [6] and in other Mössbauer spectra of $1g_{7/2}-2d_{5/2}$ transitions [3, 7], the 28 lines expected for a mixed M1/E2 transition between states with spins $7/2^+$ and $5/2^+$ coincide to form eight groups, the components of which cannot be resolved, and of which only six possess sufficient intensity to be visible in the Mössbauer spectra. The Zeeman patterns of PrO_2 at 4.2 K and 1.8 K were fitted with a superposition of 28 Lorentzian lines having the theoretical relative intensities. Generally the relative intensities of the lines in Mössbauer scattering spectra [22, 23] are different from those in absorption spectra [51], and depend on the scattering angle due to the different angular distribution of the radiation scattered by transitions between different Zeeman sublevels. Detailed calculations using the exact expressions [22, 23], however, showed that for the spins and multipolarity mixture involved in the 145.4 keV transition of ^{141}Pr and for the scattering angle of 120° the deviations from the relative intensities expected in an absorption spectrum amount to no more than 0.5%. These calculations also revealed that the contributions from the interference between the waves scattered on different Zeeman sublevels of the excited state [22, 23] are less than 1% of the intensities of the Lorentzian lines in a case like PrO_2, where Zeeman splitting $g_{7/2}\,\mu_N\,H_i$ is about 4.5 times larger than the natural linewidth $\Gamma=\hbar/\tau$. Nevertheless no good agreement with the data was obtained with a single, well defined value for the hyperfine field H_i. Fairly good fits resulted, however, when several discrete hyperfine fields or a distribution of such were assumed. The results given in Tab. 1 for PrO_2 at 4.2 K and 1.8 K and the solid curves in Fig. 4 were, for instance, obtained under the assumption that all fields in the range $\overline{H_i}\pm\Delta H_i$ are equally probable. Then, for 4.2 K, one finds $\overline{H_i}=(865\pm30)$ kOe and $\Delta H_i=(140\pm10)$ kOe. For PrO_2 at 1.8 K the results are the same within the limits of error, namely $\overline{H_i}=(900\pm60)$ kOe and $\Delta H_i=(160\pm30)$ kOe. The additional assumption of an electric quadrupole interaction does not bring a significant improvement of the fits. The single line observed in the paramagnetic state at 24 K is still slightly broadened with respect to the one observed with both source and scatterer at 77 K, but the linewidth at 24 K is less by nearly a factor of two than that derived from the split spectra even if a distribution of the hyperfine fields is assumed. Our results in this respect qualitatively agree with those of BENT et al. [13] who report even less resolved PrO_2 spectra, the difference probably being due to their use of unannealed CeO_2 sources. Non-stoichiometry of PrO_2 seems to be ruled out as a conceivable explanation for the observed line broadening, since scatterers prepared by different methods showed virtually identical spectra. A complicated magnetic structure of PrO_2 might be involved, but in any case the interpretation of the Mössbauer spectra in terms of a distribution of hyperfine fields need not be physically significant. In view of the large zero-point spin deviations which have recently been observed in some antiferromagnets [52–55] it seems conceivable that time-dependent spin fluctuations can give rise to spectra like the observed ones even at temperatures far below the Néel point. Preliminary approaches in this direction using the WICKMAN formula [42] like in the cases of $CsPrF_5$ and Cs_2PrF_6 gave reasonable agreement with the data. They will not be discussed in detail since it is felt that a more thorough understanding of the influence of spin fluctuations on Mössbauer scattering in particular is necessary before definite conclusions can be drawn. It will also be of interest to compare the present data with PrO_2 spectra obtained in the standard absorption geometry.

The values for the ratio of nuclear g-factors as obtained in the various attempts to fit the PrO_2 spectra all fell into the rather narrow range of $g_{7/2}/g_{5/2}=+(0.48\pm0.03)$. Using the groundstate magnetic moment $\mu_{5/2}=(4.136\pm0.004)\,\mu_N$ [29] we thus obtain $\mu_{7/2}=(2.8\pm0.2)\,\mu_N$ for the 145.4 keV level of ^{141}Pr.

Pr metal, like Nd metal, has the double-hexagonal lattice structure, in which half of the atoms are in a cubic nearest-neighbour environment and half in a

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hexagonal one [56, 57]. Neutron diffraction studies on polycrystalline samples [58] gave evidence for an antiferromagnetic transition at $T_N = 25$ K. The authors suggested the magnetic order to be of the same type as in metallic Nd between 7.5 and 19 K, where the spins on the hexagonal sites are antiferromagnetically ordered while those on the cubic sites remain paramagnetic. The antiferromagnetic spins are aligned in the basal planes with the magnitude of the magnetic moment sinusoidally modulated. Specific heat measurements [59] down to 0.02 K support this notion and yield $H_{i,\max} = (1030 \pm 15)$ kOe for the maximum value of the hyperfine field at the ordered sites, which corresponds to a maximum magnetic moment of 0.95 μ_B. These values are much smaller than the hyperfine field $H_i = 3370$ kOe and the magnetic moment $\mu_z = 3.20\ \mu_B$ expected for a free Pr^{+3} ion and indicate strong crystalline field effects. On the other hand recent neutron diffraction experiments with single crystals of Pr metal did not reveal any spontaneous magnetism [60]. This prompted the idea [60], that cooperative magnetism in Pr metal occurs in polycrystalline samples only, perhaps due to changes in the crystal-field splitting arising from strains in the polycrystals.

The Pr metal scatterer used to take the Mössbauer spectrum reproduced in Fig. 6 was a polycrystalline disk of 1 mm thickness and a purity of 99.8%. If the wave vector of the sinusoidal modulation of the ordered Pr^{+3} spins is incommensurate with the lattice [57–59] like in Nd [56], one expects fields in the region $-H_{i0} \leqq H_i \leqq H_{i0}$ to occur with a probability $p(H_i) \sim 1/(H_{i0}^2 - H_i^2)^{1/2}$, where H_{i0} is the maximum value of the hyperfine field. The solid curve drawn to the data points of Fig. 6 was obtained by a least squares fit assuming the Mössbauer spectrum to consist of the magnetic hyperfine pattern resulting for such a distribution of the hyperfine fields on the ordered sites plus a single line representing the paramagnetic Pr. The linewidth of the single line and that folded into the split pattern were assumed to be identical and the same isomer shift was attributed to the two lattice sites. The g-factor ratio was kept constant at $g_{7/2}/g_{5/2} = 0.48$. The isomer shift and linewidth obtained in this way are given in Table 1. For the maximum hyperfine field $H_{i0} = (860 \pm 60)$ kOe was obtained. This value is but slightly smaller than that of $H_{i0} = (1030 \pm 15)$ kOe derived from the specific heat measurements [59]. For the ratio of the areas under the single line and the magnetic pattern (0.6 ± 0.3) was obtained, in fair agreement with the value of unity expected if the Debye-Waller factors on the cubic and hexagonal sites are equal. The isomer shift found for Pr-metal coincides with that for Pr_2O_3 (Tab. 1). This raises the question, whether the single line could not partly or even totally be due to oxide impurities in the Pr metal sample. Now the single line in the Pr-metal Mössbauer spectrum has a hight of about 1.1%, whereas for pure Pr_2O_3 an effect of about 14% was observed (Figs. 3 and 6). The background in the pulse-height spectra was nearly the same in both cases. Thus an oxide impurity of about 8% would have been necessary to produce the single line in the Pr metal Mössbauer spectrum, while the oxide impurity actually present in the sample was considerably less than this. Hence our measurement seems to support the notion that the Pr spins on the cubic sites remain paramagnetic. It is, however, felt that all presently available data on Pr metal are also compatible with the alternative assumption that polycrystalline samples use to consist of a mixture of antiferromagnetic and paramagnetic crystallites, an idea which is prompted by the work of JOHANSSON [60]. Further Mössbauer work, with better statistics and both single crystal and polycrystalline scatterers, may help to clarify this matter.

4. Discussion

Recently Mössbauer measurements on ^{141}Pr by other groups [11–14] became known. The isomer shifts initially published by GROVES et al. [12] differ from our values in both sign and magnitude, but revised data reported by these authors [14] are in good agreement with our results. The isomer shifts found by BENT et al. [13] do fairly well agree with the ones observed by the present authors with unannealed CeO_2 sources. The rather broad lines observed by both GROVES et al. [12] and BENT et al. [13] may be due to the

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method of source preparation and to difficulties in correcting for the velocity smearing inherent in the back-scattering geometries employed in their experiments. Our result for the g-factor ratio, $g_{7/2}/g_{5/2} = 0.48 \pm 0.03$ is in good agreement with the value of $g_{7/2}/g_{5/2} = 0.48^{+0.02}_{-0.01}$ obtained by BENT et al. [13] from the hyperfine pattern of PrB_6.

In order to obtain the change $\Delta\langle r^2\rangle$ of the mean square nuclear charge radius $\langle r^2\rangle$ from the relation [61]

$$\Delta S = (2\pi/3)\, Z\, e^2\, \Delta\langle r^2\rangle \Delta D$$

for the isomer shift ΔS between two different scatterers, one has to know the difference ΔD of the electron densities D at the sites of the Mössbauer nuclei in the two materials. The shifts observed between divalent and trivalent rare earths have been attributed [62] to the shielding effect of the additional 4f electron in the divalent state as compared to the trivalent one. The magnitude of the corresponding decrease of the electron density at the nucleus has been estimated from optical isotope shift data in connection with either the Fermi-Segré formula [62] or $K_{\alpha 1}$ x-ray isotope shift values [63]. These methods at best yield electron density differences between free RE^{+2} and RE^{+3} ions. A recent [64] reinterpretation of optical isotope shift measurements on Eu^{+2} in CaF_2 [65], however, indicates that the electron density differences increase by no more than a factor of about 1.3 when the ions are incorporated into a solid. On the other hand non-relativistic Hartree-Fock-Slater [66] self-consistent-field calculations of electron densities in the rare earth yielded consistently larger free-ion values [2] for $\Delta D(RE^{+2} - RE^{+3})$ than the estimates based on optical isotope shifts [62–64]. This gave rise to the idea [63, 67] that configuration mixing in the excited optical states might lead to the low values for $\Delta D(RE^{+2} - RE^{+3})$ derived from isotope shift data.

The self-consistent-field value for the electron density difference between Pr^{+4} ($4f^1$) and Pr^{+3} ($4f^2$) given by SHENOY and KALVIUS [2],

$$\Delta D(Pr^{+4} - Pr^{+3}) = 3.1 \cdot 10^{26}\,\mathrm{cm}^{-3},$$

already contains the relativistic factor $S'(Z)$ [61], with which the nonrelativistic Hartree-Fock-Slater value has to be corrected for relativistic effects. It will in the following be used to obtain an estimate of $\Delta\langle r^2\rangle$ for ^{141}Pr.

The isomer shift results compiled in Tab. 1 show that the shifts for trivalent praseodymium compounds fall into a fairly narrow region between about -0.7 mm/s and -0.95 mm/s, whereas the shifts for the tetravalent compounds reveal a considerable difference between the behaviour of PrO_2 with a shift of -0.05 mm/s, and the fluorine complexes $CsPrF_5$ and Cs_2PrF_6 with shifts near $+0.5$ mm/s.

The only rare earth element for which isomer shifts for divalent, trivalent and tetravalent compounds have been observed is dysprosium. Using the 26 keV γ-rays of ^{161}Dy, HENNING et al. [68, 69] found a shift of $\Delta S = +(6.3 \pm 0.3)$ mm/s between Dy^{+3} ($4f^9$) in DyF_3 and Dy^{+2} ($4f^{10}$) in CaF_2. COHEN and WEST [70], observing satellite lines in the emission spectrum of a GdF_3 source, obtained a value of $\Delta S = +(7.0 \pm 0.4)$ mm/s for the shift between Dy^{+4} ($4f^8$) and Dy^{+3} ($4f^9$). With these data one can form the ratio

$$\frac{\Delta S(Dy^{+4}\text{ in }GdF_3 - Dy^{+3}\text{ in }GdF_3)}{\Delta S(Dy^{+3}\text{ in }DyF_3 - Dy^{+2}\text{ in }CaF_2)} = 1.11 \pm 0.08$$

for dysprosium in a fluorine environment. From Hartree-Fock-Slater electron densities [2] for Dy, on the other hand, one gets

$$\frac{\Delta D(Dy^{+4} - Dy^{+3})}{\Delta D(Dy^{+3} - Dy^{+2})} = 1.10\,.$$

The good agreement of both values supports the idea that covalency effects do not seriously affect the relative values of the isomer shifts in rare earth fluorine compounds. Experiments by KHURGIN et al. [71] with a source of ^{161}Tb in CeO_2 yielded a shift

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of $\Delta S = +(3.71 \pm 0.04)$ mm/s between Dy^{+4} and Dy^{+3} in CeO_2. The ratio

$$\frac{\Delta S(Dy^{+4} \text{ in } CeO_2 - Dy^{+3} \text{ in } CeO_2)}{\Delta S(Dy^{+4} \text{ in } GdF_3 - Dy^{+3} \text{ in } GdF_3)} = 0.53 \pm 0.03$$

resulting from this value and the shift observed by COHEN and WEST [70] may be compared with our praseodymium data, which yield

$$\frac{\Delta S(Pr^{+4} \text{ in } PrO_2 - Pr^{+3} \text{ in } Pr_2O_3)}{\Delta S(Pr^{+4} \text{ in } Cs_2PrF_6 - Pr^{+3} \text{ in } PrF_3)} = 0.50 \pm 0.04 .$$

The fact that the shifts between the oxides in both the Pr and the Dy case are only about half as large as those between the fluorides indicates strong covalency effects in the oxides, particularly for tetravalent rare earths in the fluorite lattices of PrO_2 and CeO_2. The idea that chemical bonding affects rare earth ions more strongly in the oxides than in the fluorides is supported by optical data, which show that the nephelauxetic effect is considerably larger in the oxides than in the fluorides [72].

Thus we use the mean isomer shift difference $\Delta S = +(1.4 \pm 0.1)$ mm/s between $CsPrF_5$ and Cs_2PrF_6 on the one hand and K_3PrF_6 and PrF_3 on the other to derive a value for $\Delta\langle r^2\rangle$. With the Hartree-Fock-Slater value [2]

$$\Delta D(Pr^{+4} - Pr^{+3}) = 3.1 \cdot 10^{26} \text{ cm}^{-3}$$

for the electron density difference we obtain $\Delta\langle r^2\rangle = 12 \cdot 10^{-3}$ fm^2.

An electron density calibration based on the shifts between the metal and trivalent compounds has been employed [2] for heavier rare earths like Gd or Tm but cannot be applied to the praseodymium case. This approach is based on the observation that in Sm, Eu, Dy, and Yb metal the ratio of the conduction electron density to the electron density difference between the divalent and trivalent compounds of these elements is approximately constant [2] at

$$\frac{\Delta D(\text{CE})}{\Delta D(RE^{+2} - RE^{+3})} \approx 0.4 .$$

From the present results for Pr metal and the fluorides, and taking into account that metallic Pr has to be regarded as Pr^{+3} plus conduction electrons, we find

$$\frac{\Delta D(\text{CE})}{\Delta D(Pr^{+2} - Pr^{+3})} \approx \frac{\Delta D(\text{CE})}{\Delta D(Pr^{+3} - Pr^{+4})} = 0.05 \pm 0.10$$

which indicates that the conduction electron density at the Pr nuclei is virtually zero. A rather small value of 0.2 ± 0.1 for the corresponding ratio has recently also been observed [63] for Nd. Since both metals have the same double-hexagonal type of lattice one is tempted to attribute their anomalous behaviour to this crystal structure.

The signs of the known $\Delta\langle r^2\rangle$ values for proton transitions between the low-lying $5/2^+$ and $7/2^+$ states in the ^{121}Sb to ^{151}Eu region can be understood coherently if one attributes a larger mean square charge radius to the odd proton when it occupies a $2d_{5/2}$ orbit than when it stays in a $1g_{7/2}$ orbit [1, 67]. Thus in ^{121}Sb, which contains just one proton outside the $Z = 50$ closed-shell configuration, one finds [2] $\Delta\langle r^2\rangle = \langle r^2\rangle_{7/2+} - \langle r^2\rangle_{5/2+} = -32 \cdot 10^{-3}$ fm^2 for the $1g_{7/2} - 2d_{5/2}$ single-particle transition, and for the 21 keV transition in ^{151}Eu, where the $1g_{7/2} - 2d_{5/2}$ shell is filled except for a single hole,

$$\Delta\langle r^2\rangle = \langle r^2\rangle_{7/2+} - \langle r^2\rangle_{5/2+} = +17 \cdot 10^{-3} \text{ fm}^2$$

is obtained from the isomer shift of 13.6 mm/s between EuF_3 and EuF_2 [73] and the Hartree-Fock-Slater electron density difference [2]

$$\Delta D(Eu^{+2} - Eu^{+3}) = 1.9 \cdot 10^{-26} \text{ cm}^{-3}.$$

Our result for ^{141}Pr,

$$\Delta\langle r^2\rangle = \langle r^2\rangle_{7/2+} - \langle r^2\rangle_{5/2+} = +12 \cdot 10^{-3} \text{ fm}^2$$

can be directly compared with this ^{151}Eu value since essentially the same calibration scheme has been used in both cases.

In the simple shell model, ^{141}Pr with its 82 neutrons and 59 protons is expected to have a $(1g_{7/2})^8 (2d_{5/2})^1$ groundstate configuration with the $1g_{7/2}$ shell being completely filled by eight protons. Then, with the 145 keV transition proceeding between $(1g_{7/2})^7 (2d_{5/2})^2$ and $(1g_{7/2})^8 (2d_{5/2})^1$ configurations, one expects a positive $\Delta\langle r^2\rangle$ as found for the single-hole transition in ^{151}Eu, in agreement with the present result. Obviously configuration mixing does not basically change this behaviour. It may, however, be the reason for the smaller $\Delta\langle r^2\rangle$ in ^{141}Pr as compared to ^{151}Eu.

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