

## Isomer Shift and Hyperfine Splittings of the 59.6-keV Mössbauer Resonance in $^{237}\text{Np}\dagger$

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The Mössbauer resonance of the 59.6-keV transition in  $^{237}\text{Np}$  was observed in a variety of chemical compounds, using the  $\alpha$  decay of  $^{241}\text{Am}$  as a source. The shift of the resonance as a function of the charge state of neptunium, coupled with atomic self-consistent-field calculations for the electron densities at the nucleus, leads to a change in the nuclear charge radius  $\Delta\langle r^2\rangle/\langle r^2\rangle = -3.5\times 10^{-4}$ . Using the collective nuclear model, this number can be expressed as a change in the nuclear deformation of  $\Delta\beta/\beta_0 = -6.3\times 10^{-3}$ . All compounds investigated exhibited electric quadrupole or magnetic hyperfine splitting, or both. These data confirmed the earlier results of the ratios of the nuclear moments as  $g^*/g = 0.533\pm 0.005$  and  $Q^*/Q = 1.0\pm 0.1$ .

### INTRODUCTION

IN recent years the Mössbauer effect has been extensively applied to the nuclear spectroscopy of rare-earth isotopes. Because of the large static deformations of nuclei having masses  $190\geq A\geq 150$ , the low-lying states are of a collective nature with excitation energies on the order of 100 keV, and a large number of transitions suitable for the Mössbauer effect occur. In even-even nuclei, the transition from the first excited state to the ground state is an electric quadrupole transition with a typical lifetime of several nanoseconds, leading to a Mössbauer resonance linewidth of  $\sim 2$  mm/sec. In odd- $A$  nuclei, the lowest transition in a given rotational band is typically magnetic dipole and thus somewhat faster, yielding a correspondingly larger linewidth. However, these nuclei often have several bands of collective states intermixed. The transition from the ground state of a higher energetic band to the true ground state is, in general, strongly hindered. These transitions, having relatively long lifetimes and relatively low energy, are then especially favorable for Mössbauer-effect investigations. A typical example of this case is the 26-keV transition in  $^{161}\text{Dy}$ .<sup>1</sup>

Nuclear systematics shows the existence of a second region of strongly deformed nuclei at  $A\geq 220$ , belonging to the actinide elements. These form a series of transition elements in which the  $5f$  electronic subshell is being filled, in a fashion similar to the filling of the  $4f$  subshell in the rare-earth elements. In this series, also, a large number of possible Mössbauer-effect transitions are available. The investigation of the actinides with the Mössbauer effect is of special interest because of the large amount of work that has been done on the rare earths. From a nuclear point of view, the low-lying states of both series are described by the collective nuclear model,<sup>2</sup> so that comparisons and

interrelationships can be made. From the point of view of chemistry and solid-state physics, one is interested in comparing the behavior of the  $5f$  elements with the corresponding  $4f$  elements in the rare-earth series.

As has been previously shown by Stone and Pillinger,<sup>3</sup> the 59.6-keV transition of  $^{237}\text{Np}$  is at present the most favorable case for Mössbauer-effect studies in the actinide series. Although it is a transuranium element and therefore unstable, this isotope is available in macroscopic amounts. Also, the radiation from a  $^{237}\text{Np}$  absorber is sufficiently low to allow measurements in a standard-transmission geometry. The pertinent transition has a highly favorable half-life of 63 nsec and occurs between the ground states of two  $K=\frac{5}{2}$  rotational bands. Such an intraband transition is likely to have a larger change in nuclear-charge radius than in a purely rotational (interband) transition. This, together with the fact that several different charge states of the neptunium ion can be stabilized in chemical compounds, makes this isotope a good candidate for a first investigation of isomer shifts in an actinide element.

It is hoped that an understanding of the nuclear-charge density in neptunium can be later applied to other chemically similar actinides such as plutonium and uranium. Such a scheme for interpreting isomer shifts has been successfully developed in the rare-earth series using  $^{151}\text{Eu}$  as a standard.<sup>4-8</sup> Unfortunately, the experimental situation is more difficult in the actinides because little optical spectroscopy has been done, and therefore the electronic configurations and the chemical bonding effects are much less well under-

<sup>3</sup> J. A. Stone and W. L. Pillinger, Phys. Rev. Letters **13**, 220 (1964).

<sup>4</sup> S. Hüfner, P. Kienle, D. Quitmann, and P. Brix, Z. Physik **187**, 67 (1965); Phys. Letters **13**, 140 (1964).

<sup>5</sup> P. Kienle, in Proceedings of the Conference on Nuclear Hyperfine Interactions, Asilomar, California, 1967, edited by E. Matthias and D. Shirley (North-Holland Publishing Co., to be published).

<sup>6</sup> S. G. Cohen, N. A. Blum, Y. W. Chow, R. B. Frankel, and L. Grodzins, Phys. Rev. Letters **16**, 322 (1966).

<sup>7</sup> H. Schaller, G. Kaindl, F. Wanger, and P. Kienle, Phys. Letters **24B**, 397 (1967).

<sup>8</sup> U. Atzmony, E. R. Bauminger, J. Hess, A. Mustachi, and S. Ofer, Phys. Rev. Letters **16**, 322 (1966).

<sup>†</sup> Based on work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>1</sup> R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, Phys. Rev. Letters **9**, 467 (1961).

<sup>2</sup> B. R. Mottelson and S. G. Nilsson, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Skrifter **1**, No. 8 (1959).

stood. Perhaps the determination of the isomer shifts for a wide variety of neptunium compounds may help to establish a scheme for the interpretation of bonding in neptunium materials, especially in intermetallic compounds where other forms of spectroscopy are difficult.

Very little is known about magnetic behavior in actinide materials. The high resolution available in  $^{237}\text{Np}$  allows the Mössbauer effect to be used to advantage in the study of magnetic properties in neptunium materials, as well as in other actinides. It is possible to investigate magnetic behavior even in cases where the atomic moments are very small and other methods, such as neutron diffraction, cannot be used.

Finally, it is of interest to note that the 59.6-keV level in  $^{237}\text{Np}$  can be populated both by  $\beta$  decay (from  $^{237}\text{U}$ ) and by  $\alpha$  decay (from  $^{241}\text{Am}$ ). Careful studies using both sources should allow one to investigate the effect of the recoil transferred to the neptunium nucleus from the preceding  $\alpha$  decay.

#### $\alpha$ -DECAY SOURCES

In all cases in this work the source activity was  $^{241}\text{Am}$ . The first investigation<sup>3</sup> on  $^{237}\text{Np}$  was done using the  $\beta^-$  parent  $^{237}\text{U}$  as source. However, this isotope has several disadvantages. The  $^{237}\text{U}$  lifetime is a comparatively short 6.7 days. Also, the production reaction  $^{238}\text{U}(n, \gamma)^{237}\text{U}$  produces a large amount of activity from fission products of the  $^{235}\text{U}$  present, necessitating a radiochemical separation after the irradiation. Finally, the decay scheme of  $^{237}\text{U}$  is rather complex, yielding many different  $\gamma$  rays, and high-resolution detectors are required to isolate the 59.6-keV line.

The  $^{241}\text{Am}$   $\alpha$  parent is much more convenient because of its long half-life of 458 years and because of the fact that the 59.6-keV line is produced 86% of the time. The major problem with an  $^{241}\text{Am}$  source is that almost 100 keV of recoil energy is transferred to the nucleus during the  $\alpha$  decay, which is substantially more than enough to dislocate the atom from its regular position. The lifetime of any level suitable for Mössbauer experiments certainly exceeds the time necessary to stop the recoiling nucleus. However, the heat generated in the process may not be dissipated from the immediate surroundings by the time of  $\gamma$ -ray emission. This may give rise to a locally elevated temperature and hence to a reduced recoil-free emission (the "heat-spike" picture). In addition, after coming to rest the nucleus may occupy different positions throughout the lattice, which can give rise to a variety of hyperfine interactions and may cause line broadening or multiple emission lines.

In spite of these considerations, it is found that metallic americium compounds do make suitable Mössbauer sources. The results obtained with several  $^{241}\text{Am}$  sources are given in Table I, along with the results

TABLE I. Linewidth of the 59.6-keV resonance in  $^{237}\text{Np}$  sources.

Source	$T$ (°K)	Absorber	$T$ (°K)	FWHM (mm/sec)
$\text{UO}_2$ <sup>a</sup>	4.2	$\text{NpO}_2$	4.2	6
	78	$\text{NpO}_2$	78	3
	78	$\text{NpAl}_2$	78	2
$\text{Am}$ <sup>b</sup>	4.2	$\text{NpO}_2$	4.2	4.1
	4.2	$\text{NpO}_2$	78	3.2
	78	$\text{NpO}_2$	78	2.6
	4.2	$\text{NpAl}_2$	78	3.0
$\text{Am in Th}$ <sup>b</sup>	4.2	$\text{NpO}_2$	4.2	2.5
	4.2	$\text{NpAl}_2$	78	1.1
$\text{Am in Cu}$ <sup>b</sup>	4.2	$\text{NpO}_2$	4.2	10.8
Intrinsic linewidth $2\Gamma_N$ <sup>c</sup>				0.07

<sup>a</sup> Stone and Pillinger, Ref. 3.

<sup>b</sup> Present work.

<sup>c</sup> A. H. Muir, Jr., K. J. Ando, and H. M. Coogan, *Mössbauer Effect Data Index* (John Wiley & Sons, Inc., New York, 1966), p. 108.

from the  $^{237}\text{UO}_2$  source used in Ref. 3. Americium metal has the double hexagonal structure of the rare-earth metals and may therefore be expected to show a quadrupole interaction. Nonetheless, the metallic Am source produces a linewidth as good as that obtained from the cubic  $\text{UO}_2$  source. The best linewidth thus far has been obtained by alloying 5-wt % Am into cubic thorium metal, giving a linewidth of 1.1 mm/sec against a paramagnetic  $\text{NpAl}_2$  absorber. While this is about 15 times the natural width, it is still the sharpest resonance line thus far reported for  $^{237}\text{Np}$ .

At the present stage of investigation, it is impossible to separate the contributions of source and absorber to the line broadening. Since the absorbers are also radioactive, radiation self-damage in the absorber is quite possible. However, only the over-all damage done to the lattice is of importance, not the dislocated atom itself, since an absorber nucleus which has undergone  $\alpha$  decay has lost the ability to resonantly absorb, no longer being  $^{237}\text{Np}$ . Typical spectra for these sources are shown in Fig. 1. Sources prepared by alloying small amounts (typically 1%) of Am into Al, Cu, and Au produced very wide emission lines (> 10 mm/sec), presumably due to phase separation.

Sources prepared from nonmetallic compounds such as  $\text{AmO}_2$  show multiple emission lines. These lines cannot be fitted with a hyperfine spectrum, but the positions of the individual lines agree rather well with the positions given below for the resonances of the neptunium ion in different charge states. The relative intensities of the different lines are strongly dependent on the sample history. No attempt has been made to measure the total area under the emission lines and to compare the recoil-free fractions following  $\alpha$  and  $\beta$  decay; however, it would seem that the possibility of

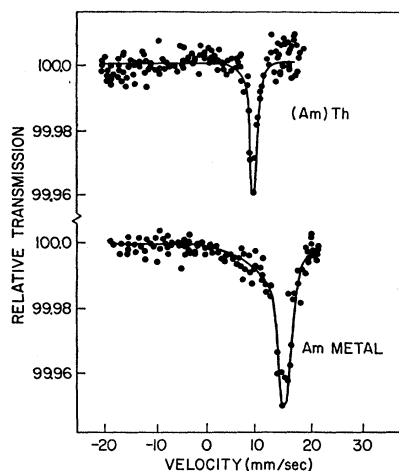


FIG. 1. Recoilless absorption spectra for metallic Am sources. The absorber is  $\text{NpAl}_2$ . Both source and absorber are at  $77^\circ\text{K}$ .

multiple emission lines weakens a previous discussion. Such a comparison was used<sup>9</sup> to support a discussion of local heating following  $\alpha$  decay. It is believed that at present there is no confirmed evidence for the heat-spike picture.

### EXPERIMENTAL

Typically, absorbers were made from  $250 \text{ mg/cm}^2$  of powdered compounds bound to a  $\frac{1}{2}$ -in.-diam disk by lucite dissolved in acetone. This was then encapsulated in a brass container having a 10-mil wall thickness. This amount of brass was thick enough to stop the  $\text{Np } \alpha$  particles, but still thin enough to easily transmit the  $\gamma$  rays. The container was then closed with vacuum-tight solder joints. The radiation density in contact with the absorber itself was of the order of  $30 \text{ mR/h}$ , and so could be handled using only moderate care.

Most measurements were performed with both source and absorber at  $4.2^\circ\text{K}$ . The experimental arrangement

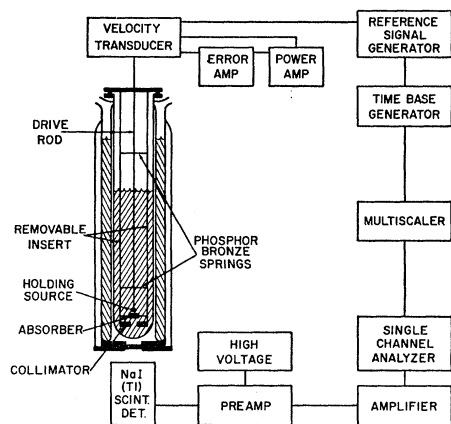


FIG. 2. Block diagram of experimental arrangement.

<sup>9</sup> J. G. Mullen, *Phys. Letters* **15**, 4 (1965).

is shown in Fig. 2. Samples were mounted inside the liquid-helium bath of a glass cryostat. Relative motion between source and absorber was introduced through a stainless-steel drive rod from an electromechanical transducer mounted on top of the cryostat. The velocity profile was sinusoidal, generated by a function generator (Hewlett Packard 3300A) and controlled by a standard negative-feedback circuit.<sup>10</sup> The spectrum was stored in a 400-channel analyzer (RIDL 34-12) which was operated in time mode and synchronized with the oscillator.

Because both source and absorber are active in this case, and because the velocity range in this work can be rather high (in excess of  $200 \text{ mm/sec}$ ), strong geometrical effects are observed regardless of whether

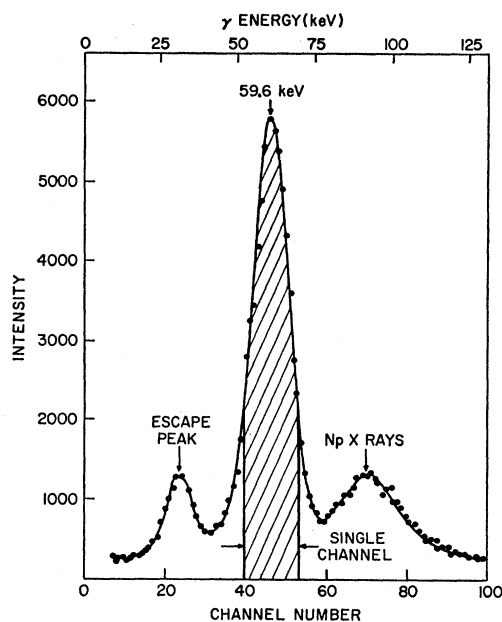


FIG. 3.  $^{237}\text{Np}$   $\gamma$ -ray spectrum, using  $\text{NaI}(\text{TI})$  scintillation counter, with resonant absorber in place.

the source or absorber is moved. Experience has shown that larger geometrical effects are obtained with a moving source, but that these are more symmetrical and hence more easily corrected. In some cases, however, the correction for a curved base line was difficult and added to the uncertainty of the measurements.

The  $59.6\text{-keV}$   $\gamma$  rays were detected in a  $\frac{3}{8}$ -in.  $\times$  2-in.  $\text{NaI}(\text{TI})$  scintillation detector. A typical pulse-height spectrum is shown in Fig. 3 with the resonant absorber in place. The signal-to-background ratio was generally about 4:1 with the absorber in place. The principal competing radiation is the  $\text{Np}$  x rays around  $100 \text{ keV}$ . Since these stem mainly from the absorber, they can be minimized by choosing a geometry with a small ab-

<sup>10</sup> E. Kankaleit, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum Press, Inc., New York, 1965), Vol. 1, pp. 47-66.

TABLE II. Hyperfine splitting parameters for neptunium compounds at 4.2°K. Isomer shifts are given with respect to  $\text{NpO}_2$ . Assuming ground-state moment of 2.7 nm, the internal magnetic fields are given by  $H_i(\text{kOe}) = 59.2(gH)$ .

Substance	Charge state	Isomer shift (mm/sec)	$gH$ (mm/sec)	$e^2qQ/4I(2I-1)$ (mm/sec)	$\eta$
$\text{NpF}_3$	+3	$41.0 \pm 0.5$	...	$0.55 \pm 0.03$	...
$\text{NpO}_2$	+4	0	$0.7 \pm 0.2$	...	...
$(\text{NpO}_2)_2\text{C}_2\text{O}_4\text{H} \cdot 2\text{H}_2\text{O}$	+5	$-17 \pm 1.0$	$115.2 \pm 0.5$	$2.8 \pm 0.2$	...
$\text{KNpO}_2\text{CO}_3$	+5	$-12 \pm 1.0$	$108.8 \pm 1.0$	$-3.1 \pm 0.5$	...
$\text{K}_3\text{NpO}_2\text{F}_5$	+6	$-46 \pm 2.0$	$39.6 \pm 1.0$	$5.0 \pm 1.0$	0.15
$\text{NpO}_2(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$	+6	$-36 \pm 2.0$	$46.0 \pm 2.0$	$1.8 \pm 1.0$	...
$\text{NpAl}_2$		$6.3 \pm 0.5$	$54.0 \pm 0.5$	...	...
$\text{NpC}$		$-12 \pm 1.0$	$84.0 \pm 0.5$	...	...

sorber-detector solid angle. The count rate in the single channel generally exceeded  $10^6/\text{sec}$ , thus allowing the observation of rather small absorption peaks in a reasonable length of time ( $\sim 40$  h).

All spectra were analyzed with a computer program in which relative line positions are constrained by the values of an appropriate Hamiltonian, rather than by the usual manner in which independent lines are fitted to the various peaks. In the present procedure, the variables for fitting were in general the off-resonance count rate, the absorption strength, the linewidth, the isomer shift, the magnetic coupling constant  $gH$ , the electric quadrupole coupling constant  $e^2qQ/4I(2I-1)$ , and the asymmetry parameter  $\eta$ .

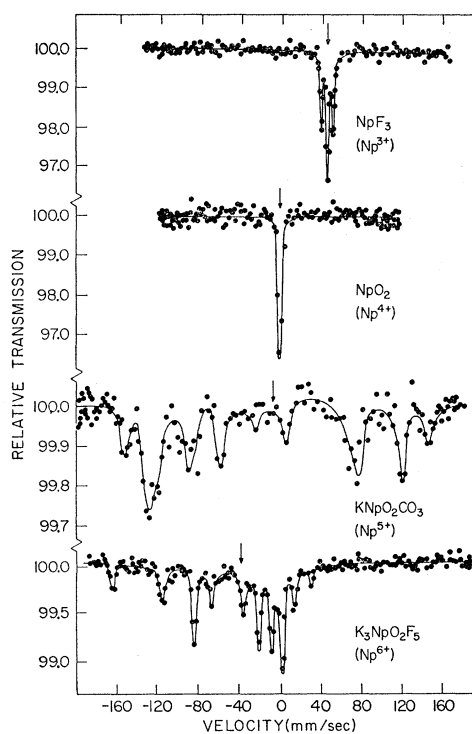


FIG. 4. Recoilless absorption spectra for Np compounds with four different valence states. The source is (Am) Th. Both source and absorber are at 4.2°K. Hyperfine-splitting parameters for the spectra are given in Table II.

### ISOMER SHIFTS

The  $5f$  electrons in the actinide series are less well localized than the  $4f$  electrons in the rare-earth series. Because of this, the actinides can exist in a variety of charge configurations, whereas the rare earths almost always occur in the tripositive state. Neptunium can be prepared in compounds with the four formal valencies +3, +4, +5, and +6. The Mössbauer resonances of  $^{237}\text{Np}$  in compounds with all these valence states have been observed, and typical spectra are shown in Fig. 4. The extraction of the isomer shifts from such spectra is complicated by the fact that most compounds show hyperfine splittings, thus requiring one to fully fit the entire spectrum in order to accurately determine the isomer shift. The results of this investigation for several compounds is given in Table II. All shifts have been referred to an  $\text{NpO}_2$  absorber in order to remove any dependence on the particular source used.

The electronic charge density at the nucleus [ $\psi_0^2$ ] for the pure configuration  $5f^4$  to  $5f^1$  have been obtained by a computer calculation using nonrelativistic Hartree-Fock wave functions.<sup>11</sup> This calculation shows that the change in  $\psi_0^2$  for the removal of one  $5f$  electron is independent of the particular  $5f$  configuration, thus showing that the self-shielding of the  $5f$  electrons is small. If we tentatively assign the configuration  $5f^4$  to  $\text{Np}^{3+}$ ,  $5f^3$  to  $\text{Np}^{4+}$ , etc., then we obtain the relation between the isomer shift and the electronic density at the nucleus shown in Fig. 5. We see that it is possible to approximate a straight line through the experimental points, although this must certainly be considered only an approximation since it neglects any possible effects due to covalency and configuration mixing. That such effects are present is shown by the spread of isomer shifts assigned to some charge states. From the slope of the straight line we obtain

$$\Delta(\text{isomer shift})/\Delta\psi_0^2 = -1.48(\text{mm/sec}) a_0^3,$$

where  $a_0$  is the Bohr radius, or

$$\Delta(\text{isomer shift})/\Delta\psi_0^2 = -22.2 \times 10^{-26}(\text{mm/sec}) \text{cm}^3.$$

<sup>11</sup> M. Wilson (private communication).

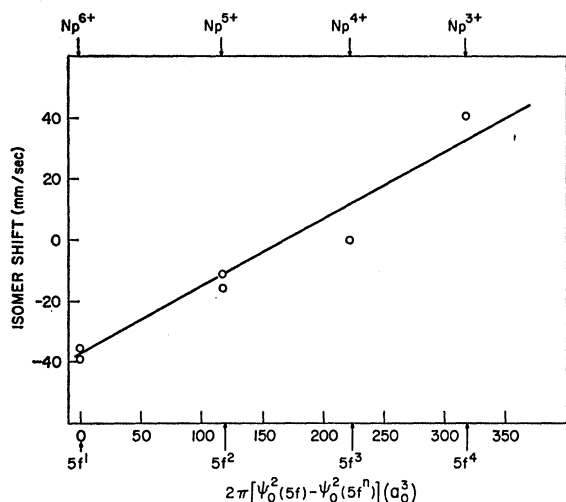


FIG. 5. Isomer shifts versus electronic density at the nucleus for free-atom Np configurations. Isomer shifts are given with respect to  $\text{NpO}_2$ .

This value may be somewhat small. From optical spectroscopy it is believed that the purely ionic configurations are rather good representations of  $\text{Np}^{3+}$  and  $\text{Np}^{4+}$ . For the higher charge states no data are available so far. The values in Fig. 5 for  $\text{Np}^{3+}$  and  $\text{Np}^{4+}$  give

$$\Delta(\text{isomer shift})/\Delta\psi_0^2 = -37.3 \times 10^{-26} (\text{mm/sec}) \text{ cm}^3.$$

Using the average value above and the relativistic correction outlined by Shirley,<sup>12</sup> we obtain the change in the nuclear charge radius between the excited and ground states to be

$$\Delta\langle r^2 \rangle / \langle r^2 \rangle = -3.5 \times 10^{-4}.$$

The fact that the isomer shifts are large (approximately 600 times natural linewidth), despite the rather small change in nuclear charge radius, can largely be attributed to the effect of the strong relativistic enhancement of the electron density at the nucleus, about a factor of 14 in this case.

As mentioned above, the 59.6-keV transition occurs between the ground states of two  $K = \frac{5}{2}$  rotational bands. Assuming that the change  $\Delta\langle r^2 \rangle$  is due to a change in the deformation parameter  $\beta$  of an axially symmetric nucleus, one finds

$$\Delta\beta/\beta_0 = -6.3 \times 10^{-3},$$

where  $\beta_0 = 0.265$  is the deformation parameter for the true ground state. This is in general agreement with the results of collective nuclear-model calculations, which obtain approximately the same deformation parameter in both  $\frac{5}{2}$  bands from the nuclear energy-level spacings.<sup>2</sup>

The 59.6-keV transition is a proton transition between the  $[642] \frac{5}{2}^+$  and  $[523] \frac{5}{2}^-$  Nilsson states. The

<sup>12</sup> D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

same states are involved in the 25.6-keV transition in  $^{161}\text{Dy}$ . However, in that case the levels represent neutron-hole states. A comparison between the results obtained for  $^{237}\text{Np}$  and  $^{161}\text{Dy}$  is given in Table III. The difference in the sign of  $\Delta\langle r^2 \rangle / \langle r^2 \rangle$  reflects the difference in proton states and neutron-hole states. The difference in the magnitude is not believed to be important, given the approximations which go into such a calculation. One thus obtains the result that the change in nuclear charge radius is roughly the same for both proton and neutron excitation.

### HYPERFINE INTERACTIONS

The compounds investigated show a variety of hyperfine spectra. The interaction parameters for various compounds are given in Table II. In contrast with rare-earth elements, where one finds predominantly the magnetic hyperfine field of the free trivalent ion, neptunium compounds show a wide variety of internal fields ranging from  $\sim 6$  MOe in  $\text{KNpO}_2\text{CO}_3$  to  $\sim 40$  kOe in  $\text{NpO}_2$ . Pure magnetic hyperfine spectra are observed in  $\text{NpAl}_2$  and in  $\text{NpC}$ . From these spectra the ratio of the  $g$  factor of the excited state to that of the ground state is found to be  $g^*/g = 0.533 \pm 0.005$ , in good agreement with a previous determination.<sup>13</sup> With a ground-state magnetic moment of  $+2.7$  nm,<sup>14</sup> we obtain  $+1.4$  nm for the magnetic moment of the 59.6-keV state. We may compare this value with that of the ground state of  $^{241}\text{Am}$ , which has the same Nilsson assignment of  $[523] \frac{5}{2}^-$ , and which has been measured by the atomic-beam method to be  $+1.58 \pm 0.03$  nm.<sup>15</sup> Since the deformation in  $^{241}\text{Am}$  is somewhat larger ( $\beta_0 = 0.27$ ) than in  $^{237}\text{Np}$ , the moment of  $^{241}\text{Am}$  may be considered an upper limit.

We may use these values for the moments of  $^{237}\text{Np}$  to calculate the effective spin  $g$  factor, according to de Boer and Rogers.<sup>16</sup> The result for the  $[523] \frac{5}{2}^-$  excited state of  $^{237}\text{Np}$  is  $g_{s,\text{eff}}/g_s = 0.69$ . This value is in good agreement with the values found for deformed

TABLE III. Comparison of  $^{237}\text{Np}$  and  $^{161}\text{Dy}$ .

	$^{237}\text{Np}$	$^{161}\text{Dy}$
$Z$	93	66
Ground state		$[642] \frac{5}{2}^+$
Excited state		$[523] \frac{5}{2}^-$
Isomeric energy (keV)	59.6	25.7
Single particle	Proton	Neutron hole
$\Delta\langle r^2 \rangle / \langle r^2 \rangle$	$-3.5 \times 10^{-4}$ <sup>a</sup>	$+2.5 \times 10^{-4}$ <sup>b</sup>

<sup>a</sup> Present work.

<sup>b</sup> P. Kienle (private communication). This number has been revised from that given in Ref. 4.

<sup>13</sup> J. A. Stone and W. L. Pillinger, Phys. Rev. **165**, 1319 (1968).

<sup>14</sup> C. A. Hutchinson, Jr., and B. Weinstock, J. Chem. Phys. **32**, 56 (1960).

<sup>15</sup> L. Armstrong, Jr., and R. Marrus, Phys. Rev. **144**, 994 (1966).

<sup>16</sup> J. de Boer and J. D. Rogers, Phys. Letters **3**, 304 (1963).

nuclei in the rare-earth region. This same Nilsson state also appears as the ground state in  $^{168}\text{Dy}$ . For this nucleus, de Boer and Rogers report a value of  $g_{s,\text{eff}}/g_s = 0.38 \pm 0.04$ , which is anomalously low in comparison to the  $^{237}\text{Np}$  value and the other rare-earth nuclei. However, a recent paper by Bochnaki and Ozaga<sup>17</sup> lists an experimental value of  $g_{s,\text{eff}}/g_s = 0.52 \pm 0.03$  for  $^{168}\text{Dy}$  and a theoretical value of 0.61, in much better agreement with the present results.

Pure quadrupole splitting is observed in the compound  $\text{NpF}_3$ . From this spectrum, and from the mixed magnetic and electric spectra of other compounds, we obtain the ratio of the quadrupole moment in the excited state to the quadrupole moment in the ground state to be  $Q^*/Q = 1.0 \pm 0.1$ , in agreement with the value given by Stone and Pillinger.<sup>18</sup> This is further confirmation that the deformation changes very little in the transition between the two states.

EPR measurements have been performed<sup>18</sup> on neptunyl ions in aqueous solutions. The hyperfine spectra have been analyzed in terms of the spin Hamiltonian

$$\mathcal{H} = A S_z' I_z + B (S_x' I_x + S_y' I_y) + P [I_z^2 - \frac{1}{3} I(I+1)],$$

where  $S'$  is the effective spin associated with an electronic Kramers doublet and  $I$  is the nuclear spin in the ground state. The values obtained for the hyperfine-interaction terms are  $A = -0.16547 \text{ cm}^{-1}$ ,  $|B| = 0.01782 \text{ cm}^{-1}$ , and  $P = 0.03017 \text{ cm}^{-1}$ . The values obtained from the Mössbauer spectrum of the neptunyl compound  $\text{K}_3\text{NpO}_2\text{F}_5$  (see Table II) are found to be  $|A| = 0.127 \text{ cm}^{-1}$  and  $P = +0.025 \text{ cm}^{-1}$ . The system is magnetic at the low temperature where the spectrum was taken. As a result, the term in  $B$  gives no hyperfine splitting. Because of the symmetry of the magnetic hyperfine splitting, the sign of  $A$  is not determined. One sees that the values for the magnitude of the hyperfine interactions are in general agreement with Eisenstein and Pryce.<sup>18</sup>

The positive quadrupole interaction is in agreement both with the EPR data and with a nuclear polarization

experiment by Hanauer, Dabbs, Roberts, and Parker.<sup>19</sup> The fact that  $P > 0$  has an important consequence already discussed by Roberts and Dabbs.<sup>20,21</sup> The linear "cigar-shaped" charge distribution along the O-Np-O axis in the neptunyl ion, assumed by Eisenstein and Pryce,<sup>18</sup> leads to a negative intrinsic quadrupole moment for the ground state of  $^{237}\text{Np}$ . However, the resulting negative nuclear deformation implied by this disagrees strongly with the established  $^{237}\text{Np}$  level scheme, as well as with the magnetic moments. Furthermore, the Mössbauer experiments show that the sign of the ground-state quadrupole moment is equal to the sign of the 59.6-keV level quadrupole moment. The 59.6-keV state in  $^{237}\text{Np}$  has the same Nilsson state as the ground state of  $^{241}\text{Am}$ , for which a quadrupole moment of +4.9 b has been given.<sup>21</sup> Thus, rather than taking the quadrupole moment to be negative, one should take the charge distribution around the neptunyl ion to be toroidally shaped. This in turn will require a revised model for bonding in the neptunyl ion.

### CONCLUSION

The Mössbauer resonance in  $^{237}\text{Np}$  has been used in an investigation of isomer shifts and hyperfine interactions in Np compounds. Although the best linewidth thus far obtained is 15 times the natural width, well resolved spectra are obtained due to the large interaction energies and larger isomer shifts. One should note that this linewidth in  $^{237}\text{Np}$  corresponds to an effective lifetime of  $\sim 4$  nsec (15 times smaller than the true lifetime). Therefore, the even-even  $2^+ \rightarrow 0^+$  transitions, having lifetimes  $t_{1/2} \sim 0.3$  nsec, should also show resolved hyperfine structure and detectable isomer shifts.

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