expect the more general Hamiltonian

$$H=\sum J_{ij}\mathbf{s}_{1i}\cdot\mathbf{s}_{2j}$$

to be required in the case of Mn^{++} pairs in ZnS:MnS, where experimental results have been analyzed on the basis of the simple exchange Hamiltonian.[36] In this case, also, the order of the spin levels in the excited state appears to be opposite to that in the ground state in the sense that a high-spin level lies lowest in the metastable excited state, whereas the low-spin level lies lowest in the ground state.

ACKNOWLEDGMENTS

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Nuclear Gamma-Ray Resonance Study of Hyperfine Interactions in ^{238}U†

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Nuclear γ-ray resonance (the Mössbauer effect) has been observed in ^{238}U using the 44.7-keV transition from the first excited state (2^+) to the ground state (0^+). The γ rays were obtained from the α decay of ^{242}Pu. The source material (PuO_2) gave a single emission line having a width of about 40 mm/sec, which is roughly 1.5 times the natural linewidth. Absorption spectra were taken in the temperature region between 77 and 4.2°K using the following absorbers: UO_2, UC, UF_4, $(UO_2)(NO_3)_2\cdot 6H_2O$, UO_3, UFe_2, and α-uranium metal. Several compounds showed partially resolved hyperfine spectra. In UO_2 the resonance line broadens by a factor of 2 when cooling from 77 to 4.2°K. By fitting a pure magnetic hyperfine spectrum to the widened line, a hyperfine field of 2700±200 kOe was deduced, using $g(2^+)=g_R=0.25$. The resonance in $(UO_2)(NO_3)_2\cdot 6H_2O$ can be explained by a pure electric quadrupole interaction of $e^2qQ=-6100\pm 225$ MHz. The isomer shift between U^{4+} and U^{6+} compounds is smaller than 2 mm/sec, thus giving a limit for the relative change in nuclear charge radius of $|\delta\langle r^2\rangle/\langle r^2\rangle|\leqslant 10^{-5}$.

I. INTRODUCTION

Nuclei of the actinide elements fall into the second region of strong nuclear deformation ($A\geqslant 220$). Because of the deformation, the lowest nuclear levels are collective in nature with rather small excitation energies. In particular, the rotational excitation energy is about 50 keV, and for this reason a large number of actinide nuclei are favorable isotopes for nuclear γ-ray resonance (Mössbauer-effect) experiments. However, a difficulty not encountered in other regions of the Periodic Table is that these nuclei are unstable, hence the absorbers will also be radioactive, and this limits substantially the number of possible candidates. The most favorable isotope for nuclear gamma-ray resonance (NGR) is the 59.6-keV resonance of ^{237}Np ($\tau_n=63$ nsec), which to the present has been the only actinide isotope extensively studied. In that high-resolution case, detailed information can be obtained due to the large hyperfine interactions and the extremely large isomer shifts.[1,2]

There is considerable interest in obtaining NGR spectra in ^{238}U because of the widespread work on uranium systems by other techniques. The appropriate γ ray here comes from the $0+\longrightarrow 2+$ transition at 44.7 keV.

As in all $E2$ transitions, the lifetime is rather short (in this case 0.23 nsec). This results in relatively poor energy resolution as compared with most NGR isotopes. However, the internal fields were expected to be large in uranium, and it seemed worthwhile to attempt the resonance measurements.

Coulomb excitation provides one method for obtaining a source of the desired γ rays. However, in many cases the technique is not simple. We have failed during the last three years in attempts to observe NGR absorption in ^{235}U using both 4-MeV α particles and 35-MeV ^{16}O bombardment ions, despite an abundance of 45-keV γ rays. The group at Johns Hopkins has been able to see the ^{238}U resonance after Coulomb excitation with 3-MeV α particles, and to observe some sign of hyperfine splitting.[3] Nonetheless, it is still quite desirable to find a radioactive source for the ^{238}U γ rays.

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The only radioactive decay populating the 44.7-keV state of ^{238}U is the α decay of ^{242}Pu. Results with ^{237}Np show that recoil-free emission is possible after α decay. However, the half-life in ^{238}U is about 300 times faster than that in ^{237}Np, and it was not obvious that sources could be found in which recoil aftereffects do not hopelessly blur the resonance. We have found that such difficulties are not serious, and in this paper we report NGR measurements in ^{238}U obtained with the α decay of ^{242}Pu.

II. EXPERIMENTAL DETAILS

The decay scheme[4] of ^{242}Pu is shown in Fig. 1. The only excited state appreciably populated is the 44.7-keV level in ^{238}U. This state is fed by 24% of the decays, with essentially all of the remaining going to the ^{238}U ground state. The long half-life of 3.79×10^5 yr in ^{242}Pu results in a very low specific activity of 2×10^8 disintegrations/sec g for the source. This disadvantage cannot be offset by simply using more source material as electronic absorption of the 44.7-keV γ ray limits the source thickness to 70–100 mg/cm^2. In addition, the γ intensity is severely reduced by a strong internal-conversion process in the 44.7-keV transition. The internal-conversion coefficient has not been measured; however, a value of 607 ± 29 has been given[5] for the 45.3-keV transition in ^{236}U. Correcting for the slight energy difference, one finds $\alpha_T=660\pm30$ for the total conversion coefficient of the 44.7-keV transition in ^{238}U. For a 1-in.-diam source containing 450 mg of ^{242}Pu, a total intensity of only 3.3×10^4 γ rays per sec (into a full 4π sr) can be expected. Using a large area detector so close that the solid angle factor is 1/60, and allowing for 60% electronic absorption in the absorber, and 50% detection efficiency in the Ge(Li) detector, one anticipates merely 110 counts/sec.

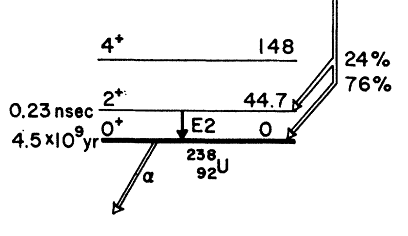

FIG. 1. Decay scheme of ^{242}Pu.

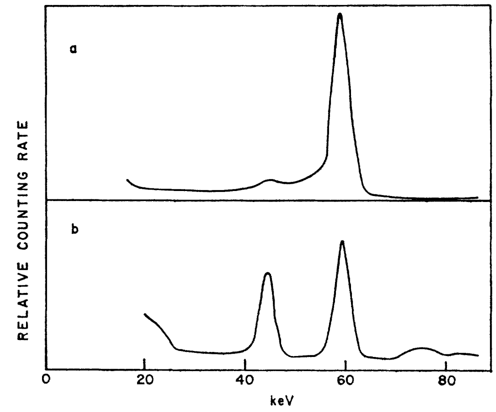

FIG. 2. γ-ray spectrum of ^{242}Pu obtained with Ge(Li)-detector: (a) before, (b) after chemical separation of americium.

The large conversion coefficient causes another problem by reducing the resonance absorption cross section to about the same size as the electronic absorption in uranium. Even at 4°K in a crystalline environment corresponding to a Debye temperature $\Theta_D\approx150$°K, an absorber of 100 mg/cm^2 of ^{238}U has an effective NGR thickness $t\approx1$. Any reduction in this effective thickness, such as would be caused by a lower Debye temperature or a hyperfine splitting of the absorption line, cannot be compensated by increasing the number of absorber atoms. If one attempts to do so, the mass absorption of the γ ray decreases the counting rate prohibitively.

The best isotopic purity of ^{242}Pu obtainable from the AEC contains 0.003% ^{238}Pu, 0.02% ^{239}Pu, 0.08% ^{240}Pu, and 0.01% ^{241}Pu. These other isotopes will give background radiation,[4] which must be considered here. The α decay of ^{238}Pu goes 28% of the time to the 43.5-keV level in ^{234}U. Since the half-life of ^{238}Pu is about 3000 times shorter than the half-life of ^{242}Pu, even a contamination of tenths of a percent of ^{238}Pu will dilute the 45-keV line severely. Similarly, ^{239}Pu gives a 51.6-keV line, and ^{240}Pu gives a 45.3-keV line, both of which will affect the usable counts in the γ-ray window. By far the most serious contamination is ^{241}Pu. This isotope undergoes β decay with a half-life of 13 yr into ^{241}Am. This in turn undergoes α decay with a half-life of 458 yr into ^{237}Np and produces a 59.6-keV γ ray which, arising from an $E1$ transition, has a low conversion coefficient ($\alpha_T\simeq1$). The net result is that the dominant radiation from any sample of ^{242}Pu is the 59.6-keV transition in ^{237}Np.

In order to adequately resolve the 44.7- and the 59.6-keV γ lines, a lithium-drifted silicon or germanium detector is necessary. Since useful sources have a rather large diameter for the reasons discussed above, detectors having areas of the order of 10 cm^2 are

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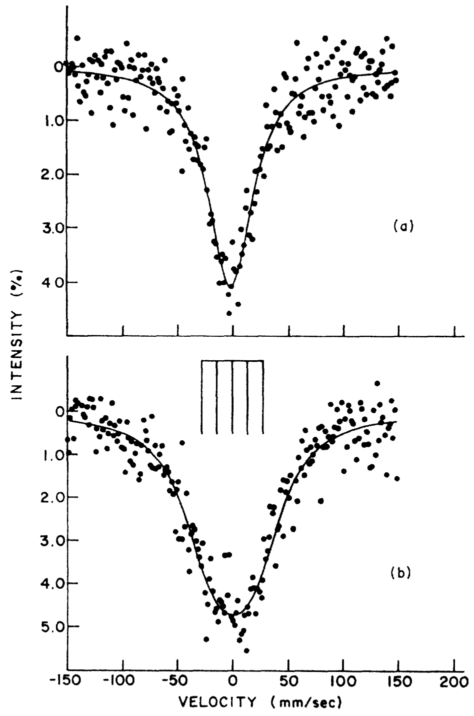

FIG. 3. Nuclear γ-ray resonance spectrum of UO_2 at 77°K (a) and at 4.2°K (b). The analysis into five magnetic hyperfine lines is indicated by the bar diagram.

required, which limits the resolution to $\sim$3 keV. This in itself would not be serious; however, detectors with thin windows tend to have large tails on the low-energy side of the photopeak when used for low-energy γ rays, and this produces a basic difficulty. Figure 2(a) shows the γ-ray spectrum of the ^{242}Pu available to us. This was obtained with a 1-cm-thick 4$\times$4-cm Ge(Li) detector having a resolution of about 4 keV and an efficiency of 85% at 45 keV. The 59.6-keV peak is roughly 50 times more intense than the 44.7-keV peak, and the resulting low-energy tail makes the 44.7-keV line barely discernible. Since such a source is not usable, a chemical separation of Am from Pu was necessary.

In the γ-ray spectrum of the cleaned ^{242}Pu source, shown in Fig. 2(b), the 44.7-keV line is practically free of background. Since the ^{241}Am is being constantly bred in, it is necessary to repeat the separation roughly once every three months. This requires the chemical form of the Pu source to be obtained from solution, and so excludes metallic sources at the present time.

The most favorable compound for a source is PuO_2, which has the cubic CaF_2 structure[6] and is nonmagnetic.[7] About 350 mg of PuO_2 were packed into a Lucite disk of 25 mm diam and sealed into a brass container having a 2-mil brass window. The ^{238}U absorbers have only a very weak radioactivity, and so could be handled nearly as normal material. Absorbers were generally pressed into 33-mm-diam Lucite disks, with a thickness of 70 mg/cm^2 of uranium.

Measurements were performed with both sources and absorbers at 77 and 4.2°K. The glass Dewar used was similar to one previously described,[1] the main difference being a 2-in.-diam Mylar window at the bottom of the helium container to allow a high transmission of the 45-keV γ ray. Cryostats of this type will run unattended for up to 70 h after a 3-l filling of liquid ^{4}He. Data were collected in a 400-channel analyzer, using a velocity spectrometer of the Kankeleit type.[8] The count rate in the channel was 80 cps with a signal-to-background ratio of about 3.5:1. The solid angle between source and detector was 2%, causing an average velocity smearing of $\pm 2\%$. Data were analyzed using a least-squares-fitting program, as previously described.[1]

III. RESULTS

Measurements have been obtained with two different sources of PuO_2. Except for a difference in the relative intensities of the 44.7 and 59.6-keV radiation, thus causing a different background in the 45-keV counting channel, the two sources gave similar results. The minimum linewidth (full width at half-maximum) obtained was 48 mm/sec, using a PuO_2 source and UO_2 absorber at 77°K. After correction for geometrical broadening, this gives $2\Gamma_{\rm expt}=42$ mm/sec. The source width did not change from 77 to 4.2°K. Using the accepted half-life of 0.23 nsec for the 45-keV state,[4] one obtains the natural linewidth to be $2\Gamma_n=27$ mm/sec, about $\frac{2}{3}$ narrower than the observed width. Whether this broadening is connected with the preceding α decay or is due to imperfections in the UO_2 and/or PuO_2, cannot be decided at the present time. However, it is clear that nonmetallic compounds are usable sources for ^{238}U despite the α decay and the short nuclear lifetime. Such is not the case for ^{237}Np. A possible explanation for this difference may be found in the fact that isomer shifts are not observable in ^{238}U (see below), whereas they are quite large in ^{237}Np. The resonance absorption is about 5% at 4.2°K. This is the value one expects for a Debye temperature $\Theta_D \simeq 150$°K under the present experimental conditions. No evidence was found for a reduction in the recoil-free fraction caused by a "heat spike" from the preceding α decay.[9]

Typical spectra are shown in Figs. 3 and 4. Approximately 5×10^4 counts per channel were obtained in each run. The following absorbers have been investigated: uranium dioxide (UO_2), uranium trioxide (UO_3), uranium monocarbide (UC), uranium tetrafluoride (UF_4), uranyl nitrate $[(UO_2)(NO_3)_2\cdot 6H_2O]$,

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TABLE I. NGR results for ^{238}U in Several compounds.

Compound	Temperature (°K)	Baseline counts/ channel	Intensity[a] (%)	FWHM (mm/sec)	$g_{ex}H_i$ (mm/sec)	$\frac{1}{4}e^2qQ$ (mm/sec)	S[b] (mm/sec)
UO_2	78	61K	4.0±0.2	48±3	···	···	2±3
	4.2	60K	7.0±0.2	45±1	14.5±1.0	···	1±1
UF_4	4.2	86K	4.6±0.2	45±4	···	20±1	1±1
UC	4.2	78K	3.3±0.1	55±3	···	···	0.5±1.0
$(UO_2)(NO_3)_2 \cdot 6H_2O$	4.2	55K	4.3±0.2	47±2	···	−42±2	3±1
$(UO_2)(NO_3)_2$ in H_2O	4.2	88K	2.5±0.2	50±6	···	−47±3	−3±2
UO_3	4.2	128K	3.0±0.2	60±6	···	40±2	−2±2
α-U	78	74K	2.7±0.2	48[c]	···	−19±2	1±1
	4.2	68K	5.1±0.2	48[c]	···	−21±1	1±1
UFe_2	4.2	137K	2.0±0.1	48[c]	4 ±3	···	2±2

[a] Total absorption amplitude of all lines in the presence of hf splitting.
[b] Isomer shift relative to PuO_2 source.
[c] Width was constrained to value listed for the analysis.

uranyl nitrate in frozen aqueous solution, α-uranium metal, and UFe_2. The experimental results are summarized in Table I.

IV. DISCUSSION

A. Tetravalent Uranium Compounds

Tetravalent ionic uranium compounds are expected to have either a $5f^2$ or $6d^2$ electronic configuration. Of the compounds containing the tetravalent uranium ion, UO_2 has been most extensively studied. Neutron diffraction results[10] show that an antiferromagnetic transition occurs at 30.8°K. This transition is first order, with no observable change in the lattice parameters. The magnetic structure consists of ferromagnetic planes coupled antiferromagnetically, with a magnetic moment per uranium ion between 1.7 and 1.8 μ_B. The experimental form factor rules out a $6d^2$ configuration and can only be explained by a $5f^2$.

The NGR spectra (Fig. 3) show a broadening of the resonance line while cooling from 77 to 4.2°K, which may well be due to a magnetic hyperfine interaction. However, the low-temperature spectrum is not well resolved and some assumptions have been made for the analysis. We assume that no hyperfine interaction is present above the transition temperature, and that below that temperature there exists only a single magnetic hyperfine field with no electric quadrupole interaction at the uranium site. The latter assumption is justified by the cubic (CaF_2) crystal structure.[11] However, even in cubic symmetry a quadrupole interaction may be induced in magnetically ordered transition-metal compounds owing to the spatial alignment of the electronic orbital momentum. This effect can be clearly seen[12] in the cubic neptunium compounds $NpAl_2$ and NpC; however, the quadrupole splitting found there is very small compared to the magnetic splitting and would be undetectable with the resolution available in ^{238}U. In addition, no asymmetry is seen in the UO_2 resonance spectrum, as would be so if quadrupolar coupling were present. We have, therefore, analyzed for a single magnetic interaction. In that case the $I=0$ ground state remains unsplit, and the $I=2$ excited state splits symmetrically into five levels. The resulting spectrum consists of five equally spaced lines having equal intensity. A computer fit of such a spectrum to the UO_2 data gives a magnetic interaction energy $g_{ex}H_i = 14.5 \pm 1$ mm/sec and a width of 45±7 mm/sec for each line. This fit seems reasonable in view of the linewidth of 48±3 mm/sec obtained in the paramagnetic state, where the spectrum should be a single line. The resulting line positions are shown in Fig. 3.

To obtain the magnetic field at the nucleus (H_i), it is necessary to assign a value to g_{ex}. If we interpret

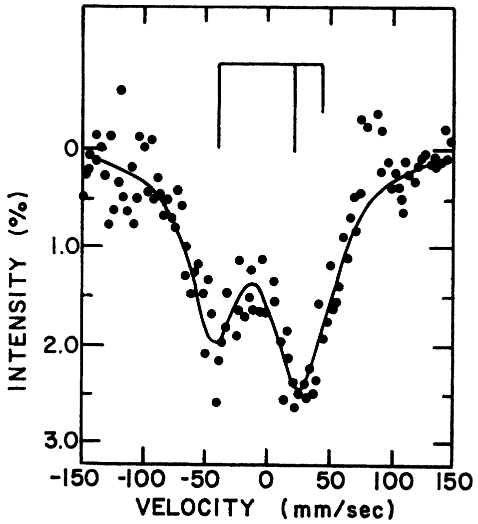

FIG. 4. Nuclear γ-ray resonance spectrum of $(UO_2)(NO_3)_2$ $6H_2O$ at 4.2°K. The spectrum is analyzed as a pure quadrupole splitting. The bar diagram shows the positions of the hyperfine components.

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the 2^+ level as a pure rotational excitation, the gyromagnetic ratio should be given by the rotational contribution alone: $g_{ex}=g_R$. In the simple model of a rigid rotator, $g_R=Z/A$. A more detailed calculation by Nilsson and Prior[13] leads to somewhat lower values. In the first region of strong deformation, these results are in satisfactory agreement with experimental results, but no comparison with experiment exists in the second region of strong deformation. Taking Nilsson and Prior's value $g_R=0.25$ for ^{238}U, we obtain $H_i=2700 \pm 200$ kOe for the magnetic hyperfine field in UO_2 at 4.2°K.

As stated above, the ionic configuration of U^{4+} is $5f^2$. We take for this configuration $\langle r^{-3}\rangle=7.82$ a.u. as obtained from nonrelativistic Hartree-Fock calculations.[14] Then the orbital contribution to the magnetic hyperfine field will be about $(H_i)_{orb}\approx 5200$ kOe. Using the optically measured[15] core polarization for Am^{2+} ($5f^7$), and proceeding in analogy with the $4f$ series,[16] we may estimate the contribution of the core polarization to the hyperfine field in actinide ions to be $H_c\approx -625(g-1)J$. For $U^{4+}(5f^2)$, this leads to $(H_i)_c\approx 500$ kOe, making the total free-ion field about 5700 kOe. This is roughly twice the observed value. A similar discrepancy exists for the atomic magnetic moments. Assuming Hund's rules, the magnetic moment should be $3.58\mu_B$. This agrees well with the value $3.20\mu_B$ obtained for $Pr^{3+}(4f^2)$, but is roughly twice the value of $1.7\mu_B$ obtained for $U^{4+}(5f^2)$ in UO_2. The reduced size of the moment, and hence also of the hyperfine field, are presumably due to the effects of crystalline-field and exchange-field splittings on the electronic ground state.[17] It thus seems plausible that fields roughly twice as large may be found in other tetravalent uranium compounds. It is interesting to note that the hyperfine fields obtained[1,2] in Np^{5+} compounds, which also have nominally the $5f^2$ configuration, are 5500 to 6000 kOe, which is much closer to the free-ion value. Unfortunately, no information on the Np^{5+} ionic moment is presently available.

So far none of the other U^{4+} compounds measured show a magnetic splitting. Uranium monocarbide, which is cubic (NaCl structure), gives an unsplit resonance line at 4.2°K. This is in agreement with magnetic susceptibility measurements which show no magnetic transition above 4.2°K.[18,19] Uranium tetrafluoride gives a slightly broadened resonance. Since it has the orthorhombic ZrF_4 structure,[6] we expect an electric field gradient (efg) at the nucleus. The observed spectrum can be fully accounted for with a pure quadrupole interaction $e^2qQ=2900\pm150$ MHz.

B. Hexavalent Uranium Compounds

The free U^{6+} ion should have a closed-shell configuration ($5f^0$). Therefore, hexavalent uranium compounds are not expected to have magnetic moments. The uranyl ion $(UO_2)^{++}$ has been studied by EPR[20] and by optical methods,[21] and indeed shows a temperature-independent paramagnetism. Because of its closed-shell configuration, the uranyl ion itself does not give an EPR signal, and the investigations were done on uranyl compounds doped with $(^{237}NpO_2)^{++}$. For this reason, a direct comparison between the EPR and NGR results are not possible. However, it is known that a large axially symmetric field gradient acts at the uranium site, so the uranyl compounds should provide good absorbers for investigating pure quadrupole interactions.

Under the influence of a rotationally symmetric field gradient, the 2^+ state splits into three hyperfine levels positioned at $+A$, $-0.5A$, and $-A$ relative to the unsplit energy, where $A=\frac{1}{4}e^2qQ$. The resulting spectrum consists of three lines at these energies having relative intensities 2:2:1, respectively. Since this spectrum is not symmetric, the sign of the quadrupolar coupling can be determined. However, in order to determine q, the efg at the nucleus, one must know the nuclear quadrupole moment Q.

As mentioned before, ^{238}U is a strongly deformed nucleus having a well-developed band of rotational levels. From the reduced matrix element $B(E2)$ obtained either by Coulomb excitation or by the radioactive decay rate of the 2^+ level, the intrinsic quadrupole moment of the ground-state band has been determined to be $Q_0=10.52\pm0.48$ b.[22,23] A determination using muonic x rays[24] gives $Q_0=11.25\pm0.15$ b, in satisfactory agreement; however, the first value is probably more reliable. Using $Q_0=10.5$ b, we obtain the spectroscopic quadrupole moment of the 2^+ state $Q(2^+)=-3.0$ b, according to the transformation scheme for strong coupling.

The NGR spectrum of the uranyl compound $(UO_2)(NO_3)_2\cdot 6H_2O$ can be fitted assuming an axially symmetric quadrupole interaction, with a coupling parameter $e^2qQ=-(169\pm6)$ mm/sec$=-6100\pm225$ MHz. The width of each hyperfine line is 47 ± 7 mm/sec, again in good agreement with the width obtained from paramagnetic UO_2. A frozen aqueous solution of uranyl

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nitrate was also investigated. Within the limits of error, it gave a resonance spectrum identical with the solid compound. In order to test the reliability of the negative sign of e^2qQ, a fit was also made by forcing a positive quadrupolar interaction. Although the interaction energy remained essentially the same, the fit was substantially worse and χ^2 was increased by about 30%. Using the quadrupole moment of -3 b, we obtain the efg $q[(\mathrm{UO_2})^{++}]=+8.5\times10^{18}$ V/cm^2.

It is of interest to compare this result with an NGR measurement of the neptunyl ion[2] which gives[25] $q[(\mathrm{NpO_2})^{++}]=12\times10^{18}$ V/cm^2. Assuming that the neptunyl ion consists of a single $5f$ electron in addition to the uranyl core, we may write

$$q[(\mathrm{NpO_2})^{++}]=q[(\mathrm{UO_2})^{++}]+(1-R_Q)q_{5f}\,,$$

where R_Q is the Sternheimer shielding factor. This separation seems well justified in the light of optical and EPR spectroscopy. In both of these cases, experimental data are well described by assuming the electronic configuration of the $(\mathrm{NpO_2})^{++}$ ion to be a single $5f$ electron. Taking $R_Q\approx0.25$, we obtain for the efg due to single $5f$ electron

$$q_{5f}=5\times10^{18}\ \mathrm{V/cm^2}\,.$$

According to Ref. 20, this can be expressed as

$$q_{5f}=\tfrac{2}{3}a\langle r^{-3}\rangle\,,$$

where $a=9.75\times10^{17}$ V/cm^2 a.u. We thus obtain $\langle r^{-3}\rangle$ for $\mathrm{Np^{6+}}(5f^1)$ to be ≈9 a.u. This number is in general agreement with values which have been calcuated for actinide ions.[14] However, it should be noted that those calculations are nonrelativistic, and have not been done for this particular configuration.

Note added in proof. Relativistic Dirac-Fock calculations by J. B. Mann (private communication) give $\langle r^{-3}\rangle=8.5$ a.u. for the $\mathrm{Np^{6+}}$ ion.

Data have also been obtained for the hexavalent uranium compound $\mathrm{UO_3}$. Uranium trioxide (α phase) forms a hexagonal lattice in which the uranium ion is coordinated with eight nearest-neighbor oxygen atoms.[26] Along the c axis, one obtains a chain of the form —O—U—O—U—O, which closely resembles a chain of uranyl ions. The other six oxygen atoms are roughly symmetrically arranged in a plane perpendicular to the c axis. In the uranyl compound $(\mathrm{UO_2})(\mathrm{NO_3})_3\cdot6\mathrm{H_2O}$, the basal plane coordination is very similar, with four of the oxygen atoms being supplied by the two nitrate groups and the other two oxygen atoms coming from two of the six waters of hydration.[27] The NGR spectrum of $\mathrm{UO_3}$ gives a quadrupole interaction of $+5800\pm200$ MHz, which is of the same magnitude as in the uranyl, but of opposite sign. As pointed out above, the efg in hexavalent uranium compounds is not due to valence electrons, but is produced by the lattice (and bonding electrons if covalency effects are present) multiplied by a Sternheimer factor. Thus the efg in $\mathrm{U^{6+}}$ compounds will be very sensitive to fine details of crystal structure.

C. Isomer Shifts

Within the limits of error, no isomer shifts (ΔS) were detected between the tetravalent source and the hexavalent absorbers. Given the accuracy of the measurements, we may take $\Delta S\leqslant2$ mm/sec. This result may be used to obtain a limit for the change in nuclear charge radius $\delta\langle r^2\rangle$ between the ground 0^+ state and the rotationally excited 2^+ state. From nonrelativistic Hartree-Fock calculations, we obtain the change in electron density at the nucleus per $5f$ electron to be

$$\Delta|\psi_0|^2=1.05\times10^{26}\ \mathrm{cm^{-3}}\,.$$

Using the correction S' for the relativistic enhancement of the electron density, as discussed by Shirley,[28] one can write

$$\frac{\delta\langle r^2\rangle}{\langle r^2\rangle}=0.13\times10^{26}\frac{(\Delta S)E_\gamma}{ZS'(\Delta|\psi_0|^2)A^{2/3}}\,.$$

With $S'=13$ and $|\Delta S|\leqslant2$ mm/sec for the shift between $5f^2$ and $5f^0$, we obtain the limit

$$|\delta\langle r^2\rangle/\langle r^2\rangle|\leqslant10^{-5}\,.$$

This value is somewhat below the size of the change in charge radius found[29] for the well-developed rotational excitations in the first region of strongly deformed nuclei (^{158}Gd to ^{182}W). This is expected, since the rotational excitation energy is lower in the second deformed region, and so the influence of centrifugal stretching will be even less observable. {*Note added in proof.* Calculations by E. R. Marshalek [Phys. Rev. Letters **20**, 216 (1968)] provide a theoretical basis for the conclusions reached here concerning the change in nuclear charge radius. Those calculations show that values of $\delta\langle r^2\rangle/\langle r^2\rangle$ in heavy rare-earth nuclei are roughly an order of magnitude larger than in actinide nuclei. For ^{238}U, the theoretical value is 0.75×10^{-5}, in excellent agreement with the present estimate.} To summarize, the change in $\langle r^2\rangle$ is very small (less than 1/300 of the value for ^{57}Fe) and the short lifetime creates a broad line. The result then is that isomer shift data will not be good enough to study chemical bonding, covalency effects, etc.

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[25] From Ref. 2, we obtain $e^2qQ=240$ mm/sec for $\mathrm{Rb(NpO_2)}\times(\mathrm{NO_3})_3$. To obtain the efg we have taken the neptunium quadrupole moment to be $Q(\frac{5}{2}^+)=4$ b.

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TABLE II. Hyperfine parameters for several uranium compounds at 4.2°K.

Compound	H_i(kOe)	e^2qQ(MHz)
UO_2	2700 ± 200	...
UF_4	...	$+2900\pm150$
$(UO_2)(NO_3)_2\cdot6H_2O$	...	-6100 ± 225
UO_3	...	$+5800\pm300$
α-U	$\leqslant300$	-2800 ± 300
UFe_2	$\leqslant300$	...

D. Metallic Compounds

The question of magnetism in α-uranium has been discussed for some time. Measurements of transport properties, such as resistivity and Hall effect, show a transition at 43°K[30]; however, the nature of this transition is still unclear. Measurements of the elastic moduli[31] in a single crystal of α-uranium are interpreted to show a crystallographic phase transition ($\alpha \rightarrow \alpha_0$) with very little change in the lattice parameters; this would explain the absence of a peak in the specific heat at the transition. Recent susceptibility measurements[32] on a single crystal rule out an earlier suggestion[33] of the formation of a localized, randomly oriented magnetic moment of $0.04\mu_B$. However, these measurements cannot choose between three other possible mechanisms: oriented magnetic moments having a small net magnetization, spin-density waves, or a temperature-dependent band structure associated with a crystallographic phase transition.

The NGR spectrum of α-uranium does not change between 77 and 4.2°K, although it is slightly broadened at all temperatures. This broadening can be explained by a quadrupole coupling $e^2qQ = -2750\pm300$ MHz due to the low site symmetry. From these data, we can further conclude that no magnetic hyperfine field larger than ~300 kOe is present in α-uranium. If we assume a linear relationship between hyperfine fields and atomic moments, then a comparison with the UO_2 data shows that this field corresponds to a moment $\mu \simeq 0.15\mu_B$. This sets an upper limit on the moment per uranium atom if an ordered magnetic structure is present. By a similar argument, if a static spin-density wave is present, the hyperfine field produced would seem to be unusually small. A phase change like the proposed α/α_0 transition is compatible with our result since the change in lattice parameters is small and would cause only a small variation of the efg.

We have also investigated the cubic Laves phase compound UFe_2, which is known to become ferromagnetic at 195°K.[34] NGR measurements of the 14.4-keV resonance in ^{57}Fe have been previously done[35] and show a poorly resolved complex hyperfine spectrum, arising from the two nonequivalent Fe sites. The internal magnetic field at the iron nucleus is $\simeq60$ kOe. The NGR spectrum of ^{238}U in UFe_2 gives a single line having a linewidth close to the minumum observed with our source. This places a limit on the internal field of $H_i \leqslant 300$ kOe, and if we again transform this into a magnetic moment on the uranium ion we obtain $\mu \leqslant 0.15\mu_B$. A very recent polarized neutron investigation[36] at 84°K obtained a magnetic moment of $0.38\mu_B$ for the Fe atom and $0.03\mu_B$ for the U atom.

V. CONCLUSION

NGR experiments with the 44.7 keV of radiation of ^{238}U using a source of ^{242}Pu have been described. Several compounds containing the U^{4+} and U^{6+} ion, as well as α-U metal and UFe_2 have been investigated. The resolution obtained is limited, but moderately accurate measurements of the hyperfine interactions can be made on compounds having large internal fields. The hyperfine coupling parameters have been interpreted using values for the nuclear moments obtained from the theory of strongly deformed nuclei. The internal fields thus obtained are summarized in Table II. No isomer shifts were detected owing to the very small change in nuclear charge radius present for a pure rotational transition.

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