

THE ACTINIDE (5*f*) GROUP

6.1. Ions and compounds of the actinide group

ALTHOUGH Bohr had suggested as early as 1923 that another paramagnetic group might occur at the upper end of the periodic table, with electrons in the 5*f* shell, it was not until much later that the point at which such a series started became clear. In a review of the evidence Seaborg (1949) postulated that the 5*f* series starts with actinium as the analogue of lanthanum, thorium that of cerium, etc., the closed shells of electrons corresponding to a radon core. Later Dawson (1952), on the basis of magnetic data, suggested that at the start of the series the magnetic electrons occupied 6*d* states rather than 5*f*, but it is now accepted that this interpretation is incorrect (see, for example, Bleaney (1955)). The number of unpaired electron spins is shown in Table 6.1 for the ions where the evidence is most complete. These electrons occupy the 5*f* states, and at 7 electrons (Am^{2+} , Cm^{3+}) we reach the half-filled shell; presumably the shell would be complete with 14 electrons at the tripositive ion of element 103. Measurements on the heavier ions are, of course, very difficult because of the high level of radioactivity, and magnetic resonance measurements have been confined to the lighter members of the group. Since most of the isotopes are α -particle emitters, radiation damage is heavy, causing magnetic resonance spectra to deteriorate rapidly in a single crystal, or even to be unobservable immediately after crystal growth. Ionic radii and some other data for the first half of the actinide group are given in Table 6.2.

In the solid state the tripositive ions have been studied mainly in the compounds LaCl_3 and $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, which have been extensively used in work on the lanthanide group. The site symmetry is C_{3h} (see the discussion in the previous chapter) and analysis of the results is similar to that for the 4*f* group. Uranium ions have been incorporated into CaF_2 , and its analogues, where charge compensation results in magnetic resonance spectra that show tetragonal or trigonal symmetry as well as cubic symmetry.

The actinide ions in higher valency states have been studied in compounds that are, in the main, different from those of the 4*f* group. The two sets of compounds of greatest importance have regular octahedral symmetry at the actinide ion site. In the gas phase the molecules UF_6 , NpF_6 , and PuF_6 have a structure in which the metal

TABLE 6.1

Number of unpaired electron spins for the principal ions of the actinide group. In addition the complex ions $(\text{UO}_2)^{2+}$, $(\text{NpO}_2)^{2+}$, $(\text{PuO}_2)^{2+}$ have 0, 1, and 2 unpaired electron spins respectively. For these ions, as for those in the table, the unpaired electrons occupy the 5f states

	0	1	2	3	4	5	6	7
Thorium	Th ⁴⁺							
Protoactinium	Pa ⁵⁺	Pa ⁴⁺						
Uranium	U ⁶⁺		U ⁴⁺	U ³⁺	U ²⁺			
Neptunium		Np ⁶⁺		Np ⁴⁺	Np ³⁺			
Plutonium			Pu ⁶⁺		Pu ⁴⁺	Pu ³⁺		
Americium							Am ³⁺	Am ²⁺
Curium								Cm ³⁺

atom is at the centre of a regular octahedral arrangement of six fluorine atoms, the metal to fluorine distances being 0.1996, 0.1981, and 0.1971 nm respectively. A magnetic resonance experiment shows that cubic symmetry is preserved in the solid state for NpF_6 (Hutchison and Weinstock 1960). Some quadrupositive ions have been studied in the diluted state in the compounds Cs_2ZrCl_6 and $[(\text{CH}_3)_4\text{N}]_2\text{PtCl}_6$, in each

TABLE 6.2

Some data for ions in the first half of the actinide series

Tripositive ions			Quadrupositive ions			
Z	Ion	Ionic radius (nm)	Spin-orbit coupling (cm ⁻¹)	Ion	Ionic radius (nm)	Spin-orbit coupling (cm ⁻¹)
90	Th ³⁺ , 5f ¹	0.108		Th ⁴⁺ , 5f ⁰	0.095	
91	Pa ³⁺ , 5f ²	0.106		Pa ⁴⁺ , 5f ¹	0.091	1490 ASJ
92	U ³⁺ , 5f ³	0.104	1666 CW 1659 GCCN	U ⁴⁺ , 5f ²	0.089	1800 JSSW
93	Np ³⁺ , 5f ⁴	0.102	2070 CW 1969 GCCN	Np ⁴⁺ , 5f ³	0.088	
94	Pu ³⁺ , 5f ⁵	0.101	2292 CW 2260 GCCN	Pu ⁴⁺ , 5f ⁴	0.086	
95	Am ³⁺ , 5f ⁶	0.100	2548 CW 2605 C	Am ⁴⁺ , 5f ⁵	0.085	
96	Cm ³⁺ , 5f ⁷		2948 CW 2842 GCCN			

The ionic radii are from Evans (1964); the other references are

ASJ Axe, Stapleton, and Jeffries (1961).

CW Carnall and Wybourne (1964), Wybourne (1964).

GCCN Gruber, Cochran, Conway, and Wong (1966).

JSSW Johnston, Satten, Schreiber, and Wong (1966).

C Conway (1964).

of which the metal ion is at the centre of a regular octahedron of chlorine ions.

The actinide series differs also from the lanthanide series in the formation of complex ions such as the uranyl ion $(\text{UO}_2)^{2+}$ and its analogues $(\text{NpO}_2)^{2+}$ and $(\text{PuO}_2)^{2+}$. These ions are linear, of the form $\text{O}-\text{U}-\text{O}$, with a rather short distance for the $\text{U}-\text{O}$ bond which provides evidence for a covalent type of bonding. Uranyl sodium acetate, $(\text{UO}_2)\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_3$ is cubic, with four (UO_2) groups per unit cell whose axes lie along the threefold axes of the cube; paramagnetic resonance has been observed in the plutonyl salt (Hutchison and Lewis 1954). A salt that has been used more extensively is uranyl rubidium nitrate, $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$. This salt is hexagonal and all the (UO_2) groups lie parallel to the c -axis, surrounded by three nitrate groups in the equatorial plane, making the c -axis a threefold axis for each (UO_2) group. Paramagnetic resonance has been observed in the neptunyl and plutonyl ions present in dilute form in uranyl rubidium nitrate (Bleaney, Llewellyn, Pryce, and Hall 1954*a, b*) and the properties of these ions have been the subject of a detailed theoretical study by Eisenstein and Pryce (1955, 1956).

6.2. Tripositive actinide ions

Optical studies have been made of a number of the tripositive ions of the actinide group, mostly incorporated in crystals of LaCl_3 . An analysis of these results together with data obtained on ions in solution shows that the behaviour is similar to that of the 4f group except that the spin-orbit coupling is considerably larger, as can be seen from a comparison of Tables 6.2 and 5.3. Two sets of values are given for the tripositive ions, which illustrate the spread in the experimental values.

The electrostatic parameters such as F_2 are rather smaller than in the 4f group, as can be seen from Tables 6.18, 6.19 in Wybourne (1964), so that departures from LS -coupling are much more pronounced. For example, Conway (1964) finds that in the ground multiplet $5f^6, {}^7F$ of Am^{3+} the level $J = 1$ lies 2720 cm^{-1} above $J = 0$, and $J = 6$ lies 12350 cm^{-1} above $J = 0$. Thus these two splittings are in the ratio 2:9.1 instead of the ratio 2:42 that is appropriate to pure LS -coupling, a departure that is far greater than those given in Table 5.2 for the corresponding 4f⁶ ions. It follows that intermediate coupling is an important factor in interpreting any resonance results; however no analysis of the crystal field will be attempted here and the resonance results given below summarize mainly the spin Hamiltonian parameters.

$5f^3$, U^{3+} in $LaCl_3$

The resonance results for this substance have been fitted to the usual spin Hamiltonian for effective spin $S = \frac{1}{2}$ with axial symmetry; they are summarized in Table 6.3.

The g -values are remarkably close to those ($g_{\parallel} = 4.00$, $g_{\perp} = 1.76$) measured for the corresponding ion $4f^3$, Nd^{3+} in $LaCl_3$, a result which in itself strongly suggests that the resonance is due to a doublet split off by the crystal field from a ground state characterized fairly accurately

TABLE 6.3

Spin Hamiltonian parameters for U^{3+} in $LaCl_3$

$ g_{\parallel} = 4.153(5)$, $ g_{\perp} = 1.520(2)$ Hutchison, Llewellyn, Wong, and Dorain (1956)		
	Isotope 233 ($I = \frac{5}{2}$)	Isotope 235 ($I = \frac{7}{2}$)
$ A_{\parallel} $	$378.6(12) \times 10^{-4} \text{ cm}^{-1}$	$176(1) \times 10^{-4} \text{ cm}^{-1}$
$ A_{\perp} $	$123.6(10) \times 10^{-4} \text{ cm}^{-1}$	$58.5(5) \times 10^{-4} \text{ cm}^{-1}$
$ P_{\parallel} $	$9.9(10) \times 10^{-4} \text{ cm}^{-1}$	$5.5(5) \times 10^{-4} \text{ cm}^{-1}$
	Bleaney, Hutchison, Llewellyn, and Pope (1956)	Dorain, Hutchison, and Wong (1957)

as $5f^3$, $^4I_{\frac{3}{2}}$. The ratio $(A_{\parallel}/A_{\perp})/(g_{\parallel}/g_{\perp})$ is 1.12, which is also very close to that for Nd^{3+} in $LaCl_3$, and suggests that crystal field strength and spin-orbit coupling are roughly in the same ratio as for Nd^{3+} . The nuclear spins of $\frac{5}{2}$ for isotope 233 and $\frac{7}{2}$ for isotope 235 are clearly established from the hyperfine structure, the ratio of the nuclear moments being $\mu_I^{235}/\mu_I^{233} = 0.66$. The quadrupole interaction is measured by observation of the 'forbidden' hyperfine lines that appear when the external magnetic field is not along the symmetry axis (cf. § 3.9). The values of P_{\parallel} are very much larger than in the case of Nd^{3+} , and the correction for the pseudo-quadrupolar interaction ΔP_{\parallel} which was quite important for Nd^{3+} (§ 4.8) should be quite small for U^{3+} . Thus the ratio of the quadrupole moments, $Q^{235}/Q^{233} = 1.17(20)$ should be quite accurate. As in the case of Nd^{3+} , the lattice may make a substantial contribution to the electric field gradient at the nucleus, since the anti-shielding factor γ_{∞} is likely to be larger for U^{3+} as well as $\langle r^{-3} \rangle$, which would increase the gradient due to the f -electrons.

 $5f^7$, Cm^{3+} in $LaCl_3$, and $La(C_2H_5SO_4)_3 \cdot 9H_2O$

This ion is expected to be in an $^8S_{\frac{7}{2}}$ state, like Gd^{3+} , where crystal field effects produce splittings only through higher-order effects. Abraham, Judd, and Wickman (1963) have shown that some spectra attributed earlier to Cm^{3+} must be due to Gd^{3+} ; they find that only a

single anisotropic resonance line is visible, with the following g -values:

$$\begin{array}{lll} \text{Cm}^{3+} \text{ in } \text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3, 9\text{H}_2\text{O} & |g_{\parallel}| = 1.925(2) & |g_{\perp}| = 7.73(2), \\ \text{Cm}^{3+} \text{ in } \text{LaCl}_3 & |g_{\parallel}| = 1.925(2) & |g_{\perp}| = 7.67(2). \end{array}$$

Since g_{\perp} is very close to $4g_{\parallel}$, this must correspond to the transition $|+\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ of $S = \frac{7}{2}$ split by an axial term $D\{S_z^2 - \frac{1}{3}S(S+1)\}$ (or $B_2^0\{3S_z^2 - S(S+1)\}$) which is large compared with the frequency at which resonance is observed ($\sim 0.3 \text{ cm}^{-1}$). The value of g_{\parallel} should be equal to the g -value of the free ion, and its rather low value is due to a fair degree of intermediate coupling, being in reasonable agreement with that calculated from the wave-functions

$$0.8884 |^8S\rangle + 0.4197 |^6P\rangle - 0.0909 |^6D\rangle + \dots$$

suggested by Carnall and Wybourne (1964) (see also Gruber, Cochran, Conway, and Nicol (1966)). The larger degree of intermediate coupling means that we should also expect the crystal field splittings to be much larger for Cm^{3+} than for Gd^{3+} , in agreement with experiment. A proportionate increase in line-width for the other transitions due to crystal imperfections would also be expected, and the damage due to the high radioactivity would readily make such lines too broad to be observed.

6.3. Actinide ions in CaF_2

The electron spin resonance and optical spectra of several actinide ions have been studied in CaF_2 and isomorphic crystals, partly in a search for suitable laser crystals.

$5f^4$, U^{2+} ; $5f^3$, U^{3+} and $5f^2$, U^{4+} in CaF_2

Magnetic resonance was observed by Bleaney, Llewellyn, and Jones (1956) due to uranium in CaF_2 and SrF_2 ; the spectra showed axial symmetry about a fourfold axis with the following g -values:

	Uranium		Neodymium	
	$ g_{\parallel} $	$ g_{\perp} $	$ g_{\parallel} $	$ g_{\perp} $
CaF_2	3.501	1.866	4.412	1.301
SrF_2	3.433	1.971	4.289	1.505

(Errors: ± 0.008 in g_{\parallel} , ± 0.002 in g_{\perp} .)

The similarity of the results suggests that the ions are U^{3+} , Nd^{3+} . A fluorine hyperfine structure was observed in the U^{3+} spectrum, but not in the Nd^{3+} spectrum, suggesting that the $5f$ electrons take part in an appreciable amount of covalent bonding.

Title *et al.* (1962) have reported resonance lines whose angular variation can be fitted to that of a Γ_8 quartet in cubic symmetry, which would be expected as the ground state for $5f^3$ in the cubic field of CaF_2 ; however the observed g -values have not been interpreted, and do not seem to correspond to those expected from simple crystal field theory using the calculations of Lea, Leask, and Wolf (1962), though this is perhaps not surprising.

A number of asymmetrical lines typical of non-Kramers doublets with $g_{\perp} < 0.1$ and axial symmetry about a threefold axis have also been observed in CaF_2 doped with uranium and, for comparison, with praseodymium. The values of g_{\parallel} are

- (a) $g_{\parallel} = 5.65(1)$ McLaughlan (1966) Pr^{3+} , $4f^2$, 3H_4 .
- (b) $g_{\parallel} = 5.83(1)$ McLaughlan (1966) Pr^{3+} , $4f^2$, 3H_4 .
- (c) $g_{\parallel} = 5.66(2)$ McLaughlan (1966) U^{4+} , $5f^2$, 3H_4 .
- (d) $g_{\parallel} = 4.02(1)$ McLaughlan (1966) U^{4+} , $5f^2$, 3H_4 .
- (e) $g_{\parallel} = 3.238(5)$ Yariv (1962); Title *et al.* (1962).

The first three lines are so similar in the value of g_{\parallel} that they are assigned to f^2 ions, where the 3H_4 manifold is split by the trigonal field to give as ground state the non-Kramers doublet (cf. eqn (5.67))

$$\alpha | \pm 4 \rangle \pm \beta | \pm 1 \rangle + \gamma | \mp 2 \rangle.$$

For this doublet the maximum possible value of g_{\parallel} is $8 \langle J \| \Lambda \| J \rangle$ (corresponding to $\alpha = 1$, $\beta = \gamma = 0$); this maximum is 6.4 for f^2 , 3H_4 but only 4.8 for f^4 , 5H_4 , so that the lines cannot be due to $5f^4$, U^{2+} ions. The last value (e), also ascribed to $5f^2$, U^{4+} ions by the authors quoted, is assigned to $5f^4$, U^{2+} by Hargreaves (1967).

In the absence of local charge compensation, an f^2 , 3H_4 ion in the purely cubic field of CaF_2 may have as ground state (see Lea, Leask and Wolf (1962)) a Γ_8 triplet with an isotropic $\tilde{g} = 2$ and an effective spin $\tilde{S} = 1$. Such an isotropic line has been observed by McLaughlan (1967), and the line (d) above is attributed to a $|+\tilde{1}\rangle \leftrightarrow |-\tilde{1}\rangle$ transition for such a triplet split by a trigonal distortion, the $|\tilde{0}\rangle$ level lying higher by some 7 cm^{-1} (McDonald 1969; Wetsel and Donoho 1965).

$5f^7$, Am^{2+} and Cm^{3+} in CaF_2

The magnetic resonance spectra of these ions at sites of cubic symmetry in CaF_2 have been observed by Edelstein and Easley (1968). At low field strengths a single resonance line with an isotropic g -value of $(-)4.492$ is observed for $^{244}\text{Cm}^{3+}$, but at higher field strengths (frequencies of 35 GHz) some anisotropy is found. Similar results are

TABLE 6.4

Magnetic resonance results for the Γ_6 doublet of the 3S_2 state split by a cubic field in CaF_2 (Edelstein and Easley 1968). Similar but slightly smaller values of $(-)\cdot 4\cdot 484(2)$ and $(-)\cdot 4\cdot 475(2)$ have been obtained for $^{244}\text{Cm}^{3+}$ in ThO_2 and CeO_2 respectively (Abraham, Finch, and Clark 1968)

Ion	$g(\Gamma_6)$	I	$ A $ (cm^{-1})
$^{244}\text{Cm}^{3+}$	$(-)\cdot 4\cdot 492(2)$	0	0
$^{241}\text{Am}^{2+}$	$(-)\cdot 4\cdot 490(2)$	$\frac{5}{2}$	0.01837(2)
$^{243}\text{Am}^{2+}$	$(-)\cdot 4\cdot 490(2)$	$\frac{5}{2}$	0.01821(2)

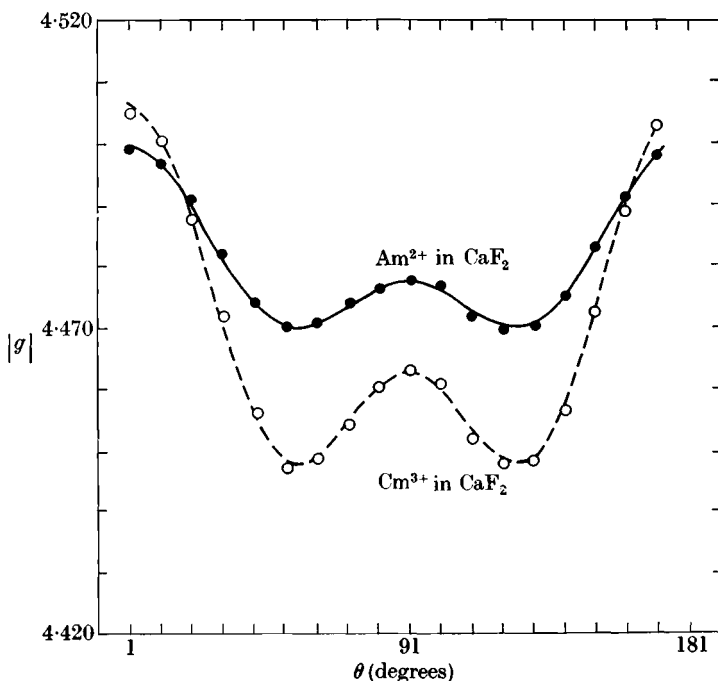


Fig. 6.1. The apparent g -factor of the Γ_6 doublet of two $5f^7$ ions on cubic sites in CaF_2 , as measured at 35 GHz. The magnetic field is rotated in an $\langle 011 \rangle$ plane, and $\theta = 0$ corresponds to a $\langle 100 \rangle$ axis. The anisotropy is due to admixture of the excited Γ_8 states by the Zeeman interaction (Edelstein and Easley 1968).

—●—●— Am^{2+} , $W(\Gamma_8) - W(\Gamma_6) = 18.6 \text{ cm}^{-1}$;
 —○—○— Cm^{3+} , $W(\Gamma_8) - W(\Gamma_6) = 13.4 \text{ cm}^{-1}$.

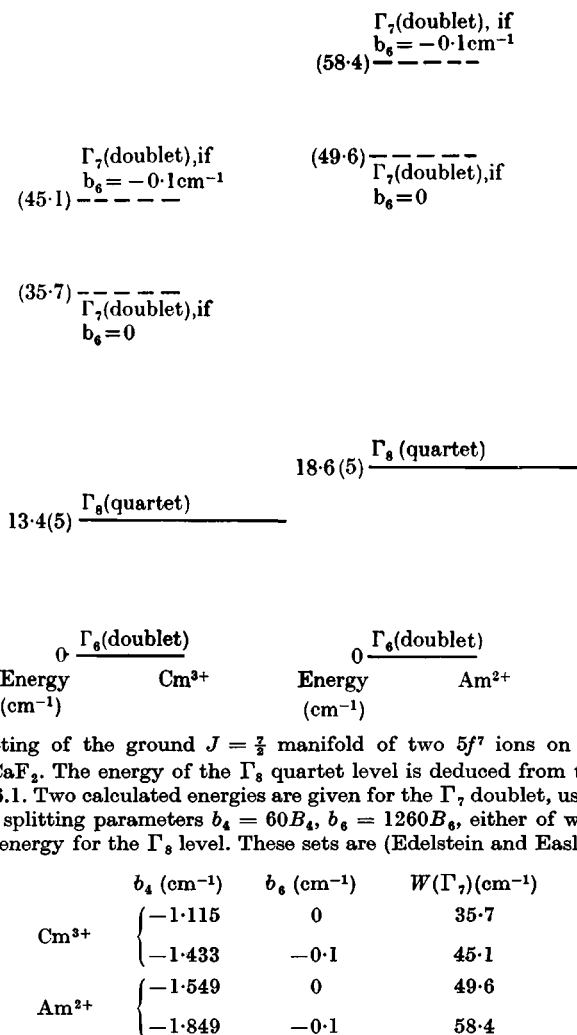


FIG. 6.2. Splitting of the ground $J = \frac{7}{2}$ manifold of two 5f⁷ ions on sites of cubic symmetry in CaF₂. The energy of the Γ_8 quartet level is deduced from the anisotropy shown in Fig. 6.1. Two calculated energies are given for the Γ_7 doublet, using two sets of values for the splitting parameters $b_4 = 60B_4$, $b_6 = 1260B_6$, either of which gives the correct energy for the Γ_8 level. These sets are (Edelstein and Easley 1968):

	b_4 (cm ⁻¹)	b_6 (cm ⁻¹)	$W(\Gamma_7)$ (cm ⁻¹)
Cm ³⁺	-1.115	0	35.7
	-1.433	-0.1	45.1
Am ²⁺	-1.549	0	49.6
	-1.849	-0.1	58.4

obtained for Am²⁺, with a hyperfine structure due to the odd isotopes 241, 243, each of which has $I = \frac{5}{2}$. The resonance is attributed to the Γ_8 doublet of an $^8S_{\frac{7}{2}}$ state with a large cubic field splitting; the effective g -value (see Table 22) is $(-\frac{7}{3})$ times the true g -value for $S = \frac{7}{2}$ at low fields, while at higher fields the anisotropy arises from admixture of the excited Γ_8 quartet by the Zeeman interaction. The energy of the Γ_8 level in zero field can be deduced from this anisotropy.

The results are listed in Table 6.4; the anisotropy is shown in Fig. 6.1 and the energy levels in Fig. 6.2. For the $S = \frac{7}{2}$ configuration the

value of g_J is deduced to be 1.9261(10) for Cm^{3+} and 1.9258(10) for Am^{2+} ; the latter is slightly smaller than the value $g_J = 1.93788(7)$ measured by Armstrong and Marrus (1966) for the free atom Am, which has the configuration $5f^7 7s^2$, $^8S_{7/2}$, but both are in good agreement with those for Cm^{3+} in C_{3h} symmetry (see § 6.2). The cubic field splittings (see Fig. 6.2) are enormously greater than those listed in Table 5.19 for the corresponding $4f^7$ ions.

6.4. Actinide ions in octahedral symmetry

We consider first the quadrivalent ions. Optical measurements on Pa^{4+} , $5f^1$ in Cs_2ZrCl_6 (Axe, reported by Raubenheimer, Boesman, and Stapleton (1965)) yields the value $\zeta = 1490 \text{ cm}^{-1}$ for the spin-orbit parameter. This is in line with values for the trivalent ions (Table 6.2) and for U^{4+} , $5f^2$ (see below). On the other hand, the fourth degree term in the crystal potential is much larger than that for trivalent actinide or lanthanide ions. For Pa^{4+} the above authors give $A_4\langle r^4 \rangle = +888 \text{ cm}^{-1}$, $A_6\langle r^6 \rangle = +42 \text{ cm}^{-1}$, and similar values are found for U^{4+} (see below).

Magnetic resonance has been observed for Pa^{4+} in Cs_2ZrCl_6 by Axe, Stapleton, and Jeffries (1961) who also measured the hyperfine structure of ^{231}Pa ($I = \frac{3}{2}$) by Endor. In an octahedral field the ground manifold of $5f^1$, $^2F_{5/2}$ is split into a doublet (Γ_7) and a quartet (Γ_8), the former lying lower (from optical measurements) by about 1900 cm^{-1} . The magnetic resonance spectrum of the doublet was fitted to the usual spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} - g^{(I)}\beta\mathbf{H} \cdot \mathbf{I} \quad (6.1)$$

with the isotropic values $|g| = 1.1423(14)$, $|A| = 1578.6(14) \text{ MHz}$, $|g^{(I)}| = 7.74 \times 10^{-4}$. After applying an 8 per cent correction for the pseudo-nuclear Zeeman effect, a value of 1.96 nuclear magnetons is obtained for the nuclear moment. The experiments show that g has the opposite sign to $g^{(I)}$, and hence also to g_I ; since the nuclear moment is expected to be positive this gives a negative sign for g (and also for A). For a pure $J = \frac{5}{2}$ manifold split by a small cubic field the g -value for the Γ_7 doublet should be $(-\frac{5}{3}) \times \langle J \parallel \Lambda \parallel J \rangle = -\frac{10}{7}$ for f^1 (cf. § 18.2 and Table 22); the observed value is rather smaller because the crystal field admixes an appreciable amount of the $J = \frac{7}{2}$, Γ_7 states into the ground doublet. In general, one can write the ground doublet as

$$\cos \alpha |J = \frac{5}{2}, \Gamma_7\rangle + \sin \alpha |J = \frac{7}{2}, \Gamma_7\rangle \quad (6.2)$$

for which

$$g = -\frac{10}{7} \cos^2 \alpha + \frac{16}{7\sqrt{3}} \cos \alpha \sin \alpha + \frac{24}{7} \sin^2 \alpha, \quad (6.3)$$

showing that g can be positive or negative according to the value of α . The hyperfine constant is

$$A = 2g_n \beta \beta_n \langle r^{-3} \rangle \left\{ -\frac{16}{7} \cos^2 \alpha - \frac{8}{7\sqrt{3}} \cos \alpha \sin \alpha + \frac{16}{7} \sin^2 \alpha - \right. \\ \left. - \kappa \left(\frac{5}{21} \cos^2 \alpha + \frac{16}{7\sqrt{3}} \cos \alpha \sin \alpha + \frac{3}{7} \sin^2 \alpha \right) \right\} \quad (6.3a)$$

where the term in κ allows for the possibility of a contribution from core polarization. An alternative approach is outlined below, in the theory for NpF_6 .

Measurements of the susceptibility of $[(\text{CH}_3)_4\text{N}]_2\text{UCl}_6$, where the U^{4+} ion is in an octahedral environment, show that it has a small temperature-independent susceptibility up to 300°K (Hutchison and Candela 1957). This is consistent with a ground term $5f^2$, 3H_4 , which in an octahedral field of the expected sign gives a Γ_1 singlet as the lowest level; the small constant susceptibility shows that the crystal field splittings are large compared with room temperature (200 cm^{-1}). Analysis of the optical spectrum (see, for example, Satten, Schreiber, and Wong (1965)) gives values of $A_4 \langle r^4 \rangle \approx 900 \text{ cm}^{-1}$, $A_6 \langle r^6 \rangle \approx 56 \text{ cm}^{-1}$, $\zeta = 1796 \text{ cm}^{-1}$; the first excited state (the Γ_4 triplet of 3H_4) lies at about 900 cm^{-1} .

The magnetic resonance spectrum of NpF_6 at dilutions of 2 and 4 per cent in UF_6 has been observed at 4°K by Hutchison and Weinstock (1960). The results are fitted to the spin Hamiltonian (6.1); g is found to be isotropic with the value $g = -0.604(3)$, the sign being determined using circularly polarized radiation (cf. § 3.2). The hyperfine structure, also isotropic, is due to the isotope ^{237}Np ($I = \frac{5}{2}$), and its value is $|A| = 0.0665(5) \text{ cm}^{-1}$. These results are consistent with a structure in which the neptunium ion is surrounded by a regular octahedron of fluorine ions, with a single electron in the $5f$ shell. This is similar to that of Pa^{4+} in Cs_2ZrCl_6 (see above, but the much smaller g -value shows that a weak crystal field approach is an even poorer approximation in this case).

The theory of NpF_6 has been considered in some detail by Eisenstein and Pryce (1960). In a cubic field the sevenfold orbital degeneracy of an f -state is lifted, giving a singlet (a_2 or Γ_2), and two triplets (t_1 or Γ_4 , and t_2 or Γ_5); the wave-functions are listed in Table 6.5. In an octahedral

TABLE 6.5

Splitting of the orbital states of an f-electron in a cubic field (Eisenstein and Pryce 1960). The wave-functions to the right are in terms of $|l_z\rangle$, and are real linear combinations of those given in Fig. 7.5. (A common factor of $\sqrt{7}$ has been omitted from the functions given in Cartesian coordinates as compared with Eisenstein and Pryce). If the orbital splitting is related to the spin operator form $B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)$, then $V = 10b_4 + 84b_6$; $V' = 18b_4 + 28b_6$, and for a single f-electron $B_4 = b_4/60 = 2A_4\langle r^4 \rangle / (11 \times 45)$, $B_6 = b_6/180 = -4A_6\langle r^6 \rangle / (11 \times 13 \times 27)$

Symmetry	Energy	Wave-functions
$t_1 (\Gamma_4)$	V'	$\begin{cases} \delta_2\rangle \equiv \frac{1}{2}x(5x^2 - 3r^2) \equiv \frac{\sqrt{3}}{4}\{ +1\rangle - -1\rangle\} - \frac{\sqrt{5}}{4}\{ +3\rangle - -3\rangle\} \\ \delta_3\rangle \equiv \frac{1}{2}y(5y^2 - 3r^2) \equiv -i\frac{\sqrt{3}}{4}\{ +1\rangle + -1\rangle\} - i\frac{\sqrt{5}}{4}\{ +3\rangle + -3\rangle\} \\ \delta_1\rangle \equiv \frac{1}{2}z(5z^2 - 3r^2) \equiv 0\rangle \end{cases}$
$t_2 (\Gamma_5)$	V	$\begin{cases} \epsilon_2\rangle \equiv \frac{1}{2}\sqrt{15}x(y^2 - z^2) \equiv \frac{\sqrt{5}}{4}\{ +1\rangle - -1\rangle\} + \frac{\sqrt{3}}{4}\{ +3\rangle - -3\rangle\} \\ \epsilon_3\rangle \equiv \frac{1}{2}\sqrt{15}y(z^2 - x^2) \equiv i\frac{\sqrt{5}}{4}\{ +1\rangle + -1\rangle\} - i\frac{\sqrt{3}}{4}\{ +3\rangle + -3\rangle\} \\ \epsilon_1\rangle \equiv \frac{1}{2}\sqrt{15}z(x^2 - y^2) \equiv \frac{1}{\sqrt{2}}\{ +2\rangle + -2\rangle\} \end{cases}$
$a_2 (\Gamma_2)$	0	$ \beta\rangle \equiv \sqrt{15}xyz \equiv \frac{1}{\sqrt{2}}\{ +2\rangle - -2\rangle\}$

field the a_2 state is lowest, since it has zero density along each fourfold axis and so avoids the negatively charged ligand ions as much as possible; the t_2 states lie next, and the t_1 states highest. In crystal field theory this is equivalent to assuming that the fourth degree terms in the octahedral potential outweigh the sixth degree terms. In terms of bonding, the a_2 orbital is non-bonding, the t_1 orbitals can form σ -bonds, and the t_2 orbitals π -bonds. If we assume that the magnetic electron occupies an anti-bonding orbital, and that σ -bonding is stronger than

TABLE 6.6

Basis functions of f^1 including spin in a cubic field (Eisenstein and Pryce 1960)

		m_j
Γ_7	$ \bar{A}\rangle = i \bar{\beta}\rangle$	$\left. \begin{array}{l} \\ \end{array} \right\} +\frac{3}{2}$
	$ B\rangle = (\frac{1}{2})^{\frac{1}{2}}[- \bar{\epsilon}_1\rangle + \epsilon_2\rangle - i \epsilon_3\rangle]$	
	$ \bar{A}\rangle = i \beta\rangle$	$\left. \begin{array}{l} \\ \end{array} \right\} -\frac{3}{2}$
	$ B\rangle = (\frac{1}{2})^{\frac{1}{2}}[\epsilon_1\rangle + \bar{\epsilon}_2\rangle + i \bar{\epsilon}_3\rangle]$	
Γ_8	$ \bar{C}\rangle = (\frac{2}{3})^{\frac{1}{2}}[-2 \bar{\epsilon}_1\rangle - \epsilon_2\rangle + i \epsilon_3\rangle]$	$\left. \begin{array}{l} \\ \end{array} \right\} +\frac{3}{2}$
	$ \bar{D}\rangle = -(\frac{1}{2})^{\frac{1}{2}}[\delta_2\rangle + i \delta_3\rangle]$	
	$ \bar{C}'\rangle = (\frac{1}{2})^{\frac{1}{2}}[\bar{\epsilon}_2\rangle - i \bar{\epsilon}_3\rangle]$	$\left. \begin{array}{l} \\ \end{array} \right\} +\frac{1}{2}$
	$ \bar{D}'\rangle = (\frac{1}{2})^{\frac{1}{2}}[2 \delta_1\rangle - \delta_2\rangle - i \delta_3\rangle]$	
	$ \bar{C}'\rangle = -(\frac{1}{2})^{\frac{1}{2}}[\epsilon_2\rangle + i \epsilon_3\rangle]$	$\left. \begin{array}{l} \\ \end{array} \right\} -\frac{1}{2}$
	$ \bar{D}'\rangle = (\frac{1}{2})^{\frac{1}{2}}[2 \delta_1\rangle + \delta_2\rangle - i \delta_3\rangle]$	
	$ C\rangle = (\frac{2}{3})^{\frac{1}{2}}[-2 \epsilon_1\rangle + \bar{\epsilon}_2\rangle + i \bar{\epsilon}_3\rangle]$	$\left. \begin{array}{l} \\ \end{array} \right\} -\frac{3}{2}$
	$ D\rangle = (\frac{1}{2})^{\frac{1}{2}}[\delta_2\rangle - i \delta_3\rangle]$	
Γ_6	$ E\rangle = (\frac{1}{2})^{\frac{1}{2}}[\delta_1\rangle + \delta_2\rangle + i \delta_3\rangle]$	$+\frac{1}{2}$
	$ E\rangle = (\frac{1}{2})^{\frac{1}{2}}[- \delta_1\rangle + \delta_2\rangle - i \delta_3\rangle]$	$-\frac{1}{2}$

The orbital functions are given in Table 6.5; the notation is that β is an orbital function combined with 'up' spin ($m_s = +\frac{1}{2}$) and $\bar{\beta}$ is an orbital function combined with 'down' spin ($m_s = -\frac{1}{2}$). The values in the column headed m_j are the values of $l_z + s_z$.

π -bonding, this gives the same order of levels as assumed above, the anti-bonding σ -orbitals t_1 lying highest, and the non-bonding orbital a_2 lowest.

When the electron spin is introduced the product wave-functions can be classified as Γ_6 (doublet), Γ_7 (doublet), and Γ_8 (quartet), where Γ_6 occurs only once, but Γ_7 and Γ_8 occur twice, as given in Table 6.6. From the energy matrices given in Table 6.7 it is clear that the ground state will be a Γ_7 doublet, which can be written as

$$\begin{aligned} |+\rangle &= \cos \theta |A\rangle - \sin \theta |B\rangle \\ |-\rangle &= \cos \theta |\bar{A}\rangle - \sin \theta |\bar{B}\rangle \end{aligned} \quad (6.4)$$

TABLE 6.7

Energy matrices for the Γ_7 (doublets), Γ_8 (quartets) and Γ_6 (doublet) states of NpF_6 . The quantities V , V' are the energies of the t_2 and t_1 levels respectively (see Table 6.5); $\sqrt{k'}$, \sqrt{k} are factors by which the amplitude of the 5f wave-functions are reduced in the t_1 and t_2 orbitals respectively. t_1 orbitals are σ -bonding, t_2 orbitals π -bonding and the remaining a_2 orbital is non-bonding (Eisenstein and Pryce 1960)

		A	B			C	D
Γ_7	A	0	$(3k)^{\frac{1}{2}}\zeta$	Γ_8	C	$V + \frac{1}{4}k\zeta$	$\frac{3}{4}(5kk')^{\frac{1}{2}}\zeta$
	B	$(3k)^{\frac{1}{2}}\zeta$	$V - \frac{1}{2}k\zeta$		D	$\frac{3}{4}(5kk')^{\frac{1}{2}}\zeta$	$V' - \frac{3}{4}k'\zeta$
E							
		Γ_6	$E \quad V' + \frac{3}{2}k'\zeta $				

whose g -value is

$$g = 2 \cos^2\theta - 4(k/3)^{\frac{1}{2}} \sin 2\theta - \frac{2}{3}(1-k) \sin^2\theta \quad (6.5)$$

if an orbital reduction factor $k^{\frac{1}{2}}$ is assumed to allow for any π -bonding in the t_2 orbitals (note that the nomenclature used by Eisenstein and Pryce differs from that normally used for bonding effects with d -orbitals). Equation (6.5) with $k = 1$ is equivalent to eqn (6.3), as can be verified by noting that in the limit of a weak crystal field the two Γ_7 states belonging to $J = \frac{5}{2}$ and $J = \frac{7}{2}$ have the form

$$\begin{aligned} J = \frac{7}{2}, \Gamma_7; & \quad \sqrt{(\frac{4}{7})} |A\rangle + \sqrt{(\frac{3}{7})} |B\rangle \\ J = \frac{5}{2}, \Gamma_7; & \quad \sqrt{(\frac{3}{7})} |A\rangle - \sqrt{(\frac{4}{7})} |B\rangle \end{aligned} \quad (6.6)$$

and

$$\begin{aligned} \cos \theta &= \sqrt{(\frac{3}{7})} \cos \alpha + \sqrt{(\frac{4}{7})} \sin \alpha \\ \sin \theta &= \sqrt{(\frac{4}{7})} \cos \alpha - \sqrt{(\frac{3}{7})} \sin \alpha. \end{aligned} \quad (6.6a)$$

In their analysis for NpF_6 Eisenstein and Pryce attempted to fit the g -value, the optical spectrum, and the temperature-independent term in the magnetic susceptibility. With $k = 1$ (and also no orbital reduction factor for the t_1 orbitals), they adopted the values

$$\zeta = 2405 \text{ cm}^{-1}, \quad V = 5442 \text{ cm}^{-1}, \quad V' = 22220 \text{ cm}^{-1},$$

which give a temperature-independent susceptibility term of 158×10^{-6} per mol, in good agreement with the value of 165×10^{-6} obtained by Hutchison, Tsang, and Weinstock (1962) for NpF_6 in UF_6 , extrapolated

to infinite dilution. These parameters are considerably larger than those for the single *f*-electron of Pa^{4+} in Cs_2ZrCl_6 of

$$\zeta = 1490 \text{ cm}^{-1}, \quad V = 1496 \text{ cm}^{-1}, \quad V' = 3656 \text{ cm}^{-1}$$

(see Raubenheimer, Boesman, and Stapleton 1965). The corresponding crystal field parameters are

$$\begin{array}{lll} \text{Pa}^{4+} \text{ in } \text{Cs}_2\text{ZrCl}_6 & A_4\langle r^4 \rangle = 888 \text{ cm}^{-1}, & A_6\langle r^6 \rangle = 41.9 \text{ cm}^{-1} \\ \text{Np}^{6+} \text{ in } \text{UF}_6 & A_4\langle r^4 \rangle = 5700 \text{ cm}^{-1}, & A_6\langle r^6 \rangle = 320 \text{ cm}^{-1}, \end{array}$$

which showed a marked rise with increasing valency. Both parameters are positive, as would be expected for an octahedral configuration.

The magnetic hyperfine constant is

$$A = -2g_n\beta\beta_n\langle r^{-3} \rangle \left\{ \frac{4}{\sqrt{3}} \sin 2\theta + \frac{1}{3}\kappa(1 + 2 \cos 2\theta) \right\} \quad (6.7)$$

and it can be verified by using eqns (6.6a) that this is identical with eqn (6.3a). The value of 2θ required to fit the experimental *g*-value of NpF_6 is 63° , for which

$$A = -2g_n\beta\beta_n\langle r^{-3} \rangle (2.06 + 0.63\kappa). \quad (6.7a)$$

6.5. Neptunyl and plutonyl ions

As mentioned in § 6.1, ions of the type $(\text{UO}_2)^{2+}$ are linear. Uranyl salts have only a temperature-independent susceptibility, suggesting that there are no unpaired electrons. The free uranium atom has a closed radon core, and six valence electrons, two of which have been lost in $(\text{UO}_2)^{3+}$. Eisenstein and Pryce (1955) postulate that the remaining electrons are used to form covalent bonds with the oxygen atoms. In a simple model which uses only σ -bonding, the six valence electrons of each oxygen are assumed to be in non-bonding orbitals formed from the $2s$, $2p$ states on the oxygens, which are thus filled. For the central uranium ion, bonding orbitals of σ -type can be formed from $5f$, $6d$, $7s$ (and perhaps $7p$) using the substates with $m_l = 0$; taking the O—U—O axis as the z -axis, this means the f , δ_1 orbital in Table 6.5, whose wavefunction $z(5z^2 - 3r^2)$ is strongly directed along the z -axis, and similarly the $(3z^2 - r^2)$ orbital belonging to the d -states. The two orbitals forming a bond with the inwardly directed sp_z orbital on each oxygen can accommodate just four electrons, which are assumed to be those originally associated with the uranium. The situation is therefore different from any considered hitherto for compounds of ions containing

f-electrons, in that we have strong bonding involving *f*-orbitals. In many respects it resembles a linear molecule (cf. Elliott 1953).

We now consider such 'actinyl' groups in the hexagonal compound $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$, where the axes of all the groups are parallel to the unique crystal axis.

$(\text{UO}_2)^{2+}$ in $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$

A strong nuclear electric quadrupole interaction with axial symmetry would be expected in this compound; this has been verified by measurements of anisotropy in the α -particle emission from ^{233}U , ^{235}U at temperatures below 1°K by Dabbs, Roberts, and Parker (1958).

$(\text{NpO}_2)^{2+}$ in $(\text{UO}_2)\text{Rb}(\text{NO}_3)_3$

The paramagnetic resonance spectrum of this compound has been measured by Bleaney, Llewellyn, Pryce, and Hall (1954b). As would be expected from the foregoing discussion, it shows strong axial symmetry, and the results have been fitted to a spin Hamiltonian with effective spin $S = \frac{1}{2}$ of the usual form with axial symmetry. The measured parameters are (see Pryce 1959)

$$\begin{aligned} g_{\parallel} &= -3.405(8), & |g_{\perp}| &= 0.205(6); \\ A_{\parallel} &= -0.16547(5) \text{ cm}^{-1}, & |A_{\perp}| &= 0.01782(3) \text{ cm}^{-1}; \\ P_{\parallel} &= +0.03015(5) \text{ cm}^{-1}. \end{aligned}$$

The hyperfine parameters are for the isotope ^{237}Np , whose nuclear spin is $I = \frac{5}{2}$. The actual signs are not determined experimentally, except for the result that A_{\parallel} , P_{\parallel} are of opposite sign. Pryce (1959) has pointed out that theoretically g_{\parallel} is negative (see below), and that A_{\parallel} should be negative provided that the nuclear magnetic moment is (as expected) positive. A negative value of A_{\parallel} and a positive value of P_{\parallel} have been confirmed by Hanauer, Dabbs, Roberts, and Parker (1961) from the temperature dependence of the anisotropy in the emission of α -particles in a nuclear alignment experiment.

The concentration of negative charge along the axis of the O—U—O complex means that any additional electron such as the extra electron in the neptunyl ion will be strongly repelled, and in the ground state it would occupy an orbital whose charge distribution is concentrated in the equatorial plane. The 5f orbitals will therefore have very different energy, according to their charge distribution. The states for which $l_z = \pm 3$ will be lowest, followed by the $l_z = \pm 2$, ± 1 and the anti-bonding $l_z = 0$ states in that order. The excited states are estimated by Eisenstein and Pryce to lie at 20000–30000 cm^{-1} , as also are the 6d

states. These splittings are large compared with the spin-orbit coupling, of order 2000 cm^{-1} , so that in a first approximation we retain only the diagonal term $\zeta l_z s_z$. Since ζ is positive for a single electron, the four states with $l_z = \pm 3$, $s_z = \pm \frac{1}{2}$ are split into two doublets, the lower doublet being that for which the axial components of orbit and spin are anti-parallel. These two states can be denoted by $j_z = l_z + s_z = |\pm \frac{5}{2}\rangle$, the other two states $|j_z = \pm \frac{7}{2}\rangle$ lying higher in energy by 3ζ . Use of the Zeeman operator $l_z + 2s_z$ shows that in this approximation the ground doublet would have $g_{\parallel} = 4$, $g_{\perp} = 0$. Such a doublet would not show a magnetic resonance line, though the similarity of the g -values to the experimental results suggests that the basic theory is correct.

We now allow for the effect of the crystal field due to other constituents, mainly the three nitrate ions symmetrically disposed in the equatorial plane. These produce a crystal field of threefold symmetry about the z -axis, of whose components V_6^0 is of vital importance because it admixes states with $l_z = \pm 3$. The ground doublet is then no longer exactly characterized by $j_z = \pm \frac{5}{2}$, but contains an admixture of the $j_z = \pm \frac{7}{2}$ states, making a resonance transition allowed. In addition off-diagonal elements of the spin-orbit coupling will admix some of the $l_z = \pm 2$, $j_z = \pm \frac{5}{2}$ states, but since the spin-orbit coupling is rather weak relative to the splitting due to the axial charge concentration, their amplitude is rather small. These two perturbations can be taken into account by writing the wave-functions of the ground doublet in terms of $|l_z, s_z\rangle$ as

$$\begin{aligned} |+\rangle &= (1+p^2+q^2)^{-\frac{1}{2}}(|-3, +\frac{1}{2}\rangle + p|+3, +\frac{1}{2}\rangle - q|-2, -\frac{1}{2}\rangle) \\ |-\rangle &= (1+p^2+q^2)^{-\frac{1}{2}}(|+3, -\frac{1}{2}\rangle + p|-3, -\frac{1}{2}\rangle - q|+2, +\frac{1}{2}\rangle) \end{aligned} \quad (6.8)$$

where q is about 0.1. Use of the Zeeman operator $l_z + 2s_z$ then gives

$$\begin{aligned} g_{\parallel} &= -(4-8p^2+6q^2)(1+p^2+q^2)^{-1} \\ g_{\perp} &= |p\{4-2\sqrt{(6)q}\}(1+p^2+q^2)^{-1}|. \end{aligned} \quad (6.9)$$

If q is fixed (and its effect is anyway rather small), the values of g_{\parallel} and g_{\perp} are related, depending only on the parameter p , and it is not possible to fit the experimental values of g_{\parallel} and g_{\perp} simultaneously. If g_{\perp} is fitted, the value of g_{\parallel} given by these equations is very close to -4 ; since most of the contribution to g_{\parallel} comes from the orbit, this suggests that an orbital reduction factor k should be introduced to allow for some covalent bonding. The g -values then become

$$\begin{aligned} g_{\parallel} &= -\{k(6-6p^2+4q^2)-2(2+2p^2-2q^2)\}(1+p^2+q^2)^{-1} \\ g_{\perp} &= |p\{4-2\sqrt{(6)kq}\}(1+p^2+q^2)^{-1}|. \end{aligned} \quad (6.10)$$

The experimental g -values can then be fitted using $k = 0.9$, $p = 0.056$.

In eqns (6.8) we have chosen as the $|+\rangle$ state that which gives a 1:1 correspondence between the matrix elements of the effective spin and of the true angular momentum $\mathbf{l} + \mathbf{s}$. This makes the sign of g_{\parallel} negative because it is dominated by the contribution from the orbit, which is opposed to the smaller spin contribution.

The theoretical expressions for the hyperfine constants given by Eisenstein and Pryce (1955) are

$$A_{\parallel} = -2g_n\beta\beta_n\langle r^{-3} \rangle \left\{ \frac{2}{3} + \frac{2}{3}\sqrt{(6)q - \frac{1}{3}p^2 + 4q^2 + \kappa(1+p^2-q^2)} \right\} (1+p^2+q^2)^{-1}$$

$$A_{\perp} = |2g_n\beta\beta_n\langle r^{-3} \rangle p \left\{ \frac{2}{3} - \frac{5}{3}\sqrt{(6)q - 2\kappa} \right\} (1+p^2+q^2)^{-1}| \quad (6.11)$$

(here the sign of A_{\parallel} has been reversed from the original, like that of g_{\parallel} ; see Pryce (1959)). With the value $q = 0.1$ assumed above, and the value $p = 0.056$ required to fit the g -values, these equations can be solved for κ and $g_n\langle r^{-3} \rangle$ using the measured hyperfine constants. To fit the anisotropy, a value of about -3.1 is required for κ , which then gives

$$g_n\langle r^{-3} \rangle = +13.7.$$

(An alternative solution, $\kappa = +120$, which leads to $g_n\langle r^{-3} \rangle = 0.4$ seems quite inadmissible.) Even if we take a value of $g_n = +2$, which corresponds to a magnetic moment close to the Schmidt limit of 4.8 n.m. for $I = \frac{5}{2}$, this result seems to give rather a large value for $\langle r^{-3} \rangle$, especially if some bonding occurs, which would tend to reduce $\langle r^{-3} \rangle$.

This result may be compared with that for NpF_6 , where a similar value of $g_n\langle r^{-3} \rangle$ might be expected. If the measured value of A is there taken to be negative, eqn (6.7a) yields the result

$$g_n\langle r^{-3} \rangle = 21/(2.06 + 0.63\kappa),$$

which would be equal to 13.7 if we take $\kappa = -0.75$. Thus to reconcile this result with that for the neptunyl ion we again need a negative value of κ , though not so large.

In the 3d and 4f groups the observed values of κ are positive but we shall not hazard a prediction of its sign for the 5f group. The theory given above for the magnetic hyperfine constants of the neptunyl ion should be accepted with reserve, since Eisenstein and Pryce (1956) have pointed out that the crystal field may contain a V_3^3 term, which could admix s -states directly to the 5f, $l_z = \pm 3$ states. This would affect the hyperfine structure in a way that cannot be represented by the addition of a κ -term, and the formulae (6.11) would no longer be correct.

The theory of Eisenstein and Pryce (1955) gives a nuclear electric quadrupole interaction

$$P_{\parallel} = -\frac{e^2Q}{I(2I-1)}\{(\frac{4}{5}\alpha - \frac{1}{2})\langle r^{-3} \rangle_{5f} + \frac{6}{7}\alpha'\langle r^{-3} \rangle_{6d}\}, \quad (6.12)$$

where α and α' are the probabilities that the bonding electrons are in the neptunyl 5f and 6d states rather than on the oxygen atoms. Since $\langle r^{-3} \rangle_{6d}$ is expected to be considerably larger than $\langle r^{-3} \rangle_{5f}$, this leads to a negative nuclear quadrupole moment for a positive value of P_{\parallel} , the field gradient at the nucleus being due mainly to the σ -bonding electrons. If there were an appreciable amount of π -bonding, this would give a contribution to P_{\parallel} of opposite sign. Shielding corrections, and lattice contributions have been omitted from (6.12).

(PuO₂)²⁺ in (UO₂)Rb(NO₃)₃

Paramagnetic resonance has been observed for this ion by Bleaney, Llewellyn, Pryce, and Hall (1954a). The line shape is asymmetrical, as expected for resonance due to a non-Kramers ion; the spin Hamiltonian parameters for a non-Kramers doublet with an effective spin of $\frac{1}{2}$ are found to be

$$|g_{\parallel}| = 5.32(2)$$

$$\text{Isotope 239}(I = \frac{1}{2}) \quad |A_{\parallel}| = 0.0862(5) \text{ cm}^{-1}$$

$$\text{Isotope 241}(I = \frac{5}{2}) \quad |A_{\parallel}| = 0.0609(4) \text{ cm}^{-1}.$$

The theory is discussed by Eisenstein and Pryce (1956). Exchange interaction between the two electrons outside the (UO₂)²⁺ type core is assumed to be strong, so that they will have parallel spin and hence must occupy different orbital states. There are then two possibilities: (a) they occupy the states $l_z = +3$ and $l_z = -3$, giving a resultant $L_z = 0$ and $S_z = \pm 1$; (b) they occupy the states $l_z = \pm 3$, $l_z = \pm 2$ with parallel spin, giving four possible states $L_z = \pm 5$, $S_z = \pm 1$, which are then split by spin-orbit coupling into two doublets, that where the spin and orbital components are anti-parallel having the lower energy. Because of the Coulomb repulsion between the two electrons, the ground state is (b), where the electrons occupy orbitals with different values of l_z . The values of $L_z + 2S_z$ for the two states of the ground doublet are then $\pm(5-2)$, so that we have $g_{\parallel} = 6$, $g_{\perp} = 0$. In the next approximation, the crystal field and spin-orbit coupling will admix some other states into the ground state wave-functions, but the amplitude of the admixtures is expected to be small and does not seriously change the value of g_{\parallel} , while g_{\perp} remains zero. To explain the

observed value of g_{\parallel} it seems necessary to introduce a reduction factor k for the orbital moment, which then gives

$$|g_{\parallel}| = 2(5k-2), \quad g_{\perp} = 0. \quad (6.13)$$

The measured value of $g_{\parallel} = 5.32$ can then be fitted with a value of k of about 0.93, which is not inconsistent with that needed to fit the corresponding neptunyl compound. Magnetic resonance has been observed by Hutchison and Lewis (1954) in another plutonyl compound, plutonyl sodium acetate; they find $g_{\parallel} = 5.92$, which would require a value of $k = 0.99$.

The magnetic hyperfine interaction arises from the 5f electrons, together with a contribution of s -like character due to core polarization and the fact that the V_3^3 term in the crystal field can directly admix s -states into the $l_z = \pm 3$ states. The two mechanisms cannot be differentiated in the present case, so that both can be combined in a single term, giving

$$A_{\parallel} = 2g_n\beta\beta_n\langle r^{-3} \rangle (\frac{3}{2} + 2\kappa) \quad (6.14)$$

with, of course, $A_{\perp} = 0$. Using the value of $-0.200(4)$ n.m. (Faust, Marrus, and Nierenberg 1965) for the nuclear moment of ^{239}Pu , a value of about 6 a.u. is found for $\langle r^{-3} \rangle$ if $\kappa = 0$, and a rather smaller value if κ is positive. A strong nuclear electric quadrupole interaction may be expected for isotopes with $I > \frac{1}{2}$, but cannot be observed in an electron spin resonance experiment. An f -electron with $l_z = \pm 2$ has

$$3l_z^2 - l(l+1) = 0,$$

so the extra electron in the plutonyl ion gives no contribution to the nuclear electric quadrupole interaction, and eqn (6.12) should apply also to the plutonyl ion.