346. *Magnetochemistry of the Heaviest Elements. Part VI.** PuO_2–ThO_2 *and* PuF_4–ThF_4 *Solid Solutions.*

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The magnetic susceptibilities of plutonium dioxide and tetrafluoride have been measured over the temperature range 90—450° K. The tetrafluoride obeys the Curie–Weiss law above 200° K but there is an upward curvature below that temperature. Measurements on solid solutions of the tetrafluoride in isomorphous thorium tetrafluoride lead to an extrapolated susceptibility at infinite dilution in agreement with a $5f^4$ electron configuration.

The susceptibility of the dioxide does not obey the Curie–Weiss law and is considerably lower than that of the tetrafluoride, but dilution in thorium dioxide shows that the susceptibility increases very rapidly between 10 atomic % and infinite dilution. The intercept at infinite dilution appears to be about the value for a $5f^4$ configuration, but some of the evidence may indicate that $6d$ levels are occupied.

ON the basis of magnetic susceptibility measurements at temperatures about 76°, 190°, and 300° K, Elliott and Lewis reported that $Rb_4Pu(SO_4)_4,2H_2O$ obeys the Curie–Weiss law, but that PuF_4 and $Pu(C_2O_4)_2,6H_2O$ show an upward curvature and $Pu(SO_4)_2,4H_2O$ shows a downward curvature away from this law [Paper 90, Symposium: Chemistry of the Actinide Elements, American Chemical Society Meeting, Chicago, September, 1950]. They noted that the observed moments were abnormally lower than the theoretical one for a $5f^4$ electron configuration but that quenching of the orbital contribution would not account for the discrepancy.

Previous experiments on uranium dioxide and tetrafluoride have shown that the technique of dilution in solid solution with an isomorphous diamagnetic compound and extrapolation of the susceptibilities to infinite dilution provides a means for better assess-

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* Part V, *J.*, 1952, 1185.

ment of the electron configuration, the result being not necessarily the one expected on the basis of measurements on the undiluted compounds (Trzebiatowski and Selwood, *J. Amer. Chem. Soc.*, 1950, **72**, 4505; Dawson, *J.*, 1952, 1185). This paper describes the results obtained by applying the same technique to plutonium dioxide and tetrafluoride.

EXPERIMENTAL

A stock solution of plutonium tetranitrate in dilute nitric acid was found by spectrographic analysis to contain negligible amounts of other elements, and the purity determined by counting and weighing an aliquot portion evaporated on to platinum foil was 100·8±2%. The absence of ferromagnetic impurities was checked further by susceptibility measurements at room temperature on the solid solutions at three field strengths: no dependence on field strength was observed.

Spectrographic analysis of a stock solution of thorium nitrate also showed negligible impurities, and a sample of thorium tetrafluoride prepared from it was found to be diamagnetic.

Aliquot portions of the plutonium and thorium nitrate solutions were mixed in quartz centrifuge tubes and the hydroxides were precipitated by addition of ammonium hydroxide. For the preparation of the oxides the tubes were centrifuged, the supernatant liquid was removed, and the tubes were placed in an oven the temperature of which was raised slowly to about 800° c. The tetrafluoride solid solutions were prepared by slurrying the hydroxides into a platinum boat which was heated to 450° c in a stream of hydrogen fluoride and oxygen in a copper furnace.

X-Ray diffraction patterns of the resulting oxides and fluorides showed that true solid solutions had been obtained. A plot of sin θ against composition for several of the most sharply defined lines showed that the plutonium percentages in the solid solutions were the same as those calculated from the amounts of stock solution taken, within the error of the measurements.

The samples (5—15 mg.) were enclosed in Pyrex capillaries and the measurements were made on the balance described in Part I of this series (Dawson and Lister, *J.*, 1950, 2177). The investigation of the effect of varying field strength was performed with the same samples on a second balance, an electromagnet being used. After the measurements, each sample container was cracked open, and the sample removed; the two parts of the container were then sealed together again and the magnetic effect on the empty container was measured.

In order to obtain the true paramagnetism of the quadrivalent plutonium ion the following diamagnetic corrections were applied: Th(IV), $31{\cdot}2 \times 10^{-6}$; Pu(IV), $40{\cdot}8 \times 10^{-6}$; O^{2-}, $11{\cdot}25 \times 10^{-6}$; F^-, $7{\cdot}25 \times 10^{-6}$. These values were calculated after the method of Angus (*Proc. Roy. Soc.*, 1932, *A*, **136**, 569), the value for Pu(IV) being a mean of the $5f^4$ and $6d^4$ electron configurations.

The experimental results and the deduced magnetic susceptibilities of the Pu(IV) ion are given in Tables 1 and 2.

TABLE 1. PuF_4–ThF_4 *Solid solutions.**

Composition: Pu, %	T, ° K	$10^6 \times \chi_g$	$10^6 \times \chi_m$	$10^6 \times \chi_{Pu(IV)}$	Composition: Pu, %	T, ° K	$10^6 \times \chi_g$	$10^6 \times \chi_m$	$10^6 \times \chi_{Pu(IV)}$
100	90	9·482	2983	3053	52·0	90	7·249	2260	4470
	201	7·384	2326	2396		201	4·949	1543	3093
	301	5·589	1760	1830		301	3·512	1095	2232
	329	5·125	1614	1684		373	2·907	906·1	1868
	370	4·677	1473	1543		442·5	2·449	763·5	1593
	415·5	4·293	1353	1423					
	453	3·984	1255	1325					
77·8	90	9·168	2874	3781	34·0	90	5·745	1784	5434
	200	6·829	2141	2839		200	3·874	1203	3727
	300	4·878	1530	2053		300	2·527	784·6	2494
	329·5	4·543	1424	1917		334	2·306	755·5	2292
	378·5	4·049	1269	1718		362	2·036	672·0	2046
	412·5	3·718	1165	1584		418	1·783	593·1	1815
	441	3·494	1095	1494		442·5	1·489	555·7	1704
					3·6	300	0·142	43·8	2900
					2·0	300	0	0	3020

* χ_g = Gram susceptibility.
χ_m = Molar susceptibility.
$\chi_{Pu(IV)}$ = Susceptibility per g.-ion corrected for diamagnetism.

TABLE 2. PuO_2–ThO_2 *Solid solutions.*

Composition : Pu, %	T, ° K	$10^6 \times \chi_g$	$10^6 \times \chi_m$	$10^6 \times \chi_{Pu(IV)}$
100	90	4·859	1317	1381
	200	3·258	883·0	946·3
	300	2·693	730·2	793·5
	333·5	2·577	698·4	761·7
	367	2·543	689·0	752·3
	406	2·426	657·3	720·6
	430	2·414	654·1	717·4
75	90	4·644	1251	1748
	200·5	2·771	746·5	1076
	300	2·168	584·0	859·8
	334·5	2·055	553·7	819·5
	372	1·942	523·0	778·5
	411·5	1·852	499·0	746·5
	446·5	1·793	482·9	725·1
	521	1·754	472·3	710·1
	592	1·675	451·2	682·7
50·0	90	3·426	943·0	1949
	199	2·034	571·1	1205
	300	1·614	458·6	980
	332	1·490	425·5	914
	372	1·436	410·9	885
	415	1·410	404·0	871
	445	1·374	394·4	852
35·3	90	2·475	659·8	2034
	200	1·548	412·5	1332
	300	1·294	344·8	1140
	328·5	1·158	308·5	1037
	371	1·117	397·6	1006
	411	1·062	283·0	965
	437	1·034	275·6	944
12·1	90	1·205	319·2	3090
	201	0·552	146·2	1660
	299	0·344	91·1	1210
	334·5	0·303	80·2	1120
	375	0·260	69·0	1020
	414	0·230	60·9	955
	462	0·194	51·3	877
8·82	300	0·280	74·1	1460
8·72	300	0·352	93·2	1580
4·31	300	0·102	26·8	1880
2·19	300	0·056	14·7	3140

DISCUSSION

The value of the dilution technique for the elucidation of the electron configuration of a paramagnetic ion lies in the fact that extrapolation to infinite dilution provides a value of the susceptibility more comparable with theoretically predicted values than that measured on the pure compounds, since the theoretical methods do not take account of any possible interaction between neighbouring ions.

The theoretical susceptibilities of the quadrivalent plutonium ion, various electron configurations being assumed and calculation being by Hund's method (*Z. Phys.*, 1925, **33**, 855), are in Table 3. Hund's method assumes that the multiplet separations are very wide compared to kT. Considering the lanthanides, Van Vleck has shown that the magnetic susceptibility may be affected by contributions from several low-lying energy states if the multiplet intervals are comparable to kT ("The Theory of Electric and Magnetic Susceptibilities," 1932, Chapter IX). His "intermediate" formula being used, and a $5f^4$ configuration being assumed with the electrons in L–S coupling, the theoretical susceptibility has been calculated at various temperatures (Table 4). Owing to the contributions from other low-lying states in addition to the predicted ground state, the theoretical susceptibility at 300° K is somewhat higher in Table 4 than in Table 3.

TABLE 3. *Theoretical magnetic susceptibilities at* 300° K (*Hund ; L–S coupling.*)

Configuration	Conditions	$10^6 \times \chi$
$5f^4$	No interaction	3,010 [a]
$5f^3 6d^1$	No orbital contribution from the 6*d* electrons	3,010
$5f^2 6d^2$		1,250
$5f^1 6d^3$		0
$6d^4$	"Spin-only" value	10,500

[a] The j–j value is about 6100×10^{-6}.

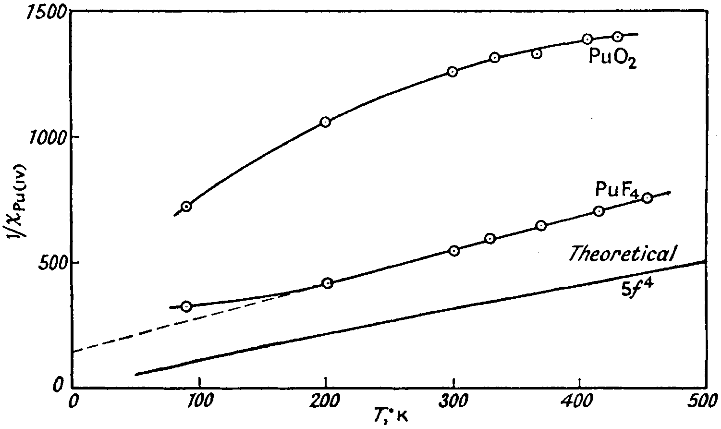
TABLE 4. *Theoretical susceptibility of* Pu(IV) *with* $5f^4$ *configuration* (*Van Vleck*).

T, ° K	50	100	200	300	400	500	600
$10^6 \chi$	17,840	9035	4632	3165	2434	2003	1724

The value of the screening constant used in the calculation was 58, this having been shown by Dawson, Mandleberg, and Davies (*J.*, 1951, 2047) to be the most probable value for plutonium. The screening constant does not have such a marked effect on the theoretical susceptibility for the Pu(IV) ion as for the Pu(III) ion. Use of the value 57 instead of 58 gives a susceptibility less than 1% lower.

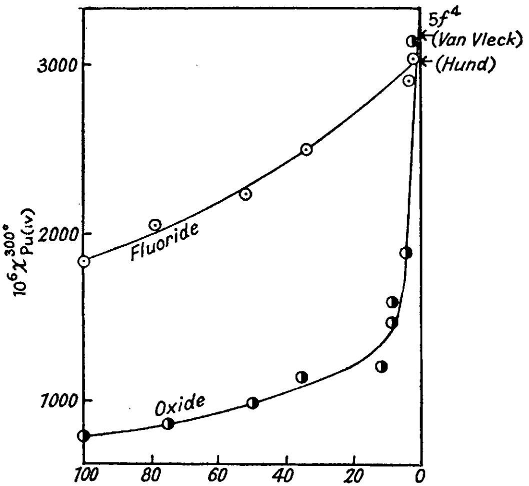
Plutonium Tetrafluoride.—The observed value of the magnetic susceptibility at 300° K (1830×10^{-6}) is somewhat lower than the value (1980×10^{-6}) quoted by Elliott and Lewis (*loc. cit.*). The variation of reciprocal susceptibility of the pure substance with temperature is shown in Fig. 1 and agrees with Elliott and Lewis's assertion that there is an upward curvature away from the straight line of the Curie–Weiss law. This occurs only below 200° K, however; above that temperature the Curie–Weiss law is a good approximation to the behaviour of the susceptibility. The theoretical curve derived from Table 4, also shown in Fig. 1, does not quite follow the Curie–Weiss law, there being a slight downward curvature scarcely visible on the reduced scale. Dilution in solid solution does not have any effect on the deviation of the experimental susceptibility at 90° K, at least down to 34% of plutonium which was the most dilute solution investigated at this temperature.

FIG. 1. *Susceptibility–temperature behaviour of* Pu(IV).



The variation of susceptibility at 300° K with plutonium concentration is shown in Fig. 2. Extrapolation to infinite dilution gives a susceptibility of about 3020×10^{-6}. This value is in reasonable agreement with that predicted for a $5f^4$ electron configuration with L–S coupling (see Tables 3 and 4). The theoretical value for a $5f^3 . 6d^1$ configuration is the same as that for $5f^4$ (Hund values) but the tetrafluoride solid solutions show no evidence of the exchange forces which would be expected from the presence of *d*-shell electrons.

FIG. 2. PuO_2–ThO_2 *and* PuF_4–ThF_4 *solid solutions.*



Direct comparison with the lanthanide series is not possible since the corresponding ion with four electrons would be Pm(III) on which no results are available. However, the tervalent praseodymium ion in the octahydrated sulphate shows an upward curvature away from the Curie–Weiss law, similar to that observed above, and Penney and Schlapp (*Phys. Review*, 1932, **41**, 194) have explained this by a consideration of the redistribution of the magnetic levels due to the effect of the crystal electric field. It is possible that the similar effect in plutonium tetrafluoride may arise in the same way.

Plutonium Dioxide.—The variation of reciprocal susceptibility with temperature of the Pu(IV) ion in the oxide lattice is quite different from that in the fluoride (Fig. 1). It is fairly closely represented over the investigated temperature range by the expression :

$$(\chi - 542{\cdot}9 \times 10^{-6})(T + 0{\cdot}14) = 0{\cdot}0756$$

This is similar to the formula used by Cabrera and Duperier (*Compt. rend.*, 1927, **185**, 414; 1929, **188**, 1640) for the susceptibility of ions of the platinum- and palladium-group elements and also of some of the lanthanides. Despite increasing dilution in thorium dioxide, this type of behaviour persists without much change down to 12% of plutonium (the most dilute solution investigated over a temperature range), which gives

$$(\chi - 276{\cdot}1 \times 10^{-6})(T + 13{\cdot}1) = 0{\cdot}2901$$

The susceptibility of the Pu(IV) ion in pure PuO_2 is considerably lower than in PuF_4 and is very low compared with the theoretical value for a $5f^4$ configuration. However, between 10% of plutonium and infinite dilution there is an extremely rapid rise in the susceptibility; in fact, it is so steep that it is difficult to fix the value of the intercept at infinite dilution. It does not appear to be as high as 10,500 × 10^{-6}, which would indicate a $6d^4$ configuration, but to be somewhere near the value to be expected for $5f^4$ or $5f^3 . 6d^1$ (Fig. 2). The above evidence might be interpreted as showing that there is a considerable amount of exchange interaction in the oxide lattice and that this persists so long as more than some critical number of lattice sites is occupied by paramagnetic plutonium ions. It is quite different from the behaviour observed in the fluoride lattice and may favour the supposition of a $5f^3 . 6d^1$ electron configuration rather than $5f^4$.

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Harwell, near Didcot, Berks.

[*Received, January* 18*th*, 1952.]