453. *Magnetochemistry of the Heaviest Elements. Part IV.* Plutonium Trifluoride and Trichloride.*

By J. K. DAWSON, C. J. MANDLEBERG, and D. DAVIES.

The magnetic susceptibilities of plutonium trifluoride and trichloride have been measured over the temperature range 90—600° K. There is a minimum between 500° and 550° K. in the susceptibility–temperature curve of the tervalent plutonium ion, and the close resemblance of this behaviour to that of the tervalent samarium ion is taken as good qualitative evidence for a $5f^5$ electronic configuration for the plutonium ion. The application of Van Vleck's method for calculating the theoretical susceptibility yields 58 as the most probable value of the spin-doublet screening constant.

IN the rare-earth series, the magnetic susceptibility of the tervalent samarium ion varies with temperature in an unusual way. Hund assumed the multiplet intervals to be large compared to kT, and calculated the magnetic susceptibilities of the rare-earth ions on this basis: his results agreed well with experiment except for samarium and europium. Van Vleck ("The Theory of Electric and Magnetic Susceptibilities," O.U.P., 1932, Chap. IX) has shown that the discrepancy can be removed satisfactorily by taking into account the possibility that in samarium and europium the multiplet intervals may be comparable with kT; the Boltzmann temperature factor enters into the calculation, and the contribution to the susceptibility of the term arising from the second-order Zeeman effect cannot then be neglected. Such an assumption accounts for the fact that the susceptibility of Sm(III) does not obey the Weiss–Curie law, and in particular that it exhibits a shallow minimum somewhat above room temperature, the exact position of which on the theoretical curves depends upon the value of the screening constant used in the calculations.

With the same number of unpaired f electrons postulated for both samarium and plutonium (Seaborg, "The Transuranium Elements," National Nuclear Energy Series, 14B, paper 21.1), their tervalent compounds might be expected to behave similarly, but no magnetic measurements have hitherto been reported on plutonium compounds over a sufficiently wide temperature range to confirm this. Howland and Calvin (U.S. Atomic Energy Commission Report, A.E.C.D. 2440) find that Pu(III) in dilute hydrochloric acid solution has a susceptibility of 370×10^{-6}, and Elliott and Lewis (American Chemical Society meeting, Chicago, September 1950) report that plutonium trifluoride has susceptibilities of 2550, 1590, and 1150×10^{-6}, at 76°, 189·5°, and 303° K., respectively (claiming that the results follow the Weiss–Curie law with $\mu = 1{\cdot}96$, $\Delta = 110°$), and that the oxalate, $Pu_2(C_2O_4)_3,9H_2O$, gives the values 1580, 850, and 620×10^{-6} at 76°, 190°, and 298° K. In the present investigation, the authors report measurements made on the Pu(III) ion in the solid fluoride and chloride over the temperature range 90—600° K.

EXPERIMENTAL.

The measurements were made on a balance described previously (Dawson and Lister, *J.*, 1950, 2177). The samples (1—10 mg.) were sealed in small Pyrex or quartz capillaries, and after the measurements these were broken open, the samples washed out, and the halves of each capillary fused together again so that the effect of the empty container could be measured. Corrections were applied for the diamagnetism of the various ions (see Angus, *Proc. Roy. Soc.*, 1932, *A*, **136**, 569). The values used were: Pu(III) = 35×10^{-6}, $Cl^- = 23 \times 10^{-6}$, and $F^- = 7{\cdot}3 \times 10^{-6}$.

Preparation of Plutonium Fluoride.—Plutonium tetraoxalate was precipitated from a pure solution of the tetranitrate by addition of oxalic acid. The centrifuged oxalate was dried by infra-red heating and transferred to a small platinum boat. A "reactive" oxide was produced by calcining it at about 600° C. in a slow stream of air, and this oxide was then allowed to react in a copper furnace at 650° C. with hydrogen fluoride containing a small partial pressure of hydrogen. The identity of the product as plutonium trifluoride was established by its *X*-ray diffraction pattern and by oxidation of a weighed amount to PuO_2; the change in weight corresponded to a fluorine content of 19·4 ± 0·2% (Calc.: 19·26%).

Preparation of Plutonium Chloride.—The reactive oxide was produced in the same way as in the preparation of the fluoride and it was then transferred to a quartz capillary tube which could be attached to a high-vacuum line. Carbon tetrachloride was used as the chlorinating agent (for details see Abraham *et al.*, National Nuclear Energy Series, 14B, p. 746).

The chloride sublimed out of the reaction zone and condensed in a cool section of the capillary where it was sealed off in a length of tube suitable for the magnetic measurements. After these had

---

* Part III, *J.*, 1951, 429.

been made, the weighed product was dissolved in dilute nitric acid and made up to a known volume in a standard flask. The solution was quite clear and had the characteristic colour of the Pu(III) ion; aliquots of this solution were evaporated to dryness and estimation by α-counting gave a plutonium content of 68·9 ± 1% (Calc.: 69·2%).

TABLE I.

Magnetic susceptibilities of PuF_3 *and* $PuCl_3$.

T, °K.	PuF_3, χ g. $\times 10^6$.	χPu(III) $\times 10^6$.	T, °K.	$PuCl_3$, χ g. $\times 10^6$.	χPu(III) $\times 10^6$.	T, °K.	$PuCl_3$, χ g. $\times 10^6$.	χPu(III) $\times 10.^6$
90	7·38	2240	90	4·35	1607	457	1·19	515
200	3·23	1014	200	2·27	887	491	1·10	484
300	2·00	651	300	1·60	658	520	1·04	464
372	1·53	508	334	1·45	606	548	1·03	462
453	1·15	398	373	1·35	571	583	1·06	472
511	0·995	351	397	1·29	548	300	1·60	659
563	1·08	375	428	1·22	525			
594	1·14	394						
300	2·00	650						

The analyses of the compounds were not in themselves sufficiently accurate to preclude the possibility of the presence of ferromagnetic impurity sufficient to make an appreciable contribution to the susceptibilities, but samples prepared from batches of plutonium nitrate solution which had been through several different purification procedures showed good agreement amongst themselves. Results from typical runs are set out in Table I. In order to check that decomposition of the samples did not take place at the highest temperature, the room-temperature reading was repeated at the end of each run.

DISCUSSION.

If there is an actinide ion with a low-lying energy term $6H_{5/2}$ and an electron configuration $5f^5$, analogous to the corresponding $4f^5$ state of Sm(III), then a similar deviation of the susceptibility from the Weiss–Curie law should exist. In this case there should be an appreciable contribution from the second-order Zeeman effect due to the multiplet intervals being comparable to $\boldsymbol{k}T$, and it is therefore necessary to use Van Vleck's general formula to calculate the theoretical susceptibility :

$$\chi = \frac{\boldsymbol{N} \sum\limits_{J=L-S}^{L+S} [g_J{}^2 \,.\, \beta^2 \,.\, J(J + 1)/3\boldsymbol{k}T + \alpha_J](2J + 1) \,.\, e^{-W_J{}^\circ/\boldsymbol{k}T}}{(2J + 1) \,.\, e^{-W_J{}^\circ/\boldsymbol{k}T}}$$

where

$$\boldsymbol{N} = \text{Avogadro's number}$$

$$g_J = [1 + J(J + 1) + S(S + 1) - L(L + 1)]/2J(J + 1)$$

$$\beta = \boldsymbol{eh}/4\pi mc = 0{\cdot}9174 \times 10^{-20} \text{ erg gauss}^{-1}$$

$$\alpha_J = \frac{\beta^2}{6(2J + 1)}\left[\frac{\mathrm{F}(J + 1)}{\boldsymbol{h}\nu(J + 1;\ J)} - \frac{\mathrm{F}(J)}{\boldsymbol{h}\nu(J;\ J - 1)}\right]$$

$$\mathrm{F}(J) = 1/J[(S + L + 1)^2 - J^2][J^2 - (S - L)^2]$$

$$W_J{}^\circ = W_J - W_{J\,\text{min.}}$$

$$\frac{1}{C}\,\Delta\nu J_{\text{max.}} - J_{\text{min.}} = \pm\,\frac{5{\cdot}82(2L + 1)}{n^3 l(l + 1)(2l + 1)} \,.\, (Z - \sigma_2)^4 \text{ cm.}^{-1}$$

$$\sigma_2 = \text{the spin-doublet screening constant}$$

The multiplet width Δν, and consequently the susceptibility derived from it, are obviously very dependent on the effect of the screening of the electrons concerned by the other electrons in the ion, as expressed by the term $(Z - \sigma_2)^4$.

A $5f^5$ electron configuration with Russell–Saunders coupling being assumed, values for the ionic susceptibility were calculated for various values of σ_2 over the temperature range 50—700° K., and the results are given in Table II.

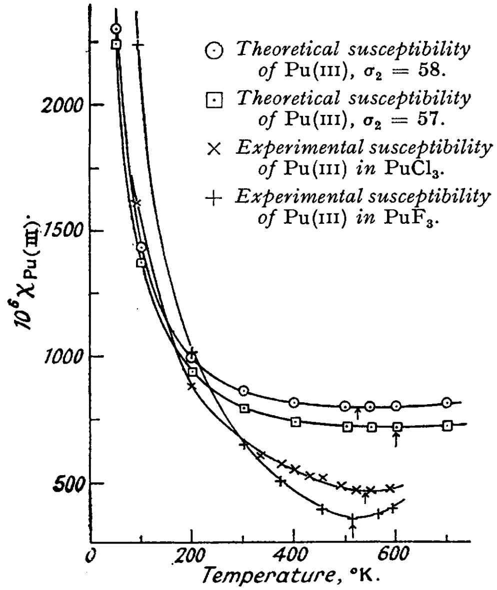
TABLE II.

Theoretical susceptibilities ($\chi \times 10^6$) *for an ion with* $5f^5$ *electron configuration.*

Screening constant σ_2 = Temp., ° K.	54.	57.	58.	59.
50	2114	2249	2306	2373
100	1241	1375	1433	1500
200	804	939	997	1065
300	659	797	860	935
400	588	739	810	896
500	551	718	796	892
550	540	714	796	895
600	533	714	799	900
700	524	718	806	911

The results for $\sigma_2 = 57$ and $\sigma_2 = 58$ are plotted in the figure, together with the experimental results on the Pu(III) ion from Table I. The theoretical curves for $\sigma_2 = 57$, 58, and 59 have shallow susceptibility minima at about 600, 530, and 480° K., respectively, whereas the experimental curves show considerably more marked minima at about 515° and 545° K. for the trifluoride and the trichloride, respectively.

The theoretical spin-only value of the magnetic moment is 5·92 Bohr magnetons, while the values obtained by Hund's method are 0·84 with Russell–Saunders coupling and 2·54 with *jj* coupling, these being independent of temperature. At room temperature the experimental moment of Pu(III) calculated from the susceptibilities by means of the formula $\mu = 2{\cdot}83\sqrt{\chi\,.\,T}$ is 1·26 in the chloride and 1·25 in the fluoride. If there is any orbital quenching due to the 5*f* electrons being less effectively sequestered than 4*f* electrons, then the moment should be higher than 0·84, becoming progressively closer to 5·92 as the quenching becomes more complete. In solution, where ionic interactions should have the least effect, Calvin, Kasha, and Sheline (National Nuclear Energy Series, 14B, paper 4.23) have found that the effective moment of Pu(III) is 1·1 Bohr magnetons. These figures may all be correlated by assuming that the Pu(III) ion has a $5f^5$ electron configuration; the "ideal" magnetic moment is 0·84, being increased to 1·1 in solution and somewhat higher in the solid compounds where the orbital interactions are greater. However, the Hund theory does not allow for any change of the moment with temperature, and in particular does not explain the susceptibility minimum above room temperature. Satisfactory correlation of theory with experiment cannot be obtained on the basis of *jj* coupling or by assuming a $5f^4 . 6d^1$ electron configuration. The Van Vleck method of calculation gives moments which are not far removed from the experimental ones, the agreement being nearest below room temperature. Table III gives the moments calculated from the susceptibilities of Table II and interpolated susceptibilities from the figure.



The similarity of the ranges of values, together with the fact that the Van Vleck calculation for a $5f^5$ configuration provides an explanation of the susceptibility minimum, may be taken as good qualitative evidence that the electronic structure of Pu(III) involves the $5f^5$ state, being closely analogous to the $4f^5$ state in Sm(III). The theoretical curve which shows a minimum susceptibility in the same temperature range as the experimental curves is the one derived by taking 58 as the value of the spin-doublet screening constant. The susceptibilities obtained by using a screening constant of 54 are in better agreement with the experimental values above room temperature but do not show a minimum in the temperature range under investigation.

If it is assumed that the theoretical curve with $\sigma_2 = 58$ is the most probable one, there remains the discrepancy that at the higher temperatures the experimental magnetic susceptibilities are lower than the theoretical ones, whereas any mechanism leading to slight orbital quenching would be expected to raise the susceptibility (towards the spin-only value). However, comparison between the molar susceptibilities of the aqueous cations of the actinide elements and those of the rare earths shows that throughout the series from one to six unpaired electrons

TABLE III.

The magnetic moment of Pu(III).

T, °K.	100	200	300	400	500
μ, $\sigma_2 = 58$	1·07	1·26	1·44	1·63	1·79
μ, PuF$_3$	1·25	1·28	1·25	1·22	1·20
μ, PuCl$_3$	1·08	1·19	1·26	1·32	1·38

those of the former are all appreciably lower than those of the latter (Howland and Calvin, *loc. cit.*).

Finally, it may be noted that the above results, where they are in the same temperature range, are in reasonable agreement with those of Elliott and Lewis on the hydrated Pu(III) oxalate but not at all with their results on plutonium trifluoride. In addition, it has been shown above that their contention that the susceptibility of plutonium trifluoride follows the Weiss–Curie law arises from the limited temperature range over which their results are quoted.

This paper was submitted in manuscript to Professor E. C. Stoner and the authors would like to express their thanks to him for his interest and for his helpful comments; however, the opinions expressed herein remain the sole responsibility of the authors.

The authors thank the Director of the Atomic Energy Research Establishment for permission to publish this paper.

A.E.R.E., HARWELL, NEAR DIDCOT, BERKS.

[*Received, March* 19*th*, 1951.]