643. *Magnetochemistry of the Heaviest Elements. Part V.* Uranium Tetrafluoride–Thorium Tetrafluoride Solid Solutions.*

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The magnetic susceptibilities of solid solutions of uranium tetrafluoride and thorium tetrafluoride have been measured over the temperature range 90—350° K., and at all dilutions the susceptibility of the U(IV) ion obeys the Weiss–Curie law. At infinite dilution the extrapolated susceptibility and the magnetic moment of U(IV) are close to the theoretical values predicted for a $5f^2$ electron configuration with the *j–j* type of coupling. This is in contrast to the corresponding oxide system in which urania is diluted with thoria, since the susceptibility and the magnetic moment of U(IV) at infinite dilution in that case correspond to theoretical values expected for a $6d^2$ electron configuration.

Magnetic susceptibility studies have been made on a considerable number of uranium compounds, and the reported magnetic moments of the U(IV) ion range from 2·7 Bohr magnetons for the chloride (Bommer, *Z. anorg. Chem.*, 1941, **247**, 249) to 3·75 for the hydrated oxalate (Hutchinson and Elliott, *J. Chem. Physics*, 1948, **16**, 920). Speculation about the electronic configuration of the U(IV) ion has favoured a $6d^2$ or a $5f^2$ stable state according to whether the observed magnetic moments have been respectively at the lower or the higher end of the observed range.

In the dioxide, the U(IV) ion has a magnetic moment of 3·20 Bohr magnetons (Dawson and Lister, *J.*, 1950, 2188). This value is intermediate between the theoretical moments calculated for the $5f^2$ and $6d^2$ electronic states, but dilution with isomorphous diamagnetic thorium dioxide produces a lowering of the moment, and the susceptibility at infinite dilution is very close to that obtained theoretically by the use of the " spin-only " formula. These facts have been taken by Trzebiatowski and Selwood (*J. Amer. Chem. Soc.*, 1950, **72**, 4504) as evidence in favour of a $6d^2$ electron configuration. The magnetic moment of uranium tetrafluoride is somewhat more remote from the " spin-only " value and nearer to the theoretical value expected for a $5f^2$ configuration (Dawson, *J.*, 1951, 429), and it was of interest to apply the dilution technique to this compound in order to determine whether the change of ionic environment from the oxide to the fluoride had any effect on the ground state of the uranous ion. The dilution was made with diamagnetic thorium tetrafluoride which is isomorphous with the uranium compound; they are both monoclinic and their cell dimensions differ by only about 3% (Zachariasen, U.S. Atomic Energy Commission Report, M.D.D.C. 1151).

Experimental.

The starting materials were commercial grades of uranyl sulphate and thorium nitrate. The uranyl sulphate was dissolved in a mixture of concentrated sulphuric acid and ethyl alcohol and reduced to the quadrivalent state by irradiation with ultra-violet light (for details, see Hutchinson and Elliott, *loc. cit.*). The insoluble uranous sulphate was centrifuged, washed with absolute ethyl alcohol, and dried in air at 80°. Analyses for uranium and sulphate led to the formula $U(SO_4)_2,3{\cdot}26H_2O$.

The solid solutions were prepared by dissolving weighed amounts of uranous sulphate and of thorium nitrate in dilute nitric acid and adding freshly distilled ammonia water. The co-precipitated hydroxides were centrifuged and washed with water distilled in quartz. Evaporation of the supernatant liquids to dryness in a weighed platinum crucible confirmed that precipitation was complete. The hydroxides were made into a sludge in a platinum boat and dried in a copper furnace at 70° in a stream of hydrogen. The fluorination was carried out in the same furnace in a stream of hydrogen fluoride and hydrogen at 500°.

Table I.

	Impurities (p.p.m.)				
Compound	Fe	Co	Ni	Cr	Mn
Uranyl sulphate	20	<4	<4	<20	<4
Thorium nitrate	<20	<10	<10	<50	<2
Uranous sulphate	20	<8	< 8	<40	<8
$U_{0{\cdot}05}Th_{0{\cdot}95}F_4$	<10	<10	10	<50	<2

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Spectrographic analyses of the materials for possible ferromagnetic contamination at various stages during the preparation are given in Table I. Magnetic measurements were restricted to one field strength only, but these amounts of ferromagnetic impurities should make only an extremely small contribution to the observed susceptibilities. The measurements were made on 2—10-mg. samples, the magnetic susceptibility balance described by Dawson and Lister (*J.*, 1950, 2177) being used. Two separate preparations were made at each dilution studied, and several samples were taken from each for the measurement of susceptibility at room temperature. The agreement was in general quite close, but there were rather wide variations in the dilute uranium solid solutions since, for instance, an error of only 0·5% on the actual measurements leads to an error of 10% in the deduced susceptibility of the U(IV) ion at 5% uranium content. The results over the temperature range 90—350° K. are given in Table II, the uranium and thorium contents being expressed as atomic percentages. Table III gives the Weiss constants of the solid solutions, obtained by plotting the reciprocal of $\chi_{U(IV)}$ against temperature, and also the effective magnetic moments calculated from the formula $\mu = 2{\cdot}83\sqrt{\chi_{U(IV)}\cdot(T + \Delta)}$.

TABLE II.

Composition, %	T, °K.	$10^6\chi_{g.}$	$10^6\chi_{m.}$	$10^6\chi_{U(IV)}$
U, 100	90	22·39	7030	7,091
	197	14·61	4588	4,649
	300	10·67	3530	3,411
	332	9·92	3117	3,176
U, 90	90	22·27	6982	7,825
Th, 10	200	13·41	4207	4,742
	301	10·01	3139	3,560
	334	9·21	2888	3,277
U, 75	90	20·60	6440	8,668
Th, 25	199	12·60	3940	5,334
	295	9·22	2881	3,922
	328	8·47	2650	3,610
U, 50	90	16·92	5261	10,640
Th, 50	200	10·11	3144	6,409
	298	7·38	2296	4,713
	334	6·62	2060	4,241
U, 25	90	10·26	3177	12,950
Th, 75	199	5·94	1839	7,579
	300	4·24	1314	5,497
	328	3·76	1165	4,901
U, 11	90	5·66	1748	16,430
Th, 89	200	2·822	871·2	8,475
	303	1·837	567·0	5,701
	355	1·579	487·5	4,979
U, 5·3	90	2·903	895·6	18,040
Th, 94·7 ...	199	1·437	443·3	9,501
	300	0·936	288·8	6,586
	330·5	0·814	251·1	5,874

$\chi_{g.}$ = Gram-susceptibility.
$\chi_{m.}$ = Molar-susceptibility.

TABLE III.

U, %	100	90	75	50	25	11	5·3
Δ	102	90	80	68	55	22	25
μ	3·30	3·34	3·43	3·68	3·93	3·86	4·12

Samples of pure thorium tetrafluoride were prepared by the same method and gave a molar diamagnetic susceptibility of 59 × 10^{-6}. This is very close to the theoretical value calculated by Angus's method, 60 × 10^{-6} (*Proc. Roy. Soc.*, 1932, *A*, **136**, 569), which was taken as the diamagnetic correction for 100% ThF_4. The value 61 × 10^{-6}, calculated by the same method, was taken as the diamagnetic correction for 100% UF_4.

DISCUSSION.

The values of the susceptibility of uranium tetrafluoride in Table II are a little higher than those already reported by the author (*loc. cit.*). This is believed to be due to a small amount of UO_2F_2 in the commercial sample used previously. This had some effect on the Weiss constant but the deduced magnetic moments are essentially the same—3·28 previously and 3·30 in the present communication. This is also in agreement with the value 3·30 reported by Elliott (*Physical Rev.*, 1949, **76**, 431), who gives the somewhat higher Weiss constant of 147°, however.

The solid solutions all obey the Weiss–Curie law over the temperature range studied, and the values of the Weiss constant, the effective magnetic moment, and the susceptibility of U(IV) at 300° K. are plotted against composition in Fig. 1. Their behaviour is different from that observed in the oxide solid-solution system as shown in Fig. 2.

Trzebiatowski and Selwood (*loc. cit.*) obtained their oxide solid solutions by co-precipitating ammonium diuranate and thorium hydroxide, followed by simultaneous ignition and reduction at 1200° in hydrogen. The present author in collaboration with Dr. M. W. Lister obtained results on the same system starting from the mechanically mixed oxides which were compressed into pellets and made homogeneous by ignition to about 2400° in a vacuum furnace. The agreement with Trzebiatowski and Selwood's results is good, and the two sets taken together show that the moment of the U(IV) ion is definitely dependent on concentration, the value falling from 3·20 in 100% UO_2 to about 3·0 Bohr magnetons at infinite dilution.

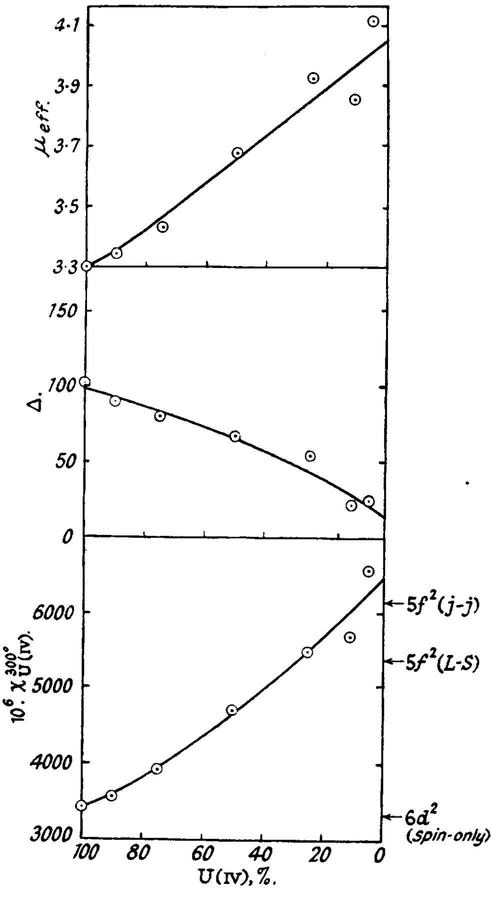
On the other hand, in the fluoride solid solution system the effective moment of the U(IV) ion rises from 3·30 in 100% UF_4 to about 4·05 at infinite dilution. The possible theoretical values which may be obtained by using Hund's formula, $\mu = g\sqrt{J(J + 1)}$ are:

Electronic configuration	Ground state	Effective moment: *L–S* coupling	*j–j* coupling	spin only
$5f^2$	$3H_4$	3·58	3·84	2·83
$6d^2$	$3F_2$	1·63	1·96	2·83

Thus it appears that at infinite dilution the magnetic moment is close to the theoretical value for two 5*f*-shell electrons in *j–j* coupling. This point is brought out even more clearly from a consideration of the susceptibility curve where the complication due to the inclusion of a Δ value does not arise. At infinite dilution, the extrapolated susceptibility of U(IV) at 300° K. is about 6360 × 10^{-6}, the theoretical value for a $5f^2$ configuration in *j–j* coupling being 6140 × 10^{-6}, compared with the theoretical values of 5390 × 10^{-6} and 3330 × 10^{-6} for a $5f^2$ configuration in *L–S* coupling and the spin-only value to be expected from a $6d^2$ configuration, respectively (in the oxide system, the extrapolated susceptibility is about 3550 × 10^{-6} in agreement with the " spin-only " value). At 90° K., the extrapolated suceptibility at infinite dilution is equal, within the limits of experimental error, to the theoretical value of 20,500 × 10^{-6} calculated for a $5f^2$ configuration with *j–j* coupling (the " spin-only " value being 11,100 × 10^{-6} at this temperature).

FIG. 1.

UF_4–ThF_4. *Solid solutions.*



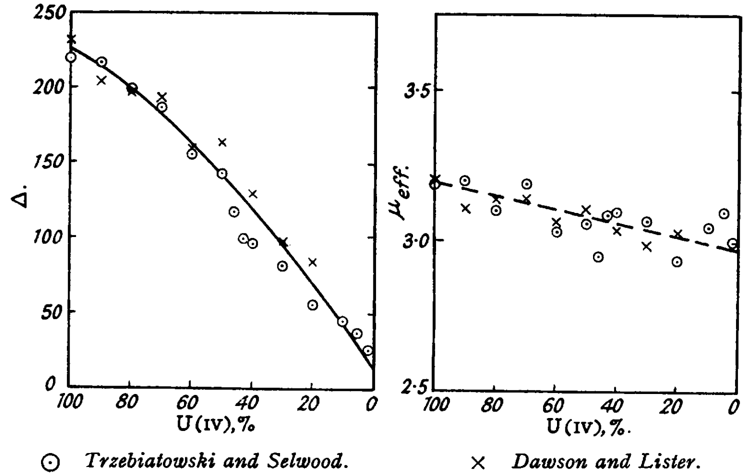
It appears that there is no correlation of the observed magnetic effects in this sytem with the presence of two unpaired electrons in the 6*d* level in the uranous ion. On the other hand, there is definite evidence in favour of the two electrons occupying the 5*f* level and having *j–j* coupling. The theoretical susceptibility for the *L–S* type of coupling is somewhat lower than the *j–j* value (see above), but consideration of the low iron content of the materials (Table I), together with the fact that the thorium fluoride is diamagnetic, indicates that the agreement with the susceptibilities derived on the assumption of *j–j* coupling is probably real and not due to an additional contribution to the susceptibility from ferromagnetic impurities.

It is usually assumed that electrons occupying the 5*f* level will be less effectively shielded from external interaction than is the case with 4*f* electrons. This probably accounts for the change in the Weiss constant as UF_4 is diluted with ThF_4. The change is intermediate between that observed by Selwood for the system Nd_2O_3–La_2O_3, Δ = 59° at 100% Nd_2O_3 to Δ = 30° at 2% Nd_2O_3 (*J. Amer. Chem. Soc.*, 1933, **55**, 3161) and that observed in the UO_2–ThO_2 system (Fig. 2), Δ = 232° at 100% UO_2 to Δ = 26° at 2% UO_2, *i.e.*, intermediate between the well-shielded 4*f*-shell type and the unshielded 6*d*-shell type. The value of the Weiss constant extrapolated to infinite dilution does not appear to be zero, but this is not inconsistent with the *f*-like nature of the unpaired electrons, since the 4*f* electrons in the Nd_2O_3–La_2O_3 system also give rise to a small positive Δ value at infinite dilution owing to the effects of the crystalline field of the diamagnetic diluent atoms.

In the elements beyond actinium, there is increasing evidence from magnetic data that thorium compounds have " unpaired " electrons in the 6*d* level; for instance, ThS is diamagnetic (Brewer *et. al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 4019), and the present author has found that ThSe has a small temperature-independent paramagnetism, these facts indicating very strong exchange coupling between (presumably) unshielded electrons. On the other hand, the plutonium tervalent ion has a $5f^5$ electron configuration (Dawson, Mandleberg, and Davies, *J.*, in the press). The uranium(IV) ion, with two unpaired electrons, lies between these two types and seems to be at the point where the energies of the 6*d* and 5*f* levels are approximately the same; the particular configuration which the ion assumes then appears to depend on the crystal environment.

FIG. 2.

UO_2–ThO_2. *Solid solutions.*



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