

16. *Magnetochemistry of the Heaviest Elements. Part IX.* The System $\text{UO}_2\text{-ThO}_2\text{-O}$.*

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The magnetic susceptibility per uranium atom of partially oxidised samples of urania-thoria solid solutions has been measured at three different urania concentrations. In each case the susceptibility decreased linearly as the average valency of the uranium increased from 4 to 5, more rapidly than in the oxidation of pure urania and at a rate that would have led to zero susceptibility before the uranium reached a valency of 6. A possible explanation is that U(IV) is replaced by U(V) in the initial stages of oxidation of these mixed crystals.

THE magnetic properties of fully reduced urania-thoria solid solutions have been investigated by several authors, the general conclusions being that all the solid solutions obeyed the Curie-Weiss law and the susceptibility of the urania at infinite dilution approached the theoretical "spin-only" value for two unpaired electrons (Trzebiatowski and Selwood, *J. Amer. Chem. Soc.*, 1950, **72**, 4504; Dawson and Lister, *J.*, 1952, 5041; Slowinski and Elliott, *Acta Cryst.*, 1952, **5**, 768). Although the Weiss constant decreased approximately linearly with uranium concentration, Slowinski and Elliott found that there was a deviation below about 30% uranium so that the Weiss constant did not fall to zero at infinite dilution.

Anderson, Edgington, Roberts, and Wait (*J.*, 1954, 3324) have recently studied the oxidation of urania-thoria solid solutions. They have shown that oxidation to an average uranium valency as high as 5.5 can take place while the lattice retains its cubic symmetry and the extra oxygen enters interstitial positions in the lattice. There were indications that the type of interaction between uranium and oxygen changed as the uranium valency increased beyond 5.0 and it was felt that magnetic susceptibility measurements on these oxidised materials could give further information on this since it should be possible to detect the difference between paramagnetic U(V) and diamagnetic U(VI) if they replace U(IV) ions as a result of the oxidation.

EXPERIMENTAL

Solid solutions containing 27.9% and 43.1% of urania in thoria were prepared by coprecipitation of ammonium diuranate and thorium hydroxide followed by ignition of the dried

Magnetic susceptibility of oxidised urania-thoria solid solutions.

U	Atomic ratio Th	O	Average U valency	$10^6 \chi_g^{300}$	Susceptibility per U atom *	Weiss constant
0.148	0.852	2	4.00	1.83	3450×10^{-6}	45
			4.68	0.93	1840	31
			4.91	0.62	1280	—
			5.19	0.36	817	30
			5.46	0.26	638	37
0.279	0.721	2	4.00	2.94	2880	35
			4.45	2.14	2130	32
			4.99	1.05	1110	42
			5.37	0.61	667	55
0.431	0.569	2	4.00	4.35	2730	57
			4.32	3.51	2220	—
			5.02	1.47	960	56
			5.20	1.02	680	60

* Calc. after correction for the diamagnetism of ThO_2 (30×10^{-6} per mole) but not for the underlying diamagnetism of the uranium ions.

precipitate in an alumina crucible at 1200° in a stream of carbon monoxide. A solid solution of 14.8% of urania in thoria was obtained by coprecipitation followed by ignition at 2000° in a vacuum-furnace.

* Part VIII, *J.*, 1954, 3393.

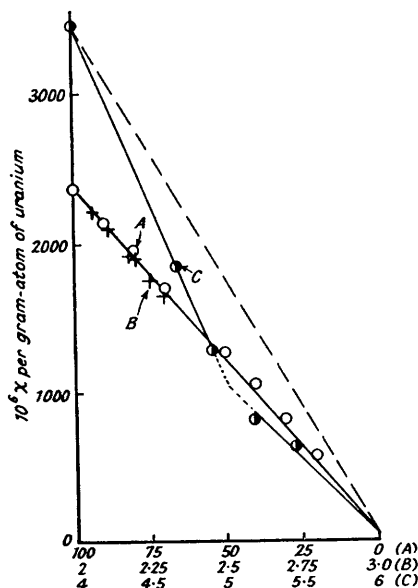
Oxidation of the solid solutions to mean uranium valencies up to 5.0 was carried out by adding known quantities of oxygen gas at 400–600° and annealing for a short time at 800°. Oxidation beyond a mean uranium valency of 5.0 required high pressures of oxygen at 500°. The products were analysed by reducing known weights with carbon monoxide and measuring the carbon dioxide evolved.

The magnetic susceptibilities were measured on the powdered samples by means of the balance described previously (Dawson and Lister, *J.*, 1950, 2177). Observations were made at 90°, 200°, and 300° K; the susceptibilities at 300° K and the variation of the Weiss constant are given in the Table.

DISCUSSION

The magnetic susceptibility of the oxidised solid solutions at three different urania concentrations decreases approximately linearly with increasing oxidation between an average uranium valency of 4 and 5; this is shown in the Figure for the 14.8% urania solid solution. Also plotted are the results of Dawson and Lister (*loc. cit.*) on reduced urania-thoria mixed crystals. The susceptibility in that system also decreased approximately

Scale A, UO_2 (%) in system, $\text{UO}_2\text{-ThO}_2$ (○).
 Scale B, $\text{UO}_2\text{-O}_2$ system, x in UO_x (+).
 Scale C. Average uranium valency in $\text{UO}_2\text{-ThO}_2\text{-O}_2$ system containing 14.8% of urania (●).



linearly as the U(IV) ions were diluted by diamagnetic Th(IV) ions over the whole concentration range. Provided that the same type of behaviour can be assumed for the dilution of U(IV) by diamagnetic U(VI), the susceptibility of a urania-thoria solid solution should fall linearly to zero on oxidation to an average uranium valency of 6.0 if U(IV) is being replaced by U(VI) as oxidation proceeds. The observed magnetic susceptibility of all the mixed crystals decreases at a greater rate than this, however, as the average uranium valency increases from 4 to 5.0.

A possible explanation of this behaviour is that in the initial stages of oxidation the oxygen enters the lattice in such a way that the uranium ions change from quadrivalent to quinquivalent, appreciable amounts of hexivalent uranium not being formed until the average uranium valency is greater than 5.0. The additional oxygen is probably doubly ionised or covalently linked to the uranium and does not exist as interstitial free atoms. Unfortunately no magnetic data exist on any other compound containing quinquivalent uranium. The magnetic susceptibility of quadrivalent uranium in dilute solution in the thoria lattice has the spin-only value, however, and if the single electron in U(V) is assumed also to have the spin-only value then the theoretical susceptibility for dilute U(V) in thoria would be less than that of an equal mixture of U(IV) and U(VI). Thus the susceptibility might decrease more rapidly if the quadrivalent uranium is replaced by U(V) than if it is replaced by U(VI) on oxidation.

There is some indication that the susceptibility-temperature relation changes at an average uranium valency of about 5.0, in agreement with the postulate made on the basis of X-ray diffraction data by Anderson and his co-workers that the type of interaction between oxygen and uranium changes at about the same point.

Anderson *et al.* (*loc. cit.*) have suggested also that the cell contraction caused by a given quantity of added oxygen per uranium atom is independent of the uranium concentration in the crystal; that is, the mechanism is similar over the range 100% urania to 15% urania-in-thoria. However, the present magnetic behaviour appears to differ from that obtained previously for the urania-oxygen system (Dawson and Lister, *J.*, 1950, 2181). The Figure compares the behaviour of 14.8% urania-in-thoria with that of pure urania on oxidation. Observations on the pure urania system are not valid beyond 30% replacement of U(IV), *i.e.*, $\text{UO}_{2.30}$, owing to the appearance of a second phase at that point; nevertheless, over the limited single-phase region it appears that the results follow very closely the theoretical line expected for the replacement of U(IV) by a diamagnetic ion [U(VI)] rather than by paramagnetic U(V). However, the magnetic interaction of interstitial oxygen with the undiluted oxide may differ from that where the oxygen is partially surrounded by quadrivalent thorium ions, and a direct comparison may not be valid.

Finally, although the number of results is rather small, it may be noted that the Weiss constant appears to pass through a minimum at an average uranium valency of about 5, being in this respect similar to the variation of cell constant as deduced from X-ray diffraction data (Anderson *et al.*, *loc. cit.*).

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