449. *Magnetochemistry of the Heaviest Elements. Part II. The Oxides of Uranium.*

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Measurements have been made of the magnetic susceptibilities of UO_2 and intermediate oxides up to U_3O_8 over the approximate temperature range 90—570° K., and the results have been correlated with tensimetric and *X*-ray studies of this system. Oxides between UO_2 and $UO_{2\cdot3}$ follow the Weiss–Curie law with high values of Δ, and the susceptibilities are consistent with the view that these oxides contain quadri- and sexi-valent, but no quinquevalent, uranium. The magnetic moment of UO_2 has a value corresponding to a $5f^2$ (or $5f^1 . 6d^1$) rather than a $6d^2$ electronic configuration.

Above $UO_{2\cdot3}$ there is a two-phase region; reproducible oxides in this middle region are difficult to obtain and give susceptibilities which do not follow the Weiss–Curie law. The exact upper limit of the two-phase region was not defined. It is necessary to express the susceptibility–temperature behaviour of U_3O_8 in the form $(\chi - k)(T + \Delta) = C$. U_3O_8 has a magnetic moment much below that predicted for $UO_2,2UO_3$; the moment agrees more nearly with that of U_2O_5,UO_3, but this requires a rather low value for quinquevalent uranium.

The susceptibility of UO has been measured in UO–UO_2 mixtures.

A STUDY of the oxides between UO_2 and $UO_{2\cdot3}$ by means of *X*-ray-diffraction measurements and observation of the kinetics of oxidation has been reported recently by Anderson and Alberman (*J.*, 1949, S 303). They find that UO_2, which has a fluorite-type structure, will react with oxygen at moderate temperatures up to a composition about $UO_{2\cdot2}$ while retaining the same structure and with very little change in cell dimensions. Further oxidation at temperatures below 230° C. leads to oxides with a composition up to $UO_{2\cdot3}$; these oxides have a tetragonal structure with a c/a ratio quite close to unity. The low-temperature oxidation stops at $UO_{2\cdot3}$, but, when heated, the latter substance disproportionates into $UO_{2\cdot2}$ and a U_3O_8 phase. The U_3O_8 is also stable over a range of compositions, extending downwards as far as U_2O_5 according to Rundle, Baenziger, and Wilson (*J. Amer. Chem. Soc.*, 1948, **70**, 99). A two-phase region probably extends from $UO_{2\cdot3}$ to U_2O_5.

It was thought that magnetic measurements would be of use in interpreting the changes involved in these oxidations. In particular, it should be possible to deduce whether quadrivalent uranium is replaced by quinque- or sexi-valent uranium as the oxidation proceeds. In addition, the susceptibility–temperature relations should be of interest, as this is a good example of the progressive dilution of a paramagnetic ion in a regular and more-or-less constant crystal environment. Finally, the magnetic measurements might also help to fix the boundaries of stability of the various phases in the uranium oxide system; this is difficult with *X*-ray measurements alone since subsidiary phases existing in a sample in proportions less than about 5% can remain undetected.

EXPERIMENTAL.

The magnetic measurements were all made on the susceptibility balance described in Part I (preceding paper), the sample size being in the region of 2—10 mg. The sources of experimental error are discussed in that paper; the root mean square errors of the susceptibilities given below are estimated to be between 0·5 and 1·0%.

The UO_2 was a pure commercial grade and there are two main possible sources of error from impurities: traces of ferro-magnetic impurities and the products of partial oxidation. Since the susceptibility measurements were made at one field strength they did not in themselves detect ferro-magnetic impurities and it was necessary to be sure of their absence by other means. Spectroscopic examinations of the UO_2 gave a content of Fe, Mn, Ni, and Co, which could have contributed about 1% to the observed susceptibility, assuming that they were present in a ferro-magnetic form. However, the consistency of the

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change in susceptibility as the sample was oxidised and the agreement of the susceptibility of the U_3O_8 eventually formed with that prepared from other sources make it improbable that these impurities were contributing more than the experimental error from other causes (*ca.* 0·5%). For a check against the products of partial oxidation a sample was weighed on a commercial micro-balance and then oxidised in air to U_3O_8; the increase in weight was measured on the quartz torsion fibre microbalance. 8·506 Mg. of UO_2 gave an increase in weight of 335·25 μg., or 3·9% (calc. for $UO_2 \longrightarrow U_3O_8$, 3·9%). The composition of the intermediate oxides was calculated from the take-up of oxygen during their oxidation from UO_2. These intermediate oxides were obtained from Anderson and Alberman, and were those used in their *X*-ray investigations (*loc. cit.*).

Measurements on UO–UO_2 Mixtures.—The mixtures were made as follows. Uranium metal, obtained in a finely divided state by heating UH_3, was allowed to react with an amount of oxygen insufficient to convert it into UO_2 and the product was heated to about 2000° in a vacuum furnace. Part of the uranium sintered to a bead of metal which effectively removed it from the reaction zone, but part formed UO according to the reaction, $U + UO_2 \longrightarrow 2UO$. The product was passed through a 200-mesh sieve and washed with dilute hydrochloric acid which dissolved the remaining metal but not the UO and UO_2. After washing and drying of the product, no metallic beads could be observed in the oxide mixture under a microscope. The composition of the samples used for susceptibility measurements was determined after the latter by measuring the increase in weight on oxidation in air to U_3O_8. The magnetic susceptibility of the U_3O_8 so formed was measured also and was identical with that of the U_3O_8 produced by oxidation of the pure UO_2: this served as a check, both on the completeness of the oxidation and on the purity of the sample.

TABLE I.

Sample A. Mean composition $UO_{1\cdot845}$.

Temp., °K.	197·5	293	335	399	453·5
$10^6\chi_m$	10·36	8·45	7·79	7·01	6·41
$10^6\chi_{UO}$	7·23	6·41	5·73	5·31	4·69

Sample B. Mean composition $UO_{1\cdot834}$.

Temp., °K.	197·5	293	332·5	398	453·5
$10^6\chi_m$	10·47	8·38	7·79	7·02	6·46
$10^6\chi_{UO}$	8·18	6·15	5·64	5·44	5·19

TABLE II.

UO_2:	Temp., °K.	90	197	293	375	423	476	525	563			
	$10^6\chi$	14·77	10·90	8·74	7·55	7·00	6·57	6·04	5·75			
$UO_{2\cdot06}$:	Temp., °K.	197	293	335	405·5	445						
	$10^6\chi$	10·20	8·15	7·49	6·64	6·27						
$UO_{2\cdot11}$:	Temp., °K.	90	197	293	335·5	397·5	449	497				
	$10^6\chi$	13·98	9·79	7·73	7·10	6·33	5·83	5·45				
$UO_{2\cdot18}$:	Temp., °K.	90	195	293	398·5	432	482·5	517	562·5			
	$10^6\chi$	13·71	9·10	7·07	5·75	5·42	5·01	4·74	4·42			
$UO_{2\cdot20}$:	Temp., °K.	293										
	$10^6\chi$	6·95										
$UO_{2\cdot25}$:	Temp., °K.	197·5	293	333	398	400	449					
	$10^6\chi$	8·33	6·41	5·88	5·20	5·18	4·78					
$UO_{2\cdot30}$:	Temp., °K.	90	198	276	293	336	349	372	399	399·5	452·5	493
	$10^6\chi$	11·52	7·90	6·32	6·02	5·49	5·35	5·11	4·85	4·84	4·42	4·13
$UO_{2\cdot365}$:	Temp., °K.	90	197	198	293	332·5	398	449·5	500·5	550		
	$10^6\chi$	9·31	5·87	5·84	4·49	4·12	3·63	3·32	3·08	2·90		
$UO_{2\cdot43}$:	Temp., °K.	90	197	293	333·5	398	447·5	482·5	498·5	514·5		
	$10^6\chi$	8·76	5·54	4·31	3·94	3·50	3·23	3·07	2·98	2·94		
$UO_{2\cdot52}$:	Temp., °K.	90	195	293	374	425	449	473·5	537	569·5		
	$10^6\chi$	5·90	3·87	2·99	2·52	2·31	2·22	2·16	1·97	1·93		
$UO_{2\cdot59}$:	Temp., °K.	202	276·5	293	312	333	354	372·5	398·5	423·5	442·5	
	$10^6\chi$	2·89	2·75	2·62	2·53	2·43	2·34	2·27	2·165	2·08	2·02	
$UO_{2\cdot67}$:	Temp., °K.	90	197	293	335·5	398	447	497	554			
	$10^6\chi$	3·28	2·09	1·64	1·51	1·38	1·29	1·21	1·15			

From the susceptibility of the samples the susceptibility of UO (see Table I) was calculated by assuming that the samples were simple mixtures of UO and UO_2 obeying Wiedermann's law, *i.e.*, by subtracting the susceptibility of UO_2 at the corresponding temperatures interpolated from the results on pure UO_2. Thus in the first sample the mean composition was $UO_{1\cdot845}$ so that 1 g. of the mixture contained 0·853 g. of UO_2 and 0·147 g. of UO. If χ_m is the g.-susceptibility of the mixture,

$$\chi_m = 0{\cdot}853\chi_{UO_2} + 0{\cdot}147\chi_{UO}$$

$$\text{or } \chi_{UO} = 6{\cdot}80\chi_m - 5{\cdot}80\chi_{UO_2} \text{ in sample } A$$

$$\text{and } \chi_{UO} = 6{\cdot}33\chi_m - 5{\cdot}33\chi_{UO_2} \text{ in sample } B$$

The calculated susceptibilities for UO are subject to relatively large errors; any error in χ_m is magnified 6—7 times in χ_{UO}. An error of 0·01 in the U : O ratio gives an error of about 0·45 in this region in the constants of the equations used to calculate χ_{UO}, and hence an error of about 0·15 in χ_{UO}. Consequently the accuracy of the results for UO is not better than about $\pm 5\%$.

The results were corrected by 43×10^{-6} per mole for the diamagnetism of the oxygen and also of the uranium atoms themselves (calculated according to Angus, *Proc. Roy. Soc.*, 1932, *A*, **136**, 569). Although the points in a plot of $1/\chi$ against T were rather widely scattered, the results seemed to follow the Weiss–Curie law and a least squares evaluation of the constants gave $\mu = 2{\cdot}76$, $\Delta = 286°$. If all the four electrons of the U(II) ions are in the $5f$ shell with normal L–S coupling, the moment may be calculated as 2·68 Bohr magnetons. The closeness of this to the measured values is probably coincidental, however, in view of the high magnetic concentration of the ions and the high value of the molecular field constant. Normal L–S coupling and a $6d^4$ configuration leads to a calculated effective moment of 0·00, while the spin-only value is 4·90. The measured value lies between these extremes and might be interpreted as incomplete orbital quenching of the $6d$ electrons, but more accurate and more numerous results are needed before any detailed discussion is possible.

Measurements on Oxides between UO_2 *and* U_3O_8.—Table II gives the g.-susceptibilities measured, no diamagnetic correction having been applied.

At the end of each series, the sample was returned to 293° K. and that measurement was repeated so as to detect any oxidation. In the cases where the measurements are not given to the highest temperatures, this usually means that oxidation by residual oxygen in the balance case set in. This could be detected by steady drifting of the balance owing to the increase in weight, and when the 293° K. reading was repeated the susceptibility was lower than that of the original sample.

DISCUSSION.

The Magnetic Moment of UO_2.—From the above results, the magnetic moment of UO_2 is found to be 3·11 Bohr magnetons and $\Delta = 219{\cdot}5°$ K. by the least squares method. After correction for the diamagnetism of the oxygen and uranium atoms, the respective values become $\mu = 3{\cdot}20$, $\Delta = 233°$ for the U(IV) ion.

Apart from the observation that the susceptibility–temperature relation follows the Curie–Weiss law, these results are not in close agreement with those published previously by other authors. Thus Wedekind and Horst (Internat. Crit. Tables, Vol. VI, p. 359) give $\chi_{17°} = 7{\cdot}5 \times 10^{-6}$, and Sucksmith (*Phil. Mag.*, 1935, **14**, 1115) obtained results which give $\Delta = 310°$, $\mu = 4{\cdot}36$ Bohr magnetons. Haraldesen and Bakken (*Naturwiss.*, 1940, **28**, 127) find $\Delta = 180°$, $\mu = 2{\cdot}92$.

For two unpaired electrons, as is the case in the U(IV) ion, the various electronic possibilities and their corresponding theoretical magnetic moments are given in Table III.

TABLE III.

		Moment (Bohr magnetons).		
Configuration.	Ground state.	L–S coupling.	Spin only.	jj coupling.
$5f^2$	$3H_4$	3·58	2·83	3·84
$6d^2$	$3F_2$	1·63	2·83	1·96
$5f^1 6d^1$	$3H_4$	3·58	2·83	3·74

In view of the high magnetic concentration in the oxide lattice one would not expect to find that experimental values of the magnetic moment of the U(IV) ion would agree with either of the two possible extreme theoretical values of 3·58 and 1·63 based on the assumption of no interaction between the ions. It is also probable that the experimental moment would not correspond exactly to the " spin only " values of 2·83 Bohr magnetons since the lattice symmetry of UO_2 is cubic, and Bethe (*Z. Physik*, 1930, **60**, 218) has shown theoretically that systems of cubic symmetry will not remove all the degeneracy. The actually determined value of 3·20 Bohr magnetons indicates that the electrons are in $5f$ (or possibly $5f6d$) states and that partial quenching of their orbital contributions occurs, the screening effect of the outer electrons being much less effective than in rare-earth ions. It is interesting to compare these results with those of Elliot (*Physical Rev.*, 1949, **76**, 431) on UF_4. Fluorides are generally considered to be similar to oxides as regards magnetic concentration, and the moment of UF_4 is 3·30—also higher than any value to be expected from a $6d^2$ configuration.

The Region UO_2 *to* $UO_{2\cdot3}$.—UO_2 and the intermediate oxides up to $UO_{2\cdot3}$ obey the Curie–Weiss law with reasonable accuracy over the temperature range studied. The values of Δ are all positive and comparatively large. The susceptibilities were corrected for diamagnetism (method of Angus, *loc. cit.*), the values used being $-11{\cdot}25 \times 10^{-6}$ per g.-ion of $O^{=}$ and $-31{\cdot}5 \times 10^{-6}$ per g. of uranium. These corrections are comparatively small and do not disturb the adherence to the Curie–Weiss law. They do alter the values of Δ and C somewhat, as may be seen in Table IV which gives the values of Δ and C in the equation $\chi(T + \Delta) = C$, calculated on a g. basis. It is usual to calculate from susceptibility data an effective moment for the paramagnetic atoms or ions by the equations

$$\chi_m = N\mu_{\text{eff.}}\beta^2/[3K(T + \Delta)]$$

$$\mu_{\text{eff.}} = 2{\cdot}83\sqrt{\chi_m(T + \Delta)}$$

Except for UO_2 itself, the difficulty is to know whether to calculate a mean magnetic moment (assuming all the uranium atoms to be equivalent) or to make assumptions as to the different species of uranium ions present. In the latter case three possibilities arise: (i) U(IV) and U(VI), (ii) U(IV) and U(V), (iii) U(IV), U(V), and U(VI).

Ignoring for the moment the question of resonance, we may assume, as a first approximation at least, that the susceptibilities obey Wiedermann's law of addition. U(VI), whether as UO_2^{++} or U^{6+}, may be taken as diamagnetic and its contribution to the susceptibility disregarded for the present purpose. (This ion is sometimes reported as having a temperature-independent paramagnetism but this is still relatively quite small.) Consequently, under assumption (i) above, χ should be approximately constant in the various compounds of composition UO_{2+x} for quantities of material containing 1 g.-mol. of U(IV), or $1/(1 - x)$ g.-mol. of U atom. The calculation of susceptibilities per g.-mol. of U(IV) from the results in Table II leads to the values quoted in Table V. The points obtained by plotting $1/\chi$ against T lie very close to a straight line for each compound and lead to the following effective moments defined by $\mu_{\text{eff.}} = 2{\cdot}83\sqrt{\chi\text{U(IV)} . (T + \Delta)}$

$(2 + x)$	2·00	2·06	2·11	2·18	2·25	2·30
$\mu_{\text{eff.}}$	3·20	3·13	3·09	3·01	2·97	2·94

Thus, while at room temperature there is reasonable constancy for χU(IV) (italicised values in Table V), sufficient to suggest that (i) is the right interpretation of the uranium valency states

TABLE IV.

$(2 + x)$	2·00	2·06	2·11	2·18	2·25	2·30
Δ_1	219·5	200·5	181	158	145·5	131
Δ_2	233·5	212·5	198	170	160·5	144
C	1·282	1·221	1·193	1·129	1·106	1·083

$(2 + x)$ is the oxygen constituent of UO_{2+x}. Δ_1 is uncorrected for diamagnetism. Δ_2 is corrected for the diamagnetism of the oxygen and the uranium.

TABLE V.

	Temp., ° K.	χ per U(IV), $\times 10^6$.	χ per U(IV) corrected for diamagnetism, $\times 10^6$.
UO_2	90	3989	4043
	197	2944	2998
	293	2362	*2416*
	375	2038	2092
	423	1891	1945
	476	1774	1828
	525	1632	1686
	563	1553	1607
$UO_{2{\cdot}06}$	197	2942	3000
	293	2350	*2408*
	335	2161	2219
	405·5	1914	1972
	445	1809	1867
$UO_{2{\cdot}11}$	90	4269	4332
	197	2985	3048
	293	2357	*2420*
	333·5	2164	2227
	397·5	1930	1993
	449	1777	1840
	497	1660	1723
$UO_{2{\cdot}18}$ ...	90	4551	4619
	195	3030	3098
	293	2355	*2423*
	398·5	1914	1982
	432	1804	1872
	482·5	1668	1736
	517	1579	1647
	562·5	1470	1538
$UO_{2{\cdot}25}$ ...	197·5	3043	3119
	293	3241	*2417*
	333	2150	2226
	398	1902	1978
	400	1895	1971
	449	1748	1824
$UO_{2{\cdot}30}$	90	4543	4625
	198	3117	3199
	293	2376	*2458*
	336	2166	2248
	349	2109	2191
	372	2013	2095
	399·5	1908	1990
	452·5	1744	1826
	493	1630	1712

present, this is to some extent a combination of two opposing variations in $\mu_{\text{eff.}}$ and Δ. This point will be discussed in more detail later.

Because of the lack of experimental data on the magnetic moment of U(V) and the uncertainty regarding the amount of coupling, it is difficult to test assumption (ii) quantitatively. Qualitatively, however, it appears that assumption (i) is in better agreement with the facts.

In connection with assumption (iii), the equilibrium

$$\mathrm{U(IV)} + \mathrm{U(VI)} \rightleftharpoons 2\mathrm{U(V)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

would involve only an electron transfer. Since UO_2 is a semi-conductor, an equilibrium distribution of electrons between the uranium atoms in the several valency states must be attained; however the proportion of U(V) appears to be too small to contribute substantially to the magnetic measurements. The reason may be that U(VI) is invariably stabilised by covalency and it seems probable that the extra oxygen in these intermediate oxides would be linked by predominantly covalent bonds.

The Decrease in $\mu_{\text{eff.}}$ *per* U(IV) *with Increasing Oxygen Content.*—As shown above, while the composition moves from UO_2 to $UO_{2\cdot 3}$, the effective moment of U(IV) decreases from 3·20 to 2·94 Bohr magnetons.

UO_2 has the fluorite structure, and extra oxygen is almost certainly accommodated in interstitial ($\frac{1}{2}$,0,0) positions. For a number of reasons, *e.g.*, the general chemistry of U(VI) compounds, the polarising effect of U^{6+} ion, the dimensional constancy of the cubic UO_{2+x} phase, it can be argued that the interstitial oxygen is so bound as to approximate to UO_2^{2+} (or UO^{4+}) groups in the structure. The dissymmetry so produced in the electric field of the crystal lattice would increase the quenching of the orbital angular momentum. This could account for the reduction in effective moment of the U(IV) ions, though the magnitude of the effect cannot be exactly computed.

Systems in which the contribution of the orbital momentum is suppressed usually obey the Curie–Weiss law $\chi(T + \Delta) = C$ with appreciable values of Δ. Table IV shows that the Δ values in the combounds under discussion are all large and positive. The Weiss theory of the internal molecular field can be shown to lead to a regularity in the behaviour of Δ similar to that found experimentally. According to this theory the atoms are assumed to be subject, in addition to the externally applied field H, to an internal field proportional to the mean resultant moment of an atom as a result of the orienting effect of H. If the atom has total angular momentum J, the resultant expression for χ_m is

$$\chi_m = \frac{NJ(J+1)g^2\mu_B{}^2}{3k} \times \frac{1}{T - \dfrac{\nu J(J+1)g^2\mu_B{}^2 n}{3k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where N = Avogadro's number, g = Lande's splitting factor, μ_B = the moment of the ion in Bohr magnetons, k = gas constant, ν = a constant, characteristic of the internal field, and n = the number of atoms per c.c.

The total internal field is taken to be $F = H + n\overline{m}$ where $\overline{m}$ is the average moment. Whence

$$\Delta = -\nu C(1 - x)/V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

where V = molar volume of 1 g. of U atoms, *i.e.*, $V/(1 - x)$ = molar volume of the U(IV) atoms in UO_{2+x}. The result (iii) is obtained by assuming that the crystals have a perfect cation lattice; for a perfect anion lattice the expression for Δ becomes

$$\Delta = \frac{-\nu C(1 - x)}{V(1 + 0{\cdot}5x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

since $V(1 + 0{\cdot}5x)/(1 - x)$ is now the molar volume of U(IV) atoms. It is evident that equations (iii) and the general form of (ii) are unaltered if only the spin moment is effective (J becomes S and $g = 2$). The applicability of (iii) or (iv) may be tested by examining the constancy of ν calculated from the data obtained. The X-ray data and the mode of preparation make it probable that (iii) should apply to these lower oxides (Anderson and Alberman, *loc. cit.*, from which source the cell dimensions were also obtained). The results for the compounds expressed as UO_{2+x} are:

$(2 + x)$	2·00	2·06	2·11	2·18	2·25	2·30
$-\nu$	4440	4510	4550	4480	4700	4590

In view of the experimental errors, these values of ν are reasonably constant: the negative sign arises from the fact that these compounds have an apparent negative Curie point. The constancy of ν shows that Δ arises from some (unspecified, as yet) interaction between the U(IV) ions and that this interaction makes them *less* liable to mutual alignment in the external field H. The interaction is proportional to the number of U(IV) ions per unit volume and presumably it must be of an exchange type in order to account for the large value of ν—magnetic interactions are much too small.

Note on an Annealed Sample, $UO_{2\cdot19}$.—According to Anderson and Alberman, oxides in the range $UO_{2\cdot2}$ to $UO_{2\cdot3}$ on prolonged heat treatment disproportionate into a pseudo-fluorite β-phase of composition close to $UO_{2\cdot2}$ and a higher phase, U_3O_8 or U_2O_5. A sample of composition $UO_{2\cdot19}$ was found to yield pure β-phase on annealing thus. Magnetic susceptibility measurements yielded a Δ value of 152·5° and $C = 1\cdot145$. According to equation (iii) above, this compound gives a ν of -4010, whilst ν from equation (iv) is -4390. The X-ray data suggest that annealed $UO_{2\cdot19}$ would have a perfect anion lattice and that equation (iv) should be applicable. It is interesting to note that this is confirmed by the closeness of the value of ν to those obtained for the unannealed oxides according to equation (iii).

The Region $UO_{2\cdot3}$ to $UO_{2\cdot67}$.—The oxides in the region $UO_{2\cdot3}$ to $UO_{2\cdot5}$, and possibly even further, are certainly mixtures. Furthermore, they are not necessarily mixtures of only the same two phases, since the lower phase may be $UO_{2\cdot2}$ or $UO_{2\cdot3}$ according to the degree of reorganisation of the crystal structure that has taken place before further oxidation. The upper phase is probably U_3O_8, but here again a range of composition is not impossible. Consequently the susceptibilities given in Table II for the oxides in this range have no very great significance, except to show that the range of stability of the UO_2-type phase certainly ends near to $UO_{2\cdot3}$, after which deviations from the previous regularities in susceptibility occur. These materials no longer obey the Curie–Weiss law, owing in part to their being mixtures of compounds with different Δ values, and also to the fact that U_3O_8 itself does not obey the same law.

The susceptibility–temperature relation of U_3O_8 very closely follows the form $(\chi - k)(T + \Delta) = C$. The actual values, expressed per g., are

$$(\chi - 0\cdot492 \times 10^{-6})(T + 51\cdot4) = 3\cdot94 \times 10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

The constant k is formally equivalent to a temperature-independent paramagnetism (as in the case of the platinum group compounds; Cabrera and Duperier, *Compt. rend.*, 1927, **185**, 414), of magnitude $133\cdot8 \times 10^{-6}$ per g.-atom of uranium, uncorrected for diamagnetism. A temperature-independent paramagnetism has been reported for U(VI) compounds by several investigators (Lawrence, *J. Amer. Chem. Soc.*, 1934, **54**, 776; Nicolau, *Compt. rend.*, 1937, **205**, 654; Tilk and Klemm, *Z. anorg. Chem.*, 1939, **240**, 355; Haraldsen and Bakken, *loc. cit.*). Consequently, the effect is quite to be expected if the U_3O_8 contains sexivalent uranium, although the magnitude is relatively large.

Using the equation

$$\mu = 2\cdot83\sqrt{(\chi - k)(T + \Delta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

the effective moment of U_3O_8 is 1·63 for a composition $UO_2,2UO_3$ and 1·15 for $UO_{2\cdot5},\frac{1}{2}UO_3$. Both these values are lower than those calculated for two and one unpaired electrons respectively, although the value obtained for the U(V)–U(VI) combination agree most nearly. Consequently the structure of U_3O_8 seems to involve a U(V)–U(IV) mixture; this agrees with the conclusion drawn by Haraldsen and Bakken, although they report that the susceptibility follows the Curie–Weiss law.

If Δ and C are taken from equation (vi) for U_3O_8, then $\nu = \Delta V/C = 10{,}200$ when C is expressed per g.-atom of U(V). There is no particular reason why this should be the same as for UO_2, but it is obviously of the same order.

Note on the Uniformity of the Samples.—It is evident that if in a sample nominally taken as $UO_{2\cdot1}$ some of the grains are, in fact, $UO_{2\cdot2}$ and others are UO_2, this would not easily be detected in the magnetic measurements. Relatively heavy contamination by an oxide of different oxygen content would have the effect of producing a curve in the $1/\chi$–T line, but the only real guarantee of homogeneity comes from the kinetic studies of the oxidation by which the samples were prepared (Anderson and Alberman, *loc. cit.*). The grain size itself, as shown by the electron-microscope is very small, each grain containing about 10^7 unit cells. The activation energy of the oxidation is about 27 kcals. and the temperature of preparation about 200°.

The oxidation is found to be rapid and the oxygen must diffuse into the cells since the surface area is insufficient for only superficial oxidation. Consequently, with these small grains and the relatively easy oxidation, it seems reasonable to suppose that there will have been time for the oxygen to become distributed during the annealing of the samples.

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