[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Susceptibilities of Urania–Thoria Solid Solutions

BY W. TRZEBIATOWSKI[1] AND P. W. SELWOOD[2]

The magnetic moment of the U^{+4} ion has been determined by several authors from magnetic susceptibilities of uranium compounds,[3–9] but the theoretical calculation of the moment is difficult, because indeterminate factors influence each value.

For elimination of some of these factors it seems to be advantageous to determine the magnetic moment of U^{+4} in a state of dilution such as may exist in solid solutions of uranium dioxide with diamagnetic thorium dioxide. These compounds, being isomorphous, may be expected to form a continuous range of solid solutions with the fluorite structure.

Experimental

Preparation of Solid Solutions.—Uranium acetate (Anal. Reag. Mallinckrodt Chem. Works) and thorium nitrate (Lindsay Light and Chem. Co.), the latter stated to contain less than 0.003% rare earths, were used. Uranium dioxide was obtained by precipitating a dilute solution of the acetate with ammonia water and reducing the diammonium uranate at 1100°, using electrolytic hydrogen which had been passed through palladium-asbestos, concd. sulfuric acid and phosphorus pentoxide. Thorium dioxide was obtained by ignition of the thorium nitrate at 1100°. For preparation of solid solutions, mixtures of about 50 g. of uranium acetate and thorium nitrate, in proportions related to the desired oxide content, were dissolved in 3 l. of water containing 20 ml. of 20% nitric acid plus 3% ammonium nitrate. Coprecipitation of an intimate mixture of ammonium uranate and thorium hydroxide was obtained with 5% ammonia water in the presence of methyl red,[10] while the solution was vigorously stirred. It was confirmed that precipitation was quantitative. The precipitate was washed with 2% ammonium nitrate solution, dried and, after preliminary ignition, reduced for three hours at 1200° in hydrogen, the solid solution being formed simultaneously. The samples were cooled in hydrogen and the structure was confirmed by X-ray powder diagrams.

Magnetic Susceptibility Measurements.—A Gouy balance was used at field strengths of 3750, 4910 and 5700 oersteds. Two different arrangements were used for temperature control. The first provided successive measurements at eight different temperatures from 25 to −128°,[11] and the second permitted measurements at liquid air temperature and at the temperature of a solid carbon dioxide-acetone freezing mixture.[12] Sample tubes, in two sizes, contained 3.6 and 17 g. of substance, respectively, and were calibrated with standard 20% nickel chloride solution for which the susceptibility at 25° was taken as 6.15×10^{-6}, and with solid ferrous ammonium sulfate for which the susceptibility at 25° was taken as 31.6×10^{-6}.[13] Both experimental arrangements provided a hydrogen atmosphere around the suspended sample tubes. No systematic dependence of the susceptibility at the three different field strengths was observed. This assured that the samples did not contain ferromagnetic impurities in appreciable amount. The average value of the susceptibilities measured as 4910 and 5700 oersteds was employed. The differences between susceptibilities obtained at these two field strengths in no case exceeded 0.08×10^{-6}.

Results

The values of the mass susceptibilities are presented in Table I. From these data, the molar susceptibility of U^{+4} was calculated according to the formulas

$$a_1\chi^{\text{mole}}_{\text{UO}_2} + a_2\chi^{\text{mole}}_{\text{ThO}_2} = \chi^{\text{gr}}_{\text{ss}}\cdot MW_{\text{ss}} = a_1(\chi^{\text{mole-para}}_{\text{U}^{+4}} + \chi^{\text{mole-dia}}_{\text{U}^{+4}} + 2\chi^{\text{mole-dia}}_{\text{O}^{=}}) + a_2\chi^{\text{mole}}_{\text{ThO}_2}$$

$$\chi^{\text{mole-para}}_{\text{U}^{+4}} = \frac{\chi^{\text{gr}}_{\text{ss}}\cdot MW_{\text{ss}} - a_2\chi^{\text{mole}}_{\text{ThO}_2}}{a_1} - 2\chi^{\text{mole-dia}}_{\text{O}^{=}} - \chi^{\text{mole-dia}}_{\text{U}^{+4}}$$

a_1, a_2 = mole fractions of UO_2 and ThO_2
χ^{mole} = molar susceptibilities
$\chi^{\text{gr}}_{\text{ss}}$ = mass susceptibilities of solid solutions
MW_{ss} = gram formula weights of solid solutions

Values for the diamagnetic corrections for $O^{=}$ and U^{+4} were taken as −12 and -35×10^{-6}, respectively. The susceptibility of pure UO_2 is about 0.7×10^{-6} higher than that calculated from the magnetic moment of UO_2 reported by Haraldsen and Bakken.[5] It was found that the magnetic susceptibility of UO_2 diminishes with increasing oxygen content, being 8.02×10^{-6} at 25° for $UO_{2.11}$.

The susceptibility for thoria was determined at 25° to be -0.04×10^{-6} and at −190° to be -0.08×10^{-6}. The mean value adopted for all temperatures was -0.06×10^{-6} for the gram susceptibility and -15.8×10^{-6} for the molar susceptibility.

In the range from 25 to −190° the solid solutions of $[U,Th]O_2$ follow the Curie–Weiss law.

Figure 1 presents the changes of the molar susceptibility, $\chi_{U^{+4}}$, as measured at 25 and −190°, and also gives the Weiss constant as a function of concentration.

There is no evidence of a discontinuity of the magnetic moment of U^{+4}, although the susceptibilities increase sharply at 55% thoria. X-Ray powder diagrams show only the reflections of the fluorite structure. Lattice constants of the whole series were determined by use of the (422) reflection, the precision being ±0.003 Å. It will be seen from Table I that the lattice constants change continuously, but that for the 50 and 54

---

[1] UNESCO-American Chemical Society Fellow.

[2] Inquiries concerning this paper should be addressed to P. W. Selwood.

[3] Sucksmith, *Phil. Mag.*, **14**, 1115 (1932).

[4] Lawrence, THIS JOURNAL, **56**, 776 (1934).

[5] Haraldsen and Bakken, *Naturwiss.*, **28**, 127 (1940).

[6] Bommer, *Z. anorg. allgem. Chem.*, **247**, 249 (1941).

[7] Howland and Calvin, Atomic Energy Commission Document No. 1895 (1948).

[8] Hutchison and Elliott, *Phys. Rev.*, **73**, 1229 (1948).

[9] Elliott, *ibid.*, **76**, 431 (1949).

[10] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 425.

[11] Selwood, *Bull. soc. chim.*, D 122 (1949).

[12] Selwood, THIS JOURNAL, **55**, 3161 (1933).

[13] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 29.

TABLE I

SUSCEPTIBILITIES (× 10^6) AND RELATED QUANTITIES FOR SOLID SOLUTIONS OF URANIA AND THORIA

This table gives the measured susceptibilities per gram of sample at various concentrations and temperatures. The table also gives the lattice constants obtained from the X-ray powder diagram. Under each measured susceptibility there is given the Curie constant per gram-ion of U^{+4} as derived from the relation $C = \chi_{U^{+4}}(T + \Delta)$. The values of the Weiss constant were deduced for each sample from the graph $1/\chi_{U^{+4}}$—T. The table also gives the average Curie constant C_{av} and the magnetic moment of the U^{+4} ion in Bohr magnetons. Thus for the sample containing 10 mole % thoria at 298°K. the mass susceptibility is 8.03×10^{-6}, the molar susceptibility is $8.03 \times 10^{-6} \times 269.48 = 2164 \times 10^{-6}$. Using -2×10^{-6} as the molar diamagnetic correction for the thoria content, the susceptibility per gram-ion of U^{+4} is then 2166×10^{-6}. For this sample the Weiss constant is $\Delta = 217°$, thus the molar Curie constant for 298°K. is 1.269. The average value of C for the whole range of temperatures at this concentration is 1.27, and the magnetic moment is $\mu = 2.84\sqrt{C_{av}} = 3.20$ Bohr magnetons. For this sample the lattice constant was found to be 5.469 Å.

Mole % ThO_2 and apparent formula weight	Temperature, °K.									Mol. diamag. corn. for thoria	Δ and C_{av}	Magnetic moment $\mu = 2.84\sqrt{C}$	Lattice constant
	298	230	215	200	184	167	148	128	83				
UO_2	8.86	10.33	10.61	10.97	11.30	11.80	12.42	13.18	15.20		220		
270.07	1.270	1.282	1.272	1.269	1.256	1.255	1.245	1.258	1.261		1.26	3.19	5.455
10	8.03	9.50	9.80	10.05	10.40	10.72	11.42	11.95	13.87	− 2	217		
269.48	1.269	1.289	1.294	1.280	1.273	1.256	1.270	1.256	1.265		1.27	3.20	5.469
20	6.89	7.90	8.15	8.57	9.15	9.51	10.07	10.64	12.62	− 3	200		
268.88	1.182	1.180	1.164	1.177	1.176	1.195	1.199	1.194	1.204		1.19	3.10	5.482
30	6.57	7.47	8.00	8.33	8.62	9.05	9.46	10.24	11.66	− 5	187		
268.28	1.279	1.222	1.259	1.260	1.251	1.251	1.237	1.259	1.225		1.25	3.18	5.492
40	5.46	6.56	6.75	7.00	7.40	7.75	8.28	8.87	10.78	− 6	156		
267.69	1.137	1.158	1.146	1.138	1.148	1.142	1.116	1.146	1.166		1.14	3.03	5.509
50	4.80	5.69	5.92	6.15	6.55	6.90	7.36	7.99	9.63	− 8	143		
267.09	1.163	1.162	1.158	1.153	1.169	1.166	1.166	1.178	1.164		1.16	3.06	diffuse
54[a]	4.30	....	....	....	5.85	....	....	....	9.04	− 9	118		
266.85	1.07				1.09				1.07		1.08	2.95	diffuse
57[a]	4.61	....	....	....	6.13	....	....	....	10.29	− 9	100		
266.68	1.17				1.21				1.18		1.18	3.09	5.526
60	4.43	5.29	5.76	5.90	6.24	6.60	7.12	7.79	9.95	−10	97		
266.50	1.199	1.180	....	1.192	1.191	1.194	1.182	1.187	1.206		1.19	3.10	5.544
70	3.40	4.12	4.39	4.59	4.85	5.19	5.62	6.31	7.78	−11	82		
265.90	1.180	1.168	1.185	1.174	1.168	1.169	1.184	1.194	1.153		1.17	3.07	5.558
80	2.20	2.76	2.93	3.19	3.35	3.53	3.87	4.33	5.86	−13	56		
265.31	1.077	1.083	1.045	1.115	1.092	1.072	1.070	1.080	1.097		1.07	2.94	5.575
90	1.21	1.50	1.62	1.69	1.79	1.98	2.16	2.45	3.35	−14	45		
264.71	1.167	1.147	1.165	1.142	1.131	1.160	1.143	1.156	1.161		1.15	3.05	5.580
95[a]	0.61	....	....	....	0.98	....	....	....	1.86	−15	37		
264.41	1.2				1.2				1.2		1.2	3.1	5.580
98[a]	0.20	....	....	....	0.31	....	....	....	0.72	−16	26		
264.24	1.1				1.1				1.1		1.1	3.0	5.589
100										−16			5.587

[a] The susceptibilities thus indicated were determined at 298, 194 and 83°K.

mole % thoria the diffraction patterns are diffuse, so that the small differences of the lattice constant cannot be established. If limited solid solutions exist in this system their compositions must differ very little. No discontinuity of lattice constants could be established.

Discussion

The results presented show that the magnetic moment of U^{+4} is independent, or almost independent, of concentration with the value of approximately 3.0 Bohr magnetons at the composition $U_{0.02}Th_{0.98}O_2$. By contrast, with increasing dilution the Weiss constant diminishes and at the composition mentioned is depressed from 220 to 26°. This appears to prove that the influence of such factors as the crystalline field, exchange effects, or the existence of multiplet levels in the energy range of kT must all be very small at such magnetic dilution. This behavior is in contrast to that found for solid solutions of paramagnetic neodymia in diamagnetic lanthana in which the Weiss constant is virtually independent of concentration.[12]

The results reported here permit certain conclusions to be drawn about the electronic configuration of U^{+4}. There have been several attempts at deduction of the electronic configuration of U^{+4} from its magnetic moment. The values of 2.91 magnetons for UO_2, 3.40 for UF_4, 3.52 for hydrated uranium sulfate, 3.75 for uranium oxalate, together with Weiss constants in the range from

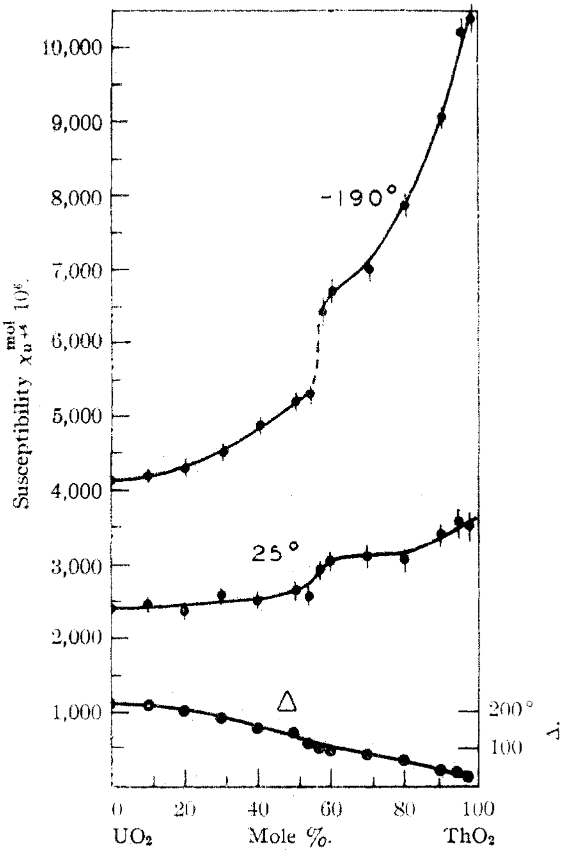

Fig. 1.—Molar susceptibilities of U^{+4} ion and Weiss constants of urania-thoria solid solutions.

108 to 290°, have all been reported.[6–9] These values, with the exception of that for UO_2, have been interpreted as proof for the $5f^2$ electron distribution in a $^3H_4$ state. The magnetic moment which may be derived for the gaseous U^{+4} ion in this state is 3.58 in *LS* coupling and 3.84 in *jj* coupling. By use of the $6d^2$ distribution with the $^3F_2$ state, analogous to the Ti^{+3} ion, there results a magnetic moment of 1.63 in *LS* coupling or 1.96 in *jj* coupling. For this reason, Hutchison and Elliott[8] rejected the 6*d* distribution.

A further possibility exists in the so-called "spin only" formula, which for two unpaired electrons gives a magnetic moment of 2.83 Bohr magnetons. The moment obtained from pure uranium dioxide is very close to this.[5] The present results with diluted solid solutions appear to confirm this result. If it is assumed that quenching of the orbital contribution occurs only for *d* electrons, then the results reported here must be interpreted as favoring the $6d^2$ distribution in tetravalent uranium.

Extrapolation of the susceptibility of U^{+4} to zero urania content permits a calculation of the magnetic moment for U^{+4} at infinite dilution. This procedure gives $\chi_{U^{+4}}^{mole} = 3600$ at 25° and 10600 ($\times 10^{-6}$) at −190°. This gives a moment for tetravalent uranium of 2.9 and 2.7, respectively, which shows even better agreement with the "spin only" formula.

Summary

The magnetic moment of tetravalent uranium has been determined in solid solutions of uranium dioxide with diamagnetic thorium dioxide in the concentration range 100 to 2% urania.

The molar susceptibility of the uranium rises sharply with increasing magnetic dilution, but this is due almost entirely to a diminution of the Weiss constant. The magnetic moment of the uranium shows little, if any, dependence on concentration. The moment at the greatest dilution is in agreement with the "spin only" formula for two unpaired electrons, and hence with the 6*d* rather than the 5*f* electron distribution.

EVANSTON, ILLINOIS RECEIVED MARCH 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Diffusion Studies on Dilute Aqueous Glycine Solutions at 1 and 25° with the Gouy Interference Method[1]

BY MARGARET S. LYONS AND JEAN V. THOMAS

The development of the Gouy interference method for diffusiometry[2–7] has provided a precise tool for the investigation of diffusion in solution. This method for the determination of diffusion coefficients makes use of the time-dependent refractive index gradient at the boundary between two solutions of different concentration. It is particularly useful in the study of non-electrolytes, since its expected accuracy of about 0.1% is much higher than that of other applicable methods.

Previous work[8] has shown that, even for systems which are nearly ideal in the thermodynamic

(1) This report is based upon theses submitted by Margaret S. Lyons and Jean V. Thomas to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degrees of Doctor of Philosophy and Bachelor of Science, respectively, in June, 1949.

(2) Gouy, *Compt. rend.*, **90**, 307 (1880).

(3) Longsworth, *Ann. N. Y. Acad. Sci.*, **46**, 211 (1945).

(4) Kegeles and Gosting, THIS JOURNAL, **69**, 2516 (1947).

(5) Longsworth, *ibid.*, **69**, 2510 (1947).

(6) Coulson, Cox, Ogston and Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

(7) Gosting, Hanson, Kegeles and Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(8) Gosting and Morris, THIS JOURNAL, **71**, 1998 (1949).