

Uranium Monosulfide. The Ferromagnetic Transition. The Heat Capacity and Thermodynamic Properties from 1.5° to 350°K*

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The heat capacity of uranium monosulfide was measured from 1.5° to 22°K by an isothermal (isoperibol) method and from 6° to 350°K by an adiabatic technique. The ferromagnetic transition at 180.1°K has a characteristic lambda shape and associated magnetic ordering entropy and enthalpy increments of 1.6 ± 0.2 cal°K⁻¹ mole⁻¹ and 231 ± 20 cal mole⁻¹, respectively, over the temperature range 0° to 230°K. The correlation of the thermal data with magnetic studies is discussed. The heat capacity below 9°K is represented by $C_p = 5.588 \times 10^{-3}T + 2.627 \times 10^{-4}T^{3/2} + 6.752 \times 10^{-6}T^3$ cal°K⁻¹ mole⁻¹, in which the successive terms represent conduction electronic, magnetic, and lattice contributions. Values of the entropy [S°], enthalpy function [$(H^\circ - H^\circ_0)/T$], and Gibbs-energy function [$(G^\circ - H^\circ_0)/T$] are 18.64 ± 0.05 , 8.94 ± 0.02 , and -9.70 ± 0.02 cal°K⁻¹ mole⁻¹, respectively, at 298.15°K. The Gibbs energy of formation at 298.15°K is -72.9 ± 3.5 kcal mole⁻¹.

I. INTRODUCTION

Recent interest in the crystal structures, vaporization, and magnetic behavior of the lanthanide and actinide monochalcogenides and the potential utilization of the latter as a reactor fuel has already produced a significant literature. The present paper is an endeavor to explore some thermal properties of uranium monosulfide and thereby establish its thermodynamic behavior. Thermodynamics of the formation process are evaluated and found to be at variance with estimates in the literature. In the course of the heat-capacity measurements a lambda-type anomaly was found near 180.1°K,¹ which was later shown to be associated with a ferromagnetic transition.² Tables of the heat capacity and other thermodynamic functions are presented, and the thermodynamic functions are resolved into the electronic, lattice, and magnetic contributions.

II. EXPERIMENTAL

A. Preparation and Characterization of the Sample

Two sets of heat-capacity measurements were made. The first, made at the University of Michigan, covered the temperature range 6° to 350°K. The second set was made four years later at the Argonne National Laboratory over the range 1.5° to 22°K. Because the composition of the sample changed slightly by exposure to

the atmosphere and consequent reaction with oxygen or moisture, individual characterization of the sample is required for each set of data.

The sample was prepared from high-purity uranium metal of natural isotopic composition in 4- and 13-g batches by Method 4 of Eastman *et al.*³ as adapted by Cater, Gilles, and Thorn.⁴ Hence, the metal was first hydrogenated, subsequently decomposed, and then reacted with hydrogen sulfide to form a loosely sintered mass of a higher sulfide and α -uranium of proper overall stoichiometry. This reaction product was ground and thoroughly mixed in a boron carbide mortar within an argon-atmosphere drybox; it was transferred to a degassed, spun tantalum crucible and homogenized by heating in high vacuum ($<10^{-6}$ torr) at 2100°C for 7.5 h. After sampling for analytical purposes, the resultant material was ground again and pelleted in a hardened steel die, annealed in a tantalum crucible at 1900°C for 1.5 h ($<10^{-6}$ torr), and allowed to cool to room temperature over a 12-h period. The three cylinders were brightly metallic, with the luster and appearance of silver.

Spectrochemical analyses of the sample resulted in the detection of the following impurities (in ppm): Fe (70), Si (60), Cu (20), Al (10), Mg (10), Ni (10), Mn (5), Pb (5), and Cr (2). The following elements were not detected, and the limits of detection were as indicated (in ppm): K, P, Ti, and Zn (<50); Ca and Mo (<20); As and Na (<10); Co and Sm (<10); Ag, B, Be, Bi, Li, and Sb (<1). A special spectrochemical analysis for tantalum after the high-tem-

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

¹ A preliminary report was given by E. F. Westrum, Jr. and F. Grönvold in *Thermodynamics of Nuclear Materials* (International Atomic Energy Agency, Vienna, 1962), pp. 3-37.

² M. A. Kanter and C. Kazmierowicz, *Bull. Am. Phys. Soc.* **7**, 556 (1962).

³ E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.* **72**, 4019 (1950).

⁴ E. D. Cater, P. W. Gilles, and R. J. Thorn, *J. Chem. Phys.* **35**, 608 (1961).

TABLE I. Heat capacity of uranium monosulfide, in cal °K⁻¹ mole⁻¹, measured at the University of Michigan. A correction for curvature has been applied to all points except those for which the temperature increment ΔT is given in a footnote. Mole wt = 270.09; 0°C = 273.15°K.

\bar{T} (°K)	C_p	\bar{T} (°K)	C_p	\bar{T} (°K)	C_p
Series I		126.29	9.602	183.92	11.89
		134.72	10.336	185.13	11.71
7.05	0.063	143.32	11.109	186.73	11.57
8.18	0.087	151.83	11.987	191.12	11.39
9.46	0.116	160.71	13.074		
10.78	0.154	169.77	14.707	Series III	
12.13	0.205	178.69	16.870 ^a		
13.52	0.272	188.34	11.530 ^b	168.33	14.39
15.00	0.364	198.74	11.27	170.54	14.91
16.59	0.477	208.39	11.31	172.71	15.60
18.26	0.619	217.30	11.38	175.74	16.89
20.09	0.809	226.36	11.47	178.53	18.88
22.15	1.043	235.73	11.63	179.85	20.54 ^c
24.45	1.310	245.08	11.72	180.86	16.51
27.03	1.632	254.34	11.74	181.96	12.74
29.81	1.990	263.52	11.80	185.27	11.71
32.80	2.335	272.64	11.90		
36.13	2.718	281.73	11.98	Series IV	
39.76	3.085				
43.84	3.474	Series II		172.81	14.10 ^d
48.61	3.904				
54.01	4.345	173.01	15.46	Series V	
59.57	4.756	174.13	16.05		
65.40	5.180	175.22	16.51	277.95	11.88
72.13	5.635	176.30	17.10	287.14	11.97
79.38	6.137	177.37	17.89	296.36	12.10
86.56	6.718	178.42	18.64	305.70	12.15
94.00	7.225	179.44	20.01 ^e	315.06	12.19
101.72	7.742	180.46	19.02 ^f	323.49	12.25
109.82	8.316	181.55	13.47	330.95	12.32
118.31	8.969	182.73	12.18	338.48	12.34
				346.15	12.38

^a $\Delta T = 8.877^\circ\text{K}$.

^b $\Delta T = 10.401^\circ\text{K}$.

^c $\Delta T = 0.961^\circ\text{K}$.

^d $\Delta T = 36.069^\circ\text{K}$.

^e $\Delta T = 1.001^\circ\text{K}$.

^f $\Delta T = 1.020^\circ\text{K}$.

perature annealing but prior to pelleting showed 14-ppm tantalum.

Analyses for sulfur were performed prior to making the final pellets by dissolving 30 to 100 mg of the sample in 3.6*N* sulfuric acid, absorbing the hydrogen sulfide produced in an ammoniacal solution containing a weighed quantity of silver nitrate, and titrating the excess silver with standard potassium thiocyanate in the presence of ferric iron as indicator.⁵ Duplicate analyses indicated 11.86±0.10 wt% sulfur (theoretical, 11.87%). As has already been pointed out by Cater *et al.*,⁴ slight oxygen contamination (e.g., 0.01%) results in the formation of uranium dioxide and uranium oxysulfide phases which remain undissolved in the course of

the sulfide analytical procedure and hence can be weighed and identified by x-ray diffraction. No insoluble residue was present in this material. X-ray powder diffraction photographs of the homogenized sample revealed only the lines characteristic of uranium monosulfide and yielded a lattice parameter a_0 of 5.4879±0.0002 Å. Although no direct analysis was made for uranium, the data indicate that the S/U ratio was 1.00±0.01 initially. (The above values characterize the sample used for the heat capacity measurements from 6° to 350°K presented in Table I.)

By the time the second set of measurements was started, the sample color had changed to a uniform bronze throughout. After the conclusion of the measurements it was again analyzed. The lattice constant a_0 was found to be 5.488±0.001 Å, in agreement with the previous value. The oxygen content was determined by inert-gas fusion⁶ to be 0.16±0.01 wt%. Total uranium was determined as 87.95±0.16 wt% from the weight gain on ignition to U₃O₈. A residue insoluble in 3.6*N* sulfuric acid amounted to 1.55±0.05 wt% of the sample. X-ray diffraction of the residue showed only two phases, uranium dioxide and uranium oxysulfide, with the former predominant. From these results the composition of the sample (for the data reported in Table II) (in mole fraction) is 0.9847 US, 1.17 UO₂, and 0.36 UOS. The theoretical values for this composition (in wt%) are 88.11 U, 11.73 S, and 0.16 O. The total sulfur determined by a method involving complete dissolution of the sample in perchloric acid and

TABLE II. Heat capacity of uranium monosulfide, in cal °K⁻¹ mole⁻¹, measured at Argonne National Laboratory. The apparent C_p values were calculated with the assumption of a pure US sample, and the corrected C_p values were adjusted for the presence of 1.17 mole % UO₂ and 0.36 mole % UOS.

\bar{T}	Apparent C_p	Corrected C_p	\bar{T}	Apparent C_p	Corrected C_p
1.568	0.00934	0.00948	6.326	0.05611	0.05680
1.709	0.01029	0.01044	6.931	0.06521	0.06596
1.879	0.01142	0.01159	7.555	0.07575	0.07656
2.052	0.01262	0.01281	8.239	0.08887	0.08973
2.249	0.01402	0.01423	9.004	0.1056	0.1065
2.473	0.01564	0.01587	9.843	0.1273	0.1282
2.709	0.01743	0.01769	10.764	0.1552	0.1560
3.043	0.02001	0.02030	11.809	0.1931	0.1939
3.340	0.02246	0.02279	13.056	0.2496	0.2502
3.685	0.02549	0.02586	14.386	0.3238	0.3241
4.054	0.02889	0.02931	15.688	0.4115	0.4116
4.474	0.03311	0.03358	15.777	0.4175	0.4176
4.659	0.03512	0.03561	17.239	0.5337	0.5334
5.130	0.04044	0.04099	18.963	0.6917	0.6905
5.693	0.04735	0.04796	20.802	0.8830	0.8806

⁵ I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* **57**, 2126 (1935).

⁶ W. G. Smiley, *Anal. Chem.* **27**, 1098 (1955).

conversion of the sulfur to barium sulfate was 11.90 ± 0.12 wt%, and the sulfur content of the soluble portion by the method described above⁵ was 12.02 ± 0.12 wt%. These values indicate that the S/U ratio in the soluble portion was 1.015 ± 0.012 . This agrees with the original ratio of 1.00 ± 0.01 within the experimental errors.

B. Calorimetric Technique, University of Michigan, 6° to 350°K

Measurements were made by the intermittent heating technique⁷ in the Mark II adiabatic calorimetric cryostat previously described⁸. This was provided with an electronic, adiabatic shield control consisting of three separate channels of recording circuitry with proportional, rate, and reset control actions which maintained temperature equality with the calorimeter within a millidegree and thereby reduced heat exchange with the surroundings to an amount negligible in comparison with other sources of error. A special gold-plated calorimeter (laboratory designation W-34) of mass 10.5 g (plus approximately 7 g of platinum-resistance thermometer, heater sleeve, and spool), machined from OFHC copper rod, was used. The sample space of 8.0 cc was sealed with Cerroseeal (indium-tin) solder. Temperatures were determined with a capsule-type, platinum-resistance thermometer (laboratory designation A-3) in a thermometer-heater well which was mounted somewhat off the axis of the sample space. The temperatures are considered to accord with the thermodynamic temperature scale within 0.03°K from 10° to 90°K and within 0.04°K from 90° to 350°K .

The heat capacity of the empty calorimeter was determined separately with appropriate small adjustments for the slight differences in the amounts of several adjuvant substances on the loaded and empty calorimeter. In particular these involved amounts of helium gas (about 100-torr pressure, used to enhance thermal contact between calorimeter and sample), of Cerroseeal solder, and of Apiezon T grease (for thermal contact between calorimeter, thermometer, heater, and thermocouples). The mass of the three cylindrical specimens comprising the sample was 15.326 g (*in vacuo*). A density of 10.87 g/cc was used for buoyancy corrections. Despite the small mass of the calorimeter, the heat capacity of the sample represented only about 27% of the total above the transition and increased to 37% at 175° and to 50% below 10°K . All determina-

tions of mass, current, voltage, time, and temperature were referred to calibrations or standardizations performed by the National Bureau of Standards.

C. Calorimetric Technique, Argonne National Laboratory, 1.5° to 22°K

The calorimetric apparatus and measuring technique have been described in detail in a previous publication,⁹ which also reports the calibration of the germanium resistance thermometer (laboratory designation Ge No. 3) used for these measurements and the results obtained in the same apparatus for a sample from the 1965 Calorimetry Conference Copper Standard. The technique is an isothermal one in which a copper ring¹⁰ to which the leads and supports are thermally anchored is held constant to $\pm 0.001^\circ\text{K}$ with an automatic control circuit.

The three cylindrical specimens used at the University of Michigan were crushed to a powder in a helium-filled dry box and then encapsulated within a thin-walled (0.06 mm) right annular copper cylinder and pressed within a hardened steel die. By this means adequate thermal conductivity was obtained between the copper capsule and the entire sample, and no helium exchange gas was required in the calorimeter.¹¹ The copper-encapsulated specimen fit over a re-entrant well in the calorimeter.¹² Thermal contact between the capsule and the calorimeter was effected by about 9 mg of Apiezon T grease which bridged the 0.003-cm inner radial clearance between the parts. After sealing the lid on the calorimeter with a weighed amount of Cerroseeal solder, the calorimeter was transferred from the helium-filled dry box to a vacuum line, where the helium was evacuated through a 0.5-mm hole provided for this purpose, and the hole was soldered shut. The mass of the sample in the capsule was 14.344 g *in vacuo*.

The heat capacity of the empty calorimeter was determined in a separate series of measurements. Small adjustments for differences in the amounts of solder, copper, and Apiezon T grease between the full and empty calorimeter were applied. These were based upon the measured heat capacities of copper⁹ and Apiezon T grease¹³ and an estimated heat capacity for the solder. The total uncertainty resulting from these calculated corrections is judged to be less than 0.1% of the reported values. The sample accounted for about 75% of the total measured heat capacity at 1.5°K , about 60% at 5°K , and about 50% above 10°K .

⁷ E. F. Westrum, Jr., G. T. Furukawa, and J. P. McCullough, "Adiabatic Low-Temperature Calorimetry," in *Experimental Thermodynamics*, J. P. McCullough and D. W. Scott, Eds. (Butterworths Scientific Publications, Ltd., London, 1967).

⁸ E. F. Westrum, Jr., and J. P. McCullough, "Thermodynamics of Crystals," in *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Labes, and A. Weissberger, Eds. (Interscience Publishers, Inc., New York, 1963), Vol. 1, pp. 1-178. [See Fig. 2 and accompanying description.]

⁹ D. W. Osborne, H. E. Flotow, and F. Schreiner, *Rev. Sci. Instr.* **38**, 159 (1967).

¹⁰ Compare Fig. 1, Ref. 9.

¹¹ H. E. Flotow and D. W. Osborne, *Rev. Sci. Instr.* **37**, 1414 (1966).

¹² Compare Fig. 4, Ref. 9.

¹³ E. F. Westrum, Jr., C. Chou, D. W. Osborne, and H. E. Flotow, *Cryogenics* **7**, 43 (1967).

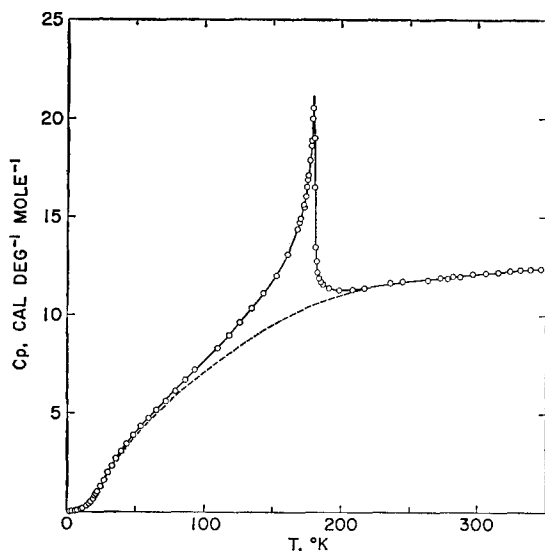


FIG. 1. The heat capacity of uranium monosulfide showing the magnetic transition. Circles represent the experimental values and the dashed curve represents the estimated lattice plus electronic contributions.

III. RESULTS AND DISCUSSION

A. Heat Capacity

The data are based upon a defined thermochemical calorie equal to 4.1840 J, an ice point of 273.15°K, and a molecular weight of 270.09 for uranium monosulfide.

Experimental values for the heat capacity from the higher temperature set of data are presented in Table I. Temperature increments employed in the measurements may usually be deduced from the differences in the adjacent mean temperatures. Values of ΔT have been indicated for certain runs for which the tabulated C_p does not represent the limiting value of $\Delta H/\Delta T$ as a consequence of the magnitude of ΔT . Except for these runs, the data have been adjusted for "curvature" occasioned by the finite temperature increments used for the measurements. The measurements are considered to have a probable error decreasing from about 5% at 8°K to 2% at 12°K and to about 0.2% above 25°K except in the region of the anomaly. These data are also presented in Fig. 1, in which the shape of the anomaly with a maximum at 180.1°K can be seen.

The data from the lower temperature set are given in order of ascending temperature in Table II. The apparent C_p values were calculated as if the sample were pure US, and the corrected C_p values were obtained from the apparent ones by applying a correction for the presence of 0.0117 mole % UO_2 and 0.0036 mole % UOS. The heat capacity of UO_2 was taken from Westrum and Huntzicker,¹⁴ and the heat capacity of UOS was taken as the average of the heat capacities of

UO_2 ¹⁴ and US_2 ,¹⁵ since the heat capacity of UOS has not been reported. It is estimated that the corrected C_p values given in Table II have a probable error of 0.5% or less. These data are represented by circles in Fig. 2 as C/T vs T^2 .

Heat-capacity values presented at selected temperatures in Table III were taken from smooth curves provided by polynomial functions fitted by least-squares to the experimental points from both sets of data, except that a large scale plot of C_p vs T was used from 170° to 190°K. This plot was drawn to accord with the runs having small temperature increments as well as with the enthalpy increments through the entire region. In the region of overlap, the two sets of data agree well within the estimated probable errors.

B. Resolution of Electronic, Magnetic, and Lattice Contributions near 0°K

The nature of the compound suggests that at the lowest temperatures the heat capacity can be represented by an equation of the form

$$C_p = \gamma T + bT^{3/2} + cT^3, \quad (1)$$

in which the term linear in T represents the conduction electrons, the $T^{3/2}$ term is the magnetic contribution, and the T^3 term is the lattice contribution reduced to the Debye limiting law.

The magnetic coefficient b was evaluated as $2.627 \times 10^{-4} \text{ cal}^\circ\text{K}^{-5/2} \text{ mole}^{-1}$ from the formula given by Dyson¹⁶ for an ideal Heisenberg ferromagnet of spin = $\frac{1}{2}$ in a rocksalt-type crystalline lattice with $T_c = 180.1^\circ\text{K}$.

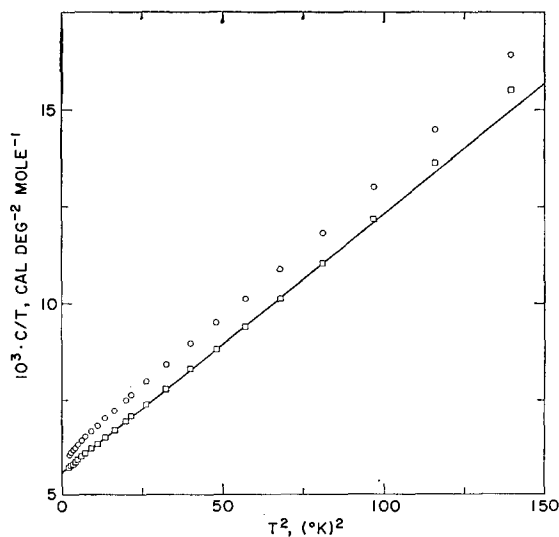


FIG. 2. C/T vs T^2 for uranium monosulfide. The circles represent the experimental heat capacity determinations corrected to the composition US. The squares show the corresponding values after adjustment for the magnetic contribution by Eq. (2). The line is the least-squares fit described in the text.

¹⁴ E. F. Westrum, Jr., and J. J. Huntzicker (unpublished data).

¹⁵ E. F. Westrum, Jr., and F. C. Grønvald (unpublished data).

¹⁶ F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

In Fig. 2 the squares represent the values of

$$C/T = C_p/T - 2.627 \times 10^{-4} T^{1/2}. \quad (2)$$

The other two coefficients were then computed from the corrected heat-capacity values between 1.5 and 9°K (cf. Table II) by least squares. The electronic coefficient γ has a value of 5.588×10^{-3} cal °K⁻² mole⁻¹; the lattice coefficient c is 6.752×10^{-5} cal °K⁻⁴ mole⁻¹, which corresponds to a Debye θ of 190°K for three degrees of freedom. The line in Fig. 2 represents the computer fit. These values of γ and c are more accurate than those given earlier ($\gamma = 4.4 \times 10^{-3}$ cal °K⁻² mole⁻¹ and $c = 8.8 \times 10^{-5}$ cal °K⁻⁴ mole⁻¹) because the earlier¹ analysis ignored the $T^{3/2}$ term, was based on less accurate data at the lowest temperatures, and used data extending to a relatively high temperature.

C. The Ferromagnetic Transition

It is of interest to calculate the magnetic contribution to the entropy and enthalpy from the experimental data. For this purpose an estimate of the sum of the electronic and lattice contributions to the heat capacity of uranium monosulfide, $C_E + C_L$, is needed. An estimate might be provided by the heat capacity of the isostructural, diamagnetic compound thorium monosulfide, but since these data were not available, the following procedure was used. The magnetic heat capacity C_M was calculated from 0° to 80°K by the equation

$$C_M = 2.627 \times 10^{-4} T^{3/2} + 1.350 \times 10^{-6} T^{5/2} + 9.949 \times 10^{-9} T^{7/2}. \quad (3)$$

Equation (3), obtained from Dyson's¹⁶ Eqs. (70) and (135) with T_c equated to 180.1°K, is expected to be valid for $T < T_c/2$.¹⁶ A curve of $(C_p - C_M)$ vs T was drawn up to 80°K and then extended to join the experimental C_p curve at 230°K. This curve, used as an approximation for $C_E + C_L$, is represented between 35° and 230°K by the dashed line in Fig. 1. Below 35°K the dashed line lies too close to the C_p curve to be distinguished in the figure.

The magnetic entropy corresponding to the difference between the two curves of Fig. 1 is 1.49 cal °K⁻¹ mole⁻¹ from 0° to 180.1°K and 0.13 cal °K⁻¹ mole⁻¹ from 180.1° to 230°K, a total of 1.6₂ cal °K⁻¹ mole⁻¹. The value of 1.6₂ for the total magnetic entropy is uncertain by about ± 0.2 but is to be preferred to the earlier estimate¹ of 1.17 cal °K⁻¹ mole⁻¹ in which no account was taken of the magnetic contribution below 80°K. Similarly, the magnetic enthalpy is 206 cal mole⁻¹ from 0° to 180.1°K and 25 cal mole⁻¹ from 180.1° to 230°K, or a total of 231 \pm 20 cal mole⁻¹.

It is also of interest to compare the present results with those obtained from magnetic studies, which may be summarized briefly as follows. After the observation that uranium monosulfide is ferromagnetic below

TABLE III. Thermodynamic functions of uranium monosulfide. Units: cal, °K, mole.

T	C_p°	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
5	0.0393	0.0327	0.0863	0.0155
10	0.1324	0.0839	0.4812	0.0358
15	0.3629	0.1748	1.6406	0.0654
20	0.7967	0.3339	4.4571	0.1110
25	1.381	0.5727	9.8616	0.1782
30	2.002	0.8795	18.323	0.2687
35	2.587	1.2327	29.819	0.3808
40	3.112	1.6130	44.087	0.5108
45	3.587	2.0074	60.853	0.6551
50	4.019	2.4080	79.884	0.8103
60	4.791	3.2106	124.02	1.1436
70	5.493	4.0023	175.47	1.4956
80	6.183	4.7808	233.84	1.8577
90	6.894	5.5498	299.21	2.2253
100	7.611	6.3135	371.76	2.5960
110	8.334	7.0726	451.46	2.9684
120	9.101	7.8303	538.59	3.3420
130	9.922	8.5909	633.67	3.7165
140	10.79	9.3577	737.19	4.0920
150	11.74	10.134	849.73	4.469
160	12.93	10.927	972.72	4.848
170	14.79	11.761	1110.4	5.229
180	20.91	12.722	1278.8	5.618
190	11.43	13.407	1405.3	6.011
200	11.27	13.988	1518.6	6.395
210	11.31	14.538	1631.3	6.770
220	11.43	15.067	1745.0	7.135
230	11.53	15.577	1859.8	7.491
240	11.62	16.070	1975.5	7.838
250	11.71	16.546	2092.2	8.177
260	11.80	17.007	2209.7	8.508
270	11.88	17.454	2328.0	8.831
280	11.95	17.887	2447.2	9.147
290	12.03	18.308	2567.1	9.456
300	12.10	18.717	2687.8	9.757
310	12.16	19.114	2809.0	10.053
320	12.23	19.502	2931.0	10.342
330	12.29	19.879	3053.6	10.625
340	12.34	20.246	3176.7	10.903
350	12.40	20.605	3300.4	11.175
273.15	11.90	17.59	2366	8.93
298.15	12.08	18.64	2665	9.70
	± 0.02	± 0.05	± 7	± 0.02

180°K,² Kazmierowicz¹⁷ found that the saturation magnetic moment at 0°K (based on an extrapolation from 4.2°K) is 1.05 ± 0.03 Bohr magnetons. This value is more reliable than a preliminary value of 1.02-Bohr magnetons reported from the same laboratory¹⁸ which was based on an extrapolation from 77°K. It is also more reliable than the value 1.61-Bohr magnetons

¹⁷ C. W. Kazmierowicz, Argonne National Laboratory Report ANL-6731 (1963).

¹⁸ M. A. Kanter and C. W. Kazmierowicz, J. Appl. Phys. **35**, 1053 (1964).

reported by Suski and Trzebiatowski,¹⁹ who stated that their value was only approximate because it involved an extrapolation from 80° to 0°K. These authors^{19,20} found that the paramagnetic moment is 2.22-Bohr magnetons, the Curie-Weiss constant is 185°K, and the Curie temperature is 180°K. Didchenko and Gortsema²¹ reported a paramagnetic moment of 2.46-Bohr magnetons and a Curie temperature of 180°K. Allbutt, Junkison, and Dell²² found that the paramagnetic moment is 2.25 ± 0.05 -Bohr magnetons, the Curie-Weiss constant 173°K, and the Curie temperature $178^\circ \pm 2^\circ\text{K}$.

These measurements of the Curie temperature are in agreement with the temperature at which the heat-capacity curve has a maximum, $180.1 \pm 0.5^\circ\text{K}$. Of course, these temperatures are not expected to agree exactly because the magnetic measurements give the temperature at which the spontaneous magnetization σ becomes zero, whereas the heat-capacity maximum occurs where $(d\sigma^2/dT) = 0$ according to the Weiss model of ferromagnetism.

If the magnetism arises entirely from electron spins, the magnitude of the saturation magnetic moment at 0°K indicates one electron spin per US molecule. On the assumption that these spins can be considered localized, the change in magnetic entropy between the ground state at 0°K with completely ordered spins to a high-temperature state with completely disordered spins is then calculated to be $R \ln 2$ or $1.38 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$. This value is somewhat lower than the experimental value, $1.62 \pm 0.2 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$, but the disagreement is only slightly larger than the estimated experimental error. This may be fortuitous, however, for the spins probably cannot be considered localized in an electrical conductor. Also, for one localized spin per molecule with $g=2$, the paramagnetic moment should be 1.73-Bohr magnetons, significantly lower than the observed values of 2.22- to 2.46-Bohr magnetons.¹⁹⁻²² A more sophisticated calculation involving band theory would be desirable, but so far none has been reported.

D. Thermodynamic Functions

The thermodynamic functions—entropy [S°], enthalpy increment [$H^\circ - H^\circ_0$], and Gibbs energy function [$-(G^\circ - H^\circ_0)/T$]—are given at selected temperatures in Table III. These were obtained by appro-

priate integrations of the polynomials representing the heat capacity data with a high-speed digital computer. The extrapolation to 0°K, where the entropy is assumed to be zero, was made by Eq. (1); the transition region was integrated by numerical quadrature. The precision of these functions is considered to correspond to a probable error of 0.25% above 100°K. An additional digit beyond those significant is given in this table for internal consistency and to permit interpolation and differentiation. Entropy and Gibbs-energy values have not been adjusted for nuclear spin and isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

E. Thermodynamics of Formation of Uranium Monosulfide

Combining the entropy of uranium monosulfide given in Table III with the entropies of α -uranium ($12.00 \pm 0.02 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$)²³ and of rhombic sulfur ($7.62 \pm 0.04 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$)²⁴ at 298.15°K, we obtain the entropy of formation of uranium monosulfide, $\Delta S_f^\circ_{298.15} = -0.98 \pm 0.07 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$. This value may be combined with values of $\Delta H_f^\circ_{298.15}$ obtained by other workers to yield $\Delta G_f^\circ_{298.15}$.

Cater, Gilles, and Thorn²⁵ have found $\Delta H^\circ_{2300} = 271.2 \pm 2.0 \text{ kcal mole}^{-1}$ and $\Delta S^\circ_{2300} = 65.49 \pm 0.88 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ for the sublimation of uranium monosulfide to uranium and sulfur atoms at 2300°K. These results were derived from measurements on the vaporization of uranium monosulfide and from mass-spectrometric measurements by Cater, Rauh, and Thorn.²⁶ Using these numbers with Rauh and Thorn's value²⁷ for the enthalpy of sublimation of α -uranium metal at 298.15°K, with estimated thermodynamic properties of uranium monosulfide between room temperature and 2300°K, and with literature values of the thermodynamic properties of gaseous uranium and sulfur atoms (including the enthalpy of formation of gaseous sulfur atoms), they calculated the enthalpy of formation of uranium monosulfide at 298.15°K to be $\Delta H_f^\circ_{298.15} = -90 \pm 5 \text{ kcal mole}^{-1}$. From this and $\Delta S_f^\circ_{298.15}$ we obtain $\Delta G_f^\circ_{298.15} = -90 \pm 5 \text{ kcal mole}^{-1}$.

Recently the enthalpy of formation at 298.15°K has been obtained more directly by burning uranium monosulfide in fluorine. O'Hare, Settle, Feder, and Hubbard²⁸ reported an enthalpy of combustion of -2708.8 ± 3.9

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cal g^{-1} for the reaction



and from this they obtained $\Delta H_f^\circ_{298.15} = -73.2 \pm 3.5$ kcal mole $^{-1}$ for the formation of $US_{1.011}$. In view of the indicated uncertainty this value will also be considered appropriate for the stoichiometric composition, $US_{1.000}$. The corresponding value for the Gibbs energy of formation is $\Delta G_f^\circ_{298.15} = -72.9 \pm 3.5$ kcal mole $^{-1}$.

The reason for the large discrepancy between the enthalpy of formation obtained from high-temperature measurements and that obtained from combustion in fluorine is not known. The present authors believe that the second of these is to be preferred.

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Analysis of the Paramagnetic Resonance and Optical Spectra of $d^{3,7}$ Ions in Tetragonal Crystal Fields. I. Orbitally Nondegenerate Ground States

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The ligand-field Hamiltonian, including spin-orbit coupling and all states of the configuration, has been diagonalized for the $d^{3,7}$ ions in tetragonal environments. The g -tensor components have been determined within the lowest two Kramers doublets in cases where the ground state is orbitally nondegenerate. The variation of D , g_{\parallel} , and g_{\perp} with the parameters of the tetragonal potential has been investigated for parameter values appropriate to the Co^{2+} ion in D_{2d} symmetry. The results are compared with those obtained from simple perturbation expressions which have been used in the literature. Parameters for the extended spin Hamiltonian are evaluated directly. Matrices for the tetragonal potential are used to discuss optical and paramagnetic resonance data for Cs_3CoCl_5 and Co^{2+} in CaF_2 . Polarized single-crystal optical data for Cs_3CoCl_5 at 4.2°K are described for the ${}^4T_1({}^4F)$ and ${}^4T_1({}^4P)$ states.

INTRODUCTION

There has been an increased interest in recent years in the effect of low-symmetry components of the crystal field on the optical spectra of transition-metal systems¹ and on the resonance properties of the ground states.^{2,3} Emphasis has been placed on the complete inclusion of all states of the configuration and of the spin-orbit coupling.

In the present paper a complete crystal-field calculation of the effects of tetragonal distortions on the optical and paramagnetic resonance properties of $d^{3,7}$ ions is presented. The problem including spin-orbit effects and all states of the configuration reduces to two 30×30 matrices corresponding to the 60 Kramers doublets of the $d^{3,7}$ configuration. The paramagnetic resonance properties are then evaluated within the

lowest or lowest two doublets depending on the orbital degeneracy of the ground state.

We consider principally the problem of Co^{2+} in an environment of D_{2d} symmetry, taking as an example the Cs_3CoCl_5 system. With appropriate variation of the magnitude and sign of the input parameters, square planar, and tetragonally distorted octahedral $d^{3,7}$ ions can also be treated.

The parameters D_s and D_t for the Y_2^0 and Y_4^0 contributions to the low-symmetry component of the field⁴ are most convenient for the treatment of the orbitally nondegenerate problem. The zero-field splitting, g anisotropy, and splitting of the 4T_2 excited state are largely determined by D_t except in cases where $D_s \gg D_t$.

Brief consideration is given to the optical and paramagnetic resonance data for the pure O_h system Co^{2+} in CaF_2 . The calculated parameters of the extended

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