

URANIUM CHALCOGENIDES—III

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF $US_{1.9}$ AND USe_2 FROM 5 TO 350°K*

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Abstract—Heat capacities have been measured and derived thermodynamic properties calculated for the structurally related $US_{1.9}$ and USe_2 phases from 5 to 350°K. Values of the heat capacity (C_p), entropy ($S^\circ - S_0^\circ$) and Gibbs energy function $[-(G^\circ - H_0^\circ)/T]$ at 298.15°K in cal mole⁻¹ °K⁻¹ are 17.68, 25.91 and 13.82 for $US_{1.9}$ and 18.92, 31.98 and 17.86 for USe_2 , respectively. Schottky-type anomalies are present in $US_{1.9}$; a λ -type thermal anomaly with $\Delta S_f = 0.19$ cal mole⁻¹ °K⁻¹ occurs at 13.1°K in USe_2 .

THE PRESENCE of paramagnetism in the uranium chalcogenides makes a study of their thermal properties seem of special interest for exploration of the mechanisms by which spin order is approached. For $US_{1.9}$ and USe_2 , both with tetragonal structures, magnetic susceptibility measurements [1–3] indicate the presence of 2 unpaired 5*f* electrons with comparatively weak atomic interactions between neighbors since the Curie–Weiss law is fulfilled at higher temperatures with a Weiss constant of about -50°K . A structural study [4] shows that some of the uranium atoms in the tetragonal US_{2-x} structure are distributed at random; this might cause further anomalies in the behavior of the heat capacity or in the zero point entropy.

EXPERIMENTAL

The preparation of the $US_{1.9}$ and USe_2 samples was carried out by reacting elements of previously described [1] purity in evacuated and sealed quartz tubes in the right proportions. In the case of the sulfide, the reaction was performed by heating the mixture to 970°C over a period of 3 weeks and keeping it at this temperature for 2 days. After cooling, the sample was then crushed and homogenized at 800°C for 1 week. After the heat capacity determinations were completed, chemical analyses were made on the $US_{1.9}$ sample by K. Jensen of the Argonne National Laboratory through the cooperation

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of H. E. Flotow. The results indicated 79.78 ± 0.10 per cent by weight of uranium, 20.15 ± 0.07 per cent by weight of sulfur by a distillation process and 20.42 ± 0.09 per cent by weight by gravimetry. (Theoretical: U = 79.62, S = 20.38). The reported results have been corrected for high recovery on standards. Hydrogen, oxygen, and nitrogen were 1.3 ± 0.4 ppm, 470 ± 30 ppm, and 25 ± 6 ppm respectively according to L. F. Krout of the same laboratory. Spectrochemical analysis by J. Lech indicated in (ppm by weight, factor of two precision): Al ~ 10 , As < 20 , Cr ~ 4 , Fe ~ 20 , K < 100 , Mg ~ 5 , Mo < 20 , P < 100 , Si ~ 60 , Ti < 200 and Zn < 50 . Spark spectral analyses from the Chemical Engineering Department of ANL indicated in (ppm atomic): Cr ~ 24 , Fe ~ 220 , K ~ 21 , Mn ~ 20 , P ~ 67 and Sc ~ 20 . Mass spectrographic results showed Al ~ 13 , Mg ~ 33 , Si ~ 1500 in the same units.

The selenide was prepared in the same way, but the temperature of homogenization was 840°C . Analyses similarly performed at the Argonne National Laboratory on the diselenide sample indicated

Uranium: 59.92 ± 0.10 per cent by weight, 3 determinations (theoretical U = 60.12)
 Selenium: 39.79 ± 0.08 per cent by weight, 6 determinations (theoretical Se = 39.88)
 Hydrogen: 5.6 ± 0.3 ppm
 Oxygen: 780 ± 20 ppm
 Nitrogen: 12 ± 1 ppm.

By spectrochemical analysis (in ppm by weight, factor of 2 precision): Al ~ 10 , As < 20 , B ~ 2 , Cr ~ 4 , Cu ~ 10 , Fe ~ 30 , K ~ 100 , Mg ~ 30 , Mo < 20 , P < 100 , Si ~ 40 , Ti < 200 and Zn < 50 .
 By spark spectrometry (in ppm atomic): Cr = 12, Fe = 220, Mn = 20, P = 67, Sc = 7.
 By mass spectrometry (in ppm atomic): Al ~ 20 , Mg ~ 25 , Na ~ 67 , Si ~ 1100 .

Measurements were made in the Mark III vacuum cryostat[5] provided with an electronic adiabatic-shield control system consisting of three separate channels of recording circuitry with proportional, rate, and reset action. These kept the temperature differences smaller than a millidegree and thereby reduced heat exchange with the calorimeter to a magnitude negligible in comparison to other sources of error. The gold-plated copper calorimeters used (laboratory designation W-29 for $\text{US}_{1.9}$ and W-28 for USE_2) had capacities of 42 and 92 cm^3 . The heat capacities of the empty calorimeters were determined separately and small corrections were applied for differences in the amounts of helium gas, indium-tin solder, and Apiezon-T grease for the loaded and empty calorimeters. The heat capacity of the $\text{US}_{1.9}$ sample (146.551 g), represented about 92 per cent of the total below 10°K and decreased to 66 per cent above 90°K . For the USE_2 sample (196.420 g), the corresponding values are 92 per cent and 60 per cent, respectively. All measurements of mass, temperature, resistance, voltage, and time were based upon calibrations or standardizations made by the U.S. National Bureau of Standards.

RESULTS AND DISCUSSION

Experimental heat capacity values for the $\text{US}_{1.9}$ and USE_2 samples are presented in Table 1 in chronological order for the mean temperatures of the determinations after correction for curvature of the heat capacity. The data are given in terms of the defined thermochemical calorie, equal to 4.1840 J, and an ice point of 273.15°K . They are considered to have probable errors decreasing from about 3 per cent at 5°K to 0.5 per cent at 10°K and to less than 0.1 per cent above 20°K . For $\text{US}_{1.9}$, the shape of the heat capacity curve (see the comparison with US_2 [6] in Fig. 1) is nearly normal, while for USE_2 a λ -shaped anomaly is present, having its maximum at 13.1°K (see Fig. 2).

The smoothed heat capacities and the thermodynamic functions derived from them by means of a digital computer using a previously described program[7]

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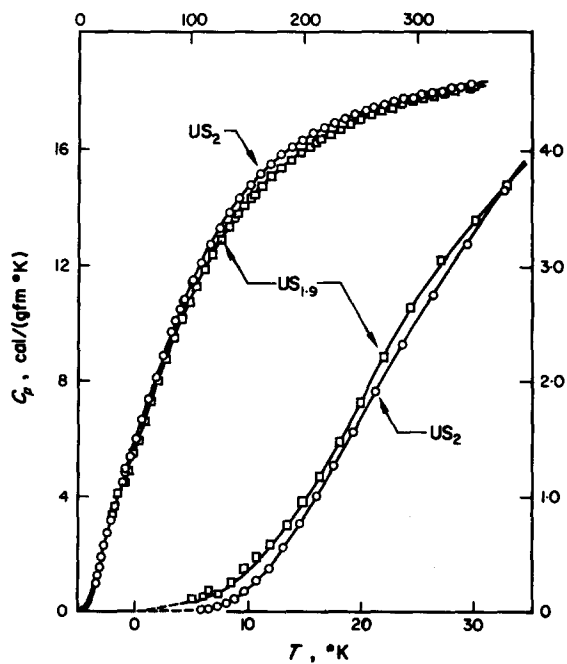
Table 1. Heat capacities of $US_{1.9}$ and USe_2^*

T	C_p	T	C_p	T	C_p
<i>Substoichiometric uranium disulfide</i> [$US_{1.9}$, 1 mole = 299.00g]					
Series I		276.54	17.42	21.93	2.199
		285.59	17.53	24.25	2.629
196.93	15.89	294.70	17.63	26.98	3.032
209.68	16.21	304.22	17.74	30.10	3.383
		314.12	17.84	32.80	3.676
Series II		324.06	17.92	36.58	4.093
		332.32	18.01	40.65	4.554
138.71	13.605	338.91	18.06	40.41	4.519
147.00	14.040	346.14	18.11	44.56	4.997
155.02	14.414			48.95	5.509
153.54	14.348	Series III		53.69	5.972
161.82	14.706			58.79	6.641
170.56	15.051	6.05	0.114	64.31	7.290
179.16	15.347	6.49	0.106	70.66	7.989
187.58	15.62	7.36	0.141	77.39	8.720
196.06	15.86	8.54	0.239	84.24	9.465
204.66	16.08	9.51	0.327	91.32	10.146
213.37	16.31	10.62	0.451	98.46	10.698
222.13	16.48	11.92	0.569	104.43	11.229
231.14	16.68	13.34	0.737	111.64	11.829
240.20	16.87	14.77	0.942	118.87	12.355
249.07	17.02	16.30	1.172	126.23	12.846
258.23	17.17	18.04	1.463	133.92	13.331
267.42	17.31	19.92	1.808	141.85	13.771
<i>Uranium diselenide</i> [USe_2 , 1 mole = 395.99g]					
Series I		Series III		Series VI	
71.10	11.478	ΔH Run A		6.14	0.051
75.90	12.041	11.33	1.028	6.94	0.111
82.30	12.746			7.96	0.302
89.97	13.476	Series IV		9.21	0.539
98.11	14.069			10.05	0.736
106.98	14.647	5.17	0.032	10.71	0.864
116.02	15.17	5.43	0.030	11.27	1.016
125.20	15.64	5.92	0.056	11.77	1.138
134.57	16.06	6.73	0.087	12.21	1.293
143.68	16.40	7.43	0.152	12.60	1.446
152.70	16.71	8.12	0.307	12.96	1.619
161.75	16.96	9.20	0.529	13.29	1.602
170.75	17.19	10.52	0.833	13.65	1.354
179.73	17.38	11.89	1.190	14.05	1.283
188.86	17.56	13.44	1.455	14.55	1.330
198.22	17.75	15.27	1.436	15.12	1.409
207.59	17.93			15.74	1.504
216.95	18.08	Series V		16.48	1.624
226.32	18.22			17.24	1.753
235.60	18.34	5.50	0.026	17.95	1.875
244.90	18.43	5.97	0.051		
254.19	18.53	6.70	0.099	Series VII	
263.53	18.61	7.50	0.150		

Table 1 (Contd.)

T	C_p	T	C_p	T	C_p
272.90	18.71	8.22	0.349	5.55	0.046
282.23	18.78	9.27	0.551	ΔH Run B	
291.58	18.87	ΔH Run B		19.29	2.118
300.86	18.99	16.30	1.595	Series VIII	
310.11	19.01	18.31	1.944		
319.33	19.08	20.34	2.312	12.49	1.432
328.53	19.14	22.71	2.761	12.63	1.445
337.59	19.17	25.40	3.283	12.75	1.481
346.00	19.21	28.62	3.925	12.87	1.541
		31.87	4.589	12.99	1.664
	Series II	34.30	5.096	13.10	1.749
		36.42	5.537	13.22	1.648
9.28	0.494	39.22	6.107	13.35	1.550
9.65	0.620	42.92	6.849	13.51	1.454
10.40	0.809	47.11	7.668	13.68	1.362
11.46	1.061	51.58	8.495	13.87	1.326
12.60	1.455	56.48	9.345	14.06	1.301
14.16	1.367	61.90	10.233		
15.93	1.533	67.83	11.084		
17.57	1.810	74.34	11.871		

*Units: cal, mole, °K.

Fig. 1. Comparison of the heat capacities of US_2 [6] and $US_{1.9}$.

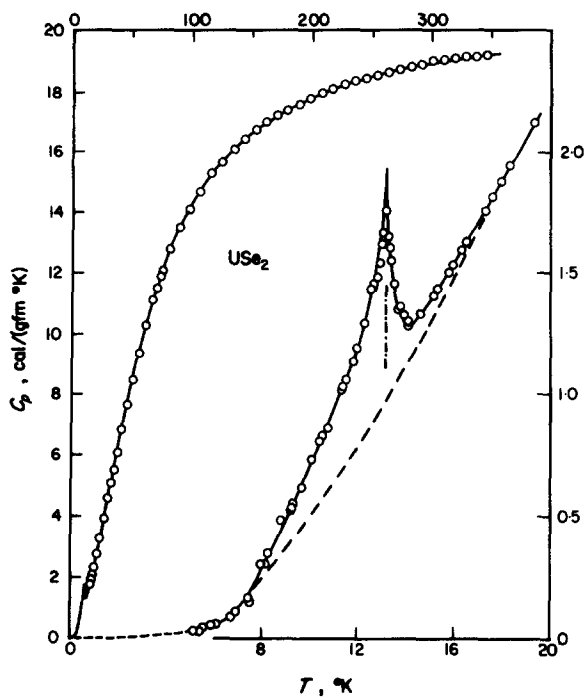


Fig. 2. The heat capacity of USe_2 showing the lambda-type anomaly.

are given in Table 2. The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1 per cent above 100°K.

Since uncertainty exists with regard to the degree of order of spins at 5°K, the entropies obtained by extrapolation in the range 0–5°K might not be correct even for use in chemical thermodynamic calculations in which nuclear spin and isotopic mixing contributions cancel. Consideration should also be given to the fact that two (1.9) of the ten uranium atoms in the tetragonal unit cell are reported to be in a four-fold position[4]. If this is also the case at low temperatures, $\text{US}_{1.9}$ has zero-point entropy of approximately

$$\Delta S = (1/5)R \ln 2 = 0.28 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}.$$

For these reasons, the entropy values are described as $(S^\circ - S_0^\circ)$ and the Gibbs energy function values must be used with caution.

Approximately one-fifth of the uranium atoms in $\text{US}_{1.9}$ are surrounded by eight sulfur atoms at the corners of a right antiprism, and the remainder (four-fifths) are surrounded by six sulfur atoms in a less regular arrangement[4]. The molal heat capacity of $\text{US}_{1.9}$ is somewhat higher than that of US_2 in the range 5–30°K, even though there are more atoms and a Schottky transition with a maximum at 25°C in the latter compound[6]. To account for the excess heat capacity in $\text{US}_{1.9}$, it appears that one-fifth of the uranium atoms have a singlet ground state and a doublet excited state corresponding to $\Delta E/k = 56^\circ\text{K}$; the other four-fifths have a double ground state and an excited singlet state separated by $\Delta E/k = 56^\circ\text{K}$.

Table 2. Thermodynamic properties of $US_{1.9}$ and USe_2^*

T	C_p	$S^\circ - S_0^\circ$	$H^\circ - H_0^\circ - (G^\circ - H_0^\circ)/T$	
<i>Substoichiometric uranium disulfide</i> [$US_{1.9}$, 1 mole = 299.00g]				
5	0.071	0.023	0.085	0.006
10	0.366	0.144	1.039	0.040
15	0.968	0.396	4.258	0.113
20	1.832	0.788	11.17	0.230
25	2.740	1.297	22.66	0.391
30	3.389	1.859	38.11	0.588
35	3.915	2.420	56.34	0.810
40	4.481	2.981	77.40	1.046
45	5.052	3.542	101.2	1.292
50	5.631	4.104	127.9	1.545
60	6.790	5.233	190.0	2.066
70	7.921	6.365	263.6	2.599
80	8.994	7.494	348.3	3.141
90	9.989	8.611	443.2	3.687
100	10.90	9.712	547.7	4.234
110	11.71	10.79	660.9	4.781
120	12.44	11.84	781.7	5.326
130	13.09	12.86	909.4	5.867
140	13.67	13.85	1043	6.402
150	14.18	14.81	1183	6.931
160	14.63	15.74	1327	7.453
170	15.03	16.64	1475	7.967
180	15.38	17.51	1627	8.473
190	15.70	18.35	1782	8.971
200	15.98	19.16	1941	9.461
210	16.23	19.95	2102	9.942
220	16.45	20.71	2265	10.41
230	16.66	21.45	2431	10.88
240	16.85	22.16	2598	11.33
250	17.03	22.85	2768	11.78
260	17.19	23.52	2939	12.22
270	17.34	24.17	3112	12.65
280	17.47	24.81	3286	13.07
290	17.59	25.42	3461	13.49
300	17.70	26.02	3637	13.90
310	17.80	26.60	3815	14.30
320	17.89	27.17	3993	14.69
330	17.98	27.72	4173	15.08
340	18.07	28.26	4353	15.46
350	18.13	28.78	4534	15.83
273.15	17.38	24.37	3166	12.78
298.15	17.68	25.91	3605	13.82

Table 2 (Contd.)

T	C_p	$S^\circ - S_0^\circ$	$H^\circ - H_0^\circ - (G^\circ - H_0^\circ)/T$	
<i>Uranium diselenide</i> [USe ₂ , 1 mole = 395.99g]				
5	0.029	0.010	0.035	0.003
10	0.676	0.158	1.289	0.029
15	1.392	0.641	7.570	0.137
20	2.250	1.155	16.60	0.325
25	3.204	1.758	30.21	0.550
30	4.205	2.430	48.71	0.806
35	5.242	3.156	72.32	1.090
40	6.267	3.923	101.10	1.396
45	7.260	4.719	134.94	1.720
50	8.206	5.533	173.6	2.061
60	9.914	7.185	264.5	2.777
70	11.343	8.824	371.0	3.524
80	12.504	10.417	490.4	4.287
90	13.439	11.946	620.3	5.054
100	14.202	13.402	758.6	5.816
110	14.840	14.787	903.9	6.569
120	15.38	16.102	1055.1	7.309
130	15.86	17.352	1211.4	8.034
140	16.26	18.543	1372.0	8.743
150	16.62	19.677	1536.5	9.434
160	16.91	20.759	1704.2	10.108
170	17.17	21.793	1874.6	10.766
180	17.40	22.781	2047.5	11.406
190	17.60	23.727	2222.5	12.030
200	17.78	24.634	2399.4	12.637
210	17.95	25.506	2578.1	13.229
220	18.12	26.345	2758.4	13.807
230	18.26	27.153	2940.3	14.369
240	18.39	27.933	3123.6	14.918
250	18.50	28.69	3308.0	15.45
260	18.59	29.41	3493.5	15.98
270	18.68	30.12	3679.8	16.49
280	18.76	30.80	3867.0	16.99
290	18.85	31.46	4055.1	17.47
300	18.94	32.10	4244.0	17.95
310	19.02	32.72	4433.8	18.42
320	19.09	33.33	4624.4	18.87
330	19.14	33.91	4815.5	19.32
340	19.18	34.49	5007.1	19.76
350	19.24	35.04	5199.2	20.19
273.15	18.70	30.33	3739	16.65
298.15	18.92	31.98	4209	17.86

*Units: cal, mole, °K.

On subtracting the heat capacity contributions of these two Schottky-type excitations from the observed heat capacities, points are obtained which compare reasonably well (see Fig. 3) with the non-transitional (or "lattice") heat capacity of $US_{1.9}$. The latter is estimated on the basis of data for US and US_3 (see Ref. [6]). A more accurate evaluation of the lattice heat capacity is obviously needed. It might well show that the estimated lattice contribution is too high and the Schottky transitions near 25°K in both $US_{1.9}$ and US_2 have singlet ground states.

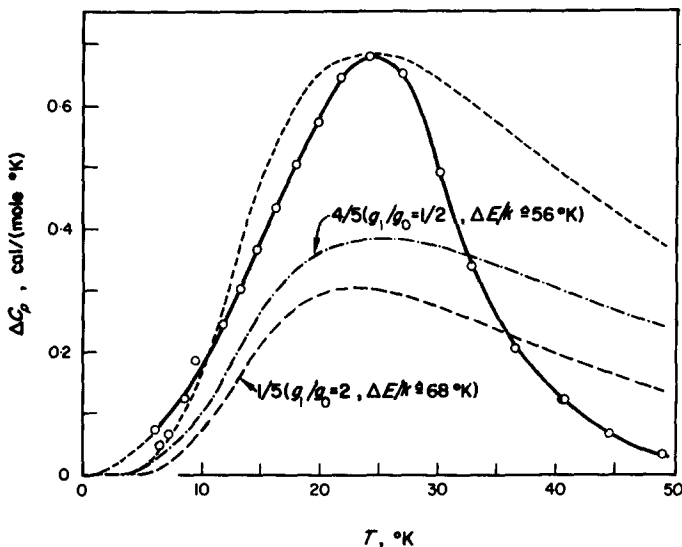


Fig. 3. Resolution of the excess heat capacity of $US_{1.9}$. The contribution from the fifth of the atoms with $\Delta E/k \cong 68^\circ K$ is shown by — —, that of the other four-fifths by - · - · - and the sum by ·····. The circles and the solid line represent the excess heat capacity obtained by subtracting a lattice contribution estimated by fitting the observed heat capacity at higher temperatures to a suitable Debye function (after trial removal of the Schottky tail), from the observed heat capacity.

In USe_2 , which has the same type of structure as $US_{1.9}$, only a cooperative transition is evident, probably because of our present inability to resolve the lattice heat capacity accurately. The entropy and enthalpy of the λ -type transition were estimated after fitting a lattice contribution through this region.

So far no magnetic or crystallographic work has been carried out below the transition, but the negative Weiss constant indicates that the compound probably becomes anti-ferromagnetic at low temperatures. The observed entropy increment, $0.19 \text{ cal mole}^{-1} \text{ }^\circ K^{-1}$, is particularly small and indicates that only a fraction of the uranium atoms are involved in the transition. The magnetic measurements indicate that at least the majority of the uranium atoms are in a triplet state. Assuming that this obtains also for the one-fifth of the uranium atoms symmetrically surrounded by selenium atoms, these would be expected to contribute an entropy increment to the cooperative transition of

$$(1/5) R \ln 3 = 0.41 \text{ cal mole}^{-1} \text{ }^\circ K^{-1}$$

or if the ground state is split into an energetic singlet and a low-lying doublet,

$$(1/5) R \ln 2 = 0.28 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}.$$

The latter alternative apparently agrees best with the observations.

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