ACTINOID PNICTIDES—II

HEAT CAPACITIES OF UAs$_2$ AND USb$_2$ FROM 5 TO 750 K AND ANTIFERROMAGNETIC TRANSITIONS†

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Abstract—The heat capacities of uranium diarsenide (UAs$_2$) and uranium diantimonide (USb$_2$), with tetragonal structures of the anti-Cu$_2$Sb-type, have been measured by adiabatic-shield calorimetry from 5 to about 750 K. Lambda-type transitions with maxima at 272.2 and 202.5 K for UAs$_2$ and USb$_2$, respectively, are related to maxima in the magnetic susceptibilities at 277 and 203 K, occasioned by transitions from antiferro- to paramagnetism in the compounds. Values of the heat capacities (C_p), entropies [$S°(T) - S°(0)$], and Gibbs energy functions $-\{[G°(T) - H°(0)]/T\}$ at 298.15 K in cal K^{-1} mole^{-1} are 19.12, 29.41 and 15.05 for UAs$_2$ and 19.16, 33.81 and 18.39 for USb$_2$. Tentative resolutions of the cooperative magnetic heat capacities of UAs$_2$ and USb$_2$ lead to the magnetic entropies ΔS(mag) = 0.99 and 1.70 cal K^{-1} mole^{-1}, respectively. The values for both are significantly lower than the spin-only magnetic entropy value $R \ln 3 = 2.18$ cal K^{-1} mole^{-1}.

INTRODUCTION

Compounds of uranium with the Group V elements (the pnigogens) exhibit a variety of solid state phenomena—consequences of the outer electron structure of uranium—which are interesting from both experimental and theoretical points of view. The compounds which are of interest currently are those of stoichiometries UX, U$_3$X$_4$ and UX$_2$. For a given stoichiometry there is a striking similarity of properties despite the large variation in pnigogen size. The UX compounds possess the NaCl structure and those of the U$_3$X$_4$ stoichiometry have the Th$_3$P$_4$ structure[1]. In the dipnictide series, UN$_2$ is an exception and is stable only under high N$_2$ pressure and has the fluorite structure[2]. The remaining members UP$_2$, UAs$_2$, USb$_2$ and UBi$_2$ are isostructural with tetragonal Cu$_2$Sb[1–5]. The unit cell and magnetic structures are shown in Fig. 1. Magnetic susceptibility[1, 6–8] and neutron diffraction measurements[9–11] have been made on the dipnictides UP$_2$ through UBi$_2$. The dependence of inverse magnetic susceptibility on temperature indicates that the compounds all order antiferromagnetically and that Curie–Weiss behavior obtains above the ordering (Néel) temperature. The paramagnetic moment increases monotonically with increasing pnigogen size, but Néel temperatures do not. The magnetic coupling may either be anomalously weak in UP$_2$ or anomalously strong in UAs$_2$.

The antiferromagnetic structures of UP$_2$, UAs$_2$ and USb$_2$ determined by neutron diffraction (in the ordered
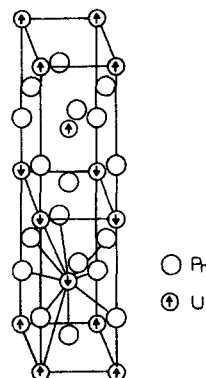

Fig. 1. Unit cell for the uranium dipnictides and magnetic unit cell for UP$_2$, UAs$_2$ and USb$_2$[12].

state) consist of ferromagnetic sheets of uranium ions stacked perpendicularly to the c-axis and in the sequence $+ - - +$ as shown in Fig. 1. The magnetic unit cell is twice as large as the chemical one due to its doubled c-axis. UBi$_2$ contrasts in that the chemical and magnetic unit cells are identical and the ferromagnetic sheets have the order $+ - + -$. The compounds display metallic conduction with $\rho(293\,\text{K}) = 1.83 \times 10^{-4}$ and $1.95 \times 10^{-4}\,\Omega$ cm for single crystal samples of UP$_2$ and UAs$_2$, respectively[12].

Enthalpy of formation ($\Delta H_f°$) measurements on lower arsenides and phosphides together with the observation that $\Delta H_f°(298\,\text{K})$ seems to be a linear function of the pnigogen to uranium radius ratio give an estimate[13] of $\Delta H_f°(298\,\text{K})$ for UP$_2$ and UAs$_2$ of -69 kcal mole^{-1} and -60 kcal mole^{-1} respectively. $\Delta H_f°(298\,\text{K})$ for USb$_2$ has been found to be $-(41.5 \pm 2.6)$ kcal mole^{-1}. However, for UBi$_2$ Lebedev et al.[14] found $\Delta H_f° = -24.7$ kcal mole^{-1}. Rice et al.[15] found -27.1 kcal mole^{-1}, and Mills[16] selected -26.0 kcal mole^{-1}.

Only the heat capacity of UP$_2$ (22.5–350 K) has been

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reported previously[17]. Here a prominent lambda anomaly at 203.2 K accords well with the transition to the antiferromagnetic state as observed in magnetic susceptibility measurements.

EXPERIMENTAL

Samples. The dipnictides were prepared in batches of about 25 g from high-purity uranium metal and pnigogens described earlier[1]. They were prepared from uranium-pnigogen mixture of molar ratio 1:2 in evacuated, sealed, silica tubes. The uranium used was in the form of turnings. The silica tubes containing uranium-antimony mixture were held at $(520 \pm 10)°C$ in a muffle furnace for 20 days, while those containing uranium-arsenic mixture were held at $(430 \pm 10)°C$ for 10 days. After complete reaction between compact uranium and pnigogen, the temperature was elevated to $(750 \pm 10)°C$ during a period of one week and kept at this temperature for another week. The tubes were then left to cool in air. The tubes containing the diantimonide batches and those containing the diarsenide batches were opened in a glove box filled with helium to avoid oxidation. The product contents were crushed under helium before being transferred to the calorimeter. The dipnictides were tempered at 550°C for one week in the calorimeter tubes before heat capacity measurement.

The samples thus prepared were handled in a glove box filled with pure, dry helium gas. X-Ray powder photographs of the samples were taken with $CuK\alpha_1$-radiation using Guinier-type focusing cameras of 8.0 cm diameter. Potassium chloride (AnalaR) was used as a calibration substance ($a_{20°C} = 629.19$ pm)[18]. The lattice constants are $a = (396.2 \pm 0.2)$, $c =$

(813.4 ± 0.4) pm for UAs$_2$ and $a = (428.3 \pm 0.2)$, $c = (875.8 \pm 0.4)$ pm for USb$_2$. They accord well with those reported earlier for UAs$_2$ by Iandelli[3] ($a = 396.2$, $c = 813.2$ pm) and Trzebiatowski *et al.*[6] ($a = 396.2$, $c = 813.6$ pm) and for USb$_2$ by Ferro[4] ($a = 428.1$, $c = 875.8$ pm).

Heat capacities 5–350 K, University of Michigan. The Mark II adiabatic cryostat described previously[19] and a vaned, gold-plated, copper calorimeter (laboratory designation W-52) were employed for both compounds. The calorimeter has a capacity of 59 cm^3 and a mass of about 33 g, and incorporates a gold gasket and screw seal. The heat capacity of the calorimeter and heater-thermometer assembly ranged from 23 to maximum of 35% of the total heat capacity observed for the UAs$_2$ sample and from 15–37% for the USb$_2$ sample; it was determined separately and small adjustments made for differences in the gold gaskets used. A capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) is contained within a re-entrant well of the calorimeter. The experimentally measured temperature increments are probably reliable to within 0.001 K after correction for quasi-adiabatic drift. The masses of the samples used were about 147 and 169 g for UAs$_2$ and USb$_2$, respectively. Helium conduction gas was added to the sample space after evacuation; the amounts employed were 75.3 torr at 299.3 K and 82.0 torr at 297 K, respectively.

Heat capacities 300–750 K, University of Oslo. The calorimetric apparatus and measuring technique have been described[20]. The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated, sealed, silica tube of about 50 cm^3 volume, tightly fitted into the
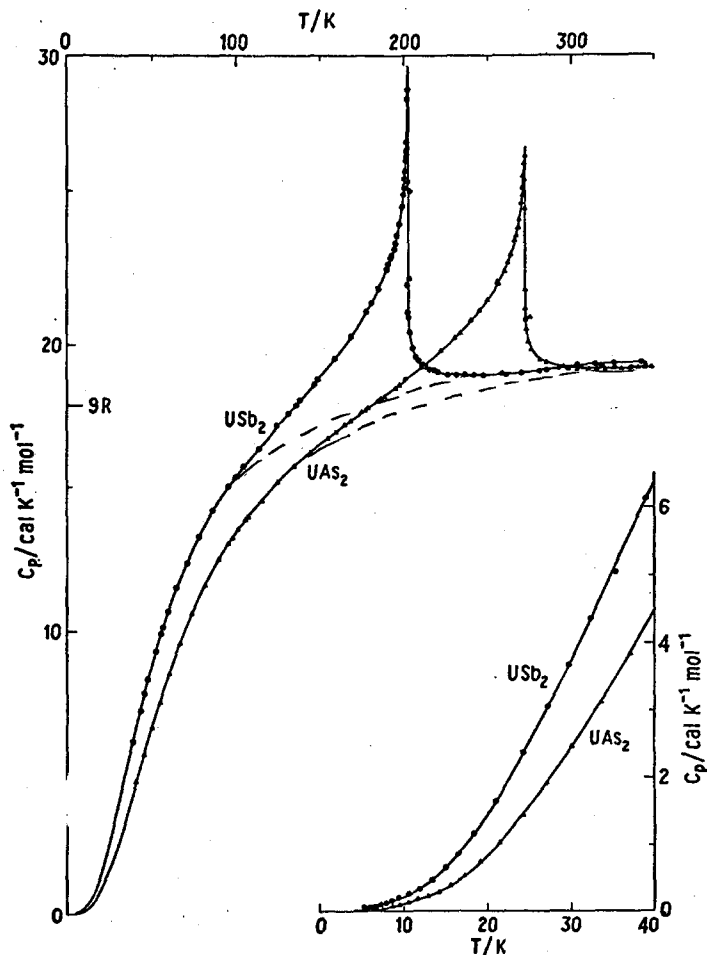

Fig. 2. Low-temperature heat capacity curves for UAs$_2$ and USb$_2$. ●, ▲ are data taken at Ann Arbor. Dashed lines represent the lattice contributions.
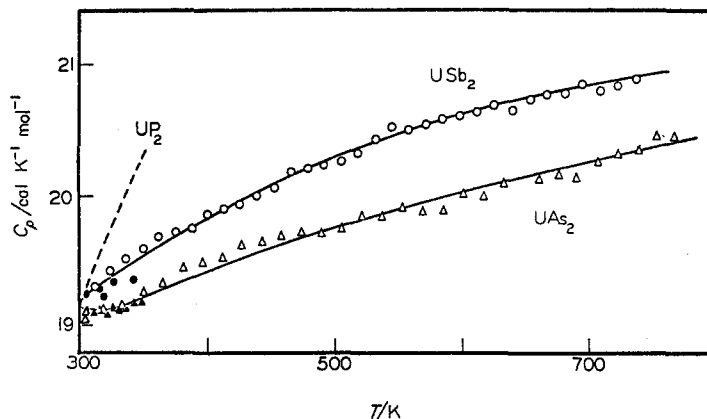
Fig. 3. Higher temperature heat capacity curves for UP$_2$[15], UAs$_2$ and USb$_2$. Dashed line represents the heat capacity of UP$_2$; ●, ▲ are data taken at Ann Arbor; and ○, △ are data taken at Oslo.

silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer. The heat capacity of the empty calorimeter assembly represents about 75% of the total heat capacity for UAs$_2$ and USb$_2$, respectively. The masses of the USb$_2$ and UAs$_2$ samples were nearly the same as those for the low-temperature calorimeter.

Calibrations and adjustments. The platinum-resistance thermometer for the low-temperature calorimeter had been calibrated by the U.S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam and zinc points. Temperatures were judged to correspond to IPTS-68 within 0.02 K from 4–300 K, and within 0.05 K above this temperature. Energy inputs were measured with reference to instruments calibrated by the U.S. National Bureau of Standards.

Small corrections were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in the masses of the gold gaskets, helium gas, and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the quartz containers for the high-temperature calorimeter.

RESULTS

The heat capacity determinations expressed in terms of the calorie defined as 4.184 J, an ice point of 273.15 K, and the atomic weight of natural uranium as 238.029 are listed in Tables 1 and 2 and shown in Figs 2 and 3. The molar masses are taken as 387.872 g mole^{-1} for UAs$_2$ and 481.429 g mole^{-1} for USb$_2$. The heat capacity values are considered to have a probable error of about 5% at 5 K, 1% at 10 K; less than 0.1% from 25–350 K, and 0.5% at higher temperatures. These results have been adjusted for curvature. Values of ΔT used in the determinations can usually be deduced from the increments between adjacent mean temperatures.

Both substances show λ-type transitions in the heat capacity. Maxima are at 272.2 and 202.5 K for UAs$_2$ and USb$_2$. Heat capacities below 5 K were extrapolated with a term proportional to T^3 (Debye lattice contribution) and one proportional to T (conduction electronic contribution, γ). The respective parameters, the Debye θ and γ, were taken from C_p/T vs T^2 plots of heat capacity points below about 20 K. Values of γ were found to be 1.36×10^{-3} and 2.98×10^{-3} cal K^{-2} mole^{-1} for UAs$_2$ and USb$_2$. Enthalpy increments over both transition and non-transition regions (compare Table 3) were made to test the accuracy of the heat capacity determinations and integration and to provide high accuracy across transition regions.

The heat capacities at constant pressure (C_p), and the derived thermodynamic functions $S°$, $[H°(T) - H°(0)]$ and $-[G°(T) - H°(0)]/T$ at selected temperatures presented in Table 4 were obtained from the experimental heat capacity points by least-squares. The curve-fitting and integration processes and the joining of low- and high-temperature segments were performed by high-speed digital computers using established programs. The thermodynamic functions are considered to have a precision indicated by a probable error of less than 0.1% from 100–350 K and 0.3% at higher temperatures. An additional digit beyond those significant is given in Tables 4 and 5 for internal consistency and to permit interpolation and differentiation. Entropies and Gibbs energies have not been adjusted for nuclear spin or isotope mixing contributions and are thus practical values for use in chemical thermodynamic calculations.

DISCUSSION

Difficulties associated with determination of magnetic heat-capacity contributions are well known and are encountered with uranium compounds involving Group IV, V and VI elements[21,22]. In the absence of heat capacity data for the isostructural diamagnetic compounds (i.e. the corresponding thorium compounds) such resolutions must be regarded as tentative and probably too low. It is interesting to note, however, that the heat capacity of USe$_2$[23] (with nearly the same molecular mass as UAs$_2$ although the crystal structures differ) agrees rather well with the heat capacity of the latter compound for some ranges both above and below the transition and with our lattice contribution described below.

The magnetic ordering contributions were determined by plotting effective θ_{Debye}'s as $f(T)$ for the total heat capacities and interpolating over the gap caused by the enhanced heat capacity in the transition region. The θ values thus obtained over this interval were used to generate "lattice" heat capacities which were then integrated. The results are shown in Table 6, together with those for UP$_2$. Magnetic quantities for the latter compound are from the analysis of Stalinski *et al.*[17] obtained by subtraction of a lattice heat capacity approximated by a trial and error sum of Debye functions.

Relevant to the interpretation of the ΔS_{mag} is the amount of entropy to be expected—despite reservations about well defined oxidation states for conducting

Table 1. Heat capacity of UAs₂. (cal = 4.184 J)

Low-Temperature Data (Ann Arbor)

T	c_p	T	c_p	T	c_p	T	c_p
K	cal K⁻¹ mole⁻¹	K	cal K⁻¹ mole⁻¹	K	cal K⁻¹ mole⁻¹	K	cal K⁻¹ mole⁻¹
Series I		340.56	19.12	ΔH_t Det'n D		24.28	1.442
211.11	19.17	347.45	18.76[a]	Series VII		27.13	1.919
222.91	19.78	Series IV		ΔH Det'n E		30.16	2.478
234.42	20.38	159.45	16.92	230.76	20.19	33.47	3.128
245.65	21.13	168.64	17.32	240.66	20.80	37.01	3.856
256.55	22.10	177.64	17.69	250.33	21.52	40.90	4.665
266.38	23.60	186.48	18.07	Series VIII		45.45	5.613
275.70	20.94	195.16	18.44	ΔH Det'n. F		50.08	6.554
285.64	19.34	201.18	18.75	Series IX		54.79	7.473
295.86	19.19	ΔH_t Det'n B		5.22	0.006	60.37	8.495
306.09	19.17	Series V		5.63	0.019	66.69	9.548
316.29	19.16	95.16	13.03	6.23	0.031	73.71	10.56
326.48	19.22	105.44	13.85	6.90	0.047	81.27	11.56
336.68	19.15	115.13	14.55	7.75	0.058	89.18	12.47
343.76	19.28	124.85	15.17	8.60	0.086	97.77	13.23
Series II		134.67	15.74	9.52	0.111	106.86	13.95
178.94	17.75	144.55	16.23	10.53	0.144	Series X	
188.36	18.15	154.80	16.72	11.64	0.169	101.03	13.52
197.61	18.55	165.07	17.17	12.88	0.222	ΔH Det'n. G	
ΔH_t Det'n. A		175.09	17.61	14.17	0.296	ΔH_t Det'n. H	
Series III		184.90	18.01	15.62	0.398	Series XI	
304.02	19.10	Series VI		17.26	0.539	305.69	19.11
310.94	19.09	ΔH Det'n. C		19.18	0.739	315.61	19.11
320.83	19.09	197.59	18.56	21.53	1.040	325.51	19.13
330.70	19.12					335.41	19.14
						343.31	19.17
						348.23	19.17

T	ΔT	$\langle c_p \rangle$[b]	c_p [c]	T	ΔT	$\langle c_p \rangle$	c_p
K	K	cal K⁻¹ mole⁻¹	cal K⁻¹ mole⁻¹	K	K	cal K⁻¹ mole⁻¹	cal K⁻¹ mole⁻¹
Series VII				Series VIII			
256.96	3.75	22.12	22.15	262.44	8.44	22.82	22.81
260.68	3.70	22.53	22.58	267.60	1.91	23.78	23.78
264.34	3.63	23.11	23.10	269.30	1.50	24.32	24.32
267.08	1.86	23.65	23.65	270.32	0.55	24.90	24.82
268.92	1.84	24.11	24.18	270.86	0.55	25.14	25.12
270.19	0.72	24.83	24.72	271.29	0.33	25.43	25.43
270.90	0.71	25.16	25.15	271.55	0.22	25.84	25.72
271.60	0.70	25.80	25.76	271.76	0.22	25.84	25.91
272.30	0.71	25.12	25.12	271.96	0.21	26.29	26.25
273.06	0.81	20.84	20.89	272.16	0.21	26.53	26.63
273.87	0.82	20.53	20.35	272.37	0.22	24.70	-----
274.70	0.83	20.09	20.08	272.59	0.24	21.89	21.76
276.16	2.10	19.81	19.79	272.82	0.25	21.24	21.25
281.83	9.28	19.44	19.34	273.06	0.25	20.94	20.92

Table 1. (Contd.)

T	c_p [b]	T	c_p	T	c_p [b]	T	c_p
K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}
				High-Temperature Data (Oslo)			
	Series I	427.20	19.62	586.18	19.89	707.57	20.27
		442.81	19.65	602.21	20.02	724.25	20.32
303.32	19.04	458.48	19.70	618.27	20.00	739.62	20.36
318.88	19.12	474.22	19.72	634.40	20.10	753.66	20.46
334.37	19.16	490.03	19.71			767.76	20.45
349.85	19.24	505.92	19.75		Series II		
365.29	19.32	521.88	19.85				
380.73	19.34	537.92	19.85	661.10	20.13		
396.17	19.48	554.04	19.92	677.51	20.17		
411.66	19.53	570.20	19.88	692.50	20.14		

[a] Subsequent determinations in this region did not confirm this value.

[b] The symbol $\langle c_p \rangle$ represents mean values of the heat capacity as calculated directly from finite $\Delta H/\Delta T$'s without curvature correction.

[c] The symbol c_p in columns adjacent to $\langle c_p \rangle$ represents the value of the heat capacity read from the smoothed curve at temperature T. Elsewhere in the table it represents c_p analytically corrected for curvature.

Table 2. Heat capacity of USb$_2$. (cal = 4.184 J)

T	c_p	T	c_p	T	c_p	T	c_p
K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}	K	cal K^{-1} mole^{-1}
				Low-Temperature Data (Ann Arbor)			
	Series I	113.29	16.35	5.60	0.042	52.39	9.247
		124.88	17.16	5.92	0.052	56.75	10.09
168.80	20.32	135.99	17.87	6.31	0.055		
180.85	21.41	146.67	18.62	6.70	0.068		Series IX
192.33	22.97	ΔH_t Det'n. A		7.28	0.096		
203.61	22.25	261.85	18.92	7.93	0.106	45.83	7.804
215.58	19.13			8.63	0.135	52.50	9.259
226.68	18.92		Series IV	9.43	0.179	55.65	9.886
		131.51	17.56	10.64	0.253	59.78	10.66
	Series II	138.16	18.03	11.94	0.329	64.78	11.51
		148.61	18.76	13.42	0.463	70.88	12.37
237.04	18.91	158.71	19.50	15.01	0.651	78.03	13.28
248.30	18.89	168.48	20.27	16.49	0.836	86.21	14.21
259.52	18.95	177.94	21.12	18.40	1.150	95.41	15.02
270.69	18.99			20.99	1.630	104.58	15.72
281.82	19.06			24.33	2.355	113.82	16.36
292.88	19.13		Series VI	27.17	3.032	124.90	17.16
303.87	19.24			29.70	3.673	ΔH_t Det'n. C	
314.82	19.28	125.34	17.18	32.26	4.349	249.15	18.92
325.75	19.33	ΔH_t Det'n. B		35.30	5.154	285.73	19.07
		242.41	18.91	38.96	6.104	298.97	19.13
	Series III			43.27	7.174	318.49	19.23
			Series VIII	47.91	8.296	342.42	19.35
100.05	15.38						

Table 2. (Contd.)

Left columns:

T (K)	ΔT (K)	$\langle C_p \rangle$ [a] (cal K^{-1} mole^{-1})	C_p (cal K^{-1} mole^{-1})
		Series IV	
185.12	5.08	21.92	21.91
190.14	4.96	22.59	22.60
195.03	4.82	23.51	23.50
199.72	4.58	25.20	25.03
204.60	5.18	21.03	-----
209.92	5.48	19.28	19.38
215.40	5.50	19.10	19.14
220.90	5.51	19.03	19.00
226.42	5.52	18.90	18.93
231.93	5.51	18.91	18.91
237.44	5.51	18.89	18.89
		Series V	
190.98	1.62	22.78	22.73
192.92	1.651	23.05	23.07
194.56	1.62	23.31	23.40
196.16	1.60	23.77	23.77
197.75	1.58	24.17	24.22
199.31	1.55	24.76	24.81
200.84	1.51	25.76	25.76
202.36	1.52	25.31	-----
204.00	1.77	20.38	20.33
205.79	1.80	19.84	19.83

Right columns:

T (K)	ΔT (K)	$\langle C_p \rangle$ [b] (cal K^{-1} mole^{-1})	C_p (cal K^{-1} mole^{-1})
207.61	1.84	19.57	19.58
209.44	1.82	19.42	19.42
211.27	1.83	19.30	19.30
213.10	1.84	19.21	19.21
214.94	1.84	19.14	19.14
216.77	1.84	19.07	19.10
218.61	1.84	19.10	19.05
		Series VII	
200.63	0.15	25.42	25.54
200.78	0.15	26.00	25.70
200.93	0.15	25.53	25.83
201.09	0.18	26.36	26.07
201.27	0.18	26.65	26.40
201.45	0.18	26.54	26.65
201.63	0.18	26.67	26.98
201.81	0.18	26.76	27.45
201.98	0.18	27.59	27.91
202.16	0.17	28.50	28.54
202.33	0.17	28.82	29.16
202.50	0.18	25.65	25.65
202.70	0.21	22.03	22.16
202.90	0.21	21.09	21.55
203.11	0.21	20.88	21.12
203.32	0.21	20.92	20.76

High-Temperature Data (Oslo)

T (K)	C_p (cal K^{-1} mole^{-1})	T (K)	C_p (cal K^{-1} mole^{-1})	T (K)	C_p (cal K^{-1} mole^{-1})	T (K)	C_p (cal K^{-1} mole^{-1})
Series I		400.43	19.86	518.76	20.33	640.11	20.66
		413.40	19.90	532.00	20.44	653.78	20.73
310.83	19.30	426.40	19.95	545.22	20.53	667.48	20.76
322.75	19.42	439.64	20.00	558.48	20.51	681.24	20.78
335.72	19.51	452.83	20.06	571.80	20.55	695.07	20.84
348.66	19.59	466.33	20.19	585.18	20.59	708.94	20.80
361.59	19.68	479.37	20.21	598.62	20.61	722.88	20.84
374.54	19.72	492.44	20.24	612.15	20.64	736.90	20.89
387.48	19.75	505.57	20.27	625.99	20.69		

[a] The symbol $\langle C_p \rangle$ represents mean values of the heat capacity as calculated directly from finite $\Delta H / \Delta T$'s without curvature correction.

[b] The symbol C_p in columns adjacent to $\langle C_p \rangle$ represents the value of the heat capacity read from the smoothed curve at temperature T. Elsewhere in the table it represents C_p analytically corrected for curvature.

Table 3. Enthalpy determinations for UAs$_2$ and USb$_2$

Designation	$\underline{T}_1$	$\underline{T}_2$	$\underline{H}(T_2)-\underline{H}(T_1)$	$\underline{H}(303 \text{ K})-\underline{H}(202 \text{ K})$
	K	K	cal mole^{-1}	cal mole^{-1}

UAs$_2$, Mark II Cryostat, Transition Region

Designation	$\underline{T}_1$	$\underline{T}_2$	$\underline{H}(T_2)-\underline{H}(T_1)$	$\underline{H}(303 \text{ K})-\underline{H}(202 \text{ K})$
Detn. A (Ser. II)	202.19	302.05	2047.3	2069.1
Detn. B (Ser. IV)	202.88	300.65	2005.9	2067.1
Detn. D (Ser. VI)	201.66	301.18	2039.8	2068.3
Detn. H (Ser. X)	201.02	300.74	2043.7	2068.0
Series I	205.14	300.96	1970.4	2068.4

Mean: (2068.2 $\pm$ 0.7)

UAs$_2$, Mark II Cryostat, Non-Transition Region

	$\underline{T}_1'$	$\underline{T}_2'$	$\underline{H}(T_2')-\underline{H}(T_1')$	
	K	K	cal mole^{-1}	
			Expt'l	Integral of curve
Detn. C	164.94	193.51	507.93	165	194	515.90	515.55
Detn. E	183.70	225.76	795.38	184	226	794.78	794.73
Detn. F	149.52	258.24	2066.28	150	258	2053.0	2052.8
Detn. G	105.91	201.02	1575.10	106	201	1573.5	1571.2

USb$_2$, Mark II Cryostat, Transition Region

				$\underline{H}(240 \text{ K})-\underline{H}(130 \text{ K})$
				cal mole^{-1}
Detn. A	151.89	255.73	2103.2	2204.4
Detn. B	131.02	237.51	2140.7	2205.6
Detn. C	130.47	243.68	2269.1	2207.8
Series IV	130.19	240.19	2204.1	2203.8

Mean: (2205.4 $\pm$ 1.8)

Table 4. Thermodynamic functions of uranium diarsenide (cal = 4.184 J, molar mass/g = 387.872)

$\underline{T}$	$\underline{C}_p$	$\{\underline{S}°(\underline{T})-\underline{S}°(0)\}$	$\{\underline{H}°(\underline{T})-\underline{H}°(0)\}$	$-\{\underline{G}°(\underline{T})-\underline{H}°(0)\}/\underline{T}$
K	cal K^{-1} mole^{-1}	cal K^{-1} mole^{-1}	cal mole^{-1}	cal K^{-1} mole^{-1}
5	0.024	(0.012)	(0.037)	(0.005)
10	0.110	0.049	0.327	0.016
15	0.353	0.132	1.398	0.039
20	0.837	0.294	4.268	0.081
25	1.559	0.555	10.172	0.148

Table 4. (*Contd.*)

T	C_p		$\{\underline{S}°(\underline{T})-\underline{S}°(0)\}$		$\{\underline{H}°(\underline{T})-\underline{H}°(0)\}$		$-\{\underline{G}°(\underline{T})-\underline{H}°(0)\}/\underline{T}$	
K	cal	K^{-1} mole^{-1}	cal	K^{-1} mole^{-1}	cal	mole^{-1}	cal	K^{-1} mole^{-1}
30		2.446		0.915		20.129		0.244
35		3.439		1.366		34.810		0.371
40		4.478		1.893		54.59		0.528
45		5.522		2.481		79.60		0.712
50		6.541		3.115		109.77		0.920
60		8.426		4.478		184.80		1.398
70		10.051		5.903		277.42		1.940
80		11.404		7.336		384.91		2.525
90		12.516		8.746		504.7		3.138
100		13.433		10.113		634.6		3.767
110		14.204		11.431		772.9		4.405
120		14.869		12.696		918.3		5.043
130		15.46		13.910		1070.0		5.679
140		16.00		15.08		1227.3		6.309
150		16.49		16.20		1389.8		6.931
160		16.95		17.28		1557.1		7.544
170		17.38		18.32		1728.8		8.147
180		17.80		19.32		1904.7		8.740
190		18.21		20.29		2084.7		9.323
200		18.68		21.24		2269.1		9.895
210		19.15		22.17		2458.2		10.464
220		19.64		23.07		2652.2		11.015
230		20.15		23.95		2851.1		11.554
240		20.74		24.83		3056.8		12.093
250		21.49		25.69		3267.7		12.619
260		22.49		26.55		3487.3		13.137
270		24.63		27.43		3720.5		13.650
272.21[a]		26.72						
280		19.42		28.20		3933.1		14.153
290		19.18		28.88		4125.8		14.653
300		19.11		29.53		4317.2		15.14
310		19.10		30.15		4508.2		15.61
320		19.10		30.76		4699.2		16.07
330		19.13.		31.35		4890.3		16.53
340		19.18		31.92		5082		16.97
350		19.22		32.47		5274		17.41
400		19.47		35.06		6241		19.45
450		19.67		37.36		7220		21.32
500		19.79		39.44		8206		23.03
550		19.87		41.33		9198		24.61
600		19.97		43.06		10194		26.08
650		20.09		44.67		11195		27.44

Table 4. (*Contd.*)

T	c_p	$\{S^\circ(T)-S^\circ(0)\}$	$\{H^\circ(T)-H^\circ(0)\}$	$-\{G^\circ(T)-H^\circ(0)\}/T$
K	cal K^{-1} $mole^{-1}$	cal K^{-1} $mole^{-1}$	cal $mole^{-1}$	cal K^{-1} $mole^{-1}$
700	20.24	46.16	12203	28.73
750	20.40	47.56	13219	29.94
273.15	(20.76)	(27.71)[b]	(3797.3)[b]	(13.808)[b]
298.15	19.12	29.41	4281.8	15.05

[a] Peak of transition

[b] The 273.15 K value is within ordering high-temperature "tail" of the transition range, but the heat capacity has nearly decreased to the normal value for Phase I.

Table 5. Thermodynamic functions of uranium diantimonide (cal = 4.184 J, molar mass/g = 481.429)

T	c_p	$\{S^\circ(T)-S^\circ(0)\}$	$\{H^\circ(T)-H^\circ(0)\}$	$-\{G^\circ(T)-H^\circ(0)\}/T$
K	cal K^{-1} $mole^{-1}$	cal K^{-1} $mole^{-1}$	cal $mole^{-1}$	cal K^{-1} $mole^{-1}$
5	0.031	(0.025)	(0.035)	(0.018)
10	0.207	0.088	0.540	0.034
15	0.651	0.246	2.554	0.075
20	1.427	0.531	7.609	0.151
25	2.504	0.961	17.332	0.267
30	3.761	1.527	32.951	0.428
35	5.069	2.204	55.02	0.632
40	6.372	2.967	83.64	0.876
45	7.607	3.789	118.62	1.153
50	8.741	4.650	159.54	1.460
60	10.090	6.423	257.04	2.139
70	12.260	8.193	372.07	2.878
80	13.529	9.916	501.2	3.650
90	14.553	11.571	641.8	4.439
100	15.38	13.148	791.6	5.232
110	16.10	14.649	949.1	6.020
120	16.81	16.08	1113.7	6.799
130	17.48	17.45	1285.3	7.566
140	18.15	18.77	1463.4	8.317
150	18.86	20.05	1648.4	9.061
160	19.60	21.29	1840.6	9.786
170	20.44	22.50	2040.5	10.497
180	21.34	23.69	2249.0	11.196
190	22.58	24.87	2468.2	11.879
200	25.16	26.08	2704.2	12.559
202.52[a]	29.80			
210	19.38	27.14	2921.4	13.229
220	19.02	28.03	3113.0	13.880
230	18.91	28.88	3302.5	14.521
240	18.90	29.68	3491.5	15.13

Table 5. (*Contd.*)

T	C_p	$\{S°(T)-S°(0)\}$	$\{H°(T)-H°(0)\}$	$-\{G°(T)-H°(0)\}/T$
K	cal K^{-1} mole^{-1}	cal K^{-1} mole^{-1}	cal mole^{-1}	cal K^{-1} mole^{-1}
250	18.91	30.46	3680.5	15.74
260	18.93	31.20	3869.7	16.32
270	18.98	31.92	4059.3	16.88
280	19.04	32.61	4249.4	17.43
290	19.10	33.28	4440.1	17.97
300	19.17	33.93	4631.5	18.49
310	19.25	34.55	4823.5	19.00
320	19.34	35.17	5017	19.49
330	19.40	35.76	5210	19.98
340	19.47	36.34	5405	20.45
350	19.53	36.91	5600	20.91
400	19.84	39.54	6584	23.08
450	20.08	41.89	7582	25.04
500	20.29	44.02	8592	26.83
550	20.47	45.96	9611	28.48
600	20.63	47.75	10638	30.02
650	20.73	49.40	11673	31.44
700	20.80	50.94	12711	32.78
273.15	19.00	32.14	4119.1	17.06
298.15	19.16	33.81	4596.0	18.39

[a] Peak of transition

Table 6. Some thermodynamic quantities for the uranium pnictides

Quantity	UP$_2$	UAs$_2$ [a]	USb$_2$ [a]	UBi$_2$
At 298.15 K				
C_p/cal K^{-1} mole^{-1}	19.12 [b]	19.11	19.16	(19.2) [c]
$S°$/cal K^{-1} mole^{-1}	24.34 [b]	29.41	33.81	(29.1) [d] (37.5) [e] (40.2) [g]
$H°-H°_0$/cal mole^{-1}	3679 [b]	4282	4596	----
$\Delta C°_{pf}$/cal K^{-1} mole^{-1}	1.12	0.73	0.60	(0.2)
$\Delta H°_f$/kcal mole^{-1}	(-69) [c,d]	(-60) [c,d]	-41.5±2.6 [c,d]	-26._1 [g]
$\Delta S°_f$/cal K^{-1} mole^{-1}·	-7.33	0.58	0.02	1 [g]
$\Delta G°_f$/kcal mole^{-1}	(-66.8) [c]	(-60.2) [c]	-41.5±3	-26._4 [g]
$\Delta V°_f$/cm^3 mole^{-1}	-1.61 [f]	-0.13	-0.82	-1.78
At other temperatures				
$T_{Néel}$/K	203.2 [b]	272.2	202.5	----
ΔH_{mag}/cal mole^{-1}	204.5	234.4	258.5	----
ΔS_{mag}/cal K^{-1} mole^{-1}	1.31 [b]	0.99	1.70	----
$\gamma \times 10^3$/cal K^{-2} mole^{-1}	5 [b]	1.36	2.98	----

[a] This research.

[b] From Stalinski et al. [17]

[c] Parentheses indicate quantities in which estimates are involved.

[d] Rand and Kubaschewski [24], based on Cosgarea et al. [25] and others.

[e] Estimated from USb$_2$ and magnetic contribution.

[f] From black phosphorus.

[g] Mills [16].

compounds involving the pnigogens. Naively, one may at least initially adopt a model with a specified oxidation state for uranium (U^{+4}) and proceed from the free-ion, ground term ($^3H_4$) under the assumption of Russell–Saunders coupling to the expected magnetic entropy of $R \ln(2J + 1) = 4.37 \, \text{cal K}^{-1} \text{mole}^{-1}$. Failure of the experimental results to account for this amount of entropy is usually attributed to crystal field quenching of the orbital moment. Occasionally in such systems the paramagnetic moment and the excess entropy can be identified more closely with spin-only values, which in the present case would be $R \ln(2S + 1) = R \ln 3 = 2.18 \, \text{cal K}^{-1} \text{mole}^{-1}$. The paramagnetic moments are all less than the free-ion values ($3.58 \, \mu_B$) and vary from below the spin-only value ($2.83 \, \mu_B$) for UP_2 to near the free-ion value for UBi_2. However, it is shown in Table 6 that the ΔS_{mag} values are well below even the spin-only values.

The UP_2 heat capacity (compare Fig. 3) already near 350 K is well above the Dulong and Petit limit and the trend of these data contrasts markedly with that for UAs_2 and USb_2. Magnetic susceptibility[26], electrical conductivity[27], and more recently X-ray crystallographic[28, 29] studies have shown the presence of a phase transition in UP_2 near 356 K where the tetragonal super-structure disappears on heating.

Lack of monotonic progression of Néel temperatures with anionic size through the pnigogens may be due to the relatively small U to X radius ratio in UP_2. Thermodynamics of the formation processes for these compounds from the elements is also indicated in Table 6. The S° values for the elements were taken from the report of the CODATA Task Group on Key Values[30].

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