Thermodynamics of uranium intermetallic compounds
II. Heat capacity of UPd$_3$ from 8 to 850 K [a]

RAMON BURRIEL,[b] MICHAEL (WING KEI) TO,[c]
HANNA ZAINEL,[d] EDGAR F. WESTRUM, JR.,

Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.

E. H. P. CORDFUNKE, R. P. MUIS, and G. WIJBENGA [e]

Netherlands Energy Research Foundation ECN,
Petten (NH), The Netherlands

The heat capacity (from 8 to 350 K) of UPd$_3$ by adiabatic calorimetry and (from 400 to 900 K) by enthalpy-increment drop calorimetry has been measured and the thermodynamic properties at 298.15 K have been evaluated as $C_{p, m}/R = 12.28$, $\Delta_0^T S_m^\circ/R = 21.21$, $\Delta_0^T H_m^\circ/(R \cdot K) = 2817$, and $\Phi_m^\circ/R = 11.76$. Our results agree with the interpretation of localized electrons with discrete energy levels and resultant Schottky contributions. The excess of heat capacity we found over the lattice and electronic contributions is compared with the theoretical values calculated from the crystal-field model proposed by Murray and Buyers. Confirmation that the conduction-electron contribution is small can be deduced from our results and this conclusion is in accord with other interpretations.

1. Introduction

As has already been emphasized[1] the thermodynamic properties of intermetallic (actinide + noble-metal) compounds are of technological importance. Understanding the formation of UPd$_3$ in nuclear-reactor fuel elements and its ability to host other high-yield fission products (Ru, Rh), the prediction of compatibilities of actinides with noble-metal containers, and the design of nuclear-waste recovery processes, all require Gibbs energies of the various intermetallics.

[b] Present address: Instituto de Ciencia de los Materiales de Aragón, Departamento de Termología, Universidad de Zaragoza, 50009 Zaragoza, Spain.
[c] Present address: 10 Kai Yuen Street, 2/F, North Point, Hong Kong.
[d] Present address: Council for Scientific Research, Petroleum Research Center, Jadria, Baghdad, Iraq.
[e] Present address: Shipley Co. Inc., Newton, Massachusetts 01262, U.S.A.

Extension of the Brewer and Wengert[2] correlation of thermodynamic stabilities with bonding configurations for transition-metal intermetallics to include actinide compounds requires further knowledge of the contributions of 5f electrons to bonding energies and the development of thermodynamic information on these materials. Indeed, although the large spatial extent of the 5f electrons gives them a more important role in bonding than the 4f electrons in the much better understood lanthanide systems, thermophysical calorimetry may be expected to play a role in resolving some of the many interesting questions regarding the electronic structure, crystal-field effects, partial orbital quenching, and existence of covalency effects. Although neutron diffraction can in principle make major contributions, and magnetic susceptibilities also provide significant information, combination with low-temperature heat-capacities permits a more detailed explanation.[3, 4] Moreover, the evaluation of band electronic structures in calorimetric quantities is a topic urgently needing further elucidation.

We have reported heat capacities of UPd_3 in this presentation to supplement those of URu_3 and URh_3 reported previously[1] because of the considerable interest recently manifest in this "key" compound. In contrast to the other two compounds, UPd_3 crystallizes in the hexagonal system ($TiNi_3$ structure, $P6_3/mmc$). Although resistivity studies have been interpreted in terms of enhanced spin fluctuations and a narrow 5f band[5] and these are not inconsistent with e.s.r. measurements,[6] neutron inelastic-scattering experiments on UPd_3 revealed several peaks identified as crystalline-field transitions[7-9] suggesting that 5f electrons might be localized on the U sites and that the U^{4+} $5f^2$ ($^3H_4$) configuration is split in the hexagonal field to give a singlet ground state. Measurements[3] of the heat capacity of UPd_3 exhibit a jump near 7 K (accompanied by two distinct small maxima at 4.6 and 7.6 K) assumed to be a cooperative phenomenon (phase transition). In samples of lower quality, the jump degenerates into a Schottky-like anomaly. Andres *et al.*[3] conclude that the transition involves quadrupole ordering leading to a sudden depopulation of the excited doublet state.

Schlabitz and others[9, 10] also measured the heat capacity of UPd_3 and $ThPd_3$ down to 0.4 K, but their values are not yet available to us.

2. Experimental

Starting materials for the preparation of UPd_3 were palladium sponge of high purity (99.99 mass per cent, Johnson Matthey Chemicals, Ltd), and uranium nitride (UN). The preparation of UN has been described.[1] Before use, the palladium sponge was dried in vacuum at 775 K to remove adsorbed moisture. UPd_3 was prepared by heating mixtures of UN with palladium in the stoichiometric ratio at about 1350 K for several h. The reaction products were then ground in a dry box and reheated; this was repeated until the reaction was complete as indicated by X-ray diffraction analysis. A high-frequency induction furnace was used for heating samples[1] in tantalum carbide crucibles. UPd_3 is a grey solid; it reacts slowly with moisture when exposed to air.

The X-ray diffraction results of the UPd_3 sample used for the calorimetric experiment showed only hexagonal UPd_3 with $a = (577.3 \pm 1)$ pm and $c = (962.7 \pm 2)$ pm. This result is in good agreement with literature[11] X-ray diffraction results. A small amount UO_2 was visible on the X-ray diffraction patterns of the UPd_3 samples. Chemical analysis of UPd_3 gave mass fractions 0.4248 of U (calculated 42.72), 0.5727 of Pd (calculated 57.28), 140×10^{-6} of N, 660×10^{-6} of O, 205×10^{-6} of C, and less than 10×10^{-6} of H.

Adiabatic techniques 5 to 350 K, University of Michigan. Measurements on about 28 g of sample were made in calorimeter W-34 in the Mark II cryostat. Details have been provided elsewhere.[1,12] The heat capacity of the sample was 56 to 87 per cent of the total measured.

The platinum resistance thermometer had been calibrated by the U.S. National Bureau of Standards, (N.B.S.). Temperatures are judged to correspond to IPTS-68 within 0.02 to 350 K. Precision is considerably better; temperature increments are probably accurate to 0.2 mK. Measurements of mass, resistance, potential, and time are referred to standardizations and calibrations performed at N.B.S.

Enthalpy increment values 400 to 875 K, The Netherlands Energy Research Foundation ECN. Measurements were made in a diphenyl-ether drop-calorimeter developed by Cordfunke *et al.*[13] Procedures used have been described elsewhere.[1] Spherical silica ampoules of mass about 1.5 g were used to contain the sample. The ampoules contained about 15 g of UPd_3. Thus, more than 85 per cent of the measured energy was due to the sample. Temperature measurements in the furnace (to ± 0.1 K) were made with {Pt-to-(Pt + 10 mass per cent of Rh)} calibrated thermocouples. The water bath was controlled within 0.002 K. The energy equivalent of the calorimeter was determined by means of calibrations with spherical pieces of α-quartz of which the enthalpies were taken from the JANAF tables.[14] A calibration factor of (79.977 ± 0.063) J·g⁻¹ of mercury was obtained. A correction was made for the difference between the final calorimeter temperature and the standard reference temperature, 298.15 K, using $C_{p,m}(298.15 K)$. The enthalpy increments have a standard deviation of 0.25 per cent.

3. Results

The measured heat capacities of UPd_3 over the low-temperature range are listed in chronological order in table 1 and presented graphically in figure 1 together with those derived from the high-temperature enthalpy increments of table 2. The approximate temperature increments used in the determinations can usually be inferred from the adjacent mean temperatures in table 1.

Twice the standard deviation in the measured low-temperature heat capacity is about 1 per cent from 8 to 30 K, 0.1 per cent from 30 to 280 K, and 0.2 per cent from 280 to 350 K. In the higher-temperature adiabatic region it is 0.5 per cent. Below 10 K we have used the $C_{p,m}$ curve of Andres *et al.*[3,15] (which gives entropy increments in good accord with our values from 4 to 10 K) to ascertain the thermodynamic functions. Below 1 K a Debye limiting-law extrapolation was used.

TABLE 1. Experimental molar heat capacities of UPd_3 ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		Series II		233.57	12.00	Series IV		26.26	1.553	Series VI	
				243.70	12.11			29.03	1.974		
87.38	9.383	53.33	6.053	253.73	12.09	5.27	0.04	31.84	2.439	7.00	0.24[a]
94.21	9.746	58.11	6.715	263.71	12.13	6.24	0.09	34.66	2.933	10.14	0.32
101.58	10.06	63.32	7.364	273.63	12.19	7.23	0.30	37.86	3.504		
109.03	10.36	69.20	7.960	283.68	12.23	9.72	0.33	41.53	4.151	Series VII	
118.38	10.66	75.46	8.500	293.86	12.29	12.43	0.36	44.96	4.736		
129.55	10.95	82.13	9.045	304.00	12.30			48.93	5.382	5.79	0.04[a]
140.32	11.17	89.24	9.513	314.08	12.33	Series V				7.94	0.48
150.80	11.35	96.86	9.871	324.13	12.36					9.62	0.31
161.05	11.50			334.10	12.42	14.39	0.429			11.32	0.33
173.38	11.63	Series III		344.45	12.50	16.04	0.507				
182.62	11.70					17.81	0.617				
192.42	11.78	203.53	11.87			19.78	0.779				
202.37	11.85	213.57	11.93			21.76	0.974				
		223.52	11.99			23.79	1.220				

[a] Enthalpy-type run.

Smoothed values of $C_{p,m}$ at selected temperatures over the entire temperature region are given in table 3.

The results of the drop calorimetric measurements for UPd_3 are given in table 4. The enthalpy increments can be represented by the polynomial expression (390 to 875 K):

$$\{H_m^\circ(T) - H_m^\circ(298.15 \text{ K})\}/(\text{J} \cdot \text{mol}^{-1})$$
$$= 98.6872(T/\text{K}) + 5.7057 \times 10^{-3}(T/\text{K})^2 - 29930.8,$$

with a standard deviation of 0.0025.

The measurements from 1 to 16 K of Andres *et al.*[3,15] join smoothly with these results and reveal the existence of a sharp cooperative-type spike in the heat capacity at about 7 K as well as smaller peaks of 4.6 and 7.6 K. Enthalpy-type runs of this research are consistent in confirming the high heat capacity in this region. Although neither of our studies provides a definitive value of γ (the electronic

TABLE 2. Molar enthalpy increments for UPd_3 ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$\Delta_{298.15\text{K}}^{T} H_m^\circ/(R \cdot \text{K})$		T/K	$\Delta_{298.15\text{K}}^{T} H_m^\circ/(R \cdot \text{K})$	
	expt	calc.		expt	calc.
392.0	1157[a]	1158	660.6	4534	4541
435.0	1688	1693	697.9	5011	5018
443.5	1795	1799	740.8	5579	5570
451.1	1901	1894	780.3	6076	6080
536.8	2961	2970	812.4	6497	6496
595.8	3699	3715	874.6	7314	7306

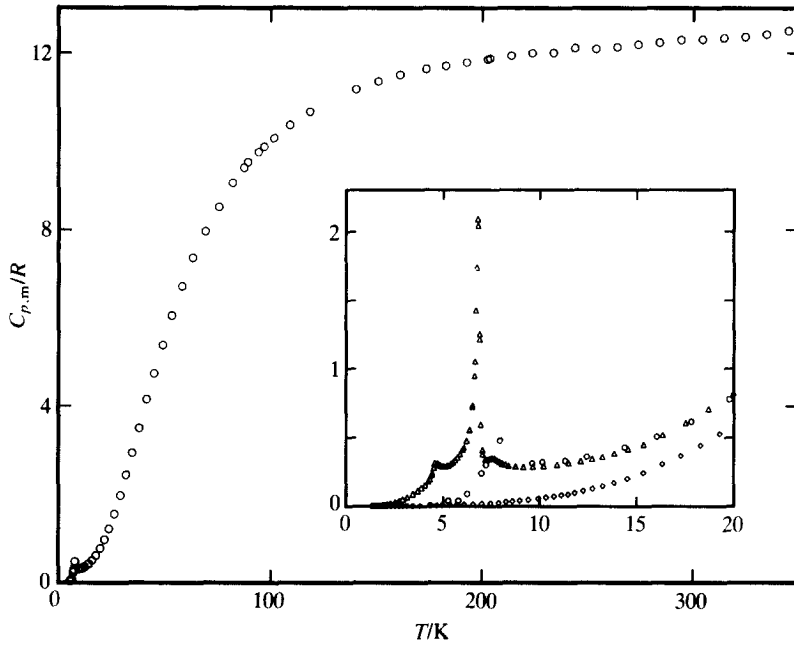[a] The standard deviation in $\Delta_{298.15\text{K}}^{T} H_m^\circ$ is 0.25 per cent.

FIGURE 1. The molar heat capacity of UPd₃. ○, From adiabatic cryogenic calorimetry; △, Andres *et al.*;[3] ◇, values for iso-structural ThPd₃.[3, 15]

TABLE 3. Thermophysical functions of UPd₃ ($R = 8.3144 \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,\,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\dfrac{\Phi_m^\circ}{R}$	$\dfrac{T}{\text{K}}$	$\dfrac{C_{p,\,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\dfrac{\Phi_m^\circ}{R}$
5	0.288	—	—	—	160	11.479	13.785	1164.6	6.507
10	0.295	0.384	2.432	0.140	180	11.691	15.150	1396.4	7.392
15	0.452	0.528	4.233	0.245	200	11.841	16.390	1631.8	8.231
20	0.801	0.700	7.275	0.337	220	11.956	17.524	1869.8	9.025
25	1.373	0.936	12.619	0.432	240	12.044	18.569	2109.9	9.778
30	2.132	1.252	21.319	0.541	260	12.130	19.54	2351.7	10.492
40	3.883	2.102	51.306	0.819	280	12.209	20.44	2595.1	11.170
50	5.551	3.152	98.659	1.179	300	12.290	21.28	2840.1	11.816
60	6.949	4.292	161.41	1.602	320	12.36	22.08	3086.6	12.43
70	8.047	5.449	236.63	2.069	340	12.40	22.83	3334.3	13.02
80	8.884	6.581	321.47	2.563	298.15	12.28	21.21	2817.4	11.76
90	9.520	7.666	431.64	3.070	400	12.42	24.84	4077.0	14.65
100	10.01	8.695	511.38	3.581	500	12.54	27.62	5324.0	16.98
120	10.702	10.586	718.99	4.594	600	12.72	29.92	6586.7	18.95
140	11.165	12.273	937.96	5.573	700	12.90	31.90	7867.8	20.66
					800	13.05	33.63	9164.9	22.17
					900	13.22	35.18	10477.9	23.54

coefficient), unpublished heat capacities of Schlabitz *et al.*[10] extending down to 0.4 K are claimed[9] to establish a value of $\gamma/(R \cdot K^{-1}) < 0.0012$ and Andres *et al.* estimate from their measurements[3] a value not larger than 0.0006. Our estimate of $\gamma'/(R \cdot K^{-1})$ based on $C_{p,m}$ above 200 K yields a value <0.0018 on the basis of the equation:

$$C_{p,m} = 3R\{1 - (\Theta_D^2/20T^2)\} + (\gamma' + \alpha)T, \tag{1}$$

involving the electronic coefficient γ', the expansivity α, and the anharmonicity together.

4. Discussion

Because this compound has been selected by others as a model compound in the elucidation of the electronic structure of the actinides and because the related question of the great stability of UPd_3 needs further elucidation, the discussion will incorporate both thermophysical and thermochemical aspects.

From neutron inelastic scattering,[7, 16, 17] resistivity, magnetic, and other results[9, 10] the electronic structure emerges as one, in sharp contrast to those[1] of URu_3 and URh_3 involving discrete energy levels and localized electrons. From thermophysical properties, confirmation of the above statement arises both from the existence of experimental Schottky levels and from the relatively low value of γ'.
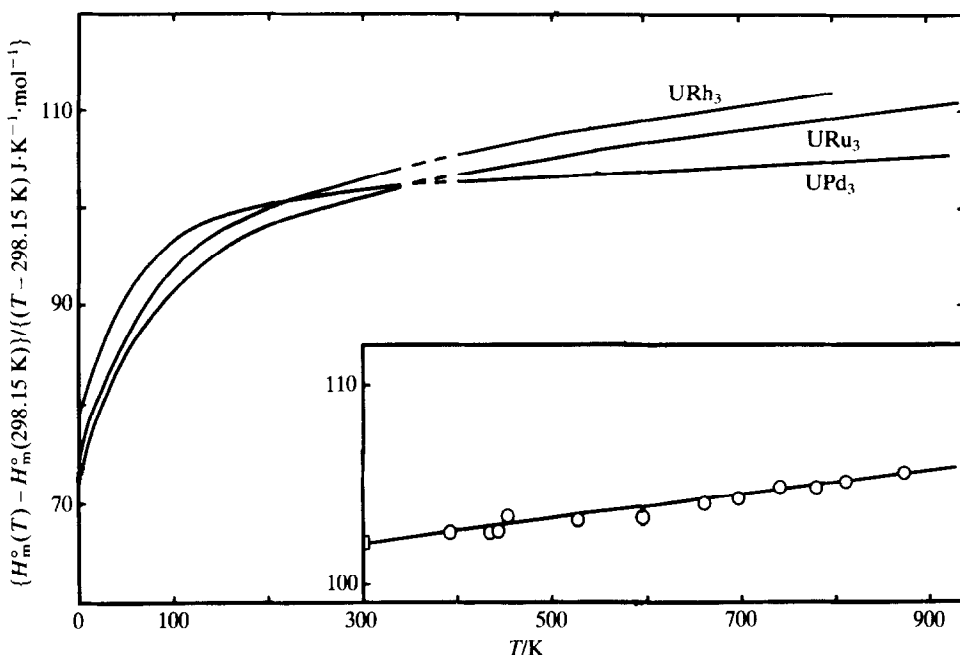

FIGURE 2. Comparison of the molar enthalpy increment divided by the temperature increment for UPd_3, URu_3,[1] and URh_3,[1] from this research. ○, Experimental values from this research.
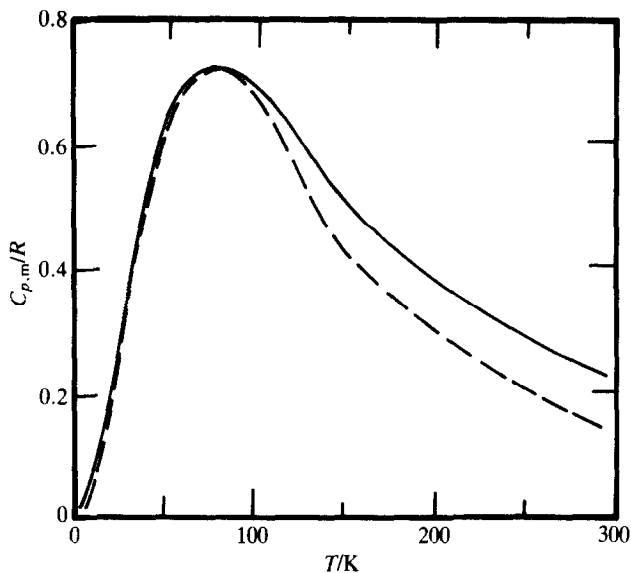
FIGURE 3. Schottky contribution to UPd₃. The curve for theoretical values derived from energy levels of figure 2 are represented by an unbroken line. See text for explanation of broken line resolved from experimental heat capacities taking into account conduction-electron coefficients.

Moreover, the essentially linear separation of $C_{p,m}/R$ for URu₃ and URh₃ from the value for UPd₃ above ambient temperature (see figure 2) is consistent with the γ' observed and the localization of the electrons in UPd₃.

Uranium atoms occur in both hexagonal and cubic sites[11] and each possesses its own levels in the crystalline electric field (C.E.F.). Several of the lower levels have been identified by neutron inelastic scattering[7] and the higher-level scheme has been delineated.[8] This scheme has been depicted in table 4. The Schottky heat-capacity contribution calculated from these levels is depicted in figure 3 (as an unbroken line). The resolution of the heat capacities to permit the evaluation of the calorimetric Schottky contribution has been achieved, noting that the apparent

TABLE 4. Schottky wavenumbers $\tilde{v}$ and degeneracies g for UPd₃

Term symbol	$\tilde{v}/\mathrm{cm}^{-1}$	g	Source[a]	Term symbol	$\tilde{v}/\mathrm{cm}^{-1}$	g	Source[a]
	Hexagonal sites				Cubic sites		
Γ_4	311	2'	T	Γ_4	363	2	T
Γ_{3a}	305	1	T	Γ_1	344	1	T
Γ_{3b}	171	1	T	Γ_3	295	2	T
$\Gamma_{2a,b}$	117	2	E	Γ_{2b}	256	1	T
$\Gamma_{5a,b}$	114	2	E	$\Gamma_{5a,b}$	16.7	2	E
Γ_1	0	1	E	Γ_{2a}	0	1	E

[a] Source: T, theoretical;[8] E, experimental from neutron scattering.[7]

Debye characteristic temperatures for URu_3 and URh_3 are substantially constant above 30 K, by the use of the Lindemann relation:

$$\Theta_D \propto T_{fus}^{1/2} V_m^{-1/3} M^{-1/2} = d,$$

in which Θ_D is the Debye characteristic temperature; V_m, the molar volume; M, the molar mass of the compound; and T_{fus}, the melting temperature of the compound. Then for URu_3, URh_3, and $ThPd_3$ a plot of Θ_D against d is linear. Although UPd_3 and $ThPd_3$ are not of the same structure as the other two, the coordination number (12) is the same. The interpolated Θ_D for UPd_3 is 236 K. Alternatively, a plot of Θ_D against V_m which has been shown to provide good correlations in lanthanide compounds[19-21] gives an almost identical value. From the interpolated Θ_D the lattice contribution of UPd_3 was estimated. Utilizing the former value and a linear term $\gamma'T$ incorporating the electronic coefficient with $\gamma'/R = 0.0006\,\mathrm{K}^{-1}$, we obtain the broken line as the experimental Schottky function in figure 3. The sensitivity of the calculation to higher terms involving anharmonicity and thermal expansion prevent any comparison above 300 K. The values are within the uncertainty to which γ' is known. In addition the parameter B_2^0 in the C.E.F. is known to change significantly with temperature due to the change in the lattice parameter quotient c/a, and this has not been taken into account in the calculation of the energy levels. The agreement provides an excellent confirmation of the reliability of the lower energy levels.

The thermal effect associated with the electric quadrupole interaction has been better delineated elsewhere[3] than in our measurements. The leveling off of the monotonic decrease with temperature of the lattice parameter c at helium temperatures points to a continuous alignment of quadrupole moments along the c

TABLE 5. Thermodynamic functions of solid UPd_3 ($R = 8.3144\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$; $T' = 298.15$ K)

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{T\Delta_0^T S_m^\circ - \Delta_{T'}^T H_m^\circ}{RT}$	$\dfrac{\Delta_{T'}^T H_m^\circ}{R\cdot K}$	$-\Delta_f G_m^\circ/(R\cdot K)$	
					Ref. 22	This work
298.15	12.28	21.21	21.21	0	63023[a]	63478[a]
300	12.28	21.29	21.21	23	63023	63480
400	12.42	24.84	21.70	1258	63086	63625
500	12.56	27.62	22.61	2506	63180	63749
600	12.69	29.92	23.64	3769	63112	63852
700	12.83	31.90	24.69	5045	63484	63928
800	12.97	33.63	25.71	6335	63705	63928
900	13.10	35.15	26.66	7638	63979	63994
942	13.16	35.75	27.05	8190	64111[a]	63992[a]
					64447[b]	63992[b]
1000	13.24	36.54	27.58	8960	64604[b]	63960[b]
1049	13.31	37.17	28.02	9606	64738[b]	62724[b]
					65310[c]	62724[c]
1100	13.38	37.80	28.45	10287	65421	63856
1200	13.52	38.98	29.28	11632	65644	63704

[a] Refers to phase III of U;[22] [b] refers to phase II of U;[22] [c] refers to phase I of U.[22]

axis.[9] The sudden decrease of a below 10 K could be a lattice distortion connected with the quadrupole ordering and producing the sudden depopulation of the Γ_5 doublet into the Γ_{2a} singlet of the cubic sites. Although our average-heat-capacity (*i.e.* enthalpy) measurements in the 4 to 25 K region provide confirmation of the overall thermodynamic functions, we note that the cooperative "depopulation" on cooling of the doubly degenerate Schottky level would require an entropy increment of $\frac{1}{2}R \ln 3$ and consider this to be within the experimental error of the combined heat-capacity determinations.

Finally, the thermochemical functions of UPd$_3$ are given in table 5 as calculated from the thermophysical results of this paper and the enthalpy of formation $\Delta_f H_m^\circ = -(15810 \pm 38) R \cdot K$ at 298.15 K from an adjuvant study.[22] A comparison of a derived enthalpy function of the results for UPd$_3$ with that for URh$_3$ and for URu$_3$ is shown in figure 2.

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