Thermodynamics of uranium intermetallic compounds

I. Heat capacities of URu$_3$ and URh$_3$ from 5 to 850 K [a]

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

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

RAMON BURRIEL,[c] MICHAEL (WING KEI) TO,[d] HANAA ZAINEL,[e]
and EDGAR F. WESTRUM, JR.

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

Heat capacities of carefully characterized samples of URu$_3$ and URh$_3$ were measured by adiabatic calorimetry from 5 to 350 K by adiabatic calorimetry and from 300 to 850 K by enthalpy-increment drop calorimetry. Values for the thermodynamic properties at 298.15 K: $C_{p,m}/R$, S_m°/R, $\{H_m^\circ(T) - H_m^\circ(0)\}/R$, and $-\{G_m^\circ(T) - H_m^\circ(0)\}/R$ are: URu$_3$: 12.20, 17.38, 2550 K, and 8.82 K; URh$_3$: 12.39, 18.31, 2639 K, and 9.46 K. Phase transitions were not observed over the entire temperature range. In contrast with UPd$_3$ with localized spins and with related materials showing localized spin fluctuations, the electronic coefficients show typical metallic behavior.

1. Introduction

Thermodynamic properties of actinide-intermetallic compounds are technologically useful since it has been found that metallic inclusions in nuclear fuel, formed during fission in a fast-breeder reactor, consist of high-stability alloys.[1] This is particularly so with the light platinum metals, which form in the nuclear-fuel matrix alloys of the type UMe$_3$ (Me = Ru, Rh, and Pd), in solid solution with one another as (U, Pu)(Ru, Rh, Pd)$_3$. For a better understanding of the formation and stability of these solid solutions thermodynamic information on these materials is necessary.

The uranium intermetallics are also of interest because of their thermophysical properties. The 5f electrons of the actinides exhibit behavior intermediate between that of the 4d itinerant electrons of the transition metals and the localized 4f electrons of the lanthanides. Moreover, 5f electrons are of considerable interest in the study of magnetism, and of crystalline electric-field levels by optical and neutron spectroscopy. This initiatory paper presents thermochemical and thermophysical properties within the context of a larger program on the determination of their chemical thermodynamics.

2. Experimental

The starting materials for the preparation of URh_3 and URu_3 were rhodium and ruthenium powders (99.99 mass per cent purity, Johnson Matthey Chemicals, Ltd.) and uranium nitride (UN) prepared by the reaction of finely divided uranium powder with nitrogen. The uranium sesquinitride that is formed at about 1000 K is decomposed in an argon atmosphere to UN at 1700 K. Before use, the rhodium and ruthenium powders were dried in vacuum at about 800 K to remove any adsorbed moisture. URu_3 and URh_3 were prepared then by heating mixtures of UN with ruthenium and rhodium in stoichiometric ratios at about 1600 and 1400 K, respectively. A high-frequency induction furnace was used for the heating of samples. The equipment consisted of a Pyrex tube with a water-cooled copper concentrator containing a TaC crucible on an alundum bar. The tube was assembled in the glove box, placed in the induction coil of the furnace, and connected with the argon purification system. After the tube had been flushed sufficiently with purified dry argon, the sample in the TaC crucible was heated. Temperatures were measured with a calibrated pyrometer on a black-body hole in the TaC crucible (accuracy ± 10 K in the temperature range 100 to 1800 K). The reaction products were ground and reheated; this was done until the reaction was complete as indicated by the X-ray diffraction results. The lattice parameters of the URu_3 and URh_3 samples are given in table 1. Since the UN starting material contained a known amount of UO_2, the URu_3 and URh_3 preparations were purified by washing them in an acid solution $\{n(HNO_3)/n(H_2O) = 1\}$ to remove any UO_2 present. URu_3 and URh_3 are insoluble in this solution. The purified preparations were dried in vacuum at 800 K. The original UN-to-Rh mole ratio was corrected for this amount of UO_2 to give finally the stoichiometric compositions.

ADIABATIC TECHNIQUES, 6 TO 350 K, UNIVERSITY OF MICHIGAN

The Mark II cryostat and the adiabatic technique were employed.[2] Gold-plated copper calorimeter W–34 with a volume of 8 cm^3 was used. The calorimeter was loaded with sample in a dry box, evacuated, and helium gas to improve thermal equilibrium added at 3 kPa pressure at 300 K to provide thermal contact between

TABLE 1. X-ray diffraction results including lattice parameters a_0 for URu_3 and URh_3

Compound	Symmetry	a_0/pm	
		Expt.	Literature
$URu_{2.9996}$	Pm3m (cubic Cu_3Au-type)	397.9	398.0[4]
$URh_{3.0000}$	Pm3m (cubic Cu_3Au-type)	399.15	399.1[5]

sample and calorimeter. It was then sealed, placed in the cryostat, and cooled. About 26 g of sample was used in each measurement.

The heat capacity of the empty calorimeter was determined in a separate set of experiments. The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type platinum resistance thermometer (A–1) located in a central well within the calorimeter. The heat capacity of the sample represented from 35 to 45 per cent of the total.

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

ENTHALPY-INCREMENT VALUES, 400 TO 850 K
(NETHERLANDS ENERGY RESEARCH FOUNDATION ECN)

Measurements were made in a diphenyl-ether drop calorimeter developed by Cordfunke et al.[3] The energy equivalent of the calorimeter was determined by means of calibrations with spherical pieces of α-quartz. A calibration factor of (79.977 ± 0.063) $J \cdot g^{-1}$ for mercury was obtained. For the drop-calorimetric studies, spherical vitreous-silica ampoules with a 0.6 mm wall thickness and 20 mm diameter were used to contain the samples. The ampoules were about 4.2 cm^3 in volume and were of mass 1 to 1.5 g empty. Heat from the sample and ampoule, when dropped into the calorimeter, melted solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether was determined by weighing the displaced mercury. Temperature measurements in the furnace were made with calibrated (Pt-to-(Pt+10 mass per cent of Rh) thermocouples to within ± 0.1 K. The enthalpy contribution of the vitreous silica was determined in a series of separate drop measurements.

The ampoules contained about 13 g of URu_3 and about 12.5 g of URh_3, respectively. In the experiments more than 85 per cent of the measured energy was due to the sample. A correction was made for the difference between the final calorimeter temperature and the standard reference temperature, 298.15 K, using $C_{p,m}(298.15 \text{ K})$.

TABLE 2. Experimental heat capacity of URu_3 and URh_3 ($R = 8.3143 \, \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

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	$C_{p,m}/R$
						URu_3					
Series I		19.02	0.300	41.57	2.514	101.90	8.446	204.86	11.37	250.44	11.838
6.92	0.022	20.58	0.502	44.67	2.896	111.21	8.929	214.22	11.50	263.68	11.871
8.83	0.045	22.29	0.502	47.80	3.303	120.03	9.360	223.48	11.61	273.67	12.050
9.67	0.048	24.19	0.646	51.68	3.833	129.50	9.745	Series III		283.58	12.111
10.59	0.061	26.39	0.825	56.21	4.387	139.65	10.07			293.42	12.170
11.66	0.079	28.68	1.019	Series II		149.46	10.36	182.46	11.030	303.40	12.239
12.59	0.092	30.68	1.218	66.87	5.634	159.0	10.60	191.74	11.171	313.14	12.310
13.74	0.120	32.62	1.385	70.91	6.056	168.35	10.82	200.22	11.289	316.75	12.293
14.77	0.147	34.74	1.680ᵃ	78.27	6.755	177.30	10.98	208.61	11.374	326.35	12.421
16.02	0.184	36.76	1.919ᵃ	86.25	7.449	186.19	11.15	216.91	11.481	335.90	12.490
17.43	0.229	38.93	2.195ᵃ	93.58	7.960	195.38	11.27	225.03	11.64	344.85	12.553
								233.45	11.710		
						URh_3					
Series I		21.89	0.517	Series II		108.73	9.249	195.91	11.518	291.77	12.366
6.79	0.025	23.90	0.686	53.57	4.603	118.66	9.708	206.34	11.639	302.53	12.432
9.57	0.044	26.37	0.926	58.15	5.194	129.14	10.091	217.10	11.763	313.23	12.496
11.05	0.068	29.05	1.245	63.69	5.871	140.25	10.438	227.97	11.860	323.88	12.550
12.79	0.094	33.31	1.760	69.84	6.515	151.48	10.719	238.74	11.965	334.44	12.647
14.56	0.142	38.29	2.449	76.32	7.116	162.40	10.963	249.34	12.057	344.96	12.728
16.29	0.196	42.08	2.993	83.39	7.740	173.06	11.190	259.85	12.123		
18.10	0.277	45.81	3.528	90.88	8.282	Series III		270.30	12.193		
20.07	0.392	50.64	4.204	99.31	8.776	185.57	11.379	280.93	12.287		

3. Results

The measured heat capacities of both compounds over the low-temperature range are listed in chronological order in table 2 and presented graphically in figure 1 together with those values obtained from the enthalpy increments from the higher-temperature results of table 4. The approximate temperature increments used in the cryogenic (adiabatic) determinations can usually be inferred from the adjacent mean temperatures in table 2. Twice the standard deviation in the measured low-temperature heat capacity is about 1 per cent from 8 to 30 K, 0.2 per cent from 30 to 300 K, and 0.3 per cent from 300 to 350 K. Below 10 K, the heat capacities were extrapolated with a $C_{p,m}/T$ against T^2 plot. The electronic (conduction) coefficients $\gamma/(R \, K)$ calculated on this basis are 0.0018 and 0.0016 for URu_3 and URh_3 at $T = 0$. Corresponding values for $\Theta_D(0)$ are 299 and 297 near $T = 0$. Our $\gamma/(R \, K)$ values for URh_3 at low temperature agree within a few per cent with the values reported by Trainor and Brodsky[6] below 14 K; they give 0.00174 and a similar temperature variation.

Values of the smoothed thermodynamic properties as derived from the fitted polynomial expressions are presented in table 3 for selected temperatures. The accuracies of the thermodynamic function values is estimated to about 0.2 per cent above 100 K.

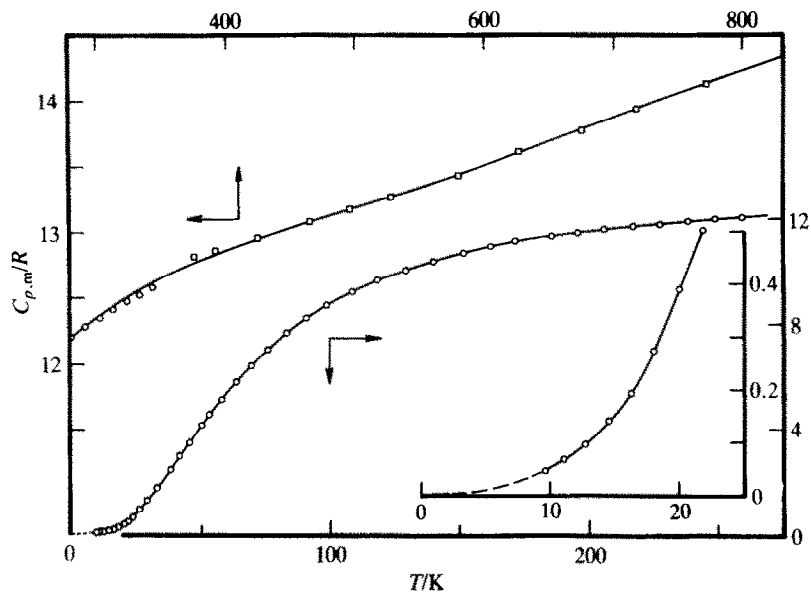The heat-capacity curves show normal behavior in both compounds, with

FIGURE 1. The heat capacity of URh_3. $\bigcirc$, Heat capacities determined in the cryogenic adiabatic calorimeter; $\square$, heat capacities derived from enthalpy determinations.

FIGURE 2. The heat capacity of URu_3. $\bigcirc$, Heat capacities determined in the cryogenic adiabatic calorimeter; $\square$, heat capacities derived from enthalpy determinations.
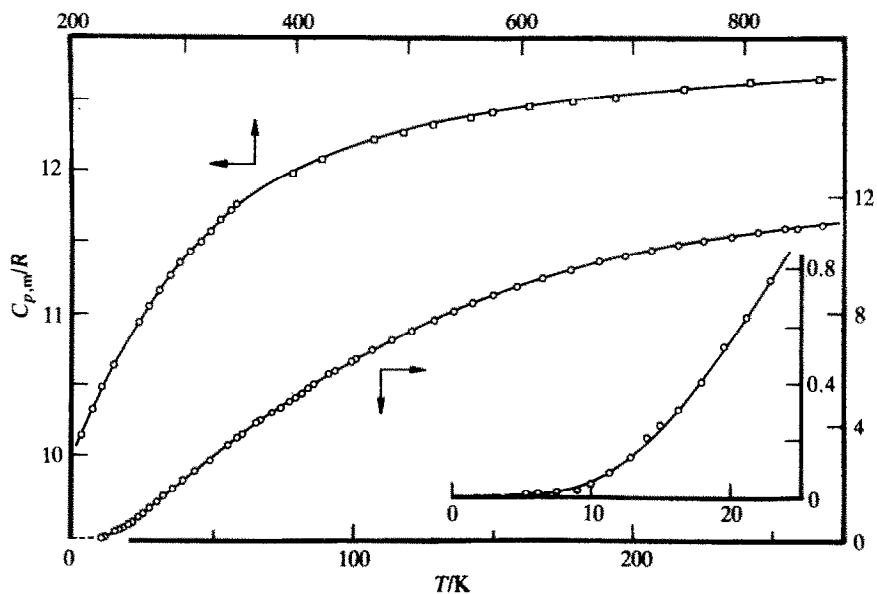
TABLE 3. Thermodynamic properties of URu$_3$ and URh$_3$ ($R = 8.3143$ J·K^{-1}·mol^{-1})

$\dfrac{T}{\mathrm{K}}$	$\dfrac{C_{p,\,m}}{R}$	$\dfrac{S_m^\circ(T)-S_m^\circ(0)}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\ \mathrm{K}}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
		URu$_3$		
5	0.015	0.013	0.033	0.006
10	0.053	0.032	0.186	0.014
15	0.152	0.070	0.663	0.026
20	0.356	0.138	1.879	0.044
25	0.692	0.251	4.443	0.074
30	1.147	0.416	9.001	0.116
40	2.278	0.895	25.897	0.247
50	3.610	1.548	55.406	0.439
60	4.847	2.317	97.786	0.687
70	5.951	3.149	151.90	0.979
80	6.903	4.007	216.30	1.304
90	7.703	4.868	289.45	1.652
100	8.368	5.715	369.91	2.016
120	9.372	7.335	547.92	2.769
140	10.077	8.836	742.80	3.530
160	10.602	10.217	949.82	4.281
180	11.010	11.490	1166.1	5.012
200	11.330	12.667	1389.6	5.719
220	11.578	13.760	1618.8	6.401
240	11.772	14.776	1852.4	7.057
260	11.930	15.72	2089.4	7.688
280	12.073	16.61	2329.5	8.294
300	12.210	17.45	2572.3	8.877
320	12.337	18.24	2817.8	9.438
340	12.445	18.99	3065.7	9.978
273.15	12.025	16.32	2247.0	8.089
298.15	12.198	17.38	2549.8	8.824
400	12.69	21.04	3819.7	11.49
500	13.03	23.91	5106.0	13.70
600	13.34	26.31	6424.8	15.60
700	13.62	28.39	7773.0	17.28
800	13.90	30.22	9149.3	18.79
900	14.18	31.88	10553.4	20.15
		URh$_3$		
5	0.022	0.008	0.030	0.002
10	0.054	0.032	0.212	0.011
15	0.150	0.068	0.675	0.023
20	0.387	0.140	1.947	0.043
25	0.793	0.267	4.827	0.074
30	1.345	0.458	10.120	0.121
40	2.693	1.025	30.141	0.271
50	4.118	1.780	64.235	0.495
60	5.421	2.648	112.07	0.780
70	6.536	3.570	172.03	1.113
80	7.458	4.505	242.15	1.478
90	8.208	5.429	320.61	1.866
100	8.822	6.326	405.86	2.268
120	9.754	8.022	592.16	3.087
140	10.426	9.579	794.29	3.905
160	10.924	11.005	1008.0	4.705

TABLE 3—*continued*

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^\circ(T)-S_m^\circ(0)}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\,K}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
180	11.292	12.314	1230.4	5.478
200	11.568	13.519	1459.1	6.223
220	11.787	14.632	1692.7	6.938
240	11.972	15.666	1930.4	7.622
260	12.133	16.63	2171.5	8.279
280	12.275	17.53	2415.6	8.908
300	12.407	18.38	2662.4	9.512
320	12.544	19.19	2911.9	10.092
340	12.682	19.96	3164.2	10.650
273.15	12.23	17.23	2331.7	8.695
298.15	12.39	18.31	2639.5	9.457
400	12.978	22.04	3932.9	12.206
500	13.340	24.98	5251.9	14.477
600	13.648	27.44	6601.6	16.438
700	13.967	29.57	7982.0	18.165
800	14.324	31.46	9396.1	19.710

contributions only from the lattice vibrations and the free-electron gas. Since the apparent Debye parameters calculated from the observed heat capacities are approximately constant above 30 K, estimates of Θ_∞ as 276 and 258 K for URu_3 and URh_3 have been made on the basis of the equation: $C_{p,m} = 3nR(1-\Theta_\infty^2/20T^2)+aT$,[7] by slopes of plots of $(C_{p,m}-12R)/T$ against T^{-3} over the region $0.7\Theta_D < T < 1.3\Theta_D$. The zero intercept of these linear curves at $T = \infty$ gives values of 0.0024 and 0.0028 for the coefficients of the linear term in T involving the conduction electronic coefficient γ', the thermal expansivity, and the anharmonicity coefficient. Hence $\gamma'/(R\ K)$ does not increase much in this region.

The results of the drop-calorimetric measurements for URu_3 and URh_3 are given in table 4. Over the range of the experimental measurements the enthalpy increments as a function of temperature can be represented by a polynomial expression of the usual form: $H_m^\circ(T) = aT+bT^2+cT^{-1}+d$, the coefficients of which have been obtained by least squares. Boundary conditions were applied so that, when $T = 298.15$ K, $\{H_m^\circ(T)-H_m^\circ(298.15\ \mathrm{K})\} = 0$ and $C_{p,m}(T) = C_{p,m}(298.15\ \mathrm{K})$. The last quantity was obtained from the low-temperature heat-capacity measurements (table 3). The high-temperature enthalpy increments correlate smoothly with the low-temperature values.

For URu_3 we obtain (298 to 890 K):

$$\{H_m^\circ(T)-H_m^\circ(298.15\ \mathrm{K})\}/(\mathrm{J}\cdot\mathrm{mol}^{-1}) = 101.224(T/\mathrm{K})+9.23014\times 10^{-3}(T/\mathrm{K})^2$$
$$+4.71814\times 10^5(T/\mathrm{K})^{-1}-32582.9,$$

with standard deviation 0.25 per cent. For URh_3 we obtain (298 to 842 K):

$$\{H_m^\circ(T)-H_m^\circ(298.15\ \mathrm{K})\}/(\mathrm{J}\cdot\mathrm{mol}^{-1}) = 104.445(T/\mathrm{K})+9.10274\times 10^{-3}(T/\mathrm{K})^2$$
$$+6.10033\times 10^5(T/\mathrm{K})^{-1}-33995.5,$$

TABLE 4. Enthalpy increments of URu_3 and URh_3 above 400 K ($R = 8.3143$ J·K^{-1}·mol^{-1})

$\dfrac{T}{K}$	$\dfrac{H_m^\circ(T) - H_m^\circ(298.15\ K)}{R\ K}$	$\dfrac{T}{K}$	$\dfrac{H_m^\circ(T) - H_m^\circ(298.15\ K)}{R\ K}$	$\dfrac{T}{K}$	$\dfrac{H_m^\circ(T) - H_m^\circ(298.15\ K)}{R\ K}$
		URu_3			
406.0	1349	607.1	3979	746.4	5875
427.8	1632	629.9	4269	764.3	6118
451.5	1938	662.9	4727	821.1	6883
481.4	2317	711.8	5375	889.7	7860
		URh_3			
423.7	1611	576.6	3645	772.4	6354
465.2	2158	627.0	4344	842.0	7363
496.6	2571	674.9	4983		
528.6	3000	717.6	5586		

with standard deviation 0.27 per cent. The thermodynamic functions of URu_3 and URh_3 are listed in table 5, as calculated from the enthalpy polynomials, as derived above, the enthalpies of formation at 298.15 K,[8] and auxiliary values for U,[9] Rh,[10] and Ru.[10]

4. Discussion

Previous measurements of the quotient χ/ρ of the magnetic susceptibility and density of URh_3 show a temperature-independent paramagnetism with a value of $\chi/\rho = 2.24 \times 10^{-8}$ m^3·kg^{-1} at 300 K.[11] This value in URh_3 suggests the existence of strong hybridization of the 6d band of the uranium with the 4d band of the

TABLE 5. Thermochemical functions for URu_3 and URh_3 ($R = 8.3143$ J·K^{-1}·mol^{-1})

Reference uranium phase	$\dfrac{T}{K}$	$\dfrac{\Delta_f H_m^\circ}{10^3 R\ K}$	$\dfrac{\Delta_f G_m^\circ}{10^3 R\ K}$	$\dfrac{\Delta_f H_m^\circ}{10^3 R\ K}$	$\dfrac{\Delta_f G_m^\circ}{10^3 R\ K}$
		URu_3		URh_3	
α	298.15	−18.141	−18.456	−36.222	−36.493
	300	−18.141	−18.458	−35.222	−36.494
	400	−18.111	−18.568	−36.217	−36.588
	500	−18.082	−18.686	−36.228	−36.678
	600	−18.069	−18.808	−36.275	−36.764
	700	−18.088	−18.930	−36.364	−36.839
	800	−18.145	−19.048	−36.507	−36.898
	900	−18.250	−19.155	−36.709	−36.935
	942	−18.310	−19.196	−36.812	−36.944
β	942	−18.646	−19.196	−37.148	−36.944
	1000	−18.700	−19.229	−37.265	−36.928
	1049	−18.747	−19.253	−37.365	−36.906
γ	1049	−19.319	−19.253	−37.937	−36.906
	1100	−19.340	−19.249	−38.016	−36.858
	1200	−19.382	−19.238	−38.176	−36.748

rhodium.[12] Measurements of the De Haas and van Alphen effect[13] and of the T^3 dependence of the resistivity at low temperatures[11] have been interpreted by a model in which a broad hybridized band between 6d and 5f uranium states overlaps the Fermi level.

Additional 5f levels in the actinide series tend to a gradual development of local-moment behavior. In the series $ThRh_3$, URh_3, $NpRh_3$, $PuRh_3$, the stabilization of the 5f energy level is clearly apparent from the magnetic susceptibilities, electric conductivities,[14] and heat-capacities. In $ThRh_3$, the 5f level is above the Fermi energy; in URh_3 a broad (6d + 5f) hybridized band overlaps the Fermi level. Addition of more 5f electrons stabilizes a nearly magnetic state in $NpRh_3$ with a reported spin-fluctuation temperature $T_S \approx 100$ K.[14] and subsequently complete localization occurs in $PuRh_3$ which presents antiferromagnetic ordering at 6.6 K.[11]

The γ values, at low temperatures, obtained from our heat-capacity measurements indicate a similar density of states in the Fermi surface for URh_3 and URu_3 intermediate between the values for $ThRh_3$ and $NpRh_3$ in accordance with the susceptibilities.[11] That and the absence of any Schottky anomaly, in contrast to UPd_3,[15] is compatible with a broad band in the Fermi surface with unlocalized electrons.

Although evidence of similar measurements for the (actinide + ruthenium) intermetallics is lacking, we predict from our results a role for the 5f electrons similar to that in the rhodium series.

Our 4d uranium compounds as well as the other non-d compounds with cubic structure presented in table 6 show a clear correlation in each group between the atomic distances and the γ values. This reflects the stabilization of the 5f electrons by band narrowing, increasing the U–U distances, and eventual magnetic ordering in UIn_3 and UPb_3. Both magnetic ordering[16] and low-energy crystal-field transitions,[17] have been unambiguously established to be present in UPd_4 which is isostructural with URu_3 and URh_3. Its lattice parameter ($a = 406.9$ pm)[18] is close to the U–U distance in UPd_3; hence similar behavior is explicable.

TABLE 6. Comparison of hexagonal actinide intermetallic compounds

Compound	M / g·mol^{-1}	a_0 / pm	$10^3\gamma$ / R K	$\Theta_D(0)$ / K	$\Theta_D(0)M^{1/2}$ / 10^3 K·g$^{1/2}$·mol$^{-1/2}$
UAl_3	26.98	428.7	5.0	378	3.4
USi_3	28.09	403.5	1.7	397	3.6
UGa_3	69.72	424.8	6.3	288	4.1
UGe_3	72.59	420.6	2.5	255	3.7
UIn_3	114.82	460.1	6.0	>174	>3.2
UPb_3	207.19	479			
URu_3	101.07	397.9	1.8	299	5.2
URh_3	102.90	399.15	1.6	297	5.2
UPd_3	106.40	410.3 ^{a}	<1.2	>237	>4.4
$ThPd_3$	106.40	417.9 ^{a}	0.2	265	4.8

^{a} U–U or Th–Th distances with the 6 nearest neighbors for hexagonal structures with the same coordination numbers.

Despite large variation in the molar masses M we find a remarkable uniformity in the $\Theta_D(0)M^{1/2}$ values indicating the dominance of low-energy vibrational modes of the lattice in which the heavy atoms do not participate.[19] This regularity permits calculation of the lattice heat-capacity contribution by the corresponding-states principle in the compounds that have thermal anomalies such as UPd_3.[15] We obtain $\Theta_D(0) = 273$ K and $\Theta_D(\infty) = 236$ K.

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