

THERMOPHYSICAL PROPERTIES OF CeB₆ AND PrB₆ AT SUBAMBIENT TEMPERATURES*

*E. F. Westrum, Jr. **, B. H. Justice, H. L. Clever and D. A. Johnson*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055 USA

Abstract

Equilibrium adiabatic heat-capacity measurements have been made on zone refined samples of CeB₆ and PrB₆. Companion measurements made on LaB₆, NdB₆, and GdB₆ have been reported elsewhere. These show cooperative lambda-type anomalies associated with antiferro-magnetic ordering. Except for lanthanum hexaboride, Schottky internal crystal field levels result in significant contributions to the thermodynamic functions. The gross thermodynamic properties at 298.15 K heat capacity (C_p/R), entropy increment ($\Delta_{0,m}^T S^0/R$), and Gibbs energy function are correlated with the nature of the lanthanide. For LaB₆, CeB₆, PrB₆, NdB₆, and GdB₆ the three properties are, respectively: {11.654, 12.014, 11.997, 11.916, 11.695} C_p/R ; {10.001, 11.803, 12.430, 12.558, 13.982} S^0/R , and finally {4.379, 5.912, 6.232, 6.451, 7.905} Φ_m^0/R .

Keywords: entropy, heat capacity, hexaborides, lanthanide metals, thermophysics, transitions

Introduction

The experimental subambient temperature heat capacity data of three lanthanide hexaborides (those of La, Nd, and Gd) have been recently presented in paper 1 [1]. Two additional heavy fermion hexaborides of particular interest are those of cerium and praseodymium, both with f-electrons. With the thermophysical values of the additional two compounds we have a better prospect of making a good evaluation of their analysis into internal and lattice degrees of freedom.

Experimental

Sample provenance

The availability of high-quality, zone-melted rods and/or composition-adjustment-samples has occasioned study of the heat capacity and related thermophysical proper-

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** Author for correspondence: E-mail: westrum@umich.edu

ties. The purification and characterization of both samples were subjected to the overall composition adjustment described earlier [2], but neither were zone melted into rods. Both samples would be expected to be about as spectroscopically pure as the GdB₆ despite the large variety of physical ground states (review in reference [3]) simple band metals (LaB₆), local moment magnets (GdB₆), or dense kondo systems (CeB₆), (NdB₆), and (PrB₆).

Cryostat, calorimeter and temperature scale

These details are expounded in paper 1 [1]. Temperatures are given in terms of IPTS-48 and accord with the thermodynamic temperature scale to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. The temperature increments are determined with higher precision and are probably correct to a few tenths of mK after correction for quasi-adiabatic drift. All measurements of mass, resistance, potential, temperature, and time are referred to calibrations and standardizations made at the National Bureau of Standards, (presently NIST).

Generation of thermodynamic functions

The evaluation of the thermophysical data were made with the internationally used fitting and averaging functions [4]. The heat capacity data for CeB₆ were extrapolated to 0 K using the data of Bredl [5] from 0.04 to 1 K resulting in a Fermi- γ of 260 mJ mol⁻¹ K⁻² and further electron and magnon contributions to the heat capacity. These data were smoothly joined to the transitional heat capacity measurements of Sullow *et al.* [6] from 0.7 to 4.5 K, done under a hydrostatic pressure of one atmosphere. This combined curve then was smoothly joined to the data of this report at 5 K.

The heat capacity values for PrB₆ were extrapolated to 0 K using the heat capacity data of McCarthy *et al.* [7] between 1.7 and 15 K. These data lead a Fermi- γ of about 280 mJ mol⁻¹ K⁻². Their data below 5 K were joined to the present curve at 5 K. The recent reevaluation and assessment of the lanthanide chalcogenides has indicated that uncertainties in chemical or in phase composition (or both) of the sample are often more serious than heat capacity measurement inaccuracy on related substances [8].

Results and discussion

The heat capacities of both hexaborides were measured from 5 to 350 K and are shown in Figs 1 and 2 with the low temperature regions depicted on an expanded scale. The experimental heat capacity values are given in Table 1 in chronological sequence so that the approximate temperature increments employed in the measurements may be inferred from the difference in the mean temperatures of adjacent results. These values have been adjusted for curvature and are based upon molar masses of 204.98 and 205.76 g mol⁻¹ for cerium and praseodymium hexaboride, respectively.

The smoothed thermodynamic properties of both hexaborides, derived from the experimental results, are summarized at selected temperatures in Table 2. The

Table 1 Experimental heat capacities of cerium hexaboride and praseodymium hexaboride ($R=8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$)

T/K	$C_{\text{p,m}}^{\circ}/R$	T/K	$C_{\text{p,m}}^{\circ}/R$	T/K	$C_{\text{p,m}}^{\circ}/R$
Cerium hexaboride, CeB ₆					
Series I		326.10	12.934	7.65	0.251
123.59	4.650	335.73	13.230	8.47	0.232
132.87	5.064	345.47	13.517	9.38	0.210
141.64	5.464			10.26	0.193
151.28	5.906	Series III		11.20	0.175
161.55	6.382	163.18	6.456		
		172.99	6.909	Series VI	
Series II		182.20	7.334	5.28	0.351
96.44	3.523	191.58	7.761	5.86	0.303
104.29	3.833	229.20	9.400	6.58	0.266
111.72	4.139	237.94	9.757	7.30	0.254
127.74	4.831			8.09	0.231
135.67	5.191	Series IV		8.94	0.221
143.32	5.541	5.30	0.413	9.85	0.201
151.00	5.893	5.60	0.337	10.79	0.185
158.58	6.243	6.40	0.287	11.78	0.168
166.15	6.596	8.01	0.231	12.80	0.164
173.91	6.955	9.70	0.204	13.80	0.165
181.77	7.318	11.60	0.167	14.78	0.168
189.48	7.670	13.52	0.165	15.70	0.176
197.15	8.010	15.35	0.174	16.88	0.187
204.88	8.353	17.18	0.199	18.38	0.224
212.58	8.689	18.99	0.240	20.16	0.279
220.39	9.027	21.11	0.315	22.30	0.366
231.07	9.473	23.41	0.389	24.61	0.474
239.55	9.830	25.60	0.524	27.04	0.601
249.82	10.229	27.94	0.650	29.47	0.736
259.22	10.598	30.40	0.789	32.04	0.883
268.67	10.959	32.91	0.933	34.92	1.046
277.77	11.293			38.39	1.235
287.85	11.643	Series V		42.54	1.444
297.21	11.983	5.27	0.379		
306.80	12.310	6.18	0.311	Series VII	
316.43	12.630	6.90	0.272	30.80	0.812

Table 1 Continued

<i>T</i> /K	$C_{p,m}^{\circ}/R$	<i>T</i> /K	$C_{p,m}^{\circ}/R$	<i>T</i> /K	$C_{p,m}^{\circ}/R$
34.21	1.007	57.26	2.074	90.77	3.305
37.94	1.211	63.12	2.304	99.32	3.636
42.18	1.426	69.28	2.518	94.64	3.452
46.92	1.649	75.74	2.748	101.20	3.707
51.94	1.863	82.97	3.015	111.13	4.115
Praseodymium hexaboride, PrB ₆					
Series I		248.25	10.271	22.75	0.516
49.86	1.978	258.90	10.614	24.72	0.613
52.52	2.109	268.03	10.971	26.84	0.724
57.88	2.366	278.26	11.318	29.24	0.857
64.08	2.656	288.58	11.675	31.58	0.993
69.45	2.910	298.79	12.032	34.45	1.161
76.57	3.235	308.92	12.352	38.02	1.360
84.08	3.573	318.85	12.656	42.31	1.591
92.37	3.937	328.63	12.901	46.60	1.815
102.48	4.377	338.26	13.167	51.17	2.041
112.21	4.793	346.81	13.378	56.48	2.295
121.64	5.198				
119.84	5.119	Series II		Series III	
129.80	5.532	4.37	0.013	7.49	0.602
139.99	5.975	4.36	0.210	4.62	0.651
150.38	6.413	4.50	0.481	4.98	0.696
160.60	6.841	4.89	0.692	5.45	0.972
170.57	7.264	5.53	1.076	5.92	1.628
180.55	7.666	6.57	0.783	6.91	0.596
190.49	8.066	8.40	0.430	7.86	0.439
200.45	8.456	10.60	0.366	8.41	0.424
198.19	8.375	11.23	0.357	8.96	0.408
208.03	8.760	12.62	0.322	9.49	0.385
218.13	9.161	17.06	0.352	10.07	0.379
228.27	9.540	18.79	0.401	10.70	0.345
238.30	9.916	20.72	0.436	11.35	0.342

Table 1 Continued

<i>T</i> /K	$C_{p,m}^{\circ}/R$	<i>T</i> /K	$C_{p,m}^{\circ}/R$	<i>T</i> /K	$C_{p,m}^{\circ}/R$
Series IV		8.97	0.513	Series VI	
8.05	0.551	16.79	0.345	4.56	0.424
12.28	0.323	17.70	0.365	8.76	0.501
17.91	0.377	18.10	0.373	19.78	0.418
		18.61	0.396	20.42	0.424
Series V		19.17	0.407		

Table 2 Thermodynamic function of cerium hexaboride and praseodymium hexaboride ($R=8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$)

<i>T</i> /K	$C_{p,m}^{\circ}/R$	$S_{0,m}^{\circ T}/R$	$H_{0,m}^{\circ T}/RK$	$\Phi_m^{\circ}(T,0)/R$
CeB ₆				
0	0	0	0	0
1.5	0.317	0.162	0.155	0.059
2.0	0.771	0.306	0.411	0.101
2.29	1.907	0.474	0.775	0.136
4	0.457	0.870	1.925	0.388
5	0.366	0.960	2.330	0.494
10	0.193	1.148	3.633	0.785
15	0.169	1.217	4.487	0.918
20	0.274	1.277	5.539	1.000
25	0.493	1.360	7.422	1.064
30	0.767	1.474	10.559	1.122
35	1.051	1.614	15.105	1.182
40	1.318	1.772	21.039	1.246
45	1.560	1.941	28.244	1.314
50	1.784	2.117	36.614	1.385
60	2.181	2.478	56.48	1.537
70	2.547	2.842	80.13	1.698
80	2.907	3.206	107.40	1.863
90	3.276	3.569	138.30	2.033
100	3.662	3.934	172.97	2.205
110	4.067	4.302	211.60	2.379
120	4.492	4.674	254.38	2.554
130	4.933	5.051	301.49	2.732

Table 2 Continued

T/K	$C_{p,m}^{\circ}/R$	$S_{0,m}^{\circ T}/R$	$H_{0,m}^{\circ T}/RK$	$\Phi_m^{\circ}(T,0)/R$
140	5.385	5.433	353.07	2.911
150	5.846	5.820	409.22	3.092
160	6.310	6.212	470.00	3.275
170	6.774	6.609	535.4	3.459
180	7.236	7.009	605.5	3.645
190	7.691	7.413	680.1	3.833
200	8.140	7.819	759.3	4.022
210	8.579	8.226	842.9	4.213
220	9.010	8.635	930.8	4.404
230	9.430	9.045	1023.0	4.597
240	9.840	9.455	1119.4	4.791
250	10.239	9.865	1219.8	4.986
260	10.628	10.274	1324.1	5.181
270	11.006	10.682	1432.3	5.378
280	11.374	11.089	1544.2	5.574
290	11.731	11.495	1659.8	5.771
298.15	12.014	11.824	1756.5	5.932
300	12.078	11.898	1778.8	5.969
325	12.899	12.898	2091.2	6.464
350	13.650	13.882	2423.2	6.958
PrB ₆				
0	0	0	0	0
1	0.034	0.034	0.017	0.017
2	0.077	0.069	0.070	0.034
3	0.170	0.115	0.187	0.053
4	0.383	0.190	0.451	0.077
5	0.725	0.311	0.999	0.111
5.92	1.628	0.486	1.968	0.154
7	0.561	0.649	2.999	0.220
8	0.435	0.712	3.471	0.278
9	0.407	0.762	3.894	0.329
10	0.368	0.803	4.280	0.375
15	0.329	0.938	5.945	0.542
20	0.423	1.043	7.782	0.654
25	0.624	1.157	10.356	0.743

Table 2 Continued

T/K	$C_{p,m}^{\circ}/R$	$S_{0,m}^{\circ T}/R$	$H_{0,m}^{\circ T}/RK$	$\Phi_m^{\circ}(T,0)/R$
30	0.901	1.295	14.149	0.823
35	1.193	1.456	19.390	0.902
40	1.465	1.633	26.040	0.982
45	1.728	1.821	34.027	1.065
50	1.982	2.016	43.305	1.150
60	2.472	2.421	65.60	1.328
70	2.940	2.838	92.67	1.514
80	3.392	3.260	124.34	1.706
90	3.833	3.685	160.47	1.902
100	4.268	4.111	200.98	2.101
110	4.698	4.538	245.82	2.304
120	5.126	4.965	294.94	2.508
130	5.552	5.393	348.33	2.713
140	5.976	5.820	405.97	2.920
150	6.398	6.246	467.87	3.127
160	6.817	6.673	533.9	3.336
170	7.232	7.098	604.2	3.544
180	7.643	7.523	678.6	3.754
190	8.047	7.947	757.0	3.963
200	8.446	8.370	839.5	4.173
210	8.838	8.792	925.9	4.383
220	9.222	9.212	1016.2	4.593
230	9.600	9.630	1110.3	4.803
240	9.971	10.047	1208.2	5.013
250	10.335	10.461	1309.7	5.222
260	10.693	10.874	1414.9	5.432
270	11.045	11.284	1523.6	5.641
280	11.390	11.692	1635.7	5.850
290	11.728	12.097	1751.3	6.058
298.15	11.997	12.426	1848.0	6.228
300	12.057	12.500	1870.3	6.266
325	12.820	13.496	2181.4	6.784
350	13.440	14.470	2510.1	7.299

smoothed heat capacities and derived properties are characterized by a probable error less than 0.1% above 40 K. Nuclear spin and isotope mixing contributions have not been included in the entropies and Gibbs energies.

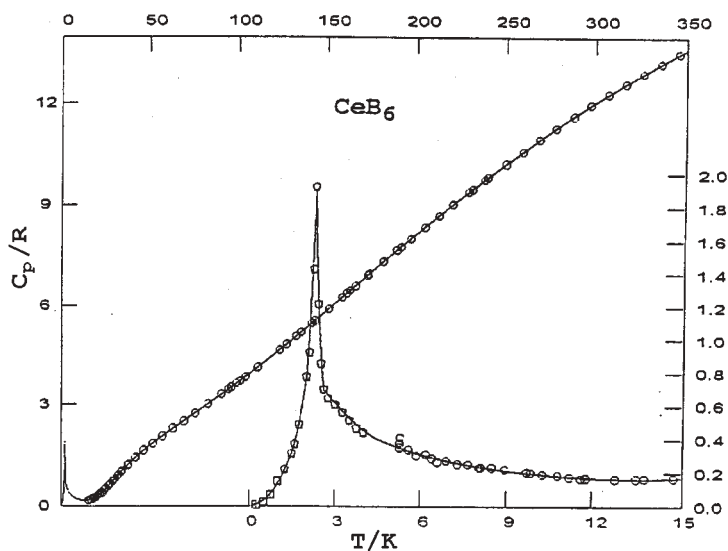


Fig. 1 C_p/R vs. T/K for CeB₆. The inset represents low temperature results of references [5] and [6] used to generate the entropy and enthalpy increments below 5 K

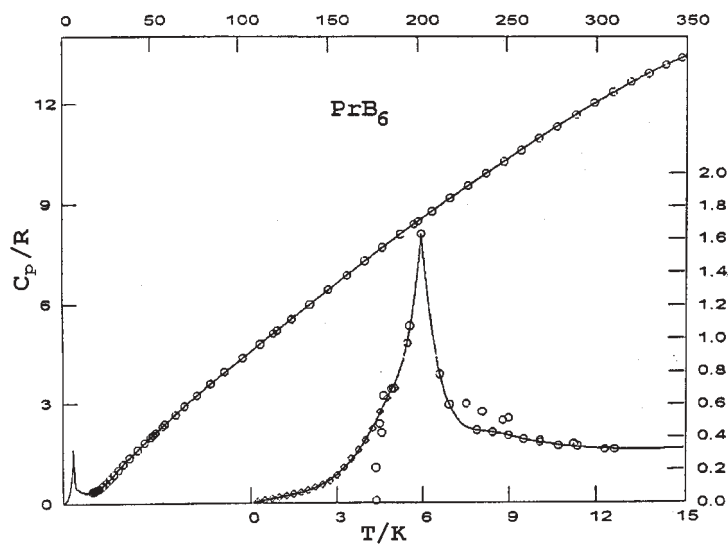


Fig. 2 C_p/R vs. T/K for PrB₆. The inset represents low temperature results of reference [7] used to generate the entropy and enthalpy increments below 5 K

Much work has been done on the electronic structure of these materials [9–12] but it is not yet possible to apply the details of these calculations to resolve specific contributions to the heat capacity results.

The greatest desideratum for making further progress on the thermophysics are electrical conductivity values on these and related hexaborides over large temperature ranges.

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