

Thermophysics of the lanthanide hydroxides

I. Heat capacities of $\text{La}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, and $\text{Eu}(\text{OH})_3$ from near 5 to 350 K. Lattice and Schottky contributions^a

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From values of the heat capacity of microcrystalline $\text{La}(\text{OH})_3$, $\text{Gd}(\text{OH})_3$, and $\text{Eu}(\text{OH})_3$ determined by precise adiabatic calorimetry from near 10 to 350 K, the Schottky contribution associated with the low-lying *J*-manifolds of $\text{Eu}(\text{OH})_3$ was resolved with the aid of a new lattice-heat-capacity approximation based upon volumetric interpolation between the lattice heat capacities of the $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$ homologs. This calorimetrically deduced Schottky contribution to the heat capacity of $\text{Eu}(\text{OH})_3$ was compared with the same contribution calculated from spectral data. Excellent accord was observed over the entire temperature range investigated. The experimental heat capacities of this study together with previously published low-temperature (0.45 to 18 K) magnetic and heat-capacity data for $\text{Gd}(\text{OH})_3$ permit evaluation of thermophysical functions relative to $T = 0$ for each compound.

1. Introduction

The resolution of the Schottky contribution (arising from thermal population of low-lying electronic energy levels) from the total heat capacity of lanthanide compounds has been thwarted primarily by the absence of an adequate method of approximating the generally much larger vibrational ('lattice') contribution. While a model does exist which enables the calculation of the Schottky contribution with reasonable accuracy from spectroscopic data, no such model exists for the lattice contribution which, therefore, must be determined empirically. It follows that the success of a lattice heat-capacity approximation historically has been judged in terms of the agreement between the calculated Schottky contribution (using spectroscopically observed electronic energy levels and degeneracies) and that deduced calorimetrically from the lattice approximation in question. Because the spectroscopically determined energy levels are often obtained for the paramagnetic ion of interest doped into a diamagnetic host lattice rather than for the concentrated compound and because no

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allowance is made for such effects as shifts of the energy levels with temperature, near perfect agreement between the two independently deduced Schottky contributions is generally an unreasonable expectation. In the lanthanide trihydroxide series $\text{Eu}(\text{OH})_3$ is the exception to this generalization.

We here present the results of heat-capacity measurements from 5 to 350 K on $\text{La}(\text{OH})_3$ and $\text{Eu}(\text{OH})_3$ and from 15 to 350 K on $\text{Gd}(\text{OH})_3$. The Schottky contribution to the heat capacity of $\text{Eu}(\text{OH})_3$ is resolved using a lattice approximation involving an interpolation (weighted by the fractional molar volume increment) between the lattice heat capacities of $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$. The lattice-approximation method used in this paper was previously employed in the analysis of the Schottky contribution to the heat capacity of $\text{Pr}(\text{OH})_3$.⁽¹⁾ Presentation herein of the heat capacities of $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$ allows verification of the results then achieved.

2. Experimental

PREPARATION AND CHARACTERIZATION OF SAMPLES

Ln_2O_3 ($\text{Ln} = \text{La}, \text{Eu}, \text{and Gd}$; 99.99 moles per cent purity, Research Chemicals, Phoenix, Arizona) starting materials were calcined at about 1200 K and stored in a desiccator containing both Drierite and Ascarite. The lanthanide sesquioxides were transferred into crimped gold tubes for direct reaction with water at 110 to 125 MPa and 650 to 870 K using the hydrothermal technique previously described by Haschke and Eyring.⁽²⁾ A detailed description of the hydrothermal apparatus is reported in the doctoral dissertation of Lance-Gomez.⁽³⁾ The gold tubes were crimped with a three-jawed chuck to allow direct communication between the pressurized water in the reactor and the sesquioxide. Reaction conditions for the individual compounds are listed in table 1. Powder X-ray diffraction results using a 114.6 mm Hagg-type Guinier camera ($\text{Cu K}\alpha_1$ radiation, $\lambda = 0.15405$ nm) with silicon ($a = 0.543062$ nm) as an internal standard showed only the hexagonal UCl_3 -type crystal structure reported for all of the lanthanide trihydroxides.⁽⁴⁾ Thermogravimetric analyses were performed on the three $\text{Ln}(\text{OH})_3$ samples. All of these compounds exhibited the thermal decomposition path previously reported by Fricke and Seitz:⁽⁵⁾

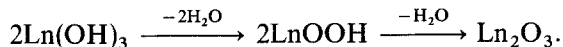


TABLE 1. Preparation and sample characteristics of lanthanide trihydroxides

Compound	$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$\frac{t}{\text{h}}$	Composition	$\frac{m}{\text{g}}$	$\frac{M}{\text{g mol}^{-1}}$ ^a
$\text{La}(\text{OH})_3$	870	110	20	$\text{La}(\text{OH})_{2.995 \pm 0.003}$	86.3347	189.932
$\text{Eu}(\text{OH})_3$	650	125	20	$\text{Eu}(\text{OH})_{3.002 \pm 0.003}$	81.0196	202.982
$\text{Gd}(\text{OH})_3$	650	110	20	$\text{Gd}(\text{OH})_{2.996 \pm 0.003}$	92.3487	208.2721

^a Based on 1971 IUPAC relative atomic masses.

Possible formation of a fourth compound, La₃O₄OH, was observed in the La(OH)₃ decomposition curve; however, none of the other trihydroxides exhibited this behavior. The formation of this fourth compound was originally reported by Lance-Gomez.⁽³⁾ No attempt was made to characterize the fourth compound crystallographically. The stoichiometries of the prepared lanthanide trihydroxides were determined by direct ignition of samples to the sesquioxides. The stoichiometries shown in table 1 are the result of at least five separate determinations; reported error limits represent one standard deviation.

THE CALORIMETER AND CRYOSTAT

The calorimetric samples were loaded into a gold-plated copper calorimeter (laboratory designation W-54) provided with a screw-type closure involving a stainless-steel knife edge and an annealed gold gasket. The loaded calorimeter was evacuated and then—after the addition of 3.1 to 3.5 kPa of purified He gas to facilitate thermal equilibration—was sealed. A small mass of Apiezon-T grease was placed in the thermocouple and heater-thermometer wells of the calorimeter to provide good thermal contact between the heater, the temperature sensors, and the calorimeter. Loading quantities for the compounds are shown in table 1. Buoyancy corrections used to obtain the vacuum masses were based on crystallographic densities implied in table 2.

Heat-capacity measurements were made in the range 5 to 350 K in the Mark II adiabatic cryostat, which has been described previously.⁽⁶⁾ A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature and temperature-increment determinations. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S.) against the IPTS-1948 (as textually revised in 1960)⁽¹⁴⁾ for temperatures above 90.2 K, against the N.B.S. provisional scale from 10 to 90 K, and by the technique of McCracken and Chang⁽¹⁵⁾ below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K from 10 to 90 K and to within 0.04 K above 90 K. Determinations of mass, current, potential, and time are based upon calibrations performed at the N.B.S. The accuracy of a single heat-capacity measurement is judged to be

TABLE 2. Hexagonal lattice constants of some lanthanide trihydroxides

Compound	a/pm	c/pm	Reference
La(OH) ₃	652.3	385.0	7, 8
	652.3	385.5	9
	652	386	10
	652.3	384.9	11
	654.7	385.4	12
Eu(OH) ₃	635.2	365.3	11
	636.5	364.5	13
	632	363	10
Gd(OH) ₃	632.9	363.1	12
	633	363	11
	630	361	10

approximately 1 per cent at 10 K. This decreases to 0.1 per cent at 25 K and to near 0.06 per cent between 25 and 350 K even though precision is significantly better, especially at low temperatures.

3. Results and discussion

HEAT CAPACITIES AND THERMOPHYSICAL FUNCTIONS

The heat capacities of all the lanthanide trihydroxides of this investigation may be represented by simple sigmate curves in the temperature range 15 to 350 K, as shown in figures 1, 2, and 3. Measurements were obtained to approximately 5 K for $\text{La}(\text{OH})_3$ and $\text{Eu}(\text{OH})_3$. This, however, was not possible for $\text{Gd}(\text{OH})_3$, because proper adiabatic conditions could not be maintained. The problem seems related to the crystallite size and may have been due to absorption of the helium exchange gas by the finely powdered sample.

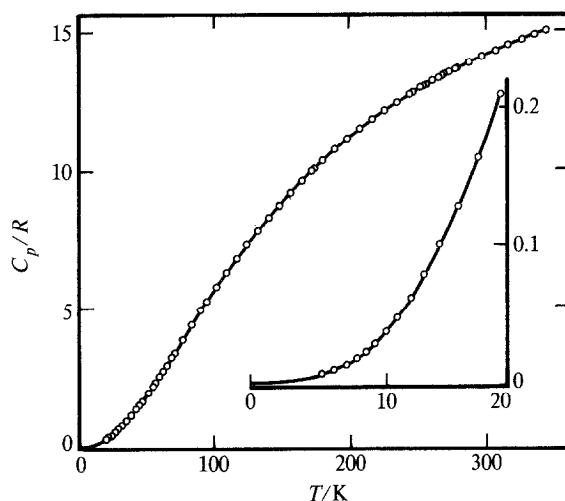


FIGURE 1. Experimental heat capacity of $\text{La}(\text{OH})_3$. \circ , This work.

The experimental heat capacities were processed by subtraction of the heat capacity due to the empty calorimeter (determined separately) and corrected for small differences in the amounts of helium gas, 50 mass per cent Pb+Sn solder, and stainless steel, relative to the calorimeter as run empty. The calorimeter and heater-thermometer assembly commonly represented between 20 to 40 per cent of the total measured heat capacity. Curvature corrections were applied to obtain true heat capacities [*i.e.* $\lim(\Delta H/\Delta T)_p = C_p$ as $\Delta T \rightarrow 0$] from the measured $\Delta H/\Delta T$ values. The experimental heat-capacity values for each compound (based on the molar masses listed in table 2) are listed in chronological sequence in table 3 so that the ΔT 's

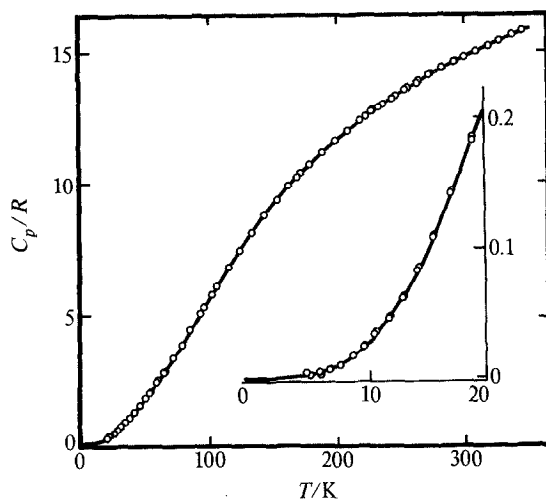


FIGURE 2. Experimental heat capacity of $\text{Eu}(\text{OH})_3$. \circ , This work.

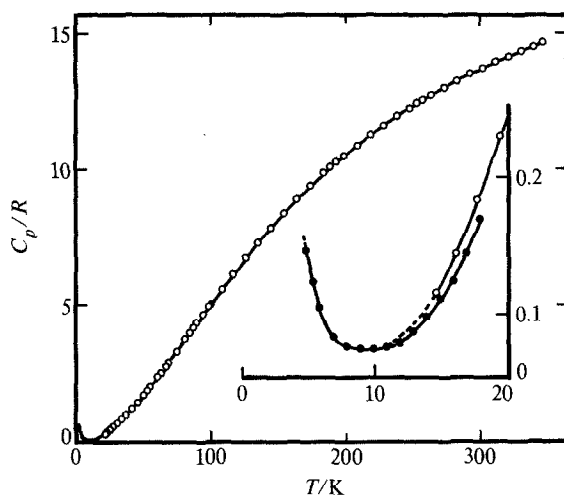


FIGURE 3. Experimental heat capacity of $\text{Gd}(\text{OH})_3$. \circ , This work; \bullet , Skjeltop *et al.*; ---, chosen to join the two sets.

employed usually can be estimated from adjacent mean temperatures.† These results were curve fitted to a power series in orthogonal polynomials in reduced temperature as described by Justice.⁽¹⁷⁾ The thermophysical functions, listed in table 4, were derived through appropriate integration of the fitted polynomials. These functions do not include contributions from nuclear spin and isotopic mixing and are thus suitable for use in ordinary thermochemical calculations. The method for evaluation of the

† The value of R used throughout is $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$.⁽¹⁶⁾

TABLE 3. Experimental heat capacities of La(OH)₃, Eu(OH)₃, and Gd(OH)₃

T/K	C _p /R	T/K	C _p /R	T/K	C _p /R	T/K	C _p /R
La(OH) ₃							
Series 1		132.45	7.817	266.27	13.353	11.03	0.045
254.50	13.017	140.56	8.305			12.02	0.060
261.51	13.215	148.72	8.771	Series 6		13.06	0.078
268.04	13.381	156.88	9.214	260.91	13.195	14.24	0.101
273.98	13.537	165.22	9.641	270.28	13.466	15.57	0.129
279.87	13.689	173.87	10.067	279.60	13.686	17.05	0.164
				288.96	13.905	18.70	0.209
Series 2		Series 4		298.45	14.119	20.50	0.266
54.46	2.163	172.11	9.978	308.33	14.334	22.45	0.334
59.75	2.551	180.76	10.380	318.40	14.545	24.62	0.420
64.98	2.952	189.66	10.771	328.27	14.725	27.04	0.524
70.60	3.377	198.75	11.142	338.12	14.912	29.46	0.636
76.80	3.858	207.92	11.497	346.58	15.083	32.07	0.766
83.18	4.369	217.17	11.842	Series 7		35.14	0.929
89.80	4.883	226.45	12.159			38.65	1.129
		235.74	12.458	5.34	0.005 ^a	42.42	1.354
Series 3		245.06	12.749	6.30	0.008 ^a	46.59	1.625
94.49	5.230	254.42	13.015	7.16	0.012	51.26	1.940
101.70	5.747			7.92	0.016	56.41	2.310
109.20	6.280	Series 5		8.61	0.021	62.08	2.729
117.01	6.818	247.33	12.812	9.30	0.026	68.49	3.216
124.67	7.324	256.78	13.091	10.12	0.035		
Eu(OH) ₃							
Series 1		Series 3		172.34	10.397	346.69	15.803
227.88	12.759	53.10	1.950	Series 8		Series 12	
237.22	13.053	Series 4		169.35	10.241	4.99	0.006 ^a
246.47	13.347	54.38	2.032	179.38	10.744	6.23	0.002 ^a
255.80	13.635	59.24	2.363	189.32	11.209	6.95	0.007
265.21	13.926	64.58	2.751	199.20	11.636	7.69	0.011
274.61	14.167	Series 5		209.02	12.032	8.65	0.018 ^a
283.88	14.403	55.01	2.074	218.83	12.418	9.58	0.024
293.24	14.632	60.32	2.440	228.64	12.759	10.46	0.035
Series 2		65.93	2.850	Series 9		11.50	0.046
5.32	0.002	72.09	3.308 ^a	223.45	12.574	12.67	0.063
6.11	0.005	78.72	3.838 ^a	233.43	12.922	13.89	0.084
6.88	0.007	85.89	4.438 ^a	243.34	13.245	15.13	0.110
7.79	0.010 ^a	93.71	5.066	253.21	13.549	16.51	0.142
8.70	0.014 ^a	102.16	5.741	263.14	13.854	18.07	0.183
9.61	0.025	Series 6		273.01	14.128	19.80	0.234
10.59	0.037	96.33	5.275	282.84	14.373	21.72	0.297
11.59	0.048	Series 7		292.65	14.623	23.82	0.377
12.66	0.063	106.53	6.083	Series 10		26.12	0.471
13.79	0.083	115.66	6.792	300.45	14.793	28.69	0.580
15.09	0.110	124.69	7.469	310.20	15.020	31.50	0.718
16.56	0.144	134.07	8.128	320.18	15.238	34.42	0.864
18.14	0.186	143.83	8.774	Series 11		37.74	1.038
19.88	0.236	153.28	9.349	328.82	15.446	41.72	1.256
21.67	0.296	162.65	9.883	338.78	15.644	46.01	1.504
23.77	0.375					50.04	1.759
26.20	0.474					54.60	2.048
28.76	0.588					60.27	2.437

TABLE 3—continued

T/K	C_p/R	T/K	C_p/K	T/K	C_p/R	T/K	C_p/R
$\text{Gd}(\text{OH})_3$							
Series 1		66.74	2.771	98.94	4.958	228.77	11.561
14.70	0.116			108.16	5.570	238.52	11.887
16.19	0.144	Series 2		117.07	6.146	248.16	12.204
17.76	0.183	53.14	1.904	126.09	6.713	257.73	12.509
19.48	0.231	57.74	2.176	135.58	7.283		
21.39	0.292	62.82	2.512	145.19	7.832	Series 6	
23.44	0.364	68.43	2.877	154.80	8.360	253.96	12.373
25.73	0.457	74.45	3.276	164.51	8.863	263.59	12.689
28.30	0.565	80.92	3.730	174.35	9.349	273.47	12.963
31.09	0.697	87.36	4.186	184.19	9.801	283.45	13.204
34.16	0.848	94.76	4.681	193.91	10.222	293.36	13.450
37.47	1.018					303.18	13.690
41.21	1.216	Series 3		Series 5		312.93	13.918
45.49	1.453	99.75	5.010	189.49	10.029	322.57	14.124
50.16	1.727			199.44	10.449	331.91	14.322
55.12	2.022	Series 4		209.35	10.846	340.98	14.503
60.65	2.372	89.82	4.353	219.11	11.218	347.72	14.635

^a This point was not included in the curve-fitting calculations.

TABLE 4. Thermophysical functions for $\text{La}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, and $\text{Gd}(\text{OH})_3$

T K	C_p R	$S^\circ(T) - S^\circ(0)$ R	$H^\circ(T) - H^\circ(0)$ R K	$- \{G^\circ(T) - H^\circ(0)\}$ RT
$\text{La}(\text{OH})_3$				
5	0.004	0.001	0.005	0.000
10	0.034	0.011	0.081	0.003
15	0.115	0.038	0.430	0.009
20	0.250	0.088	1.322	0.022
25	0.435	0.163	3.016	0.043
30	0.662	0.262	5.744	0.071
35	0.922	0.383	9.693	0.106
40	1.209	0.525	15.009	0.150
45	1.519	0.685	21.819	0.200
50	1.852	0.862	30.239	0.257
60	2.572	1.262	52.31	0.391
70	3.334	1.716	81.82	0.547
80	4.116	2.212	119.06	0.724
90	4.889	2.742	164.10	0.918
100	5.633	3.295	216.74	1.128
110	6.342	3.866	276.65	1.351
120	7.017	4.447	343.47	1.585
130	7.660	5.034	416.88	1.827
140	8.269	5.624	496.55	2.077
150	8.843	6.215	582.1	2.334
160	9.380	6.803	673.3	2.595
170	9.880	7.387	769.6	2.859
180	10.346	7.965	870.8	3.127
190	10.782	8.536	976.4	3.397
200	11.191	9.099	1086.3	3.668

TABLE 4—continued

$\frac{T}{K}$	$\frac{C_p}{R}$	$\frac{S^\circ(T) - S^\circ(0)}{R}$	$\frac{H^\circ(T) - H^\circ(0)}{RK}$	$-\frac{\{G^\circ(T) - H^\circ(0)\}}{RT}$
210	11.576	9.655	1200.2	3.940
220	11.937	10.202	1317.8	4.212
230	12.277	10.740	1438.9	4.484
240	12.595	11.269	1563.2	4.756
250	12.893	11.789	1690.7	5.027
260	13.174	12.301	1821.0	5.297
270	13.440	12.803	1954.1	5.565
280	13.694	13.296	2089.8	5.833
290	13.933	13.781	2227.9	6.098
300	14.159	14.257	2368.4	6.362
310	14.369	14.725	2511.1	6.625
320	14.568	15.18	2655.8	6.885
330	14.760	15.64	2802.4	7.143
340	14.952	16.08	2951.0	7.400
350	15.14	16.52	3101.5	7.654
273.15	13.522	12.959	1996.6	5.650
298.15	14.118	14.170	2342.3	6.314
Eu(OH) ₃				
5	0.002	0.001	0.003	0.000
10	0.029	0.008	0.061	0.002
15	0.107	0.033	0.378	0.007
20	0.241	0.080	1.226	0.019
25	0.423	0.153	2.867	0.038
30	0.645	0.249	5.524	0.065
35	0.893	0.367	9.358	0.100
40	1.161	0.503	14.487	0.141
45	1.447	0.657	20.999	0.190
50	1.751	0.825	28.984	0.245
60	2.419	1.202	49.764	0.372
70	3.154	1.629	77.58	0.521
80	3.943	2.101	113.02	0.688
90	4.762	2.613	156.56	0.873
100	5.570	3.156	208.23	1.074
110	6.359	3.724	267.89	1.289
120	7.120	4.311	335.32	1.516
130	7.845	4.910	410.18	1.754
140	8.524	5.516	492.06	2.001
150	9.155	6.126	580.5	2.256
160	9.738	6.736	675.0	2.517
170	10.276	7.342	775.1	2.783
180	10.775	7.944	880.4	3.053
190	11.238	8.539	990.5	3.326
200	11.669	9.127	1105.0	3.601
210	12.073	9.706	1223.8	3.878
220	12.451	10.276	1346.4	4.156
230	12.807	10.838	1472.7	4.435
240	13.142	11.390	1602.5	4.713
250	13.459	11.933	1735.5	4.991
260	13.758	12.467	1871.6	5.268
270	14.040	12.991	2010.6	5.545
280	14.305	13.507	2152.3	5.820

TABLE 4--*continued*

$\frac{T}{K}$	$\frac{C_p}{R}$	$\frac{S^\circ(T) - S^\circ(0)}{R}$	$\frac{H^\circ(T) - H^\circ(0)}{RK}$	$-\frac{\{G^\circ(T) - H^\circ(0)\}}{RT}$
290	14.554	14.013	2296.6	6.094
300	14.790	14.510	2443.4	6.366
310	15.02	14.999	2592.4	6.636
320	15.24	15.48	2743.7	6.905
330	15.46	15.95	2897.2	7.172
340	15.67	16.42	3052.8	7.437
350	15.88	16.87	3210.6	7.700
273.15	14.125	13.155	2055.0	5.631
298.15	14.748	14.419	2416.1	6.316
$\text{Gd}(\text{OH})_3$				
10	(0.075)	(2.074)	(2.516)	(1.839)
15	0.121	2.126	2.958	1.929
20	0.247	2.177	3.853	1.984
25	0.426	2.250	5.516	2.029
30	0.645	2.347	8.180	2.074
35	0.889	2.464	12.005	2.121
40	1.151	2.600	17.100	2.172
45	1.428	2.751	23.543	2.228
50	1.716	2.916	31.397	2.288
60	2.330	3.283	51.58	2.423
70	2.985	3.691	78.13	2.574
80	3.666	4.133	111.37	2.741
90	4.354	4.605	151.48	2.922
100	5.031	5.099	198.41	3.115
110	5.690	5.609	252.03	3.318
120	6.330	6.132	312.16	3.531
130	6.948	6.663	378.57	3.751
140	7.539	7.200	451.02	3.979
150	8.103	7.740	529.3	4.211
160	8.635	8.280	613.0	4.449
170	9.138	8.819	701.9	4.690
180	9.610	9.354	795.6	4.934
190	10.054	9.886	894.0	5.181
200	10.473	10.412	996.6	5.429
210	10.869	10.933	1103.3	5.679
220	11.246	11.447	1213.9	5.930
230	11.604	11.955	1328.2	6.180
240	11.944	12.456	1446.0	6.432
250	12.266	12.951	1547.0	6.682
260	12.569	13.438	1691.2	6.933
270	12.855	13.917	1818.3	7.183
280	13.124	14.390	1948.2	7.432
290	13.377	14.855	2080.8	7.680
300	13.617	15.31	2215.7	7.927
310	13.847	15.76	2353.1	8.172
320	14.068	16.21	2492.7	8.416
330	14.281	16.64	2634.4	8.659
340	14.485	17.07	2778.3	8.900
350	14.678	17.49	2924.1	9.140
273.15	12.942	14.067	1859.0	7.261
298.15	13.574	15.23	2190.6	7.881

entropy and enthalpy increments developed below the lowest temperatures reached in this study are described below.

LOW-TEMPERATURE ENTROPY AND ENTHALPY INCREMENTS

La(OH)₃. The ¹S₀ ground state of La(OH)₃ implies the absence of a cooperative magnetic or Schottky contribution over the entire temperature range studied. Assuming the low-temperature limiting form of the Debye heat-capacity equation, $C_p/R = aT^3$, a plot of C_p/RT against T^2 was made to determine a . Theoretically this equation is valid⁽¹⁸⁾ only for T less than about 4 K (*i.e.* T less than about $\theta_D/50$); however, the plot remained linear for temperatures as high as 12 K. The parameter a was found to be $3.2 \times 10^{-5} \text{ K}^{-3}$. The heat capacity of La(OH)₃ between 0.5 and 15 K has been determined by Skjeltorp *et al.*⁽¹⁹⁾ and an identical analysis indicated a to be $(3.9 \pm 0.3) \times 10^{-5} \text{ K}^{-3}$. It can be seen below that the choice of a has very little effect on the calculated entropy and enthalpy contributions below 5 K. The enthalpy and entropy increments calculated using the results of the current study were used in compiling table 4.

Source	a/K^3	$S(0 \text{ to } 5 \text{ K})/R$	$H(0 \text{ to } 5 \text{ K})/R \text{ K}$
Skjeltorp <i>et al.</i> ⁽¹⁹⁾	3.9×10^{-5}	0.0016	0.0061
This research	3.2×10^{-5}	0.0013	0.0050

Eu(OH)₃. Although Eu(OH)₃ is paramagnetic, the results may be treated in a manner completely analogous to that used for La(OH)₃. The Eu³⁺ ground J -state is a singlet (⁷F₀) and the first excited J -state is a triplet (⁷F₁), whose degeneracy is reduced by the crystalline electric field of Eu(OH)₃ to a doublet at 334.98 cm^{-1} and a singlet at 435.81 cm^{-1} .⁽²⁰⁾ Because of the relatively high energy of the first excited Stark component, the Schottky contribution to the Eu(OH)₃ heat capacity is essentially zero below 25 K. This implies that, like La(OH)₃, the total heat capacity of Eu(OH)₃ below 25 K is due entirely to lattice vibrations. A plot of C_p/RT against T^2 for results below 10 K yielded a straight line with slope equal to $(2.1 \pm 0.2) \times 10^{-5} \text{ K}^{-3}$ from which entropy and enthalpy increments below 5 K were derived and used in compiling table 4.

Gd(OH)₃. The ⁸S_{7/2} ground state of Gd(OH)₃ implies a low-temperature cooperative magnetic ordering of the Gd³⁺ ions with an associated entropy contribution equal to $(R \ln 8)$. As was previously mentioned, the measurements of this study were limited to temperatures above 15 K. These results, however, are complemented by those of Skjeltorp *et al.*,⁽¹⁹⁾ who have performed extensive magnetic and thermophysical measurements on Gd(OH)₃ between 0.4 and 18 K. Through both low-temperature heat capacity and susceptibility measurements, Skjeltorp *et al.* have found that Gd(OH)₃ undergoes an antiferromagnetic ordering transition at $(0.94 \pm 0.02) \text{ K}$. Two complementary techniques were used to estimate the cooperative magnetic contribution to the total heat capacity. In the vicinity of the Néel temperature, the heat capacity of diamagnetic La(OH)₃ was used to estimate the lattice contribution. At temperatures high relative to the Néel temperature the cooperative magnetic heat capacity was derived from the magnetic field dependence

of the adiabatic differential susceptibility using the method of Casimir and du Pré.⁽²¹⁾ By this analysis, Skjeltorp *et al.* found that the cooperative magnetic heat capacity above the Néel temperature could be expressed by the expansion:

$$C_p(\text{magnetic})/R = (4.09 \pm 0.05)(\text{K}/T)^2 - (4.2 \pm 0.7)(\text{K}/T)^3 \\ + (4 \pm 2)(\text{K}/T)^4 - (1 \pm 3)(\text{K}/T)^5 - (2 \pm 6)(\text{K}/T)^6,$$

while the lattice heat capacity below 10 K could be expressed as:

$$C_p(\text{lattice})/R = (3.4 \pm 0.3) \times 10^{-5} (T/\text{K})^3.$$

The heat capacities of the present research were joined with those of Skjeltorp *et al.*⁽¹⁹⁾ as shown in figure 3. The entropy and enthalpy increments between 10 and 15 K were obtained by numerical integration of this curve. The total cooperative magnetic entropy and enthalpy contributions were approximated as $(R \ln 8)$ and $(0.94R \ln 8)$, respectively. The portion of these increments developed above 10 K was calculated by integration of the above $\{C_p(\text{magnetic})/R\}$ expansion from $T/\text{K} = 10$ to ∞ . The lattice contribution to the entropy and enthalpy below 10 K was calculated in the usual manner using the expression for $C_p(\text{lattice})/R$ given by Skjeltorp *et al.*

RESOLUTION OF THE SCHOTTKY CONTRIBUTION

Determination of the excess electronic (Schottky) heat capacity requires a basis for interpolation of the lattice heat capacity along the lanthanide series between end members. Although only the lanthanum(III) and lutetium(III) analogs within any lanthanide series are diamagnetic and, therefore, have heat capacities involving only a lattice contribution, the heat capacity of the gadolinium(III) analog at temperatures above about 30 K can also be considered to entail only a lattice contribution. For both GdCl_3 and $\text{Gd}(\text{OH})_3$ Wolf *et al.*^(19, 22) have shown that the cooperative magnetic heat-capacity contribution is essentially zero above 25 K. (In cubic Gd_2O_3 , the $^8\text{S}_{7/2}$ J -state is slightly split by the crystalline field. Justice and Westrum⁽²³⁾ have estimated the total splitting to be approximately 10 cm^{-1} ; the resulting excess heat capacity approaches zero near 40 K.) The first excited J -state of Gd^{3+} is near 32000 cm^{-1} ,⁽²⁴⁾ and, therefore, much too high to produce a Schottky contribution below 350 K. Hence, the heat capacity of the gadolinium(III) analog for nearly all series of lanthanide compounds can be assumed to consist of only a lattice contribution above about 30 K. In addition, with the aid of very low-temperature heat-capacity measurements, it is possible to estimate the cooperative magnetic contribution and, thereby, to extend knowledge of the lattice heat capacity of the gadolinium(III) compound to lower temperatures. The heat capacities and susceptibilities of Skjeltorp *et al.*⁽¹⁹⁾ between 0.45 and 18 K enable such an extension for the lattice contribution of $\text{Gd}(\text{OH})_3$ to be made.

The difference between the total heat capacities of $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$ is depicted in figure 4. The large positive ΔC_p observed below 20 K is due to the onset of magnetic ordering in $\text{Gd}(\text{OH})_3$. The dashed curve represents the approximate difference between the respective lattice heat capacities upon removing the

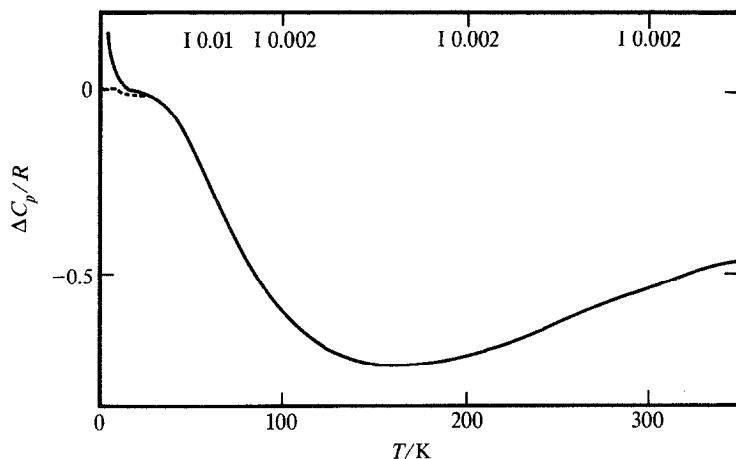


FIGURE 4. $[C_p\{\text{Gd}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]/R = \Delta C_p/R$. The dashed curve represents the approximate difference between the respective lattice heat capacities.

cooperative magnetic contribution using the formulae of Skjeltorp *et al.* mentioned earlier. The shape of this curve is typical for lanthanide compounds. Analogous plots of $\{C_p(\text{GdCl}_3) - C_p(\text{LaCl}_3)\}$,⁽²⁵⁾ $\{C_p(\text{Gd}_2\text{O}_3) - C_p(\text{Lu}_2\text{O}_3)\}$,⁽²⁶⁾ and $\{C_p(\text{GdCl}_3 \cdot 6\text{H}_2\text{O}) - C_p(\text{LuCl}_3 \cdot 6\text{H}_2\text{O})\}$ ⁽²⁷⁾ are similar, with minima between 80 and 150 K. (The heat capacity of $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$ is complicated by an unexplained anomaly near 282 K; however, the general shape of the difference plot remains similar to those for the other series.) The magnitude of the variation in lattice heat capacity of the trihydroxides between the lanthanum and gadolinium analogs ($\Delta C_p/R \approx 0.75$ at 160 K) is relatively large; therefore, the trihydroxides are particularly sensitive to the weighting of the interpolation used.

Indeed, as previously discussed,⁽¹⁾ we consider that for the present an adequate interpolation scheme for the lattice heat capacities of the lighter lanthanide trihydroxides can be formulated in terms of molar volumes; for $\text{Eu}(\text{OH})_3$:

$$C_p\{\text{lattice, Eu}(\text{OH})_3\} = (1-f)[C_p\{\text{La}(\text{OH})_3\} + f\{C_p^*\{\text{Gd}(\text{OH})_3\}\}],$$

in which f may be expressed in terms of the molar volumes V_i , of the homologous lanthanide trihydroxides as

$$f = f\{\text{Eu}(\text{OH})_3\} = [V\{\text{Eu}(\text{OH})_3\} - V\{\text{La}(\text{OH})_3\}] / [V\{\text{Gd}(\text{OH})_3\} - V\{\text{La}(\text{OH})_3\}].$$

Here f is the increment in molar volume for the lighter lanthanide trihydroxide divided by the volume increment between the end members. The value of $f\{\text{Eu}(\text{OH})_3\}$ based upon the mean of the lattice parameters listed in table 3 is found to be 0.87. The asterisk indicates that the heat capacity associated with the antiferromagnetic ordering of $\text{Gd}(\text{OH})_3$ has been deleted. (Heat-capacity measurements in progress for several of the heavier $\text{Ln}(\text{OH})_3$'s as well as for $\text{Y}(\text{OH})_3$ will permit a more extended

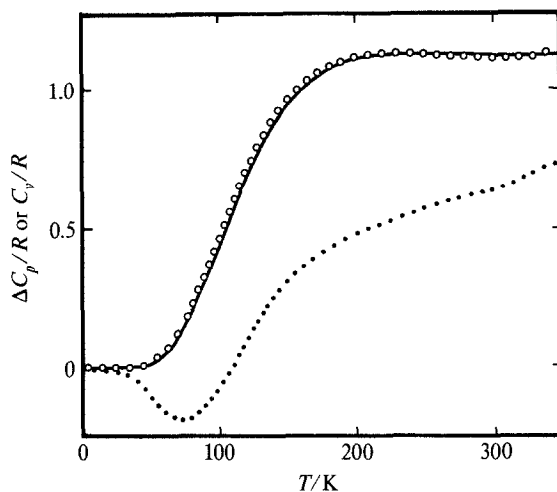


FIGURE 5. The Schottky contribution to the heat capacity of Eu(OH)_3 . The uninterrupted curve and \circ 's represent the 'spectroscopic' and 'calorimetric' Schottky contributions, respectively. (See text for explanation.) The dotted curve represents the Schottky contribution had the heat capacity of La(OH)_3 been used as an estimate for the lattice heat capacity of Eu(OH)_3 .

test of the proper volume and mass dependence. It is, however, already evident that the scheme can be successfully applied to other trihydroxides as well as to the light trichlorides.⁽²⁸⁾ Deduction of the lattice contribution from the Eu(OH)_3 total heat capacity results in the curve designated the 'calorimetric' Schottky contribution in figure 5. The solid curve, the 'spectroscopic' Schottky contribution, was derived using spectroscopically determined energy levels and degeneracies in the general Schottky heat-capacity expression:

$$C_V/R = \sum_i g_i (E_i/kT)^2 \exp(-E_i/kT)/Q - \left\{ \sum_i g_i (E_i/kT) \exp(-E_i/kT)/Q \right\}^2,$$

in which E_i represents the energies of the Stark levels of degeneracies g_i ; k , R , and Q are the Boltzmann constant, the gas constant, and the electronic partition function, respectively. The energy levels of pure 'concentrated' Eu(OH)_3 were determined by Cone and Faulhaber⁽²⁰⁾ from absorption and fluorescence spectra at 4.2 and 77 K. Stark levels arising from the 7F_0 , 7F_1 , 7F_2 , and 7F_3 J -states all contribute to the Schottky heat capacity below 350 K. The Stark levels of the lowest three manifolds are listed in table 5. As can be seen in figure 5, the agreement between the calorimetric and spectroscopic Schottky contributions is excellent. Indeed, the two curves lie within the experimental uncertainty of the heat-capacity measurements from 5 to 350 K. Also shown in figure 5 is the excess obtained when the heat capacity of La(OH)_3 is used as an estimate of the lattice contribution for Eu(OH)_3 . The large difference between this and the calorimetric Schottky curve emphasizes the large variation in the lattice heat capacity across the lanthanide trihydroxide series.

The excellence of the agreement between the calorimetric and spectroscopic Schottky contributions achieved for Eu(OH)_3 is, in fact, essential if the lattice

TABLE 5. Spectroscopically determined wavenumbers σ of $\text{Eu}(\text{OH})_3$ ^a

<i>J</i> -State	σ/cm^{-1}	μ	<i>g</i>
⁷ F ₀	0	0	1
⁷ F ₁	334.98	1	2
	435.81	0	1
⁷ F ₂	1012.19	2	2
	(1028.19) ^b	1	2
	(1151.30) ^b	0	1
The next level is at 1833.39 cm ⁻¹ .			

^a Reference 20.^b Bracketed energies were calculated.

approximation is to be considered successful for this compound. The Schottky contribution to the heat capacity of the europium(III) analog within any lanthanide series is unique in that it arises totally from the thermal population of excited *J*-manifolds. The wavenumber of the first excited *J*-state of the Eu^{3+} ion is approximately 370 cm⁻¹,⁽²⁴⁾ which invariably results in the lowest excited Stark levels being much higher in energy for the europium(III) analog than for any other series member. Consequently, the spectroscopic Schottky contributions of europium(III) compounds are relatively insensitive to small errors or shifts in the Stark level energies (compare reference 1). Therefore, the spectroscopic and calorimetric Schottky contributions must be in excellent agreement if the resolution is to be deemed successful.

It is unfortunate that this is the only compound for which the spectroscopic data allow unequivocal corroboration of the lattice heat-capacity approximation over the entire temperature range. The Schottky heat capacity is too sensitive to small energy shifts in the much lower-lying Stark levels of compounds containing other lanthanide ions to allow such good agreement, discounting coincidence, between the calorimetric and spectroscopic Schottky curves even if the lattice contributions were precisely known.

4. Conclusions

The thermophysical properties of $\text{La}(\text{OH})_3$ arise solely from a vibrational (lattice) contribution, while those of $\text{Gd}(\text{OH})_3$ are the summation of a vibrational contribution and a cooperative antiferromagnetic anomaly near 0.94 K. Thermophysical functions were evaluated for both compounds.

On the basis of a lattice heat-capacity contribution interpolated on the molar volume variation between $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$, excellent resolution of the Schottky heat capacity of $\text{Eu}(\text{OH})_3$ is obtained. The large high-temperature Schottky contribution, which rises about 10 per cent above the lattice contribution near 300 K, produces no observable decrease in the total heat capacity as is often associated with a Schottky 'anomaly'. Thermophysical functions are also evaluated for $\text{Eu}(\text{OH})_3$.

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