

Thermophysics of the lanthanide trihydroxides

III. Heat capacities from 5 to 350 K of the related compound $Y(OH)_3$. Lattice contribution^a

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Heat-capacity measurements between 5 and 350 K have been performed upon a microcrystalline sample of $Y(OH)_3$. The heat capacities can be represented by a simple sigmoid curve; no anomalous behavior was observed. Comparison with previously published results for the iso-anionic compounds $La(OH)_3$ and $Gd(OH)_3$ provides insight into the physical origins of experimentally observed trends in the lattice contributions of lanthanide compounds and suggests a rationale for the volume-weighted lattice-approximation scheme, which has been applied with great success to the lighter lanthanide trihydroxides.

1. Introduction

Excellent resolution of the Schottky contributions to the heat capacities of $Pr(OH)_3$,⁽¹⁾ $Eu(OH)_3$,⁽²⁾ $Tb(OH)_3$,⁽³⁾ and the light lanthanide trichlorides,⁽⁴⁾ has recently been achieved through application of a lattice heat-capacity approximation based upon an interpolation between the lattice contributions of the appropriate lanthanum and gadolinium compounds weighted by the molar volumes along each lanthanide iso-anionic series. This lattice approximation effectively emphasizes the apparent dominance of volume over mass⁽⁵⁾ as a determining term in the trend of the lattice contribution along the series over the temperature region of major cryogenic entropic increments and electronic Schottky contributions. Decreasing lattice heat capacity with increasing atomic number of the lanthanide obtains for every such lanthanide series investigated. We here present heat-capacity measurements between 5 and 350 K performed upon the analogous isostructural diamagnet, $Y(OH)_3$, to provide insight into the physical origins of the observed trends in the lattice contributions of lanthanide compounds and hence to provide a rationale for the volume-weighted lattice approximation.

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2. Experimental

PREPARATION AND CHARACTERIZATION OF THE SAMPLE

Y_2O_3 (99.99 moles per cent purity, Research Chemicals, Phoenix, Arizona) was calcined at about 1200 K and stored in a desiccator containing both Drierite and Ascarite. The sesquioxide was transferred into crimped gold tubes for direct reaction with water at 110 MPa and 620 K for 20 h using the hydrothermal technique previously described by Haschke and Eyring.⁽⁶⁾ Powder X-ray diffraction results using a 114.6 mm Hagg-type Guinier camera (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 structure reported for all of the lanthanide trihydroxides.⁽⁷⁾ Thermogravimetric analysis revealed the same decomposition path for $Y(OH)_3$ as that reported by Fricke and Seitz⁽⁸⁾ for the iso-anionic lanthanides. The stoichiometry of the yttrium trihydroxide, $Y(OH)_{2.992 \pm 0.002}$, was determined by direct ignition of samples to the sesquioxide. The error limits represent one standard deviation.

THE CALORIMETER AND CRYOSTAT

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 was loaded 86.511 g of finely powdered $Y(OH)_3$. The loaded calorimeter was evacuated and then, after the addition of 2.87 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. Buoyancy corrections used to obtain the mass were based upon the crystallographic density (3.59 g cm^{-3}) calculated from the mean of the lattice parameters available in the literature.^(7, 9, 10) Heat-capacity measurements were made in the 5 to 350 K range in the Mark II adiabatic cryostat, which has been described previously,⁽¹¹⁾ with calibrations and constraints already noted.⁽³⁾

3. Results and discussion

LOW-TEMPERATURE ENTHALPY AND ENTROPY INCREMENTS

The 1S_0 ground state of $Y(OH)_3$ implies the absence of a cooperative magnetic or Schottky contribution in the temperature range studied. Assuming the validity of 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 . Although on theoretical grounds⁽¹²⁾ this equation is strictly valid only for $T \leq 4.5$ K (*i.e.* $T < \theta_D/50$), the plot was linear for temperatures as high as 10 K and the parameter a was found to be $2.2 \times 10^{-5} \text{ K}^{-3}$. Appropriate integration of the Debye heat-capacity equation between 0 and 5 K yielded the low-temperature enthalpy and entropy increments subsequently listed at 5 K.

TABLE 1. Experimental values of the heat capacity of Y(OH)₃; $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Series 1		15.06	0.054	64.92	2.125	Series 5	
63.82	2.061	16.51	0.071	71.23	2.526	205.17	10.252
70.08	2.453	18.09	0.095	77.92	2.973	214.16	10.587
76.24	2.857	19.88	0.125	85.03	3.470	223.26	10.927
82.73	3.308	21.76	0.162	93.05	4.014	232.42	11.254
89.87	3.807	23.84	0.209	101.76	4.592	241.80	11.573
97.80	4.336	26.14	0.267	111.07	5.204	251.24	11.880
106.35	4.903	28.67	0.340	120.57	5.820	260.78	12.190
114.98	5.469	31.33	0.426	129.82	6.405	270.29	12.495 ^a
		33.94	0.521	138.94	6.951	279.80	12.712
		37.03	0.642			289.45	12.958
Series 2				Series 4		Series 6	
5.28	0.001 ^a	40.68	0.797	135.20	6.731		
5.79	0.002 ^a	44.72	0.984	144.24	7.259	284.81	12.845
6.53	0.003	48.97	1.201	153.47	7.771	294.46	13.090
7.67	0.005	52.80	1.407	162.71	8.261	304.05	13.329
8.67	0.008	57.18	1.654	172.04	8.732	313.30	13.554
9.52	0.012	62.58	1.984	181.35	9.177	322.03	13.745
10.51	0.016			190.56	9.585	330.69	13.939
11.50	0.022	Series 3		199.82	9.993	339.49	14.113
12.57	0.030	54.37	1.491	209.36	10.383	346.82	14.250
13.73	0.041	59.35	1.779				

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

HEAT CAPACITIES AND THERMOPHYSICAL FUNCTIONS

The heat capacity of Y(OH)₃ can be represented by a simple sigmate curve between 5 and 350 K. 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 (lead + tin) solder, and stainless steel, relative to that of the empty calorimeter. The Y(OH)₃ sample represented between 60 and 80 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 (based on a molar mass of $139.927 \text{ g mol}^{-1}$) are listed in chronological sequence in table 1† so that ΔT 's employed usually can be estimated from adjacent mean temperatures. These results were curve fitted by a power series in orthogonal polynomials in reduced temperature as described by Justice.^(1,2) Appropriate integration of this polynomial yielded the thermophysical functions listed in table 2. The functions do not include contributions from nuclear spin or isotope mixing and are thus suitable for use in ordinary thermochemical calculations. The accuracy of a single heat-capacity measurement is judged to be 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.

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

TABLE 2. Thermophysical functions of $Y(OH)_3$; $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T K	C_p R	$S^\circ(T) - S^\circ(0)$ R	$H^\circ(T) - H^\circ(0)$ R K	$- \{G(T) - H(0)\}$ RT
5	0.001	0.001	0.003	0.000
10	0.014	0.004	0.032	0.001
15	0.053	0.016	0.186	0.004
20	0.127	0.041	0.623	0.010
25	0.237	0.080	1.519	0.020
30	0.383	0.136	3.054	0.034
35	0.560	0.208	5.400	0.054
40	0.767	0.296	8.707	0.078
45	1.000	0.400	13.114	0.108
50	1.254	0.518	18.739	0.143
60	1.822	0.795	34.052	0.228
70	2.448	1.123	55.38	0.332
80	3.119	1.493	83.15	0.453
90	3.811	1.900	117.81	0.591
100	4.481	2.337	159.29	0.744
110	5.138	2.795	207.39	0.909
120	5.786	3.270	262.02	1.086
130	6.415	3.758	323.04	1.273
140	7.015	4.255	390.22	1.468
150	7.583	4.759	463.24	1.671
160	8.120	5.265	541.8	1.879
170	8.628	5.773	625.5	2.093
180	9.110	6.280	714.3	2.312
190	9.568	6.785	807.7	2.534
200	10.002	7.287	905.5	2.759
210	10.413	7.785	1007.6	2.987
220	10.802	8.278	1113.7	3.216
230	11.170	8.767	1223.6	3.447
240	11.518	9.250	1337.0	3.679
250	11.847	9.726	1453.9	3.911
260	12.156	10.197	1573.9	4.144
270	12.446	10.661	1696.9	4.376
280	12.718	11.119	1822.8	4.609
290	12.978	11.570	1951.3	4.841
300	13.228	12.014	2082.3	5.073
310	13.471	12.452	2215.8	5.304
320	13.705	12.883	2351.7	5.534
330	13.923	13.308	2489.8	5.763
340	14.123	13.727	2630.1	5.991
350	14.309	14.139	2772.2	6.218
273.15	12.533	10.806	1736.3	4.450
298.15	13.182	11.932	2057.9	5.030

4. Discussion

The continuous and dashed curves of figure 1 represent $[C_p\{\text{Gd}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ and $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ with the cooperative magnetic contribution to the $\text{Gd}(\text{OH})_3$ heat capacity deleted. The dotted curve is an estimate of the quantity $[C_p\{\text{Lu}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ derived by extrapolation of the

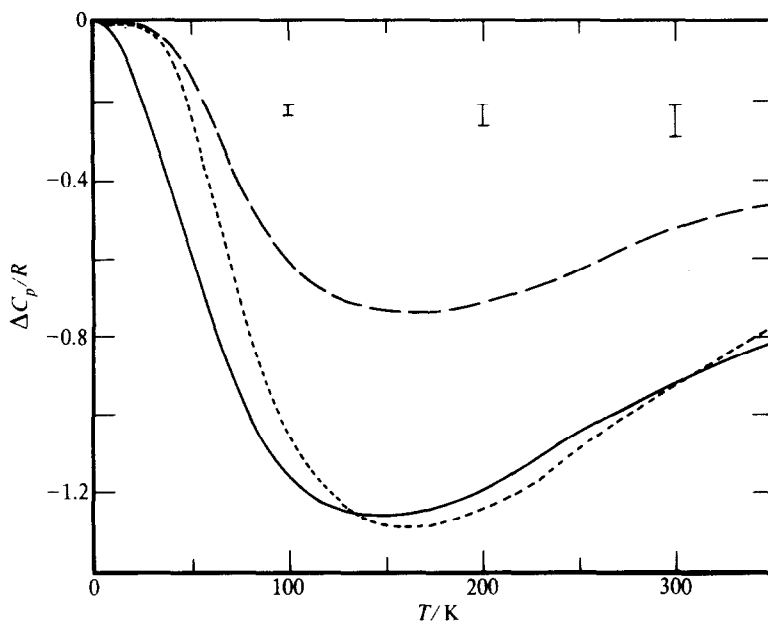


FIGURE 1. Temperature dependence of $\Delta C_p/R$ for the trihydroxide pairs. —, $[C_p\{\text{Gd}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$; ---, $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$; ···, $[C_p\{\text{Lu}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ (estimated). The error bars represent 0.5 per cent of $C_p\{\text{La}(\text{OH})_3\}$.

experimentally observed lattice heat-capacity variation between $\text{La}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3$ (e.g. see reference 3). If the lattice heat-capacity contribution for the lanthanide trihydroxides were exclusively a linear function of the molar volume, then the $[C_p\{\text{Y}(\text{OH})_3\} - C_p\{\text{La}(\text{OH})_3\}]$ curve would lie almost exactly midway between the dashed and dotted curves from 5 to 350 K. In contrast, if the trend in the lattice contributions was determined principally by the molar-mass variation it would lie entirely below the dotted curve instead of only for temperatures below about 120 K. From the results obtained for $\text{Y}(\text{OH})_3$, a shift in the relative importance of the cationic mass and volume in determining the trend in the lattice contributions across the series occurs near 100 K. The experimental observations may be rationalized by considering the type and nature of the lattice vibrational modes being activated at each temperature.⁽¹³⁾ At very low temperatures low-frequency modes, roughly characterized as unit-cell vibrations, are those primarily activated. The lanthanide contraction, which is an intramolecular contraction, has little effect upon these vibrations. In essence the force constants between the unit cells are unchanged, while the cell masses increase across the series. This occasions a decrease in the vibrational frequencies of the unit cells with increasing atomic number and, therefore, a corresponding increase in lattice contribution at a given temperature.

At higher temperatures an increasing proportion of the observed heat capacity is due to thermal activation of optical vibrational modes. The effect of the lanthanide contraction upon these modes is to increase their frequency by increasing the intramolecular force constants to such an extent that the counteracting effect of the

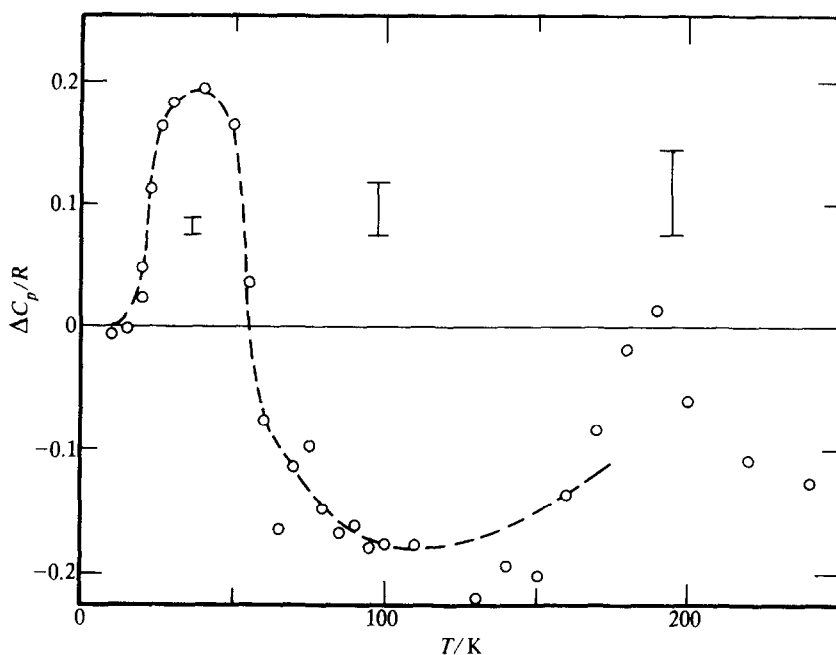


FIGURE 2. Temperature dependence of
 $\Delta C_p = [C_p\{\text{Lu}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}\} - C_p\{\text{Y}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}\}]$.^(13,14)
 The error bars represent 0.1 per cent of either molar heat capacity.

increased cation mass is largely overshadowed. [An analogous effect is routinely observed in temperature dependence of vibrational spectra. As the temperature is decreased (*i.e.* as the molecule contracts), the vibrational mode frequencies are generally seen to increase.] In the case of the lanthanide trihydroxides the molar-mass variation between the lanthanum and gadolinium iso-anionic compounds is small enough to be insignificant in determining the trend in lattice contribution across the series between 10 and 350 K. Even when considering $\text{Y}(\text{OH})_3$, which has a molar mass approximately 2/3 that of the lanthanide compounds, the effect of molar mass is clearly dominant only below 80 K. Figure 2, which shows the difference between the heat capacities of lutetium and yttrium ethylsulfates,^(14,15) clearly exhibits the same type of behavior as that of the corresponding trihydroxides.

The apparent differences with temperature of the functional dependence of the lattice contribution upon molar mass and volume makes it imperative that lattice approximations (*e.g.* the method of "corresponding states"), which employ observations made at high temperatures to imply low-temperature properties or *vice versa*, be applied with caution. Related problems have been discussed by Saxena,⁽¹⁶⁾ by Cantor⁽¹⁷⁾ and by Kieffer.⁽¹⁸⁾

Thus the trend in lattice heat capacities of iso-anionic series of lanthanide compounds may be rationalized in terms of two competing factors: molar mass and molar volume. At low temperatures, the lattice contribution is due primarily to

thermal activation of acoustic lattice modes and molar mass is the dominant factor. At higher temperatures increasing thermal activation of optical lattice modes, which are strongly affected by the lanthanide contraction, results in lattice heat-capacities which are related predominantly to the trend in molar volume. For the light lanthanide trihydroxides the molar-mass variation is dominated by the molar-volume effect at least above 50 K. Only for much lighter $Y(OH)_3$, is the mass effect clearly visible and then only below 100 K.

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