Thermophysics of the lanthanide trihydroxides
IV. The heat capacity of Ho(OH)$_3$ from 11 to 350 K. Lattice and Schottky contributions [a]

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From values of the heat capacity of microcrystalline Ho(OH)$_3$ determined by precise adiabatic calorimetry from 11 to 350 K, the Schottky contribution associated with the Stark splitting of the ground J-manifold ($^5I_8$) was resolved by means of an extrapolation of the known lattice heat-capacity variation between La(OH)$_3$ and Gd(OH)$_3$. This calorimetrically deduced Schottky contribution is compared with that calculated from spectroscopically derived energy levels of Ho^{3+} doped Y(OH)$_3$. Because the lattice parameters of Y(OH)$_3$ and Ho(OH)$_3$ are nearly identical it is assumed that the electronic energy levels of the Ho^{3+} ions are the same in either host lattice. These results together with independent heat-capacity measurements made at lower temperatures were used to adjust the low-temperature thermophysical functions to evaluate C_p/R, S°/R, and $-[\{G^\circ - H^\circ(0)\}/RT]$, at 298.15 K as 13.80, 15.64, and 7.855.

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 been achieved through application of a lattice heat-capacity approximation scheme based upon an interpolation between the lanthanum and gadolinium analogs weighted by the molar volumes along the lanthanide isoanionic series.[1–3] This empirical approximation effectively emphasizes the apparent dominance of volume over mass[5] as a determining factor of the lattice-contribution trend along the series over the temperature region of major cryogenic entropy augmentation. Recent heat-capacity measurements performed upon the isostructural diamagnet Y(OH)$_3$ provide significant insight into the physical origins of the observed trends.[6] We here present heat-capacity measurements between 11 and 350 K performed upon the heaviest

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lanthanide trihydroxide yet investigated, $Ho(OH)_3$, to determine whether the lattice approximation scheme can be successfully extrapolated to include the heavier series members.

Experimental

PREPARATION AND CHARACTERIZATION OF THE SAMPLE

The calorimetric sample was obtained as a loan from S. Mroczkowski of Yale University (Becton Center, Yale University, New Haven, Connecticut 06520, U.S.A.). The preparative technique has been described previously.[7] Powder X-ray diffraction (performed at the University of Michigan) using a 114.6 mm Hägg-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.[8] The most probable impurity, HoOOH, exhibits an intense (001) reflection which would have been detected readily if present.

THE CALORIMETER AND CRYOSTAT

A mass 41.323 g of finely powdered $Ho(OH)_3$ were loaded into a gold-plated copper calorimeter (laboratory designation W-50) 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 2.87 kPa of purified He gas to facilitate thermal equilibrium, 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 calculated from the mean of the lattice parameters (6.02 g cm^{-3}) listed in table 1. Heat-capacity measurements were made over the 12 to 350 K range in the Mark II adiabatic cryostat, which has been described previously[14] with calibrations and constraints already noted.[1]

TABLE 1. Lattice parameters of $Ho(OH)_3$

a/nm	c/nm	ref.	a/nm	c/nm	ref.	a/nm	c/nm	ref.
62.68	35.51	9	62.66	35.53	11	62.5	35.3	13
62.55	35.45	10	62.4	35.3	12			

Results

HEAT CAPACITIES AND THERMOPHYSICAL FUNCTIONS

The heat capacity of $Ho(OH)_3$ may be represented by a simple sigmoid curve from 11 to 350 K. Below 11 K thermal equilibration was much too slow to allow proper maintenance of adiabatic conditions. This problem was previously noted during measurements performed on other finely powdered lanthanide trihydroxides and may

have been due to absorption of the He exchange gas by the sample.[1-3] The experimental heat capacities were processed by subtraction of the heat capacity due to the empty calorimeter (determined separately) and by correction for small differences in the amounts of helium gas, of 50 mass per cent (lead + tin) solder, and of stainless steel, relative to that of the empty calorimeter. Curvature corrections were applied to obtain true heat capacities [i.e. $\lim (\Delta H/\Delta T)_p = C_p$ as $\Delta T \to 0$] from the measured $\Delta H/\Delta T$ values.

The experimental heat capacities (based on a molar mass of Ho(OH)$_3$ of 215.95 g mol^{-1}) are listed in chronological sequence in table 2. Throughout this

TABLE 2. Experimental heat capacities of Ho(OH)$_3$; $R = 8.3143$ J K^{-1} mol^{-1}

| T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Series I		27.27	0.862	59.77	3.134	110.48	6.375	184.89	10.187	270.48	13.103
11.03	0.279	30.13	1.061	60.43	3.177	119.59	6.916	189.77	10.389	280.00	13.350
12.31	0.273	33.28	1.287	64.77	3.472	123.96	7.168	194.13	10.566	289.44	13.587
13.60	0.271	36.78	1.545	66.02	3.553	128.49	7.429	203.92	10.943	298.81	13.820
14.93	0.297	40.83	1.837	67.68	3.662	132.62	7.658	213.57	11.299	308.20	14.036
16.48	0.326	45.85	2.188	71.80	3.920	141.76	8.152	223.11	11.646	317.55	14.260
18.29	0.380	50.23	2.493	78.34	4.354	151.26	8.639	232.61	11.957	326.92	14.460
20.26	0.457	Series II		85.50	4.839	160.89	9.115	241.74	12.270	336.37	14.658
22.39	0.563	51.12	2.550	93.16	5.323	170.58	9.571	251.08	12.563	345.46	14.858
24.70	0.697	55.12	2.820	101.51	5.833	180.29	9.996	260.86	12.840		
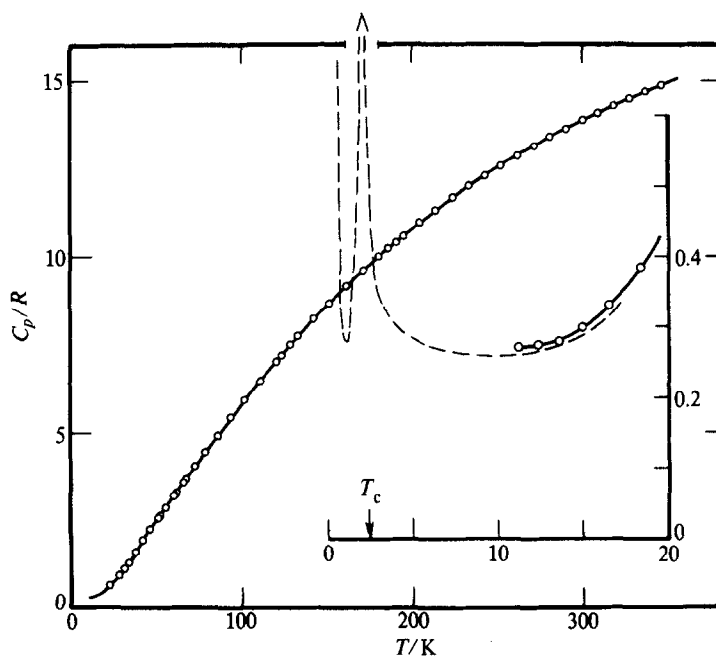
FIGURE 1. ○, The experimental heat capacities of Ho(OH)$_3$; – – –, the values of Catanese and Meissner.[14]

paper $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ so that ΔT's employed usually can be estimated from adjacent mean temperatures. Figure 1 shows our experimental heat capacity of $Ho(OH)_3$ between 11 and 350 K and the curve of Meissner[13] from 1 to 19 K. These results were curve-fitted to a power series in the range 0.66 to 19 K as interpreted by Catanese and Meissner.[15] Meissner's measurements[13] had been adversely criticized by Catanese.[17] Our results were curve-fitted to a power series in orthogonal polynomials in reduced temperature as described by Justice.[16] Appropriate

TABLE 3. Thermophysical functions of $Ho(OH)_3$

$\dfrac{T}{K}$	$\dfrac{C_p}{R}$	$\dfrac{S°(T)-S°(0)}{R}$	$\dfrac{H°(T)-H°(0)}{R\,K}$	$\dfrac{-\{G°(T)-H°(0)\}}{RT}$
10	0.271	0.940	1.265	0.814
15	0.299	1.053	2.655	0.876
20	0.445	1.155	4.458	0.932
25	0.714	1.282	7.315	0.989
30	1.053	1.441	11.716	1.050
35	1.412	1.630	17.872	1.119
40	1.776	1.843	25.850	1.197
45	2.131	2.073	35.622	1.281
50	2.477	2.315	47.145	1.372
60	3.149	2.826	75.291	1.571
70	3.811	3.362	110.10	1.789
80	4.465	3.913	151.48	2.020
90	5.111	4.477	199.37	2.262
100	5.704	5.048	253.64	2.512
110	6.351	5.624	314.11	2.768
120	6.941	6.202	380.59	3.030
130	7.510	6.780	452.86	3.296
140	8.057	7.357	530.7	3.566
150	8.579	7.930	613.9	3.837
160	9.075	8.500	702.2	4.111
170	9.542	9.064	795.3	4.386
180	9.983	9.622	893.0	4.661
190	10.398	10.173	994.9	4.937
200	10.793	10.717	1100.9	5.213
210	11.170	11.253	1210.7	5.488
220	11.532	11.781	1324.2	5.762
230	11.880	12.301	1441.3	6.034
240	12.211	12.814	1561.7	6.307
250	12.524	13.319	1685.4	6.577
260	12.817	13.816	1812.2	6.846
270	13.092	14.305	1941.7	7.114
280	13.352	14.785	2074.0	7.378
290	13.602	15.258	2208.7	7.642
300	13.845	15.724	2346.0	7.904
310	14.082	16.181	2485.6	8.163
320	14.311	16.632	2627.6	8.421
330	14.527	17.076	2771.8	8.677
340	14.733	17.513	2918.1	8.930
350	14.936	17.943	3066.4	9.182
273.15	13.18	14.46	1983.1	7.197
298.15	13.80	15.64	2320.4	7.855

integration of this polynomial yielded the thermophysical functions listed in table 3. The functions do not include contributions from nuclear spin and isotope mixing and are thus suitable for use in ordinary thermochemical calculations.

LOW-TEMPERATURE ENTHALPY AND ENTROPY INCREMENTS

The measurements of Meissner clearly exhibit a λ-transition at 2.54 K (see figure 1) associated with the magnetic ordering of the Ho^{3+} ions. The ground state of Ho(OH)$_3$ is a doublet; therefore, this ordering will result in an $R \ln 2$ entropy contribution. Below 30 K the lattice contribution is approximated by the method described in this paper while the Schottky contribution is calculated from the reported Stark levels. The cooperative magnetic entropy and enthalpy increments at 30 K were taken as $(R \ln 2)$ and $(2.54\,\mathrm{K}\,R \ln 2)$, respectively. By summing the lattice, Schottky, and cooperative magnetic contributions, the thermophysical functions are evaluated at 30 K. Values below this temperature are obtained by subtracting the calorimetrically obtained increments from the values deduced for 30 K. No significant cooperative magnetic entropy contribution is anticipated above 30 K.

RESOLUTION OF THE LATTICE AND SCHOTTKY CONTRIBUTIONS

The lattice heat-capacity contribution of Ho(OH)$_3$ was resolved by extrapolation of the observed variation of the lattice heat capacity between La(OH)$_3$ and Gd(OH)$_3$, weighted by the fractional molar-volume variation along the series:

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

in which f may be expressed in terms of the molar volumes of La(OH)$_3$, Gd(OH)$_3$, and Ho(OH)$_3$.[2] The asterisk indicates that the heat capacity associated with the cooperative antiferromagnetic anomaly of Gd(OH)$_3$ has been deleted.

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

The value of $f\{\text{Ho(OH)}_3\}$ based upon the mean of the lattice parameters listed in table 1 is found to be 1.31. The heat capacities and lattice parameters of La(OH)$_3$ and Gd(OH)$_3$ have been reported previously.[2] Deduction of the approximate lattice contribution from the Ho(OH)$_3$ total heat capacity results in the curve designated the "calorimetric" Schottky contribution in figure 2.

The absorption spectrum of concentrated Ho(OH)$_3$ has been investigated by Scott[18] at both 77 and 4.2 K. However, as seen in table 4, only the lowest 2 of an anticipated 10 excited Stark wavenumbers within the ground $^5I_8$ J-manifold were observed. Several Stark wavenumbers associated with higher-lying J-manifolds were also observed; however, the overall spectrum was, "too sparse to permit a reliable determination of the crystal-field parameters".[18] These would have been useful for estimation of the wavenumbers of the unobserved Stark levels. Absorption-spectral measurements on Y(OH)$_3$ crystals doped with approximately 1 mass per cent of Ho^{3+} at 77 K were more successful. As noted in the light lanthanide trichlorides,[4] assuming the Stark-level wavenumbers of doped crystals equal to those of their
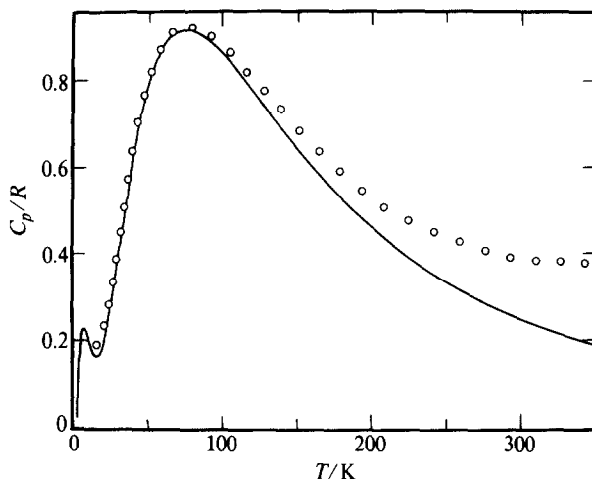
FIGURE 2. The Schottky contribution for Ho(OH)$_3$. O, $--$, the "calorimetric" and "calculated" (spectroscopic) Schottky contributions, respectively. See text for explanation.

TABLE 4. Ho : Ln(OH)$_3$ wavenumbers for $J = {}^5I_8$

σ/cm^{-1}							
obs.[a]		calc.		obs.[a]		calc.	
Ho(OH)$_3$	Ho:Y(OH)$_3$	Ho:Y(OH)$_3$	g	Ho(OH)$_3$	Ho:Y(OH)$_3$	Ho:Y(OH)$_3$	g
—	—	364.8	1	—	—	127.5	2
—	—	342.4	2	—	102.1	102.5	2
—	—	274.1	2	73.2	72.8	75.6	1
—	—	222.3	2	11.0	11.3	11.4	1
—	—	220.8	1	0.0	0.0	0.0	2
—	—	147.3	1				

[a] Reference 18.

concentrated analog (e.g. Pr^{3+}-doped LaCl$_3$ against concentrated PrCl$_3$) can lead to discrepancies in the calculated Schottky contribution which may be readily detected calorimetrically. This difference is anticipated to be small for {Y(OH)$_3$ − Ho(OH)$_3$} because the lattice parameters of both are nearly identical. Indeed, the first two excited Stark wavenumbers of the ${}^5I_8$ manifold for Ho^{3+}-doped Y(OH)$_3$ and concentrated Ho(OH)$_3$ are within 0.4 cm^{-1} of each other. This does not necessarily prove that higher wavenumbers will be as nearly identical; however, it is a strong indication that Ho^{3+}-doped Y(OH)$_3$ Stark-level wavenumbers may be used to estimate those of concentrated Ho(OH)$_3$.

Scott[18] observed a total of 31 transitions originating from 4 levels of the ${}^5I_8$ ground J-manifold and terminating in 13 levels of the ${}^5F_5$, ${}^5F_4$, and ${}^5F_3$ excited J-manifolds. The energy-level assignments were confirmed by Zeeman experiments. The four observed wavenumbers within the ${}^5I_8$ J-manifold are listed in table 4. Although only one additional Stark level within the ground J-manifold was observed, the results (on 17 levels) are sufficient to allow deduction of the four crystal-field

parameters necessary to estimate the wavenumbers of the unobserved Stark levels. The crystal-field parameters deduced by Scott are listed in table 5. Because Scott reported only the center of gravity calculated for the $^5I_8$ J-manifold, we use the deduced crystal-field parameters to calculate the individual wavenumbers of the $^5I_8$ Stark levels of Ho^{3+}-doped $Y(OH)_3$. Our calculations follow the procedures detailed by Stevens,[19] Elliot and Stevens,[20] Judd,[21] and Hutchings,[22] and do not include the effect of J-mixing. Scott's calculations did include J-mixing; however, he found this effect to be quite small. Indeed, the largest relative shift of any two levels within the same manifold caused by J-mixing was less than $2\,\text{cm}^{-1}$. These shifts readily explain the small difference in the center of gravity that we calculate $(174.0\,\text{cm}^{-1})$ and that calculated by Scott $(174.4\,\text{cm}^{-1})$ for the $^5I_8$ J-manifold. Uncertainties of this magnitude in the Stark-level wavenumbers have a negligible effect on the calculated Schottky heat-capacity contribution. The calculated wavenumbers and degeneracies of the $^5I_8$ manifold are listed in table 4 and were used to derive the "calculated" Schottky contribution represented by the uninterrupted line in figure 2.

TABLE 5. Crystal-field parameters for Ho^{3+} doped $Y(OH)_3$[a]

B_2^0/cm^{-1}	B_4^0/cm^{-1}	B_6^0/cm^{-1}	B_6^6/cm^{-1}
246.0	−56.7	−39.8	543.6

[a] From reference 18.

Discussion

Below the maximum Schottky contribution (near 90 K) the agreement between the "calculated" and "calorimetric" curves is seen to be excellent. The small positive deviation of the "calorimetric" relative to the "calculated" curve near the lowest temperatures of this study almost certainly arises from neglect of the small cooperative magnetic contribution anticipated in this region (since $Ho(OH)_3$ orders ferromagnetically near 2.54 K). Above 90 K the "calorimetric" and "calculated" curves gradually diverge until they differ by approximately $0.18C/R$ near 350 K. Although this quantity is only 1.2 per cent of the total measured heat capacity of $Ho(OH)_3$ at this temperature, it is well outside the experimental uncertainty of about $0.03C/R$ (i.e. 0.2 per cent of the measured C_p). This result is in direct contrast to the excellent quantitative agreement observed for $Pr(OH)_3$,[1] $Eu(OH)_3$,[2] $Tb(OH)_3$,[3] and the light lanthanide trichlorides.[4]

The origin of the observed divergence can be attributed to one of three effects. 1. The lattice approximation method employed may not be entirely valid when an extrapolation of the magnitude necessary in this instance must be used. 2. Since only the lowest-energy Stark levels of the $^5I_8$ manifold were actually observed, significant deviations between the Ho^{3+}-doped $Y(OH)_3$ and $Ho(OH)_3$ $^5I_8$ Stark may have been undetected. It is interesting to note that at low temperatures, where the experimentally observed levels are predominantly responsible for the Schottky contribution, the agreement with the calorimetrically deduced curve is excellent. 3.

The additional excess heat capacity observed for $Ho(OH)_3$ at high temperatures may be due to an unforeseen contribution which has not been taken into account (*e.g.* the low-temperature "tail" of a structural phase transition). Planned heat-capacity measurements on $Er(OH)_3$ could lend important insight into the source of the divergence between Schottky heat-capacity curves for $Ho(OH)_3$. The principal advantage is that the spectroscopic properties of $Er(OH)_3$ are well known[23] and do not present the problems associated with the coupled $^5I_8$ ground state of $Ho(OH)_3$.

In conclusion, the relatively large uncertainty in the spectroscopically deduced Schottky contribution for $Ho(OH)_3$ precludes definitive ascertainment of the success of the lattice approximation above 100 K, when applied to the heavier lanthanide trihydroxides; however, at lower temperatures the lattice approximation is shown to be excellent. Experiments planned for $Er(OH)_3$ will provide a better test of the lattice approximation at higher temperatures for the heavier series members.

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