

## Thermophysics of the lanthanide trihydroxides

### II. Heat capacities from 10 to 350 K of $\text{Nd}(\text{OH})_3$ and $\text{Tb}(\text{OH})_3$ . Lattice and Schottky contributions<sup>a</sup>

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Heat capacities have been measured from near 7 to 350 K for  $\text{Nd}(\text{OH})_3$  and  $\text{Tb}(\text{OH})_3$  and the derived thermophysical properties evaluated using previously reported heat capacities at lower temperatures. At 298.15 K the values of  $C_p/R$ ,  $S^\circ/R$ , and  $-\{G^\circ - H^\circ(0)\}/RT$  are 14.15, 15.62, and 7.484 for  $\text{Nd}(\text{OH})_3$  and 13.72, 15.44, and 7.525 for  $\text{Tb}(\text{OH})_3$ . The resolution of the lattice and Schottky contributions for both compounds is discussed. The  $\text{Tb}(\text{OH})_3$  calorimetric Schottky contribution is correlated with spectroscopically deduced energy levels for  $\text{Tb}(\text{OH})_3$  and  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$ , while that of  $\text{Nd}(\text{OH})_3$  is used to estimate the crystal-field splitting of the  $^4I_{9,2}$  *J*-manifold. The effect of temperature upon the Schottky heat capacities is discussed.

### 1. Introduction

Recent studies on the lanthanide trihydroxides have emphasized the validity of a lattice heat-capacity approximation method based upon fractional molar-volume increments. Application of this method to  $\text{Eu}(\text{OH})_3$ <sup>(1)</sup> and  $\text{Pr}(\text{OH})_3$ <sup>(2)</sup> yielded Schottky contributions in excellent accord with those calculated from spectroscopically determined energy levels and degeneracies. (The former are designated the "calorimetric" Schottky contributions and the latter the "spectroscopic".) Because 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 allowance is made for shifts of the Stark levels with temperature, perfect agreement between the "calorimetric" and "spectroscopic" Schottky contributions is generally an unreasonable expectation. The exception to this generalization is  $\text{Eu}(\text{OH})_3$  for which excellent agreement is found between 5 and 350 K<sup>(1)</sup> through use of the lattice approximation technique mentioned above. Because of the sensitivity of the Schottky heat capacity to small shifts in the lower-

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lying energy levels of other lanthanide compounds, corroboration of the lattice approximation over the entire temperature range cannot, at present, be achieved. Moreover, at very low temperatures, relative ionic masses may be expected to play a large role.

In this paper we present the results of heat-capacity measurements from 5 to 350 K on  $\text{Tb}(\text{OH})_3$  and from 10 to 350 K on  $\text{Nd}(\text{OH})_3$ . The calorimetric Schottky contribution derived for  $\text{Tb}(\text{OH})_3$  is compared with that calculated from spectroscopically determined energy levels and degeneracies of  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$  and with concentrated  $\text{Tb}(\text{OH})_3$ . Spectroscopic quantities are not known for  $\text{Nd}(\text{OH})_3$ . In their absence the Stark splitting of the  ${}^4\text{I}_{9/2}$  ground  $J$ -manifold of  $\text{Nd}(\text{OH})_3$  is estimated from the calorimetrically derived Schottky contribution. The magnitude of this Stark splitting is compared with that calculated from the crystal-field parameters spectroscopically deduced for the nearby trihydroxides  $\text{Pr}(\text{OH})_3$  and  $\text{Eu}(\text{OH})_3$ .

## 2. The Schottky heat-capacity model

The molar (Schottky) heat capacity  $C_x$  for systems with energy levels  $\varepsilon_i$  and degeneracies  $g_i$  is

$$C_x/R = \sum_i g_i (\varepsilon_i/kT)^2 \exp(-\varepsilon_i/kT)/Z - \left\{ \sum_i (g_i \varepsilon_i/kT) \exp(-\varepsilon_i/kT)/Z \right\}^2, \quad (1)$$

in which  $k$ ,  $T$ , and  $Z$  are the Boltzmann constant, thermodynamic temperature, and electronic partition function. The subscript  $x$  represents any parameter upon which the energy levels and their degeneracies depend (*e.g.*  $x =$  volume, magnetic field, or electric field, *etc.*). In deriving the above expression it has been tacitly assumed that the energy levels are temperature independent. This assumption may be the single largest source of error in the application of the Schottky heat-capacity model to lanthanide compounds since the spectroscopically derived energy levels used in the calculation of Schottky heat capacities are frequently determined only near 4 K and/or 77 K. The temperature effect may be rationalized as follows. As the lattice expands with increasing temperature the interionic distances increase, thereby lowering the crystal-field intensity at the cation, which in turn results in a decreased splitting of the individual  $J$ -manifolds and a simultaneous shift of the barycenters of the excited  $J$ -manifolds to slightly lower energies. A superposition of these two effects may cause individual Stark levels of excited  $J$ -manifolds to shift either to lower or higher energies relative to the ground Stark level. The effect on the Stark levels of the ground  $J$ -manifold, however, is gradually to shift them closer to the ground Stark level as the crystal-field intensity is decreased.

Johnson *et al.*<sup>(3)</sup> determined the Stark splitting of several excited  $J$ -manifolds of  $\text{Nd}^{3+}$  doped  $\text{LaF}_3$  as a function of temperature between approximately 70 and 160 K. As anticipated, wavenumber differences between Stark levels of the same parent  $J$ -state decreased with increasing temperature, while the absolute wavenumber (*i.e.* determined relative to the ground Stark level) did not vary monotonically. The overall splittings of the  $J$ -manifolds were decreased by approximately  $5 \text{ cm}^{-1}$  in the temperature range investigated.

Levshin and Pirinchieva<sup>(4)</sup> determined the wavenumber levels of Er<sup>3+</sup>-doped Y<sub>2</sub>O<sub>3</sub> at 4, 77, 130, 195, and 295 K and found results very much in accord with those of Johnson *et al.*<sup>(3)</sup> Of particular interest is their determination of the Stark splitting of the <sup>4</sup>I<sub>15/2</sub> ground *J*-manifold. Between 4 and 77 K, shifts of only  $\approx 1 \text{ cm}^{-1}$  were detected; however, between 77 and 295 K a near linear decrease in the crystal-field splitting was observed. The total observed shifts between 77 and 295 K for the <sup>4</sup>I<sub>15/2</sub> Stark components (in order of increasing wavenumber were 1, 2, 4, 4, 5,  $\approx 13$ , and  $\approx 13 \text{ cm}^{-1}$ , respectively, as would be anticipated due to a gradual compression of the ground *J*-manifold as the crystal field is weakened. The shifts correspond to an approximately 3 per cent decrease in the wavenumbers of the <sup>4</sup>I<sub>15/2</sub> Stark components. The two highest Stark levels could not be resolved at 295 K due to temperature broadening; consequently, the  $13 \text{ cm}^{-1}$  shift reported for these levels is that of their center of gravity.

The magnitudes of the wavenumber level shifts so far discussed would have only a small effect on the calculated Schottky heat capacity. However, the temperature-dependent spectroscopic data for the lanthanide trihydroxides indicate that generalizations concerning the magnitude of this effect cannot be made on the basis of the Er<sup>3+</sup>-doped Y<sub>2</sub>O<sub>3</sub> and Nd<sup>3+</sup>-doped LaF<sub>3</sub> data alone.

Chirico *et al.*<sup>(2)</sup> found the wavenumber of the first excited Stark level of Pr(OH)<sub>3</sub> to be  $13 \text{ cm}^{-1}$  from optical measurements made at 95 K, while independent measurements made by Gruber<sup>(5)</sup> at 4 K determined this level to be shifted downward—possibly as low as  $8 \text{ cm}^{-1}$ . (The direction of this shift is opposite to that anticipated; however, the spectroscopic data of Dorman<sup>(6)</sup> and McLaughlin and Conway<sup>(7)</sup> indicate that the wavenumber of the first excited Stark level ( $\mu = -3$ ) of the Pr<sup>3+</sup> ion in C<sub>3h</sub> lattice sites decreases as the crystal-field intensity increases.) Moreover, unpublished spectral results of Scott<sup>(8)</sup> show the wavenumber of the first excited Stark level of Dy(OH)<sub>3</sub> to increase from  $7.5 \text{ cm}^{-1}$  at 77 K to  $16 \text{ cm}^{-1}$  at 4 K as a consequence of the increasing crystal-field intensity. The magnitudes of the shifts found by Chirico *et al.* and by Scott for only the first excited Stark levels of Pr(OH)<sub>3</sub> and Dy(OH)<sub>3</sub> are comparable to the shifts for the entire *J*-manifolds found by Johnson *et al.*<sup>(3)</sup> and Levshin and Pirinchieva.<sup>(4)</sup> No spectral results are available for the temperature dependence of higher-lying Stark levels for the trihydroxides.

Because the Schottky heat capacity is generally calculated from spectral data near 4 or 77 K, errors introduced by ignoring shifts of the Stark levels with temperature are expected to be increasingly important at higher temperatures. This is offset to some extent by the decreased sensitivity of the Schottky heat capacity to small wavenumber shifts; however, the large shifts implied by the limited results available for the lanthanide trihydroxides clearly cannot be ignored.

### 3. Experimental

#### PREPARATION AND CHARACTERIZATION OF SAMPLES

Nd(OH)<sub>3</sub>. Nd<sub>2</sub>O<sub>3</sub> (99.99 moles per cent purity, Research Chemicals, Phoenix, Arizona) starting material was calcined at about 1200 K and stored in a desiccator

containing both Drierite and Ascarite. The calcined  $\text{Nd}_2\text{O}_3$  was transferred into crimped gold tubes for direct reaction with water at 110 MPa and 840 K for about 20 h using the hydrothermal technique previously described by Haschke and Eyring.<sup>(9)</sup> The gold tubes were crimped with a three-jawed chuck to allow direct communication between the pressurized water in the reactor and the sesquioxide. A detailed description of the hydrothermal apparatus is reported in the doctoral dissertation of Lance-Gomez.<sup>(10)</sup>

Powder X-ray diffraction patterns obtained with a 114.6 mm Hagg-type Guinier camera ( $\text{Cu K}\alpha_1$  radiation,  $\lambda = 15405$  nm) with silicon ( $a = 0.543\ 062$  nm) as an internal standard showed only the hexagonal  $\text{UCl}_3$ -type crystal structure reported for all of the lanthanide trihydroxides.<sup>(11)</sup> Upon thermogravimetric analysis the prepared  $\text{Nd}(\text{OH})_3$  exhibited the two-step decomposition path previously reported by Fricke and Seitz:<sup>(12)</sup>



No evidence for the possible formation of a fourth compound analogous to that observed in the  $\text{La}(\text{OH})_3$  decomposition curve was detected.<sup>(1,10)</sup> The stoichiometry was determined by direct ignition of samples to the sesquioxide. The reported stoichiometry,  $\text{Nd}(\text{OH})_{(2.994 \pm 0.002)}$ , is the mean of six separate determinations. The reported error limits represent the standard deviation.

$\text{Tb}(\text{OH})_3$ . The  $\text{Tb}(\text{OH})_3$  sample used in this research was obtained on loan from S. Mroczkowski (Becton Center, Yale University, New Haven, Connecticut). The synthetic method employed by Mroczkowski involves precipitation of amorphous  $\text{Tb}(\text{OH})_3$  by aqueous  $\text{NaOH}$  from a solution of the oxide dissolved in 20 mass per cent nitric acid (heated to evaporate excess  $\text{HNO}_3$ ) followed by hydrothermal crystallization from a nearly saturated aqueous  $\text{NaOH}$  solution. The reported stoichiometry,  $\text{Tb}(\text{OH})_{(3.000 \pm 0.001)}$ , was determined using a slight variation of the back-titration method of Flaschka.<sup>(13)</sup> Details of the preparation and characterization are available in the literature<sup>(14)</sup> and in the doctoral dissertation of Meissner.<sup>(15)</sup>

#### THE CALORIMETERS AND CRYOSTAT

The  $\text{Nd}(\text{OH})_3$  (93.6043 g) and  $\text{Tb}(\text{OH})_3$  (48.6344 g) samples were loaded into gold-plated copper calorimeters (laboratory designation W-54 and W-50, respectively) provided with screw-type closures involving a stainless-steel knife edge and an annealed gold gasket.<sup>(16)</sup> The calorimeters were evacuated and then—after the addition of about 4 kPa of purified He gas to facilitate thermal equilibration—were sealed. A small amount of Apiezon-T grease of known mass was placed in the thermocouple and heater + thermometer wells of the calorimeter to provide good thermal contact between the heater, temperature sensors, and the calorimeters. Buoyancy corrections used to obtain the masses listed above were based on the crystallographic densities implied in table 1.

TABLE 1. Hexagonal lattice constants, sample mass *m*, and molar mass *M* for Ln(OH)<sub>3</sub>

Compound	<i>a</i> /nm	<i>c</i> /nm	Reference	<i>m</i> /g	<i>M</i> /g mol <sup>-1</sup>
Nd(OH) <sub>3</sub>	642.1	374	17	93.6043	195.262
	642.2	374.2	18		
	641.8	374.3	19		
	642.5	373.9	9		
	643	375	20, 21		
	642	367	22		
Tb(OH) <sub>3</sub>	630.8	360.0	23	48.6344	209.9461
	631.2	360.1	24		
	628	357	22		
	631.5	360.3	19		
	627.0	356.0	25		

Heat-capacity measurements were made in the range 5 to 350 K in the Mark II adiabatic cryostat, which has been described previously.<sup>(16)</sup> 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)<sup>(26)</sup> 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<sup>(27)</sup> below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K between 10 and 90 K and 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 approximately 1 per cent at 10 K. This decreases to 0.1 per cent at 25 K and to about 0.06 per cent between 25 and 350 K even though precision is significantly better, particularly at low temperatures.

#### 4. Results and discussion

##### HEAT CAPACITIES AND THERMOPHYSICAL FUNCTIONS

The heat capacities of Tb(OH)<sub>3</sub> and Nd(OH)<sub>3</sub> given in table 2 may be represented by simple sigmate curves between 10 and 350 K, as shown in figures 1 and 2. Because proper adiabatic conditions could not be maintained at lower temperatures, measurements on Nd(OH)<sub>3</sub> were limited to temperatures above 11.4 K. The problem seems due to crystallite size and may have been due to absorption of the He exchange gas by the finely-powdered sample. No experimental difficulties were encountered at temperatures as low as 4.5 K during measurements with the Tb(OH)<sub>3</sub> sample, which was composed of significantly larger crystals.

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 He 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 and 40 per cent of the total

TABLE 2. Experimental values of the heat capacities of Nd(OH)<sub>3</sub> and Tb(OH)<sub>3</sub>

T/K	C <sub>p</sub> /R	T/K	C <sub>p</sub> /R	T/K	C <sub>p</sub> /R	T/K	C <sub>p</sub> /R
Nd(OH) <sub>3</sub>							
Series 1		110.20	6.928	239.27	12.706	Series 8	
243.41	12.826	117.77	7.433	248.58	12.974	16.82	0.158
251.87	13.052	125.68	7.924			18.44	0.203
260.79	13.338 <sup>a</sup>			Series 5		20.22	0.259
269.89	13.577 <sup>a</sup>	Series 3		280.19	13.759	22.10	0.326
278.88	13.730	128.68	8.109	288.97	13.952	24.24	0.411
287.96	13.941	137.47	8.618			26.61	0.522
297.30	14.146	146.54	9.105	Series 6		29.15	0.652
307.00	14.344	155.61	9.565	303.67	14.260	31.92	0.808
		164.75	9.995	312.04	14.437	34.64	0.980
Series 2		174.00	10.409	321.21	14.611	37.76	1.187
58.75	2.857	183.32	10.791	330.78	14.791	41.58	1.459
63.32	3.255	192.59	11.159			45.80	1.785
68.32	3.680			Series 7		50.41	2.155
73.61	4.120	Series 4		11.38	0.057	55.49	2.577
78.87	4.569	192.86	11.174	12.45	0.069	60.83	3.036
84.22	5.025	202.02	11.516	13.45	0.085		
90.03	5.492	211.24	11.826	14.80	0.110	Series 9	
96.23	5.942	220.54	12.155	16.21	0.141	338.49	14.936
102.94	6.243	229.90	12.435	17.79	0.182	346.25	15.080
Tb(OH) <sub>3</sub>							
Series 1		34.29	1.071	Series 3		247.78	12.453
4.72	0.072 <sup>a</sup>	37.48	1.301	99.12	6.214	257.64	12.723
4.84	0.069 <sup>a</sup>	41.03	1.564	107.93	6.757	267.34	12.981
5.38	0.053 <sup>a</sup>	45.04	1.880	117.59	7.307	276.89	13.222
6.51	0.041 <sup>a</sup>	49.64	2.257	126.97	7.804	286.45	13.453
7.77	0.036 <sup>a</sup>	54.71	2.688	136.00	8.257		
8.89	0.038 <sup>a</sup>	59.93	3.143	145.05	8.687	Series 5	
9.97	0.048 <sup>a</sup>	65.46	3.650	154.48	9.113	281.57	13.333
11.04	0.052			164.14	9.532	291.07	13.550
12.12	0.063	Series 2		173.77	9.926	300.73	13.774
13.32	0.081	56.94	2.887	183.40	10.302	310.57	13.980
14.59	0.107	62.07	3.344	193.03	10.664	320.60	14.196
15.98	0.135	67.60	3.824	202.69	11.012	330.52	14.387
17.50	0.177	73.62	4.324			340.33	14.568
19.21	0.233	80.21	4.868	Series 4		347.66	14.703
21.13	0.307	87.45	5.436	199.36	10.880		
23.29	0.404	95.44	5.980	208.91	11.219	Series 6	
25.60	0.525	104.24	6.534	218.49	11.549	78.70	4.744
28.18	0.671			228.14	11.856	85.98	5.324
31.16	0.858			237.91	12.161	93.11	5.825
						110.17	6.284

<sup>a</sup> This point was not included in the curve-fitting calculations.

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 capacities for each compound are listed in chronological sequence in table 2† so that the  $\Delta T$ 's employed usually can be estimated from adjacent mean temperatures. These results were curve fitted to a power series in

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

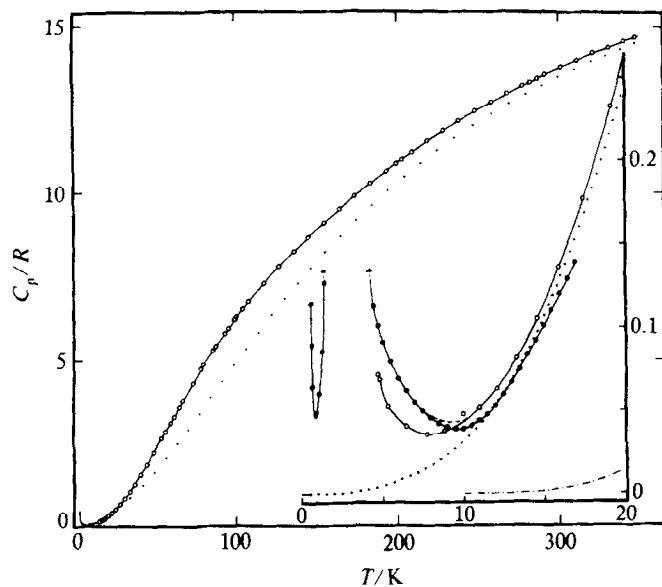


FIGURE 1. Experimental heat capacity of  $\text{Tb}(\text{OH})_3$ .  $\circ$ , This work;  $\bullet$ , Catanese *et al.*<sup>(30)</sup> -----, Chosen to join the two sets of results;  $\cdots$ , the approximate lattice contribution;  $-\cdot-, the calculated Schottky contribution below 20 K.$

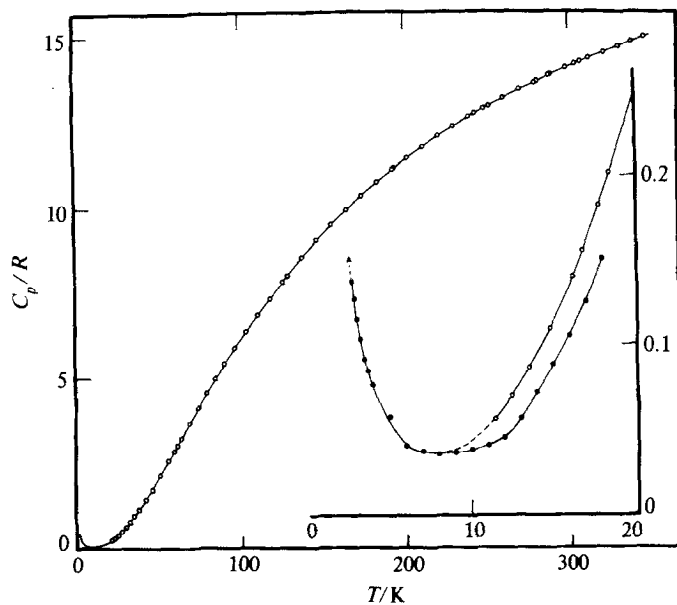


FIGURE 2. Experimental heat capacity of  $\text{Nd}(\text{OH})_3$ .  $\circ$ , This work;  $\bullet$ , Meissner.<sup>(42)</sup> -----, Chosen to join the two sets of results.

TABLE 3. Thermophysical functions of  $\text{Nd}(\text{OH})_3$  and  $\text{Tb}(\text{OH})_3$ 

$\frac{T}{\text{K}}$	$\frac{C_p}{R}$	$\frac{S^\circ(T) - S^\circ(0)}{R}$	$\frac{H^\circ(T) - H^\circ(0)}{R \text{ K}}$	$-\frac{\{G^\circ(T) - H^\circ(0)\}}{RT}$
$\text{Nd}(\text{OH})_3$				
10	(0.042)	(0.695)	(0.336)	(0.661)
15	0.114	0.723	0.699	0.676
20	0.250	0.773	1.585	0.694
25	0.446	0.849	3.301	0.717
30	0.698	0.952	6.138	0.747
35	1.000	1.081	10.362	0.785
40	1.344	1.237	16.208	0.832
45	1.721	1.417	23.860	0.886
50	2.120	1.619	33.456	0.949
60	2.964	2.079	58.83	1.098
70	3.820	2.600	92.75	1.275
80	4.666	3.166	135.21	1.476
90	5.472	3.762	185.94	1.696
100	6.222	4.378	244.46	1.934
110	6.918	5.004	310.20	2.184
120	7.568	5.634	382.66	2.445
130	8.179	6.264	461.43	2.715
140	8.751	6.892	546.1	2.991
150	9.284	7.514	636.3	3.272
160	9.776	8.129	731.7	3.556
170	10.231	8.736	831.7	3.843
180	10.655	9.332	936.2	4.132
190	11.054	9.919	1044.7	4.421
200	11.432	10.496	1157.2	4.710
210	11.789	11.063	1273.3	4.999
220	12.124	11.619	1392.9	5.287
230	12.437	12.165	1515.7	5.575
240	12.728	12.700	1641.6	5.860
250	13.001	13.225	1770.2	6.145
260	13.260	13.740	1901.5	6.427
270	13.508	14.246	2035.4	6.707
280	13.746	14.741	2171.7	6.985
290	13.973	15.23	2310.3	7.261
300	14.185	15.70	2451.1	7.535
310	14.385	16.17	2593.9	7.806
320	14.576	16.63	2738.7	8.074
330	14.766	17.08	2885.4	8.341
340	14.955	17.53	3034.0	8.604
350	15.14	17.96	3184.5	8.866
273.15	13.584	14.403	2078.0	6.795
298.15	14.147	15.62	2424.8	7.484
$\text{Tb}(\text{OH})_3$				
10	0.043	(0.700)	(2.563)	(0.444)
15	0.113	0.728	2.923	0.533



TABLE 3—continued

$\frac{T}{K}$	$\frac{C_p}{R}$	$\frac{S^\circ(T) - S^\circ(0)}{R}$	$\frac{H^\circ(T) - H^\circ(0)}{R K}$	$-\{G^\circ(T) - H^\circ(0)\}$ RT
20	0.262	0.779	3.826	0.588
25	0.491	0.861	5.678	0.634
30	0.784	0.976	8.843	0.681
35	1.121	1.121	13.590	0.733
40	1.487	1.295	20.099	0.792
45	1.877	1.492	28.499	0.859
50	2.287	1.711	38.900	0.933
60	3.156	2.204	66.07	1.103
70	4.028	2.756	102.00	1.299
80	4.856	3.349	146.48	1.518
90	5.606	3.965	198.85	1.755
100	6.276	4.590	258.32	2.007
110	6.880	5.217	324.14	2.271
120	7.436	5.840	395.76	2.542
130	7.957	6.456	472.75	2.820
140	8.449	7.064	554.8	3.101
150	8.915	7.663	641.6	3.385
160	9.356	8.253	733.0	3.671
170	9.774	8.832	828.7	3.958
180	10.171	9.402	928.4	4.244
190	10.549	9.962	1032.0	4.531
200	10.911	10.513	1139.3	4.816
210	11.260	11.054	1250.2	5.100
220	11.595	11.585	1364.5	5.383
230	11.917	12.108	1482.1	5.664
240	12.224	12.622	1602.8	5.943
250	12.515	13.126	1726.5	6.221
260	12.790	13.623	1853.0	6.496
270	13.049	14.110	1982.2	6.769
280	13.296	14.589	2114.0	7.040
290	13.530	15.06	2248.1	7.308
300	13.756	15.52	2384.5	7.574
310	13.973	15.98	2523.2	7.838
320	14.180	16.42	2664.0	8.099
330	14.377	16.86	2806.8	8.358
340	14.563	17.30	2951.5	8.615
350	14.744	17.72	3098.0	8.869
273.15	13.128	14.262	2023.5	6.854
298.15	13.715	15.44	2359.1	7.525

orthogonal polynomials in reduced temperature as described by Justice.<sup>(28)</sup> The thermophysical functions, listed in table 3, were derived by integration of the fitted polynomials. These functions do not include contributions from nuclear spin and isotope mixing and are thus suitable for use in ordinary thermochemical calculations.

The method of evaluation of the entropy and enthalpy increments developed below 10 K are described below.

### LOW-TEMPERATURE ENTHALPY AND ENTROPY INCREMENTS

$\text{Tb}(\text{OH})_3$ . The crystal-field analysis of Scott, Meissner, and Crosswhite<sup>(29)</sup> has shown the two lowest lying electronic states of  $\text{Tb}(\text{OH})_3$  to be singlets separated by approximately  $0.3 \text{ cm}^{-1}$ . Because the next excited Stark level is relatively high in wavenumber ( $118.2 \text{ cm}^{-1}$ ), each  $\text{Tb}^{3+}$  ion can be represented by an effective spin  $S = 1/2$  as is customary for systems with a well separated Kramers-doublet ground state. Through both low-temperature heat capacity and susceptibility measurement, Catanese *et al.*<sup>(30)</sup> determined that  $\text{Tb}(\text{OH})_3$  orders ferromagnetically at  $(3.72 \pm 0.01) \text{ K}$  with an associated total entropy contribution of  $(R \ln 2)$ . Catanese *et al.* employed two complementary techniques to estimate the cooperative magnetic contribution to the total heat capacity. Near the Curie temperature the heat capacity of diamagnetic  $\text{La}(\text{OH})_3$  was used to estimate the lattice contribution. At temperatures high relative to the Curie temperature, the cooperative magnetic contribution was determined directly from the magnetic-field dependence of the adiabatic differential susceptibility using the method of Casimir and du Pré.<sup>(31)</sup> This analysis yielded the expansion for the cooperative magnetic contribution to the heat capacity of  $\text{Tb}(\text{OH})_3$  above the Curie temperature:

$$C_p(\text{magnetic})/R = (1.00 \pm 0.10)(\text{K}/T)^2 + (1.6 \pm 0.8)(\text{K}/T)^3 + (7 \pm 2)(\text{K}/T)^4 + (60 \pm 40)(\text{K}/T)^5. \quad (2)$$

The lattice contribution below 10 K, derived from a plot of  $T^2 C_p(\text{total})/R$  against  $T^5$  for results above the Curie temperature, may be expressed as

$$C_p(\text{lattice})/R = (3.8 \pm 0.2) \times 10^{-5} (T/\text{K})^3. \quad (3)$$

The heat capacities of the present research were joined with those of Catanese *et al.* as shown in figure 1. The total cooperative magnetic entropy and enthalpy contributions were estimated as  $(R \ln 2)$  and  $3.72 \text{ K } R \ln 2$ , respectively. The portions of these increments developed above 10 K were calculated by integration of equation (2) from 10 K to  $\infty$ . The lattice entropy and enthalpy contributions were derived using equation (3). The sharp increase in the  $\text{Tb}(\text{OH})_3$  total heat capacity below 1 K is due to thermal population of nuclear energy levels. The effect of this nuclear Schottky contribution has not been considered in the calculation of the  $\text{Tb}(\text{OH})_3$  thermophysical functions.

$\text{Nd}(\text{OH})_3$ . The ground state of  $\text{Nd}(\text{OH})_3$  is a Kramers doublet, which implies the presence of a low-temperature  $\lambda$ -type anomaly with an associated entropy of  $(R \ln 2)$ . The fact that the first excited Stark level is more than  $120 \text{ cm}^{-1}$  above the ground state ensures that below 10 K only the cooperative magnetic and lattice contributions need be considered in the determination of the low-temperature enthalpy and entropy increments. As previously mentioned, heat-capacity measurements of this research were limited to temperatures above 11.4 K; however, these results are complemented by those of Meissner,<sup>(15)</sup> who measured the heat capacity of  $\text{Nd}(\text{OH})_3$  from 0.62 to

18 K. The curve chosen to join the two sets of results is shown in figure 2. Meissner was able to observe only the high-temperature 'tail' of the magnetic ordering transition; however, judging from  $(\partial C_p/\partial T)_p$  at 0.62 K (the lowest temperature attained) the transition maximum, clearly, is quite near. For the purpose of estimating the enthalpy increment below 10 K, a transition temperature of 0.6 K has been assumed.

Below 18 K, Meissner assumed the total heat capacity could be written in the form:

$$C_p(\text{total})/R = aT^3 + bT^{-2} + cT^{-3}. \quad (4)$$

Above 11 K the third term was assumed to be insignificant. For results between 11 and 18 K a plot of  $\{C_p(\text{total})/R\}T^2$  against  $T^5$  yielded the lattice coefficient  $a = (2.57 \pm 0.17) \times 10^{-5} \text{ K}^{-3}$ . The lattice contribution calculated using this value of  $a$  was subtracted from  $C_p(\text{total})$  between 1.5 and 10 K and the excess was designated the cooperative magnetic contribution,  $C_p(\text{mag})$ . A plot of  $\{C_p(\text{mag})/R\}T^2$  against  $1/T$  yielded a straight line and thus allowed determination of the magnetic coefficients  $b = (1.50 \pm 0.25) \text{ K}^2$  and  $c = (-1.25 \pm 0.40) \text{ K}^3$  in equation (4).

The total cooperative magnetic entropy and enthalpy contributions were estimated as  $(R \ln 2)$  and  $(0.6 \text{ K } R \ln 2)$ , respectively. Meissner's estimation of the lattice and magnetic coefficients enabled the entropy and enthalpy increments below 10 K for Nd(OH)<sub>3</sub> to be calculated in a manner analogous to that used for the Tb(OH)<sub>3</sub> low-temperature increments.

## RESOLUTION OF THE SCHOTTKY CONTRIBUTIONS

Excellent resolution of the Schottky contributions to the heat capacities of Pr(OH)<sub>3</sub><sup>(2)</sup> and Eu(OH)<sub>3</sub><sup>(1)</sup> has been achieved using a lattice approximation technique involving an interpolation between the lattice heat capacities of La(OH)<sub>3</sub> and Gd(OH)<sub>3</sub>. As discussed previously,<sup>(1)</sup> the relatively large variation in the lattice heat capacity of the lanthanide trihydroxides between the lanthanum and gadolinium homologs results in the resolved Schottky contributions for this series being particularly sensitive to the weighting of the interpolation used. Indeed, it has been determined that an adequate interpolation scheme for the lattice heat capacities of the lighter lanthanide trihydroxides can be formulated in terms of their molar volumes:

$$C_p\{\text{lattice, Ln(OH)}_3\} = (1-f)[C_p\{\text{La(OH)}_3\}] + f[C_p\{\text{Gd(OH)}_3^*\}]. \quad (5)$$

Here the superscript \* indicates that the cooperative magnetic contribution associated with the antiferromagnetic ordering of Gd(OH)<sub>3</sub> has been deleted, and  $f$  is the fractional increment in molar volume for the lanthanide trihydroxide in question compared with the volume increment between the La and Gd homologs. The value of  $f\{\text{Nd(OH)}_3\}$  and  $f\{\text{Tb(OH)}_3\}$  based upon the mean of the lattice parameters listed in table 1 are 0.55 and 1.12, respectively. [The Tb(OH)<sub>3</sub> lattice heat capacity is deduced by means of an extrapolation of the observed trend in the lattice heat capacity of the lighter members of the series.] The experimental heat capacities of La(OH)<sub>3</sub> and Gd(OH)<sub>3</sub> have been published previously.<sup>(1)</sup>

TABLE 4. Wavenumbers  $\sigma$  of  $\text{Tb}(\text{OH})_3$  and  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$  for  $J$ -State  ${}^7\text{F}_6$ <sup>a</sup>

$\mu$	$g$	$\sigma/\text{cm}^{-1}$	
		$\text{Tb}(\text{OH})_3$	$\text{Tb}^{3+}$ -doped $\text{Y}(\text{OH})_3$
0	1	0.0	0.0
0	1	0.0	0.0
1	2	118.2	111.1
2	2	206.0	196.0
0	1	224.4	202.7
1	2	233.7	213.1
3	1	(235.5) <sup>b</sup>	(220.4) <sup>b</sup>
2	2	252.3	237.0
3	1	(281.4) <sup>b</sup>	(267.3) <sup>b</sup>

<sup>a</sup> Reference 29. The next levels are at 2082.0 and 2065.9  $\text{cm}^{-1}$ .

<sup>b</sup> The wavenumbers in parentheses were calculated by the authors of reference 29.

$\text{Tb}(\text{OH})_3$ . The energies and degeneracies of the Stark levels arising from the four lowest-lying  $J$ -manifolds of  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$  and concentrated  $\text{Tb}(\text{OH})_3$  have been determined by Scott, Meissner, and Crosswhite.<sup>(29)</sup> They observed the Stark level energies of the  ${}^5\text{D}_4$   $J$ -manifold through absorption spectra at 4 K and then deduced the crystal-field splitting of the lower  $J$ -manifolds from fluorescent transitions originating from the  ${}^5\text{D}_4$  Stark levels at 77 K. The wavenumber levels of the  ${}^7\text{F}_6$  ground  $J$ -manifold of concentrated  $\text{Tb}(\text{OH})_3$  and  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$  are listed in table 4. The spectroscopic Schottky contributions calculated from these levels, plus the  ${}^7\text{F}_5$  levels, are shown in figure 3. The two  $\mu = 3$  singlets were not observed experimentally for either system; therefore, the calculated energies were

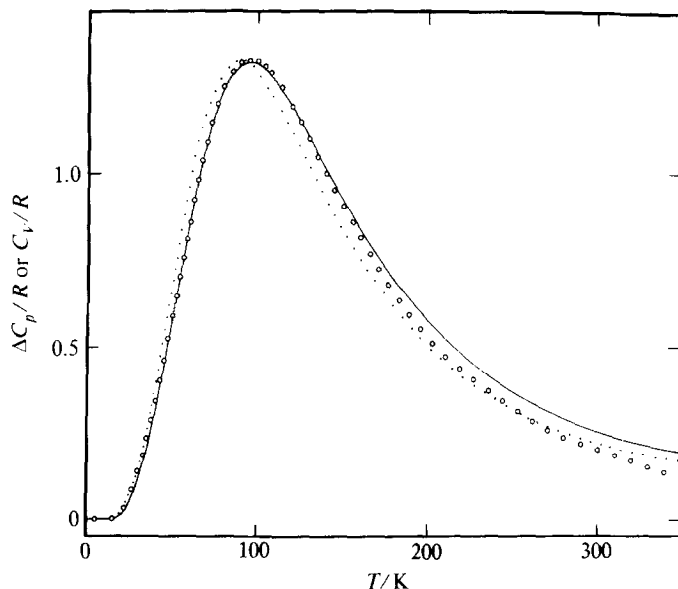


FIGURE 3. The Schottky contribution to the heat capacity of  $\text{Tb}(\text{OH})_3$ . —,  $\circ$ , represent the "spectroscopic" and "calorimetric" Schottky contributions, respectively. (See text for explanation.)  $\cdots$ , the Schottky contribution calculated from the  $\text{Tb}^{3+}$ -doped  $\text{Y}(\text{OH})_3$  energy levels.

used in the Schottky heat-capacity calculation. The error limits for the crystal-field parameters deduced by Scott *et al.* were used to estimate the uncertainty in the  $\mu = 3$  Stark level wavenumbers. The uncertainties deduced in this manner were found to be approximately  $\pm 6 \text{ cm}^{-1}$ . The effect of these uncertainties upon the calculation of the spectroscopic Schottky contribution is generally about  $0.005C_p/R$  and is, therefore, negligible.

Although the lattice parameters of Y(OH)<sub>3</sub> are significantly smaller than those of Tb(OH)<sub>3</sub>, the crystal-field splitting is clearly greater within the concentrated host. We know of no explanation for the relative intensity of these crystalline fields.

Deduction of the lattice contribution, derived using equation (2), from the heat capacity of Tb(OH)<sub>3</sub> results in the curve designated the "calorimetric" Schottky contribution in figure 3. (The cooperative magnetic contribution to the heat capacity of Tb(OH)<sub>3</sub> has been deleted using the formulae of Catanese *et al.*,<sup>(30)</sup> equation 2.)

The calorimetric Schottky contribution and the concentrated Tb(OH)<sub>3</sub> spectroscopic curve are in excellent agreement below 160 K, while at higher temperatures the calorimetric curve trends below the calculated contribution. Indeed, the calorimetric curve eventually intersects the Schottky contribution calculated from the Tb<sup>3+</sup>-doped Y(OH)<sub>3</sub> energy levels near 270 K and continues below it. Above 160 K the combined uncertainty in the  $\mu = 3$  Stark-level energies and the experimental heat capacities could at most account for approximately one third of the observed discrepancy between the calorimetric and concentrated Tb(OH)<sub>3</sub> spectroscopic curves. The observed difference, however, may be accounted for if the Stark levels are assumed to undergo a gradual (approximately 7 per cent) shift to lower energies between 77 and 350 K. A gradual shift of this magnitude may be postulated as being due to the decrease in the crystal-field intensity as the lattice expands with increasing temperature. Indeed, these proposed shifts are quite comparable to those observed by Levshin and Pirinchieva<sup>(4)</sup> for Er<sup>3+</sup>-doped Y<sub>2</sub>O<sub>3</sub> and by Johnson *et al.*<sup>(3)</sup> for Nd<sup>3+</sup>-doped LaF<sub>3</sub>.

Nd(OH)<sub>3</sub>. Although spectroscopic quantities necessary to evaluate fully the calorimetric Schottky heat capacity of Nd(OH)<sub>3</sub> are not known, some interesting comparisons with the results achieved for Tb(OH)<sub>3</sub> can be made. Deduction of the lattice contribution, derived using equation (2), from the experimental heat capacity of Nd(OH)<sub>3</sub> results in the curve designated the "calorimetric" Schottky contribution in figure 4. (The cooperative magnetic contribution to the heat capacity of Nd(OH)<sub>3</sub> has been deleted using the formulae of Meissner,<sup>(15)</sup> equation 4.) Also shown in figure 4 is the spectroscopic Schottky curve calculated from the energy levels of Nd<sup>3+</sup>-doped LaCl<sub>3</sub> crystals.<sup>(32)</sup> The maxima of the Schottky contributions for these two systems are within  $\approx 0.015C_p/R$ , while the stronger crystal field within the trihydroxide shifts the Nd(OH)<sub>3</sub> curve to higher temperatures. The observed Schottky contributions for these compounds are due almost entirely to thermal population of the Stark levels arising from the ground (<sup>4</sup>I<sub>9/2</sub>) J-manifold. The site symmetry of the Nd<sup>3+</sup> ion is C<sub>3h</sub> in both the trichloride and trihydroxide host lattices, therefore, it is anticipated that the relative energies of the <sup>4</sup>I<sub>9/2</sub> Stark levels will be quite similar for these systems. Indeed, it may be shown that if the energy levels arising from a single multi-degenerate system all undergo the same fractional shift in

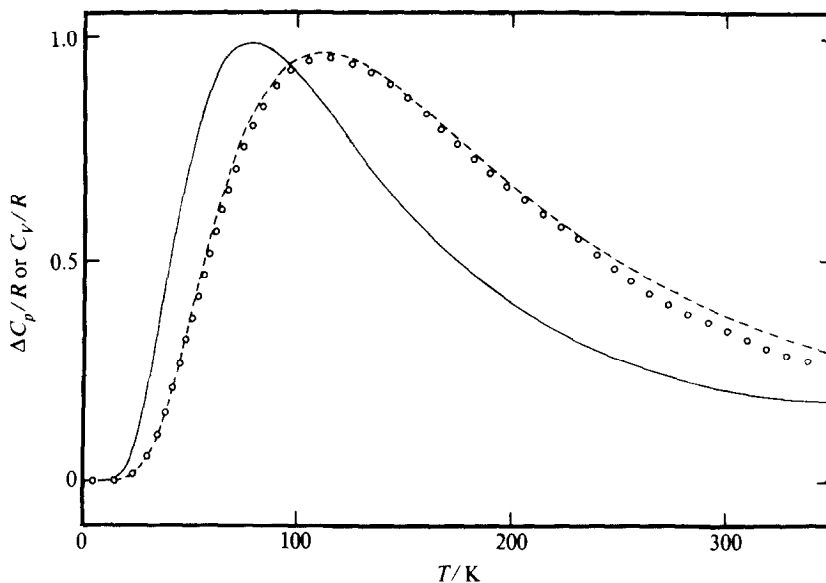


FIGURE 4. The Schottky contribution to the heat capacity of  $\text{Nd}(\text{OH})_3$ .  $\circ$ , The  $\text{Nd}(\text{OH})_3$  "calorimetric" Schottky contribution. ----, —, the Schottky contributions calculated from the calorimetrically deduced  $\text{Nd}(\text{OH})_3$  energy levels and those of  $\text{Nd}^{3+}$ -doped  $\text{LaCl}_3$ ,<sup>(32)</sup> respectively.

energy, the maximum of the derived Schottky heat capacity is unchanged. Moreover, the fractional shift in the energies is identical to the fractional shift in the temperature of the maximum of the derived Schottky heat capacity. Therefore, the fact that the  $\text{Nd}(\text{OH})_3$  calorimetric and  $\text{Nd}^{3+}$ -doped  $\text{LaCl}_3$  spectroscopic Schottky curves have nearly identical maxima (near 113 and 78 K, respectively) implies that the  $\text{Nd}(\text{OH})_3$   $^4\text{I}_{9/2}$  Stark level energies may be approximated by simply increasing the energies of the corresponding  $\text{Nd}^{3+}$ -doped  $\text{LaCl}_3$  Stark levels by a factor of about 1.45 (*i.e.*  $113/78 \approx 1.45$ ). Small adjustments of less than  $5 \text{ cm}^{-1}$  were made in the wavenumbers derived in this manner so as to optimize the agreement between the calorimetric Schottky heat capacity and that calculated from the estimated  $\text{Nd}(\text{OH})_3$  wavenumbers over the entire temperature range investigated. The estimated wavenumbers of the Stark levels arising from the  $^4\text{I}_{9/2}$   $J$ -state of  $\text{Nd}(\text{OH})_3$  are listed in table 5. An energy level extrapolation scheme such as this may be used only if the lanthanide ions of the compounds involved are located in sites of the same symmetry. Different site symmetries may lead to radically different splitting patterns (compare reference 3).

The energy levels estimated for  $\text{Nd}(\text{OH})_3$  were chosen so as to yield a derived Schottky contribution in reasonable agreement with that deduced calorimetrically over the entire temperature range studied. The results achieved for  $\text{Tb}(\text{OH})_3$  suggest that this may not be the proper approach. Indeed, it was observed that although a set of energy levels could be found which yielded a Schottky curve in excellent agreement with the calorimetric curve below about 150 K, the same set of energy levels at higher temperatures produced a Schottky contribution in excess of that determined calorimetrically, as would be anticipated due to the effect of thermal expansion of the

TABLE 5. Wavenumbers  $\sigma$  for Nd(OH)<sub>3</sub> ( $J = {}^4I_{9/2}$ )

$\sigma/\text{cm}^{-1} \text{ }^a$	$\sigma/\text{cm}^{-1} \text{ }^b, \text{ }^d$	$\sigma/\text{cm}^{-1} \text{ }^b, \text{ }^e$	$\sigma/\text{cm}^{-1} \text{ }^c, \text{ }^d$	$\sigma/\text{cm}^{-1} \text{ }^c, \text{ }^e$
365	340	358	340	336
355	320	356	330	323
175	203	235	188	195
165	178	214	173	186
0	0	0	0	0

<sup>a</sup> Calorimetrically deduced. <sup>b</sup> Calculated from Pr(OH)<sub>3</sub> CEF parameters. <sup>c</sup> Calculated from Eu(OH)<sub>3</sub> CEF parameters. <sup>d</sup> First-order perturbation calculations. <sup>e</sup> Calculations with  $J$ -mixing.

lattice. The fractional shift in the Stark level energies necessary to produce the observed trend in the Nd(OH)<sub>3</sub> calorimetric Schottky contribution is—like that found for Tb(OH)<sub>3</sub>—approximately 7 to 8 per cent between 10 and 350 K.

### CRYSTAL-FIELD CALCULATIONS

To obtain an independent estimate of the crystal-field splitting of the  ${}^4I_{9/2}$   $J$ -manifold of Nd(OH)<sub>3</sub>, crystal-field calculations using intermediate coupling were performed both with and without the  $J$ -mixing effect of the  ${}^4I_{11/2}$   $J$ -manifold.<sup>(33-35)</sup>

The Hamiltonian for a trivalent lanthanide ion at a site of C<sub>3h</sub> symmetry can be expressed as:

$$H = H_0 + (B_2^0 V_2^0 + B_4^0 V_4^0 + B_6^0 V_6^0 + B_6^6 V_6^6).$$

$H_0$  is the free-ion Hamiltonian and the crystal-field parameters  $B_2^0$ ,  $B_4^0$ ,  $B_6^0$ , and  $B_6^6$  are defined and normalized by the procedures of Stevens,<sup>(36)</sup> of Elliot and Stevens,<sup>(34)</sup> and of Judd.<sup>(34)</sup> First-order perturbation calculations with sets of crystal-field parameters deduced from spectroscopic measurements on Pr(OH)<sub>3</sub><sup>(2)</sup> and Eu(OH)<sub>3</sub><sup>(37)</sup> were performed. The wavenumbers obtained from these calculations, as well as those deduced calorimetrically, are listed in table 5. The  $J$ -mixing effect between the  ${}^4I_{9/2}$  and  ${}^4I_{11/2}$   $J$ -manifolds was then calculated using the general formulae for the interaction matrix elements tabulated by Elliot and Stevens<sup>(35)</sup> and by Judd.<sup>(34)</sup> The crystal-field parameters deduced for Pr(OH)<sub>3</sub> and Eu(OH)<sub>3</sub> were also used in the  $J$ -mixing calculations. The wavenumbers derived from these calculations are also listed in table 5. Although the calculations do not provide unequivocal corroboration of the calorimetrically deduced wavenumbers, the overall magnitude of the  ${}^4I_{9/2}$  crystal-field splitting (about 350 cm<sup>-1</sup>) is reproduced.

### 5. Conclusions

On the basis of a lattice heat-capacity contribution interpolated on the molar-volume variation between La(OH)<sub>3</sub> and Gd(OH)<sub>3</sub>, the Schottky contributions to the heat capacities of Tb(OH)<sub>3</sub> and Nd(OH)<sub>3</sub> are resolved. Below 160 K excellent agreement between the calorimetric and spectroscopic Schottky contributions for Tb(OH)<sub>3</sub> is observed. Above 160 K it is postulated that the observed discrepancy is due to a

reduction of  $\approx 7$  per cent in the  ${}^1F_6$  Stark splitting resulting from thermal expansion of the lattice between 77 and 350 K. In the absence of spectroscopic results for  $\text{Nd}(\text{OH})_3$ , the crystal-field splitting of the ground  ${}^4I_{9/2}$   $J$ -manifold was estimated calorimetrically and compared with that calculated from crystal-field parameters deduced spectroscopically for nearby trihydroxides. Although the uncertainties in the calculations are too great to allow precise calculation of the  $\text{Nd}(\text{OH})_3$  energy levels, corroboration of the overall magnitude of the crystal-field splitting of the  ${}^4I_{9/2}$   $J$ -manifold deduced calorimetrically is obtained.

The heat-capacity measurements of this research, in conjunction with the low-temperature heat-capacity and magnetic measurements of Catanese *et al.* and of Meissner, allow calculation of thermophysical functions for  $\text{Tb}(\text{OH})_3$  and  $\text{Nd}(\text{OH})_3$ .

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