

Thermodynamics of the lanthanide halides

I. Heat capacities and Schottky anomalies of LaCl_3 , PrCl_3 , and NdCl_3 from 5 to 350 K^a

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The heat capacities of LaCl_3 , PrCl_3 , and NdCl_3 have been measured from 5 to 350 K by adiabatic calorimetry. No co-operative thermal anomalies were seen in the temperature range investigated but substantial magnetic heat-capacity contributions of the non-co-operative (Schottky) type were found. Subtraction of the heat capacity of the diamagnetic and isostructural LaCl_3 from those of the paramagnetic members yields experimental Schottky heat-capacity contributions which are compared with heat capacities derived from spectroscopically determined energy levels. Small discrepancies between the calculated and experimental contributions are probably due to differences in lattice heat capacities between LaCl_3 and the others. The values of $\{(S^\circ(298.15 \text{ K}) - S^\circ(0))\}/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ are for LaCl_3 and NdCl_3 , 32.88 and 36.67. Due to the possibility of a low-temperature phase transition, the entropy of PrCl_3 covers only the experimental range of this research and that of Colwell, Mangum, and Utton. $\{S^\circ(298.15 \text{ K}) - S^\circ(0.294 \text{ K})\}$ for PrCl_3 is 36.64 $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$.

1. Introduction

Although insufficient thermophysical data exist on any of the lanthanide(III) halides to permit calculation of the thermodynamic properties, the trichlorides are of special interest because abundant spectroscopic and other studies facilitate correlation and interpretation. The lighter, UCl_3 -type⁽¹⁾ hexagonal isostructural trichlorides (LaCl_3 through GdCl_3) have lanthanide ions with C_{3h} point symmetry. This paper reports heat capacities of diamagnetic LaCl_3 , and of paramagnetic PrCl_3 and NdCl_3 ; a subsequent paper⁽²⁾ treats SmCl_3 , EuCl_3 , and GdCl_3 .

The electronic states of these ions can be designated after Hund as $(2S+1)L_J$ ($J = L - S$) for the $4f^n$ configurations ($n = 1$ through 7). The $(2J+1)$ -fold degeneracies of the multiplets characterized by J are removed by the crystalline electric field of the chloride ions (Stark effect); the resulting crystal-field levels are around 100 cm^{-1} and thus provide important Schottky contributions⁽³⁾ over the range, 5 to 350 K, of the present measurements.

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The differences between the heat capacities of diamagnetic LaCl_3 and those of PrCl_3 and NdCl_3 can be expressed in terms of the calculated Schottky contributions of the latter evaluated from the spectroscopic energy levels of Dieke.⁽⁴⁾ Moreover, PrCl_3 and NdCl_3 , characterized by cooperative magnetic ordering below 5 K, were studied⁽⁵⁾ and the major part of the expected cooperative entropy was accounted for by Colwell and Mangum.⁽⁶⁾ Spectroscopic data exist which delineate each of these important contributions to the total heat capacities for the paramagnetic members, *i.e.* cooperative-magnetic, non-cooperative-magnetic (Schottky), and lattice heat capacities. The resolution of the magnetic contribution into cooperative and non-cooperative parts (which is seldom successful) is simplified for these salts by the fact that cooperative-magnetic ordering occurs at very low temperatures and involves only the lowest doublet of the crystal-field levels; relatively large energies separate the higher levels. Thus, the cooperative phenomena are between ions in the ground crystalline state.

Indicative of the inferences which can be made from optical spectroscopy alone are studies related to the magnetic ordering reported by Prinz^(7,8) for NdCl_3 . These led to the interpretation⁽⁹⁾ of the magnetic-ordering process in terms of a linear Ising chain involving the antiferromagnetic ordering of spins along the crystal *c*-axis. The elucidation of the optical spectrum of Pr(III) and Nd(III) in LaCl_3 , summarized by Dieke⁽⁴⁾ provides the information necessary for evaluation of the Schottky heat capacities over the entire temperature range. This is the focal point of the present study which endeavors to account for the major differences between the heat capacities of PrCl_3 and NdCl_3 and that of LaCl_3 .

Although the lattice heat capacity may not be evaluated unambiguously, substantial information bears upon this feature. The enumeration of the $k = 0$ lattice vibrations by Murphy, Caspers, and Buchanan⁽¹⁰⁾ provides a framework for i.r.⁽¹¹⁻¹³⁾ and Raman studies⁽¹⁴⁻²¹⁾ of lattice-vibrational frequencies. In addition, studies of the vibronic spectra of Pr(III) in LaCl_3 and PrCl_3 ,⁽²²⁾ and of Pr(III) and Nd(III) in NdCl_3 ,⁽²³⁾ and of Pr(III) in LaCl_3 , PrCl_3 , and GdCl_3 ,⁽²⁴⁾ give information on the lattice-vibrational frequencies. These vibronic studies also strengthen the identification of portions of the lattice heat capacities as sums of Einstein functions for the frequencies.

2. Experimental

PREPARATION AND CHARACTERIZATION OF SAMPLES

Samples were prepared in this laboratory to insure proper treatment, detailed knowledge of sample history, and minimum elapsed time from preparation to measurement. Reportedly 99.99 mass per cent pure La_2O_3 and Pr_6O_{11} , 99.9 mass per cent pure Nd_2O_3 , reagent-grade hydrochloric acid and ammonium chloride were reactants in a Carter-and-Taylor-type process⁽²⁵⁾ modified to minimize oxychloride formation. Oxide corresponding to 0.1 mol of Ln(III) was dissolved in 50 cm³ of concentrated hydrochloric acid. Although most of the oxide dissolved quickly, the solution was warmed to 343 K and stirred until all of the oxide dissolved. Then a 50 cm³ portion of 6 mol dm⁻³ HCl(aq) was added, followed by 0.75 mol of NH_4Cl

[7.5 mol of NH_4Cl per mol of Ln(III)]. The mixture was heated with stirring and addition of another 30 cm^3 of concentrated hydrochloric acid until all the ammonium chloride dissolved. This solution was evaporated carefully on a hot-plate with constant stirring over a period of 1 h. To hasten the evaporation, a stream of nitrogen was directed over the mixture. In view of the extensive loss of water occurring at the fairly low temperatures, extreme caution was taken in the latter stages of this evaporation to keep the temperature of the ever-thickening slurry below 363 K. The Carter and Taylor procedure in which the evaporated mixture was heated to 473 K in air was omitted. After the break-seal tip of the evacuation cell was plugged with a small wad of platinum foil the moist solid was placed in the inner chamber of the cell and the cell mounted on the vacuum line. The system was evacuated and the heating process begun. The sample was gradually heated to 473 K over 4.5 h, and the temperature was maintained for 1 h, although most of the water was removed at lower temperatures. The temperature was now raised to 700 K over about 7 h, during which time the ammonium chloride sublimed off leaving the trichloride as a polycrystalline material. A brief cooling period was allowed to check for the presence of residual ammonium chloride in the sample (indicated by the appearance of a condensate on the side of the reaction cell). Once the absence of ammonium chloride was ascertained, the cell was allowed to cool to 300 K, sealed off, and removed to the dry box. This procedure, with care taken to insure uniformity, was used for the preparation of all batches. Once the success of the preparative steps was confirmed for a trial batch by chemical and crystallographic methods, the final four batches for the calorimetric samples were prepared and crystallographically checked to verify the absence of ammonium chloride, LnOCl , and hydrated phases.

The salts are very hygroscopic, readily forming hydrates upon exposure to air. Heptahydrates are attributed to the trichlorides of La, Ce, and Pr; the remaining members form hexahydrates.⁽²⁶⁾ Samples left in air deliquesced quickly. Hence the samples were handled in a nitrogen-filled dry box.

Chemical analyses were used to determine both chlorine and metal content. The former was accomplished gravimetrically by precipitation of the chloride with silver nitrate solution. Sodium chloride samples were determined as blanks with each analysis. Since ignition of the trichloride in air at 1270 K gave a phase approximating LnOCl , a procedure was designed to overcome this difficulty by removal of the chloride with silver nitrate, precipitation of any excess Ag^+ ion with ammonium bromide, and evaporation and ignition in air of the residue, now composed of the less stable bromide and nitrate salts. Although adequate, this method was extremely inconvenient, involving several filtration and transfer steps and evaporations which could not be reliably accomplished with the aid of heating or vacuum aspiration due to the risk of splattering. It was applied only to the analysis of NdCl_3 , the first sample prepared. A system of hydrolysis at elevated temperatures was devised and proved to be much more convenient and reliable. Samples of the trichloride were placed in platinum boats and allowed to stand in air but not to deliquesce, since heating of deliquescent samples led to splattering and loss of material. Boats were supported on ceramic chips in a long tube of vitreous silica which was placed in a muffle furnace. Nitrogen gas was bubbled through a flask of heated water and the saturated gas passed

through the tube. The furnace was heated to 1270 K over 4 h, maintained at or above this temperature for 2 h, and then cooled. The samples, converted quantitatively to the oxide, were weighed and then tested for the presence of chloride with silver nitrate. The analytical results are shown in table 1. The uncertainties indicated are twice the standard deviation of the mean.

TABLE 1. Analysis of the lanthanide trichloride samples; w denotes mass fraction^a and n amount of substance

Compound	Cl		Ln		$10^2 \Sigma w$	$n(\text{Cl})/n(\text{Ln})$
	obs.	calc. ^b	obs.	calc. ^b		
LaCl ₃	43.39 ± 0.08	43.36	56.66 ± 0.02	56.63	100.05 ± 0.08	3.000 ± 0.005
PrCl ₃	43.02 ± 0.10	43.01	56.99 ± 0.08	56.99	100.01 ± 0.14	3.000 ± 0.006
NdCl ₃	42.42 ± 0.14	42.44	57.57 ± 0.04	57.56	99.99 ± 0.14	2.998 ± 0.010

^a The uncertainties are two standard deviations.

^b Based on 1971 IUPAC atomic weights.

TABLE 2. Lattice parameters of the lanthanide trichlorides

	LaCl ₃		PrCl ₃		NdCl ₃	
	a_0/nm	c_0/nm	a_0/nm	c_0/nm	a_0/nm	c_0/nm
Zachariasen ^a	0.7468 ± 0.0003	0.4366 ± 0.0003	0.741 ± 0.001	0.425 ± 0.001	0.7381 ± 0.0004	0.4231 ± 0.0003
Others	0.74779 ^b	0.43745 ^b	0.7422 ± 0.0005 ^c	0.4275 ± 0.0004 ^c	0.73988 ^b	0.42423 ^b
ASTM File ^d	0.7483	0.4364	0.7423	0.4272	0.7400	0.4240
This work	0.7484 ± 0.0004	0.4375 ± 0.0002	0.7410 ± 0.0006	0.4276 ± 0.0003	0.7398 ± 0.0004	0.4246 ± 0.0003
$\rho/\text{g cm}^{-3}$	3.863		4.063		4.169	

^a References 1 and 27.

^b Reference 28.

^c Reference 29.

^d Reference 30; ASTM File card numbers: LaCl₃, 12-605; PrCl₃, 12-787; NdCl₃, 12-785.

In addition to the crystal-structure studies of Zachariasen,^(1,27) those of Templeton and Dauben,⁽²⁸⁾ Morosin,⁽²⁹⁾ and the ASTM file⁽³⁰⁾ list lattice parameters of several of the light lanthanide trichlorides. These results are given in table 2 together with those obtained from the Guinier-Hagg powder pattern using Cu K α_1 radiation ($\lambda = 0.154051$ nm) which were corrected for film shrinkage by reference to a silicon internal standard. The measured $\sin^2 \theta$ values were least-squares fitted by computer to give the lattice parameters tabulated and their uncertainties.

HEAT-CAPACITY MEASUREMENTS

Heat-capacity measurements were made in the range 5 to 350 K in the Mark II adiabatic cryostat.⁽³¹⁾ Each sample was loaded into the calorimeter and its heat

capacity determined before the next sample was prepared. The calorimeter (laboratory designation W-28) had an internal volume of 92 cm³ and a mass of 61 g. It was of gold-plated copper closed by a cap sealed on to a monel metal neck by a known mass of low-melting (393 K) Cerroseal solder. Once the cap was sealed on to the filled calorimeter, the nitrogen atmosphere from the dry box was evacuated through a small hole atop a thin-walled monel tube on the calorimeter top. A small pressure of helium gas was then admitted and the hole sealed off with Cerroseal solder. This helium gas, together with vertical copper vanes within the calorimeter, enhanced the attainment of thermal equilibrium. Loading data for the compounds are shown in table 3. Buoyancy corrections are based upon the calculated crystallographic densities listed in table 2.

TABLE 3. Calorimeter loading data: m denotes mass of sample, M molar mass,^a and p pressure of helium

Compound	m/g	$M/g\ mol^{-1}$	p/kPa
LaCl ₃	74.5391	245.264	7.9
PrCl ₃	62.7227	247.267	6.6
NdCl ₃	88.8150	250.60	8.9

^a Based on 1971 IUPAC atomic weights.

A capsule-type platinum resistance thermometer (laboratory designation A-5) was inserted within a sleeve with a non-inductively wound calorimeter heater and this thermometer + heater assembly was mounted within an entrant well in the calorimeter. A small measured amount of Apiezon-T grease established thermal contact. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S.) according to the IPTS-48 (as textually revised in 1960)⁽³²⁾ for the temperature range above 90.2 K, according to the N.B.S. provisional scale from 10 to 90 K, and according to a provisional scale of Carlson⁽³³⁾ 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.

3. Results

THERMODYNAMIC FUNCTIONS

No cooperative thermal phenomena were encountered despite substantial magnetic heat-capacity contributions present in these compounds. The only apparent manifestation of non-cooperative effects was a slight increase in the period required to reach a constant quasi-adiabatic drift following energy inputs in the temperature regions of the Schottky maxima.

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 and of Cerroseal solder relative to the calorimeter

as run empty. The calorimeter and heater + thermometer assembly represented about 30 to 50 per cent of the total measured heat capacity. Curvature corrections were applied to obtain true heat capacities $C_p = \lim_{\Delta T \rightarrow 0} (\Delta H / \Delta T)$ from $\Delta H / \Delta T$ measured for finite increments of temperature.

The heat capacities are listed in chronological sequence in table 4 so that the ΔT 's employed usually can be estimated from adjacent mean temperatures. These results are depicted in figure 1. Those points indicated in table 4 as having been omitted from the curve-fitting process represent values deviating from the curve

TABLE 4. Experimental heat capacities of LaCl_3 , PrCl_3 , and NdCl_3
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Lanthanum trichloride							
Series I		Series II		63.18	9.450	13.03	0.332
98.56	15.26	230.42	22.30	68.63	10.53	14.30	0.440
107.11	16.23	240.21	22.51	74.68	11.64	15.63	0.565
116.22	17.14	249.92	22.68	81.31	12.82	17.06	0.692
126.18	18.02	259.73	22.83	88.50	13.98	18.58	0.839
136.44	18.78	269.64	23.01	96.28	14.98	20.16	1.008
146.34	19.39	279.71	23.20	104.09	15.89	22.03	1.232
155.96	19.90	289.95	23.29			24.36	1.550
165.35	20.34	300.11	23.48			26.85	1.920
174.96	20.74	310.21	23.58	Series IV		29.64	2.379
185.09	21.10	320.28	23.61	5.63	0.017	33.10	3.005
195.38	21.41	330.29	23.76	6.18	0.024	36.78	3.723
205.53	21.68	340.28	23.81	6.87	0.039	40.44	4.486
215.56	21.95	347.26	23.79 ^a	7.53	0.054	44.74	4.978
225.49	22.19			8.30	0.083	45.54	5.589
235.33	22.39			9.24	0.064 ^b	50.18	6.611
		Series III		10.05	0.153	54.38	7.530
		54.64	7.602	10.78	0.193	58.96	8.541
		58.56	8.458	11.83	0.248		
Praseodymium trichloride							
Series I		Series II		72.40	12.40	20.42	1.623
84.84	14.53	235.83	22.70	79.73	13.67	22.27	1.889
92.44	15.55	246.07	22.93	87.97	14.96	24.41	2.225
100.95	16.51	256.63	23.06			26.77	2.637
110.00	17.41	267.11	23.21	Series IV		29.26	3.039 ^b
119.57	18.26	277.54	23.34	5.52	0.046	31.96	3.654
129.36	19.01	287.90	23.52	6.33	0.085	35.40	4.379
139.04	19.62	298.21	23.65	6.88	0.109	39.74	5.378
148.81	20.16	308.45	23.76	7.59	0.180	44.56	6.487
158.70	20.61	318.66	23.92	8.53	0.268	50.08	7.770
168.87	21.03	328.88	24.00	9.43	0.399	55.64	9.013
179.12	21.37	339.06	24.02	10.39	0.459		
189.21	21.67	346.13	24.05	11.49	0.565		
199.16	21.92			12.75	0.704	Series V	
209.25	22.17			14.10	0.865	5.44	0.046
219.47	22.41	Series III		15.54	1.037	6.08	0.071
229.60	22.59	54.39	8.755	17.10	1.216	6.88	0.105
239.64	22.78	59.77	9.944	18.74	1.411	7.58	0.200
		65.80	11.20			8.18	0.212

TABLE 4—continued

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Praseodymium trichloride (cont.)							
Series V (cont.)		14.16	0.875	25.19	2.359	46.50	6.947
9.05	0.322	15.62	1.049	27.71	2.808	51.45	8.086
9.90	0.417	17.21	1.229	30.70	3.392		
10.83	0.523	18.89	1.428	34.16	4.127		
11.75	0.592	20.75	1.669	38.00	4.978	63.66	10.82 ^b
12.82	0.710	22.88	1.979	42.14	5.924	70.36	12.01
Neodymium trichloride							
Series I		Series III		105.42	17.56	14.98	0.491
127.37	19.43	276.16	23.47			16.61	0.624
134.72	19.88	286.18	23.60		Series V	18.50	0.818
143.19	20.37	296.17	23.69	71.61	12.67	20.63	1.068
152.84	20.83	306.13	23.80	77.66	13.79	22.92	1.396
162.90	21.23	316.06	23.89	84.32	14.97	25.51	1.830
172.78	21.58	325.94	24.01	91.76	16.04	28.42	2.378
182.51	21.86	333.97	24.08	100.24	17.03	31.55	3.044
192.34	22.11	340.16	24.10	109.69	18.00	34.88	3.817
202.29	22.34	345.11	24.14	119.42	18.85	38.38	4.684
212.59	22.54	348.81	24.16	129.20	19.56	42.29	5.683
223.24	22.75			138.88	20.15	46.55	6.850
233.80	22.93	Series IV		148.27	20.63	51.50	8.059
244.28	23.10	58.92	9.877			57.22	9.486
254.70	23.19	62.14	10.68		Series VI	63.23	10.89
		65.83	11.52	5.31	0.025	69.80	12.31
		69.63	12.28	6.18	0.046	77.45	13.77
Series II		73.48	13.02	6.75	0.058		
219.76	22.69	77.32	13.74	7.51	0.072		
230.30	22.86	81.39	14.47	8.42	0.096	74.08	13.14
240.76	23.05	85.54	15.18	9.20	0.124	81.06	14.41
251.14	23.18	89.51	15.75	10.07	0.162	88.99	15.68
261.47	23.30	93.34	16.22	11.12	0.207	98.30	16.82
271.73	23.44	97.08	16.66	12.30	0.290		
281.95	23.56	101.02	17.10	13.60	0.377		
292.11	23.71						

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

^b These points were given lesser weight in the curve-fitting process.

determined by adjacent points. In all cases these were either not confirmed by replicated measurements or were the last point below the upper limit of measurement (350 K).

The curve-fitting process involved computer regression of the measured heat capacities to a power series of orthogonal polynomials in reduced temperature as described by Justice.⁽³⁴⁾ The power series was integrated appropriately to produce the derived thermodynamic functions at rounded temperature intervals. These functions, listed in table 5, do not include contributions from nuclear spin or isotopic mixing and are thus suitable for use in ordinary thermochemical calculations.

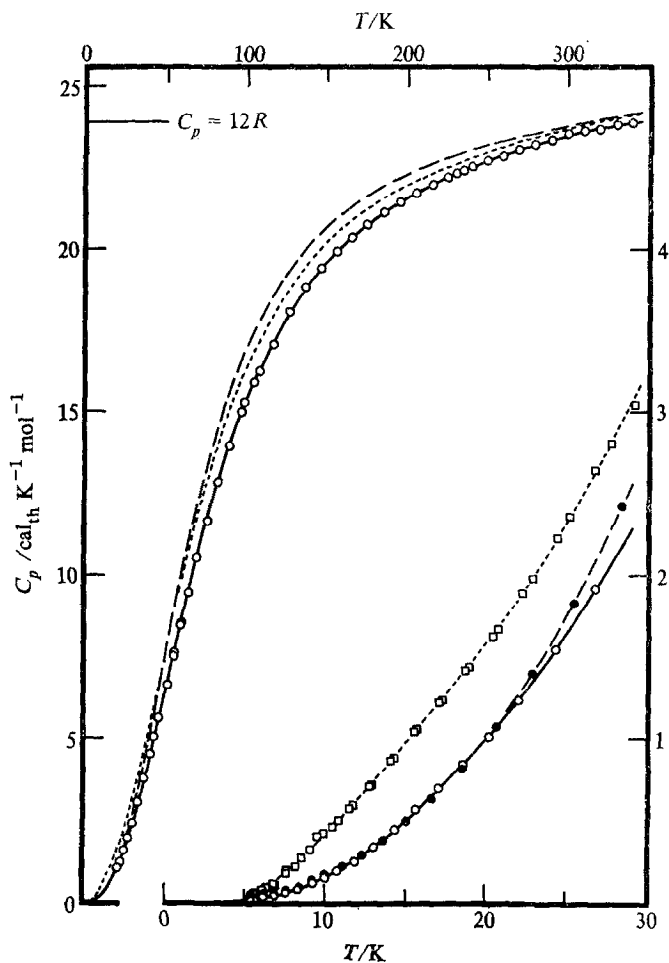


FIGURE 1. Experimental heat capacity curves. \circ , LaCl_3 ; \square , PrCl_3 ; \bullet , NdCl_3 .

LANTHANUM TRICHLORIDE

While the 1S_0 ground state of La(III) implies the absence of magnetic contributions to the thermodynamic functions, PrCl_3 and NdCl_3 will have contributions from the ground-state doublet amounting to about $R \ln 2$ below the temperature range of this investigation. Fortunately, the heat-capacity studies of Colwell and Mangum⁽⁶⁾ and Colwell, Mangum, and Utton⁽³⁵⁾ account for most of this entropy. Extrapolation by the Debye T^3 -dependence of the heat capacity below 5 K was used for LaCl_3 . Varsanyi and Maita⁽³⁶⁾ and Landau, Doran, and Keen⁽³⁷⁾ report Θ_D values of (149.5 ± 1.5) K and (155.2 ± 1.3) K for LaCl_3 . These values, adjusted by the factor $Z^{-1/3}$ ($Z = 2$ for the UCl_3 -type structure) to make them appropriate to LnCl_3 ,⁽³⁸⁾ become (118.7 ± 1.0) K and (123.3 ± 1.0) K and are in good agreement with that from this study, (119 ± 8) K.

TABLE 5. Thermodynamic functions of LaCl_3 , PrCl_3 , and NdCl_3
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T K	C_p $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$S^\circ(T) - S^\circ(0)$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$H^\circ(T) - H^\circ(0)$ $\text{cal}_{\text{th}} \text{mol}^{-1}$	$-\{G^\circ(T) - H^\circ(0)\}/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
Lanthanum trichloride				
5	0.011	(0.005)	(0.017)	(0.001)
10	0.150	0.042	0.326	0.010
15	0.496	0.163	1.866	0.038
20	0.996	0.370	5.538	0.094
25	1.640	0.659	12.066	0.177
30	2.438	1.026	22.199	0.286
35	3.371	1.471	36.675	0.423
40	4.395	1.987	56.06	0.586
45	5.469	2.566	80.71	0.773
50	6.571	3.199	110.80	0.984
60	8.767	4.593	187.57	1.467
70	10.795	6.100	285.57	2.020
80	12.584	7.661	402.67	2.627
90	14.123	9.234	536.4	3.274
100	15.43	10.792	684.4	3.948
110	16.55	12.317	844.4	4.640
120	17.50	13.798	1014.8	5.342
130	18.31	15.23	1193.9	6.048
140	19.00	16.61	1380.5	6.753
150	19.59	17.95	1573.5	7.455
160	20.10	19.23	1772.1	8.151
170	20.54	20.46	1975.3	8.839
180	20.92	21.64	2182.7	9.518
190	21.25	22.78	2393.6	10.186
200	21.55	23.88	2607.6	10.844
210	21.81	24.94	2824.5	11.490
220	22.06	25.96	3043.8	12.125
230	22.28	26.95	3265.5	12.748
240	22.49	27.90	3489.4	13.359
250	22.68	28.82	3715.2	13.959
260	22.86	29.71	3943.0	14.548
270	23.03	30.58	4172.4	15.13
280	23.18	31.42	4403.5	15.69
290	23.32	32.24	4636.0	16.25
300	23.45	33.03	4869.9	16.80
310	23.56	33.80	5105	17.33
320	23.66	34.55	5341	17.86
330	23.74	35.28	5578	18.38
340	23.81	35.99	5816	18.88
350	23.87	36.68	6054	19.38
273.15	23.08	30.85	4245.1	15.31
298.15	23.43	32.88	4826.5	16.70

TABLE 5—continued

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	$S^\circ(T) - S^\circ(0)$ cal _{th} K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(0)$ cal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
Praseodymium trichloride ^b				
5	(0.109)	(1.180) ^a	(1.368) ^a	(0.906) ^a
10	0.421	1.313	2.405	1.073
15	0.972	1.583	5.822	1.195
20	1.566	1.943	12.155	1.335
25	2.328	2.371	21.806	1.498
30	3.251	2.874	35.681	1.685
35	4.309	3.454	54.55	1.895
40	5.432	4.102	78.88	2.130
45	6.588	4.808	108.92	2.388
50	7.746	5.562	144.76	2.667
60	9.980	7.175	233.53	3.282
70	11.996	8.868	343.63	3.959
80	13.736	10.586	472.52	4.680
90	15.20	12.291	617.4	5.431
100	16.42	13.958	775.8	6.201
110	17.45	15.57	945.3	6.980
120	18.31	17.13	1124.2	7.761
130	19.05	18.62	1311.1	8.539
140	19.67	20.06	1504.7	9.311
150	20.21	21.44	1704.2	10.074
160	20.67	22.76	1908.7	10.826
170	21.06	24.02	2117.4	11.565
180	21.40	25.23	2329.7	12.291
190	21.69	26.40	2545.2	13.003
200	21.95	27.52	2763.5	13.701
210	22.19	28.60	2984.2	14.385
220	22.40	29.63	3207.2	15.05
230	22.60	30.63	3432.2	15.71
240	22.78	31.60	3659.2	16.35
250	22.95	32.53	3887.8	16.98
260	23.10	33.43	3118.1	17.60
270	23.25	34.31	4349.8	18.20
280	23.39	35.16	4583.0	18.79
290	23.54	35.98	3817.7	19.37
300	23.67	36.78	5054	19.94
310	23.80	37.56	5291	20.49
320	23.89	38.32	5530	21.04
330	23.97	39.05	5769	21.57
340	24.02	39.77	6009	22.10
350	24.09	40.47	6249	22.61
273.15	23.29	34.58	4423.1	18.39
298.15	23.65	36.64	5010	19.83

TABLE 5—continued

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{S^\circ(T) - S^\circ(0)}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{H^\circ(T) - H^\circ(0)}{\text{cal}_{\text{th}} \text{mol}^{-1}}$	$\frac{-\{G^\circ(T) - H^\circ(0)\}/T}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Neodymium trichloride				
5	0.041	(1.335) ^a	(1.060) ^a	(1.123) ^a
10	0.161	1.390	1.460	1.244
15	0.489	1.512	3.021	1.311
20	0.989	1.716	6.625	1.385
25	1.737	2.012	13.328	1.479
30	2.713	2.412	24.376	1.600
35	3.840	2.913	40.704	1.750
40	5.094	3.507	62.98	1.932
45	6.429	4.183	91.78	2.144
50	7.714	4.928	127.17	2.385
60	10.146	6.552	216.63	2.942
70	12.351	8.285	329.34	3.580
80	14.238	10.062	462.58	4.279
90	15.78	11.831	612.9	5.020
100	17.02	13.560	777.2	5.788
110	18.03	15.23	952.6	6.571
120	18.87	16.84	1137.2	7.360
130	19.59	18.38	1329.6	8.149
140	20.20	19.85	1528.7	8.933
150	20.71	21.26	1733.3	9.708
160	21.13	22.61	1942.6	10.473
170	21.48	23.91	2155.7	11.225
180	21.78	25.14	2372.1	11.964
190	22.05	26.33	2591.3	12.689
200	22.29	27.46	2812.9	13.400
210	22.50	28.56	3036.9	14.096
220	22.70	29.61	3262.9	14.777
230	22.87	30.62	3490.8	15.44
240	23.02	31.60	3720.2	16.10
250	23.16	32.54	3951.1	16.74
260	23.29	33.45	4183.3	17.36
270	23.41	34.33	4416.8	17.97
280	23.53	35.19	4651.5	18.57
290	23.64	36.01	4887.4	19.16
300	23.73	36.82	5124	19.74
310	23.84	37.60	5362	20.30
320	23.95	38.35	5601	20.85
330	24.04	39.09	5841	21.39
340	24.11	39.81	6082	21.92
350	24.17	40.51	6323	22.45
273.15	23.45	34.60	4491	18.16
298.15	23.72	36.67	5080	19.63

^a Based on data of Colwell, Mangum, and Utton.⁽³⁵⁾^b Values for PrCl₃ are referred to $T = 0.294$ K rather than to $T = 0$ (see text).

PRASEODYMIUM TRICHLORIDE

The temperature range 0.29 to 4 K was covered in the study of Colwell, Mangum, and Utton.⁽³⁵⁾ No impurity effects are noted, but an appreciable difference in the heat capacities for the two samples investigated (called 5N's and 3N's by these authors) exists. They favor the 5N's data, so these have been used in the present evaluation. Natural Pr is essentially all ¹⁴¹Pr and there is a substantial nuclear contribution to the entropy. Holley, Huber, and Baker,⁽³⁹⁾ in their review of the thermodynamic properties of the lanthanide metals and oxides, note that such nuclear contributions usually have been omitted (or subtracted if they were large). They specifically cite experimental results on Pr metal which show that the nuclear entropy is negligible above 2 K and that the thermodynamic functions do not include nuclear contributions below 2 K. We also omit the contribution in the corresponding trihalide. The functions reported for the metals in this review are those listed in N.B.S. T.N. 270-7,⁽⁴⁰⁾ which are used also in the calculations of the present investigation. The possibility of a very low-temperature phase transition in this salt, raised in the experiments of Hessler and Carlson,⁽⁴¹⁾ is a serious deterrent to the specification of the low-temperature increments, at least along lines identical to those applied to Kramers' salts. Although such a lattice distortion would evidently be a subtle one, the effect on the entropy is not unambiguously predictable. The measured entropy is about 0.2 cal_{th} K⁻¹ mol⁻¹ less than $R \ln 2$.† The tabulation of the thermodynamic functions is constrained to the measured heat capacity only and is referred to 0.294 K.

Re-evaluation of the results from 0.294 to 4 K gives a value for $\{S^\circ(4 \text{ K}) - S^\circ(0.294 \text{ K})\}$ of 1.196 cal_{th} K⁻¹ mol⁻¹, which is only about 0.6 per cent (0.007 cal_{th} K⁻¹ mol⁻¹) higher than that of Colwell *et al.*⁽³⁵⁾ The nuclear entropy was

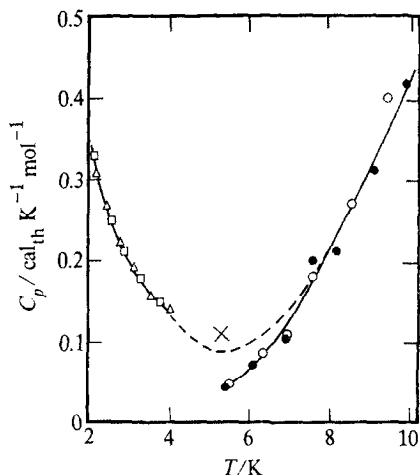


FIGURE 2. Low-temperature heat capacity of PrCl₃. This research: ○, Series IV; ●, Series V; Δ, □, reference 35; ----, selected heat-capacity curve.

† Throughout this paper cal_{th} = 4.184 J.

re-calculated and was found to be identical with the value of those authors, $0.042 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. Enthalpy contributions were found directly from the results and were corrected for nuclear contributions. The increments over the temperature range 4 to 8 K were found from a large plot similar to figure 2. The values of the present investigation below about 7 K are somewhat lower than those of Colwell *et al.*,⁽³⁵⁾ and than the calculations and the findings of Varsanyi and Maita.⁽³⁶⁾ These sources are in good agreement over this range; the second of these incorporates the lattice, Schottky, and high-temperature cooperative contributions; the third source reports a minimum in the heat capacity with a value of $0.11 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at about 5 K. A "broad" curve including all reasonable possibilities results in an entropy spread of only $0.020 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. The chosen curve is consistent with the statement of Varsanyi and Maita that "The specific heat of PrCl_3 has a minimum value of $1100 \cdot 10^{-4} \text{ cal deg}^{-1} \text{ mol}^{-1}$ around 5 K. . .". Summaries of the entropy and enthalpy increments are given in table 6.

TABLE 6. Low-temperature entropy and enthalpy increments for PrCl_3 and NdCl_3
($\text{cal}_{\text{th}} = 4.184 \text{ J}$)

T_1 K	T_2 K	$S^\circ(T_2) - S^\circ(T_1)$ $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$H^\circ(T_2) - H^\circ(T_1)$ $\text{cal}_{\text{th}} \text{ mol}^{-1}$	Source
Praseodymium trichloride				
0	0.294	—	—	<i>a</i>
0.294	4	1.196	1.274	<i>b</i>
0.294	4	- 0.042	- 0.024	<i>c</i>
4	5	0.026	0.118	<i>d</i>
5	8	0.063	0.400	<i>d</i>
8	298.15	35.41	5008	<i>e</i>
0.294	298.15	36.64	5010	Σ
Neodymium trichloride				
0	0.298	0.236	0.063	<i>f</i>
0.298	4	1.09	0.953	<i>g</i>
4	5	0.010	0.044	<i>b</i>
5	7	0.024	0.098	<i>d</i>
7	298.15	35.31	5079	<i>d</i>
0	298.15	36.67	5080	Σ

^a Not specified due to possibility of low-temperature transition, see reference 41.

^b From reference 35.

^c Nuclear contribution, model used in reference 35; data of reference 49.

^d Graphical evaluation of selected curve.

^e Integration of fitted curve through values of this investigation.

^f Calculation, two-chain model of reference 43.

^g Graphical extrapolation.

NEODYMIUM TRICHLORIDE

The heat-capacity data of Colwell *et al.*⁽³⁵⁾ cover the range from 0.298 to 4.102 K. The nuclear entropy, based upon the isotopic abundances of ^{143}Nd and ^{145}Nd of 12.7 and 8.3 per cent,⁽⁴²⁾ is $0.015 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. The small impurity peaks, deleted from the heat-capacity curve, are found to account for about 1 per cent of the total

entropy at 4 K and are ignored. The present treatment includes the small ($0.003 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$) contributions to the lattice entropy which was subtracted in the published account of Colwell *et al.* The present evaluation of $\{S^\circ(4 \text{ K}) - S^\circ(0.298 \text{ K})\}$ yields $1.09 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ compared with the value of $0.79R \ln 2 = 1.09 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ found by Colwell *et al.* The enthalpy increments over this region represent direct integration of the heat-capacity curve which was graphically evaluated as $0.953 \text{ cal}_{\text{th}} \text{ mol}^{-1}$. Determination of the increments below 0.298 K involves a closer inspection of the models chosen to represent the measured heat capacity. Despite varied quality of fit with the results, all have a common feature in that they yield $R \ln 2$ as the value of $S_\infty(\text{mag})$. The use of the Ising linear-chain interpretation, whose simple heat-capacity expression is identical to a Schottky function, guarantees this. While this expression mimics the expected entropy, the probable effect in the heat capacity (due to long-range ordering) is a sharp spike, similar to that found for PrCl_3 . It is certainly inadequate to describe the morphology of the cooperative magnetic heat capacity, despite satisfaction of the lesser condition (in this case) of giving the "correct" entropy. The chief merit of such models is that they involve only a single parameter which is available from three sources: susceptibility data, the temperature of the measured heat-capacity maximum, or from spectroscopy. The three values of this parameter—an exchange constant—found by Colwell *et al.*⁽³⁵⁾ from these three sources are, respectively, $J/k = -1.32 \text{ K}$, -1.13 K , and -1.02 K . These determine $\{S^\circ(0.298 \text{ K}) - S^\circ(0)\}$ values of 0.129, 0.217, and 0.284 $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$, respectively. The two-parameter fit from the two-chain model of Hunt and Newman⁽⁴³⁾ leads to an increment of $0.236 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. This value is between the second and third of the one-parameter values (the former is the weaker determination) and is selected to represent $\{S^\circ(0.298 \text{ K}) - S^\circ(0)\}$. The increment $\{H^\circ(0.298 \text{ K}) - H^\circ(0)\}$ was estimated by graphical extrapolation to be only $0.063 \text{ cal}_{\text{th}} \text{ mol}^{-1}$.

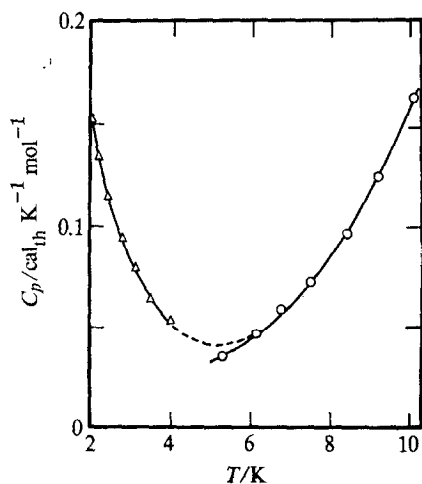


FIGURE 3. Low-temperature heat capacity of NdCl_3 . O, This research; Δ , reference 35; ----, selected curve.

The determination of the heat capacity immediately above 4 K is hampered by the fact that the curves for NdCl_3 and for PrCl_3 have a minimum in the region between 4 and 8 K. This region lies above that of the other studies and is the least accurate of this investigation. From the results for LaCl_3 below 7 K the points of the present study appear to be systematically low, possibly by as much as 50 per cent at 5 K. It is, therefore, very difficult to specify the exact location of this minimum in the heat capacity. Judicious use of the low-temperature studies together with theoretical considerations minimize the uncertainty in the thermodynamic functions.

Curves were drawn by visual inspection to represent the extremes of variation consistent with the data of Colwell *et al.*⁽³⁵⁾ at 4 K and with that of this study near 7 K. The curve determined by means of these two was compared with that calculated from the lattice contribution and the high-temperature ($1/T^2$) expression of the cooperative heat capacity (the Schottky contribution is zero here). Since excellent agreement was found, a mean curve was adopted and integrated to give the entropy and enthalpy increments. Above 7 K, the computer-calculated values from the "normal" data processing were employed. It is evident from figure 3 that little variance is involved. Two extreme curves (not shown) differed only by $0.0008 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. This treatment effectively disregards only the single lowest-temperature point of the present investigation. The various contributions and their sources are shown in table 6.

4. Discussion

SCHOTTKY HEAT CAPACITIES

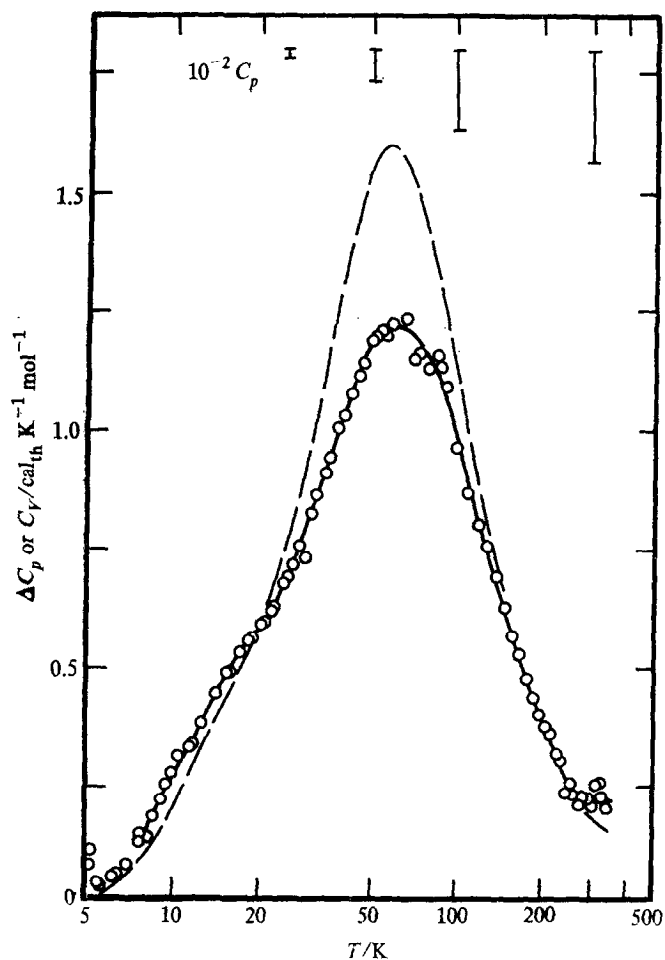
Schottky contributions occur in PrCl_3 and NdCl_3 . Of the six methods Van Vleck⁽⁴⁴⁾ listed for determining the Schottky levels for paramagnetic salts of the lanthanides (directly from i.r. spectroscopy, indirectly from optical spectroscopy, microwave resonance through the Zeeman effect (e.p.r.), magnetic susceptibility, heat capacity, and activation energies for Orbach processes in paramagnetic relaxation) each has been applied to some of the light lanthanide trihalides; however, the discussion will be based largely upon the optical spectroscopic data presented by Dieke.⁽⁴⁾ Many of these data were determined in Dieke's laboratory and his tables often summarize several experimental determinations. The experimental energy levels have been measured for LaCl_3 crystals in which a paramagnetic cation was present as an impurity of 0.1 to 2 mole per cent.

PRASEODYMIUM TRICHLORIDE

The energy-level scheme for the Pr^{3+} ion in LaCl_3 shown in table 7 yields a heat-capacity curve which reaches a maximum of $1,595 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 58.60 K as shown in the plot of figure 4. The curve of $\{C_p(\text{PrCl}_3) - C_p(\text{LaCl}_3)\}$ is also shown and designated as the "experimental" (Schottky) curve. The abscissa of the plot is the logarithm of the temperature, since this choice emphasizes the most interesting region of the curves. The points on the experimental curve represent deviations of the PrCl_3 values from the smoothed LaCl_3 curve and thus attribute a "perfectly" smooth curve to this substance used as an approximation to the lattice heat capacity.

TABLE 7. Crystal-field levels for PrCl_3 and NdCl_3 ; ΔE denotes energy above ground, μ denotes crystal quantum number, and g denotes degeneracy of level

<i>J</i> -state term	PrCl_3^a			<i>J</i> -state term	NdCl_3^b		
	$\Delta E/hc \text{ cm}^{-1}$	μ	<i>g</i>		$\Delta E/hc \text{ cm}^{-1}$	μ	<i>g</i>
$^3\text{H}_4$	0.0	2	2	$^4\text{I}_{9/2}$	0.0	5/2	2
	33.1	3 ⁻	1		115.39	1/2	2
	96.4	2'	2		123.21	3/2	2
	130.2	1	2		244.4	5/2	2
	137.0	3 ⁺	1		249.4	3/2	2
	199.1	0	1				
Next level at 2137.2 cm^{-1}				Next level at 1973.85 cm^{-1}			

^a Reference 45.^b Reference 58.FIGURE 4. Schottky heat capacity for PrCl_3 . \circ , $\{C_p(\text{PrCl}_3) - C_p(\text{LaCl}_3)\}$; ----, C_v (Schottky, calc.) for PrCl_3 .

The first excited level is found spectroscopically at 33.1 cm^{-1} ($\mu=3^-$) and is responsible for the slight bulge on the low-temperature side of the calculated Schottky maximum. The calculated curve includes the effect of the next higher J -state, 3H_5 , the lowest level and center of gravity of which are at 2137.2 and about 2203 cm^{-1} . At 350 K, the Boltzmann factor between the 3H_4 and 3H_5 states is about 2×10^{-4} so that at this temperature, the 3H_5 levels make effectively no contribution to the heat capacity; higher levels will have correspondingly less effect. At higher temperatures, the 3H_5 state will become important; indeed, calculations show that the curve should have a minimum at about 365 K, slightly beyond the upper limit of the present study. Above 365 K it begins to rise due to the population increase in the higher state.

The experimental curve shows qualitative agreement with the calculated one and virtual coincidence from near 150 K to about 250 K. Beyond 250 K, a systematic departure is seen; the experimental curve lies higher by about 0.2 per cent of the total C_p for PrCl_3 and is concave upwards. On the low-temperature side of the maximum, the bulge noted in the calculated curve is even more prominent in the experimental curve. The calculated heat capacity is quite sensitive to the placement of the lowest level and the enhanced contribution is an indication that the $\mu=3^-$ level deduced from heat capacity is rather lower than the value obtained from spectroscopy. Downward adjustment of the $\mu=3^-$ level (not shown) by about 9 per cent to 30 cm^{-1} gives a better fit to the heat capacity from about 7 to 17 K, and causes the calculated maximum to shift upwards about 1 K, and lowers it by about 2.2 per cent relative to the calculated curve shown. Although the thus improved fit is encouraging, it is not enhanced by extension of the comparison much above 17 K, since substantial difference in the lattice heat capacities between PrCl_3 and LaCl_3 begins near this temperature. Such an adjustment of the spectroscopic levels causes only minor changes in the calculated entropy. Of perhaps greater significance is that the lattice differences obscure a detailed picture of the higher-lying levels, *i.e.* those above about 100 cm^{-1} , since these give the largest heat-capacity contributions in regions where the lattice differences are largest. Shifts in the spectroscopic levels of several per cent could go unnoticed and would only be suspected where the lack of conformity to a scheme of lattice heat capacity (or entropy) is pronounced. Possible evidence of such variation will be presented later.

The most conspicuous feature of figure 4 is the lesser height (only 76 per cent of the calculated value) of the experimental curve in the region of the maximum. The Schottky contribution amounts to about 5 per cent of $C_p(\text{total})$ at this temperature. This deviation gradually diminishes on either side until good agreement is found at 20 K and again near 150 K. Likewise, the experimental and calculated maxima do not coincide, the former occurring at 61.65 K and the latter at 58.60 K. As mentioned before, shifting the $\mu=3^-$ level does move T_{max} in the expected direction although the resulting shift is only about 1 K. It is difficult to specify an exact value for T_{max} from the experimental curve, since the latter is fairly flat over a range of about 3 K. Nevertheless, the closeness of the agreement between the experimental and calculated T_{max} values, together with the good fit at high temperatures and the fairly good fit at lower temperatures, indicates that the application of spectroscopic data to describe the heat-capacity behavior is "appropriate", *i.e.* that no level has been "missed" or

incorrectly introduced; and that even the greatest deviation in the plot is not damaging to the Schottky interpretation. This deviation is probably due to differences in lattice heat capacities of the members of the series and hence provides information useful in developing a better approximation for the heat capacities of lanthanide salts. It is believed that the same argument also applies, with modifications, to all members of the series.

PrCl_3 has been intensively studied. The energy-level values taken from Dieke⁽⁴⁵⁾ derive from the experiments of Sarup and Crozier⁽⁴⁶⁾ and of Dieke and Sarup.⁽⁴⁷⁾ The earlier-measured values of Freed and Sayre⁽⁴⁸⁾ were used by Hutchison and Wong⁽⁴⁹⁾ as a source of crystal-field-potential parameters from which the levels of the remaining salts could be calculated from the parameters measured in their e.p.r. studies. The latter study is influenced by the work of Freed and Sayre—though Hutchison and Wong present calculated energy levels both with and without correction of the crystal-field parameters (derived from PrCl_3) for cations with different values of Z . Schneider^(50,51) used the results of the variation of the paramagnetic susceptibility with temperature to calculate values of the levels; his values are somewhat higher than those of the spectroscopic studies. Hougen and Singh,⁽¹⁴⁾ in one of the early observations of the electronic Raman effect, found values for the first three excited crystal-field levels which are in fairly good agreement with those of the optical spectroscopic studies. Of considerable interest to the present study is the work of Dorman⁽⁵²⁾ on the line shapes and oscillator strengths of PrCl_3 as a function of Pr(III) concentration. This work provides data on the variation of the levels of $^3\text{H}_4$ with composition. For $\mu = 2'$ and 3^- the observed wavenumbers are shown elsewhere.⁽⁵³⁾ The variation is not monotonic, although the comparison of the results from 0.26 to 2 per cent with the "100 per cent values" show that $\mu = 3^-$ has shifted to lower values and the $\mu = 2'$ to higher values. The increments from increased concentration of dopant would improve the agreement between calculated and experimental curves. The change in the $\mu = 3^-$ value is somewhat less (30 cm^{-1}) than that needed to ensure good agreement. Without further information on the variation of the other crystal-field levels, it is not possible to say that the upward shift of T_{max} found experimentally is due to the $\mu = 2'$ shift, since an identical or an indistinguishable one could be achieved by a shift in one of the higher-lying levels.

Some experimental scatter is evident in the region of the maximum. This is possibly due to increased drift time (mentioned previously) which Lyon⁽⁵⁴⁾ has suggested as possible evidence for a relatively low-level spin-lattice interaction in this temperature region.

As the most-studied member of the present series, it is perhaps not surprising for PrCl_3 —or at least for Pr(III) in LaCl_3 —that several studies have disclosed evidence of higher-order interactions which must surely complicate a simple "additive-thermodynamic model". Among these is the study of German and Kiel⁽⁵⁵⁾ on the concentration variation of fluorescence decay lifetimes. These authors also found an anomalous temperature dependence in the fluorescence linewidths below 100 K for transitions whose terminal state is a magnetic doublet (e.g. $\mu = 2$ of $^3\text{H}_4$).⁽⁵⁶⁾ They suggest that the broadening is caused by cooperative interaction between ground-state and excited-state ions. This is confirmed by the very recent work of Allen⁽⁵⁷⁾ whose

investigation of Pr(III) in LaF_3 , in which the crystal-field components are non-magnetic, finds no such broadening. It is not to be implied that difficulties in interpreting one type of experiment can be disposed of by pointing to similar ones in other experiments, but the attempted resolution of the Schottky heat-capacity contributions must involve either the assumption that such interactions do not exist, or that they do not affect the heat capacity. Proof of the validity of the latter assumption is not at hand.

NEODYMIUM TRICHLORIDE

The energy-level scheme of Dieke for Nd(III) in LaCl_3 is also shown in table 7. These values and assignments are from the experimental work of Carlson and Dieke.^(58,59) They were found for LaCl_3 crystals containing 0.2 and 2 per cent of

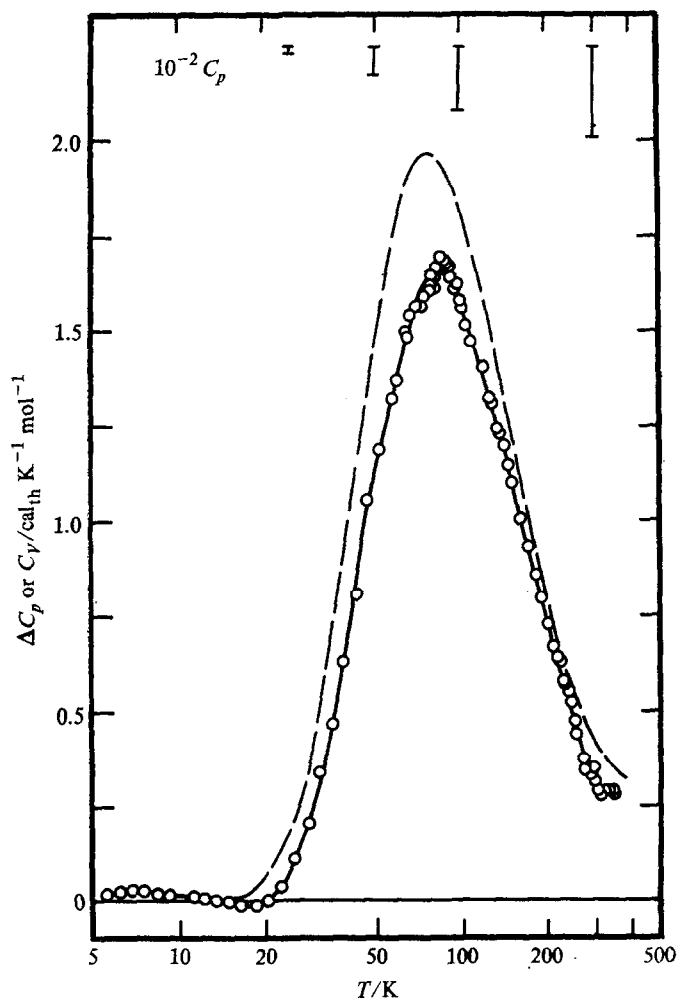


FIGURE 5. Schottky heat capacity for NdCl_3 . O, $\{C_p(\text{NdCl}_3) - C_p(\text{LaCl}_3)\}$; ----, $C_v(\text{Schottky, calc.})$.

Nd(III). The second of these studies is a "direct" infrared absorption study and is thus an independent determination. Also, the article of Hutchison and Wong⁽⁴⁹⁾ presents a comparison of the levels of Carlson and Dieke,⁽⁵⁸⁾ with values calculated by three methods from e.p.r. data. In reference 58, the upper $\mu = 3/2$ level (at 249.4 cm^{-1}) had not yet been found. The energy-level scheme consists of five Kramers' doublets with the first excited state at 115.39 cm^{-1} and the highest at 249.4 cm^{-1} . The next J -state, $^4I_{11/2}$, was included in the calculated Schottky heat capacity, although its lowest level and center of gravity are at 1973.85 and 2028 cm^{-1} , respectively.

The experimental and calculated Schottky heat-capacity contributions shown in figure 5 have the same appearance as those for PrCl_3 . The maximum in the heat capacity occurs at rather higher temperatures than for PrCl_3 since the levels for NdCl_3 are substantially higher. The experimental T_{max} value of 84.7 K is higher than the calculated value of 78.15 K; but as for PrCl_3 , exact level-placement would seem to be in fair agreement. This accords well with the findings of Gray and Stapleton⁽⁶⁰⁾ on the spin-lattice relaxation behavior of Nd(III) in LaCl_3 ; this work extends to the "high" (for such experiments) temperature of 29 K and places the average of the first two doublets at 117.6 cm^{-1} compared with the spectroscopic value of 119.3 cm^{-1} . The calculated Schottky heat capacity is effectively zero below about 15 K (less than 0.001 $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$). The experimental curve shows a slight bulge below about 10 K, but is still quite close to zero. Above 10 K, the curve is seen to dip below zero briefly, with a minimum near 18 K. This negative excursion is due to the difference in apparent lattice heat capacity and is quickly lost in the rapid increase in the Schottky heat capacity. Above 250 K, the experimental curve deviates substantially below the calculated one. This deviation is in the opposite sense to that for PrCl_3 , but since such deviations arise—at least in part—from the accumulated uncertainty in the several subtractions necessary to determine the curve, may not be significant.

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