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# Thermodynamics of the lanthanide halides II. Heat capacities and Schottky anomalies of $SmCl_3$, $EuCl_3$, and $GdCl_3$ from 5 to 350 K[a]

JAMES A. SOMMERS[b] AND EDGAR F. WESTRUM, JR.

*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.*

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The heat capacities of $SmCl_3$, $EuCl_3$, and $GdCl_3$ have been measured from 5 to 350 K by adiabatic calorimetry. For $SmCl_3$ and $EuCl_3$, the calculated Schottky heat capacities may be compared with the difference in heat capacity between $LaCl_3$ and the paramagnetic members, as before. For $GdCl_3$ which lacks a Schottky contribution, the difference between the heat capacity of $LaCl_3$ and $GdCl_3$ may be discussed in terms of spectroscopic data on lattice vibration. Comparison between the measured entropies and the results of estimation schemes is presented. The values of $\{S^\circ(298.15\ \mathrm{K}) - S^\circ(0)\}$ for $SmCl_3$, $EuCl_3$, and $GdCl_3$ are 35.88, 34.43, and 36.19 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$, respectively.

## 1. Introduction

The compounds $SmCl_3$, $EuCl_3$, and $GdCl_3$ differ from the preceding lanthanide trihalides(1) in several respects. Sm(III) and Eu(III) are characterized by low-lying $J$-states which make significant contributions in the temperature range under investigation here. The $^8S_{7/2}$ ground state of Gd(III) is little affected by the crystalline field and its next $J$-state is too energetic to contribute heat capacities below 350 K. The thermal properties in the temperature range 10 to 350 K (where the contribution due to its ferromagnetic ordering transition(2) at 2.2 K is small) provides a measure of the lattice heat capacity which may be compared with that of $LaCl_3$. All three salts show the increasing influence of the lanthanide contraction on their thermal properties. This paper will treat the resolution of the heat capacities of $SmCl_3$ and $EuCl_3$ similarly to those of the first paper, compare the heat capacity of $LaCl_3$ and $GdCl_3$, and discuss the overall energies of these trihalides based on spectroscopic and calorimetric data.

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[b] Present address: Monsanto Polymers and Petrochemicals Co., 800 N. Lindbergh Blvd, Saint Louis, Missouri 63166, U.S.A.

## 2. Experimental

### SAMPLE PREPARATION AND CHARACTERIZATION

The methods of the previous paper(1) were applied to the samples of this series except for $EuCl_3$. The sesquioxides were obtained from American Potash and Chemical Co. and were of 99.99 mass per cent stated purity. A slight deficiency of chlorine despite the fact that heating was stopped at 623 K was found in the initial $EuCl_3$ preparation. This deficiency was reflected in the analytical results which gave a composition of $EuCl_{2.989\pm0.003}$. There was no chemical or crystallographic evidence of contamination; it was concluded that the method was inadequate for europium. This observation is in good agreement with the work of Polyachenok and Novikov(3) on the decomposition pressure of $EuCl_3$. A crude extrapolation of their results beyond the range of their determination gives an equilibrium chlorine pressure of about 0.1 Pa at 623 K and implies certain chlorine depletion under the conditions of synthesis employed. This result is similar to that of Haschke(4) for $EuBr_3$. Hence, the hypostoichiometric $EuCl_3$ sample was chlorinated in a Pyrex cell connected through a vacuum line with stopcocks to a trap bathed in a $CCl_4$-slush bath and then to a tank of chlorine gas with a short piece of Tygon tubing. The system and cell were evacuated and briefly purged with chlorine at atmosphere pressure. The cell was isolated and surrounded by the furnace. The temperature was slowly taken to 633 K, held there for 1 h, and then allowed to cool slowly over 4 h with the turned-off furnace in place. The cell was then evacuated, filled with pre-purified nitrogen gas, and sealed off under flame. The treatment gave a stoichiometric product.

In applying the method for lanthanide analysis to the series of this article, it was noted that the masses of recovered oxide samples were slightly high (by about 2 to 5 per cent) but that silver chloride was not precipitated from nitric acid solutions upon addition of $AgNO_3(aq)$. Since firing for several hours in air would bring the sesquioxide masses down to the theoretical, the discrepancy was possibly due to the formation of hydrous oxide phases which dried out on further heating. All three sesquioxides (samarium, europium, and gadolinium) required longer heating periods to reach the theoretical mass. For the oxides of this series, the increased period to convert to sesquioxide (up to 48 h) may have been partly due to an increased tendency of the oxide phase to retain chlorine; it was observed that the extra firing time increased in the order Sm > Eu > Gd. The analytical results obtained are shown in table 1.

TABLE 1. Analysis of the lanthanide trichloride samples; $w$ denotes mass fraction[a]

| Compound | $10^2w$ | | | | $10^2\Sigma w$ | $n(\mathrm{Cl})/n(\mathrm{Ln})$ |
|---|---|---|---|---|---|---|
| | Cl | | Ln | | | |
| | obs. | calc.[b] | obs. | calc.[b] | | |
| $SmCl_3$ | 41.41 ± 0.06 | 41.42 | 58.61 ± 0.28 | 58.58 | 100.02 ± 0.28 | 2.997 ± 0.010 |
| $EuCl_3$ | 41.17 ± 0.04 | 41.17 | 58.85 ± 0.10 | 58.83 | 100.02 ± 0.11 | 2.999 ± 0.003 |
| $GdCl_3$ | 40.34 ± 0.06 | 40.35 | 59.70 ± 0.20 | 59.65 | 100.04 ± 0.21 | 2.997 ± 0.006 |

[a] Uncertainty indices are two standard deviations.

[b] Based on 1971 IUPAC atomic weights.

The only ambiguity in the assignment of the hexagonal $UCl_3$-type crystal structure to all the light lanthanide trichlorides is presented in the work of Harris and Veale(5) on $GdCl_3$. Their observations on the occurrence of the orthorhombic $PuBr_3$-type structure seem consistent with this structure being a metastable one for $GdCl_3$. Nevertheless, an attempt was made to obtain the orthorhombic modification. A $GdCl_3$ sample, prepared as usual, was found to give only $UCl_3$-type diffraction lines. Samples were sealed in small vials under 3.8 MPa of He gas. One was immersed in liquid nitrogen for 7 h, the other annealed in a drying oven at 367 K for 7 d. Guinier-Hägg-type powder X-ray patterns taken on these samples revealed only lines due to the $UCl_3$-type structure, with no trace of lines due to a $PuBr_3$-type phase. It was concluded that the results of subsequent heat-capacity measurements could be unambiguously attributed to hexagonal $GdCl_3$. The lattice parameters found for these halides and a comparison with literature values are shown in table 2.

TABLE 2. Lattice parameters of the lanthanide trichlorides

| | $SmCl_3$ | | $EuCl_3$ | | $GdCl_3$ | |
|---|---|---|---|---|---|---|
| | $a_0$/nm | $c_0$/nm | $a_0$/nm | $c_0$/nm | $a_0$/nm | $c_0$/nm |
| Templeton and Dauben[a] | 0.7378<br>± 0.0007 | 0.4171<br>± 0.0004 | 0.7369<br>± 0.0004 | 0.4133<br>± 0.0002 | 0.7363<br>± 0.0004 | 0.4105<br>± 0.0002 |
| Morosin[b] | | | 0.73746 | 0.41323 | 0.73663 | 0.41059 |
| ASTM File[c] | 0.7380 | 0.4169 | 0.7375 | 0.4134 | | |
| This work | 0.7380<br>± 0.0007 | 0.4175<br>± 0.0001 | 0.7370<br>± 0.0002 | 0.4137<br>± 0.0004 | 0.7367<br>± 0.0002 | 0.4108<br>± 0.0001 |
| $\rho$/g cm$^{-3}$ | 4.330 | | 4.414 | | 4.542 | |

[a] Reference 6.
[b] Reference 7.
[c] Reference 8: ASTM File card numbers: $SmCl_3$, 12-789; $EuCl_3$, 12-387.

## HEAT-CAPACITY MEASUREMENTS

The heat-capacity measurements were obtained in the chronological order $SmCl_3$, $GdCl_3$, and $EuCl_3$ by the same method as reported earlier.(1) The loading data are given in table 3.

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 |
|---|---|---|---|
| $SmCl_3$ | 79.2313 | 256.8 | 8.1 |
| $EuCl_3$ | 80.4073 | 258.319 | 7.9 |
| $GdCl_3$ | 76.1415 | 263.61 | 7.6 |

[a] Based on 1971 IUPAC atomic weights.

## 3. Results

### THERMODYNAMIC FUNCTIONS

No cooperative thermal phenomena were encountered and the only apparent manifestation of non-cooperative effects was a slight increase in the duration of time required for establishment of constant quasi-adiabatic drifts following energy inputs that occurred in the temperature regions of the maxima in these contributions.

The experimental heat capacities were processed by subtraction of the heat capacity due to the empty calorimeter (determined separately) and correction for small differences in amounts of helium gas and 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 in order to adjust the mean values of $\Delta H/\Delta T$ to the limit ($\mathrm{d}H/\mathrm{d}T = C_p$). The heat capacities are listed in chronological sequence in table 4 so that the $\Delta T$'s employed usually can be estimated from adjacent mean temperatures.

These results are depicted in figure 1. The curve-fitting involved computer regression of the measured heat capacities to a power series of orthogonal polynomials in reduced

TABLE 4. Experimental heat capacities of $SmCl_3$, $EuCl_3$, and $GdCl_3$
($\mathrm{cal_{th}} = 4.184$ J)

| $\frac{T}{\mathrm{K}}$ | $\frac{C_p}{\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_p}{\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_p}{\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_p}{\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}}$ |
|---|---|---|---|---|---|---|---|
| | | | Samarium trichloride | | | | |
| Series I | | 265.60 | 23.15 | 10.91 | 0.309 | 5.96 | 0.021 |
| 68.05 | 10.86 | 275.76 | 23.35 | 11.98 | 0.424 | 6.58 | 0.040 |
| 74.65 | 11.95 | 285.99 | 23.56 | 13.10 | 0.581 | 7.22 | 0.055 |
| 82.80 | 13.27 | 296.16 | 23.75 | 14.25 | 0.755 | 7.94 | 0.080 |
| 92.30 | 14.58 | 306.26 | 23.94 | 15.44 | 0.953 | 8.74 | 0.127 |
| 102.15 | 15.70 | 316.28 | 24.10 | 16.76 | 1.168 | 9.63 | 0.208 |
| 111.69 | 16.68 | 326.28 | 24.24 | 18.18 | 1.417 | 10.79 | 0.306 |
| 121.82 | 17.59 | 336.24 | 24.38 | 19.76 | 1.706 | 12.04 | 0.431 |
| 132.25 | 18.42 | 343.17 | 24.44 | 21.67 | 2.071 | 13.39 | 0.624 |
| 142.27 | 19.09 | 347.13 | 24.45[a] | 23.93 | 2.514 | 14.75 | 0.842 |
| 151.97 | 19.66 | | | 26.30 | 2.984 | 16.17 | 1.065 |
| 161.77 | 20.14 | Series III | | 29.03 | 3.507 | 17.65 | 1.325 |
| 171.70 | 20.58 | 58.97 | 9.204 | | | 18.87 | 1.536 |
| 181.45 | 20.96 | 64.36 | 10.21 | Series V | | 20.91 | 1.926 |
| 191.56 | 21.32 | 69.78 | 11.13 | 35.56 | 4.769 | 23.27 | 2.385 |
| 202.03 | 21.64 | 75.95 | 12.14 | 39.07 | 5.425 | 25.94 | 2.908 |
| 212.37 | 21.94 | | | 42.84 | 6.132 | 28.90 | 3.480 |
| 222.59 | 22.24 | Series IV | | 46.58 | 6.847 | 32.16 | 4.116 |
| 232.71 | 22.47 | | | 50.41 | 7.578 | 35.61 | 4.772 |
| 242.73 | 22.72 | 5.62 | 0.023 | 54.87 | 8.416 | 39.18 | 5.444 |
| | | 6.64 | 0.055 | 59.89 | 9.367 | 42.97 | 6.157 |
| Series II | | 7.46 | 0.078 | | | 47.04 | 6.924 |
| 235.42 | 22.51 | 8.36 | 0.117 | | | 51.31 | 7.742 |
| 245.35 | 22.75 | 9.14 | 0.169 | Series VI | | 56.45 | 8.718 |
| 255.51 | 22.99 | 9.92 | 0.235 | 5.18 | 0.018 | 62.60 | 9.874 |

TABLE 4.—*continued*

| $T$/K | $C_p$/cal$_{th}$ K$^{-1}$ mol$^{-1}$ | $T$/K | $C_p$/cal$_{th}$ K$^{-1}$ mol$^{-1}$ | $T$/K | $C_p$/cal$_{th}$ K$^{-1}$ mol$^{-1}$ | $T$/K | $C_p$/cal$_{th}$ K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | Europium trichloride | | | | |
| Series I | | 226.30 | 24.31 | 346.44 | 26.09 | 20.42 | 1.034 |
| 85.05 | 13.38 | 236.27 | 24.54 | | | 22.43 | 1.287 |
| 92.12 | 14.56 | 246.16 | 24.80[a] | Series III | | 24.68 | 1.604 |
| 99.72 | 15.70 | | | 4.95 | 0.012 | 27.12 | 1.962 |
| 107.97 | 16.84 | Series II | | 6.06 | 0.030 | 29.57 | 2.351 |
| 116.87 | 17.97 | 239.80 | 24.62 | 6.98 | 0.043 | 32.15 | 2.807 |
| 126.22 | 19.04 | 249.67 | 24.78 | 8.03 | 0.071 | 35.19 | 3.341 |
| 136.02 | 19.98 | 259.48 | 24.97 | 9.08 | 0.108 | 38.95 | 4.052 |
| 145.95 | 20.80 | 269.35 | 25.11 | 10.07 | 0.157 | 43.32 | 4.917 |
| 155.87 | 21.51 | 279.28 | 25.29 | 11.11 | 0.203 | 48.12 | 5.905 |
| 165.84 | 22.10 | 289.13 | 25.46 | 12.18 | 0.269 | 53.99 | 7.161 |
| 175.77 | 22.61 | 298.94 | 25.58 | 13.25 | 0.353 | 60.50 | 8.550 |
| 185.69 | 23.04 | 308.84 | 25.71 | 14.39 | 0.444 | 66.80 | 9.861 |
| 195.79 | 23.42 | 318.76 | 25.81 | 15.65 | 0.556 | 73.16 | 11.11 |
| 206.08 | 23.76 | 328.66 | 25.95 | 17.03 | 0.678 | 79.80 | 12.41 |
| 216.24 | 24.07 | 338.56 | 26.04 | 18.62 | 0.834 | 86.98 | 13.75 |
| | | | Gadolinium trichloride | | | | |
| Series I | | 311.38 | 23.54 | 151.04 | 19.27 | 14.37 | 0.493 |
| 152.40 | 19.35 | 321.61 | 23.69 | 160.73 | 19.77 | 15.71 | 0.612 |
| 162.90 | 19.89 | 332.05 | 23.78 | Series III | | 17.21 | 0.745 |
| 172.98 | 20.34 | 342.02 | 23.82 | 52.73 | 6.836 | 18.95 | 0.916 |
| 182.85 | 20.73 | 348.36 | 23.77[a] | 58.35 | 7.975 | 20.83 | 1.131 |
| 192.79 | 21.08 | | | 64.04 | 9.132 | 22.83 | 1.383 |
| 202.79 | 21.40 | Series II | | 69.68 | 10.18 | 24.98 | 1.686 |
| 212.67 | 21.66 | 66.21 | 9.548 | | | 27.29 | 2.025 |
| 222.49 | 21.93 | 73.32 | 10.82 | Series IV | | 29.81 | 2.420 |
| 232.28 | 22.17 | 80.39 | 12.07 | 4.90 | 0.086 | 32.40 | 2.865 |
| 242.18 | 22.38 | 87.77 | 13.28 | 5.41 | 0.087 | 35.23 | 3.371 |
| 252.16 | 22.56 | 95.76 | 14.33 | 6.49 | 0.111 | 38.51 | 3.979 |
| 262.07 | 22.75 | 104.14 | 15.34 | 7.87 | 0.156 | 42.31 | 4.702 |
| 271.90 | 22.94 | 112.76 | 16.27 | 9.26 | 0.185 | 46.52 | 5.553 |
| 281.78 | 23.10 | 121.90 | 17.17 | 10.65 | 0.243 | 51.00 | 6.485 |
| 291.73 | 23.26 | 131.44 | 17.96 | 11.88 | 0.296 | 56.16 | 7.536 |
| 301.60 | 23.44 | 141.21 | 18.66 | 13.11 | 0.389 | 62.31 | 8.792 |

[a] This point was given less weight in the curve-fitting process.

temperature. The resulting power series was integrated appropriately to produce the derived thermodynamic functions at round temperature intervals. These functions (listed in table 5) do not include contributions from nuclear spin or isotropic mixing and are thus suitable for use in ordinary thermochemical calculations. Above 25 K the heat capacities are considered to have standard deviations no greater than 0.1 per cent and the derived thermodynamic properties are considered to be even more reliable over this range, apart from allowance for the presence of effects below the lowest temperature of measurement.

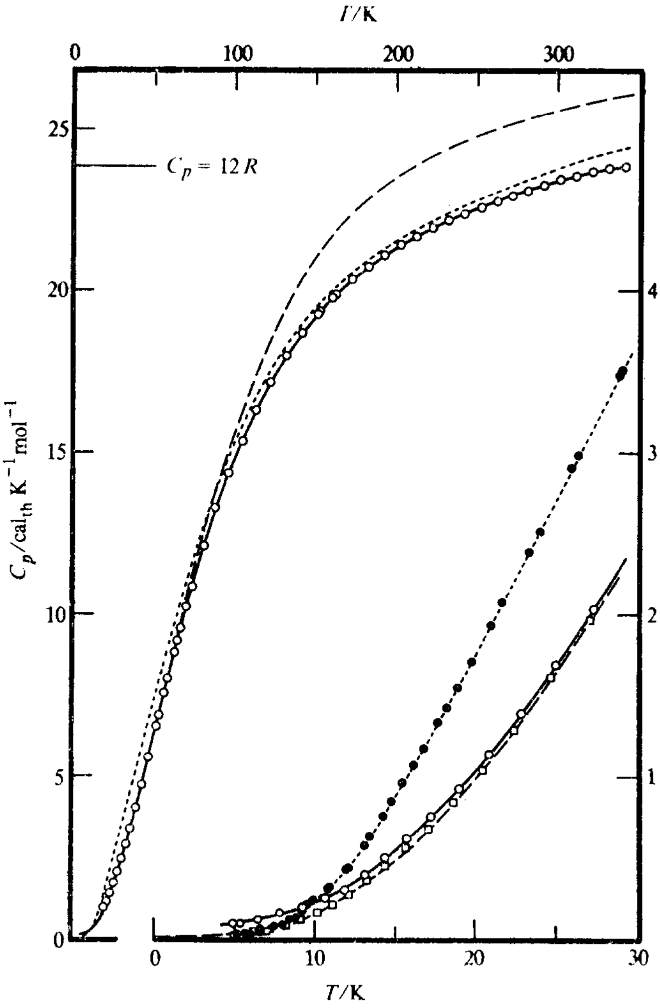

FIGURE 1. Experimental heat-capacity curves. ●, $SmCl_3$; □, $EuCl_3$; ○, $GdCl_3$.

## SAMARIUM TRICHLORIDE

The findings of Colwell, Mangum, and Utton(9) are in substantial disagreement with those of this study. Their heat capacities show a large spike (which they do not believe is a true feature of $SmCl_3$). They found long relaxation times during measurements. Furthermore, they find a minimum in the heat capacity between 3 and 4 K, and attribute "turn around" in the heat capacity to the lower-temperature side of the Schottky heat capacity. The cause of this rise, the first Kramers' doublet, has been found at 40.7 $cm^{-1}$ for Sm(III) in $LaCl_3$.(10) Colwell *et al.*'s data require it to be some 20 per cent lower to produce a minimum to match that observed in their heat-capacity experiments. The heat capacity behavior found at the upper limit of their temperature range (4 K) fits poorly with that of this study. Even allowing

TABLE 5. Thermodynamic functions for $SmCl_3$, $EuCl_3$, and $GdCl_3$
($cal_{th} = 4.184$ J)

| $T$ / K | $C_p$ / $cal_{th}\ K^{-1}\ mol^{-1}$ | $\{S^\circ(T) - S^\circ(0)\}$ / $cal_{th}\ K^{-1}\ mol^{-1}$ | $\{H^\circ(T) - H^\circ(0)\}$ / $cal_{th}\ mol^{-1}$ | $-\{G^\circ(T) - H^\circ(0)\}/T$ / $cal_{th}\ K^{-1}\ mol^{-1}$ |
|---|---|---|---|---|
| | | Samarium trichloride | | |
| 5 | 0.017 | (1.383) | (0.415) | (1.300) |
| 10 | 0.229 | 1.437 | 0.864 | 1.351 |
| 15 | 0.875 | 1.638 | 3.449 | 1.408 |
| 20 | 1.750 | 2.006 | 9.962 | 1.508 |
| 25 | 2.726 | 2.501 | 21.134 | 1.656 |
| 30 | 3.694 | 3.084 | 37.194 | 1.844 |
| 35 | 4.660 | 3.726 | 58.08 | 2.066 |
| 40 | 5.597 | 4.410 | 83.73 | 2.316 |
| 45 | 6.543 | 5.123 | 114.08 | 2.588 |
| 50 | 7.496 | 5.862 | 149.18 | 2.879 |
| 60 | 9.388 | 7.397 | 233.64 | 3.503 |
| 70 | 11.186 | 8.981 | 336.62 | 4.172 |
| 80 | 12.819 | 10.583 | 456.80 | 4.873 |
| 90 | 14.249 | 12.178 | 592.3 | 5.596 |
| 100 | 15.48 | 13.744 | 741.1 | 6.333 |
| 110 | 16.53 | 15.27 | 901.3 | 7.076 |
| 120 | 17.44 | 16.75 | 1071.2 | 7.821 |
| 130 | 18.24 | 18.18 | 1249.7 | 8.563 |
| 140 | 18.94 | 19.55 | 1435.7 | 9.299 |
| 150 | 19.55 | 20.88 | 1628.3 | 10.027 |
| 160 | 20.07 | 22.16 | 1826.4 | 10.746 |
| 170 | 20.51 | 23.39 | 2029.4 | 11.454 |
| 180 | 20.90 | 24.58 | 2236.5 | 12.150 |
| 190 | 21.25 | 25.72 | 2447.4 | 12.834 |
| 200 | 21.58 | 26.81 | 2661.5 | 13.506 |
| 210 | 21.88 | 27.87 | 2878.9 | 14.165 |
| 220 | 22.16 | 28.90 | 3099.1 | 14.812 |
| 230 | 22.41 | 29.89 | 3321.9 | 15.45 |
| 240 | 22.64 | 30.85 | 3547.2 | 16.07 |
| 250 | 22.85 | 31.78 | 3774.7 | 16.68 |
| 260 | 23.05 | 32.68 | 4004.2 | 17.28 |
| 270 | 23.25 | 33.55 | 4235.7 | 17.86 |
| 280 | 23.44 | 34.40 | 4469.1 | 18.44 |
| 290 | 23.63 | 35.23 | 4704.5 | 19.00 |
| 300 | 23.82 | 36.03 | 4941.8 | 19.56 |
| 310 | 24.00 | 36.81 | 5181 | 20.10 |
| 320 | 24.16 | 37.58 | 5422 | 20.64 |
| 330 | 24.30 | 38.32 | 5664 | 21.16 |
| 340 | 24.41 | 39.05 | 5908 | 21.68 |
| 350 | 24.50 | 39.76 | 6152 | 22.18 |
| 273.15 | 23.31 | 33.82 | 4309.0 | 18.04 |
| 298.15 | 23.79 | 35.88 | 4897.7 | 19.46 |

TABLE 5.—*continued*

| $\frac{T}{\mathrm{K}}$ | $\frac{C_p}{\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}}$ | $\frac{\{S^\circ(T) - S^\circ(0)\}}{\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}}$ | $\frac{\{H^\circ(T) - H^\circ(0)\}}{\mathrm{cal_{th}\ mol^{-1}}}$ | $\frac{-\{G^\circ(T) - H^\circ(0)\}/T}{\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}}$ |
|---|---|---|---|---|
| Europium trichloride | | | | |
| 5 | 0.013 | (0.005) | (0.019) | (0.002) |
| 10 | 0.150 | 0.045 | 0.341 | 0.011 |
| 15 | 0.488 | 0.163 | 1.860 | 0.039 |
| 20 | 0.993 | 0.369 | 5.502 | 0.094 |
| 25 | 1.644 | 0.658 | 12.037 | 0.177 |
| 30 | 2.426 | 1.025 | 22.164 | 0.287 |
| 35 | 3.310 | 1.465 | 36.472 | 0.423 |
| 40 | 4.260 | 1.968 | 55.38 | 0.584 |
| 45 | 5.256 | 2.527 | 79.15 | 0.768 |
| 50 | 6.299 | 3.134 | 108.01 | 0.974 |
| 60 | 8.444 | 4.473 | 181.76 | 1.444 |
| 70 | 10.519 | 5.932 | 276.67 | 1.979 |
| 80 | 12.449 | 7.464 | 391.65 | 2.569 |
| 90 | 14.200 | 9.034 | 525.1 | 3.200 |
| 100 | 15.76 | 10.612 | 675.0 | 3.862 |
| 110 | 17.14 | 12.181 | 839.7 | 4.547 |
| 120 | 18.35 | 13.726 | 1017.3 | 5.248 |
| 130 | 19.40 | 15.24 | 1206.2 | 5.958 |
| 140 | 20.31 | 16.71 | 1404.9 | 6.674 |
| 150 | 21.09 | 18.14 | 1612.0 | 7.391 |
| 160 | 21.76 | 19.52 | 1826.3 | 8.106 |
| 170 | 22.32 | 20.86 | 2046.8 | 8.817 |
| 180 | 22.81 | 22.15 | 2272.6 | 9.522 |
| 190 | 23.22 | 23.39 | 2502.8 | 10.219 |
| 200 | 23.58 | 24.59 | 2736.8 | 10.908 |
| 210 | 23.88 | 25.75 | 2974.2 | 11.587 |
| 220 | 24.15 | 26.87 | 3214.4 | 12.257 |
| 230 | 24.39 | 27.95 | 3457.1 | 12.916 |
| 240 | 24.61 | 28.99 | 3702.1 | 13.564 |
| 250 | 24.80 | 30.00 | 3949.2 | 14.201 |
| 260 | 24.98 | 30.97 | 4198.1 | 14.828 |
| 270 | 25.15 | 31.92 | 4448.8 | 15.44 |
| 280 | 25.30 | 32.84 | 4701.0 | 16.05 |
| 290 | 25.45 | 33.73 | 4954.8 | 16.64 |
| 300 | 25.59 | 34.59 | 5210 | 17.23 |
| 310 | 25.72 | 35.43 | 5467 | 17.80 |
| 320 | 25.85 | 36.25 | 5724 | 18.36 |
| 330 | 25.96 | 37.05 | 5983 | 18.92 |
| 340 | 26.05 | 37.83 | 6243 | 19.46 |
| 350 | 26.13 | 38.58 | 6504 | 20.00 |
| 273.15 | 25.20 | 32.21 | 4528.1 | 15.63 |
| 298.15 | 25.57 | 34.43 | 5163 | 17.12 |

TABLE 5.—*continued*

| $T$ / K | $C_p$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$ | $\{S^\circ(T) - S^\circ(0)\}$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$ | $\{H^\circ(T) - H^\circ(0)\}$ / $\mathrm{cal_{th}\,mol^{-1}}$ | $-\{G^\circ(T) - H^\circ(0)\}/T$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$ |
|---|---|---|---|---|
| Gadolinium trichloride | | | | |
| 5 | (0.209)[a] | (3.939)[a] | (5.9)[a] | (2.75)[a] |
| 10 | 0.218 | 4.059 | 6.858 | 3.373 |
| 15 | 0.536 | 4.201 | 8.658 | 3.623 |
| 20 | 1.038 | 4.419 | 12.524 | 3.793 |
| 25 | 1.688 | 4.718 | 19.284 | 3.947 |
| 30 | 2.456 | 5.092 | 29.597 | 4.106 |
| 35 | 3.321 | 5.535 | 44.004 | 4.278 |
| 40 | 4.262 | 6.039 | 62.94 | 4.466 |
| 45 | 5.252 | 6.598 | 86.71 | 4.671 |
| 50 | 6.271 | 7.204 | 115.50 | 4.894 |
| 60 | 8.319 | 8.529 | 188.50 | 5.387 |
| 70 | 10.255 | 9.959 | 281.51 | 5.937 |
| 80 | 12.003 | 11.445 | 392.97 | 6.532 |
| 90 | 13.540 | 12.949 | 520.9 | 7.162 |
| 100 | 14.871 | 14.446 | 663.1 | 7.816 |
| 110 | 16.01 | 15.92 | 817.7 | 8.486 |
| 120 | 17.00 | 17.36 | 982.8 | 9.165 |
| 130 | 17.84 | 18.75 | 1157.1 | 9.849 |
| 140 | 18.57 | 20.10 | 1339.3 | 10.533 |
| 150 | 19.20 | 21.40 | 1528.2 | 11.215 |
| 160 | 19.74 | 22.66 | 1722.9 | 11.891 |
| 170 | 20.22 | 23.87 | 1922.8 | 12.560 |
| 180 | 20.63 | 25.04 | 2127.1 | 13.221 |
| 190 | 20.99 | 26.16 | 2335.2 | 13.873 |
| 200 | 21.31 | 27.25 | 2546.8 | 14.515 |
| 210 | 21.60 | 28.30 | 2761.4 | 15.15 |
| 220 | 21.86 | 29.31 | 2978.7 | 15.77 |
| 230 | 22.10 | 30.28 | 3198.6 | 16.38 |
| 240 | 22.32 | 31.23 | 3420.7 | 16.98 |
| 250 | 22.53 | 32.14 | 3645.0 | 17.56 |
| 260 | 22.72 | 33.03 | 3871.2 | 18.14 |
| 270 | 22.90 | 33.89 | 4099.4 | 18.71 |
| 280 | 23.07 | 34.73 | 4329.3 | 19.27 |
| 290 | 23.24 | 35.54 | 4560.8 | 19.81 |
| 300 | 23.40 | 36.33 | 4794.0 | 20.35 |
| 310 | 23.54 | 37.10 | 5029 | 20.88 |
| 320 | 23.67 | 37.85 | 5265 | 21.40 |
| 330 | 23.76 | 38.58 | 5502 | 21.91 |
| 340 | 23.82 | 39.29 | 5740 | 22.41 |
| 350 | 23.87 | 39.98 | 5978 | 22.90 |
| 273.15 | 22.96 | 34.16 | 4171.6 | 18.89 |
| 298.15 | 23.37 | 36.19 | 4750.8 | 20.25 |

[a] Based on thesis data of A. F. G. Wyatt, Oxford, 1963.

for some 50 per cent error at 5 K, the curve of this investigation is lower by a factor of 3 to 4 than any reasonable extrapolation of their curve. No reasonable join could be found even were the points of the present study to be called into question at temperatures as high as 10 K. Indeed, the curve found here implies that the first Schottky level should be some 30 per cent higher than the spectroscopic value. Furthermore, the downward shift of the level suggested by Colwell *et al.* would displace the maximum of the Schottky peak to lower temperatures whereas an upward shift is required to reproduce the Schottky behavior noted in this work over a much wider range of temperature. The $SmCl_3$ cooperative magnetic-ordering transition occurs at much lower temperatures than for either $PrCl_3$ or $NdCl_3$. Colwell *et al.* report little success in attempts to fit their results to a theoretical model. The entropy between 0.313 K and 4 K is about 0.68 $cal_{th}\ K^{-1}\ mol^{-1}$.† Since the transition occurs at low temperatures, the separation of cooperative and non-cooperative entropy contributions is evident; the entropy increments below 5 K will be taken as $R \ln 2$ (in preference to the measured values of Colwell *et al.*) plus a small lattice contribution (0.005 $cal_{th}\ K^{-1}\ mol^{-1}$ as that for $LaCl_3$ and $EuCl_3$). An approximation in keeping with these results is made in specifying the attendant enthalpy increment; the excess entropy is regarded as a spike of zero width at $T = 0.3$ K and the enthalpy approximated as $R \ln 2 \times 0.3\ K = 0.4\ cal_{th}\ mol^{-1}$. This is reasonable in comparison with the values for $PrCl_3$ and $NdCl_3$ (about 1 $cal_{th}\ mol^{-1}$) but is probably a slight overestimate since the "average" magnetic ordering temperature is probably somewhat lower than 0.3 K.

The values of Colwell *et al.* have been ignored almost entirely for $SmCl_3$ in favor of the theoretically formulated values.

## EUROPIUM TRICHLORIDE

The ground state of Eu(III), $^7F_0$, is non-degenerate and the first component of the next *J*-state occurs at 355 $cm^{-1}$ above the ground state.(11) At 5 K, the Boltzmann factor between the ground state and the center of gravity of the $^7F_1$ state shows that the relative population of the $^7F_0$ and $^7F_1$ states is about $10^{47}$, so that the upper state has negligible effect. Therefore, both $LaCl_3$ and $EuCl_3$ are characterized by lattice-only heat-capacity contributions—below 20 K—due mostly to acoustical contributions. This can be justified by the use of the $\Theta_D$ value of Varsanyi and Maita(12) and the lattice vibrational frequencies of Stedman and Newman.(13) Since heat capacity due to the 21 optical-branch frequencies is very small at the lowest temperatures, the optical contribution is effectively zero at 5 K, 2 per cent of the total at 10 K, 13 per cent at 15 K, and 25 per cent at 20 K. Thus, in the absence of extreme differences in the optical-branch frequencies between $LaCl_3$ and $EuCl_3$, such differences in the heat capacities as exist for these two compounds are largely due to differences in acoustical vibrations. A plot of $C_p/T$ against $T^2$ for both $LaCl_3$ and $EuCl_3$ is given in figure 2. The value of Varsanyi and Maita of (118±1) K is in good agreement with the value of this study, (119±8) K. Despite the large uncertainty in the $\Theta_D$, it is clear from figure 2 that $LaCl_3$ and $EuCl_3$ have nearly identical

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

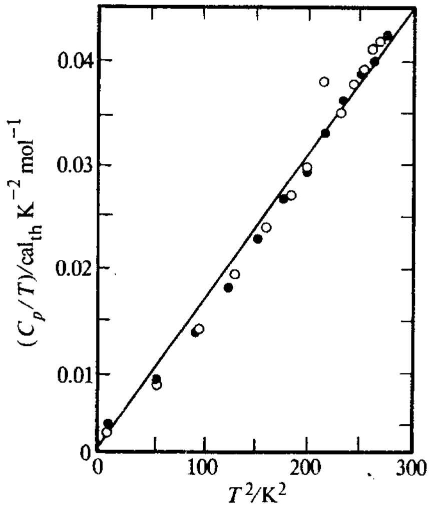

FIGURE 2. Plot of $C_p/T$ against $T^2$. ○, $LaCl_3$; ●, $EuCl_3$.

heat capacities over this range. The range of variation of the molecular weight and molar volume covered by this pair is nearly the entire range of this study. Thus, this pair should show almost the maximum variation in $\Theta_D$ but no variation is found. Application of the Lindemann melting formula(14) is precluded by decomposition of solid $EuCl_3$ with loss of $Cl_2$. Although the relative magnitude of $\Theta_D$ cannot be specified for this pair, application of the Lindemann melting rule to the pair $LaCl_3$ and $GdCl_3$ yields the quantity $\Theta_D(GdCl_3)/\Theta_D(LaCl_3) = 0.874$, or a $\Theta_D$ for $GdCl_3$ of about 102 K. The $LaCl_3$-$GdCl_3$ pair spans the entire range of parameters involved in the Lindemann comparison but should be fairly close to that for the pair $LaCl_3$-$EuCl_3$; a direct comparison for the former pair is not possible due to the enhanced heat capacity from the magnetic ordering found at the lowest temperatures of this study. The near coincidence of the curves for $LaCl_3$ and $EuCl_3$ below about 20 K shows much less dependence of $\Theta_D$ for this series on the various parameters than the Lindemann rule which suggests no variation at all in the $\Theta_D$ values for these compounds; and hence, no difference in the acoustical heat capacity. In the light of figure 2, it seems reasonable to attribute identical $\Theta_D$'s to each member of the series. Certainly, in terms of the low-temperature augmentation of the thermodynamic functions, such an assumption will not be serious since the increments will be small.

## GADOLINIUM TRICHLORIDE

The high-temperature tail of the prominent ferromagnetic transition at 2.2 K is clearly evident in the heat capacity of this experiment below about 20 K. Even though the experimental measurements of Leask, Wolf, and Wyatt(2) extend only to 1.2 K, the magnetic entropy is established by higher-temperature magnetic heat capacity and interaction studies. Leask *et al.* present the heat capacities of Wyatt's thesis,(15) used the experimentally derived value of $\{S°(4.2\ \mathrm{K})-S°(1.2\ \mathrm{K})\} = 2.397$

$\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$ and an extrapolation of the $T^{-2}$-dependent high-temperature magnetic heat capacity to find $\{S^\circ(1.2\text{ K})-S^\circ(0)\}$ by subtraction from $R\ln 8$; this gave a value of 1.592 $\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$. Several later studies have concentrated on the measurement of the magnetic heat capacity and its expression, valid for $T > T_c$, as a power series:(16)

$$C_{\text{mag}} = R\sum_{n=2}^{n=\infty} C_n/T^n.$$

The $C_n$'s are related to exchange constants. Only $C_2$ and $C_3$ are needed and the resulting expression $C_{\text{mag}} = RC_2/T^2+RC_3/T^3$ has served as the basis for analyzing the high-temperature magnetic heat capacity. Two of the most recent studies are in good agreement on the values of $C_2$ and $C_3$; Clover and Wolf,(17) and Birgeneau, Hutchings, and Wolf,(18) find $C_2$ and $C_3$ values of $(3.36\pm0.012)$ $K^2$ and $(-5.3\pm0.4)$ $K^3$, and $(3.2\pm0.3)$ $K^2$ and $(-4.9\pm1.0)$ $K^3$, respectively. The values allow a better value of $\{S^\circ(\infty)-S^\circ(4.2\text{ K})\}$ and hence a more reliable estimate of $\{S^\circ(1.2\text{ K})-S^\circ(0)\}$ with reference to a total of $R\ln 8$. The former values of $C_2$ and $C_3$ were chosen and determine $\{S^\circ(\infty)-S^\circ(4.2\text{ K})\} = 0.236$ $\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$, and $\{S^\circ(1.2\text{ K})-S^\circ(0)\} = 1.499$ $\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$. The choice of $C_2$ and $C_3$ is somewhat arbitrary, but the difference in the entropy increments which it implies is very small. In either case, the value of $\{S^\circ(1.2\text{ K})-S^\circ(0)\}$ is specified within rather narrow limits. An attempt was made to extrapolate judiciously the plot of $C_p/T$ against $T$ for Wyatt's data to $T = 0$. The entropy was found to be about 1.5 $\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$ below 1.2 K in good agreement with the calculation. From the curve, it seems that such a plot will have a broad maximum at about 1.2 K. One may infer from the heat-capacity plot of Hovi, Vuola, and Salmonpera(19) that the curve of Wyatt's data has too small a temperature dependence as $T \rightarrow 0$ and that a shoulder rather than a maximum might be a more "natural" description of the $C_p/T$ against $T$ plot. However, the estimate from the extrapolation of 1.5 $\text{cal}_{\text{th}}$ $K^{-1}$ $\text{mol}^{-1}$ is quite reasonable. The enthalpy increment in this region was obtained by a similar extrapolation, and is given rather wide error limits; the enthalpy increment in the region 1.2 to 4.2 K was found directly.

The total heat capacity in the region near 5 K was approximated with the aid of other experiments. The lowest three points of this study seem to be in substantial error, as shown in figure 3. If the high-temperature magnetic-heat-capacity studies are to be regarded as correct, this contribution plus any reasonable lattice estimate forces the curve to reach a minimum between 7 and 8 K. Such calculations, using the $\Theta_D$ value of 118 K and the $C_2$ and $C_3$ values above were used to arrive at the short-dash curve of figure 3 as the probable heat capacity in the region 4.2 to about 8 K. This curve joins very well on the low-temperature side with Wyatt's data and on the high-temperature side with the curve of the present study at about 8 K. A further check on this drawn curve is that the difference in the heat capacity between $GdCl_3$ and $EuCl_3$ agrees fairly well with the calculated magnetic-heat-capacity in the region near 8 K. At higher temperatures, the experimental $GdCl_3$ curve lies higher but shows similar temperature dependence. This difference could be due to appreciably different acoustical heat-capacity contributions, although this would be

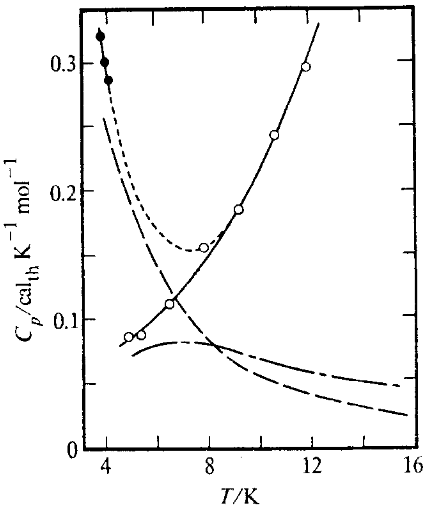

FIGURE 3. Low-temperature heat capacity of $GdCl_3$. ○, This research; ●, Wyatt;(2, 15) – – –, selected heat-capacity curve; ——, $C_{mag}$ (reference 16); –·–·–, $\{C_p(GdCl_3) - C_p(EuCl_3)\}$ for comparison with $C_{mag}$.

in contradiction to assumptions made for the other lighter halides of this study. There is also strong evidence that the lower lattice vibrational frequencies are smaller for $GdCl_3$ than for $EuCl_3$.(20) The dashed curve patching the two sets of calorimetric heat capacities, which, as seen above, has strong justification, was used to evaluate the entropy and enthalpy increments between 4.2 and 9 K as summarized in table 6.

TABLE 6. Low-temperature entropy and enthalpy increments for $GdCl_3$ ($\mathrm{cal_{th}} = 4.184$ J)

| $\frac{T_1}{\mathrm{K}}$ | $\frac{T_2}{\mathrm{K}}$ | $\frac{S^\circ(T_2) - S^\circ(T_1)}{\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}}$ | $\frac{H^\circ(T_2) - H^\circ(T_1)}{\mathrm{cal_{th}\,mol^{-1}}}$ | Source |
|---|---|---|---|---|
| 0 | 1.2 | 1.499 | 1.2 | *a,b* |
| 1.2 | 4.2 | 2.397 | 4.463 | *c* |
| 4.2 | 5 | 0.043 | 0.261 | *d* |
| 5 | 9 | 0.099 | 0.734 | *d* |
| 9 | 298.15 | 32.15 | 4744.1 | *e* |
| Total | | | | |
| 0 | 298.15 | 36.19 | 4750.8 | |

[a] By difference between [c] and $R \ln 8$ (see text) based upon high-temperature expansion of $C_{mag}$ of reference 16 using coefficients of reference 17.

[b] Graphical estimation.

[c] Data of Wyatt, references 2 and 15.

[d] Graphical evaluation of selected curve.

[e] Integration of fitted curve of points of this investigation.

## 4. Discussion

### COMPARISON WITH ENTROPY ESTIMATION SCHEMES

In predicting the cation contribution to $S^\circ(298.15\ \mathrm{K})$ to vary logarithmically with mass, the refined Latimer method[21] implies that Gd(III) will contribute 14.3 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ in comparison with 13.8 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ for La(III). This trend is perhaps the failure of this method in its application to lanthanide salts. It appears that a universal feature of lanthanide-compound thermophysical behavior is that the heat capacity of the Gd(III) salt is lower over most of the temperature range than its La(III) analog. This requires the entropy of the Gd(III) salt to be lower, which is properly taken into account in the method of Westrum;[22] which originated from extension of an earlier scheme for transition element chalcogenides in an analysis of the heat-capacity data for the lanthanide sesquioxides. The scheme proposes a gradual decrease in the cation contribution with atomic number, from 15.2 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ for La(III) to 13.0 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ for Lu(III). The Latimer scheme is still useful in its prediction of the anion contribution. Latimer takes the value of 6.9 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ for $\mathrm{Cl^-}$ ion in salts of the formula $\mathrm{MCl_3}$; this value was deduced from measurements on only two compounds, $\mathrm{CrCl_3}$ and $\mathrm{VCl_3}$, and thus is drawn from a limited data base which is without lanthanide "representation". The values of $S^\circ(298.15\ \mathrm{K})$ available from Latimer scheme information are presented in table 7 under the heading "Latimer". Since the method of Westrum is correct in predicting the decrease in cation contribution and comes from lanthanide sources, it is of interest immediately to compare the $\mathrm{Cl^-}$ contribution implied by the present study with that of the Latimer scheme; such a comparison shows that a contribution of 5.9 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ obtains against that of 6.9 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ proposed by Latimer.

The magnetic contribution, as suggested by Westrum, can be approximated as $R\ln(2J+1)$. Addition of these approximate magnetic contributions to the Latimer

TABLE 7. Comparison of some trihalide entropy estimation schemes ($\mathrm{cal_{th}} = 4.184$ J)

| Compound | $S^\circ(298.15\ \mathrm{K}) - S^\circ(0)$ / $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ | | | | |
|---|---|---|---|---|---|
| | Latimer | Latimer augmented[a] | Westrum[a, b] augmented | "Spectroscopic" | This investigation |
| $\mathrm{LaCl_3}$ | 34.5 | 34.5 | 33.1 | 32.47 | 32.88 |
| $\mathrm{CeCl_3}$ | 34.5 | 38.1 | 36.1 | 35.99 | (36.0)[c] |
| $\mathrm{PrCl_3}$ | 34.5 | 38.9 | 36.8 | 36.74 | 36.64[d] |
| $\mathrm{NdCl_3}$ | 34.6 | 39.2 | 36.8 | 36.84 | 36.67 |
| $\mathrm{PmCl_3}$ | 34.7 | 39.5 | 36.8 | 36.82 | (37.0)[c] |
| $\mathrm{SmCl_3}$ | 34.8 | 38.4 | 35.7 | 36.10 | 35.88 |
| $\mathrm{EuCl_3}$ | 34.8 | 37.3 | 34.5 | 34.70 | 34.43 |
| $\mathrm{GdCl_3}$ | 35.0 | 39.1 | 36.0 | 36.60 | 36.19 |

[a] By $R\ln(2J+1)$; the $(\mathrm{Cl_3})^{3-}$ ion contribution is taken as 20.7 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$.

[b] By $R\ln(2J+1)$; the $(\mathrm{Cl_3})^{3-}$ ion contribution is taken as 17.9 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$.

[c] Parentheses denote values involving interpolated lattice and calculated Schottky contributions.

[d] Based on 0.294 K.

and Westrum cation values (the latter augmented with the adjusted $Cl^-$ contribution) appear in table 7 as "Latimer$+R\ln(2J+1)$" and "Westrum, augmented", respectively.

A further option represents values obtained by recourse to spectroscopic information. Employing the $\Theta_D$ value of Varsanyi and Maita(12) of 118 K for $LaCl_3$ as the only "calorimetric" input and using the energy levels of Ln(III) ions in $LaCl_3$ of Dieke(23) and the calculated frequencies of Stedman and Newman(13) for $LaCl_3$, the entropies of the salts can be derived as shown under the heading "Spectroscopic". This last and rather convoluted estimate does not display the established decrease with cation mass but further refinement—although within the bounds of spectroscopic information—would be too heavily biased by hindsight. Hence, this estimate incorporates only previously available information and the cation-attendant decrease is used in proposing the entropy values for $CeCl_3$ and $PmCl_3$; these latter are left as a benchmark for comparison with future determinations.

## THERMODYNAMICS OF FORMATION AT 298.15 K

The values of $\Delta H_f^\circ(298.15\ K)$ reported by Schumm, Wagman, Bailey, Evans, and Parker(24) in the recent N.B.S. Technical Note 270–7 are used in calculating the values of $\Delta G_f^\circ(298.15\ K)$. For $Cl_2(g)$ the recommended value from CODATA Bulletin 10(25) (53.29 $cal_{th}\ K^{-1}\ mol^{-1}$) is used for $S^\circ(298.15\ K)$; this value is identical to that listed in the JANAF tables(26) which is the source of $C_p^\circ$ at 298.15 K (8.111 $cal_{th}\ K^{-1}\ mol^{-1}$). The estimates of $C_p^\circ$ and $S^\circ$ at 298.15 K of this study are used for $CeCl_3$. The values for $\Delta G_f^\circ$ shown in table 8, are invariably quite negative, well below

TABLE 8. Thermodynamics of formation for $LnCl_3$ at 298.15 K
$Ln(c) + \frac{3}{2}Cl_2(g) = LnCl_3(c)$[a]
($cal_{th} = 4.184$ J)

| Compound | $\Delta H_f^\circ$ $kcal_{th}\ mol^{-1}$ | $\Delta S_f^\circ$ [b, c] $cal_{th}\ K^{-1}\ mol^{-1}$ | $\Delta G_f^\circ$ $kcal_{th}\ K^{-1}\ mol^{-1}$ | $\Delta C_{p,f}$ [d] $cal_{th}\ K^{-1}\ mol^{-1}$ |
|---|---|---|---|---|
| $LaCl_3$ | −256.0 | −60.65[e] | −237.9 | 4.78 |
| $CeCl_3$ | −251.8 | (−61.14)[f] | (−233.6) | (4.89) |
| $PrCl_3$ | −252.6 | −60.79 | −234.5 | 4.98 |
| $NdCl_3$ | −248.8 | −60.36 | −230.8 | 4.99 |
| $PmCl_3$ | (−245)[g] | (−60.2)[h] | (−277) | — |
| $SmCl_3$ | −245.2 | −60.68 | −227.1 | 4.56 |
| $EuCl_3$ | −223.7 | −63.79 | −204.7 | 6.79 |
| $GdCl_3$ | −241 | −60.01 | −223 | 2.35 |

[a] Parentheses indicate estimated values employed.

[b] Reference 24.

[c] Table 7 for $S^\circ(LnCl_3, 298.15\ K)$; reference 24 for Ln(c); Stuve, J. M. U.S. Bur. Mines, Rept. Invest. No. 6640 1965, for $Cl_2(g)$.

[d] $C_p^\circ(Cl_2, g)$ taken from reference 26.

[e] α-form of La(c), reference 24.

[f] γ-form of Ce(c), reference 24.

[g] Estimated in Feber, R. C. U.S. At. Energy Comm. Rept. LA-3164 1964.

[h] $S^\circ$(Pm, c, 298.15 K) estimated in Wicks, C. E.; Block, F. E. Thermodynamic properties of 65 elements—their oxides, halides, carbides and nitrides. Bur. Mines Bull. 605. U.S. Government Printing Office: Washington D. C. 1963.

$-200$ $\mathrm{kcal_{th}\ mol^{-1}}$. The effect of the $T\Delta S_f^\circ$ term is to raise the $\Delta G_f^\circ$ values relative to the $\Delta H_f^\circ$ ones due to the large entropy of $Cl_2(g)$. The trend in $\Delta G_f^\circ$ parallels that for $\Delta H_f^\circ$, and indeed $\Delta G_f^\circ \approx \Delta H_f^\circ$.

## OTHER THERMODYNAMIC MEASUREMENTS

Serious gaps exist in enthalpy measurements above 298.15 K for the series. Walden and Smith(27) have measured the enthalpy of $CeCl_3$ from 273.15 to 1200 K by the method of mixtures with a Bunsen ice calorimeter receiver. Using a copper-block drop calorimeter, Dworkin and Bredig made enthalpy measurements through the melting temperatures ($T_m$) for $LaCl_3$, $PrCl_3$, and $NdCl_3$,(28) and for $GdCl_3$,(29) but report only the quantities $\{H^\circ(T_m)-H^\circ(298.15\ \mathrm{K})\}$, $\Delta H_m$, and $\Delta S_m$. Data exist on the high-temperature vaporization behavior but the information available concerning gas-phase vibration frequencies is inadequate to allow a third-law analysis of these values.

## SAMARIUM TRICHLORIDE

As noted previously, the results of the present investigation seem to disagree with other studies. Unfortunately, the spectroscopic information is somewhat limited compared with that of other members of the series. Experiments which might be able to reconcile the apparent differences have not been performed.

The energy level scheme for Sm(III) (and for Eu(III)) in $LaCl_3$ is shown in table 9. This is taken from Dieke(23) based on measurements of Magno and Dieke.(10) Their data shows the $^6H_{5/2}$ ground state to consist of three Kramers' doublets at 0.0 ($\mu = 1/2$), 40.7 ($\mu = 3/2$), and 66.1 $\mathrm{cm^{-1}}$ ($\mu = 5/2$). These levels are quite low and this implies a large Schottky heat capacity at low temperatures. In contrast to the situation for $PrCl_3$ and $NdCl_3$, the next $J$-state, $^6H_{7/2}$, is not insignificantly populated at 350 K; its lowest level and center of gravity lie at 992.8 and 1080.3 $\mathrm{cm^{-1}}$, respectively. The second-higher $J$-state, $^6H_{9/2}$, makes an insignificant contribution, with its lowest level and center of gravity at 2211.7 and 2290.3 $\mathrm{cm^{-1}}$. The calculated

TABLE 9. Crystal-field levels for $SmCl_3$ and $EuCl_3$; $\Delta E$ denotes the energy above ground, $\mu$ crystal quantum number, and $g$ degeneracy of level

| | $SmCl_3$[a] | | | | $EuCl_3$[b] | | |
|---|---|---|---|---|---|---|---|
| $J$-state term | $\Delta E/\mathrm{cm^{-1}}$ | $\mu$ | $g$ | $J$-state term | $\Delta E/\mathrm{cm^{-1}}$ | $\mu$ | $g$ |
| $^6H_{5/2}$ | 0.0 | 1/2 | 2 | $^7F_0$ | 0.00 | 0 | 1 |
| | 40.7 | 3/2 | 2 | $^7F_1$ | 355.05 | 1 | 2 |
| | 66.1 | 5/2 | 2 | | 405.27 | 0 | 1 |
| $^6H_{7/2}$ | 992.8 | 3/2 | 2 | $^7F_2$ | 1022.54 | 2 | 2 |
| | 1051.2 | 5/2 | 2 | | 1027.54 | 1 | 2 |
| | 1104.7 | 1/2 | 2 | | 1084.33 | 0 | 1 |
| | 1172.6 | 5/2 | 2 | | | | |
| | Next level at 2211.7 $\mathrm{cm^{-1}}$ | | | | Next level at 1846.77 $\mathrm{cm^{-1}}$ | | |

[a] Reference 23. [b] Reference 40.

Schottky heat capacity reaches a minimum at 173.2 K and continues to rise beyond the highest temperature of the heat-capacity measurements (350 K) as a consequence of the $^6H_{7/2}$ levels. The lower-temperature maximum, due mostly to $^6H_{5/2}$ levels, occurs at 28.16 K and has the value 1.386 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$.

The comparison of the calculated and experimental curves is shown in figure 4. The qualitative features of the calculated curve, including the minimum, are reproduced by the experimental one, but there is serious disagreement between the two $T_{\max}$ values and in the heat capacities below 20 K. In this region the differences between lattice heat capacities should be small, so that the discrepancy in the region near 10 K, where the experimental Schottky heat capacity is too small by a factor of 2, together with the upward shift of nearly 20 per cent in the value of $T_{\max}$ argues strongly against the location of the $\mu = 3/2$ level at 40.7 $\mathrm{cm^{-1}}$. (The single bad point seen in the figure 4 at about 32 K is the result of a mistake in switching on the adiabatic shields in the changeover from manual to automatic operation.) A slight shift in $T_{\max}$ might result from a marked difference in lattice heat capacities between $LaCl_3$ and $SmCl_3$, but as seen from the figure, this would hardly account for the

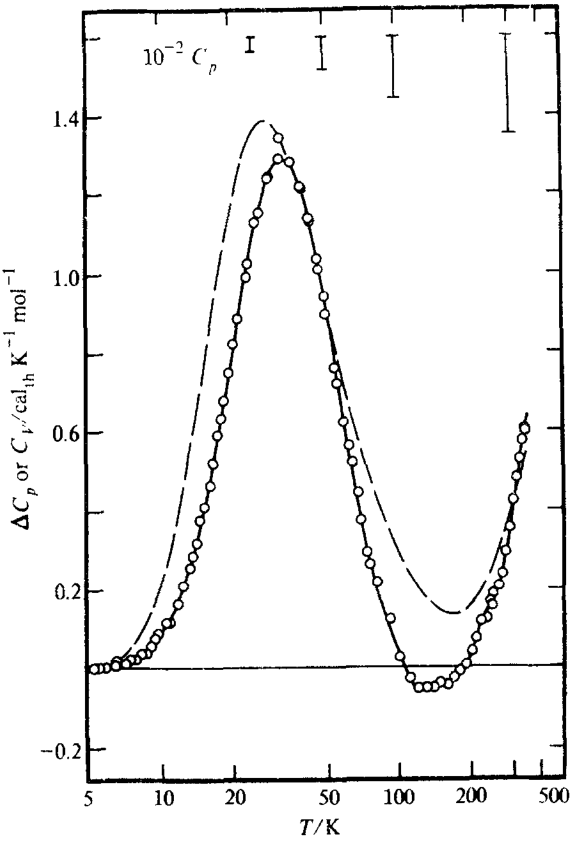

FIGURE 4. Schottky heat capacity for $SmCl_3$. ○, $\{C_p(SmCl_3) - C_p(LaCl_3)\}$; ——, $C_V$(Schottky, calc.).

region of near-coincidence which occurs from about 38 to about 55 K. To find the type of behavior observed for $PrCl_3$ and $NdCl_3$, the experimental curve must be "shrunk" but not greatly displaced relative to the calculated one.

In view of the qualitative agreement found between the calculated and experimental curves, and of the solid footing upon which both may be presumed to rest, it is suggested that the rather stark discrepancy stems not from any inaccuracy in either of the two methods, but rather from a failure to meet the "appropriateness" criterion, demonstrated for $PrCl_3$ and $NdCl_3$,(1) whereby the spectroscopic energy levels are assumed not to vary in the process of extrapolation from, say, 2 per cent to 100 per cent of Ln(III). Why this should be so for Sm(III) but not for Nd(III) or Pr(III) is puzzling.

The studies which through measurements or otherwise bear on the positions of the energy levels of $^6H_{5/2}$ in $SmCl_3$ are summarized in table 10. These include the optical spectra of Magno and Dieke,(10) on which the calculated curve is based, the e.p.r. work of Hutchison and Wong,(30) and far-i.r. absorption study of Hadni,(31) the heat-capacity results of Colwell, Mangum, and Utton,(9) the spin-lattice relaxation experiments of Mikkelson and Stapleton(32) and of Mangum and Hudson,(33) and the paramagnetic susceptibility study of Thomas.(34) Also shown are the values which provide the best fit to the heat capacities of the present investigation below about 17 K and best reproduce the experimental value of $T_{max}$ .These are found to be $(55 \pm 3)$ $cm^{-1}$ for $\mu = 3/2$ and $(70 \pm 5)$ $cm^{-1}$ for $\mu = 5/2$. Several alternatives were explored; the heat capacity below 17 K proved to be fairly sensitive to the choice for $\mu = 3/2$ and the value of $T_{max}$ rather less so. This trial-and-error fitting process produced no combination of the two excited levels which fitted the experimental difference well. The difference between the experimental and calculated Schottky curves requires a marked upward shift in the $\mu = 3/2$ level. As for the less-serious

TABLE 10. Energy levels of $^6H_{5/2}$ for $SmCl_3$,[a] $\Delta E/cm^{-1}$, and crystal quantum number $\mu$

| | | | | | | Spin-lattice relaxation | | | $C_p$ |
|---|---|---|---|---|---|---|---|---|---|
| $\mu$ | Opt. spect.[b] | e.p.r.[c] | | i.r. Absorp.[d] | Paramag. Suscept.[e] | Ref. *f* | Ref. *g* | Ref. *h* | This study[i] |
| 5/2 | 66.1 | 52.6[j] | 38.5[k] | 65 | Possibly between 11 and 99 $cm^{-1}$ | — | — | — | $70 \pm 5$ |
| 3/2 | 40.7 | 49.9 | 39.0 | 40 | Possibly between 10.7 and 66 $cm^{-1}$ | Apparently consistent with Dieke and Magno(10) | 30.8 | 32 | $55 \pm 3$ |

[a] In all cases, $\mu = 1/2$ is taken at 0.0 $cm^{-1}$. [b] By optical spectroscopy; Magno and Dieke, reference 10. [c] By e.p.r.; Hutchison and Wong, reference 30. [d] By far-infrared absorption; reference 31. [e] By paramagnetic susceptibility; Thomas, reference 34. [f] By spin-lattice-relaxation; Mikkelson and Stapleton, reference 32. [g] By spin-lattice-relaxation; Mangum and Hudson, reference 33. [h] By heat-capacity data: Colwell *et al.*, reference 9. [i] By heat-capacity data; this research. [j] Without correction of $PrCl_3$ crystal field parameters to $Z = 62$ [Sm(III)]. [k] With this correction.

discrepancy observed for $PrCl_3$,$^{(1)}$ the most favorable temperature region over which to compare the trial level spacings and the experimental curve is from about 7 K to 19 K. The shape of the curve is such that it seems to be "too high" at the lower end and "too low" at the high-temperature end. Indeed, by choosing values for $\mu = 3/2$ which fit over successive limited temperature ranges, the experimental curve can be mimicked by a Schottky function in which the $\mu = 3/2$ level rises in value by about 1 $cm^{-1}$ $K^{-1}$. There is certainly no provision for this type of behavior in the simple Schottky model. The studies of references 10 and 30 to 33 employed Sm(III)-doped $LaCl_3$ in mole percentages of less than 5. References 9 and 34 report studies carried out on pure $SmCl_3$. Some of the authors acknowledge the presence of Sm(II) as impurity in the crystal preparations. The Sm(II) fluorescence spectrum was first studied by Dieke and Sarup$^{(35)}$ in an effort to account for some unclassified lines in the spectra of Sm(III) and Tm(III) in $LaCl_3$. Eisenstein, Hudson, and Mangum$^{(36)}$ reported serious contamination by Sm(II) in their attempts to grow crystals of $SmCl_3$. Mikkelson and Stapleton$^{(32)}$ note that their crystals of Sm(III) in $LaCl_3$ were orange in color. Sm(II) salts are reddish-brown, whereas $SmCl_3$ is cream-colored. The existence of Sm(II) in the crystals should not give rise to spurious levels of low energies since it is isoelectronic with Eu(III) and its lowest level is at 272 $cm^{-1}$. A more serious consideration is the local distortion in the crystal lattice caused by the presence of the Sm(II), possibly by the occurrence of an interstitial positive ion, as suggested by Dieke,$^{(37)}$ which would disturb the hexagonal symmetry of the Ln(III) ion.

The paramagnetic-susceptibility studies were hampered in their flexibility to adjust energy levels to fit the susceptibilities, which unfortunately go down only to about 80 K, somewhat above the temperature region where the levels are being populated most rapidly. The equation used to describe the susceptibility is limited to a definite relation between the $\mu = 3/2$ and $\mu = 5/2$ levels and trial values between rather wide limits ($\mu = 3/2$; 10.7 to 66 $cm^{-1}$; $\mu = 5/2$; 11 to 99 $cm^{-1}$) do not give good agreement with the experimental data.

Spin-lattice relaxation measurements are limited in elucidating the separation between the ground and first excited state. For Kramers' salts, this is dependent upon the resolution of the relaxation rate, $\tau^{-1}$, into contributions for each of the three relaxation processes, the direct, the Orbach, and the Raman processes,$^{(38)}$ by an equation of the form:

$$\tau^{-1} = AT + B\exp(-\Delta/kT) + CT^9,$$

where $A$, $B$, and $C$ are constants and $\Delta$ is the energy increment between the ground and first excited levels ($\mu = 3/2$ in the case of $SmCl_3$). In their study of $LaCl_3$ containing 0.2 to 0.5 per cent Sm(III) from 1 to 4.2 K, Hudson and Mangum$^{(33)}$ found that subtraction of direct and Raman rates left an Orbach contribution consistent with $\Delta = 30.8$ $cm^{-1}$, a value which is in good agreement with a 20 per cent reduction (to 32 $cm^{-1}$) of the spectroscopic value implied by the heat-capacity data.$^{(9)}$ In measurements with the magnetic field parallel to the crystal c-axis, Mikkelson and Stapleton$^{(32)}$ find, over the temperature range 1.65 to 4.2 K, a fairly good fit to the above equation for samples containing 0.1 per cent Sm(III). They take the spectroscopic value for $\Delta$, yet their $A$ and $B$ constants differ from those of Hudson and Mangum. Thus, the two experiments lead to somewhat different conclusions regarding $\Delta$. The authors of reference 33, in commenting upon their results for Er(III), Ce(III), Nd(III), Ho(III), and Sm(III) ask the questions, also of concern to the present study, ". . . is $\Delta$ actually invariant for a particular ion . . .?" and "Can variations in the preparations of dilute crystals cause real variations in $\Delta$?"

If the higher displacement of the spectroscopic levels suggested by the present study is to be attributed to variation with composition, spectroscopic studies on variable mole fractions of Sm(III) might be expected to resolve the discrepancies. In the absence of such information it is of interest to speculate on possible effects of substitution of the paramagnetic cation into $LaCl_3$. For the lighter trihalides this substitution is into a matrix which, although isostructural, is characterized by larger lattice parameters; the effects should be greater for the members of larger atomic number. McLaughlin and Conway(39) have investigated the shifts in spectral lines of Pr(III) for appreciable mole fractions in $LaCl_3$, $CeCl_3$, $NdCl_3$, $SmCl_3$, and $GdCl_3$. The only crystal-field level of $^3H_4$ which was measured was $\mu = 3$ and it was seen to shift nearly linearly to lower energies with decreasing cation radius of the host, from 33.8 $cm^{-1}$ in $LaCl_3$ to 25 $cm^{-1}$ in $GdCl_3$; this shift to lower energies was found for all of the lines studied. The solution of Sm(III) in $LaCl_3$, on this argument, would be accompanied by a shift towards higher energies relative to that for pure $SmCl_3$. Since the spectroscopic levels are so low, no explanation for the observed heat capacity results. The position of $T_{max}$ is not highly dependent on the choice of this lattice heat capacity.

## EUROPIUM TRICHLORIDE

The calculated heat capacity for $EuCl_3$ must include the non-degenerate $^7F_0$ ground state and also the $^7F_1$, $^7F_2$, and $^7F_3$ $J$-states; the lowest levels and centers of gravity of the last three are at 355.05 and 371.79, 1022.54 and 1036.89, 1846.77, and 1887.13 $cm^{-1}$, respectively.(40) The calculated curve is shown in figure 5 together with the difference of the curves for $EuCl_3$ and $LaCl_3$. Since the lowest level is so energetic, the Schottky maximum will occur at a relatively high temperature and will be enhanced in width with respect to those for smaller level spacings. Hence, the experimental (total) heat capacity of $EuCl_3$ (see figure 1) lies above all the others at temperatures above about 150 K. The calculated maximum (2.286 $cal_{th}$ $K^{-1}$ $mol^{-1}$) is at 251 K. The experimental curve reaches a plateau centered at about 250 K, then begins to rise slightly near 300 K. This latter feature may be occasioned in part by the accumulated error in the subtractions which bring out small irregularities in the heat capacities of both $EuCl_3$ and $LaCl_3$. If the experimental curve were drawn with the proper curvature through the region where it appears to dip (near 270 K), only the point at 269 K lies outside the 0.2 per cent error limit (the high point at 246 K was not reproduced in subsequent redeterminations). There are no deviations greater than 0.08 per cent from the fitted curve. The third derivative of the total heat capacity will go to zero at about 292 K, and irregularities are exaggerated when the curve for $LaCl_3$ (which is about 92 per cent of the heat capacity of $EuCl_3$) is subtracted. None-

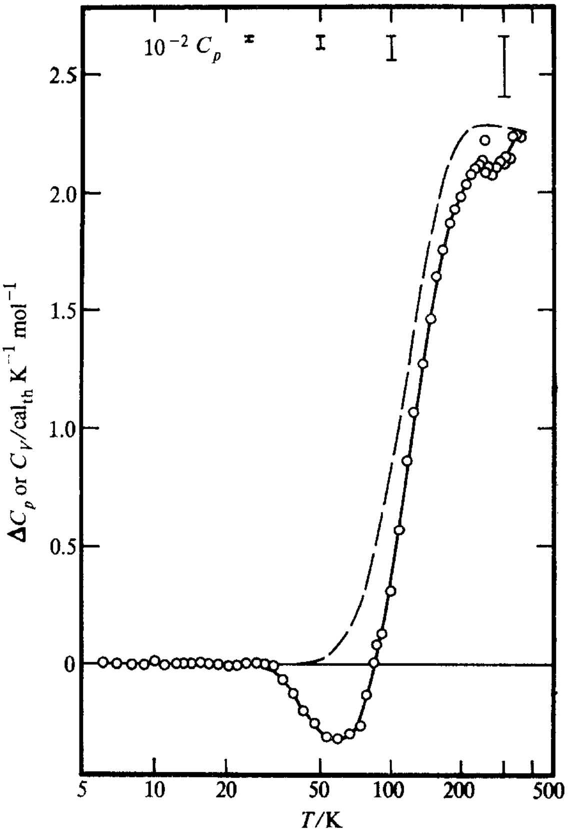

FIGURE 5. Schottky heat capacity for EuCl$_3$. ○, $\{C_p(\mathrm{SmCl_3}) - C_p(\mathrm{LaCl_3})\}$; – –, $C_v$ (Schottky, calc).

theless, the dip is slightly outside the stated error limits for the total heat capacity of EuCl$_3$.

The calculated Schottky heat capacity is effectively zero (less than 0.001 cal$_{th}$ K$^{-1}$ mol$^{-1}$) below about 39 K. This allows the effect of the difference in lattice heat capacity of EuCl$_3$ and LaCl$_3$ to be strikingly apparent since the experimental difference reaches a minimum at about 90 K before the rise of the Schottky contribution forces the curve rapidly upward. Similar—but more subtle—behavior was found for NdCl$_3$ near 20 K; it clearly demonstrates the inadequacy of LaCl$_3$ as a suitable lattice heat-capacity contribution. The minimum in the experimental Schottky heat capacity for EuCl$_3$ corresponds to the diminished heat capacity in the same temperature region for the other Schottky-containing compounds. When the lattice heat-capacity differences and experimental errors are allowed for, the irregularities in the experimental Schottky curves are quite small.

Upon heating EuCl$_3$ it transforms from a pale lemon-yellow color at 300 K to a darker and much more intense color. Near 570 K, the color was very intense, and the luster almost metallic. This intensification could be due to increased population of the $^7F_1$ *J*-state (the $^7F \rightarrow {}^5D$ transition is responsible for the color) since it was found that the compound becomes white upon immersion in liquid nitrogen. It might, however, be speculated that some other process becomes important near 300 K. The population change is entirely within the bounds of the Schottky phenomenon and would not be expected to cause anomalous heat-capacity behavior. This would, however, not necessarily be true for a more complicated electronic event. Noting the temperature-dependent color of $EuBr_3$, Haschke(4) has suggested a charge-transfer process for that compound, which culminates in the loss of $Br_2$. Since the same is true for $EuCl_3$ (although significant loss of $Cl_2$ occurs only at appreciably higher temperatures), such a mechanism might be responsible for the heat-capacity behavior observed at the high-temperature end of the present investigation. Charge-transfer spectra have been found by Barnes and Pincott(41) for $SmCl_3$ and $EuCl_3$; these occur as broad bands in the 300 K powder, reflection spectra at 37200 and 28000 $cm^{-1}$, respectively, and correlate roughly with the reduction potentials of Ln(III) ions.

## LATTICE HEAT CAPACITIES OF $LaCl_3$ AND $GdCl_3$

Although there is no Schottky contribution for $GdCl_3$, the difference in heat capacity between $LaCl_3$ and $GdCl_3$ is informative. The experimental difference will be strongly affected by the extended "tail" of the ferromagnetic ordering transition, which gives a significant contribution up to about 30 K, as found from the measurements of Clover and Wolf.(17) Over the rest of the temperature region, the difference should

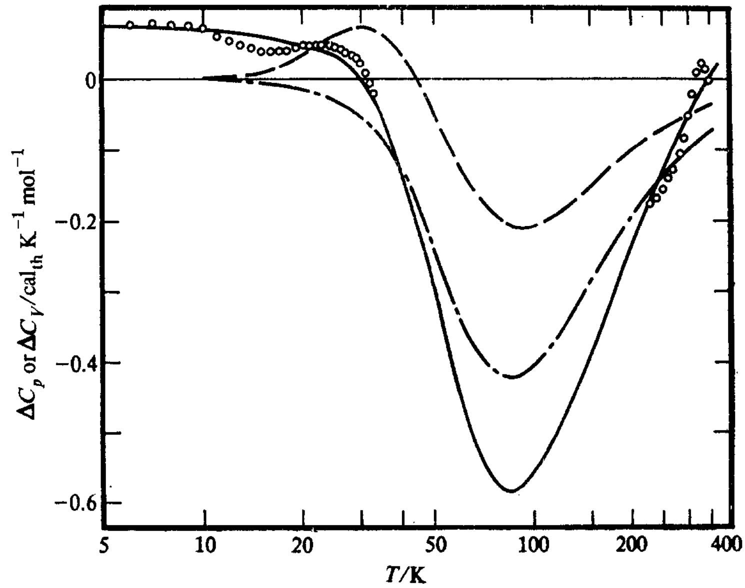

FIGURE 6. Lattice heat capacity for $GdCl_3$. ○, $\{C_p(GdCl_3) - C_p(LaCl_3)\}$; ——, $\{C_V(GdCl_3) - C_V(LaCl_3)\}$ based on Raman frequencies; —·—, $\{C_V(GdCl_3$, calculated, frequencies of reference 42) $- C_V(LaCl_3$, calculated, frequencies of reference 13)$\}$.

be a good indication of the difference in lattice heat capacity across the series, for this pair of compounds should exhibit the maximum difference in the series. The quantity $\{C_p(GdCl_3)-C_p(LaCl_3)\}$ is plotted as the solid line in figure 6. Also shown in this figure as the dashed line is the difference in heat capacity calculated by the use of Einstein heat-capacity functions of the 10 Raman frequencies for $GdCl_3$,(20, 42) and for $LaCl_3$.(43, 44) As expected, this difference is less pronounced since only 10 of the 21 optical frequencies are included. The dot-dash line in the figure is the difference in the complete set of frequencies which have been calculated for $LaCl_3$ by Stedman and Newman(13) and for $GdCl_3$ by Dawson and Schaack.(42) It is seen that the values of $T_{min}$ determined by the experimental and the two calculated methods agree quite closely, so that spectroscopic values indicate not only that the heat capacity of $LaCl_3$ is greater than that of $GdCl_3$, but semi-quantitatively account for the difference. The findings of Cohen and Moos(45, 46) from the vibronic spectra of Pr(III) in some of the other salts provide another point of comparison, even though the transitions observable in the spectra cannot be unambiguously assigned. If a direct average over the frequencies which have the same assignment (or "ambiguity" of assignment) for $LaCl_3$ and $GdCl_3$ is taken, an "average vibronic" frequency results which can be compared with weighted (according to the degeneracy of each mode) "average Raman" and "average calculated" frequencies. The results are summarized in table 11. It is seen that the different experimental methods produce roughly the same average frequency with approximately the same difference in these quantities for the two compounds. Similar correlations can be made between $LaCl_3$ and the other members of the series, though the effect of differences in lattice heat capacity are not so pronounced as for the $LaCl_3$-$GdCl_3$ pair.(47)

TABLE 11. Comparison of averaged assigned wavenumbers $\sigma$

| Summations | $\sigma/cm^{-1}$<br>$LaCl_3$ | <br>$GdCl_3$ | <br>Difference |
|---|---|---|---|
| Average Raman[a] | 176.9 | 182.7 | 5.8 |
| Average vibronic | 171.5 | 176.2 | 4.7 |
| Average calculated[a] | 177.5 | 184.0 | 6.5 |

[a] Weighted by degeneracies of each mode.

## LATTICE ENTROPIES

The confidence with which the lattice entropy deduced from the total heat capacity can be specified up to 298.15 K is somewhat limited, since it depends on the quality of the Schottky resolution. By restricting the region of comparison to the interval 10 to 298.15 K. the difficulties associated with extended short-range ordering contributions to the magnetic heat capacity can be avoided (except for $GdCl_3$ for which the magnetic entropy implied by the expansion formula of Marquard(16) using the coefficients of Clover and Wolf(17) must be deducted). The calculated Schottky entropies are deducted from the total (except for $SmCl_3$ where the optimal energy levels inferred from the best fit to the experimental difference between the heat capacity of $SmCl_3$ and $LaCl_3$ are used). The remaining monotonic decreasing quantities, designated $S^\circ_{\mathrm{lattice}}(LnCl_3)$, or lattice entropies, have values 32.84, 32.48, 32.28, 32.20, 32.16, and 32.10 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$ for $LaCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, and $GdCl_3$, respectively. These may be compared graphically with Westrum's cation contributions as in figure 7 by plotting the cation values as the abscissa and the quantity $\{S^\circ_{\mathrm{lattice}}(LnCl_3) - S^\circ_{\mathrm{lattice}}(LaCl_3)\}$ as the ordinate. The points (except for $NdCl_3$) fall fairly close to the line drawn. The deviation of $NdCl_3$ (lattice entropy too large by about 0.1 $\mathrm{cal_{th}\ K^{-1}\ mol^{-1}}$) could arise from an imperfect resolution of the Schottky contribution, although no strong argument is made for this. If the experimental differences in $S^\circ_{\mathrm{lattice}}$ as measured by this investigation were identical to the Westrum values, the line determined by the points would subtend a 45° angle with the abscissa, shown as the dashed line. That this is not the case is not surprising. Coincidence would require at a minimum, that the $Ln^{3+}$—$Cl^-$ and the $Cl^-$—$Cl^-$ force constants remain the same over the series and that the crystal structure be as "good" for $GdCl_3$ as for $LaCl_3$; available evidence seems to deny this. The figure is used to obtain corrected values for $S^\circ_{\mathrm{lattice}}$ for $CeCl_3$ and $PmCl_3$; these are used as the basis for estimation of $S^\circ(298.15\ \mathrm{K})$ in the last column of table 7.

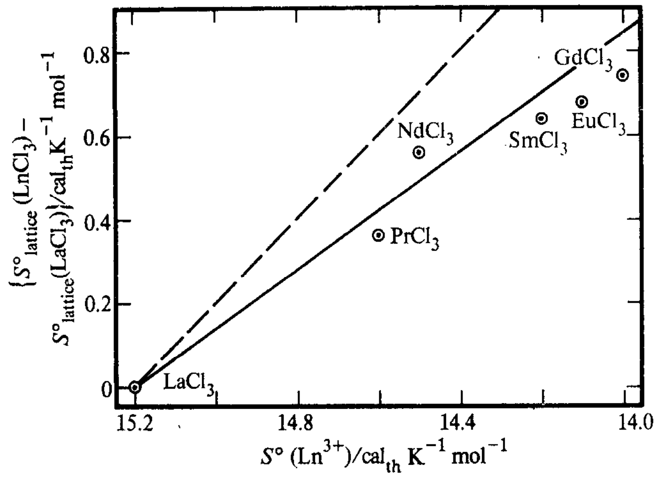

FIGURE 7. Lattice entropy comparison. ——, relationship between lattice entropies of this study and those of Westrum;(22) - - -, hypothetical line of equality of measured entropy and Westrum's cation lattice-entropy contributions.

An attempt was made to correlate the $S^\circ_{\mathrm{lattice}}$ values with several parameters such as molar volume, Ln(III) cation radius, density, atomic number, *etc.* As might be expected from the near-linearity of the plot in figure 7, the best correlation was found with the Ln(III) cation radius, though its superiority to those with other parameters was not great. Further correlations of the trends in lattice heat capacities are discussed elsewhere.(47)

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## REFERENCES

1. Sommers, J. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1976,** 8, 1115.
2. Leask, M. J. M.; Wolf, W. P.; Wyatt, A. F. G. *Proc. Int. Conf. Low. Temp Phys.*, 8th, London, **1962,** (pub. 1963) p. 230.
3. Polyachenok, O. G.; Novikov, G. I. *Zh. Neorg. Khim.* **1964,** 9, 773; cf. Russ. *J. Inorg. Chem.* **1964,** 9, 429.
4. Haschke, J. M. *J. Chem. Thermodynamics* **1973,** 5, 283.
5. Harris, A. L.; Veale, C. R. *J. Inorg. Nucl. Chem.* **1965,** 27, 1437.
6. Templeton, D. H.; Dauben, C. H. *J. Am. Chem. Soc.* **1954,** 76, 5237.
7. Morosin, B. *J. Chem. Phys.* **1968,** 49, 3007.
8. *Catalog of X-Ray Powder Data, American Society for Testing and Materials*, file card numbers: SmCl$_3$, 12–789; EuCl$_3$, 12–387.
9. Colwell, J. H.; Mangum, B. W.; Utton, D. B. *Phys. Rev.* **1969,** 181, 842.
10. Magno, M. S.; Dieke, G. H. *J. Chem. Phys.* **1962,** 37, 2354.
11. DeShazer, L. C.; Dieke, G. H. *J. Chem. Phys.* **1963,** 38, 2190.
12. Varsanyi, F.; Maita, J. P. *Bull Am. Phys. Soc.* **1965,** 10, 609.
13. Stedman, G. E.; Newman, D. J. *J. Phys. Chem. Solids* **1970,** 31, 1587.
14. Blackman, M. The Specific Heat of Solids. In *Encyclopedia of Physics*, Vol. 7, Part 1. Springer: New York. **1955,** 377.
15. Wyatt, A. F. G., Ph.D. Thesis, Oxford University, Oxford, England. **1963.**
16. Marquard, C. D. *Proc. Phys. Soc. London* **1972,** 92, 560.
17. Clover, R. B.; Wolf, W. P. *Solid State Commn.* **1968,** 6, 331.
18. Birgeneau, R. J.; Hutchings, M. T.; Wolf, W. *P. Phys. Rev.* **1969,** 179, 275.
19. Hovi, V.; Vuola, R.; Salmonperä, L. *J. Low Temp. Phys.* **1970,** 2, 383.
20. Schaack, G.; Koningstein, J. A. *J. Phys. Chem. Solids* **1970,** 31, 2417.
21. Latimer, W. M. *J. Am. Chem. Soc.* **1951,** 73, 1480.
22. Westrum, E. F., Jr. In Lanthanide actinide chemistry *Adv. Chem. Ser.* **1967,** 71, 25.
23. Dieke, G. H. *Spectra and Energy Levels of Rare Earth Ions in Crystals* Chapter 13. John Wiley and Sons: New York. 1968.
24. Schumm, R. H.; Wagman, D. D.; Bailey, S.; Evans, W. H.; Parker, V. B. Selected values of chemical thermodynamic properties. Tables for the lanthanide (rare earth) elements. *Nat. Bur. Stand. (U.S.) Tech.* Note 270–7 (April **1793).**
25. *CODATA Recommended Key Values for Thermodynamics.* CODATA Bulletin No. 10, CODATA, Paris, France, December **1973.**
26. JANAF Thermochemical Tables. The Dow Chemical Company: Midland, Michigan and U.S. Government Printing: Washington, D.C. **1971.**
27. Walden, G. E.; Smith, D. F. U.S. *Bur. Mines. Rep. Invest.* No. 5859. **1961.**
28. Dworkin, A. S.; Bredig, M. A. *J. Phys. Chem.* **1963,** 67. 697.
29. Dworkin, A. S.; Bredig, M. A. *J. Phys. Chem.* **1963,** 67, 2499.
30. Hutchison, C. A., Jr.; Wong. E. Y. *J. Chem. Phys.* **1958.** 29, 754.
31. Hadni, A. *Phys. Rev.* **1964,** 136, A758.
32. Mikkelson, R. C.; Stapleton, H. J. *Phys. Rev.* **1965,** 140, A1968.
33. Mangum, B. W.; Hudson, R. P. *J. Chem. Phys.* **1966,** 44, 704.
34. Thomas, H. H., Jr., Ph.D. Thesis Syracuse University, Syracuse, New York **1968,** Chapter III.
35. Dieke, G. H.; Sarup, R. *J. Chem. Phys.* **1962,** 36, 371.
36. Eisenstein, J. C.; Hudson, R. P.; Mangum, B. W. *Phys. Rev.* **1965,** 137, A1886.
37. Dieke, G. H. *Spectra and Energy Levels of Rare Earth Ions in Crystals.* John Wiley and Sons: New York. **1968,** 196.
38. Taylor, K. N. R.; Darby, M. I. *Physics of Rare Earth Solids.* Chapman and Hall: London. **1972,** p. 37.

39. McLaughlin, R. D.; Conway, J. G. *J. Chem. Phys.* **1963,** 38, 1037.
40. DeShazer, L. C.; Dieke, G. H. *J. Chem. Phys.* **1963,** 38, 2190.
41. Barnes, J. C.; Pincott, H. J. *J. Chem. Soc. A* **1966,** 7, 842.
42. Dawson, P.; Schaack, G. *J. Phys. Chem. Solids* **1973,** 34, 2193.
43. Asawa, C. K.; Satten, R. A.; Stafsudd, O. M. *Phys. Rev.* **1968,** 168, 957.
44. Damen, T. C.; Kiel, A.; Porto, S. P. S.; Singh, S. *Solid State Commun.* **1968,** 6, 671.
45. Cohen, E.; Moos, H. W. *Phys. Rev.* **1967,** 161, 258.
46. Cohen, E.; Moos, H. W. *Phys. Rev.* **1967.** 161, 268.
47. Detailed supplementary information on lattice heat capacities, correlation of Raman spectroscopic data with differences between calculated and experimental Schottky heat capacities, and lattice anharmonicity, etc. are presented in NAPS document No. 02847 with 40 pages of text and tables. This document may be ordered from ASJS/NAPS c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016 U.S.A. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications. Photocopies are $10.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $2.00 for a photocopy or $1.00 for a fiche.