

Entropy and heat capacity of europium(III) bromide from 5 to 340 K ^a

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The heat capacity of a polycrystalline sample of EuBr_3 has been measured from 5 to 340 K and found to be without transitions in this region. Values of the thermodynamic functions $C_p(T)$, $\{S^\circ(T) - S^\circ(5 \text{ K})\}$, and $\{H^\circ(T) - H^\circ(5 \text{ K})\}/T$ are 26.44, 43.70, and 19.66 $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$ respectively at 298.15 K. A value of $S^\circ(298.15 \text{ K}) = 41.42 \text{ cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$, for EuBr_3 from which the Schottky contribution has been deleted, is compared with an estimate of the lattice heat capacity by an empirical method.

1. Introduction

Enhanced interest in research on atomic energy levels of the lanthanide compounds has been evident recently.⁽¹⁻³⁾ Thermodynamics also provides increasingly precise and reliable data on the energetic behavior of transition⁽⁴⁾ and lanthanide compounds⁽⁵⁾ and supplements the earlier data. However, empirical evaluations are still the only values extant for many important binary compounds.^(6, 7) Hope that a measured value of the entropy of EuBr_3 would resolve the discrepancy existing in the correlation of second- and third-law entropies for EuBr_3 ⁽⁸⁾ provided a major motivation for this study of the low-temperature heat capacity of EuBr_3 . A further dividend arises from the utility of the results in estimating values for other lanthanide trihalides.

2. Experimental

PREPARATION AND CHARACTERIZATION OF EuBr_3

A 60 g sample of europium tribromide was prepared from the sesquioxide (99.99 moles per cent purity, American Potash Chemical Corp., Code 1014) by bromination of the dibromide. The previously described^(9, 10) ammonium-bromide-matrix procedure was scaled for the preparation of larger EuBr_2 samples. Employed in this procedure were 48.1 mass per cent aqueous HBr (J. T. Baker Chemical Company, containing 0.03 mass per cent Cl^- as the major contaminant) and analytical grade NH_4Br (Mallinckrodt Chemical Works). The dibromide was treated with analytical

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grade Br_2 (Mallinckrodt Chemical Works) in a sealed Pyrex vessel at 600 K and 150 kPa, a pressure which is approximately ten times the equilibrium value for the dibromide = tribromide equilibrium.⁽⁸⁾ The pressure was controlled with a bromine reservoir which extended beyond the 600 K sample zone and was maintained at a minimum of 355 K. The product was subjected to both chemical and crystallographic analyses. The europium tribromide sample was a dark rust-brown polycrystalline solid. The bromine content was determined by a gravimetric silver halide procedure, and the europium analysis was obtained by direct ignition of samples to the sesquioxide. The elemental analysis indicated (38.78 ± 0.05) mass per cent Eu and (61.22 ± 0.01) mass per cent Br (theoretical: Eu, 38.80; Br, 61.20), or $\text{EuBr}_{3.002 \pm 0.004}$. Powder X-ray diffraction results obtained with a 114.6 mm Hagg-type Guinier camera (Cu $K\alpha_1$ radiation, $\lambda = 0.154051$ nm) with silicon ($a = 0.543062$ nm) as an internal standard showed only the presence of the orthorhombic PuBr_3 structure with lattice parameters: $a = (0.9108 \pm 0.0009)$ nm, $b = (1.270 \pm 0.001)$ nm, and $c = (0.4010 \pm 0.0005)$ nm. All manipulations of the anhydrous bromides were conducted in an inert-atmosphere glove box purged of both water and oxygen.

CRYOGENIC APPARATUS

Heat-capacity measurements were made in the Mark III adiabatic cryostat which is similar in design to one previously described.⁽¹¹⁾ A gold-plated copper calorimeter (laboratory designation W-42) of about 93 cm³ volume and 41.9 g mass was employed for measurements on the sample. Temperatures determined with a capsule-type platinum resistance thermometer (laboratory designation A-3) are considered to be thermodynamic temperatures to within 0.03 K from 10 to 90 K and to within 0.04 K from 90 to 340 K. The heat capacity of the empty calorimeter was determined separately and appropriate small adjustments were made for the slight differences in the quantities of helium and Apiezon-T grease applied between determinations. The heat capacity of the 59.8352 g sample varied from about 78 per cent of the total at 15 K to about 64 per cent at 300 K. Helium gas (5.60 kPa) was used to enhance the thermal equilibrium between sample and calorimeter. All determinations of mass, potential, current, and temperature were referred to calibrations performed by the National Bureau of Standards.

3. Results and discussion

The experimentally determined heat capacities for EuBr_3 are presented in table 1. The temperatures given in the table represent the mean temperatures for the temperature increments employed in the individual runs and are considered to have a probable error ranging from 3 per cent at 5 K to 0.5 per cent at 10 K to less than 0.1 per cent above 20 K. The results are based on a molar mass of 391.67 g mol⁻¹ for EuBr_3 (1968 atomic weights). All temperatures are on the IPTS-48.

The smoothed heat capacities and thermodynamic functions at selected temperatures are presented in table 2. The heat-capacity values were taken from a smooth curve obtained by a digital computer least-squares fitted polynomial function through the experimental points. The values below 12 K are the result of extrapolation using

TABLE 1. Heat capacity of europium tribromide
(cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{th} K^{-1} \text{mol}^{-1}}$
Series I		20.55	0.500	62.91	3.894	169.88	7.676
5.18	0.015	22.56	0.618	68.04	4.254	179.94	7.797
5.77	0.018	24.56	0.747	72.77	4.558	189.87	7.902
6.43	0.024	26.52	0.884	77.21	4.830	199.67	7.995
7.15	0.032	28.82	1.054	82.05	5.113	209.36	8.080
7.80	0.046	31.63	1.277	88.69	5.473	219.42	8.164
8.53	0.063	34.71	1.537			229.84	8.241
9.27	0.082	37.51	1.780			240.60	8.315
9.98	0.104	40.54	2.044	Series III		251.70	8.381
10.79	0.113	43.62	2.314	88.46	5.456	262.72	8.445
11.74	0.135	46.70	2.585	98.16	5.878	273.66	8.500
12.72	0.163	50.86	2.941	107.28	6.228	283.54	8.547
13.69	0.195	55.56	3.326	116.67	6.550	293.35	8.595
14.82	0.233	60.09	3.683	127.34	6.853	306.11	8.639
16.15	0.286			138.45	7.135	316.82	8.681
17.46	0.343	Series II		149.18	7.350	327.48	8.719
18.83	0.409	58.01	3.517	159.64	7.522	338.08	8.760

the Debye limiting law. The estimated error in the thermodynamic functions is less than 0.1 per cent above 100 K.

The quantum number J resulting from spin-orbit (Russell-Saunders) coupling prevails with 4f elements. Eu^{3+} (or Eu IV in spectroscopic notation) has a ground term of 7F_0 which is diamagnetic. However, the other terms of the ground multiplet (${}^7F_{1, 2, 3, 4, 5, 6}$) contribute to the thermodynamic properties of trivalent europium significantly at 298.15 K. In fact, estimates show that the separation between the $J = 0$ ground state and the $J = 1$ first excited state is about $(5/3)kT$ at room temperature. Hence, Schottky contributions to the heat capacity are to be expected in EuBr_3 even below 340 K, but Boltzmann statistics show that Schottky contributions to the heat capacity below 5 K are negligible. Absence of discontinuities in the heat capacity from 5 to 340 K is conclusive evidence for the lack of cooperative phenomena in this temperature range. Nuclear magnetic contributions to the heat capacity from below 5 K are possible.

Haschke has noted the dark brown color of EuBr_3 (in contrast with the colorless nature of other europium(III) compounds) and that the color in EuBr_3 tends to fade at low temperatures.⁽⁸⁾ He speculates that the color might be due to the excitation of electrons into low-lying energy levels of the Eu^{3+} ion. Consideration of the wavenumber of the light absorbed (about 20000 cm^{-1}), however, shows that energy levels would have to involve D states with wavenumbers lying about 18000 cm^{-1} above the ground state. This speculation is supported by the data of McClure.⁽¹²⁾ The results suggest that the alternative possibility,⁽⁸⁾ a bromide to europium(III) charge transfer, is the probable origin of the visible absorption.

In the absence of data on the crystal field levels on EuBr_3 , we have selected spectroscopic data for the Eu IV levels in EuYVO_4 ⁽¹⁾ as an approximation to free ion levels.

TABLE 2. Thermodynamic functions for europium tribromide
 (cal_{th} = 4.184 J)

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{S^\circ(T) - S^\circ(0)\}}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{\{H^\circ(T) - H^\circ(0)\}}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{-\{G^\circ(T) - H^\circ(0)\}/T}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
5	0.06	0.019	0.07	0.005
10	0.44	0.148	1.18	0.03
15	1.266	0.486	5.39	0.127
20	2.373	0.995	14.36	0.277
25	3.739	1.667	29.56	0.485
30	5.256	2.481	52.00	0.748
35	6.822	3.409	82.20	1.061
40	8.361	4.421	120.18	1.417
45	9.826	5.492	165.68	1.810
50	11.180	6.598	218.25	2.233
60	13.580	8.857	342.48	3.149
70	15.60	11.11	488.7	4.125
80	17.29	13.30	653.4	5.136
90	18.72	15.42	833.6	6.162
100	19.92	17.46	1027.0	7.191
110	20.93	19.41	1231.4	8.213
120	21.77	21.27	1445.0	9.224
130	22.48	23.04	1666.4	10.219
140	23.08	24.73	1894.3	11.196
150	23.59	26.34	2127.7	12.152
160	24.02	27.87	2365.8	13.087
170	24.38	29.34	2607.9	14.000
180	24.69	30.74	2853.3	14.891
190	24.96	32.09	3101.6	15.761
200	25.19	33.37	3352.4	16.610
210	25.39	34.61	3605.3	17.438
220	25.56	35.79	3860.0	18.245
230	25.71	36.93	4116.4	19.033
240	25.85	38.03	4374.2	19.802
250	25.97	39.09	4633.3	20.552
260	26.08	40.11	4893.6	21.285
270	26.18	41.09	5155	22.000
280	26.27	42.05	5417	22.700
290	26.37	42.97	5680	23.382
300	26.46	43.86	5944	24.050
310	26.54	44.73	6209	24.703
320	26.63	45.58	6475	25.343
330	26.72	46.40	6742	25.968
340	26.80	47.20	7010	26.581
273.15	25.21	41.40	5237	22.222
298.15	26.44	43.70	5896	23.928

The Schottky contribution evaluated from these: (T/K , $C_{p,i}/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$, $S_i/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$): 50, 0.019, 0.002; 100, 0.859, 0.200; 200, 2.24, 1.38; 300, 2.24, 2.30; 500, 2.26, 3.44; 1000, 2.30, 5.04, when deducted from the observed $\{S^\circ(300 \text{ K}) - S^\circ(5 \text{ K})\}$ yields a lattice entropy of $41.5 \text{ cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$ in reasonable accord with 41.1 estimated by Latimer's⁽¹³⁾ scheme.

The measured value of $S^\circ(298.15\text{ K})$ for EuBr_3 ($43.86\text{ cal}_{\text{th}}\text{ K}^{-1}\text{ mol}^{-1}$) is significantly lower than the estimated value ($48\text{ cal}_{\text{th}}\text{ K}^{-1}\text{ mol}^{-1}$) employed in the third-law calculation for the vaporization of the tribromide.⁽⁸⁾ In the light of these results, a reevaluation of the estimates for $\text{EuBr}_2(\text{s})$ and the third-law calculations may be merited.

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