

Heat capacity of deuterated ammonium tetrafluoroborate ND_4BF_4 from 7 K to 348 K ^a

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The heat capacity of deuterated ammonium tetrafluoroborate ND_4BF_4 was measured from 7 K to 348 K by adiabatic calorimetry. The curve for heat capacity against temperature is smooth with a broad maximum between 120 K and 165 K, and the peak value in $C_{p,m} \approx 14.9 \cdot R$ occurs between 145 K to 155 K. The shape of the broad maximum is similar to that found in other anisotropic salts and is believed to be a result of contributions both from the rotation of the ND_4^+ ion and from a larger than usual dilation of the unit cell. Values of the standard thermodynamic quantities are tabulated up to 350 K.

1. Introduction

Heat-capacity results for the ammonium perchlorates and metaperiodates NH_4ReO_4 , ND_4ReO_4 , NH_4IO_4 , and ND_4IO_4 , show a broad maximum in the plot of heat capacity against temperature. This maximum occurs around 200 K in each compound,^(1–4) but does not appear in the heat capacities of KReO_4 ,⁽¹⁾ or KIO_4 .⁽⁵⁾ In addition, a large excess molar heat capacity in each of the ammonium salts also peaks around 200 K,^(6,7) due in part to the NH_4^+ or ND_4^+ ion and in part to the contribution of the $(C_{p,m} - C_{v,m})$ correction term for the anisotropic lattice in these crystals with the scheelite structure.

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The observed heat capacities of the ammonium tetrafluoroborates also show a broad maximum in their heat capacity against temperature plot, although the peak is somewhat lower around 140 K in both NH_4BF_4 ,^(8, 10) and ND_4BF_4 .^(9, 10) Not surprisingly, the heat capacity of the potassium analogue KBF_4 is without the broad maximum or peak.⁽¹¹⁾ Because the thermal expansion of the orthorhombic NH_4BF_4 is negative along the c -axis for part of the temperature range below 200 K,⁽¹²⁾ the dilation contribution to the heat capacity is probably larger than otherwise expected,^(6, 7) a situation comparable with that in the phases discussed above. It is therefore reasonable to expect a significant contribution to this peak from both the ammonium-ion rotation and the $(C_{p,m} - C_{v,m})$ correction.

As part of our ongoing study of ammonium salts, an analysis of the heat capacities of NH_4BF_4 and ND_4BF_4 was begun. However, it was discovered that numerical values of the heat capacity for the deuterated salt had not been published; rather only graphs of heat capacity against temperature have appeared in the literature for ND_4BF_4 .^(9, 10) These graphs were used initially to extract $C_{p,m}$ values. We compared the heat capacities for NH_4BF_4 tabulated by White *et al.*⁽⁸⁾ with a plot of results for the undeuterated NH_4BF_4 on the same graph in reference 9. However, the graphical values lay above the tabulated numbers by 26 to 28 per cent. No such comparison is possible for ND_4BF_4 . As a result of this confusing situation, it was decided to measure the heat capacity of ND_4BF_4 and to extend the measurements to higher and lower temperatures than shown on the graphs in references 9 and 10. These results, together with the thermodynamic functions and their interpretation, are described in this paper.

2. Experimental

The sample of ND_4BF_4 was prepared from NH_4BF_4 , supplied commercially as 99.99 mass per cent pure with a certificate of analysis indicating the impurity as 0.01 mass per cent of elemental silicon. The NH_4BF_4 was dissolved in 125 cm³ of D_2O (99.8 moles per cent minimum nuclidic purity) within a container made of (ethene + tetrafluoroethylene) copolymer, which is inert to virtually all chemicals. The 25 g of salt dissolved sparingly at 295 K, but when the solution was warmed to 343 K all the crystals dissolved readily. A partially deuterated product was obtained on recrystallization. This procedure, carried out in a nitrogen atmosphere, was repeated four times, with 25.5 g of ND_4BF_4 being produced. To remove most of the D_2O trapped in the lattice upon recrystallization, the crystals were placed under an infrared lamp within the dry box and warmed gently for 4 d as the temperature was increased gradually to 353 K. A t.g.a. was done on 10 mg samples removed at intervals.

The Guinier-de Wolff X-ray diffraction patterns of our ND_4BF_4 samples were in agreement with the standard pattern for this compound: No. 15-745 as determined by the Joint Committee for Powder Diffraction Standards (J.C.P.D.S.) for the undeuterated salt.⁽¹³⁾ The structure was found to be orthorhombic at room temperature with $a = 0.5672$ nm, $b = 0.7267$ nm, and $c = 0.9055$ nm. The structure of our starting material NH_4BF_4 was also in agreement with the standard pattern for

that compound, an orthorhombic structure with $a = 0.5677$ nm, $b = 0.7272$ nm, and $c = 0.9066$ nm, which compares favourably with the J.C.P.D.S. values of $a = 0.5686$ nm, $b = 0.7272$ nm, and $c = 0.9063$ nm.⁽¹³⁾

As a check for D_2O trapped within our "dried" sample of ND_4BF_4 , the final t.g.a. was done with 12 mg of the sample that was loaded into the calorimeter. On heating to 436 K, a mass loss of 0.2 per cent occurred. Above 436 K, the mass loss increased markedly and decomposition began. The platinum resistance thermometer used in the t.g.a. instrument to measure temperature was calibrated with reference to the ice point and the fixed points of the Curie transitions in Alumel at 422.5 K, in nickel at 631.2 K, and in Trafoperm (97 mass per cent of Fe + 3 mass per cent of Si) at 1018.8 K. The precision of the measurements was estimated to be ± 2 K and $\pm 1 \times 10^{-6}$ g.

The molar heat capacity of ND_4BF_4 was measured from 7 K to 348 K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark II cryostat described previously.⁽¹⁴⁾ A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature measurements. The thermometer was calibrated on the IPTS-1948 (as revised in 1960)⁽¹⁵⁾ for temperatures above 90 K, against the N.B.S. provisional scale from 10 K to 90 K, and by the technique of McCrackin and Chang⁽¹⁶⁾ below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K between 10 K and 90 K and within 0.04 K above 90 K.⁽¹⁷⁾ Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S. The acquisition of heat capacities from about 6 K to 350 K was computer assisted.^(18,19) The computer was programmed for a series of determinations. During the drift periods, both the calorimeter temperature and the first and second derivatives of temperature with time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. During energy input, the current through and potential difference across the heater and the duration of the heating interval were obtained. Also recorded were the apparent heat capacity of the system which included the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-62) with four internal vertical vanes and a central entrant well for (heater + thermometer) was loaded with ND_4BF_4 within a dry box. The sample had been broken into fine particles in a mortar and pestle. Following the loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that no free D_2O remained within the sample. Helium gas was then added to the vessel to a pressure of about 3.6 kPa at 300 K so as to facilitate thermal equilibration. The vessel was then sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top using a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density of $1.937 \text{ g} \cdot \text{cm}^{-3}$ derived from the unit-cell edge of our sample. The mass of the ND_4BF_4 was 25.06416 g ($\cong 0.2302267$ mol, based on its molar mass of $108.8673 \text{ g} \cdot \text{mol}^{-1}$ from IUPAC 1983 relative atomic masses).

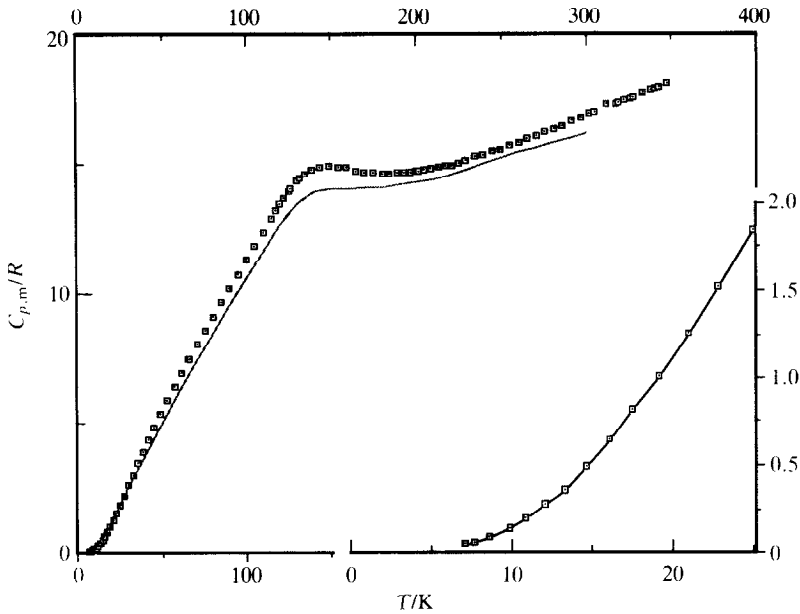


FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature for \square , ND_4BF_4 . Values —, for NH_4BF_4 are from reference 8.

rise in our heat-capacity values is evident around 270 K to 275 K, where fusion of any D_2O trapped in the lattice would be expected to occur. However, the 0.2 mass per cent of trapped D_2O would have been expected to give about a 10 per cent increment in the heat capacity over the 5 K interval of a single run. This was not detected and it is, therefore, presumed that the volatile contaminant was adsorbed water removed in the evacuation of the sample at room temperature prior to measurement.

The broad maximum in our results in figure 1 is similar in shape to that which occurs in NH_4BF_4 ,⁽⁸⁻¹⁰⁾ and in NH_4ReO_4 , NH_4IO_4 , and their deuterated analogues ND_4ReO_4 and ND_4IO_4 , although the temperature of the maximum in this latter group of four salts is higher, approximately 200 K.⁽¹⁻⁴⁾ The undeuterated NH_4BF_4 crystallizes at room temperature to a stable orthorhombic phase with space group Pnma (or No. 62 D_{2h}^{16})^(13,20-22) and transforms into a cubic phase at 472 K.^(23,24) For ND_4BF_4 at room temperature, our work shows an orthorhombic phase identical with that for the NH_4BF_4 salt. ND_4BF_4 also transforms into a cubic phase near 478 K based on d.s.c.⁽²⁵⁾ For both NH_4BF_4 and ND_4BF_4 , Schutte and Van Rensburg⁽²⁶⁾ reported a phase transition around 173 K, although the lack of marked changes in the i.r. spectra ruled out any gross structural transformation. A subsequent X-ray study of NH_4BF_4 by Van Rensburg and Boeyens⁽¹²⁾ led to the conclusion that its structure was orthorhombic above and below 173 K, but the volume of the unit cell increased by 1.5 per cent on cooling below 173 K. Below this temperature, some differences were also noted in the thermal motion of the BF_4 and

NH_4^+ tetrahedra. Caron *et al.*⁽²⁴⁾ had previously concluded from n.m.r. that a subtle structural change took place between 141 K and 187 K. However, the heat-capacity results for NH_4BF_4 fail to show any evidence of a phase transition at 173 K,^(8,9) and our results confirm this to be the case for ND_4BF_4 as well. Moreover, the temperature region of the broad maximum in our heat-capacity results corresponds to the temperatures where the discontinuities in the heights of the i.r. bands occur in ND_4BF_4 , at 118 K to 122 K and 168 K to 173 K.⁽²⁶⁾ This reinforces the argument that the source of the broad maximum in the heat capacity for both NH_4BF_4 and ND_4BF_4 , and the ammonium perchlorates and periodates, is the same. In the latter salts, ammonium-ion rotation is only one of the significant contributions; the other arises from the changes in the volume of the unit cell. In addition, for these perchlorates and periodates, the thermal expansion coefficients have opposite signs and become numerically large near 160 K and 200 K, respectively.^(6,7,27-29) Similarly, as NH_4BF_4 is cooled below 173 K, the *b*-axis shortens, the *a*-axis lengthens, and the *c*-axis remains unchanged.^(1,2)

TABLE 2. Standard molar thermodynamic functions for ND_4BF_4 ; $M = 108.8673 \text{ g} \cdot \text{mol}^{-1}$.

$$p^\circ = 101.325 \text{ kPa}, R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \Phi_m^{\circ \text{def}} = \Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ / T$$

T K	$C_{p,m}$ R	$\Delta_0^T S_m^\circ$ R	$\Delta_0^T H_m^\circ$ R · K	Φ_m° R	T K	$C_{p,m}$ R	$\Delta_0^T S_m^\circ$ R	$\Delta_0^T H_m^\circ$ R · K	Φ_m° R
0	0	0	0	0	146	14.93	13.88	1153.8	5.981
5	(0.0130)	(0.0126)	(0.0380)	(0.0050)	147	14.93	13.99	1168.7	6.035
10	0.141	0.0523	0.360	0.016	148	14.93	14.09	1183.7	6.089
15	0.515	0.169	1.87	0.045	150	14.93	14.29	1213.5	6.197
20	1.120	0.397	5.90	0.102	155	14.91	14.78	1288.1	6.466
25	1.829	0.721	13.24	0.192	160	14.85	15.25	1362.5	6.733
30	2.596	1.122	24.29	0.312	165	14.76	15.70	1436.6	6.998
35	3.365	1.580	39.20	0.460	170	14.69	16.14	1510.2	7.261
40	4.101	2.077	57.87	0.630	175	14.65	16.57	1583.5	7.520
45	4.817	2.601	80.16	0.820	180	14.64	16.98	1656.7	7.778
50	5.495	3.143	105.9	1.025	185	14.65	17.38	1730.0	8.032
55	6.168	3.698	135.1	1.242	190	14.66	17.77	1803.2	8.283
60	6.796	4.262	167.5	1.470	195	14.69	18.16	1876.6	8.531
65	7.400	4.830	203.0	1.707	200	14.72	18.53	1950.1	8.777
70	7.975	5.399	241.4	1.950	210	14.83	19.25	2097.9	9.258
75	8.535	5.968	282.7	2.199	220	14.94	19.94	2246.7	9.728
80	9.096	6.537	326.8	2.452	230	15.18	20.61	2397.4	10.19
85	9.665	7.106	373.7	2.709	240	15.41	21.26	2550.3	10.64
90	10.22	7.674	423.4	2.969	250	15.62	21.89	2705.4	11.07
95	10.75	8.241	475.8	3.232	260	15.74	22.51	2862.4	11.50
100	11.30	8.807	531.0	3.497	270	15.99	23.11	3021.6	11.92
105	11.86	9.371	588.9	3.763	280	16.34	23.70	3183.5	12.33
110	12.39	9.935	649.5	4.031	290	16.64	24.28	3348.4	12.73
115	12.93	10.50	712.8	4.300	300	16.93	24.85	3516.3	13.13
120	13.46	11.06	778.8	4.570	310	17.11	25.41	3686.4	13.51
125	13.95	11.62	847.3	4.840	320	17.40	25.95	3858.9	13.89
130	14.35	12.18	918.2	5.112	330	17.70	26.49	4034.4	14.27
135	14.64	12.72	990.7	5.384	340	17.97	27.03	4212.7	14.64
140	14.83	13.26	1064.5	5.655	350	18.23	27.55	4393.8	15.00
145	14.92	13.78	1138.9	5.927	298.15	16.88	24.74	3485.0	13.05
						± 0.02	± 0.03	± 3.5	± 0.02

Stammler *et al.*⁽³⁰⁾ suggested from X-ray measurements that another phase transition occurred in NH₄BF₄ at 83 K. This proposed phase transition was not confirmed in heat-capacity measurements,^(8,9) and also is not seen in our heat-capacity results for ND₄BF₄. It is noteworthy that Stammler *et al.*^(30,31) also claimed a phase transition in NH₄ClO₄ at 83 K, but neither the heat-capacity results for this salt,⁽³²⁾ nor those for ND₄ClO₄,⁽³³⁾ support this thesis. A detailed analysis⁽³³⁾ of all the available thermal information for NH₄ClO₄ and ND₄ClO₄ showed that in the region of 83 K, one of the thermal expansion coefficients (*b*-axis) of these orthorhombic salts had changed sign and become negative while those for the *a*- and *c*-axes remained positive, and it is this feature that Stammler *et al.*^(30,31) interpreted as a phase transition. Further evidence supporting the absence of a phase transition either in NH₄ClO₄ or NH₄BF₄ is provided by a successful interpretation of spectra on the basis of continuous changes in the crystal over the entire range of temperature from 7 K to 300 K.^(34,35)

Integration of the smoothed values for heat capacity and for the enthalpy and entropy increments through the anomalies yielded the thermodynamic functions. Values of $C_{p,m}/R$ and the derived functions are presented at selected temperatures in table 2. The heat capacities of ND₄BF₄ below 7 K were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T^3$ against T^2 and extrapolating to $T \rightarrow 0$. Such a plot can provide additional information about the lattice. The heat capacity of an insulator at very low temperatures can be written as a power series of the form:

$$C_{v,m} = aT^3 + bT^5 + cT^7 + \dots \quad (1)$$

in which the coefficients *a*, *b*, and *c* are directly related to the corresponding power series for the frequency spectrum at low frequencies.⁽³⁶⁾ However, the quantity measured calorimetrically is $C_{\text{sat},m}$, the heat capacity of the solid or liquid in equilibrium with its saturated vapour. For crystalline ND₄BF₄, $C_{\text{sat},m}$ is in effect identical with $C_{p,m}$ listed in tables 1 and 2, since the right-hand side is negligible in the equation:

$$C_{\text{sat},m} - C_{p,m} = (\partial p / \partial T)_{\text{sat}} \{ (\partial H / \partial p)_T - V_m \}. \quad (2)$$

In turn, the $C_{p,m}$ is related to the $C_{v,m}$ of equation (1) by

$$C_{p,m} - C_{v,m} = V_m T \alpha^2 / \kappa_T, \quad (3)$$

where $\alpha = V_m^{-1}(\partial V_m / \partial T)_p$ is the isobaric expansivity, V_m is the molar volume, and $\kappa_T = -V_m^{-1}(\partial V_m / \partial p)_T$ is the isothermal compressibility. At temperatures below 20 K, $(C_{p,m} - C_{v,m}) \approx 0$. As $T \rightarrow 0$, the lattice heat capacity of the crystal should equal that of an elastic continuum, which can be described by the Debye T^3 law as the low temperature limit of equation (1):

$$C_{v,m} = aT^3, \quad (4)$$

$$\Theta_D^C = (12\pi^4 Nk/5a)^{1/3}. \quad (5)$$

The Θ_D^C is the Debye temperature derived from heat capacities.

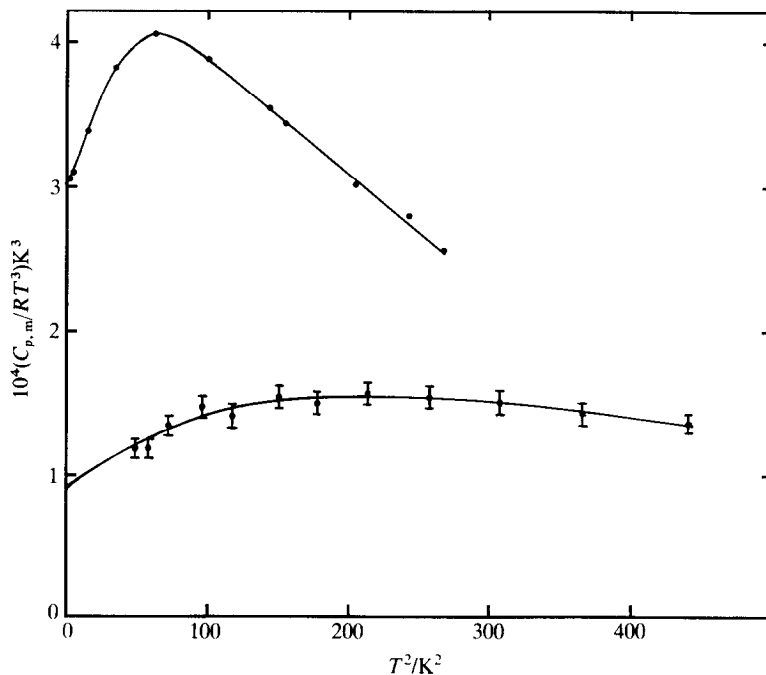


FIGURE 2. The quantity $10^4 C_{p,m}/RT^3$ plotted against T^2 for ND_4BF_4 (lower curve). The results for argon (upper curve) are from references 34 and 35. The error bars correspond to 5 per cent.

A useful plot for identifying any nonvibrational contributions to the heat capacity at low temperature is that of $C_{p,m}/T^3$ against T^2 in figure 2. In the region $50 < (T/K)^2 < 400$, *i.e.* $7 < (T/K) < 20$, the graph of our experimental heat capacities for ND_4BF_4 has the same shape as that of argon,^(37,38) suggesting that only lattice vibrations make significant contributions to the heat capacity in this range of temperature. By extrapolating the points below $T^2 = 50 K^2$ in figure 2 to intercept the $T^2 = 0$ axis, we found that $10^4 a = (0.900 \pm 0.100) \cdot R \cdot K^{-3} = (7.48 \pm 0.83) J \cdot K^{-1} \cdot mol^{-1}$, which yields $\Theta_D^C = (138 \pm 5) K$ from equation (5). This compares with 93.5 K for argon.

From the available information for NH_4BF_4 and ND_4BF_4 , a fairly consistent picture emerges describing the ionic motion in both salts. Within the orthorhombic phase of each, gross structural changes do not take place as the temperature is lowered to at least 10 K. Motion by the BF_4^- ion remains rapid down to 90 K, but not below this temperature.^(24,39) In the deuterated compound, the spin-lattice relaxation times of the ^{19}F , which are true values because of the removal of the proton-fluorine cross-relaxation upon deuteration, show no anomaly down to 50 K. However, the second moment of the ^{19}F in both ND_4BF_4 and NH_4BF_4 undergoes a rapid change between 190 K and 140 K. For the ammonium ions, rapid motion persists down to 90 K for both NH_4^+ ,^(24,39) and ND_4^+ .^(24,40) However, one n.m.r. study⁽³⁹⁾ of NH_4BF_4 below this temperature suggested rapid NH_4^+ motion about a

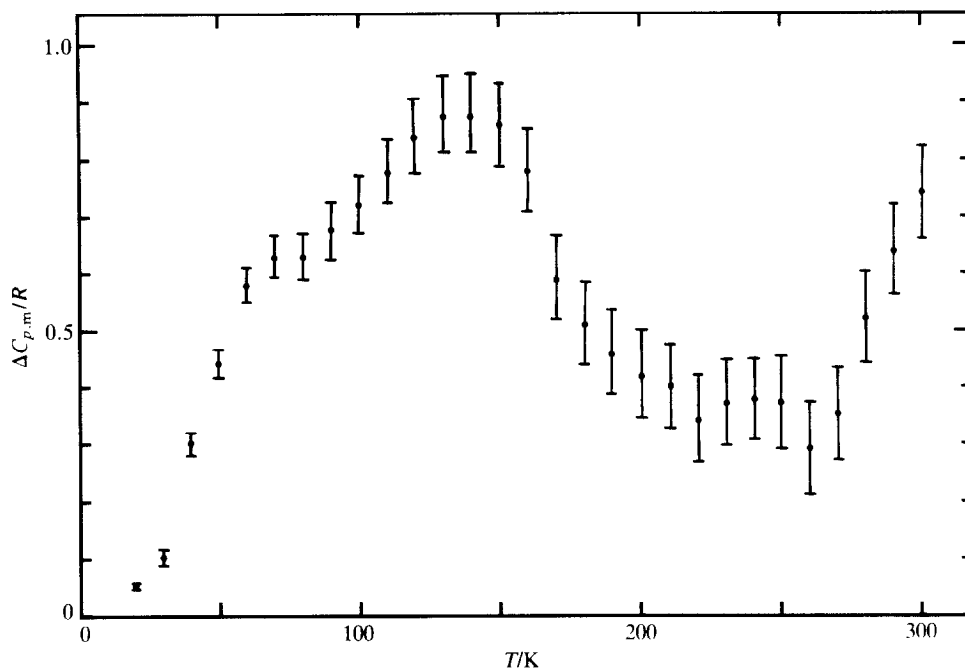


FIGURE 3. The experimental difference between the heat capacities of ND₄BF₄ and NH₄BF₄, $\Delta C_{p,m}/R = \{(C_{p,m}/R)_{\text{ND}_4\text{BF}_4} - (C_{p,m}/R)_{\text{NH}_4\text{BF}_4}\}$, plotted against T . Results for ND₄BF₄ are from this work and for NH₄BF₄ from reference 8. The error bars represent 0.5 per cent in the experimental heat capacities of each salt.

single C_2 -axis down to 20 K, which conflicts with the findings of another study⁽²⁴⁾ in which slow isotropic motion was reported to set in for the ammonium ions in both NH₄BF₄ and ND₄BF₄ somewhere between 83 K and 20 K.

A determination of the librational frequency of the NH₄⁺ in NH₄BF₄ and ND₄⁺ in ND₄BF₄ from an analysis of heat-capacity results depends upon the availability of ancillary experimental results for both salts. Because the thermal expansion of both salts is anisotropic, the method of estimating their lattice heat capacities by means of the alkali analogue is not applicable.⁽⁶⁾ The limited experimental information available for NH₄BF₄ and ND₄BF₄ about spectroscopic properties, thermal expansion, and compressibility rule out the calculation of the lattice heat capacity from i.r. and Raman spectra.^(6, 7, 33) Even though the lattice heat capacity could be estimated from a sum of Debye and Einstein functions,⁽⁴¹⁻⁴³⁾ the derived librational heat capacity cannot be separated from the $(C_{p,m} - C_{v,m})$ correction for the anisotropic lattice. The variant method by which the measured $C_{p,m}$ values of the hydrogen-containing salts are subtracted from those of the deuterated salt still does not eliminate entirely the need for spectroscopic or thermal expansion information. For ND₄BF₄ and NH₄BF₄, such a subtraction yields

$$\Delta C_{p,m} = \Delta C_{\text{lat},m} + \Delta C_{\text{int},m} + \Delta C_{\text{lib},\text{NH}_4/\text{ND}_4} + \Delta(C_{p,m} - C_{v,m}) \quad (6)$$

where $\Delta C_{p,m}$ is the difference in the experimental heat capacities, $\Delta C_{\text{lat},m}$ represents the difference in the lattice contributions to the heat capacity, $\Delta C_{\text{int},m}$ is the difference in the contribution to the heat capacities of the internal vibrations of ND_4^+ and NH_4^+ , and $\Delta(C_{p,m} - C_{v,m})$ is the difference for each salt defined by equation (3). The $C_{\text{lat},m}$ can be estimated for each salt as noted above, and the $C_{\text{int},m}$ for ND_4^+ and NH_4^+ calculated from available spectroscopic information,^(26,44,45) but the last two terms in equation (6) cannot be calculated. The $\Delta C_{p,m}$ based on experimental heat capacities of ND_4BF_4 and NH_4BF_4 is shown in figure 3. By assuming the $\Delta(C_{p,m} - C_{v,m})$ term in equation (6) to be negligible, the calculation of $C_{\text{lib},\text{NH}_4^+/\text{ND}_4^+}$ by difference for some anisotropic crystals resulted in two peaks in the librational heat capacity against temperature plot.⁽⁴⁶⁾ Finally, it is difficult to draw firm conclusions from the librational wavenumber of the NH_4^+ : $\tilde{\nu}_6 = 186 \text{ cm}^{-1}$, calculated from the combination bands based on i.r. spectra at room temperature because of the unreliability of these bands.⁽⁴⁵⁾

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