The thermodynamics of perchlorates. I. Heat capacity of ND_4ClO_4 from 7 to 345 K and the analysis of heat capacities and related data of NH_4ClO_4 and ND_4ClO_4

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The heat capacity of the orthorhombic salt: deuterated ammonium perchlorate, ND_4ClO_4, was measured from 7 to 345 K using adiabatic calorimetry. The heat capacity against temperature curve is smooth, continuous and without anomaly. Values of the standard molar thermodynamic quantities are presented up to 340 K. The heat capacities of ND_4ClO_4 and NH_4ClO_4 have been analyzed. The contributions to the vibrational heat capacity from the external optical modes of NH_4^+ or ND_4^+, ClO_4^- and libration from the external modes of ClO_4^- along with those of vibration from the internal optical modes of NH_4^+ or ND_4^+ and ClO_4^-, and the acoustic lattice modes for these ions have been calculated. The difference between the experimental and calculated heat capacity, called the residual heat capacity, equals the contribution from ammonium ion rotation and the thermal expansion of the lattice. With recent thermal expansion data, the correction from constant stress to constant strain has been applied and the derived rotational heat capacities of the NH_4^+ and ND_4^+ are determined to be in qualitative agreement with those derived from various rotational models.

I. INTRODUCTION

Disorder in ionic solids containing polyatomic ions arises when two or more orientations can exist in the lattice. In ammonium salts with a polyatomic anion, the distribution of charge on this anion over several atoms must weaken the electrostatic attraction between any of these atoms and a hydrogen atom of an NH_4^+ ion. The barrier to reorientation of the NH_4^+ in such salt is, therefore, predicted to be low, thereby allowing the ammonium ion at higher temperatures to approach free rotation. A considerable effort has been devoted to experimental work on NH_4ClO_4 to determine the barrier to rotation by the NH_4^+ ion and how its movement is affected by changes in temperature. Various studies have indicated that the experimental values of the barrier hindering NH_4^+ rotation range are below 4.2 kJ mol^{-1},[1-5] but despite this agreement, the details concerning the dynamics remain uncertain and even controversial.

Ammonium perchlorate NH_4ClO_4 undergoes a reversible crystallographic transition from the low-temperature orthorhombic structure to a cubic structure at 513 K.[6,7] The orthorhombic unit cell has a space group [P_{nma} or No. 62 D_{2h}^{16}] with $Z = 4$ retained to temperatures at least as low as 10 K.[8-12] Stammler *et al.*[13,14] proposed that both NH_4ClO_4 and isostructural NH_4BF_4 undergo a polymorphic phase transition near 83 K, based upon x-ray diffraction work. However, neither the heat capacity experiments by Westrum

and Justice[15] for NH_4ClO_4 nor those by Stephenson *et al.*[16] for NH_4BF_4 support this thesis. Peyronel and Pignedoli[17] have suggested that the x-ray data at room temperature refine better under the noncentrosymmetric space group P_{na2}, (C_{2v}^9) but this was disproved by Choi, Prask, and Prince.[10]

In the analysis of the heat capacity of NH_4ClO_4, Westrum and Justice[15] subtracted the C_p of this isostructural $KClO_4$ salt to derive the C_p due to NH_4^+ rotation. This produced a small shoulder in the C_p around 30–40 K. For anisotropic lattices, which include NH_4ReO_4, ND_4ReO_4, and ND_4IO_4, this procedure has been shown to be invalid as a large part of the C_p formerly ascribed to NH_4^+ rotation is due to contributions from the correction of the experimental heat capacity at constant pressure to the heat capacity at constant strain.[18,19] For the NH_4ClO_4 salt, its lattice parameters show the crystal to be anisotropic from 10 to 300 K with the greatest changes occurring between 20 and 100 K.[8,9,20,21] In addition, measurements of inelastic neutron scattering and the interpretation of the tunnel splitting[22,24] are consistent with the highly anisotropic thermal motions described by the diffraction measurements at low temperature.[9] As a consequence, the shoulder in the C_p around 30–40 K from Westrum and Justice[15] cannot be interpreted as due solely, if at all, to rotation of the ammonium ion; indeed, careful inspection of the NH_4ClO_4 data shows no discernible shoulder, and the feature may be better attributed to the $KClO_4$ heat capacity data.

A recent Raman study of Chakraborty *et al.*[25] of

NH_4ClO_4 noted anomalous changes in intensities of some of the internal modes of NH_4^+ and ClO_4^- as well as some lattice modes at 40 and 180 K. These authors claimed that these anomalies were due to phase transitions at the two temperatures using as support the C_p shoulder from the work of Westrum and Justice[15] and from an assumed break in the lattice parameters at 200 K, which is not supported by experiment.[21] The powder neutron diffraction, coherent neutron inelastic scattering and Raman measurements by Prask et al.[21] show the NH_4^+ internal mode splittings to vary smoothly, which is consistent with motional averaging rather than with the presence of a phase transition.

In the light of this controversy and the absence of reported heat capacity measurements, it seemed worthwhile (a) to carry out such determinations on deuterated ammonium perchlorate ND_4ClO_4 to determine whether anomalies or transitions are present and (b) to analyze the heat capacity and related data of both NH_4ClO_4 and ND_4ClO_4 using the method developed recently.[18,19]

II. EXPERIMENTAL

A. Deuterated ammonium perchlorate sample

The sample of ND_4ClO_4 was prepared from NH_4ClO_4 as follows. The NH_4ClO_4, 99.8% pure, without further purification was dissolved completely in D_2O which was 99.8 mol % minimum isotopic purity. A partially deuterated product was obtained on recrystallization. This procedure, carried out in a dry atmosphere, was repeated six times. The extent of deuteration was measured by solid-state proton nuclear magnetic resonance (NMR) using a dilute mixture of NH_4Cl in NaCl as an intensity standard. The fraction of protons was estimated at 0.75%. In addition, no peaks due to species such as ND_3H^+ were seen in the Raman spectrum, although peaks due to H_2O were present in the product from the first few cycles. The H_2O was determined to have come from moisture within the KBr used to prepare the pellets for the spectra and from the atmosphere when the spectra were being run. Corrective measures were taken[26] after which the H_2O peaks virtually disappeared. To remove most of the D_2O trapped in the lattice upon recrystallization, the sample was placed under an infrared lamp within the dry box and warmed gently for a few days with temperature increased gradually to 90 °C. Finally, the sample was held at 96 °C for four hours but no further weight loss occurred.

The Guinier–de Wolff diffraction pattern of our sample was found to be in excellent agreement with the standard pattern for this compound as determined by the Joint Committee for Powder Diffraction Standards.[27] The lattice dimensions were not determined.

As a check on any D_2O trapped within our "dried" sample of ND_4ClO_4, two thermogravimetric analyses were made using about 12 and 13 mg of the sample in a Mettler TA 3000. On heating each sample to about 468 K, a mass loss of 0.04% and 0.06% occurred. This loss of 0.05% is in excellent agreement with our attribution of D_2O as the solute obtained from the small rise in the heat capacity curve around 275 K (see below). When the sample was heated to 523 K, decomposition ensued.

B. Calorimetry

The heat capacity, $C_{p,m}$ was measured from 7.2 to 345 K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark X cryostat described previously.[28] The acquisition of heat capacities from about 9 to 349 K was computer assisted.[29,30] 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. While the calorimeter heater was on, the current and potential of the heater and the duration of the heating interval were obtained. Also recorded were the apparent heat capacity of the system including the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-139) with four internal vertical vanes and a central re-entrant well for (heater + thermometer) was loaded with ND_4ClO_4 within a dry box. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure moisture was no longer freed from the sample. Helium gas was then added to the vessel to about 3 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 derived from the single crystal x-ray diffraction study on the salt (2.022 g cm^{-3}).[21] The mass of the ND_4ClO_4 amounted to 13.7197 g, i.e., 0.112 907 mol based on its molar mass of 121.513 g mol^{-1} from IUPAC 1983 atomic masses.

III. RESULTS

A. Heat capacity

The experimental values of the molar heat capacities of our ND_4ClO_4 sample are shown in Table I. There is no evidence that the $C_{p,m}$ values depended on the thermal history of the sample so that our results are presented in order of increasing temperature. The probable errors are estimated to drop from about 1% at 10 K to less than 0.15% temperatures above 30 K. Our raw data are smooth to within 0.1% over the range 7.2–345 K.

These data have been plotted in Fig. 1 as the open circles. The resulting curve is smooth and without discontinuities or obvious anomalies. The very slight rise in the heat capacity around 270 K is presumed to result from melting a saturated aqueous (D_2O) salt solution trapped in the lattice. By interpolating the background heat capacity curve from about 260 to 285 K, the excess enthalpy associated with the anomaly was determined. The D_2O impurity amounted to 0.05 mass %, which is in excellent agreement with the 0.05% determined from the thermogravimetric analysis. The experimental $C_{p,m}/R$ values for our ND_4ClO_4 given in Table I were not adjusted for this impurity. For comparison, the heat capacity curve[15] for the undeuterated NH_4ClO_4 is shown in Fig. 1 as the broken line.

TABLE I. Experimental molar heat capacity of ND_4ClO_4 ($M = 121.513$ g mol^{-1}; $R = 8.3144$ J K^{-1} mol^{-1}).

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$
7.23	0.1284	54.84	6.709	186.11	13.03
8.12	0.1667	58.35	7.125	192.28	13.21
8.96	0.2092	62.12	7.542	198.44	13.39
9.88	0.2640	66.02	7.932	204.62	13.56
10.86	0.3350	69.94	8.283	210.79	13.73
11.85	0.4191	74.14	8.626	216.97	13.92
12.85	0.5176	78.59	8.970	223.14	14.10
13.99	0.6442	83.06	9.288	229.31	14.30
15.24	0.7986	87.55	9.567	235.79	14.50
16.51	0.9688	92.31	9.819	242.57	14.69
17.80	1.155	97.35	10.05	249.34	14.89
19.23	1.373	102.40	10.26	256.11	15.13
20.80	1.624	107.46	10.47	262.85	15.39
22.38	1.887	112.53	10.67	269.60	15.62
23.98	2.198	117.62	10.86	276.30	15.80
25.77	2.545	122.96	11.05	282.25	15.97
27.71	2.896	128.57	11.25	288.25	16.11
29.72	3.221	134.18	11.43	295.03	16.31
31.97	3.547	139.80	11.62	302.04	16.53
34.37	3.883	145.42	11.80	309.22	16.77
36.79	4.266	151.05	11.97	316.41	16.96
39.41	4.652	156.69	12.15	323.62	17.18
42.23	5.054	162.33	12.33	330.86	17.38
45.07	5.448	167.92	12.50	338.08	17.58
48.15	5.862	173.77	12.68	345.29	17.79
51.49	6.293	179.94	12.85		

B. Thermodynamic functions

Values of the thermodynamic functions obtained by integration of the smooth data are presented in Table II. The smoothed curve between 260 and 285 K was drawn by interpolating the background heat capacity as though D_2O were
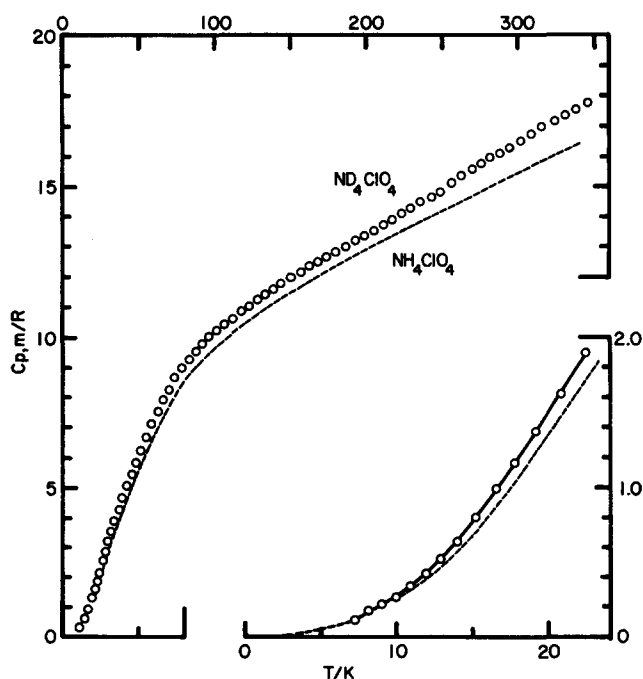

FIG. 1. Molar heat capacities of ND_4ClO_4 (open circles, this work) and NH_4ClO_4 [broken line, Westrum and Justice (Ref. 15)].

TABLE II. Standard molar thermodynamic quantities for ND_4ClO_4[a] [$M = 121.513$ g mol^{-1}; $p^0 = 101.325$ kPa; $R = 8.3144$ J K^{-1} mol^{-1}; $\Phi_m^0(T,0) \overset{def}{=} -\Delta_0^T H_m^\circ/T + \Delta_0^T S_m^\circ$].

$\dfrac{T}{K}$	$\dfrac{C_{p,m}^0}{R}$	$\dfrac{\Delta_0^T S_m^\circ}{R}$	$\dfrac{\Delta_0^T H_m^\circ}{RK}$	$\dfrac{\Phi_m^0(T,0)}{R}$
0	(0.0)	(0.0)	(0.0)	(0.0)
5	(0.0450)	(0.0160)	(0.605)	(0.00397)
10	0.2780	0.106	0.781	0.0283
15	0.7697	0.301	3.27	0.0833
20	1.488	0.618	8.86	0.1748
25	2.400	1.044	18.58	0.3006
30	3.263	1.556	32.74	0.4645
35	3.993	2.113	50.88	0.6593
40	4.736	2.694	72.70	0.8766
45	5.442	3.293	98.15	1.112
50	6.104	3.900	127.0	1.360
55	6.729	4.511	159.1	1.619
60	7.307	5.122	194.2	1.885
65	7.833	5.727	232.0	2.157
70	8.284	6.324	272.3	2.434
75	8.693	6.910	314.8	2.713
80	9.066	7.483	359.2	2.993
85	9.411	8.043	405.4	3.274
90	9.706	8.590	453.2	3.555
95	9.959	9.121	502.3	3.834
100	10.17	9.638	552.6	4.111
105	10.37	10.14	604.0	4.387
110	10.57	10.63	656.3	4.659
115	10.77	11.10	709.7	4.929
120	10.95	11.56	764.0	5.196
125	11.12	12.01	819.1	5.460
130	11.29	12.45	875.2	5.720
135	11.46	12.88	932.1	5.978
140	11.62	13.30	989.8	6.232
145	11.78	13.71	1048.3	6.483
150	11.94	14.11	1107.6	6.731
160	12.26	14.90	1228.6	7.217
170	12.56	15.65	1352.7	7.691
180	12.86	16.37	1479.8	8.153
190	13.14	17.08	1609.8	8.604
200	13.43	17.76	1742.7	9.045
210	13.71	18.42	1878.3	9.476
220	14.01	19.07	2017.0	9.897
230	14.31	19.70	2158.6	10.31
240	14.62	20.31	2303.2	10.72
250	14.91	20.91	2450.9	11.11
260	15.22	21.50	2601.6	11.50
270	15.53	22.08	2755.3	11.88
280	15.83	22.65	2912.1	12.25
290	16.15	23.22	3072.0	12.62
300	16.48	23.77	3235.2	12.99
310	16.78	24.31	3401.5	13.34
320	17.06	24.85	3570.8	13.69
330	17.35	25.38	3742.8	14.04
340	17.64	25.90	3917.8	14.38
298.15	16.43 ± 0.02	23.67 ± 0.030	3204.8 ± 4.1	12.92 ± 0.02

[a] As noted in Sec. III B, the values of this table have not been corrected for the heat capacity of 0.05 mass per cent D_2O present as ice or liquid. This correction would result in lowering the heat capacity by 0.07% to 0.10%. However, the effect of fusion of the ice has been eliminated.

not present. However, the heat capacities were not then corrected for the contribution by the 0.05 mass % D_2O. This correction would lower the $C_{p,m}/R$ in Table II by 0.07%–0.10%, based upon the heat capacity values of D_2O given by Long and Kemp.[31]

The heat capacities of ND_4ClO_4 below 7 K were ob-

tained by fitting our experimental values below 20 K to the limiting form of the Debye equation, using a plot of $C_{p,m}/T$ against T^2 and extrapolating to $T \to 0$. A plot of $C_{p,m}T^{-3}$ against T^2 was not used because our results do not extend to temperatures low enough to pass below the maximum value of $C_{p,m}T^{-3}$. It is the linear portion of the curve below the maximum $C_{p,m}T^{-3}$ that is needed for the extrapolation of $T \to 0$.

IV. ANALYSIS

A. Analysis of heat capacity data

The experimental heat capacity is written as

$$C_{\exp,m} = (C_{p,m} - C_{\epsilon,m}) + C_{\text{vib},m} + C_{\text{lat},m} + C_{\text{rot},m}. \quad (1)$$

The $(C_{p,m} - C_{\epsilon,m})$ is the correction term applied to the heat capacity $C_{p,m}$ at constant stress or constant pressure to yield heat capacity at constant strain $C_{\epsilon,m}$ and is calculated from the anisotropic thermal expansion. The $C_{\text{vib},m}$ is the heat capacity determined from known vibrational frequencies at 12–18 K and includes the internal modes of the cation and anion plus external modes except for the rotational or librational modes of the ammonium ion. The $C_{\text{lat},m}$ represents the heat capacity for the acoustic modes and the $C_{\text{rot},m}$ is the rotational heat capacity from the librational or rotational movement of the ammonium ion. The resulting calculated heat capacity by summing these contributions corresponds to that for constant geometry since frequencies at a fixed temperature are used to calculate $C_{\text{vib},m}$.

However, the heat capacity measured in the calorimeter is actually $C_{\text{sat},m}$, which is that of the liquid or solid in equilibrium with its saturated vapor, and is linked to $C_{p,m}$ via

$$C_{\text{sat},m} - C_{p,m} = -\left(\frac{dP}{dT}\right)_{\text{sat}} T\left(\frac{dV}{dT}\right)_p. \quad (2)$$

For the solid ammonium perchlorates, the $(C_{\text{sat},m} - C_{p,m})$ is negligible. Our procedure for analyzing the data will be to calculate the residual heat capacity $(C_{\exp,m} - C_{\text{vib},m} - C_{\text{lat},m})$ for $0 < T/\text{K} < 350$, which by inspection of Eq. (1) leaves $\{(C_{p,m} - C_{\epsilon,m}) + C_{\text{rot},m}\}$. The correction to conditions of constant strain will then be determined, thereby yielding numerical values for $C_{\text{rot},m}$.

The space group for the orthorhombic ammonium perchlorate is P_{nma} or No. 62 D_{2h}^{16} with four formula units per primitive cell. Each of the salts NH_4ClO_4 and ND_4ClO_4 has a total of 120 unit cell vibrations which are categorized as 72 internal modes[25] viz. $10A_g + 8B_{1g} + 10B_{2g} + 8B_{3g} + 8A_u + 10B_{1u} + 8B_{2u} + 10B_{3u}$, 33 external optical modes (excluding librational modes) viz. $5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$, 12 ammonium ion librational optical modes viz. $A_g + 2B_{1g} + B_{2g} + 2B_{3g} + 2A_u + B_{1u} + 2B_{2u} + B_{3u}$, and three acoustic modes. The assignments and wave numbers are summarized in Table III.

The assignment of all 72 frequencies for the internal vibrations has been grouped according to the frequency of the free ions with the average frequency taken from the literature.[21] For ND_4ClO_4, the assignment for 19 of the 33 external modes was made from the data of Prask et al.[21] which are derived from Raman and from coherent neutron inelastic

TABLE III. Assignment of vibrational frequencies[a] expressed as wave number v in cm^{-1}.

Mode	Ammonium ion internal modes				Perchlorate ion internal modes			
	v_1	v_2	v_3	v_4	v_1	v_2	v_3	v_4
Degeneracy	4	8	12	12	4	8	12	12
NH_4ClO_4	3204	1680	3306	1418	940	465	1102	630
ND_4ClO_4	2310	1198	2468	1121	940	465	1102	630

External modes (except librations)

NH_4ClO_4	A_g	175, 60, 220, 70.3, 93.5
	B_{1g}	113, 40,[b] 81, 97[c]
	B_{2g}	140, 65, 158, 115, 118
	B_{3g}	168, 65
	A_u	28[b,c]
	unassigned	$2B_{3g}$, $3A_u$, $4B_{1u}$, $3B_{2u}$, $4B_{3u}$
ND_4ClO_4	A_g	157, 60, 200, 70.5, 95.5
	B_g	109, 40,[b] 76.5, 97[c]
	B_{2g}	135, 64.5, 155, 92, 116
	B_{3g}	152, 195,[c] 128,[c] 67
	A_u	28[b,c]
	unassigned	$3A_u$, $4B_{1u}$, $3B_{2u}$, $4B_{3u}$

Librational modes

NH_4ClO_4	A_g	157.5
	B_{1g}	174
	B_{2g}	199
	B_{3g}	112, 54[b]
	unassigned	$1B_{1g}$, $2A_u$, $1B_{1u}$, $2B_{2u}$, $1B_{3u}$
ND_4ClO_4	A_g	131
	B_{1g}	173,[c] 198[c]
	B_{2g}	183
	B_{3g}	48[b]
	unassigned	$1B_{3g}$, $2A_u$, $1B_{1u}$, $2B_{2u}$, $1B_{3u}$

[a] Data primarily from Tables VII–IX, Ref. 21 except as noted.
[b] Estimated average over Brillouin zone, see Fig. 16, Ref. 21.
[c] CNIS data, Ref. 21.

scattering (CNIS) measurements. However, for two modes, B_{1g} and A_u, we have averaged the frequency across the zone using as weight the square of the reduced wave vector with data in their Fig. 16 rather than use the values quoted at the center of the Brillouin zone. The heat capacity is sensitive to contributions across the entire zone and not only at the center. Unassigned are the 14 external modes listed in Table III. With the numerical values of the frequency assignments, the $C_{\text{vib},m}$ was calculated as a sum of Einstein functions to include the 72 internal modes and 19 of the external modes. The remaining 14 unassigned external modes were placed with the $C_{\text{vib},m}$ by multiplying the external heat capacity by 33/19 for ND_4ClO_4 (or 33/16 in the case of NH_4ClO_4).

To determine the $C_{\text{lat},m}$, advantage is taken of the fact that rotational motion of the ammonium ion at low temperature turns up in the Raman spectrum as well-defined librational modes. As a result at low temperatures, $C_{\text{rot},m}$, which

is calculated using the Einstein function with the observed librational frequencies of the ammonium ion at low temperatures.

At low temperatures where the contribution of the thermal expansion $(C_{p,m} - C_{\epsilon,m})$ to the heat capacity is very small, $(C_{\exp,m} - C_{\mathrm{vib},m} - C_{\mathrm{lib},m})$ is dominated by the heat capacity of the acoustic modes and is fitted to a Debye function. For the ammonium perchlorates, the $(C_{p,m} - C_{\epsilon,m})$ has been calculated by us in Sec. IV B below, but unfortunately the values below 20 K are unreliable because of inadequate data for thermal expansion as well as for elastic constants. In addition, it is likely that the $(C_{p,m} - C_{\epsilon,m})$ values are not negligible below 20 K. Given this dilemma of dealing with the $(C_{\exp,m} - C_{\mathrm{vib},m} - C_{\mathrm{lib},m})$ to get at the lattice modes by either correcting it using $(C_{p,m} - \mathrm{C}_{\epsilon,m})$ data known to be inadequate below 20 K or making no correction realizing that the resulting Debye temperature must be interpreted with caution, the latter course was considered more appropriate. Therefore, the uncorrected $(C_{\exp,m} - C_{\mathrm{vib},m} - C_{\mathrm{lib},m})$ values were fitted to a Debye function for 0.75 degrees of freedom, corresponding to three acoustic degrees of freedom per unit cell containing four formula units.

Of the 12 low temperature vibrational frequencies of the ammonium ions, six are known[21] and are given in Table III. The B_{3g} mode was averaged over the Brillouin zone as done for the external modes and the B_{1g} modes are from CNIS data.[21] The six unassigned modes were incorporated by multiplying the $C_{\mathrm{lib},m}$ by 12/6 for use in the $(C_{\exp,m} - C_{\mathrm{vib},m} - C_{\mathrm{lib},m})$ calculation. The resulting Debye Θ_D values are 300 K for NH_4ClO_4 and 129 K for ND_4ClO_4.

If the Debye model were followed, the Debye temperature $\Theta_D(T)$ should be constant for any crystal. However, for real crystals even when the thermal expansion correction is negligible, the model does not describe what is observed experimentally. For metals and diatomic lattices, $\Theta_D(T)$ asymptotically approaches a constant value at high temperatures where all the vibrational modes contribute to the heat capacity. For other crystals including insulators, $\Theta_D(T)$ increases as temperature rises to reach a maximum value and then falls. To obtain the contribution of the lattice vibrations to the heat capacity in these crystals, the $\Theta_D(T)$ is plotted and the asymptotic value at the peak $\Theta_D(T)$ is drawn to extend to high temperatures. The resulting curve is then used with Debye tables. At temperatures below that where

TABLE IV. Heat capacity analysis for NH_4ClO_4. $C_{\exp,m}$, smoothed experimental molar heat capacity: $C_{\mathrm{vib},m}$, estimated vibrational contribution from internal optical modes of NH_4^+ and ClO_4^- ions and all external optical modes except librational modes of NH_4^+; $C_{\mathrm{lib},m}$, contribution from librational modes of NH_4^+ ions; $C_{\mathrm{lat},m}$, lattice contribution from NH_4^+ and ClO_4^- (Debye heat capacity for acoustic modes); $C_{\mathrm{res},m} = (C_{\exp,m} - C_{\mathrm{vib},m} - C_{\mathrm{lat},m}) = \{(C_{p,m} - C_{\epsilon,m}) + C_{\mathrm{rot},m}\}$ (see the text); $(C_{p,m} - C_{\epsilon,m})$, correction for thermal expansion; $C_{\mathrm{rot},m}$, rotational contribution from NH_4^+; $R = 8.3144$ J K^{-1}.

$\dfrac{T}{\mathrm{K}}$	$\dfrac{C_{\exp,m}}{R}$	$\dfrac{C_{\mathrm{vib},m}}{R}$	$\dfrac{C_{\mathrm{lib},m}}{R}$	$\dfrac{C_{\mathrm{lat},m}}{R}$	$\dfrac{C_{\mathrm{res},m}}{R}$	$\dfrac{(C_{p,m} - C_{\epsilon,m})}{R}$	$\dfrac{C_{\mathrm{rot},m}}{R}$
10.0	0.254	0.213	0.015	0.025	0.015	···	···
20.0	1.362	1.135	0.208	0.017	0.210	···	···
30.0	2.829	2.303	0.466	0.057	0.469	1.128	− 0.66
40.0	4.210	3.388	0.758	0.122	0.700	1.003	− 0.30
50.0	5.508	4.295	1.064	0.199	1.015	0.881	0.13
60.0	6.661	5.024	1.351	0.276	1.360	0.782	0.56
70.0	7.635	5.606	1.603	0.346	1.682	0.707	0.98
80.0	8.417	6.079	1.815	0.406	1.932	0.652	1.28
90.0	9.081	6.474	1.991	0.456	2.150	0.615	1.54
100.0	9.565	6.818	2.135	0.497	2.250	0.594	1.66
110.0	10.004	7.128	2.253	0.531	2.345	0.586	1.76
120.0	10.404	7.416	2.350	0.559	2.428	0.590	1.84
130.0	10.786	7.691	2.431	0.583	2.513	0.602	1.91
140.0	11.140	7.956	2.498	0.603	2.582	0.621	1.96
150.0	11.462	8.214	2.555	0.619	2.629	0.644	1.99
160.0	11.769	8.467	2.603	0.633	2.668	0.671	2.00
170.0	12.066	8.717	2.644	0.645	2.704	0.703	2.00
180.0	12.354	8.963	2.679	0.655	2.736	0.742	1.99
190.0	12.635	9.206	2.709	0.664	2.765	0.792	1.97
200.0	12.905	9.445	2.735	0.672	2.788	0.859	1.93
210.0	13.164	9.683	2.758	0.679	2.802	0.946	1.86
220.0	13.420	9.918	2.779	0.685	2.818	1.049	1.77
230.0	13.675	10.149	2.796	0.690	2.836	1.157	1.68
240.0	13.940	10.379	2.812	0.695	2.866	1.250	1.62
250.0	14.198	10.607	2.826	0.699	2.893	1.316	1.58
260.0	14.453	10.832	2.839	0.702	2.920	1.404	1.52
270.0	14.702	11.054	2.850	0.706	2.943	···	···
280.0	14.944	11.274	2.860	0.709	2.961	···	···
290.0	15.197	11.492	2.869	0.711	2.993	···	···
300.0	15.444	11.708	2.878	0.714	3.022	···	···
310.0	15.698	11.921	2.885	0.716	3.061	···	···
320.0	15.942	12.132	2.892	0.718	3.092	···	···
330.0	16.179	12.340	2.898	0.720	3.119	···	···
340.0	16.423	12.546	2.904	0.722	3.156	···	···

Θ_D is reached, values of Θ_D based upon experimental heat capacities are used to obtain $C_{\mathrm{lat},m}$.

What are the effects of our not correcting for the $(C_{p,m} - C_{\epsilon,m})$? Although the shape of the $\Theta_D(T)$ curve is unchanged and the typical asymptote results, the $\Theta_D(T)$ values are too low because the values of $(C_{\mathrm{exp},m} - C_{\mathrm{vib},m} - C_{\mathrm{lib},m})$ are too high. The resulting values of Θ_D for NH_4ClO_4 and ND_4ClO_4 must, therefore, be interpreted with caution as they include contributions from both lattice vibrations and lattice expansion. The various calculated quantities are presented in Tables IV and V. The residual heat capacity $C_{\mathrm{res},m} = C_{\mathrm{exp},m} - C_{\mathrm{vib},m} - C_{\mathrm{lat},m}$ equals $(C_{p,m} - C_{\epsilon,m}) + C_{\mathrm{rot},m}$ which is also given in these tables and plotted in Figs. 2(a) and 2(b).

B. Anisotropic thermal expansion

The contribution of thermal expansion to the heat capacity of any material is defined by

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

where $\alpha = V_m^{-1}(dV_m/dT)_p$ is the isobaric expansivity, V_m

is the molar volume, and $K_T = -V_m^{-1}(dV_m/dp)_T$ is the isothermal compressibility. Heat capacities calculated via statistical mechanics are usually thought to refer to conditions of constant volume. However, for ammonium ions in noncubic crystals, this procedure is inadequate and the calculations must be made under conditions of constant geometry in which the atoms near each ammonium ion are held at constant position relative to the ammonium ion and independent of temperature. To use the results of statistical mechanics in analyzing experimental heat capacities, the measured $C_{p,m}$ must be corrected to a heat capacity at constant geometry. A condition of constant volume is equivalent to that of constant geometry only for cubic crystals, with all the atoms in special positions.

For noncubic crystals, the best that can be achieved through a thermodynamic description is a calculation of the heat capacity at constant strain[18] i.e., constant unit-cell dimensions and angles. Processes at constant strain may be described as *isomeric*. When the thermodynamic equations used to drive Eq. (3) are generalized to incorporate the anisotropic stresses and strains, the connection between heat

TABLE V. Heat capacity analysis for ND_4ClO_4. $C_{\mathrm{exp},m}$, smoothed experimental molar heat capacity; $C_{\mathrm{vib},m}$, estimated vibrational contribution from internal optical modes of ND_4^+ and ClO_4^- ions and all external modes except librational modes of ND_4^+; $C_{\mathrm{lib},m}$, contribution from librational modes of ND_4^+ ions; $C_{\mathrm{lat},m}$, lattice contribution from ND_4^+ and ClO_4^- (Debye heat capacity for acoustic modes); $C_{\mathrm{res},m} = (C_{\mathrm{exp},m} - C_{\mathrm{vib},m} - C_{\mathrm{lat},m}) = \{(C_{p,m} - C_{\epsilon,m}) + C_{\mathrm{rot},m}\}$ (see the text); $(C_{p,m} - C_{\epsilon,m})$, correction for thermal expansion; $C_{\mathrm{rot},m}$, rotational contribution from ND_4^+; $R = 8.3144$ J K^{-1}.

$\dfrac{T}{K}$	$\dfrac{C_{\mathrm{exp},m}}{R}$	$\dfrac{C_{\mathrm{vib},m}}{R}$	$\dfrac{C_{\mathrm{lib},m}}{R}$	$\dfrac{C_{\mathrm{lat},m}}{R}$	$\dfrac{C_{\mathrm{res},m}}{R}$	$\dfrac{(C_{p,m} - C_{\epsilon,m})}{R}$	$\dfrac{C_{\mathrm{rot},m}}{R}$
10.0	0.278	0.191	0.029	0.059	0.029	···	···
20.0	1.488	1.044	0.246	0.172	0.273	···	···
30.0	3.263	2.185	0.459	0.345	0.733	1.128	− 0.40
40.0	4.736	3.281	0.700	0.469	0.986	1.003	− 0.02
50.0	6.104	4.212	0.975	0.549	1.343	0.881	0.46
60.0	7.307	4.963	1.252	0.602	1.742	0.782	0.96
70.0	8.284	5.563	1.505	0.637	2.084	0.707	1.38
80.0	9.066	6.049	1.723	0.661	2.356	0.652	1.70
90.0	9.706	6.454	1.906	0.678	2.574	0.615	1.96
100.0	10.170	6.804	2.058	0.691	2.675	0.594	2.08
110.0	10.570	7.119	2.184	0.701	2.751	0.586	2.17
120.0	10.950	7.411	2.289	0.708	2.831	0.590	2.24
130.0	11.290	7.688	2.376	0.714	2.887	0.602	2.29
140.0	11.620	7.958	2.449	0.719	2.943	0.621	2.32
150.0	11.940	8.222	2.511	0.723	2.996	0.644	2.35
160.0	12.260	8.482	2.563	0.726	3.051	0.671	2.38
170.0	12.560	8.742	2.608	0.729	3.089	0.703	2.39
180.0	12.850	9.001	2.646	0.731	3.118	0.742	2.38
190.0	13.140	9.261	2.679	0.733	3.146	0.792	2.35
200.0	13.430	9.521	2.708	0.735	3.174	0.859	2.32
210.0	13.710	9.782	2.733	0.736	3.192	0.946	2.25
220.0	14.010	10.044	2.756	0.737	3.229	1.049	2.18
230.0	14.310	10.307	2.775	0.738	3.265	1.157	2.11
240.0	14.620	10.570	2.792	0.739	3.311	1.250	2.06
250.0	14.910	10.833	2.808	0.740	3.337	1.316	2.02
260.0	15.220	11.095	2.822	0.741	3.383	1.404	1.98
270.0	15.530	11.358	2.834	0.742	3.431	···	···
280.0	15.830	11.619	2.845	0.742	3.469	···	···
290.0	16.150	11.878	2.855	0.743	3.530	···	···
300.0	16.480	12.134	2.865	0.743	3.602	···	···
310.0	16.780	12.390	2.873	0.744	3.647	···	···
320.0	17.060	12.641	2.880	0.744	3.675	···	···
330.0	17.350	12.870	2.887	0.744	3.717	···	···
340.0	17.640	13.134	2.894	0.745	3.761	···	···

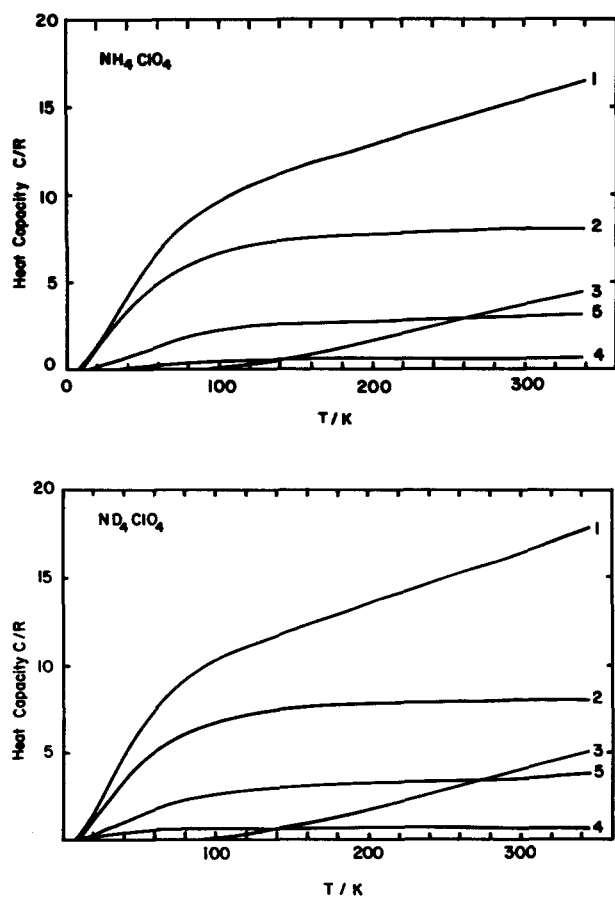FIG. 3. Linear thermal expansion coefficients of ND_4ClO_4.

FIG. 2. Molar heat capacity (a) for NH_4ClO_4 and (b) for ND_4ClO_4. (1) Experimental heat capacity for the pure salt; (2) vibrational heat capacity from all external modes except for NH_4^+ librational modes; (3) vibrational heat capacity from internal optical modes of NH_4^+ or ND_4^+ and ClO_4^-; (4) lattice heat capacity from NH_4^+ or ND_4^+ and ClO_4^- (Debye heat capacity for acoustic modes); (5) residual heat capacity $C_{res,m} = (C_{exp,m} - C_{vib,m} - C_{lat,m}) = \{(C_{p,m} - C_{\epsilon,m} + C_{rot,m})\}$, (see the text for discussion of vibrational and lattice contributions).

capacities at constant stress $C_{\sigma,m}$ and constant strain $C_{\epsilon,m}$ is given by[32,33]

$$C_{\sigma,m} - C_{\epsilon,m} = V_m T \Sigma\, c_{ijkl}\alpha_{ij}\alpha_{kl}, \qquad (4)$$

where c_{ijkl} is the isothermal elastic constant tensor and α_{ij} is the thermal expansion tensor. Essentially, the condition of constant stress can be considered as constant pressure. For orthorhombic crystals, which include the ammonium perchlorates, Eq. (4) becomes in Voigt notation:

$$C_{p,m} - C_{\epsilon,m} = V_m T\{c_{11}\alpha_1^2 + 2c_{12}\alpha_1\alpha_2 + 2c_{13}\alpha_1\alpha_3$$
$$+ c_{22}\alpha_2^2 + 2c_{23}\alpha_2\alpha_3 + c_{33}\alpha_3^2\}. \qquad (5)$$

The three diagonal components of the thermal expansion tensor α_1 (α_a), α_2 (α_b), and α_3 (α_c) have been determined for ND_4ClO_4 and are shown in Fig. 3. The α's were obtained by fitting empirical functions to the unit cell data provided by Segel[34] for ND_4ClO_4. These data are very similar to those of Prask et al.,[21] but are taken at more closely spaced temperatures and are highly self-consistent between 30 and 250 K. However, below 30 K, there are features in the data which prevent extraction of accurate thermal expansion coeffi-
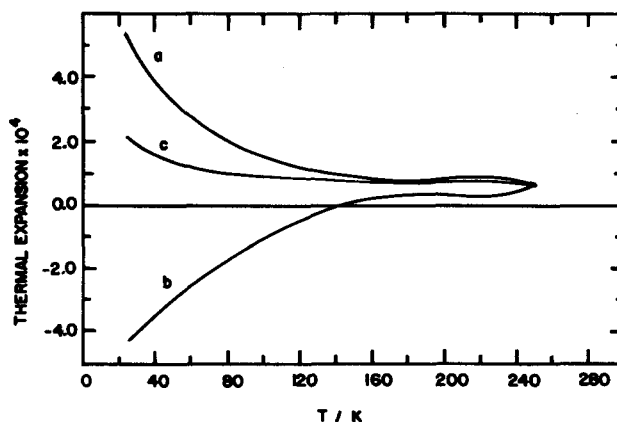
cients, although the coefficients approach zero at absolute zero. The unit cell dimensions were fitted to a sixth order polynomial in $(T-150)$ in Kelvin:

$$\text{lattice parameter} = \sum_{i=1}^{7} a_i(T - 150)^{i-1}. \qquad (6)$$

The values of the coefficients defined by Eq. (6) are given in Table VI.

The thermal expansion coefficients α_i shown in Fig. 3 were obtained by differentiation of Eq. (6). The resulting α_i values are approximately equal and constant between 150 and 250 K, but at lower temperatures α_a increases and α_b decreases to become negative. Although not shown in Fig 3, all the coefficients turn over below 30 K to head towards zero as absolute zero is approached. This behavior is expected and borne out experimentally in other cases.[35]

To obtain the expansion coefficients for NH_4ClO_4, the unit cell data by Prask et al.[21] were first used. However, a comparison of their unit cell data for NH_4ClO_4 and ND_4ClO_4 shows the thermal expansion behavior to be similar for these two salts. Because the unit cell data by Segel[34] for ND_4ClO_4 are so highly self-consistent, are spaced at such close intervals and agree with the data of Prask et al. for ND_4ClO_4, which in turn are very similar to their data for NH_4ClO_4, the data by Segel for ND_4ClO_4 were assumed to be valid for NH_4ClO_4. Equation (6) with coefficients shown in Table VI was applied to NH_4ClO_4 for our subsequent calculations of thermal expansion corrections.

TABLE VI. Coefficients used to calculate the lattice parameters in Angstroms[a] for ND_4ClO_4 and NH_4ClO_4.

| Coefficient | Lattice parameter | | |
	a	b	c
a_1	9.1190	5.7848	7.378 9
$a_2\times10^4$	8.2702	0.5449	5.827 4
$a_3\times10^6$	− 4.0854	4.2603	− 1.286 0
$a_4\times10^8$	3.7071	− 4.2890	0.548 7
$a_5\times10^{10}$	1.7481	− 0.5793	1.097 8
$a_6\times10^{12}$	− 0.4202	1.1261	0.000 61
$a_7\times10^{14}$	− 1.6315	0.7537	− 0.681 4

[a] $1\,\text{Å} = 10^{-10}\,\text{m}$.

The elastic constants in Eq. (5) have been measured at 298 K by Vazquez et al.[36] for NH_4ClO_4, who obtained values in units of 10^{10} Pascals as follows: $c_{11} = 2.51, c_{12} = 1.63$, $c_{13} = 1.15, c_{22} = 2.46, c_{23} = 0.76$, and $c_{33} = 3.15$ which are stated to be accurate within 4%. Values could neither be located at other temperatures for NH_4ClO_4 nor at any temperature for ND_4ClO_4. In the absence of other information, the elastic constants for NH_4ClO_4 were applied to ND_4ClO_4 and were assumed to be independent of temperature for both salts.

The remaining term needed to calculate the $(C_{p,m} - C_{\epsilon,m})$ of Eq. (5) is the molar volume which was evaluated using the lattice parameters from Eq. (6). The values of $(C_{p,m} - C_{\epsilon,m})/R$ are shown in Tables IV and V as calculated from Eq. (5) and are plotted in Fig. 4.

Thus common values of $(C_{p,m} - C_{\epsilon,m})$ were used for the two salts evaluated using thermal expansion coefficients of ND_4ClO_4 between 30 and 250 K, and the elastic constants of NH_4ClO_4 at room temperature.

The final column in Tables IV and V contains the $C_{rot,m}$ for the ammonium and was obtained by subtracting $(C_{p,m} - C_{\epsilon,m})$ from the $C_{res,m}$. The results are plotted in Fig. 5.

V. DISCUSSION

The experimental heat capacity curves shown in Fig. 1 for the ND_4ClO_4 salt reported in this paper along with that for NH_4ClO_4 by Westrum and Justice[15] are smooth and without evidence of a phase transition or anomaly. When the heat capacity contributions to the internal and external vibrations together with the lattice vibrations are subtracted from the experimental values for each salt, the resultant curve of $C_{res,m}$ also remains smooth and without anomaly, which is line 4 in Figs. 2(a) and 2(b). We can find no evidence to support the claim by Chakraborty et al.[25] of phase transitions in NH_4ClO_4 at 40 and 180 K which they deduced from their Raman study. Our conclusions are, therefore, in agreement with those of Prask et al.[21] who were unable to find any sign of a phase transition in either NH_4ClO_4 or ND_4ClO_4 from their crystallographic, Raman and coherent neutron inelastic scattering, and with those of Bastow et al.[39] who have reported ^2H and ^{35}Cl relaxation time measurements.
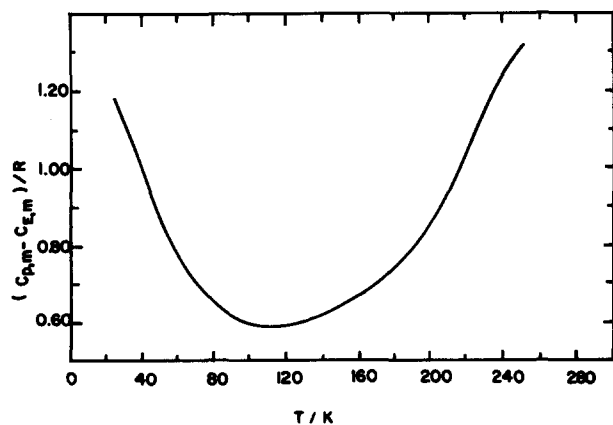

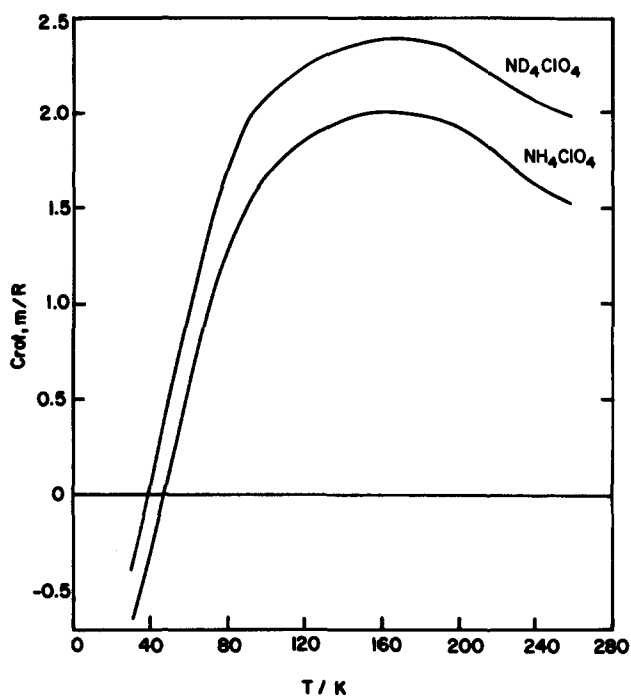FIG. 4. Heat capacity correction due to thermal expansion in ND_4ClO_4.

FIG. 5. Rotational heat capacity of the ammonium ion in NH_4ClO_4 and ND_4ClO_4.

Chakraborty et al.[25] used the anomalous shoulder in the C_p vs T curve presented in Fig. 2 of Westrum and Justice[15] to reinforce their claim. We have reanalyzed these C_p data using the procedure followed by Westrum and Justice in which the C_p data for the $KClO_4$ salt measured by Latimer and Ahlberg[37] were subtracted from those measured by Westrum and Justice for the NH_4ClO_4 salt in order to isolate the rotational heat capacity of the ammonium ion. However, the C_p data for the $KClO_4$ salt at low temperature may be causing the spurious bump since they are not smooth. Recent data by Zalukaev et al.[38] show that the data of Latimer and Ahlberg are high by about 0.3 J K^{-1} mol^{-1} between 32 and 45 K.

Returning to Figs. 2(a) and 2(b) for the ammonium perchlorates, it is evident the heat capacities for both salts are dominated by the external modes (curve 2) and that the thermal expansion + rotational contribution increases very slowly above 130 K (curve 5). The rising $C_{int,m}$ is due to the increasing excitation of the internal modes (curve 3) primarily v_2 for ClO_4.

The uncertainty in the heat capacity due to the internal modes (curve 3) is thought to be negligible, since these frequencies are well known.[21] The uncertainty in the contribution of the external modes (excluding NH_4^+ librations) due to uncertain and unknown frequencies is somewhat larger. At temperatures above about 140 K and at very low temperatures, the curve is insensitive to moderate changes in the assigned frequencies. The uncertainty is likely to be greatest between 40 and 80 K; bearing in mind that the curve must lie below the experimental curve and be reasonably smooth (since it is a superposition of 33 separate Einstein curves), the maximum error in C_v /R is estimated visually as $\pm$ 0.5 at 60 K. A corresponding maximum uncertainty of $\pm$ 0.5 follows in C_{resid} /R at 60 K.

The contribution of the rotational heat capacity for the ammonium ion in Fig. 5 is in qualitative agreement with calculated heat capacities. The shape of the curve suggests a hindered potential with the peak around 160 K. It is in reasonable agreement with that given in Fig. 2 by Smith[39] for a tetrahedron in a tetrahedral crystal field with a barrier to rotation of 6.69 kJ. The fact that the actual barrier in the ND_4ClO_4 salt is 4 kJ from NMR measurements[40] will shift the peak in Smith's Fig. 2 from 250 K to the vicinity of 160 K, but because the crystal field for the ammonium perchlorates is of lower symmetry than tetrahedral, its exact position is unknown. However, our $C_{rot,m}/R$ curve offers insight into the qualitative nature of its temperature dependence. The rotational heat capacity, calculated by difference, seems to be heading for the high temperature limit of $3R/2$ within close limits, the value expected for a free rotor. This rotational contribution is only 10% of the total heat capacity and the good agreement gives confidence that the contributions of the optical modes, the acoustic modes, the thermal expansion have been evaluated with sufficient accuracy.

However, some caution is needed in assessing the quantitative aspect of the $C_{rot,m}$ at low temperatures because of the problems in evaluating the $(C_{p,m} - C_{\epsilon,m})$ correction. The negative values in C_{rot}/R below about 40 K reinforce our stated uncertainty in the $(C_{p,m} - C_{\epsilon,m})$ due to incomplete data on thermal expansion coefficients and elastic constants at these low temperatures. At temperatures above 40 K, the expansion coefficients are known accurately and uncertainties in the $(C_{p,m} - C_{\epsilon,m})$ in this temperature region arise from the assumptions made in the elastic constants, whose values were assumed to be those for NH_4ClO_4 at room temperature and independent of temperature for both salts. This procedure must lead to an overestimated $(C_{p,m} - C_{\epsilon,m})$ as temperature falls, since the elastic constants decrease, so that $C_{rot,m}/R$ must be underestimated. Probably the underestimation becomes significant below 100 K. Clearly, the entire curve of C_{rot}/R can be enchanced by improving the quality of the thermal expansion data at $T < 40$ K, and by obtaining experimental values for the elastic constants of both salts as a function of temperature as well as for the vibrational frequencies not yet known.

ACKNOWLEDGMENTS

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