The thermodynamics of perchlorates. I. Heat capacity of $\text{ND}_4\text{ClO}_4$ from 7 to 345 K and the analysis of heat capacities and related data of $\text{NH}_4\text{ClO}_4$ and $\text{ND}_4\text{ClO}_4$

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The heat capacity of the orthorhombic salt: deuterated ammonium perchlorate, $\text{ND}_4\text{ClO}_4$, 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 $\text{ND}_4\text{ClO}_4$ and $\text{NH}_4\text{ClO}_4$ have been analyzed. The contributions to the vibrational heat capacity from the external optical modes of $\text{NH}_4^+$ or $\text{ND}_4^+$, $\text{ClO}_4^-$ and libration from the external modes of $\text{ClO}_4^-$ along with those of vibration from the internal optical modes of $\text{NH}_4^+$ or $\text{ND}_4^+$ and $\text{ClO}_4^-$, 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 $\text{NH}_4^+$ and $\text{ND}_4^+$ 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 $\text{NH}_4^+$ ion. The barrier to reorientation of the $\text{NH}_4^+$ 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 $\text{NH}_4\text{ClO}_4$ to determine the barrier to rotation by the $\text{NH}_4^+$ ion and how its movement is affected by changes in temperature. Various studies have indicated that the experimental values of the barrier hindering $\text{NH}_4^+$ rotation range are below 4.2 kJ mol$^{-1}$ but despite this agreement, the details concerning the dynamics remain uncertain and even controversial.

Ammonium perchlorate $\text{NH}_4\text{ClO}_4$ undergoes a reversible crystallographic transition from the low-temperature orthorhombic structure to a cubic structure at 513 K. The orthorhombic unit cell has a space group $[P_{nma}$ or No. 62 $D_{2h}^{11}]$ with $Z = 4$ retained to temperatures at least as low as 10 K. Stammler et al. proposed that both $\text{NH}_4\text{ClO}_4$ and isostructural $\text{NH}_4\text{BF}_4$ undergo a polymorphic phase transition near 83 K, based upon x-ray diffraction work. However, neither the heat capacity experiments by Westrum and Justice for $\text{NH}_4\text{ClO}_4$ nor those by Stephenson et al. for $\text{NH}_4\text{BF}_4$ support this thesis. Peyronel and Pignedoli have suggested that the x-ray data at room temperature refine better under the noncentrosymmetric space group $P_{nma}$ ($C^*_6$) but this was disproved by Choi, Prask, and Prince.

In the analysis of the heat capacity of $\text{NH}_4\text{ClO}_4$, Westrum and Justice subtracted the $C_p$ of this isostructural $\text{KClO}_4$ salt to derive the $C_p$ due to $\text{NH}_4^+$ rotation. This produced a small shoulder in the $C_p$ around 30-40 K. For anisotropic lattices, which include $\text{NH}_4\text{ReO}_4$, $\text{ND}_4\text{ReO}_4$, and $\text{ND}_2\text{IO}_4$, this procedure has been shown to be invalid as a large part of the $C_p$ formerly ascribed to $\text{NH}_4^+$ rotation is due to contributions from the correction of the experimental heat capacity at constant pressure to the heat capacity at constant strain. In addition, measurements of inelastic neutron scattering and the interpretation of the tunnel splitting are consistent with the highly anisotropic thermal motions described by the diffraction measurements at low temperature. As a consequence, the shoulder in the $C_p$ around 30-40 K from Westrum and Justice cannot be interpreted as due solely, if at all, to rotation of the ammonium ion; indeed, careful inspection of the $\text{NH}_4\text{ClO}_4$ data shows no discernible shoulder, and the feature may be better attributed to the $\text{KClO}_4$ heat capacity data.

A recent Raman study of Chakraborty et al. of
NH₄ClO₄ noted anomalous changes in intensities of some of the internal modes of NH₄⁺ and ClO₄⁻ 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 Cₚ shoulder from the work of Westrum and Justice₂⁹ 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 NH₄⁺ 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 ND₄ClO₄ to determine whether anomalies or transitions are present and (b) to analyze the heat capacity and related data of both NH₄ClO₄ and ND₄ClO₄ using the method developed recently.₁₈,₁₉

II. EXPERIMENTAL

A. Deuterated ammonium perchlorate sample

The sample of ND₄ClO₄ was prepared from NH₄ClO₄ as follows. The NH₄ClO₄, 99.8% pure, without further purification was dissolved completely in D₂O which was 99.8 mol % minimum isotopic purity. A partially deuterated product was obtained on recrystallization. The extent of deuteration was measured by solid-state proton nuclear magnetic resonance (NMR) using a dilute mixture of NH₄Cl in NaCl as an intensity standard. The fraction of protons was estimated at 0.75%. In addition, no peaks due to species such as ND₄⁺H⁺ were seen in the Raman spectrum, although peaks due to H₂O were present in the product from the first few cycles. The H₂O 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 after which the H₂O peaks virtually disappeared. To remove most of the D₂O 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 excellent 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 D₂O trapped within our "dried" sample of ND₄ClO₄, 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 D₂O 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, Cₚ,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 ND₄ClO₄ 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 ND₄ClO₄ 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 ND₄ClO₄ sample are shown in Table I. There is no evidence that the Cₚ,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 (D₂O) 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 D₂O impurity amounted to 0.05 mass %, which is in excellent agreement with the 0.05% determined from the thermogravimetric analysis. The experimental Cₚ,m /K values for our ND₄ClO₄ given in Table I were not adjusted for this impurity. For comparison, the heat capacity curve for the undeuterated NH₄ClO₄ is shown in Fig. 1 as the broken line.
TABLE I. Experimental molar heat capacity of Nd2ClO4 (M = 121.513 g mol⁻¹; R = 8.3144 J K⁻¹ mol⁻¹).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Cₐₚₒₐₜ (R K)</th>
<th>T (K)</th>
<th>Cₐₚₒₐₜ (R K)</th>
<th>T (K)</th>
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<td>6.293</td>
<td>51.49</td>
<td>6.293</td>
<td>51.49</td>
<td>6.293</td>
</tr>
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</table>

**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 D₂O were not present. However, the heat capacities were not then corrected for the contribution by the 0.05 mass % D₂O 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.

![FIG. 1. Molar heat capacities of Nd₂ClO₄ (open circles, this work) and NH₄ClO₄ (broken line, Westrum and Justice (Ref. 15)).](image-url)
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 \( T=0 \).

### IV. ANALYSIS

#### A. Analysis of heat capacity data

The experimental heat capacity is written as

\[
C_{\mathrm{exp},m} = (C_{p,m} - C_{e,m}) + C_{\mathrm{vib},m} + C_{\mathrm{lat},m} + C_{\mathrm{rot},m}.
\]

The \((C_{p,m} - C_{e,m})\) is the correction term applied to the heat capacity \(C_{\text{exp},m}\) at constant stress or constant pressure to yield heat capacity at constant strain \(C_{\text{sat},m}\) 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

\[
C_{\text{sat},m} - C_{p,m} = -\left(\frac{dP}{dT}\right)_{s} T \left(\frac{dV}{dT}\right)_{p}.
\]

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 \((C_{\text{exp},m} - C_{\text{vib},m} - C_{\text{lat},m})\) for \(0 < T/K < 350\), which by inspection of Eq. (1) leaves \((C_{p,m} - C_{e,m}) + C_{\text{rot},m}\). 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 \(D_{2h}^{18}\) with four formula units per primitive cell. Each of the salts \(\text{NH}_4\text{ClO}_4\) and \(\text{ND}_4\text{ClO}_4\) has a total of 120 unit cell vibrations which are categorized as 72 internal modes, viz. \(10A_u + 8B_{1g} + 10B_{1u} + 8B_{2g} + 8A_u + 10B_{1g} + 8B_{2g} + 10B_{1u}\), 33 external optical modes (excluding librational modes) viz. \(5A_g + 4B_{1g} + 5B_{1g} + 4B_{2g} + 4A_u + 4B_{1u} + 3B_{2u} + 4B_{1u}\), 12 ammonium ion librational optical modes viz. \(A_u + 2B_{1g} + B_{2g} + 2B_{1u} + 2A_u + B_{1u} + 2B_{2u} + B_{3u}\), 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 \(\text{ND}_4\text{ClO}_4\), 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 scattering (CNIS) measurements. However, for two modes, \(B_{1u}\) 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. The remaining 14 unassigned external modes were placed with the \(C_{\text{lat},m}\) by multiplying the external heat capacity by 33/19 for \(\text{ND}_4\text{ClO}_4\) (or 33/16 in the case of \(\text{NH}_4\text{ClO}_4\)).

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

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**Table III. Assignment of vibrational frequencies\(^*\) expressed as wave number \(v\) in cm\(^{-1}\).**

<table>
<thead>
<tr>
<th>Mode</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_4)</th>
<th>(v_5)</th>
<th>(v_6)</th>
<th>(v_7)</th>
<th>(v_8)</th>
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<tbody>
<tr>
<td>NH(_4)ClO(_4)</td>
<td>175</td>
<td>60</td>
<td>200</td>
<td>70.3</td>
<td>95.5</td>
<td>109</td>
<td>40.0</td>
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<tr>
<td>(B_{1g})</td>
<td>135</td>
<td>65</td>
<td>155</td>
<td>92</td>
<td>116</td>
<td>152</td>
<td>195</td>
<td>128</td>
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<tr>
<td>(A_u)</td>
<td>28(^{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>200</td>
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<td>(B_{1g})</td>
<td>135</td>
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<tr>
<td>(A_u)</td>
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<td>(\text{Liberational modes})</td>
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</tr>
<tr>
<td>(\text{NH}_4)ClO(_4)</td>
<td>112</td>
<td>54(^{2})</td>
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<td>(\text{ND}_4)ClO(_4)</td>
<td>113</td>
<td>54(^{2})</td>
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<tr>
<td>(\text{B},\text{g})</td>
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<td>198 (^{2})</td>
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<tr>
<td>(\text{B},\text{u})</td>
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<tr>
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\(^{2}\)Data primarily from Tables VII–IX, Ref. 21 except as noted.

\(^{2}\)Estimated average over Brillouin zone, see Fig. 16, Ref. 21.

\(^{2}\)CNIS data, Ref. 21.

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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 \((C_{p,m} - C_{vib,m})\) to the heat capacity is very small, \((C_{p,m} - C_{vib,m} - C_{lib,m})\) is dominated by the heat capacity of the acoustic modes and is fitted to a Debye function. For the ammonium perchlorates, the \((C_{p,m} - C_{vib,m})\) has been calculated by us in Section 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 \((C_{p,m} - C_{vib,m})\) values are not negligible below 20 K. Given this dilemma of dealing with the \((C_{exp,m} - C_{lib,m})\) to get at the lattice contributions by either correcting it using \((C_{p,m} - C_{vib,m})\) 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 \((C_{exp,m} - C_{vib,m} - C_{lib,m})\) 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\(^{1}\) and are given in Table III. The \(B_{\|}\) mode was averaged over the Brillouin zone as done for the external modes and the \(B_{\perp}\) modes are from CNIS data.\(^{2}\) The six unassigned modes were incorporated by multiplying the \(C_{lib,m}\) by 12/6 for use in the \((C_{exp,m} - C_{lib,m})\) calculation. The resulting Debye \(\Theta_{D}\) values are 300 K for \(\text{NH}_4\text{ClO}_4\) and 129 K for \(\text{ND}_4\text{ClO}_4\).

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

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**Table IV. Heat capacity analysis for \(\text{NH}_4\text{ClO}_4\), \(C_{vib,m}\), smoothed experimental molar heat capacity; \(C_{lib,m}\), estimated vibrational contribution from internal optical modes of \(\text{NH}_4^+\) and \(\text{ClO}_4^-\) ions and all external optical modes except librational modes of \(\text{NH}_4^+\); \(C_{res,m}\), contribution from librational modes of \(\text{NH}_4^+\) ions; \(C_{rot,m}\), lattice contribution from \(\text{ NH}_4^+ \) and \(\text{ClO}_4^-\) (Debye heat capacity for acoustic modes); \(C_{lib,m} = (C_{exp,m} - C_{vib,m} - C_{res,m}) = (C_{exp,m} - C_{vib,m} - C_{rot,m})\) (see the text); \(C_{rot,m} = C_{res,m} = (C_{exp,m} - C_{lib,m})\) for thermal expansion; \(C_{res,m} = (C_{exp,m} - C_{rot,m})\) rotational contribution from \(\text{NH}_4^+\); \(R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}\).**

<table>
<thead>
<tr>
<th>(T)</th>
<th>(C_{res,m})</th>
<th>(C_{vib,m})</th>
<th>(C_{lib,m})</th>
<th>(C_{rot,m})</th>
</tr>
</thead>
<tbody>
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<td>0.123</td>
<td>0.015</td>
<td>0.015</td>
</tr>
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<td>0.057</td>
<td>0.020</td>
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<tr>
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<td>0.112</td>
<td>0.113</td>
</tr>
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<td>0.160</td>
<td>0.193</td>
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<td>140.0</td>
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<td>150.0</td>
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<td>0.406</td>
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<td>9.081</td>
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</tr>
<tr>
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</tr>
</tbody>
</table>

---

\( \Theta_p \) is reached, values of \( \Theta_p \) based upon experimental heat capacities are used to obtain \( C_{\text{lat,m}} \).

What are the effects of our not correcting for the \( (C_{p,m} - C_{\text{vib,m}}) \)? Although the shape of the \( \Theta_p (T) \) curve is unchanged and the typical asymptote results, the \( \Theta_p (T) \) values are too low because the values of \( (C_{\text{exp,m}} - C_{\text{vib,m}} - C_{\text{ib,m}}) \) are too high. The resulting values of \( \Theta_p \) for \( \text{NH}_4 \text{ClO}_4 \) and \( \text{ND}_4 \text{ClO}_4 \) 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 \( C_{\text{rem,m}} = C_{\text{exp,m}} - C_{\text{vib,m}} - C_{\text{lat,m}} \) equals \( (C_{p,m} - C_{\text{vib,m}}) + C_{\text{rem,m}} \) 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

\[
C_{\alpha,m} - C_{\alpha,m} = V_m a(T^2 / K_T),
\]

where \( a = V_m (dV_m / dT) \) 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 *isometric*. When the thermodynamic equations used to drive Eq. (3) are generalized to incorporate the anisotropic stresses and strains, the connection between heat capacities for ND\(_4\)ClO\(_4\) and \( \text{ND}_4 \text{ClO}_4 \) is

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( C_{\text{exp,m}} ) ( R )</th>
<th>( C_{\text{vib,m}} ) ( R )</th>
<th>( C_{\text{lat,m}} ) ( R )</th>
<th>( C_{\text{rem,m}} ) ( R )</th>
<th>( (C_{p,m} - C_{\text{vib,m}}) ) ( R )</th>
<th>( (C_{p,m} - C_{\text{vib,m}}) ) ( R )</th>
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FIG. 2. Molar heat capacity (a) for NH₄ClO₄ and (b) for ND₄ClO₄. (1) Experimental heat capacity for the pure salt; (2) vibrational heat capacity from all external modes except for NH₄⁺ librational modes; (3) vibrational heat capacity from internal optical modes of NH₄⁺ or ND₄⁺ and ClO₄⁻; (4) lattice heat capacity from NH₄⁺ or ND₄⁺ and ClO₄⁻ (Debye heat capacity for acoustic modes); (5) residual heat capacity \[ C_m = C_{\text{m,n}} - C_{\text{l,n,m}} = (C_{\text{p,m}} - C_{\text{m}} + C_{\text{rot,m}}) \], (see the text for discussion of vibrational and lattice contributions).

The three diagonal components of the thermal expansion tensor \( \alpha_1 (\alpha_a), \alpha_2 (\alpha_b), \) and \( \alpha_3 (\alpha_c) \) have been determined for ND₄ClO₄ and are shown in Fig. 3. The \( \alpha_i \)'s were obtained by fitting empirical functions to the unit cell data provided by Segel for ND₄ClO₄. These data are very similar to those of Prask et al. 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 coefficients, although the coefficients approach zero at absolute zero. The unit cell dimensions were fitted to a sixth order polynomial in \((T-150)\) in Kelvin:

\[
\text{lattice parameter} = \sum_{i=1}^{7} a_i (T - 150)^{i-1}.
\]

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

To obtain the expansion coefficients for NH₄ClO₄, the unit cell data by Prask et al. were first used. However, a comparison of their unit cell data for NH₄ClO₄ and ND₄ClO₄ shows the thermal expansion behavior to be similar for these two salts. Because the unit cell data by Segel for ND₄ClO₄ are so highly self-consistent, are spaced at such close intervals and agree with the data of Prask et al. for ND₄ClO₄, which in turn are very similar to their data for NH₄ClO₄, the data by Segel for ND₄ClO₄ were assumed to be valid for NH₄ClO₄. Equation (6) with coefficients shown in Table VI was applied to NH₄ClO₄ for our subsequent calculations of thermal expansion corrections.

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

The thermal expansion coefficients \( \alpha_i \), shown in Fig. 3 were obtained by differentiation of Eq. (6). The resulting \( \alpha_i \) values are approximately equal and constant between 150 and 250 K, but at lower temperatures \( \alpha_a \) increases and \( \alpha_b \) 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.

To obtain the expansion coefficients for NH₄ClO₄, the unit cell data by Prask et al. were first used. However, a comparison of their unit cell data for NH₄ClO₄ and ND₄ClO₄ shows the thermal expansion behavior to be similar for these two salts. Because the unit cell data by Segel for ND₄ClO₄ are so highly self-consistent, are spaced at such close intervals and agree with the data of Prask et al. for ND₄ClO₄, which in turn are very similar to their data for NH₄ClO₄, the data by Segel for ND₄ClO₄ were assumed to be valid for NH₄ClO₄. Equation (6) with coefficients shown in Table VI was applied to NH₄ClO₄ for our subsequent calculations of thermal expansion corrections.

The three diagonal components of the thermal expansion tensor \( \alpha_1 (\alpha_a), \alpha_2 (\alpha_b), \) and \( \alpha_3 (\alpha_c) \) have been determined for ND₄ClO₄ and are shown in Fig. 3. The \( \alpha_i \)'s were obtained by fitting empirical functions to the unit cell data provided by Segel for ND₄ClO₄. These data are very similar to those of Prask et al. 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 coefficients, although the coefficients approach zero at absolute zero. The unit cell dimensions were fitted to a sixth order polynomial in \((T-150)\) in Kelvin:

\[
\text{lattice parameter} = \sum_{i=1}^{7} a_i (T - 150)^{i-1}.
\]

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

To obtain the expansion coefficients for NH₄ClO₄, the unit cell data by Prask et al. were first used. However, a comparison of their unit cell data for NH₄ClO₄ and ND₄ClO₄ shows the thermal expansion behavior to be similar for these two salts. Because the unit cell data by Segel for ND₄ClO₄ are so highly self-consistent, are spaced at such close intervals and agree with the data of Prask et al. for ND₄ClO₄, which in turn are very similar to their data for NH₄ClO₄, the data by Segel for ND₄ClO₄ were assumed to be valid for NH₄ClO₄. Equation (6) with coefficients shown in Table VI was applied to NH₄ClO₄ for our subsequent calculations of thermal expansion corrections.
The elastic constants in Eq. (5) have been measured at 298 K by Vazquez et al.\textsuperscript{36} for NH\textsubscript{4}ClO\textsubscript{4}, who obtained values in units of 10\textsuperscript{10} Pascals as follows: $c_{11} = 2.51$, $c_{12} = 1.63$, $c_{11} = 1.15$, $c_{23} = 2.46$, $c_{23} = 0.76$, and $c_{13} = 3.15$ which are stated to be accurate within 4%. Values could neither be located at other temperatures for NH\textsubscript{4}ClO\textsubscript{4} nor at any temperature for ND\textsubscript{4}ClO\textsubscript{4}. In the absence of other information, the elastic constants for NH\textsubscript{4}ClO\textsubscript{4} were applied to ND\textsubscript{4}ClO\textsubscript{4} and were assumed to be independent of temperature for both salts.

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

Thus common values of $(C_{p,m} - C_{e,m})$ were used for the two salts evaluated using thermal expansion coefficients of ND\textsubscript{4}ClO\textsubscript{4} between 30 and 250 K, and the elastic constants of NH\textsubscript{4}ClO\textsubscript{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 $(C_{p,m} - C_{e,m})$ 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\textsubscript{4}ClO\textsubscript{4} salt reported in this paper along with that for NH\textsubscript{4}ClO\textsubscript{4} by Westrum and Justice\textsuperscript{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.\textsuperscript{25} of phase transitions in NH\textsubscript{4}ClO\textsubscript{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.\textsuperscript{21} who were unable to find any sign of a phase transition in either NH\textsubscript{4}ClO\textsubscript{4} or ND\textsubscript{4}ClO\textsubscript{4} from their crystallographic, Raman and coherent neutron inelastic scattering, and with those of Bastow et al.\textsuperscript{39} who have reported $^2$H and $^{35}$Cl relaxation time measurements.

FIG. 5. Rotational heat capacity of the ammonium ion in NH\textsubscript{4}ClO\textsubscript{4} and ND\textsubscript{4}ClO\textsubscript{4}.

Chakraborty et al.\textsuperscript{25} used the anomalous shoulder in the $C_p$ vs $T$ curve presented in Fig. 2 of Westrum and Justice\textsuperscript{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 KCIO\textsubscript{4} salt measured by Latimer and Ahlberg\textsuperscript{27} were subtracted from those measured by Westrum and Justice for the NH\textsubscript{4}ClO\textsubscript{4} salt in order to isolate the rotational heat capacity of the ammonium ion. However, the $C_p$ data for the KCIO\textsubscript{4} salt at low temperature may be causing the spurious bump since they are not smooth. Recent data by Zalukaev et al.\textsuperscript{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 $C_{ins,m}$ is due to the increasing excitation of the internal modes (curve 3) primarily $\nu_2$ for ClO\textsubscript{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.\textsuperscript{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 $C_p / R$ 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.

FIG. 4. Heat capacity correction due to thermal expansion in ND\textsubscript{4}ClO\textsubscript{4}.
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\(^3\) 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\(_4\)ClO\(_4\) salt is 4 kJ from NMR measurements\(^4\) 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 perchlorate is of lower symmetry than tetrahedral, its exact position is unknown. However, our \(C_{\text{rot},m}/R\) 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 \(C_{\text{rot},m}\) at low temperatures because of the problems in evaluating the (\(C_{\text{rot},m} - C_{\text{e,m}}\)) correction. The negative values in \(C_{\text{rot}}/R\) below about 40 K reinforce our stated uncertainty in the (\(C_{\text{rot},m} - C_{\text{e,m}}\)) 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 (\(C_{\text{rot},m} - C_{\text{e,m}}\)) in this temperature region arise from the assumptions made in the elastic constants, whose values were assumed to be those for NH\(_4\)ClO\(_4\) at room temperature and independent of temperature for both salts. This procedure must lead to an overestimated (\(C_{\text{rot},m} - C_{\text{e,m}}\)) as temperature falls, since the elastic constants decrease, so that \(C_{\text{rot},m}/R\) must be underestimated. Probably the underestimation becomes significant below 100 K. Clearly, the entire curve of \(C_{\text{rot}}/R\) 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.

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\(^6\) D. Vorlaender and E. Kasacht, Ber. 56B, 1157 (1923).
\(^27\) R. D. Heyding (personal communication, 1987).
\(^34\) S. L. Segel (personal communication, 1988).