

The thermodynamics of ammonium scheelites

VI. An analysis of the heat capacity and ancillary values for the metaperiodates KIO_4 , NH_4IO_4 , and ND_4IO_4

R. JULIAN C. BROWN,

*Department of Chemistry, Queen's University,
Kingston, Ontario, K7L 3N6, Canada*

JANE E. CALLANAN,

*Centre for Chemical Engineering, National Bureau of Standards,
Boulder, Colorado 80303, U.S.A.*

RON D. WEIR,^a

*Department of Chemistry and Chemical Engineering,
Royal Military College of Canada,
Kingston, Ontario, K7K 5L0, Canada*

and EDGAR F. WESTRUM, JR.

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

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An analysis of the heat capacity of NH_4IO_4 , ND_4IO_4 , and KIO_4 has been carried out in which the effects of the anisotropy of the thermal expansion have been considered, an approach hitherto used successfully for the perrhenates KReO_4 , NH_4ReO_4 , and ND_4ReO_4 . In the ammonium scheelites, the axial expansivities are very large, but of opposite sign, and as a result the molar volume of the scheelite lattice is nearly independent of temperature. It is shown that the correction from constant stress to constant strain results in a major contribution to the heat capacity of this highly anisotropic lattice. The difference between the experimental and calculated heat capacities, referred to as $\Delta C_{p,m}$, is expressed as the sum of the contributions from the anisotropy and the rotational heat capacity. The results of the analysis show that the rotational contribution is much smaller than had previously been thought. However, the exact contribution of the anisotropy cannot yet be calculated because the elastic constants are not known. In calculating the heat capacity, maximum use has been made of external optical-mode frequencies derived from spectroscopic measurements.

^a To whom correspondence should be sent.

1. Introduction

Recent experimental and theoretical studies on the thermodynamic properties of the ammonium perrhenates, NH_4ReO_4 and ND_4ReO_4 , both of which are tetragonal scheelite crystals, have shown that the rotational contribution to the excess heat capacity is much smaller than had previously been thought.⁽¹⁾ In each of these compounds, there is a broad peak in the graph of heat capacity against temperature, which is absent from the potassium salt of the perrhenate.^(2,3) The origin of the peak is now known to include a substantial contribution from the highly anisotropic lattice in addition to the rotational energy of the NH_4^+ ion. Because the elastic constants are not yet known for these perrhenates, the exact contribution of the anisotropy cannot be calculated. However, there is optimism that once this contribution has been determined, the remaining rotational energy can be modelled accurately.

The ammonium metaperiodates NH_4IO_4 and ND_4IO_4 share several common features with the isostructural perrhenates. These include axial expansivities, large and of opposite sign, resulting in the unit-cell volume remaining constant to within about 1 per cent,^(4,5) and nuclear quadrupole resonance (n.q.r.) frequencies whose temperature and pressure dependences are peculiar.^(4,6-8) The experimental heat capacities of NH_4IO_4 and ND_4IO_4 recently reported as IV and V in our series on the scheelites^(9,10) show a broad peak in each salt around 200 K when plotted against temperature, which is similar to that in the perrhenates, a result that was not unexpected.

The present paper contains the analysis of the heat capacities of both the deuterated and non-deuterated NH_4IO_4 , their interpretation, and discussion. The revised procedure to account for the anisotropy of the thermal expansion, which has been used with the perrhenates, has been applied to the metaperiodates to include the potassium salt KIO_4 .

2. Anisotropic thermal expansion

For any material, the standard equation for the contribution of thermal expansion to the heat capacity at constant pressure $C_{p,m}$ is

$$C_{p,m} - C_{v,m} = V_m T \alpha^2 / \kappa_T, \quad (1)$$

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. Heat capacities calculated from quantum energy levels *via* statistical mechanics normally refer to conditions of constant volume. However, this is not adequate for ammonium ions in non-cubic crystals with atoms located in general positions, in which case these calculations are usually made under restrictive conditions of "constant geometry" in which the atoms near each ammonium ion are held at constant positions relative to the ammonium ion, independent of temperature. This requires that the unit-cell dimensions, angles, and all atomic positions, except those of the H atoms in the ammonium ion, be kept constant. To use the results of statistical mechanics in

analyzing our experimental heat capacities, the measured $C_{p,m}$ must be corrected to constant geometry. Only for cubic crystals with all atoms in special positions does constant geometry correspond to constant volume.

Changes in the unit-cell dimensions and angles give rise to elastic strains, and are linked to stresses on the crystal through the elastic constants. Elastic strain and the corresponding stress are subject to thermodynamic analysis, but the atomic-position parameters correspond to "internal strain", which cannot be altered by the application of any external stress.^(1,2) As a result the best that can be achieved through a thermodynamic description is a calculation of the heat capacity of the crystal constrained to constant unit-cell dimensions and angles, *i.e.* the heat capacity at constant strain.

When the thermodynamics used to derive equation (1) is generalized to account for the anisotropic stresses and strains, the relation between heat capacities at constant stress $C_{\sigma,m}$, and constant strain $C_{\epsilon,m}$ is described by^(11,13)

$$C_{\sigma,m} - C_{\epsilon,m} = V_m T \sum c_{ijkl} \alpha_{ij} \alpha_{kl}, \quad (2)$$

in which c_{ijkl} is the isothermal elastic-constant tensor and α_{ij} is the expansivity tensor. For our purposes, the condition of constant stress is equivalent to constant pressure. For a crystal of scheelite structure with tetragonal symmetry, the last equation becomes, in Voigt notation:

$$C_{p,m} - C_{\epsilon,m} = V_m T \{2(C_{11} + C_{12})\alpha_1^2 + 4C_{13}\alpha_1\alpha_3 + C_{33}\alpha_3^2\}. \quad (3)$$

Hence $(C_{p,m} - C_{\epsilon,m})$ is quadratic in the diagonal components of the expansivity tensor α , and may be large even in a case where the cubic expansivity (*i.e.* the trace of α) is small, as for the ammonium scheelites.

The expansivity tensor for ammonium metaperiodate is known in detail over a wide temperature range,⁽⁵⁾ but the elastic-constant tensor is not known at any temperature, so the right-hand side of equation (3) cannot be evaluated numerically.

The two independent diagonal components of the expansivity tensor of NH_4IO_4 are known at several temperatures below room temperature.^{5,6} However, the uncertainty in the lattice parameters a and c is greater for this salt than for ammonium perrhenate.⁽¹⁵⁾ Below about 100 K, both α_1 and α_3 (α_a and α_c , respectively, in reference 5) are small and positive: $1.0 \times 10^{-5} \text{ K}^{-1}$ and $4 \times 10^{-5} \text{ K}^{-1}$, respectively. Above 100 K, these coefficients become large and of opposite sign. Segel *et al.*⁽⁵⁾ concluded that the greatest values were reached at 160 K when $\alpha_1 = -7 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_3 = 1.8 \times 10^{-4} \text{ K}^{-1}$. As the temperature reaches 298 K, the coefficients become substantially smaller ($\alpha_1 = -2.0 \times 10^{-5}$ and $\alpha_2 = 1.1 \times 10^{-4}$) as both tend towards positive values again. Unfortunately, lattice parameters are unknown above 298 K. The anomalous and highly anisotropic values between 100 and 300 K are qualitatively similar to those for NH_4ReO_4 , although in the perrhenate the peak in α_1 and α_3 occurs around 200 K and their values are about double those in the ammonium metaperiodate.⁽¹⁾ For NH_4IO_4 , the $(C_{p,m} - C_{\epsilon,m})$ from equation (3) must show a maximum near 160 K, provided the elastic-constant tensor c does not show some unusually strong dependence on temperature.

The magnitude of $(C_{p,m} - C_{\epsilon,m})$ can be estimated from equation (3) if the elastic constants for NH_4IO_4 are assumed to be similar to those for related crystals.⁽¹⁴⁻¹⁶⁾ By using the elastic constants for ammonium sulphate:⁽¹⁷⁾ $C_{11} = 36.1$, $C_{12} = 16.5$, $C_{13} = 15.8$, and $C_{33} = 35.3$ GPa, together with the molar volume of NH_4IO_4 : $6.78 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$, the contributions of the first, second, and third terms to $(C_{p,m} - C_{\epsilon,m})$ are estimated to be approximately 5.59, -8.60 , and $12.41 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively, in the vicinity of 160 K. The resulting value of $(C_{p,m} - C_{\epsilon,m})$ is about $9.39 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Because the α_1 and α_3 are unknown above 300 K, where they appear to be heading towards small positive values, the $(C_{p,m} - C_{\epsilon,m})$ cannot be calculated in this temperature region, but it seems highly likely that it will be as small as for ammonium perrhenate.⁽¹⁾

3. Analysis of the heat capacities

The experimental heat capacity is written as

$$C_{\text{expt},m} = (C_{p,m} - C_{\epsilon,m}) + C_{\text{vib},m} + C_{\text{lat},m} + C_{\text{rot},m}, \quad (4)$$

where $C_{\text{vib},m}$ is the heat capacity calculated from known vibrational frequencies at 77 or 83 K, including internal modes of both ions and external modes except for the ammonium-ion rotational or librational modes; $C_{\text{lat},m}$ is the heat capacity for the acoustic modes; and for the ammonium salts $C_{\text{rot},m}$ is the rotational heat capacity corresponding to the librational or rotational motion of the ammonium ion. Because frequencies at a fixed temperature are used in the calculation of $C_{\text{vib},m}$, this quantity is, in effect, a heat capacity at constant geometry.

The quantity actually measured calorimetrically is $C_{\text{sat},m}$ which is the heat capacity of the solid or liquid in equilibrium with its saturated vapour. This is linked to $C_{p,m}$ by

$$C_{\text{sat},m} - C_{p,m} = -(\partial p / \partial T)_{\text{sat}} T (\partial V_m / \partial T)_p. \quad (5)$$

For these solid scheelites $(C_{\text{sat},m} - C_{p,m})$ is negligible.

The space group of the scheelite structure is $I4_1/a$ or No. 88 C_{4h}^6 with 4 formula units per crystallographic unit cell and 2 formula units per primitive cell. KIO_4 has 36 unit-cell vibrations that can be classified as $(2A_g + 3B_g + 2E_g + 3A_u + 2B_u + 2E_u)$ internal modes, $(A_g + 2B_g + 3E_g + A_u + B_u + 2E_u)$ external optical modes, and $(A_u + E_u)$ external acoustic modes.⁽¹⁸⁾ For NH_4ReO_4 and ND_4ReO_4 , each has 60 unit-cell vibrations that can be classified as $(4A_g + 6B_g + 4E_g + 6A_u + 4B_u + 4E_u)$ internal modes, $(2A_g + 2B_g + 4E_g + A_u + 2B_u + 3E_u)$ external optical modes, and $(A_u + E_u)$ external acoustic modes.⁽¹⁹⁾ The assignments and wavenumbers are summarized in table 1.

The assignments of the *gerade* (g) mode wavenumbers of both internal and external modes based upon Raman spectra⁽¹⁹⁻²¹⁾ have been used. The u internal modes have been assumed to have the same wavenumbers as the corresponding g modes and, because these wavenumbers are high, no serious error is introduced by this procedure. Details of the assignments will be described in the following sections.

The first step in the analysis is to calculate $C_{\text{vib},m}$ from spectroscopic information at low temperatures, including translational external modes for both ions and

TABLE I. Assignments of spectroscopic wavenumbers $\bar{\nu}$

Salt	$\bar{\nu}/\text{cm}^{-1}$							
	IO_4^- internal modes							
	$A_g + B_u$	$A_g + B_u$	$B_g + A_u$	$B_g + A_u$	$E_g + E_u$	$B_g + A_u$	$E_g + E_u$	
KIO_4	792	278	293	858	844	346	337.9	
NH_4IO_4	794.9	296.8	285	847.6	840.3	337.9	337.9	
ND_4IO_4	795.3	295.7	275.1	847.9	840.2	336.2	336.2	
	NH_4^+ internal modes							
	$A_g + B_u$	$A_g + B_u$	$B_g + A_u$	$B_g + A_u$	$E_g + E_u$	$B_g + A_u$	$E_g + E_u$	
NH_4IO_4	3144	1654	1654	3204	3204	1445	1445	
ND_4IO_4	2269	1192	1192	2399	2399	1099	1099	
	External modes							
	A_g	E_g	E_g	B_g	E_g	B_g	$E_g + E_u$	$A_g + B_u$
KIO_4	145	179	93.2	72.2	122	122	--	
NH_4IO_4	147.2	140.3	89.1	63.9	216	194.5	240	258.6
ND_4IO_4	141.8	135.9	89.0	63.2	196.7	176.1	176.1	196.7
	A_u	E_u	E_u	B_u				
KIO_4	98	140	<i>a</i>	<i>a</i>				
NH_4IO_4	88	190	<i>a</i>	<i>a</i>				
ND_4IO_4	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>				

^a Unassigned.

librational external modes for the anion. At low temperatures, the rotational motion of the ammonium ion appears in the Raman spectrum as well-defined librational modes. As a result, for temperatures below about 120 K, $C_{\text{rot,m}}$ is replaced by the librational heat capacity $C_{\text{lib,m}}$ computed using the Einstein function and the observed low-temperature librational wavenumbers of the ammonium ion. At $T < 70$ K, the contribution of thermal expansion to the heat capacity is very small, so that $(C_{\text{expt,m}} - C_{\text{vib,m}} - C_{\text{lib,m}})$ in this temperature region is dominated by the heat capacity of the acoustic modes. The low-temperature values of $(C_{\text{expt,m}} - C_{\text{lib,m}})$ were therefore fitted to a Debye function corresponding to 3 acoustic degrees of freedom per unit cell containing 2 formula units.

When the Debye model is obeyed, the Debye temperature $\Theta_D(T)$ remains constant for any crystal. However, for real crystals, the model fails to describe what is observed experimentally. For many metal and diatomic lattices, $\Theta_D(T)$ asymptotically approaches a constant value at high temperature where all the modes of vibration contribute to the heat capacity. For other solids, $\Theta_D(T)$ rises as temperature increases, reaches a maximum value, and then decreases. To obtain the contribution of the lattice vibrations to the heat capacity of these crystals, the $\Theta_D(T)$ is plotted and the asymptotic value at the peak Θ_D^∞ is drawn to extend to high temperatures. The resulting curve is then used with Debye tables. At temperatures below the point where Θ_D^∞ is reached, values of Θ_D based on the experimental heat capacities were used to obtain $C_{\text{lat,m}}$. Then, by difference, $\{(C_{p,m} - C_{e,m}) + C_{\text{rot,m}}\}$ is calculated over the entire range of temperature.

KIO₄

The 18 internal modes were assigned wavenumbers at 77 K.⁽²⁰⁾ The 15 external optical modes were assigned as follows: 9 g-modes were taken at 77 K,⁽²⁰⁾ the A_u and an E_u were taken at room temperature,⁽²¹⁾ and the B_u is inactive while another E_u could not be assigned.⁽²¹⁾ With these assignments, C_{vib} was calculated as a sum of Einstein functions, including a factor for degeneracy, to include the 18 internal degrees of freedom and 12 of the 15 external optical modes, the 3 external acoustic modes being considered separately as acoustic lattice modes. The remaining inactive B_u external mode and the doubly degenerate E_u external mode were placed with the C_{vib,m} by multiplying the external heat capacity by 15/12.

Using the experimental heat capacity of pure KIO₄ from reference 22, the difference (C_{expt,m} - C_{vib,m}) was then calculated, and the values for low temperatures were fitted to a Debye function for 1.5 degrees of freedom per molecule, corresponding to the 3 acoustic modes per unit cell containing 2 formula units. The value of Θ_D^x is 125.6 K, and this value was then used to compute the lattice heat capacity over the entire temperature range above 50 K.

The residual heat capacity C_{res,m} = (C_{expt,m} - C_{vib,m} - C_{lat,m}) is just (C_{p,m} - C_{e,m}), since there can be no rotational heat capacity in the potassium salt. The results of this analysis are shown in figure 1 and table 2. In the calculated values in columns 3 to 5, the results are reported with three decimal places for consistency with the experimental values. At 300 K, C_{res,m} = 9.50 J · K⁻¹ · mol⁻¹ or C_{res,m}/R = 1.142. This value is double that obtained for (C_{p,m} - C_{v,m}) using equation (1), which is equivalent to (C_{p,m} - C_{e,m}) for an isotropic lattice. For use in equation (1), the V_m⁽²³⁾, κ_T⁽²⁴⁾ and α_v⁽²⁵⁾ were taken as 6.2877 × 10⁻⁵ m³ · mol⁻¹,

TABLE 2. Heat-capacity analysis for pure KIO₄. C_{expt,m}, smoothed experimental molar heat capacity; C_{vib,m}, estimated vibrational contribution from all internal and external optical modes; C_{lat,m}, lattice contribution (Debye heat capacity for acoustic modes);

$$C_{res,m} = (C_{expt,m} - C_{vib,m} - C_{lat,m}) = (C_{p,m} - C_{e,m}); \quad R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

T K	$\frac{C_{expt,m}}{R}$	$\frac{C_{vib,m}}{R}$	$\frac{C_{lat,m}}{R}$	$\frac{C_{res,m}}{R}$	T K	$\frac{C_{expt,m}}{R}$	$\frac{C_{vib,m}}{R}$	$\frac{C_{lat,m}}{R}$	$\frac{C_{res,m}}{R}$
10	0.074	0.002	0.072	0.000	170	11.730	9.797	1.460	0.473
20	0.750	0.220	0.530	0.000	180	12.051	10.093	1.464	0.494
30	1.788	0.972	0.816	0.000	190	12.364	10.370	1.467	0.527
40	2.998	1.992	1.007	0.000	200	12.665	10.631	1.471	0.563
50	4.129	3.013	1.116	0.000	210	12.941	10.876	1.473	0.592
60	5.179	3.947	1.217	0.015	220	13.230	11.110	1.476	0.645
70	6.150	4.787	1.283	0.080	230	13.495	11.330	1.478	0.687
80	7.005	5.543	1.330	0.131	240	13.771	11.540	1.479	0.752
90	7.754	6.228	1.364	0.162	250	14.036	11.741	1.482	0.813
100	8.443	6.844	1.388	0.212	260	14.300	11.931	1.483	0.886
110	9.059	7.399	1.407	0.253	270	14.553	12.113	1.484	0.956
120	9.627	7.900	1.420	0.307	280	14.733	12.286	1.485	0.962
130	10.111	8.352	1.432	0.327	290	14.986	12.452	1.487	1.048
140	10.560	8.762	1.441	0.357	300	15.238	12.609	1.487	1.142
150	10.980	9.136	1.449	0.395	310	15.479	12.760	1.488	1.232
160	11.377	9.480	1.455	0.441					

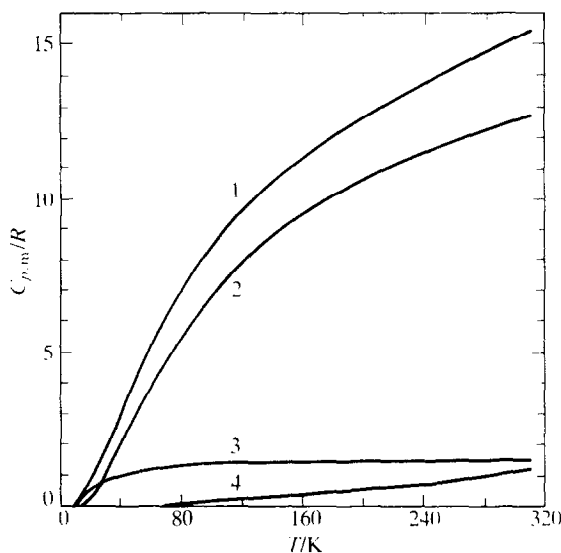


FIGURE 1. Molar heat capacity for KIO_4 . 1, Experimental heat capacity for pure salt; 2, vibrational heat capacity from (internal+external) optical modes; 3, lattice heat capacity (Debye heat capacity for acoustic modes); 4, residual heat capacity $= (C_{\text{expt.},m} - C_{\text{vib.},m} - C_{\text{lat.},m}) = (C_{p,m} - C_{v,m})$. (See the text for full discussion of vibrational and lattice contributions.)

$4.1284 \times 10^{-11} \text{ Pa}^{-1}$, and $10.08 \times 10^{-5} \text{ K}^{-1}$, respectively, to give $(C_{p,m} - C_{v,m}) = 4.64 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

NH_4IO_4

The 36 internal modes were assigned wavenumbers at 83 K,⁽¹⁹⁾ and these were kept constant in calculating their contributions to the heat capacity, since the contributions of all the vibrational modes at constant geometry are required. The 9 external optical g-modes were assigned wavenumbers also taken at 83 K,⁽¹⁹⁾ but the values for A_u and E_u : 88 and 190 cm^{-1} , were available only at room temperature.⁽²¹⁾ With these wavenumber assignments, C_{vib} was computed as a sum of Einstein functions to include the 36 internal modes and 15 of the 24 external modes. An inactive external B_u mode and an unassigned doubly-degenerate external E_u mode were incorporated with the internal modes by multiplying the external heat capacity by 15/12. The librational wavenumbers of 240 and 258.6 cm^{-1} at 83 K,⁽¹⁹⁾ were used to calculate $C_{\text{lib},m}$ at low temperatures corresponding to their 6 degrees of freedom. This completes the accounting of the 21 external optical modes leaving the 3 external acoustic modes to be considered separately as lattice modes.

The experimental heat capacities for pure NH_4IO_4 were used⁽⁹⁾ to calculate the difference $(C_{\text{expt.},m} - C_{\text{vib.},m} - C_{\text{lib.},m})$, and the values for low temperatures were fitted to a Debye function for 1.5 degrees of freedom per molecule, corresponding to the 3 acoustic modes per unit cell containing 2 formula units. The resulting value of Θ_D^∞ was 91.8 K, and this value was employed to compute the lattice heat capacity over the entire temperature range above 20 K.

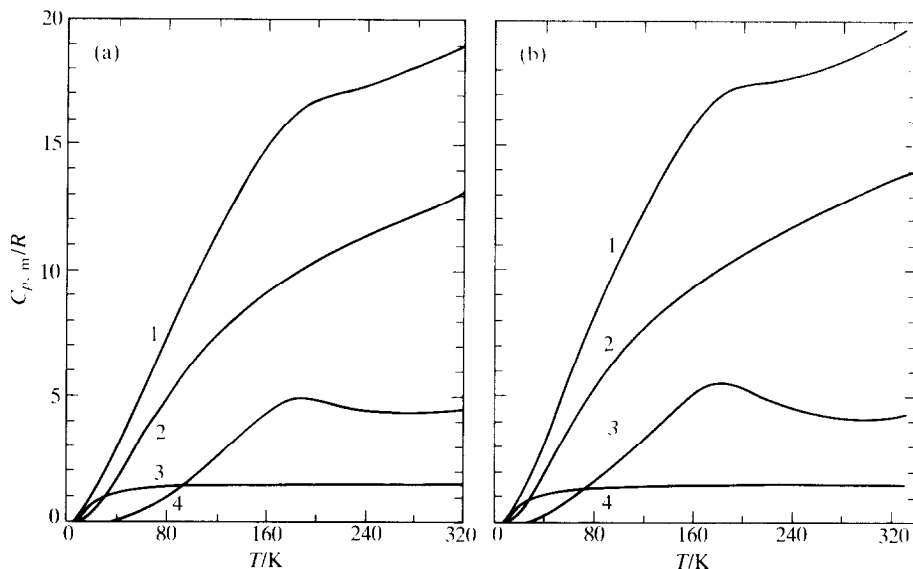


FIGURE 2. Molar heat capacity (a) for NH_4IO_4 and (b) for NH_4IO_4 . 1, Experimental heat capacity for pure salt; 2, vibrational heat capacity from (internal+external) optical modes of NH_4^+ or ND_4^+ and IO_4^- and libration from external modes of IO_4^- ; 3, lattice heat capacity from NH_4^+ or ND_4^+ and IO_4^- (Debye heat capacity for acoustic modes); 4, residual heat capacity $C_{\text{res},m} = (C_{\text{expt},m} - C_{\text{vib},m} - C_{\text{lat},m}) = \{(C_{p,m} - C_{\epsilon,m}) + C_{\text{rot},m}\}$. (See the text for full discussion of vibrational and lattice contributions.)

TABLE 3. Heat-capacity analysis for NH_4IO_4 . $C_{\text{expt},m}$, smoothed experimental molar heat capacity for pure NH_4IO_4 ; $C_{\text{vib},m}$, estimated contribution from internal optical modes of NH_4^+ and IO_4^- ions and all external optical modes except librational modes of NH_4^+ ; $C_{\text{lib},m}$, contribution from librational modes of NH_4^+ ions; $C_{\text{lat},m}$, lattice contribution from NH_4^+ and IO_4^- (Debye heat capacity for acoustic modes);

$$C_{\text{res},m} = (C_{\text{expt},m} - C_{\text{vib},m} - C_{\text{lat},m}) = \{(C_{p,m} - C_{\epsilon,m}) + C_{\text{rot},m}\} \text{ (see the text); } R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

T K	$C_{\text{expt},m}$ R	$C_{\text{vib},m}$ R	$C_{\text{lib},m}$ R	$C_{\text{lat},m}$ R	$C_{\text{res},m}$ R	T K	$C_{\text{expt},m}$ R	$C_{\text{vib},m}$ R	$C_{\text{lib},m}$ R	$C_{\text{lat},m}$ R	$C_{\text{res},m}$ R
10	0.149	0.006	0.000	0.143	0.000	170	15.635	9.523	2.114	1.478	4.634
20	0.904	0.273	0.000	0.630	0.001	180	16.189	9.847	2.194	1.481	4.861
30	1.898	0.913	0.004	0.979	0.006	190	16.536	10.147	2.264	1.483	4.906
40	2.936	1.691	0.035	1.169	0.076	200	16.772	10.434	2.325	1.484	4.854
50	3.991	2.511	0.129	1.275	0.205	210	16.957	10.703	2.379	1.485	4.769
60	5.090	3.336	0.289	1.339	0.415	220	17.087	10.960	2.427	1.487	4.640
70	6.168	4.142	0.496	1.378	0.647	230	17.218	11.206	2.470	1.488	4.525
80	7.279	4.911	0.722	1.406	0.962	240	17.373	11.442	2.509	1.489	4.443
90	8.394	5.630	0.945	1.425	1.339	250	17.567	11.669	2.544	1.490	4.408
100	9.457	6.291	1.157	1.439	1.727	260	17.739	11.888	2.575	1.490	4.361
110	10.390	6.896	1.350	1.449	2.045	270	17.978	12.101	2.604	1.491	4.386
120	11.450	7.444	1.520	1.457	2.550	280	18.170	12.307	2.629	1.493	4.370
130	12.429	7.939	1.673	1.464	3.026	290	18.349	12.507	2.653	1.493	4.349
140	13.354	8.389	1.805	1.469	3.496	300	18.553	12.703	2.674	1.493	4.357
150	14.207	8.799	1.922	1.472	3.935	310	18.768	12.893	2.693	1.494	4.382
160	14.963	9.176	2.025	1.476	4.312	320	18.996	13.080	2.711	1.494	4.422

The residual heat capacity $C_{\text{res},m} = (C_{\text{expt},m} - C_{\text{vib},m} - C_{\text{lat},m})$ is equal to $\{(C_{p,m} - C_{\varepsilon,m}) + C_{\text{rot},m}\}$, and is plotted against temperature in figure 2(a) with the results contained in table 3.

ND₄IO₄

The same procedure was followed for the deuterated salt using experimental heat capacities for pure ND₄IO₄.⁽¹⁰⁾ However, none of the external optical A_u, E_u, E_u modes has wavenumbers assigned so these plus the inactive B_u mode were included with the internal modes by multiplying the external heat capacity by 15/9. The librational wavenumbers of 176.1 and 196.7 cm⁻¹ at 83 K,⁽¹⁹⁾ were used to determine the C_{lib,m} at low temperatures.

By fitting the $(C_{\text{expt},m} - C_{\text{vib},m} - C_{\text{lib},m})$ at low temperatures to a Debye function for 1.5 degrees of freedom per molecule, the resulting $\Theta_D^{\alpha} = 118.1$ K, and this value was used to calculate the lattice heat capacity over the entire temperature range above 50 K. The results of the analysis are shown in figure 2(b) and table 4.

4. Discussion

The residual heat capacities $C_{\text{res},m}$ presented in figure 2 show the characteristic peak found for ammonium salts. This $C_{\text{res},m}$ contains contributions from the anisotropic thermal expansion and the rotational motion of the ammonium ion, which cannot be separated without information on the elastic-constant tensor.

The effect of deuteration on $C_{\text{res},m}/R$ is to raise its value at the peak from 4.906 at 190 K to 5.521 at 184 K. This small downward shift in the temperature where the

TABLE 4. Heat-capacity analysis for ND₄IO₄. $C_{\text{expt},m}$, smoothed experimental molar heat capacity for pure ND₄IO₄; $C_{\text{vib},m}$, estimated contribution from internal optical modes of ND₄⁺ and IO₄⁻ ions and all external optical modes except librational modes of ND₄⁺; $C_{\text{lib},m}$, contribution from librational modes of ND₄⁺ ions; $C_{\text{lat},m}$, lattice contribution from ND₄⁺ and IO₄⁻ (Debye heat capacity for acoustic modes); $C_{\text{res},m} = (C_{\text{expt},m} - C_{\text{vib},m} - C_{\text{lib},m}) = \{(C_{p,m} - C_{\varepsilon,m}) + C_{\text{rot},m}\}$ (see the text), $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T K	$C_{\text{expt},m}$ R	$C_{\text{vib},m}$ R	$C_{\text{lib},m}$ R	$C_{\text{lat},m}$ R	$C_{\text{res},m}$ R	T K	$C_{\text{expt},m}$ R	$C_{\text{vib},m}$ R	$C_{\text{lib},m}$ R	$C_{\text{lat},m}$ R	$C_{\text{res},m}$ R
10	0.147	0.008	0.000	0.138	0.001	180	17.010	10.043	2.517	1.468	5.499
20	0.922	0.313	0.001	0.608	0.001	190	17.287	10.352	2.562	1.471	5.464
30	1.960	1.018	0.037	0.904	0.038	200	17.427	10.648	2.602	1.475	5.304
40	3.142	1.885	0.185	1.072	0.185	210	17.500	10.935	2.635	1.477	5.088
50	4.371	2.781	0.440	1.150	0.440	220	17.583	11.213	2.665	1.478	4.892
60	5.713	3.650	0.741	1.235	0.828	230	17.679	11.485	2.692	1.481	4.713
70	6.910	4.473	1.038	1.305	1.132	240	17.775	11.749	2.716	1.482	4.544
80	8.144	5.239	1.307	1.347	1.558	250	17.871	12.009	2.737	1.483	4.379
90	9.364	5.945	1.540	1.377	2.042	260	18.014	12.264	2.755	1.484	4.266
100	10.359	6.589	1.736	1.400	2.370	270	18.218	12.514	2.772	1.485	4.219
110	11.417	7.172	1.900	1.417	2.828	280	18.410	12.760	2.788	1.487	4.164
120	12.418	7.699	2.039	1.429	3.290	290	18.639	13.000	2.801	1.498	4.151
130	13.367	8.175	2.154	1.440	3.752	300	18.890	13.236	2.814	1.489	4.165
140	14.281	8.609	2.252	1.448	4.224	310	19.118	13.468	2.825	1.489	4.161
150	15.135	9.007	2.334	1.454	4.674	320	19.419	13.694	2.836	1.490	4.235
160	15.928	9.375	2.405	1.460	5.093	330	19.695	13.915	2.846	1.490	4.290
170	16.541	9.718	2.466	1.464	5.359						

peak occurs is not observed for NH_4ReO_4 and ND_4ReO_4 or for NH_4BF_4 and ND_4BF_4 .⁽²⁷⁾ Calculations of rotational heat capacities suggest that the rotational heat-capacity peak should not shift with temperature upon deuteration.⁽²⁸⁾ The temperature at which the lattice constants for the metaperiodates undergo their maximum change with temperature was given by Segel *et al.*⁽⁵⁾ as 160 K, but there is some uncertainty in this value since the major sets of lattice-constant measurements are inconsistent in this temperature region. It is not worthwhile to fit theoretical models of rotational motion to our experimental results until the contribution of thermal expansion is separated reliably from the rotational motion of the ammonium ion, and this requires measurements of the elastic constants of the crystals.

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