The thermodynamics of ammonium scheelites. III. An analysis of the heat capacity and related data of deuterated ammonium perrhenate ND$_4$ReO$_4$

R. J. C. Brown
Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

J. E. Callanan
Center for Chemical Engineering, National Bureau of Standards, Boulder, Colorado 80303

R. D. Weir[a]
Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario, K7K 5LO, Canada

E. F. Westrum, Jr.
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

An analysis of the heat capacity of deuterated and undeuterated NH$_4$ReO$_4$ has been carried out in which the effects of the anisotropy of the thermal expansion have been considered, an approach hitherto not used for ammonium compounds. In the ammonium scheelites, the axial thermal expansion coefficients are very large, but of opposite sign, and as a result the 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 values of heat capacity, referred to as ΔC_p, 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 then previously thought. However, the exact contribution of the anisotropy cannot be calculated at this time 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.

I. INTRODUCTION

Thermodynamic properties provide a rigorous test of theories of the dynamics of solids. In the case of ammonium salts, it is not unusual to find a broad peak in the graph of heat capacity vs temperature which is not present for the alkali metal salts of the same anion. The origin of the peak is thought to be the rotational energy levels of the ammonium ion, which can be computed from quantum theory if the rotational potential energy function of the ammonium ion is known or assumed.

The reliability of heat capacity data as a test of theoretical models for the rotation of the ammonium ion depends upon being able accurately to separate the ammonium ion rotational heat capacity from various other contributions to the measured heat capacity. The rotational contribution is a small part of the total heat capacity, and so any uncertainty in other contributions drastically reduces the reliability of the "experimental" value of the rotational heat capacity.

Ammonium perrhenate, NH$_4$ReO$_4$, provides an excellent test of the analysis procedures. The heat capacities of KReO$_4$ and NH$_4$ReO$_4$ have been measured and analyzed previously.[1] The rotational heat capacity peak in NH$_4$ReO$_4$ deduced from such an analysis is larger than that of any other known peak,[2] and no adequate explanation in terms of the ammonium ion rotational motion has been published to date. To elucidate this problem, the heat capacity of ND$_4$ReO$_4$ was recently measured.[3] In attempting to under-

stand these and the previous results, the method of analysis used formerly has been reexamined and revised in this paper designated III in the series of our continuing study on the scheelites. Previous papers are designated I[1] and II[3].

In the present analysis of the heat capacity of both deuterated and undeuterated NH$_4$ReO$_4$ the effect of the anisotropy of the thermal expansion has been considered. In ammonium perrhenate, the axial thermal expansion coefficients are very large, but of opposite sign, and the volume is almost independent of temperature.[4,5] In this paper the effects of this gross anisotropy are considered and shown to be a major contributor to the heat capacity; the exact contribution cannot be calculated because the elastic constants are not known. A revised procedure for the analysis of heat capacity data is used, in which maximum use is made of known spectroscopic data. It appears that the rotational heat capacity peak is much smaller than was previously thought.

II. ANISOTROPIC THERMAL EXPANSION

For an isotropic material, the contribution of thermal expansion to the heat capacity at constant pressure C_p is described by the standard equation

$$C_p - C_v = VT\alpha^2/\kappa_T, \tag{1}$$

where $\alpha = V^{-1}(\partial V/\partial T)_P$ is the volume thermal expansion coefficient, V is the molar volume, and $K_T = -V^{-1}(\partial V/\partial P)_T$ is the isothermal compressibility. Heat capacities calculated from quantum energy levels through statistical mechanics usually refer to constant volume conditions. For

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[a] Author to whom correspondence should be sent.

ammonium ions in a noncubic crystal with atoms in general positions, the calculations are normally made under very restrictive "constant geometry" conditions in which the atoms in the vicinity of each ammonium ion are held at constant positions relative to the ammonium ion, independent of temperature. This requires that the unit cell dimensions and angles, and all atomic position parameters other than those of the hydrogen atoms in the ammonium ion, be kept constant. In order to use the results of statistical mechanics in analyzing observed heat capacity data, the measured C_p values 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 correspond to elastic strains, and are related 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 changed by the application of any external stress.[6] Therefore the best that can be achieved by a thermodynamic description is a calculation of the heat capacity of a model constrained to constant unit cell dimensions and angles, i.e., the heat capacity at constant strain.

The relationship between the heat capacities at constant stress C_σ and constant strain C_ϵ for an anisotropic crystal is an extension of Eq. (1)[7,8]:

$$C_\sigma - C_\epsilon = VT \sum c_{ijkl} \alpha_{ij} \alpha_{kl}, \qquad (2)$$

in which c_{ijkl} is the isothermal elastic constant tensor and α_{ij} is the thermal expansion tensor. For the present purposes, the condtion of constant stress means constant pressure. For the case of the scheelite structure with tetragonal symmetry, the last equation becomes, in Voigt notation,

$$C_p - C_\epsilon = VT\{(2c_{11} + c_{12})\alpha_1^2 + 2c_{13}\alpha_1\alpha_3 + c_{33}\alpha_3^2\}. \qquad (3)$$

Thus $C_p - C_\epsilon$ is quadratic in the diagonal components of the thermal expansion tensor α, and can be large even in a situation where the bulk thermal expansion (i.e., the trace of α) is small, as for the ammonium scheelites. The thermal expansion tensor for ammonium perrhenate is known in detail over a wide temperature range,[4,5] but the elastic constant tensor is not known at any temperature, so the right-hand side of Eq. (3) cannot be evaluated numerically at present.

Shown in Fig. 1 are the two diagonal components of the thermal expansion tensor of the NH_4ReO_4 as a function of temperature. These curves were determined by fitting a polynomial to the unit cell data,[4,5] and then differentiating the polynomial. Below about 100 K, both thermal expansion coefficients are small and positive, but from that temperature to 300 K, $\alpha_1(\alpha_a)$ and $\alpha_3(\alpha_c)$ are of opposite sign, and become numerically large near 200 K. Therefore $C_p - C_\epsilon$ must have a maximum in the vicinity of 200 K, unless the elastic constant tensor c has a very strong temperature dependence.

The magnitude of $C_p - C_\epsilon$ can be estimated from Eq. (3) if estimates of the elastic constants are made based upon published data for related crystals.[9] For instance, the diagonal components of the elastic constant tensor for ammonium sulphate are close to 30 GPa, and if this value is used for c_{33} in Eq. (3), together with the molar volume of NH_4ReO_4, 6.7×10^{-5} m^3 mol^{-1}, the contribution of the last term in braces to $C_p - C_\epsilon$ is found to be approximately 40 J K^{-1} mol^{-1} in the vicinity of 200 K. Some cancellation can be expected due to the negative cross term in $\alpha_1\alpha_3$, but even so, it is clear that $C_p - C_\epsilon$ is likely to very much larger than the previous estimates[1] of $C_p - C_v$ made using Eq. (1). These were 5.1 J K^{-1} mol^{-1} at 300 K for $KReO_4$, and 1.3 J K^{-1} mol^{-1} at 300 K for NH_4ReO_4. Further, because of the temperature dependence of α_1 and α_3, $C_p - C_\epsilon$ is peaked at about 200 K and may be responsible for a large part of the observed broad peak in C_p.
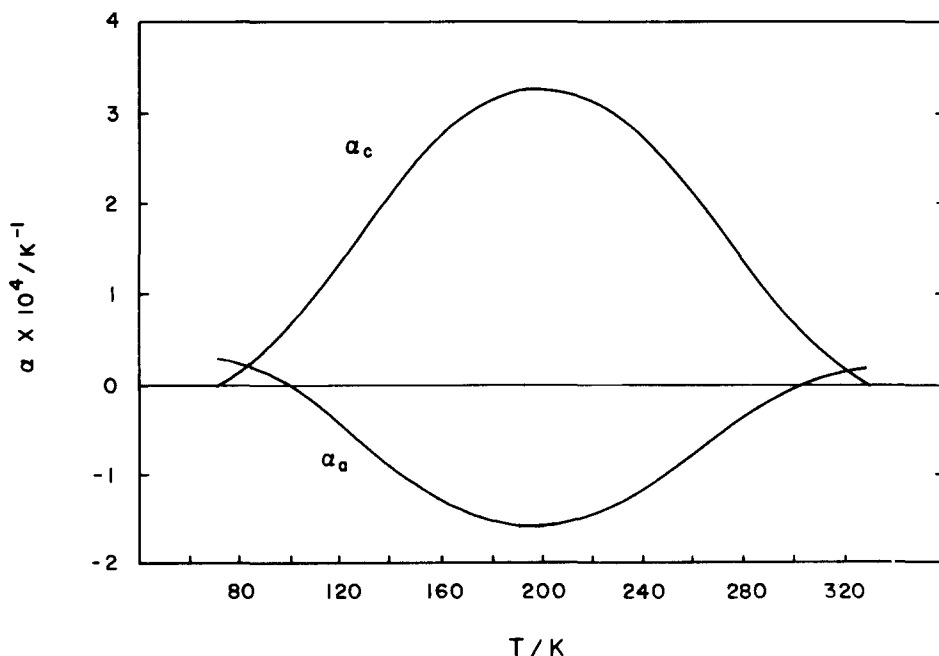

FIG. 1. Thermal expansion coefficients α_a, α_c for NH_4ReO_4.

TABLE I. Assignments of spectroscopic frequency v in cm^{-1}.

ReO$_4^-$ internal modes

	$A_g + B_u$	$A_g + B_u$	$B_g + A_u$	$B_g + A_u$	$E_g + E_u$	$B_g + A_u$	$E_g + E_u$
KReO$_4$	966	350	350	924	897	332	337
NH$_4$ReO$_4$	969	335	328	910	893	351	351
ND$_4$ReO$_4$	969	335	328	910	893	351	351

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$_4$ReO$_4$	3128	1658	1658	3182	3182	1438	1431
ND$_4$ReO$_4$	2258	1198	1191	2382	2382	1081	1081

External modes

	A_g	E_g	E_g	B_g	E_g	B_g	$E_g + E_u$	$A_g + B_u$
KreO$_4$	127.9	114.4	72.5	59.1	160.1	151	...	...
NH$_4$ReO$_4$	135.3	120.3	67.6	49.3	210.1	189.7	272	263.3
ND$_4$ReO$_4$	134.5	117.1	66.9	48.6	193.7	174.2	203	193.7

	A_u	E_u	E_u	B_u
KReO$_4$	90	125	158	a
NH$_4$ReO$_4$	108	134	170	a
ND$_4$ReO$_4$	106	140	169	a

^{a} Unassigned.

III. ANALYSIS OF HEAT CAPACITY DATA

The heat capacity data for KReO$_4$ and NH$_4$ReO$_4$, which have already been published, will be treated first, as a check on the consistency of the revised procedure. Then the new data on ND$_4$ReO$_4$ will be analyzed.

The experimental heat capacity C_{exp} is written in the form

$$C_{exp} = (C_p - C_\epsilon) + C_{vib} + C_{lat} + C_{rot}, \qquad (4)$$

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

The quantity actually measured calorimetrically is C_{sat}, the heat capacity of the solid or liquid in equilibrium with its saturated vapor. This is related to C_p by

$$C_{sat} - C_p = \left(\frac{\partial P}{\partial T}\right)_{sat} \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]. \qquad (5)$$

For the solid scheelites, $C_{sat} - C_p$ is negligible.

The space group of the scheelite structure is $I4_1/a$ or No. 88 C_{4h}^6 with four formula units per crystallographic unit cell and two formula units per primitive cell. KReO$_4$ has 36 unit cell vibrations which 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 modes, and $A_u + E_u$ acoustic modes.[10] NH$_4$ReO$_4$ has 60 unit cell vibrations which 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 modes, and $A_u + E_u$ acoustic modes.[11] The assignments and wave numbers are summarized in Table I.

The assignments of the g mode frequencies of both internal and external modes based upon Raman spectra[10–14] have been used. The u internal modes have been assumed to have the same frequencies as the corresponding g modes and, because these frequencies are high, no serious error is introduced by this procedure. Assignment of the u external modes is more tentative. The B_u modes are inactive in both IR and Raman spectra. Some information about the other modes has been obtained from IR spectra,[15] but the assignment of the frequencies is uncertain. Details of the assignments will be given in the sections to follow.

The first step in the analysis is to compute C_{vib} from spectroscopic data at low temperatures, including translational external modes for both ions and librational external modes for the anion. At low temperatures, the rotational motion of the ammonium ion manifests itself in the Raman spectrum as well-defined librational modes. Hence for temperatures below 120 K, C_{rot} is replaced by the librational heat capacity C_{lib}, which is calculated using the Einstein function with the observed low temperature librational frequencies of the ammonium ion. At low temperatures, the contribution of thermal expansion to the heat capacity is very small, so $C_{exp} - C_{vib} - C_{lib}$ at low temperature is dominated by the heat capacity of the acoustic modes. The low temperature values of $C_{exp} - C_{vib} - C_{lib}$ were therefore fitted to a Debye function corresponding to three acoustic degrees of freedom per unit cell containing two formula units.

If the Debye model were obeyed, the $\theta_D(T)$ should be constant for any crystal. However for real crystals, the model does not describe what is observed experimentally. For many metal and diatomic lattices, $\theta_D(T)$ asymptotically approaches a constant value at high temperatures where all the modes of vibration contribute to the heat capacity. For other crystals, $\theta_D(T)$ rises as temperature increases, reaches a maximum and then falls. To obtain the contribution of the
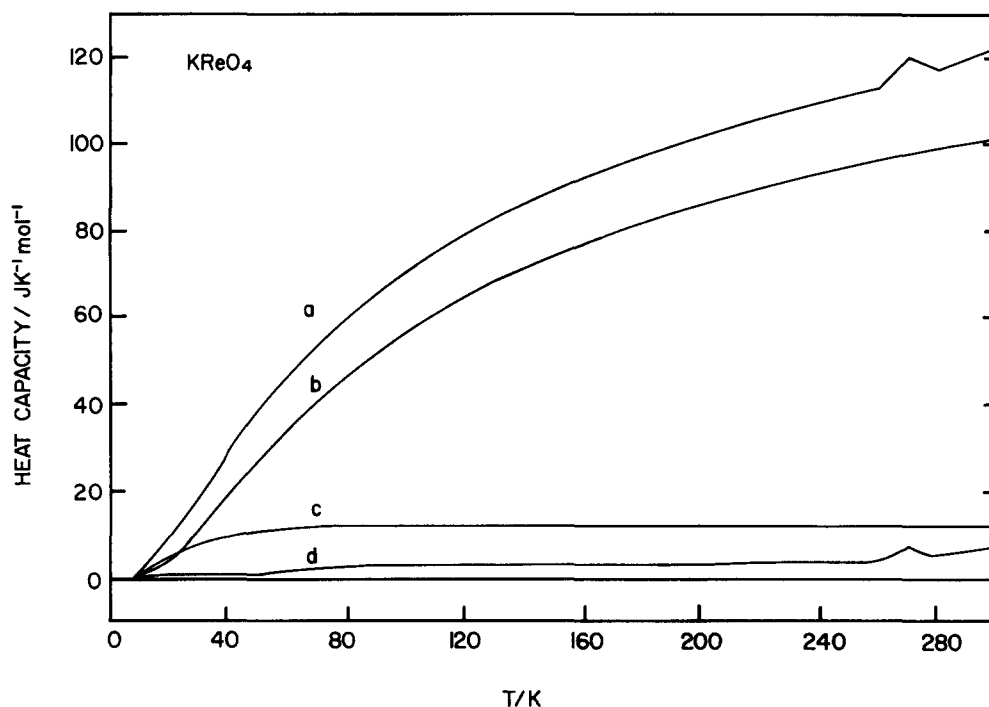
FIG. 2. Molar heat capacity of $KReO_4$. Curves: a = experimental (Ref. 1), b = vibrational contribution from internal + external optical modes, c = lattice contribution (Debye heat capacity for acoustic modes), d = residual heat capacity $C_{resid} = C_{exp} - C_{vib} - C_{lat} = (C_p - C_\epsilon)$ (see the text for full discussion of vibrational and lattice contributions)

lattice vibrations to the heat capacity in these crystals, the $\theta_D(T)$ is plotted and the asymtotic value at the peak $\theta_{\tilde{D}}$ is drawn to extend to high temperatures. The resulting curve is then used in conjunction with Debye tables. At temperatures below the point where $\theta_{\tilde{D}}$ is reached, values of θ_D based on experimental heat capacities were used to obtain C_{lat}. Then by difference, $C_p - C_\epsilon + C_{rot}$ is calculated over the whole temperature range.

A. KReO$_4$

All internal modes and the external g modes were assigned frequencies from the literature.[11,13,14] Two IR frequencies[15] were assigned as E_u and an unobserved frequency was assigned A_u and estimated as 90 cm^{-1} by comparison with corresponding spectra of $NaReO_4$ and $RbReO_4$. 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 14 of the 18 external modes, the 3 external acoustic modes being considered separately as the acoustic lattice modes. The remaining inactive B_u external mode was placed with the C_{vib} by multiplying the external heat capacity by 15/14.

The difference $C_{exp} - C_{vib}$ was then computed, and the data for low temperatures were fitted to a Debye function for 1.5 degrees of freedom per mole, corresponding to the three acoustic modes per unit cell containing two formula units. The value of the Debye $\theta_{\tilde{D}}$ was 94.4 K, and this value was then used to calculate the lattice heat capacity over the entire temperature range.

The residual heat capacity $C_{resid} = C_{exp} - C_{vib} - C_{lat}$ is just $C_p - C_\epsilon$, as there is no rotational heat capacity in the potassium salt. The resuts of this analysis are shown in Fig. 2 and Table II. The peak near 270 K results from the fusion of water and should be ignored. Apart from the effects of this slight water contamination above 270 K, the limiting high

temperature value of C_{resid} is 4.3 J K^{-1} mol^{-1}, (Table II) which agrees well with the value 5.1 J K^{-1} mol^{-1} estimated for $C_p - C_v$.[1] This shows that all degrees of freedom have been satisfactorily accounted for. The thermal expansion tensor in $KReO_4$ is only slightly anistropic.[4]

B. NH$_4$ReO$_4$

All internal modes and the external g modes were assigned frequencies from the literature.[10-12] Values at 77 K or lower were used and the frequencies were kept constant in calculating their contributions to the heat capacity, since the contributions of the vibrational modes at constant geometry are required. The external mode frequencies are quite strongly dependent on temperature.[10,11] Three IR wave numbers[15] of 108, 134, and 170 cm^{-1} were assigned as A_u, E_u, and E_u respectively. With these frequency assignments, C_{vib} was calculated as a sum of Einstein functions to include the 36 internal modes and 14 of the 24 external modes. An inactive B_u mode was then incorporated with the internal modes by multiplying the external heat capacity by 15/14. The low temperature librational frequencies of 272 and 263.3 cm^{-1} for the ammonium ion were used to calculate C_{lib} at low temperatures corresponding to their six degrees of freedom.

The difference $C_{exp} - C_{vib} - C_{lib}$ was then computed, and the data for low temperatures were fitted to a Debye function for 1.5 degrees of freedom per mole, corresponding to the three acoustic modes per unit cell containing two formula units. The value of the Debye $\theta_{\tilde{D}}$ was 81.8 K, and this value was then used to calculate the lattice heat capacity over the entire temperature range above 30 K.

The residual heat capacity $C_{resid} = C_{exp} - C_{vib} - C_{lat}$ is equal to $(C_p - C_\epsilon) + C_{rot}$, and is plotted against temperature in Fig. 3 and Table III. The kink near 270 K results because of the slight water impurity.

TABLE II. Heat capacity analysis for $KReO_4$. C_{exp}, smoothed experimental molar heat capacity; C_{vib}, estimated vibrational contribution from all internal + external optical modes; C_{lat}, lattice contribution (Debye heat capacity for acoustic modes) $C_{resid} = C_{exp} - C_{vib} - C_{lat} = (C_p - C_e)$.

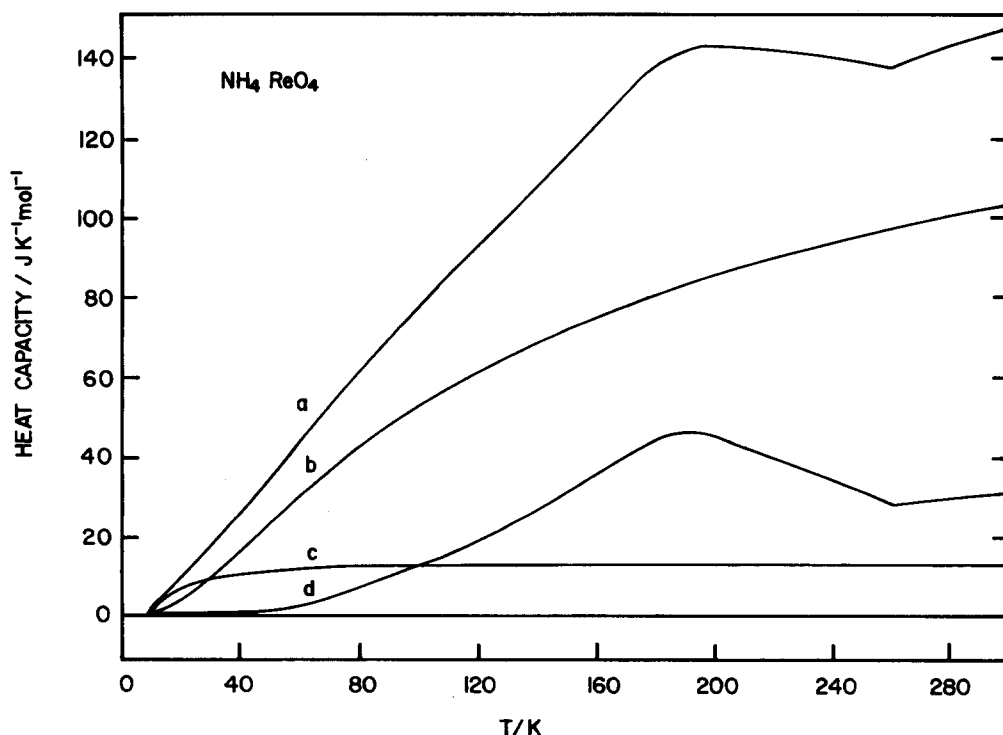| T (K)	C_{exp} (J K^{-1} mol^{-1})	C_{vib} (J K^{-1} mol^{-1})	$C_{exp} - C_{vib}$ (J K^{-1} mol^{-1})	C_{lat} (J K^{-1} mol^{-1})	C_{resid} (J K^{-1} mol^{-1})
10	1.20	0.10	1.10	1.11	0.00
20	9.00	3.12	5.88	5.03	0.85
30	18.60	10.01	8.59	7.96	0.63
40	28.70	18.38	10.32	9.59	0.73
50	37.90	26.48	11.42	10.50	0.91
60	46.00	33.72	12.28	11.06	1.23
70	53.20	40.13	13.07	11.41	1.67
80	59.60	45.88	13.72	11.65	2.07
90	65.25	51.11	14.14	11.81	2.32
100	70.40	55.89	14.51	11.93	2.58
110	75.00	60.24	14.76	12.02	2.74
120	79.20	64.20	15.00	12.09	2.91
130	82.95	67.81	15.14	12.15	3.00
140	86.30	71.09	15.21	12.19	3.02
150	89.25	74.09	15.16	12.23	2.93
160	92.20	76.85	15.35	12.26	3.09
170	94.80	79.40	15.40	12.28	3.12
180	97.25	81.76	15.49	12.30	3.19
190	99.70	83.97	15.73	12.32	3.41
200	102.00	86.04	15.96	12.33	3.62
210	104.10	88.00	16.10	12.35	3.75
220	106.20	89.85	16.35	12.36	3.99
230	108.00	91.62	16.38	12.37	4.02
240	109.70	93.30	16.40	12.38	4.03
250	111.40	94.90	16.50	12.38	4.11
260	113.10	96.44	16.66	12.39	4.27
270	120.20	97.91	22.29	12.40	9.89
280	117.60	99.32	18.28	12.40	5.87
290	119.80	100.68	19.12	12.41	6.72
300	122.40	101.97	20.43	12.41	8.02

FIG. 3. Molar heat capacity of NH_4ReO_4. Curves: a = experimental (Ref. 1), b = vibrational contribution from internal + external optical modes of NH_4^+ and ReO_4^- and librational from external modes of ReO_4^-, c = lattice contribution from NH_4^+ and ReO_4^- (Debye heat capacity for acoustic modes), d = residual heat capacity $C_{resid} = C_{exp} - C_{vib} - C_{lat} = (C_p - C_e) + C_{rot}$ (see the text for full discussion of vibrational and lattice contributions).

TABLE III. Heat capacity analysis for NH_4ReO_4. C_{exp} smoothed experimental molar heat capacity; C_{vib}, estimated contribution from internal optical modes of NH_4^+ and ReO_4^- ions and all external optical modes except librational modes of NH_4^+; C_{lib}, contribution from librational modes of NH_4^+ ions; C_{lat}, lattice contribution from NH_4^+ and ReO_4^- (Debye heat capacity for acoustic modes) $C_{resid} = C_{exp} - C_{vib} - C_{lat} = C_p - C_\epsilon + C_{rot}$ (see the text).

T (K)	C_{exp} (J K^{-1} mol^{-1})	C_{vib} (J K^{-1} mol^{-1})	C_{lib} (J K^{-1} mol^{-1})	$C_{exp} - C_{vib} - C_{lib}$ (J K^{-1} mol^{-1})	C_{lat} (J K^{-1} mol^{-1})	C_{resid} (J K^{-1} mol^{-1})
10	1.48	0.24	0.00	1.24	1.24	0.00
20	10.20	3.68	0.00	6.52	6.52	0.00
30	18.40	9.56	0.01	8.83	8.83	0.01
40	26.90	16.49	0.15	10.26	10.21	0.20
50	35.70	23.55	0.65	11.50	10.95	1.20
60	43.70	30.26	1.64	11.80	11.39	2.06
70	52.10	36.53	3.05	12.52	11.66	3.91
80	60.80	42.37	4.70	13.73	11.84	6.59
90	69.60	47.80	6.42	15.38	11.97	9.83
100	76.80	52.81	8.12	15.87	12.06	11.92
110	85.00	57.42	9.71	17.87	12.13	15.45
120	93.00	61.63	11.18	20.20	12.19	19.19
130	100.50	65.46	...	...	12.23	22.81
140	107.70	68.96	...	...	12.26	26.47
150	115.00	72.16	...	...	12.29	30.55
160	122.70	75.10	...	...	12.31	35.29
170	130.40	77.81	...	...	12.33	40.26
180	136.40	80.34	...	...	12.34	43.72
190	141.40	82.70	...	...	12.36	46.34
200	142.80	84.93	...	...	12.37	45.50
210	142.00	87.04	...	...	12.38	42.58
220	140.90	89.06	...	...	12.39	39.46
230	139.90	91.00	...	...	12.39	36.51
240	139.20	92.86	...	...	12.40	33.94
250	138.50	94.67	...	...	12.41	31.42
260	136.50	96.43	...	...	12.41	27.66
270	139.50	98.14	...	...	12.41	28.95
280	141.30	99.81	...	...	12.42	29.07
290	144.00	101.44	...	...	12.42	30.13
300	146.90	103.04	...	...	12.43	31.43

C. ND$_4$ReO$_4$

The same procedure was followed for the deuterated salt. An unobserved E_g librational mode of the ND_4^+ ion was estimated as 203 cm^{-1} by comparison with the recently reported spectrum of the undeuterated salt at 10 K.[12] The value of the Debye θ_D^∞ was 75.4 K. The results of the analysis are shown in Fig. 4 and Table IV.

IV. DISCUSSION

The residual heat capacities C_{resid} shown in Figs. 3 and 4 have the characteristic peak found for ammonium salts. The C_{resid} contains contributions from both the anisotropic thermal expansion and the rotational motion of the cation, and these two components cannot be separated without further information on the elastic constant tensor. The effect of deuteration on C_{resid} is to increase the residual heat capacity at the peak from 46.34 J K^{-1} mol^{-1} to 56.54 J K^{-1} mol^{-1} without any measurable shift in the position of the peak. The absence of any shift in the temperature at which the peak is found is consistent with observations in other ammonium salts such as NH_4BF_4 and ND_4BF_4,[16] and with calculations of rotational heat capacities.[17]

One method for obtaining the rotational heat capacity of

the ammonium ion is to use an alkali metal salt as a reference material, from which the lattice heat capacity of the ammonium salt can be deduced. This technique may be useful in cases where the thermal expansion coefficients of the ammonium salt are similar to those of the alkali metal salt, but it is clear from the present analysis that the contribution of thermal expansion, including anisotropy, will not cancel by subtraction if there is an appreciable difference in the thermal expansion tensors of the two salts. Analyses using the potassium salts as reference materials have been published for the cases of NH_4ReO_4,[18] in which thermal expansion is highly anisotropic,[19] and NH_4ClO_4,[20] in which one of the thermal expansion coefficients is actually negative.[21] It appears that the rotational heat capacities determined in those cases should be interpreted with caution.

Until the contribution of thermal expansion can be reliably separated from the rotational heat capacity of the ammonium ion, it does not seem to be profitable to try to fit theoretical models of rotational motion to experiment. However, the influence of ammonium ions on thermal expansion properties[22] is at least as interesting as their influence on heat capacity. Experimental studies to obtain the elastic constants of crystals in support of thermodynamic measurements should be initiated. Elastic constants for crystals that are rotationally disordered are especially needed.
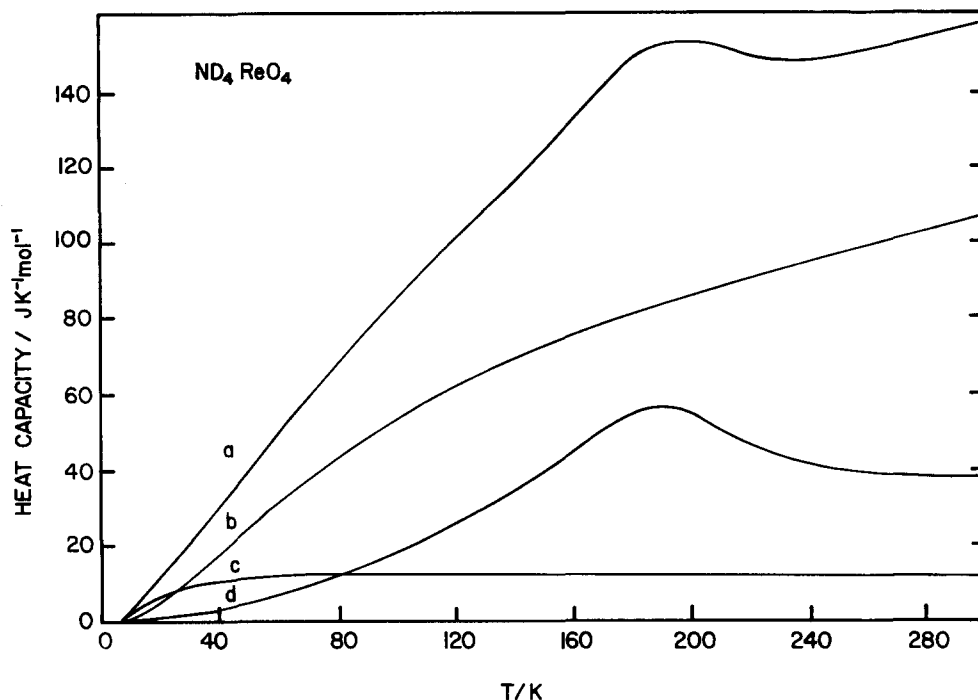
FIG. 4. Molar heat capacity of ND_4ReO_4. Curves: a = experimental (Ref. 3), b = vibrational contribution from internal + external optical modes of ND_4^+ and ReO_4^- and librational from external modes of ReO_4^-; c = lattice contribution from ND_4^+ and ReO_4^- (Debye heat capacity for acoustic modes), d = residual heat capacity C_{resid} $= C_{exp} - C_{vib} - C_{lat} = (C_p - C_\epsilon)$ $+ C_{rot}$ (see the text for full discussion of vibrational and lattice contributions).

TABLE IV. Heat capacity analysis for ND_4ReO_4. C_{exp}, smoothed experimental molar heat capacity; C_{vib}, estimated contribution from internal optical modes of ND_4^+ and ReO_4^- ions and all external optical modes except librational modes of NH_4^+; C_{lib}, contribution from librational modes of ND_4^+ ions; C_{lat}, lattice contribution from of ND_4^+ and ReO_4^- (Debye heat capacity for acoustic modes) $C_{resid} = C_{exp} - C_{vib} - C_{lat} = C_p - C_\epsilon + C_{rot}$ (see the text).

T (K)	C_{exp} (J K^{-1} mol^{-1})	C_{vib} (J K^{-1} mol^{-1})	C_{lib} (J K^{-1} mol^{-1})	$C_{exp} - C_{vib} - C_{lib}$ (J K^{-1} mol^{-1})	C_{lat} (J K^{-1} mol^{-1})	C_{resid} (J K^{-1} mol^{-1})
10	2.25	0.26	0.00	1.99	1.99	0.00
20	11.25	3.80	0.00	7.45	6.71	0.74
30	20.85	9.76	0.16	10.93	9.28	1.81
40	30.20	16.85	0.98	12.37	10.51	2.84
50	40.15	24.08	2.64	13.42	11.16	4.91
60	49.50	30.93	4.83	13.74	11.54	7.03
70	58.30	37.26	7.15	13.88	11.78	9.26
80	67.15	43.12	9.36	14.67	11.94	12.10
90	76.00	48.53	11.34	16.14	12.05	15.43
100	83.75	53.50	13.06	17.19	12.12	18.12
110	91.90	58.07	14.53	19.31	12.18	21.65
120	99.90	62.23	15.78	21.89	12.23	25.44
130	107.80	66.04	⋯	⋯	12.26	29.50
140	115.80	69.52	⋯	⋯	12.29	33.99
150	124.30	72.72	⋯	⋯	12.32	39.27
160	132.60	75.69	⋯	⋯	12.33	44.58
170	140.80	78.46	⋯	⋯	12.35	49.99
180	148.10	81.08	⋯	⋯	12.36	54.65
190	152.50	83.58	⋯	⋯	12.37	56.54
200	153.40	85.98	⋯	⋯	12.38	55.14
210	151.80	88.30	⋯	⋯	12.39	51.11
220	149.50	90.56	⋯	⋯	12.40	46.54
230	148.20	92.77	⋯	⋯	12.41	43.02
240	148.30	94.94	⋯	⋯	12.41	40.95
250	149.10	97.07	⋯	⋯	12.42	39.62
260	150.50	99.16	⋯	⋯	12.42	38.92
270	152.30	101.23	⋯	⋯	12.42	38.65
280	154.00	103.26	⋯	⋯	12.43	38.31
290	155.90	105.26	⋯	⋯	12.43	38.21
300	157.90	107.23	⋯	⋯	12.43	38.23

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