Heat Capacity of Ammonium Chloride between 8 and 300 K

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Heat capacity of NH_4Cl was measured between 8 and 300 K with an adiabatic calorimeter. The low-temperature limit of the Debye temperature is 352 K and its high-temperature limit in the harmonic approximation is 285 K. The λ transition point T_λ is 242.502 ± 0.004 K with the heat of transition 1168 J mol^{-1} and the entropy of transition 5.00 $JK^{-1} mol^{-1}$. It is very close to the first-order transition. From the analysis of the heat capacity between 242 and 300 K, an extra contribution to the heat capacity that amounts to 11.5 $JK^{-1} mol^{-1}$ at 300 K is extracted and explained by a simple model which assumes an additional type of order-disorder in the arrangment of NH_4 ions above T_λ. The energy difference between the parallel and the antiparallel pairs of NH_4 ions is estimated to be 1.46 kJ mol^{-1} from the low-temperature tail of the heat capacity anomaly near T_λ.

Ammonium chloride undergoes a diffuse phase transition at 242.5 K (hereafter designated by T_λ) and an abrupt phase transition at 457.6 K (hereafter designated by T_c). Detailed experimental and theoretical investigations[1] have been made concerning the lower phase transition at T_λ.[2-8] It is generally agreed that this transition is associated with disordering of ammonium ions between two possible orientations. Such mechanism has been established by experiments on the neutron diffraction[9] and infrared absorption[2,3] on single crystals of NH_4Cl as well as ND_4Cl.

Heat capacity measurements have been reported by many investigators[10-13] particularly below room temperature and they are fully analyzed in the paper by Sakamoto.[8] The earlier measurements, however, were not sufficiently closely spaced to reveal the shape of the heat capacity anomaly in the vicinity of T_λ. We have undertaken the precision measurements of the heat capacity between 8 and 300 K using an adiabatic calorimeter and found the results suggesting that T_λ is merely the starting point of the higher temperature transition at T_c.

Experimental

Material. Ammonium chloride (Yashima Chemicals Co., stated purity 99.9%) was recrystallized from aqueous solution and purified further by vacuum sublimation.

Calorimeter. The cryostat and calorimeter used for the present study is a modification of the one described earlier.[14] To employ larger amount of specimen, the larger calorimeter vessel (gold) and the larger adiabatic shield were newly machined, the refrigerant container being the same as before. Helium exchange gas was used to aid in the attainment of the equilibrium within the calorimeter, its amount corresponding to less than 1 Torr at room temperature. The correction to the solid heat capacities due to dissociative vaporization of NH_4Cl in the calorimeter was negligibly small even at room temperature.[15]

Temperature scales. The working thermometer above 11 K was a Leeds & Northrup platinum thermometer calibrated at the U. S. National Bureau of Standards; This was based on 1948 International Temperature Scales. A carbon resistor (Allen-Bradley, 1/8 W, 10Ω at room temperature) was used for the region below 11 K. It was calibrated by comparison with the platinum thermometer *in situ* at five different temperatures between 11 and 21 K. The results of comparison were fitted to the Clement-Quinell formula in the form

$$\log R + \frac{K}{\log R} = A + \frac{B}{T} \qquad (1)$$

for the purpose of extrapolation below 11 K. The calibration was carried out immediately after each series of measurements. The primary heat capacity values reported in the present paper are based on this temperature scale.

Since there was no fixed points below 11 K, the resulting temperature scale may be in error below about 6 K. After the experiments were concluded, the carbon scale was reexamined by comparing the carbon resistance with ^4He vapor pressure at 4.2 K in addition to the five comparisons above 11 K. The carbon scale was found to depend to a small extent on whether or not the fixed point at 4.2 K was included in the determination of the constants in Eq. (1). Further, an additional term, $C/(\log R)^2$, on the left-hand side of Eq. (1) improved the fitting of the equation. The probable error in the heat capacity values that arises from this type of uncertainty in the temperature scale were estimated to be about 10% at 4.0 K, 7.5% at 5 K, 2.5% at 6 K, 1.7% at 7 K, and 0.3% at 10 K in the present case. In view of rather large uncertainties below 8 K, the measured points below 8 K will be omitted from Table 1.

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[1] Since the number of papers on ammonium chloride is very large, only more recent references are given here which will lead one to earlier papers.

[2] N. E. Schumaker and C. W. Garland, *J. Chem. Phys.*, **53**, 392 (1970).

[3] E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

[4] C. C. Stephenson, R. W. Blue, and J. W. Stout, *ibid.*, **20**, 1046 (1952).

[5] H. C. Teh and B.N. Brockhouse, *Phys. Rev.*, **B3**, 2733 (1971).

[6] D. E. Woessner and B. S. Snoden, Jr., *J. Phys. Chem.*, **71**, 952 (1967).

[7] T. Nagamiya, *Proc. Phys.-Math. Soc. Japan*, **24**, 137 (1942).

[8] Y. Sakamoto, *J. Sci. Hiroshima Univ.* **A18**, 95 (1954).

[9] H. A. Levy and S. W. Peterson, *Phys. Rev.*, **83**, 1270 (1951); **86**, 766 (1952).

[10] F. Simon, *Ann. Phys.*, **68**, 241 (1922).

[11] F. Simon, Cl. v. Simson, and M. Ruhemann, *Z. Physik. Chem.*, **A129**, 339 (1927).

[12] W. T. Ziegler and C. E. Messer, *J. Amer. Chem. Soc.*, **63**, 2694 (1941).

[13] C. C. Stephenson, private communication.

[14] T. Shinoda, H. Chihara, and S. Seki, *J. Phys. Soc. Japan*, **19**, 1637 (1964).

[15] H. Wagner and K. Neumann, *Z. Physik. Chem.*, *N. F.*, **28**, 51 (1961).

TABLE 1. MOLAR HEAT CAPACITIES OF AMMONIUM CHLORIDE
Weight of specimen 37.3304 g. Molecular weight 53.49. 1948 International Temperature Scales.

T/K	C_p/JK^{-1} mol^{-1}
Series I	
12.394	0.2339
14.253	0.3883
15.590	0.5305
16.605	0.6514
17.498	0.7858
18.312	0.9297
19.080	1.074
19.821	1.222
20.602	1.400
21.465	1.625
22.463	1.884
23.586	2.214
24.840	2.607
26.223	3.087
27.709	3.638
29.143	4.226
30.588	4.853
32.134	5.556
33.778	6.360
35.453	7.222
37.116	8.071
38.758	8.929
40.630	9.920
42.668	11.037
44.407	12.012
Series II	
46.198	13.02
47.980	13.97
49.826	14.98
51.700	16.02
53.569	17.11
Series III	
53.539	17.05
55.536	18.13
57.482	19.15
59.516	20.20
61.617	21.24
Series IV	
61.754	21.29
63.853	22.33
66.063	23.45
68.390	24.61
70.689	25.64
72.942	26.68
75.181	27.61
77.463	28.73
79.854	29.85
82.299	30.92
84.854	32.02
87.490	33.15
90.062	34.14
92.573	35.06
95.032	36.07
97.481	36.99
99.950	37.91
Series V	
101.802	38.49
104.227	39.29
106.812	40.14
109.421	41.06
111.852	41.92
114.378	42.78
116.998	43.60
119.577	44.47
122.121	45.25
124.701	46.11
127.318	46.94
129.902	47.70
132.453	48.45
Series VI	
8.12	0.0573
9.02	0.0803
9.97	0.104
10.91	0.145
11.79	0.192
12.619	0.2397
Series VII	
134.480	49.08
137.179	49.87
139.845	50.67
142.479	51.46
145.083	52.22
147.659	52.93
Series VIII	
149.941	53.47
152.573	54.39
155.377	55.15
158.236	55.94
161.055	56.78
163.855	57.49
166.628	58.32
169.372	59.12
172.094	59.87
174.791	60.63
177.565	61.38
180.418	62.47
183.236	63.55
186.146	64.52
189.153	65.48
Series IX	
191.360	66.27
194.509	67.40
197.612	68.58
200.677	69.71
203.706	71.09
206.687	72.34
209.622	73.93

Table 1. Continued

T/K	C_p/JK^{-1} mol^{-1}
212.509	75.44
215.345	77.07
218.133	78.95
220.869	81.25
Series X	
222.942	82.89
225.044	85.02
226.590	86.48
228.112	88.37
229.607	90.54
231.073	92.76
232.509	95.35
233.910	98.58
Series XI	
(Transition region, run 1)	
234.895	101.1
236.219	105.5
237.497	110.7
238.715	119.0
239.853	130.8
240.881	144.6
241.502	179.2
241.765	205.8
241.995	246.3
242.181	328.4
242.311	569
242.395	786
242.454	1251
242.497	1372
242.547	954
242.672	275.7
242.935	144.7
243.307	112.5
243.741	97.78
244.213	90.50
244.836	85.94
245.604	83.05
246.518	81.42
247.593	80.33
Series XII	
(Transition region, run 2. Continuous heating)	
Series XIII	
248.661	80.08
250.254	79.66
252.381	79.58
256.117	79.70
260.601	80.08
264.156	80.46
268.267	80.96
272.350	81.46
276.213	82.13
280.232	82.72
284.450	83.30
288.861	84.10
293.238	84.64
297.581	85.35
301.890	85.94

Results

Measured values of the heat capacity are given in Table 1 and the smoothed values at rounded temperatures in Table 2. Curvature corrections were not applied, but may be computed from Table 1 since each series is result of continuous measurements. In the transition region, the temperature was constant at worst to within 5/10000 K when equilibrium has been reached and the smallest temperature rise in a single heating was about 2/100 K; the maximum error in $E/\Delta T$ that comes from the smallness of ΔT was therefore about 5%.

The present results are compared in Fig. 1 with previously published results of Simon,[10] Simon, Simson, and Ruhemann,[11] and Ziegler and Messer.[12] More recent unpublished measurements by Stephenson[13] above 19 K agree more satisfactorily with the present measurements. Fractional deviations from our smoothed values are compared in Table 3.

The temperature T_λ was determined from the point of maximum slope in the enthalpy *vs.* temperature graph as 242.502±0.004 K. The heat of transition was evaluated by estimating 'normal' heat capacity curve as indicated in Fig. 1. It was 1168 J mol^{-1} and the corresponding entropy of transition was 5.00 JK^{-1} mol^{-1} or 0.601 R where R is the gas constant. Table 4 is the comparison of different measurements.

Table 2. Molar heat capacities of ammonium chloride at rounded temperatures

T/K	C_p/JK^{-1} mol^{-1}	T/K	C_p/JK^{-1} mol^{-1}
8	0.0548	130	47.74
9	0.0782	140	50.75
10	0.1088	150	53.60
12	0.2046	160	56.40
14	0.3594	170	59.20
16	0.5766	180	62.26
18	0.8719	190	65.81
20	1.269	200	69.45
25	2.659	210	74.06
30	4.581	220	80.42
35	6.975	230	91.13
40	9.590	240	130.29
50	15.07	250	79.71
60	20.48	260	80.04
70	25.36	270	81.21
80	29.90	280	82.63
90	34.11	290	84.14
100	37.88	298.15	85.40
110	41.41	300	85.69
120	44.56		

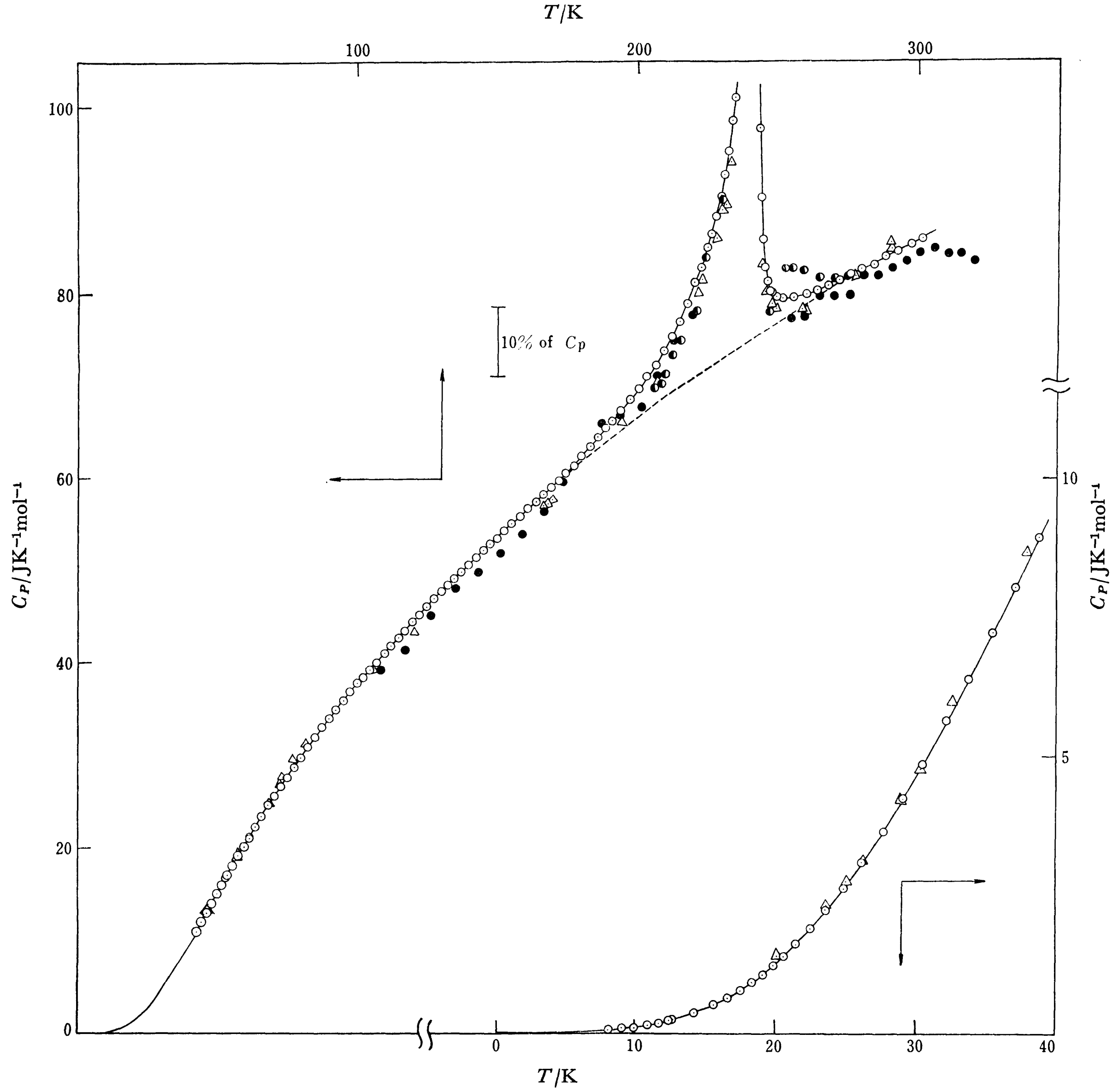

Fig. 1. Molar heat capacities of ammonium chloride; ○ present results, △ Simon,[10] ◐ Simon *et al.*,[11] ● Ziegler *et al.*[12]

Table 3. Percent deviations from the present measurements

Author	Deviation (%)			
	T=50K	100K	200K	300K
Simon[10,11]	+1.6	−0.7	−1.8	+2.0
Ziegler[12]	—	−2.8	−1.2	−2.0
Stephenson[13]	−0.8	−0.8	−0.9	−0.7

Table 4. Comparison of the transition temperature and the heat of transition

	T_λ/K	ΔH_λ/J mol^{-1}
Simon[10]	242.65	1490
Klug and Johnson[22]	242.61±0.10	—
Ziegler and Messer[12]	242.55±0.15	1117
This research	242.502±0.004	1168

Conversion of C_p to C_v

One of the crucial procedure in the analysis of experimental heat capacities is the conversion of C_p to C_v. Very rarely, reliable values of thermal expansion coefficient and isothermal compressibility are available over a sufficiently wide temperature range. We plotted available data of the molar volume on a large graph paper and found that the data by Staveley *et al.*[16] Lawson,[17] Hüllsmann-Biltz,[18] and Vegard-Hillesund[19] are mutually consistent below T_λ whereas those by Dinichert[20] and Adenstadt[21] deviate con-

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16) D. G. Thomas and L. A. K. Staveley, *J. Chem. Soc.*, **1951**, 1420.

17) A. W. Lawson, *Phys. Rev.*, **57**, 417 (1940).

18) O. Hüllsmann and W. Biltz, *Z. anorg. allg. Chem.*, **219**, 357 (1934).

19) L. Vegard and S. Hillesund, *Avhandl. Norske Videnskaps-Akad. Oslo*, **1**, *Mat. Naturv. Kl.* No. 8 (1942).

20) P. Dinichert, *Helv. Phys. Acta*, **15**, 462 (1942).

21) H. Adenstadt, *Ann. Physik*, [5] **26**, 69 (1936).

siderably in the opposite directions. We then adopted the temperature of 150 K as the reference temperature to fix C_p-C_v because the effect of the transition is barely seen at this temperature.

The adiabatic compressibility χ_S at 150 K was calculated from an extrapolation of Garland's values on c_{11} and c_{44} and it was converted to the isothermal compressibility χ_T by using the formula

$$\chi_T = \chi_S + (V\alpha^2 T/C_p) \qquad (2)$$

where V is the molar volume, α the volume expansion coefficient, and T the absolute temperature. The reference values at 150 K were thus V=33.806 cm^3 mol^{-1}, $\alpha=1.005\times10^{-4}$K^{-1}, C_p=53.58JK^{-1}mol^{-1}, $\chi_S=3.8596\times10^{-7}$ cm^{-2} N^{-1}, and $\chi_T=3.9551\times10^{-7}$ cm^{2}N^{-1}. These values give

$$C_p - C_v = \frac{V\alpha^2 T}{\chi_T} = 1.294\mathrm{JK^{-1}mol^{-1}}$$

at 150 K. Because few experimental determinations have been reported of α and χ below 150 K, an approximate formula

$$C_p - C_v = AC_p{}^2T \qquad (3)$$

was applied below 150 K, where the value of A was fixed as 3.004×10^{-6} mol J^{-1} so as to reproduce the correction at 150 K. Between 150 and 230 K, we adopted Lawson's length data[17] and normalized them so that they become consistent with the molar volume at 273.2 K (34.826 cm^3), thus estimating the values of α which are shown in Fig. 2. χ_S was derived from the measured elastic constants.[23] Above T_λ, Sakamoto's calculated values[8] of α and Garland's χ_S values were used to obtain the C_p-C_v correction. The results of such computations and the estimated C_v values are listed in Table 5.

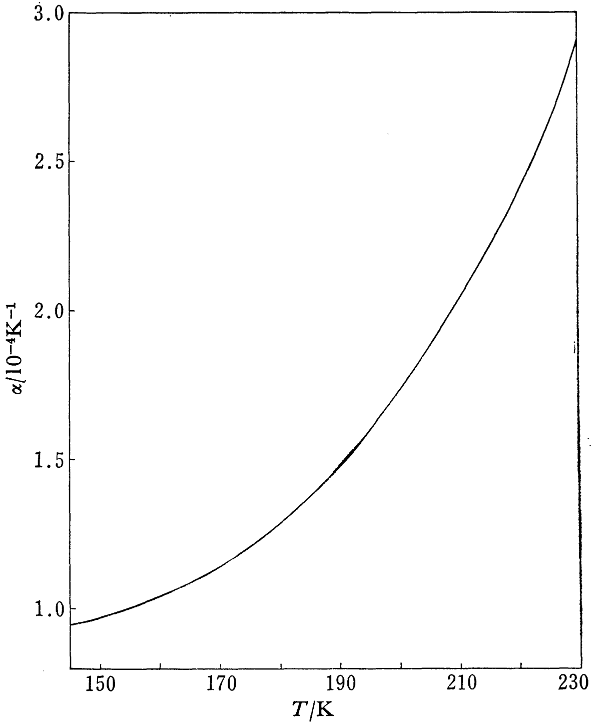

Fig. 2. Thermal expansion coefficient of ammonium chloride used for the evaluation of C_p-C_v.

Table 5. Estimates of the C_p-C_v correction and the C_v values derived therefrom (in JK^{-1} mol^{-1})

T/K	C_p-C_v	C_v	T/K	C_p-C_v	C_v
40	0.013	9.577	200	4.757	64.71
60	0.075	20.41	220	9.046	67.46
80	0.213	29.69	250	3.360	76.36
100	0.431	37.45	260	3.184	76.83
120	0.715	43.85	270	3.523	77.67
140	1.084	49.65	280	3.996	78.65
160	1.464	54.95	290	4.531	79.59
180	2.427	59.84	300	5.272	80.41

Low-temperature Heat Capacities

The low-temperature C_v was converted to the equivalent Debye temperature Θ_D^C for six degrees of freedom per unit cell after the contributions[2,3] of the intra-ionic vibrations at 1403 cm^{-1} (triply degenerate) and 1683 cm^{-1} (doubly degenerate) and of librations of ammonium ions at 391 cm^{-1} (triply degenerate, below T_λ) have been subtracted from C_v. The plot of Θ_D^C *vs* temperature (Fig. 3) shows a shallow minimum around 35 K with Θ_D^C (min)=279 K. The Debye temperature at the high temperature limit in the harmonic approximation was estimated to be Θ_∞^C=285 K corresponding to the Debye cut-off frequency of 198 cm^{-1} or 5.9×10^{12} Hz. This cut-off frequency is in good agreement with that obtained from the analysis of coherent inelastic scattering results for ND$_4$Cl.[24] The cut-off frequency is not affected by the deuterium substitution. The limiting low-temperature Θ_0 was obtained from the plot of C_vT^{-3} against T^2 at 352±6 K.

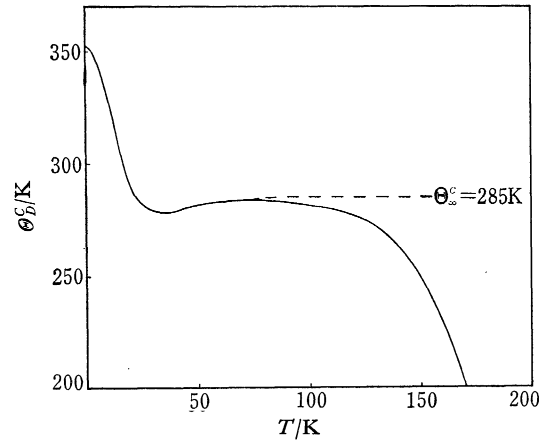

Fig. 3. Equivalent Debye temperature of ammonium chloride based on C_v for 6N degrees of freedom.

High-temperature Heat Capacities

Inspection of Fig. 3 shows that Θ_D^C tends to decrease above 100 K. Because the intra-ionic and the libra-

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[22] H. P. Klug and W. W. Johnson, *J. Amer. Chem. Soc.*, **59**, 2061 (1937).

[23] C. W. Garland and R. Renard, *J. Chem. Phys.* **44**, 1130 (1966).

[24] E. R. Cowley, *Phys. Rev.* **B3**, 2743 (1971).

tional contributions in the harmonic approximation have been subtracted from C_v which was used in deriving Θ_D^C, the descending trend of Θ_D^C must be due either to onset of the phase transition and/or to some anharmonic effect.

To visualize the behavior near T_λ, the 'rotational' part of C_v, defined by

$$C_R = C_v - C_i - C_D(285\,\mathrm{K}) \tag{4}$$

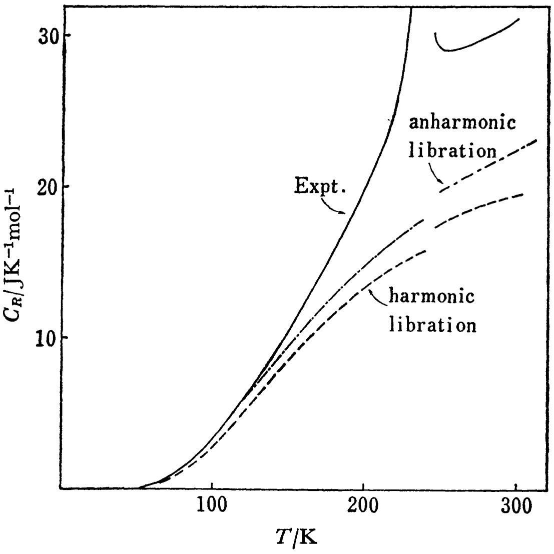

Fig. 4. Rotational contribution to the molar heat capacity.

was calculated, were C_i is the heat capacity due to intra-ionic vibrations and C_D (285 K) is the Debye heat capacity corresopnding to Θ_∞^C. The results are shown in Fig. 4. In the same figure, a curve is drawn that corresponds to the harmonic libration of NH_4^+ ions (391 cm^{-1} for $T<T_\lambda$ and 359 cm^{-1} for $T>T_\lambda$). The use of Einstein heat capacity for the libration mode may be justified by the flatness of the dispersion relation observed by the inelastic neutron scattering experiments.[5] It is apparent that the harmonic libration model can account for C_R only up to about 130 K where C_R begins to curl up rapidly. Such deviation may be taken as indicating on-set of the order-disorder transition, but what seems to be abnormal is the large discrepancy between C_R and the harmonic librational heat capacity above T_λ which amounts to as great as 11.5 J K^{-1} mol^{-1}. The existence of this extra heat capacity was already pointed out by Sakamoto[8] although his estimate was somewhat smaller (8.95 J K^{-1} mol^{-1} at 298.15 K) than ours. We shall now examine some possibilities that could account for the extra contribution.

a) Anharmonic Librations. Woessner and Snoden[6] derived a value of 19.7 kJ mol^{-1} ($T<200$ K and $T<T_\lambda$) for the activation energy of the reorientation of ammonium ions from their measurements of the NMR spin-lattice relaxation time. Since the activation energy is only eight times as large as the average thermal energy of a single ammonium ion at 300 K, the anharmonic contribution to the librational heat capacity could be significant.

If we assume the potential energy of an ammonium ion of the form

$$\begin{aligned} V(\phi) &= \frac{1}{2}V_0(1-\cos n\phi) \\ &= c\phi^2 + f\phi^4 + \cdots \end{aligned} \tag{5}$$

where V_0 is the barrier height and ϕ is the angle of rotation, the anharmonic Einstein heat capacity then becomes[25]

$$\frac{c_v}{R} = \frac{c_v^h}{R} - \frac{3}{2}\frac{fRT}{c^2} + \cdots \tag{6}$$

Equation (6) is also plotted in Fig. 4 by the dot-dash curve. It still falls short of the C_R values. The situation is almost the same if we use Eq. (5) and calculate the heat capacity of a triply degenerate hindered rotor with the help of Pitzer-Gwinn's tables.[26] Recently, Garland and Weiner[27] introduced a more anharmonic potential function that can account for the optical spectra.[1] However, the use of their energy level scheme (with $\omega=391$ cm^{-1} and $x=29$ cm^{-1}) gave too small a heat capacity, only 16.6 J K^{-1} mol^{-1} to be compared with 19.6 J K^{-1} mol^{-1} obtained at 300 K in the harmonic approximation.

b) Subsidiary Minima in the Potential Energy. At the upper transition point (T_c), NH_4Cl is transformed into NaCl type of structure probably because the reorientation rate of NH_4 cations becomes progressively larger at higher temperatures, finally reaching a point where the molecular field an NH_4 cation sees is made effectively spherical. The shape of the heat capacity curve near T_c is such that the heat capacity drops abruptly at T_c by as much as about 22.5 J K^{-1}·mol^{-1} (5.38 cal K^{-1} mol^{-1}). If the transition were simply associated with the change from reorientation to nearly free rotation of NH_4 cations, the heat capacity drop would be about $^3/_2\,R$ or 12.5 J K^{-1} mol^{-1}, about half of the decrease found experimentally. The sum of contributions 76 J K^{-1} mol^{-1}, Debye lattice heat capacity 25 J K^{-1} mol^{-1}, C_p—C_v correction *ca.* 30, rotation of NH_4 cations 12.5, and internal vibrations of NH_4 8.6, roughly account for the observed heat capacity, *ca.* 81 J K^{-1} mol^{-1}, immediately above T_c. The fact that the distance (3.27 Å) between the nearest N and Cl atoms is equal to the sum (3.29 Å) of the ionic radii also suggests that ammonium ions undergo almost free rotation above T_c. This in turn will indicate that there must be some extra contribution to the heat capacity below T_c. Therefore, the observed heat capacity contains such extra persistently between T_λ and T_c.

To interpret the extra contribution to the heat capacity we shall assume a simple model in which ammonium ions can assume additional type of disorder other than the one that is responsible for the transition at T_λ. Below T_λ the NH_4 cations are rather rigidly held in one of the two possible orientations but as the complete disorder is attained immediately above T_λ,

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25) A. J. E. Foreman and A. B. Lidiard, *Phil. Mag.* **8**, 97, (1963).

26) K. S. Pitzer, 'Quantum Chemistry', Prentice Hall, New York (1953).

27) C. W. Garland and B. B. Weiner, *J. Chem. Phys.*, **53**, 1609 (1970).

the ions will execute a kind of rattling motion as a result of frequent reorientational motion. The lowest potential barrier over which an NH_4 ion can reverse its orientation will be such that the ion is rotated through about 60° around one of its N–H bond (threefold axis) and then 60° around the axis perpendicular to the bond. The first type of rotation will lead the ion to a shallow minimum of the potential energy—here, three hydrogen bonds are broken but they are replaced by electrostatic attraction between hydrogen and chloride ions. At such an intermediate orientation, the remaining $N–H \cdots Cl^-$ hydrogen bond will become shortened giving rise to eightfold position of the N atom, slightly displaced from (½½½) toward one of the eight neighboring chloride ions. If we now assume that those subsidiary eight minima have energy ε relative to the principal minima, we shall obtain a Schottky type anomaly in the heat capacity, *i.e.*

$$C_{\text{Sch}} = \frac{N\varepsilon^2}{kT^2}\,\frac{g_0}{g_1}\,\frac{\exp(\varepsilon/kT)}{[1+(g_0/g_1)\exp(\varepsilon/kT)]^2} \qquad (7)$$

where $g_0=2$ and $g_1=8$ for the model proposed. Equation (7) is plotted in Fig. 5 for $g_0/g_1=1/4$, $\varepsilon=7.5$ kJ mol^{-1}. The maximum of C_{Sch} was fixed at 300 K as Sakamoto's analysis suggested the existence of a broad maximum here. At 300 K, Eq. (7) gives 10.36 J K^{-1} mol^{-1} whereas the experimental extra heat capacity is 11.50 J K^{-1} mol^{-1} if we assume harmonic librational modes or 8.57 J K^{-1} mol^{-1} if we assume Eq. (5) for the potential energy function. The agreement with Eq. (5) appears satisfactory in the absence of reliable estimates for the anharmonicity. Our measurements of the heat capacity did not extend beyond 300 K and therefore Eq. (5) would not deserve more detailed fitting at present. However, the existence of large extra heat capacities between T_λ and T_c is beyond doubt and they must be associated with some additional degrees of freedom in the crystal. We have proposed a possible interpretation here which may have consequences in other properties of NH_4Cl at high temperatures, *e.g.* inelastic neutron scattering, Raman spectra, and dielectric dispersion.

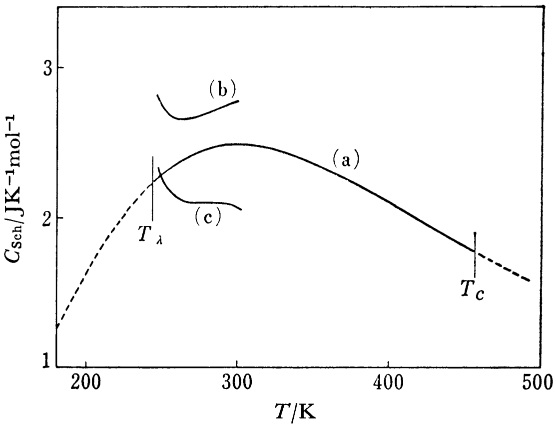

Fig. 5. Schottky heat capacity [Eq. (7)]. Comparison with 'experimental' estimates of the anomalous heat capacity above T_λ. Curve a: theoretical calculation for $g_0/g_1=1/4$, $\varepsilon=7.5$ kJ mol^{-1}, Curve b: estimate based on the harmonic libration model, Curve c: estimate based on the anharmonic libration model.

A similar type of anomaly was reported[28] in the case of stoichiometric AgI, in which case positional disorder of Ag cations were assumed to explain an anomalously large heat capacity after it has transformed to the α form at 150°C.

Anomaly Associated with the λ Transition

Garland and Schumaker[29] confirmed a good correlation between the intensity of the 1444 cm^{-1} infrared band and the anomalous part of the heat capacity using Stephenson's unpublished results. Since our results agree satisfactorily with Stephenson's heat capacities, we shall not attempt to repeat the analysis but merely point out that the transition is very close to the first order transition as may be inferred from Series XI, Table 1.

The Energy to Reorient an NH_4 ion in the Ordered Matrix

It is possible to estimate the energy required to rotate an NH_4^+ ion through 180° from the low temperature tail of the λ transition. Assuming that the number of NH_4^+ in the wrong orientation n is very small compared with the total number of the ions N, we have

$$\frac{n}{N} = \exp(s/k)\exp(-\varepsilon/kT) \qquad (8)$$

where ε is such energy and the anomalous heat capacity ΔC is given by

$$\Delta C = \frac{1}{T^2}\cdot\frac{\varepsilon^2}{k}e^{s/k}e^{-\varepsilon/kT} \qquad (9)$$

in an analogous way to the case of vacancy formation.[30]

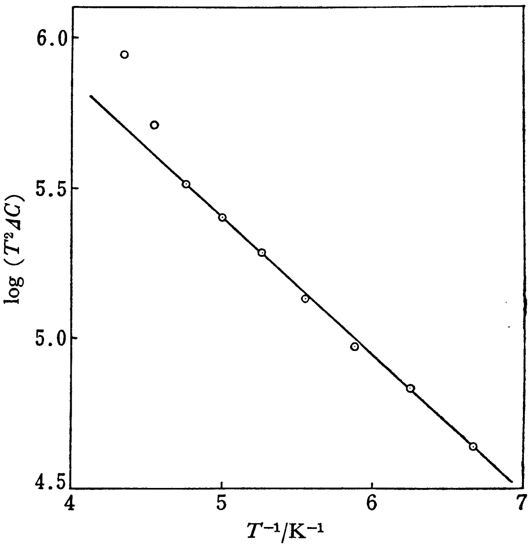

Fig. 6. Evaluation of the energy to reorient an NH_4 cation in almost perfectly ordered lattice.

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28) C. M. Perrott and N. H. Fletcher, *J. Chem. Phys.* **48**, 2143, 2681 (1968).

29) C. W. Garland and N. E. Schumaker, *J. Phys. Chem. Solids*, **28**, 799 (1967).

30) R. H. Beaumont, H. Chihara, and J. A. Morrison, *Proc. Phys. Soc.* (London), **78**, 1462 (1961).

ΔC was evaluated as the difference between C_R and C_{IIb} in Fig. 4 and a plot is made of log $(T^2\Delta C)$ *versus* $1/T$ in Fig. 6. A good straight line is obtained between 150 and 210 K, the slope of which gives $\varepsilon=$ 8.77 kJ mol^{-1}. The deviation of the points for 220 and 230 K is due to rapid increase of the heat capacity in the transition region. Eq. (8) then reads

$$\frac{n}{N} = 5.32 \exp(-1055/T) \qquad (10)$$

which leads to a value of $n/N=0.035$ at 210 K. The magnitude of ε (8.77 kJ mol^{-1}) corresponds to the difference in energy between six parallel pairs and six antiparallel pairs; the energy difference between one parallel and one antiparallel pair is then 1.46 kJ mol^{-1}, about 3/4 of kT_λ ($=2.02$ kJ mol^{-1}).

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