Heat Capacity and Thermodynamic Functions of $K_2CuCl_4\cdot 2H_2O$ and $(NH_4)_2CuCl_4\cdot 2H_2O$ from 13 to 310°K*

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There have been many investigations of the orientational order-disorder phenomena of ammonium ions in the crystalline state. Among these, the most comprehensive have been those of ammonium halides. In the case of ammonium chloride, it has been revealed from various experimental facts[1-4] and from theoretical considerations[5] that a λ-type anomaly at $-38°C$ in the heat capacity curve can be explained by the co-operative transition from an uniquely defined orientational state to two equally-probable states with respect to the NH_4^+ ion.

X-Ray structural study of the $(NH_4)_2CuCl_4\cdot 2H_2O$ crystal[6] shows that the crystal lattice is, roughly speaking, composed of three units NH_4^+, Cl^-, and $CuCl_2\cdot 2H_2O$, with the result that the inter-ammonium distance of ammonium chloride is enlarged two-dimensionally by the introduction of $CuCl_2\cdot 2H_2O$. It will, therefore, be of some interest to study an orientational ordering process of such a linearly-arranged ammonium ion system and to compare the results with those of an isotropically-arranged one found in ammonium chloride.

The present paper will report on the thermodynamic properties of $(NH_4)_2CuCl_4\cdot 2H_2O$ and $K_2CuCl_4\cdot 2H_2O$ crystals from 13 to 310°K. The latter crystal was selected as a reference material because it belongs to the same crystal system (D_{4h}^{14}-P4/mnm) as the former and involves a spherical cation, K^+, with an ionic radius nearly equal to that of the NH_4^+ ion.

Experimental and Results

The Preparation of Samples.—The potassium copper chloride dihydrate, $K_2CuCl_4\cdot 2H_2O$, is the double salt of KCl and $CuCl_2\cdot 2H_2O$, while the ammonium copper chloride dihydrate, $(NH_4)_2CuCl_4\cdot 2H_2O$, is that of NH_4Cl and $CuCl_2\cdot 2H_2O$. $(NH_4)_2CuCl_4\cdot 2H_2O$ (NH_4-salt) was prepared from a mixed solution of their component substances and was purified by repeated recrystallizations.[7] In the case of $K_2CuCl_4\cdot 2H_2O$ (K-salt), the crystal was prepared according to the phase diagram[8] of the $KCl-CuCl_2-H_2O$ system. Commercial analytical reagents of the Wakō Pure Chemical Industry Company were used for the preparation.

Differential Thermal Analysis.—The freshly prepared specimens of NH_4-salt are reported to exhibit a thermal anomaly at about $-22°C$ on cooling.[9] This anomaly is due to the freezing of occluded water, since there is no thermal anomaly in partly-dehydrated samples. In order to eliminate the excess water, the sample was dried over partly-dehydrated NH_4-salt in a desiccator for several weeks. In order to determine the temperature of dehydration, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) methods were applied to both crystals; some interesting features due to the process of dehydration were thus found. The results are shown in Fig. 1. As the temperature is raised, K-salt exhibits two apparently separate peaks, at about 93°C and 116°C. In the case of NH_4-salt, however, only one peak appears, at about 143.5°C, with a shoulder at 138°C.

Meyerhoffer[10] has found, from dilatometric study, a phase change for K-salt at 92.4°C and has suggested the following decomposition mechanism*:

$$K_2CuCl_4\cdot 2H_2O \rightleftarrows KCuCl_3+KCl+2H_2O$$

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

[2] H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 634 (1954).

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

[4] H. A. Levy and S. W. Peterson, *Phys. Rev.*, **86**, 766 (1952); G. H. Goldschmidt and D. G. Hurst, ibid., **83**, 88 (1951); **86**, 797 (1952).

[5] Y. Nagamiya, *Proc. Phys. Math. Soc. Japan*, **24**, 137 (1942).

[6] L. Chrobak, *Z. Krist.*, **88**, 35 (1934); A. Narasimhamurty and D. Premaswarup, *Proc. Phys. Soc.*, **83**, 199 (1964).

[7] A. Seidell, "Solubilities of Inorganic and Organic Compounds," Vol. I, 3rd. Ed., Van Nostrand Co., New York (1940).

[8] A. Chretien and R. Weil, *Bull. Soc. Chim.*, **2**, 1577 (1935).

[9] N. Nakamura, H. Suga and S. Seki, presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[10] W. Meyerhoffer, *Z. physik. Chem.*, **3**, 336 (1887).

* This decomposition mechanism was recently confirmed by us from Debye-Scherrer photographs taken below and above 93°C. Fairly intensive diffraction lines ascribed to KCl crystal appeared on the photograph taken at about 100°C. We are greatly indebted to Mr. Takemi Yamada of our University for his kind arrangements for taking high-temperature X-ray photographs.

This mechanism was also verified by Vriens[11] from vapor pressure measurements of K-salt and saturated solutions containing K-salt, KCl and $KCuCl_3$. This transition corresponds just to the first peak in the DTA curve. The released water dissolves parts of the crystals and forms a saturated solution, so shat the solution evaporates at a much higher temperature than does the free water. The second peak which appeared on the DTA curve seems to correspond to the evaporation process, because its temperature depends markedly on the pressure of the surroundings. The temperature of the first peak, on the other hand, is almost not influenced at all when the pressure is reduced to 350 mmHg. The thermo-gravimetric analysis of K-salt revealed that the weight of the sample is the same, within the range of experimental error, before and after the first peak I, corresponding to the A- and B-stages in Fig. 1(a) respectively. However, when passing through the second peak II, at the C-stage in the figure, the sample loses weight nearly equal in amount to the crystalline water involved. From these facts we may regard the phase changes at the I and II peaks to be as follows:

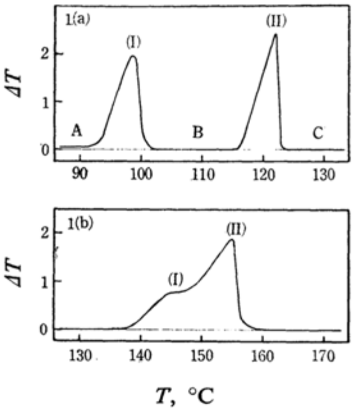

Fig. 1. Curves of the differential thermal analysis: 1(a) for $K_2CuCl_4 \cdot 2H_2O$ and 1(b) for $(NH_4)_2CuCl_4 \cdot 2H_2O$.

$$\text{(I)}\quad K_2CuCl_4 \cdot 2H_2O \rightarrow KCuCl_3 + KCl + 2H_2O \text{ (satd. soln.)}$$

$$\text{(II)}\quad 2H_2O \text{ (satd. soln.)} \rightarrow 2H_2O \text{ (vapor)}$$

The occurrence of extra peaks in the DTA curve of hydrates due to the formation of a saturated solution is not uncommon.[12]

In the case of NH_4-salt, the first peak appears on a shoulder of the second, so that a similar TGA method can not be applied to this salt. From the fact that the crystal structure of NH_4-salt is isomorphous with that of K-salt, we may also assume similar phase changes at the two successive peaks.

The Heat Capacity of $(NH_4)_2CuCl_4 \cdot 2H_2O$ and $K_2CuCl_4 \cdot 2H_2O$. — The low temperature calorimeter and the method of measurement are the same as those described in the previous report.[13] The calorimeter contains 26.967 g. (0.09719 mol.) of $(NH_4)_2CuCl_4 \cdot 2H_2O$ and 31.127 g. (0.09740 mol.) of $K_2CuCl_4 \cdot 2H_2O$ with helium exchange gas, respectively, in each experiment,

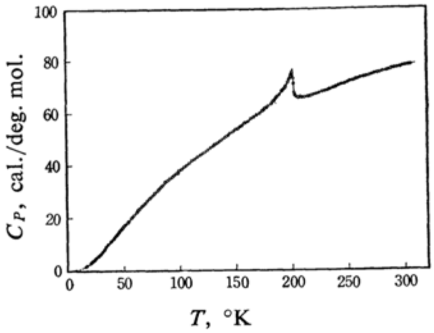

Fig. 2. Heat capacities of $(NH_4)_2CuCl_4 \cdot 2H_2O$ between the temperature range from 13°K to 310°K.

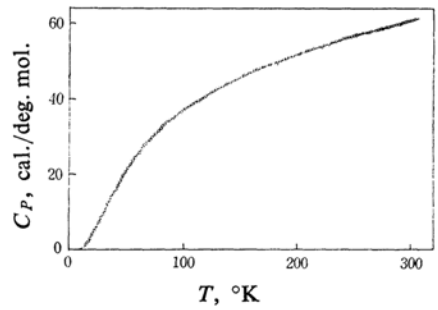

Fig. 3. Heat capacities of $K_2CuCl_4 \cdot 2H_2O$ between the temperature range from 13°K to 310°K.

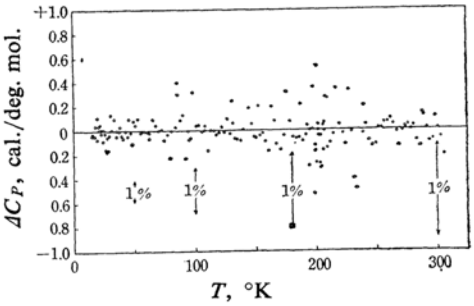

Fig. 4. Deviation of experimental heat capacities of $(NH_4)_2CuCl_4 \cdot 2H_2O$ from a smoothed curve.

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[11] J. G. C. Vriens, *Z. physik. Chem.*, **7**, 194 (1891).

[12] H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **61**, 917 (1957).

[13] H. Suga and S. Seki, This Bulletin, **38**, 1000, (1965).

TABLE I. HEAT CAPACITIES OF $(NH_4)_2CuCl_4 \cdot 2H_2O$

T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg.mol.
	Series I	
155.34	2.458	55.634
157.79	2.437	56.296
165.38	2.605	58.679
167.97	2.584	59.336
173.10	2.534	60.998
178.23	2.550	62.867
180.78	2.527	63.679
183.30	2.499	64.724
185.79	2.471	65.796
189.27	2.508	67.220
191.77	2.479	68.580
196.71	2.401	71.949
199.09	2.353	74.057
201.47	2.407	71.516
206.55	2.528	66.219
211.62	2.524	66.209
219.39	2.499	67.186
221.89	2.492	67.424
229.43	2.613	68.580
236.88	2.427	69.763
241.78	2.547	70.638
246.85	2.528	71.263
251.43	2.507	72.148
258.91	2.479	73.135
268.66	2.511	74.141
276.00	2.423	75.181
288.03	2.390	76.401
291.42	2.425	76.792
293.85	2.417	77.084
305.86	2.390	78.102
	Series II	
95.90	2.421	37.099
100.66	2.342	38.739
102.98	2.307	39.526
105.27	2.275	40.249
107.52	2.243	41.026
121.36	2.553	45.345
123.89	2.523	46.073
128.88	2.464	47.592
130.73	1.220	48.259
132.56	2.301	48.731
134.85	2.278	49.410
139.36	2.231	50.898
141.66	2.364	51.997
146.34	2.326	53.114
150.95	2.287	54.370
153.23	2.267	55.017
	Series III	
192.52	2.467	69.114
194.97	2.431	70.589
199.15	1.174	74.175
200.32	1.156	75.825
201.50	1.202	71.568
202.72	1.253	67.151
203.98	1.261	66.482
	Series IV	
197.39	1.200	71.944
198.59	1.186	73.194
199.77	1.168	74.836
200.94	1.169	74.834
202.14	1.242	68.118
	Series V	
62.62	2.650	23.548
67.74	2.455	25.857
72.51	2.306	27.940
77.02	2.189	29.785
81.92	2.078	31.818
87.94	1.963	34.241
94.21	2.065	36.417
96.26	2.037	37.067
	Series VI	
15.38	2.545	1.230
17.72	1.812	2.066
21.78	2.571	3.691
22.82	2.253	4.114
26.21	1.785	5.452
28.31	2.247	6.392
30.71	2.547	7.816
33.23	2.505	9.008
35.64	2.243	10.159
38.00	2.419	11.379
42.85	2.752	13.794
45.48	2.528	15.240
48.29	2.355	16.436
50.57	2.218	17.628
52.96	2.588	18.853
55.49	2.456	20.016
57.89	2.341	21.214
60.18	2.245	22.313
62.38	2.160	23.358
	Series VII	
15.15	1.998	1.146
17.34	1.825	1.857
19.33	1.768	2.555
21.06	1.412	3.354
22.79	1.774	4.058
24.49	1.432	4.835
25.94	1.331	5.460
27.57	1.846	6.168
29.50	1.997	7.093
31.40	1.788	8.025
33.24	1.904	8.917
35.28	2.197	9.913
37.37	2.005	11.018
39.57	2.412	12.102
41.88	2.220	13.261
44.33	2.681	14.515
46.91	2.488	15.843

TABLE II. HEAT CAPACITIES OF $K_2CuCl_4\cdot 2H_2O$

T_{av} °K	Approx. ΔT	$\Delta H/\Delta T$ cal./deg.mol.
	Series I	
90.40	2.229	35.221
94.81	2.174	36.239
99.11	2.126	37.159
105.39	2.068	38.335
109.91	2.309	39.191
114.47	2.269	40.023
121.18	2.210	41.395
125.68	2.389	42.205
129.30	2.357	42.902
136.32	2.315	43.753
143.29	2.434	44.909
152.94	2.374	46.357
157.68	2.350	46.958
164.83	2.632	47.944
172.67	2.539	48.879
177.83	2.567	49.537
188.01	2.524	50.668
197.02	2.493	51.571
204.47	2.469	52.170
214.28	2.425	53.480
219.14	2.415	53.740
223.96	2.399	54.218
235.96	2.360	55.426
240.88	2.565	55.870
248.58	2.554	56.054
256.35	2.762	56.827
261.81	2.729	57.807
267.25	2.714	58.150
278.06	2.688	58.783
280.75	2.679	59.029
286.11	2.657	59.706
288.77	2.651	59.831
291.43	2.646	59.954
294.08	2.637	60.219
296.73	2.631	60.371
299.37	2.622	60.629
302.00	2.614	60.852
	Series II	
61.44	2.102	25.837
63.69	2.424	26.622
66.08	2.336	27.844
68.39	2.281	28.551
70.64	2.229	29.226
75.08	2.286	30.715
77.35	2.240	31.385
79.57	2.202	31.874
81.76	2.162	32.610
83.91	2.128	33.157
86.02	2.091	33.886
88.10	2.062	34.450
	Series III	
21.41	1.296	4.343
24.09	3.894	5.821
27.50	3.000	7.769
30.27	2.538	9.340
32.65	2.216	10.957
34.76	1.998	12.255
36.86	2.216	13.636
39.00	2.043	14.861
40.98	1.910	15.958
43.10	2.337	17.077
45.37	2.185	18.358
47.51	2.056	19.619
49.70	2.316	20.480
54.12	2.109	22.647
56.31	2.242	23.557
58.51	2.159	24.541
60.64	2.087	25.474
62.70	2.028	26.227
64.90	2.343	27.121
	Series IV	
16.41	2.486	1.951
18.62	1.806	3.060
20.39	1.478	3.872
	Series V	
15.15	2.985	1.502
17.67	2.059	2.569
19.56	1.545	3.840
21.49	1.833	4.385
23.25	1.533	5.421
24.75	1.349	6.240
26.07	1.212	7.050

The experimental heat capacities listed in Tables I and II are the ratios of the increase in enthalpy, ΔH, to the rise in temperature, ΔT, and are equal to the differential heat capacity, C_P, only when the correction for curvature is negligible. Here, a defined calorie equal to 4.1840 absolute joules is used, and the ice point temperature is taken as 273.15°K. Also listed in Tables I and II are T_{av}, the arithmetic mean of the initial and final temperatures of each measurement, and the approximate temperature rise, ΔT. The experimental heat capacities and the smoothed curves of both crystals are shown in Figs. 2 and 3.[14] The deviation plot of measured points from the smoothed curve are given in Fig. 4 for the sake of reference.

As is shown in Fig. 2, the $(NH_4)_2CuCl_4\cdot 2H_2O$ crystal exhibits a heat capacity maximum at 200.50°K. The shape of the heat capacity curve around this temperature is similar to that of

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[14] The only heat capacity data on K-salt available for comparison is given by Kopp ("Landolt-Börnstein Physikalisch-Chemische Tabellen II," Berlin, 1923), whose value, 63.0 cal./deg. mol. at about 35°C, lies on the extrapolated curve of the present data.

TABLE III. THERMODYNAMIC PROPERTIES OF $(NH_4)_2CuCl_4\cdot 2H_2O$ (in cal./deg. mol.)

T, °K	C^0_P	S^0	$\frac{(H^0-H^0_0)}{T}$	$-\frac{(G_0-H^0_0)}{T}$
10	0.322	0.201	0.102	0.099
15	1.152	0.458	0.292	0.166
20	2.902	1.016	0.714	0.302
25	5.052	1.890	1.364	0.526
30	7.358	3.014	2.169	0.845
40	12.364	5.807	4.085	1.722
50	17.342	9.108	6.247	2.861
60	22.248	12.701	8.052	4.199
70	26.838	16.479	10.796	5.683
80	31.052	20.340	13.067	7.273
90	34.935	24.224	15.283	8.941
100	38.478	28.088	17.426	10.662
110	41.782	31.913	19.492	12.421
120	44.900	35.683	21.481	14.202
130	47.968	39.398	23.400	15.998
140	51.094	43.088	25.267	17.821
150	54.182	45.999	27.092	18.907
160	57.060	49.585	28.873	20.712
170	60.080	53.134	30.619	22.515
180	63.437	56.659	32.345	24.314
190	67.762	60.201	34.092	26.109
200	75.378	63.838	35.934	27.904
200.50	76.290	Transition point		
210	66.220	67.150	37.453	29.697
220	67.190	70.249	38.780	31.469
230	68.675	73.268	40.046	33.222
240	70.300	76.225	41.273	34.952
250	71.855	79.127	42.466	36.661
260	73.205	81.972	43.623	38.349
270	74.432	84.758	44.741	40.017
280	75.614	87.487	45.823	41.664
290	76.752	90.160	46.870	43.290
298.15	77.588	92.302	47.701	44.601

TABLE IV. THERMODYNAMIC PROPERTIES OF $K_2CuCl_4\cdot 2H_2O$ (in cal./deg. mol.)

T, °K	C^0_P	S^0	$\frac{(H^0-H^0_0)}{T}$	$-\frac{(G^0-H^0_0)}{T}$
10	0.484	0.226	0.149	0.077
15	1.463	0.579	0.401	0.178
20	3.650	1.276	0.920	0.356
25	6.322	2.372	1.875	0.497
30	9.260	3.783	2.860	0.923
40	15.448	7.312	5.249	2.063
50	20.758	11.354	7.843	3.511
60	25.210	15.541	10.374	5.167
70	29.040	19.726	12.777	6.949
80	32.188	23.812	15.010	8.802
90	35.090	27.774	17.083	10.691
100	37.320	31.593	19.001	12.592
110	39.285	35.243	20.757	14.486
120	41.148	38.741	22.378	16.363
130	42.900	42.106	23.891	18.215
140	44.484	45.344	25.306	20.038
150	45.932	48.463	26.634	21.829
160	47.310	51.472	27.883	23.589
170	48.580	54.378	29.064	25.314
180	49.760	57.188	30.181	27.007
190	50.900	59.909	31.242	28.667
200	51.880	62.545	32.249	30.296
210	52.840	65.100	33.207	31.893
220	53.790	67.580	34.120	33.460
230	54.720	69.992	34.996	34.996
240	55.646	72.340	35.837	36.503
250	56.550	74.630	36.648	37.982
260	57.418	76.872	37.430	39.442
270	58.265	78.955	38.186	40.769
280	59.120	81.190	38.918	42.272
290	59.920	83.279	39.629	43.650
298.15	60.524	84.950	40.194	44.756

the aniline hydrobromide crystal[15] at the λ-point, indicating that the phase transition is of a higher order. On the other hand, the $K_2CuCl_4\cdot 2H_2O$ crystal does not show any thermal anomaly over the entire temperature range investigated.

Thermodynamic Propertier of $(NH_4)_2CuCl_4\cdot 2H_2O$ and $K_2CuCl_4\cdot 2H_2O$.—The values of the heat capacity, entropy, enthalpy and the free energy function for NH_4-salt and K-salt have been derived from the experimental heat capacities with the standard technique; they are summarized in Tables III and IV. The extrapolation to 0°K was made by using the Debye formula. The error of the smoothed heat capacity data is estimated to be ±1% below 60°K and ±0.3% above 60°K. The values of entropy and free energy listed in Tables III and IV do not include the magnetic contributions from copper ions. Haseda[16] has recently reported the magnetic transition of K-salt at about 0.8°K, corresponding to the magnetic transition of the copper ion from the antiferromagnetic to the paramagnetic state. If the magnetic contributions were included in the thermodynamic functions of Tables III and IV, the values of entropy would become greater than the present values by about 1.3 e. u., while the values of free energy would be scarcely changed. On the other hand, the corresponding magnetic transition of NH_4-salt has not yet been reported. The NH_4-salt has an isomorphous crystal structure with the K-salt, and has lattice constants nearly equal to that of the K-salt, that is, $a_0=7.58$ Å and $c_0=7.96$ Å for the former and $a_0=7.45$ Å and $c_0=7.88$ Å

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[15] H. Suga, This Bulletin, 34, 426 (1961).

[16] T. Haseda, private communication.

for the latter. The corresponding magnetic transition can, accordingly, also be expected for the NH_4-salt around 1°K.

The Anomalous Heat Capacity of $(NH_4)_2CuCl_4\cdot 2H_2O$.—As is mentioned above, NH_4-salt gives a heat capacity anomaly. The excess heat capacity seems to rise at about 120°K, reaches a maximum value at 200.50°K, and then drops rather rapidly. The anomalous heat capacity, $(\Delta C_p)_{tr}$, at this maximum temperature amounts to 13.24 cal. deg^{-1} mol^{-1}. On the other hand, K-salt does not show any such thermal anomaly. Accordingly, the thermal anomaly seems to be associated with a movement of the ammonium group of NH_4-salt.

The entropy of transition, ΔS_{tr}, amounts to 1.945 e. u., and the enthalpy of transition, ΔH_{tr}, to 387.7 cal. $mol.^{-1}$ The procedure for calculating these values may be worth mentioning in more detail, so it will be described below.

In order to calculate the entropy and the enthalpy of transition, as well as the heat capacity associated with the ordering phenomena of the ammonium group, it is necessary to subtract the "normal" heat capacity from the experimentally-measured one. An ammonium ion has an excess of twelve internal degrees of freedom compared with a potassium ion. First of all, the contributions from these internal and torsional vibrations must be subtracted from the experimental heat capacity. Infrared or Raman data are, unfortunately, not yet known for this substance. However, it may not be unreasonable to assume that the values of the vibrational frequencies of the ammonium group in NH_4-salt will be replaced by those of other ammonium salts, in which the situation of the ammonium ion is similar to that of the present salt; i. e., each of ammonium ions is surrounded by a slightly distorted cube consisting of eight chlorine ions. The present crystal has an N-Cl distance of 3.35 Å and an N-N distance of 3.98 Å, distances which are comparable with those for ammonium chloride, where the N-Cl distance is 3.32 Å and the N-N distance, 3.87 Å. Thus, the values of the vibrational frequencies of the ammonium chloride crystal[3] may be assumed for the present crystal in calculating the contributions arising from the ammonium groups. The adopted values are as follows: $\nu_1=3040\ cm^{-1}$ (1), $\nu_2=1670$ (2), $\nu_3=3100$ (3), $\nu_4=1403$ (3), and ν_6 (torsional) = 310 (3) (the numbers in parentheses indicate degeneracy).

Now, $C_{int}(NH_4^+)$, the contribution from the internal vibrations and torsional oscillations of the ammonium ions to the heat capacity, can be calculated by using the Einstein function:

$$C_{int}(NH_4^+) = 2\boldsymbol{R}\sum_i d_i \frac{x_i^2\ e^{-x_i}}{(1-e^{-x_i})^2} \qquad (1)$$

where d_i is the degeneracy of an i-th mode of vibration and $x_i=\boldsymbol{h}\,\nu_i/\boldsymbol{k}T$. The ΔC_P(anomal) = $C_P(NH_4\text{-salt}) - C_{int}(NH^+{}_4) - C_P$(normal) quantity should be approximately the extra heat capacity contribution from the orientational motion of the ammonium ion as a whole. Usually the C_P (normal) quantity is estimated graphically rather arbitrarily. In the present case, however, the anomalous heat capacity extends over a considerable temperature range, and there is some latitude in drawing the normal heat capacity of the ammonium salt.

Osborne and Westrum[17,18] have assumed that the lattice contribution to the heat capacities of UO_2 and NpO_2 equals the heat capacity of the isomorphous diamagnetic, ThO_2, in estimating the anomalous magnetic contribution, and also, in another example, that the heat capacity of ThF_4 represents the lattice contribution for UF_4. This kind of assumption is not tenable for the present case, however, since at a low temperature the observed heat capacity of *K*-salt exceeds that of NH_4-salt, and a high temperature the situation is reversed. Stout and Catalano[19] have applied a law of corresponding states in order to estimate the normal heat capacity of antiferromagnetic MnF_2, FeF_2, COF_2 and NiF_2 by utilizing the heat capacity data of isomorphous, diamagnetic ZnF_2. Although the difference in structural parameters between the present two crystals is not very large,[6] the crystal structure of these salts is too complicated to apply such a simplified treatment in the present case.

In order to carry out a tentative but rather

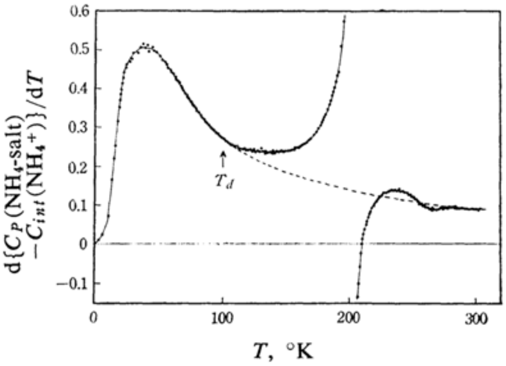

Fig. 5. $d\{C_P(NH_4\text{-salt}) - C_{int}(NH_4^+)\}/dT$ vs. temperature plot for $(NH_4)_2CuCl_4\cdot 2H_2O$ crystal.

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[17] D. W. Osborne and E. F. Westrum, Jr., *J. Chem. Phys.*, **21**, 1884 (1953).

[18] H. R. Lohr, D. W. Osborne and E. F. Westrum, Jr., *J. Am. Chem. Soc.*, **76**, 3837 (1954).

[19] J. W. Stout and E. Catalano, *J. Chem. Phys.*, **23**, 2013 (1955).

agreeable treatment for estimating the normal heat capacity of the NH_4-salt, the following procedure was adopted. The differential quantity, $d\{C_P(NH_4\text{-salt}) - C_{int}(NH_4{}^+\}/dT$, was plotted against the temperature over the entire temperature range; the results are drawn in Fig. 5. The corresponding value for K-salt, $dC_P(\text{K-salt})/dT$, is given in Fig. 6 for the sake of comparison. This procedure magnifies the effect of the phase transition on the graph. If there is no heat capacity anomaly, the behavior of the dC_P/dT in the NH_4-salt should be similar to that of K-salt, which is a monotonous function of the temperature.

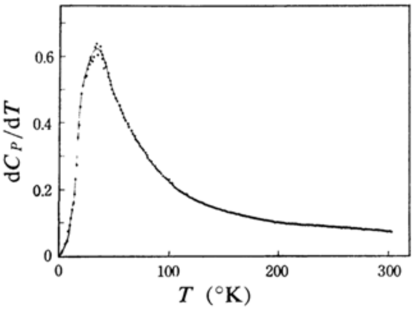

Fig. 6. $dC_P(\text{K-salt})/dT$ vs. temperature plot for $K_2CuCl_4 \cdot 2H_2O$ crystal.

There is also some latitude in drawing the dotted curve in Fig. 5, which represents the trend of the normal heat capacity of the NH_4-salt. However, there are at least two restrictions to eliminating some of the arbitrariness involved. One is that the curve corresponding to the normal heat capacity, the dotted curve in Fig. 5, must be a monotonously decreasing function; the other is that the normal heat capacity obtained by integrating the differential quantity should not exceed the value, $C_P(NH_4\text{-salt}) - C_{int}(NH_4{}^+)$, at any temperature. This means that the anomalous heat capacity, $\Delta C_P(\text{anomal})$, can not be negative. Consequently, the normal heat capacity at T°K was calculated as follows:

$$C_P(\text{normal}) \text{ at } T\text{°K}$$
$$= \{C_P(NH_4\text{-salt}) - C_{int}(NH_4{}^+)\} \text{ at } T_d\text{°K} + \int_{T_d}^{T} \frac{dC_P(\text{normal})}{dT}\, dT \qquad (2)$$

where T_d is the temperature at which the $dC_P(\text{normal})/dT$ curve deviates from the $d\{C_P(NH_4\text{-salt}) - C_{int}(NH_4{}^+)\}/dT$ curve. The anomalous heat capacity, estimated by using Eqs. 1 and 2 and the experimental heat capacity data, is shown in Fig. 7. This curve presumably corresponds to the lower limit of the anomalous heat capacity, in view of the two assumed requirements mentioned above. Above 300°K the dotted curve in Fig. 7 was extrapolated somewhat arbitrarily. The contribution from this part to the entropy of the transition amounts merely to 2.5 per cent of the total. The values of ΔS_{tr} and ΔH_{tr} were then calculated from the $\Delta C_P(\text{anomal})$ versus temperature curve.

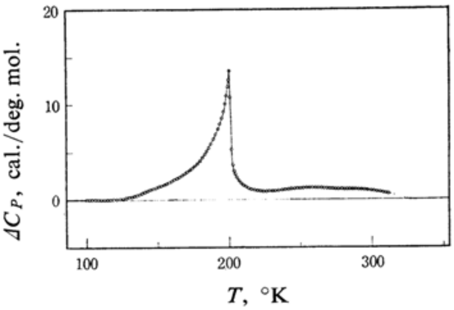

Fig. 7. Anomalous heat capacity of $(NH_4)_2CuCl_4 \cdot 2H_2O$ around 200.50°K.

Discussion

In order to discuss the nature of the phase transition of NH_4-salt, it is desirable to compare with each other the crystal structures of the two crystals.[6] The crystallographic data are summarized in Tables V, while the projections on the (010) and (001) planes of the crystal structure of NH_4-salt are depicted in Figs. 8 and 9. As has been mentioned already, each ammonium ion is surrounded by a slightly distorted cube consisting of eight chlorine ions. The N–Cl and N–N distances in the NH_4-salt are comparable to those of the ammonium chloride crystal. Therefore, an orientational order-disorder-type phase transition associated with the ammonium ions in ammonium chloride may also be expected for this NH_4-salt.

TABLE V. CRYSTALLOGRAPHIC DATA OF NH_4-SALT AND K-SALT[6]

	$(NH_4)_2CuCl_4 \cdot 2H_2O$	$K_2CuCl_4 \cdot 2H_2O$
	D_{4h}^{14} (P4/mnm)	
	Z=2	
	$a_0=7.58$ Å	$a_0=7.45$ Å
	$c_0=7.96$ Å	$c_0=7.88$ Å
Cu:	0,0,0; 1/2,1/2,1/2,	
NH_4 or K:	0,1/2,1/4; 1/2,0,1/4; 0,1/2,3/4,	
Cl (1):	$\pm(u,u,0;\ u+1/2,1/2-u,1/2)$	
Cl (2):	$\pm(v,v,1/2;\ v+1/2,1/2-v,0)$	
H_2O:	$\pm(0,0,w;\ 1/2,1/2,w+1/2)$	
	$u=0.217$	$u=0.220$
	$v=0.221$	$v=0.220$
	$w=0.250$	$w=0.250$

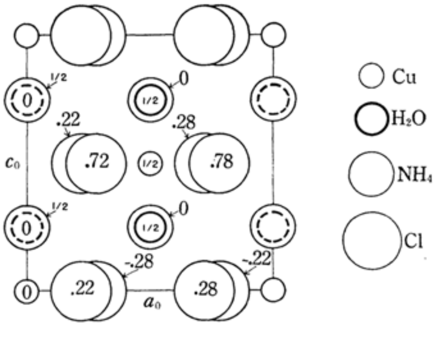

Fig. 8. A projection on the (010) plane of the crystal structure of $(NH_4)_2CuCl_4\cdot2H_2O$ (after Wyckoff).

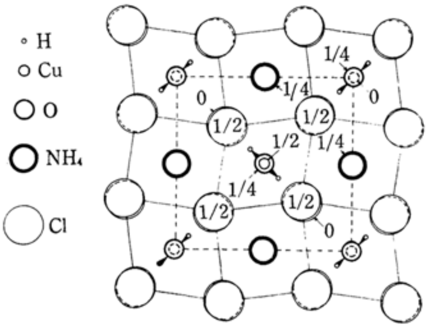

Fig. 9. A projection on the (001) plane of the crystal structure of $(NH_4)_2CuCl_4\cdot2H_2O$.

Itoh and Kamiya[20] have recently reported on the temperature variation of the proton nuclear magnetic resonance spectra of the NH_4-salt and have observed a motional narrowing associated with the protons of the ammonium group at about 150°K. They found that the situation of the barrier height hindering the flipping motion of the ammonium ion is very similar to that with ammonium chloride. If the nature of the transition of this crystal is very similar to that of the ammonium chloride, the entropy of transition could amount to 2.68 ($2\boldsymbol{R}\ln 2$) e. u. The experimental value is, however, 1.945 e. u., about two thirds of 2.68 e. u.

In the case of ammonium chloride, all chlorine ions are equivalent with respect to the $NH_4{}^+$ ion, while for the present crystal, Itoh et al.[21] have reported that there are two kinds of chlorine ions; one makes a hydrogen bond with the proton of crystalline water, while the other does not. Other differences from the ammonium chloride are that the present crystal has a tetragonal symmetry and that the N–N distance is quite different in each direction. The N–N distance along the [001] axis is 3.98 Å, while along the [110] axis it is 5.36 Å. Thus, only along the direction of the c-axis is the N–N distance comparable with that of ammonium chloride.

In other words, the principle of the framework of the present crystal is that the NH_4Cl is diluted by $CuCl_2\cdot2H_2O$ and the interaction between the ammonium ions is weakened two-dimensionally. In such a pseudo-linear chain of $NH_4{}^+$ ions, the order parameter describing the randomness with respect to the orientation of ammonium ions is expected to change much less co-operatively than a three-dimensionally-arranged system, as in the case of ammonium chloride. The extraordinary broadness of the anomaly, as well as the much smaller jump of C_P at the transition point, may be ascribed to the weakened interaction between the ammonium ions in this crystal. The maximum anomalous heat capacity of the present crystal amounts merely to 13.24 cal. deg^{-1} mol^{-1}, while in the case of ammonium chloride[1] it reaches about 159 cal. deg^{-1} mol^{-1}.

It should be mentioned that above the transition point there is a rather broad and small hump in the ΔC_P(anomal) versus temperature curve. It is more magnified in the curve of the derivative of the heat capacity than in the heat capacity curve itself (see Fig. 5). If the residual anomalous part of the heat capacity curve above the phase transition point is exclusively due to the short range order remaining, it may not show such a maximum point. Therefore, we may assume, as one explanation, that the hump arises from the Shottky anomaly, based on the population difference of the individual ammonium ion between the two sites of different energies, associated with the different chlorine ions in the disordered state; in one possible orientation of the ammonium ion, all four protons are directed to the chlorine ions hydrogen-bonded with the crystalline water, while in the other all protons are directed to the free chlorine ions. If the hump is ascribed to the Shottky anomaly, the energy difference between the two possible orientations of the ammonium ions is calculated to be about 1.3 kcal. mol^{-1}.

We have not given here the theoretical treatment needed to interpret the transition mechanism of the pseudo one-dimensional ionic array of the present crystal. In order to develop such a treatment, the ordered structure of ammonium ions must be known precisely. Because of the rather small value of the apparent transition entropy ($\fallingdotseq 2/3\times 2\boldsymbol{R}\ln 2$), however, it is supposed that there still

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[20] J. Itoh and Y. Kamiya, *J. Phys. Soc. Japan*, **17**, Supplement B-I, 512 (1962).

[21] J. Itoh, R. Kusaka, R. Kiriyama and Y. Saito, *Memoirs of the Institute of Scientific and Industrial Research, Osaka Univ.*, **XIV**, 1 (1957).

remains a much larger degree of disorder with respect to the orientation of ammonium groups in the low temperature phase. Further investigations of, for example, neutron diffraction, neutron inelastic scattering, or some other spectroscopic techniques will be useful in understanding more quantitatively the nature of the phase transition.

Summary

The heat capacity of copper potassium chloride dihydrate and copper ammonium chloride dihydrate crystals have been measured between 13 and 310°K. The latter crystal shows a λ-type anomaly in the heat capacity curve which seemed to be due to the orientational order-disorder process of ammonium groups. The heat capacity of $(NH_4)_2CuCl_4\cdot 2H_2O$ exhibits a maximum value of 76.290 cal. deg.$^{-1}$ mol^{-1} at 200.50°K. By plotting the temperature derivative of heat capacities, the normal contribution from the lattice to the heat capacity of $(NH_4)_2CuCl_4\cdot 2H_2O$ has been estimated. In this case the corresponding values for $K_2CuCl_4\cdot 2H_2O$ has been taken as a reference. By subtracting the estimated normal heat capacity from the experimentally measured one, approximate values of the entropy change, $\Delta S=$ 1.945 cal. deg.$^{-1}$ mol^{-1}, and the heat capacity jump, $\Delta C_P=13.24$ cal. deg^{-1} mol^{-1}, associated with the orientational ordering of the linearly-arranged ammonium ion system have been given.

The values of the heat capacity, entropy, enthalpy, and Gibbs free energy of both crystals have been tabulated at selected temperatures. The standard values of the entropy and enthalpy are: $K_2CuCl_4\cdot 2H_2O$, $S^0=84.95$ cal. deg^{-1} mol^{-1}, $H^0-H^0_0=11980$ cal. mol^{-1}; $(NH_4)_2\cdot CuCl_4\cdot 2H_2O$, $S^0=92.30$ cal. deg.$^{-1}$ mol^{-1}, $H^0-H^0_0=14220$ cal. mol^{-1}.

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