Heat capacities of bis-tetraethylammonium tetrachloronickelate and tetrachlorozincate I. Structural transitions and thermophysical results[a]

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The heat capacities of bis-tetraethylammonium tetrachloronickelate (BEAN) and tetra-chlorozincate (BEAZ) were measured over the temperature range 5 to 350 K by adiabatic calorimetry. Bifurcated anomalies were found for both compounds with the temperatures of the maxima occurring at (222.1 ± 0.1) K and (222.7 ± 0.1) K for BEAN and at (227.9 ± 0.2) K and (228.9 ± 0.2) K for BEAZ. The excess entropies associated with the transition regions were 9.16 and 9.96 cal_{th} K^{-1} mol^{-1} respectively. Both transition regions were characterized by equilibrium times of several days. Selected thermal functions C_p°, S°, and $-\{G^\circ(T) - H^\circ(0)\}/T$ at 298.15 K are, respectively, 151.7, 185.33, and 92.16 cal_{th} K^{-1} mol^{-1} for BEAN and 153.0, 181.52, and 88.53 cal_{th} K^{-1} mol^{-1} for BEAZ.

1. Introduction

In 1965 Ham[1] proposed a model of the dynamic Jahn-Teller effect in which electron-lattice coupling, though insufficiently strong to produce a static distortion, could partially quench orbital angular momentum. A Ni^{2+} ion in tetrahedral symmetry was suggested as one likely to exhibit such an effect.

A nearly tetrahedral $NiCl_4^{2-}$ group was found in bis-tetraethylammonium tetra-chloronickelate (BEAN) during the 300 K structure determination of that compound by Stucky, Folkers, and Kistenmacher.[2] The powder susceptibility and single-crystal anisotropies of this compound were measured between 90 and 300 K by Gerloch and Slade[3] and revealed an anomaly in the crystal anisotropy at about 220 K. This decrease in anisotropy was interpreted as indicating a change in the geometry of the complex ion. Gerloch and Slade's analysis of the susceptibilities predicted almost perfect tetrahedral coordination of the nickel ion below 220 K. Quenching of the orbital angular momentum in Ni^{2+} would reduce splitting of the $^3T_{1g}$ ground state by the spin-orbit interaction. Should the quenching be sufficiently

large, the excited states would become thermally accessible at temperatures low enough to produce recognizable contributions to the total heat capacity.

Heat-capacity measurements have been made on the tetrahedral nickel compound discussed above as well as on the isostructural[4, 5] zinc analog (BEAZ). The heat capacity of the latter provides an estimate of the non-electronic contributions to the heat capacity of the nickel compound. The discussion of these measurements in terms of Ham's theory will be published subsequently.[6] This paper presents the experimental results and discusses the significance of the bifurcated transitions found near 220 K in both compounds.

2. Experimental

SAMPLE PREPARATION

Both the BEAN sample and the BEAZ sample were prepared by the technique of Gill and Nyholm.[7] The BEAN sample consisted of approximately equal portions of powder and small flat dark-blue plates 1 to 5 mm in length. The BEAZ sample, white in color, was similarly composed. Chemical analysis for the metal and chlorine agreed to within 0.1 per cent for both compounds. Both compounds were crystallized from anhydrous ethanol, dried in a high vacuum, and handled in the anhydrous atmosphere of a glove box. Duplicate chemical analyses for all non-metallic constituents yielded mean mass percentages of the constituents of BEAN: C, (41.75 $\pm$ 0.05), (theor. 41.71); H, (9.16 $\pm$ 0.09), (theor. 8.68); N, (6.12 $\pm$ 0.08), (theor. 6.08); Cl, (30.45 $\pm$ 0.06), (theor. 30.78). Those of BEAZ were: C, (41.19 $\pm$ 0.05), (theor. 41.12); H, (8.72 $\pm$ 0.09), (theor. 8.56); N, (5.93 $\pm$ 0.08), (theor. 6.00); Cl, (30.14 $\pm$ 0.06), (theor. 30.34). The figures are estimates of the accuracy of the determinations by the commercial analysts employed. The magnitude of the average deviation from theoretical values of the analyses is thus 0.22 per cent for BEAN and only 0.12 per cent for BEAZ and, therefore, slightly exceeds the uncertainties in the individual determinations themselves. Both samples are clearly of the claimed stoichiometry and the high hydrogen determinations are probably evidence that insufficient precautions were taken by the analysts in protecting the hygroscopic nickel compound from water absorption.

HEAT-CAPACITY MEASUREMENTS

Heat-capacity measurements were made in the Mark II adiabatic cryostat described elsewhere.[8] The calorimeter, laboratory designation W-52, was a gold-plated OFHC copper can of internal volume 59.11 cm^3. Table 1 lists the mass of sample used, pressure of helium exchange gas in the calorimeter, and molar masses used to convert

TABLE 1. Sample loading data; m is the sample mass, M is the molar mass of the sample, and p the partial pressure of the helium used in the calorimeter

Compound	Formula	m/g	M/g	p/kPa
BEAN	R_2NiCl_4	36.1019	461.03	11.1
BEAZ	R_2ZnCl_4	22.6082	467.70	6.9

the experimental results to molar quantities. A density of 1.25 g cm^{-3} was used for the buoyancy correction.[2] The results are presented in terms of the IPTS-48 temperature scale.[9]

During measurements in the regions of the transition temperature, special care was taken to adjust the adiabatic shields for minimal net thermal exchange between the shields and calorimeter. This action was necessitated by the long equilibrium times in this region.

3. Results and discussion

THERMOPHYSICAL FUNCTIONS

The experimental heat capacities for BEAN and BEAZ are shown in figure 1. The C_p values have a normal sigmate shape except for the large sharp bifurcated anomalies occurring at (222.1 ± 0.1) and (222.7 ± 0.1) K for BEAN and (227.9 ± 0.1) and (228.9 ± 0.2) K for BEAZ. In figure 2 these anomalies are shown in more detail.

The heat capacities of BEAN and BEAZ are given also in table 2 in chronological sequence so that the temperature increments can be deduced approximately from the adjacent mean temperatures. Series of points have had slight adjustments made for curvature. The direct enthalpy determinations through the transition regions have been summarized in table 3.
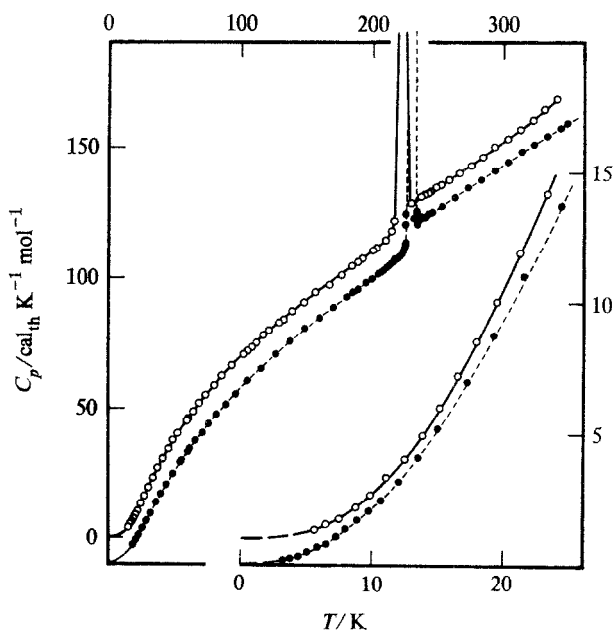

FIGURE 1. The experimental heat capacities: ○, BEAN; ●, BEAZ. For clarity, points in the transition region have been omitted (but see figure 2). The BEAZ curves have been displaced downward by 10 cal$_{th}$ K^{-1} mol^{-1} against the scale at the left and 1 cal$_{th}$ K^{-1} mol^{-1} against the scale at the right to separate the curves.

TABLE 2. Experimental molar heat capacities of [(CH₃CH₂)₄N]₂MCl₄ compounds
(cal$_{th}$ = 4.184 J)

$\dfrac{<T>}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{<T>}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{<T>}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{<T>}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$
			bis-Tetraethylammonium tetrachloronickelate (BEAN)				
Series I		220.01	285.8	221.19	542	217.25	120.02
104.80	71.96	220.64	333.7	221.45	813	218.35	142.7
108.30	73.13	221.00	1668	221.56	243	219.31	170.0
117.71	78.15	221.24	569	221.97	998	220.15	201.9
129.02	83.08	221.62	512	222.11	1052	220.73	461
138.95	87.16	222.07	406	222.30	659	221.10	510
148.48	90.89	222.45	757	222.49	1275	221.51	278
157.83	94.56	222.74	741	222.65	966	221.86	1863
167.05	97.82	223.04	634	222.93	504	221.99	1184
176.05	101.04	223.42	477	223.37	347	222.20	734
184.92	104.39	223.95	315.5	223.92	294.5	222.42	918
193.56	107.68	224.74	182.6	224.75	144.11	222.64	807
202.00	110.92	225.85	135.4	225.66	127.35	222.76	7822
210.25	114.54	229.24	128.51	226.42	127.56	222.95	511
216.60	241.4	234.77	130.18	227.00	127.44	223.37	345
220.05	504					223.93	232
ΔH$_t$ Detn. A^a		Series V		Series IX		224.73	167.6
239.63	131.65	59.04	45.88	5.67	0.34	225.73	138.7
248.94	134.66	63.60	49.02	6.59	0.52	226.84	125.21
258.06	137.40	68.42	52.21	7.51	0.75	227.98	127.79
266.97	140.51	73.52	55.21	8.74	1.22		
275.74	143.33	79.30	58.78	9.82	1.75	Series XII^a	
284.37	146.46	85.71	62.53	11.06	2.38	204.86	111.91
293.58	150.02	93.22	66.45	12.46	3.07	206.11	112.57
303.38	153.5	102.20	70.85	13.79	3.98	ΔH$_t$ Detn. I	
312.98	157.4	111.29	75.14	15.04	5.06	ΔH$_t$ Detn. J	
322.42	161.1	121.11	79.68	16.46	6.21		
331.69	164.4	131.44	84.10	17.92	7.59	Series XIII^a	
340.80	168.9			19.44	9.10	211.90	115.99
		Series VI		21.24	10.98	218.79	219.4
Series II		ΔH$_t$ Detn. C		23.34	13.21	221.62	1019
189.28	105.99			25.92	16.07	ΔH$_t$ Detn. K	
200.86	110.56	Series VII		29.14	19.69		
ΔH$_t$ Detn. B		189.61	106.03	32.67	23.33	Series XIV^a	
		200.28	110.26	36.33	27.04	ΔH$_t$ Detn. L	
Series III		ΔH$_t$ Detn. D		40.20	30.68		
202.89	111.30			44.22	34.32	Series XV^a	
211.01	114.89	Series VIII		48.51	37.92	ΔH$_t$ Detn. M	
217.29	239.6	204.38	111.93	53.32	41.66		
220.91	428	210.26	114.42	58.62	45.53	Series XVI^a	
224.56	235.5	213.31	115.61			ΔH$_t$ Detn. N	
230.52	128.9	214.44	116.50	Series X			
237.82	131.06	215.56	117.33	ΔH$_t$ Detn. E		Series XVII^a	
		216.67	118.21	ΔH$_t$ Detn. F		211.34	115.10
Series IV		217.75	126.63	ΔH$_t$ Detn. G		218.27	239.0
208.53	113.78	218.70	165.9	ΔH$_t$ Detn. H			
214.35	118.97	219.45	231.0			Series XVIII^a	
217.78	153.13	220.04	305.2	Series XI		212.04	115.43
218.73	243.9	220.52	366.4	214.89	116.23	ΔH$_t$ Detn. O	
219.42	315.8	220.88	559	216.08	117.37	ΔH$_t$ Detn. P	

TABLE 2—*continued*

bis-Tetraethylammonium tetrachlorozincate (BEAZ)

$\langle T\rangle$ K	C_p cal$_{th}$ K^{-1} mol^{-1}	$\langle T\rangle$ K	C_p cal$_{th}$ K^{-1} mol^{-1}	$\langle T\rangle$ K	C_p cal$_{th}$ K^{-1} mol^{-1}	$\langle T\rangle$ K	C_p cal$_{th}$ K^{-1} mol^{-1}
Series I		228.46	1226	5.44	0.291	205.64	111.86
241.99	134.17	229.65	444	6.17	0.430	212.87	114.76
252.66	137.58	232.23	179.1	6.93	0.631	217.83	117.04
262.74	140.93	236.06	132.38	7.60	0.761	220.91	118.01
272.92	144.25	240.27	133.51	8.30	1.023	221.87	118.62
283.25	147.83			9.11	1.319	222.82	119.10
293.47	151.19	Series III		9.92	1.675	223.76	121.70
303.50	154.79	200.45	109.38	10.73	2.104	224.69	120.66
313.38	158.36	ΔH_t Detn. A		11.79	2.452	225.62	122.74
323.28	161.52	245.38	135.19	13.05	3.171	226.52	134.60
333.20	164.56			14.45	4.121	227.20	269.86
342.98	167.77	Series IV		16.00	5.217	227.51	731
348.73	169.70	208.50	112.99	18.19	7.035	227.68	745
Series II		214.26	115.43	20.11	8.784	227.96	455
53.70	39.35	219.65	117.91	22.46	11.014	228.21	1123
60.28	44.03	223.39	119.65	25.26	13.726	228.42	632
65.53	47.63	225.51	123.75	27.99	16.52	228.64	943
70.69	50.86	227.16	267.7	31.09	19.69	228.81	1100
75.86	54.03	228.00	830	35.01	23.52	228.97	1041
81.63	57.71	228.46	801	38.99	27.20	229.12	660
88.14	61.64	228.93	818	43.25	30.92	229.26	1136
95.77	65.61	229.38	853	47.98	34.80	229.42	1101
105.28	70.52	229.84	761	53.48	39.05	229.57	1063
115.56	75.55	230.44	518	59.84	43.74	229.74	962
126.00	80.45	231.43	236.80			230.05	351.40
137.43	85.45	233.05	135.73	Series VII		230.31	776
149.01	90.20	235.00	131.80	104.26	69.91	230.52	507
159.76	94.40	236.96	132.44	ΔH_t Detn. D		230.81	216.8
170.02	98.37			ΔH_t Detn. E		231.41	249.8
180.13	102.10	Series V		199.14	109.38	232.04	183.8
189.29	105.56	199.75	109.49	ΔH_t Detn. F		232.83	132.74
199.39	109.38	ΔH_t Detn. B		248.28	136.08	233.71	132.74
206.73	112.03	ΔH_t Detn. C				234.59	130.97
211.43	114.30	242.53	134.37			235.47	134.17
216.06	116.36			Series VIII		236.35	132.89
225.05	130.39	Series VI		185.68	104.18	237.22	133.53
227.65	879	4.28	0.139	195.79	108.02		
		4.81	0.198				

a These determinations are considered to have been made on the sample incompletely converted to the low-temperature phase. Not included in final fit.

The experimental heat capacities in non-transition regions were curvature corrected and fitted to polynomials in reduced temperature by the method of least squares and integrated to yield values of the thermodynamic functions at selected temperature intervals. Within the transition regions, the thermal functions were obtained by numerical integration of heat-capacity points checked against large-scale plots. Values for the thermal functions thus obtained are presented in table 4 for both compounds. Entropy and enthalpy increments below the lowest measured temperature were obtained by a Debye limiting-law extrapolation.
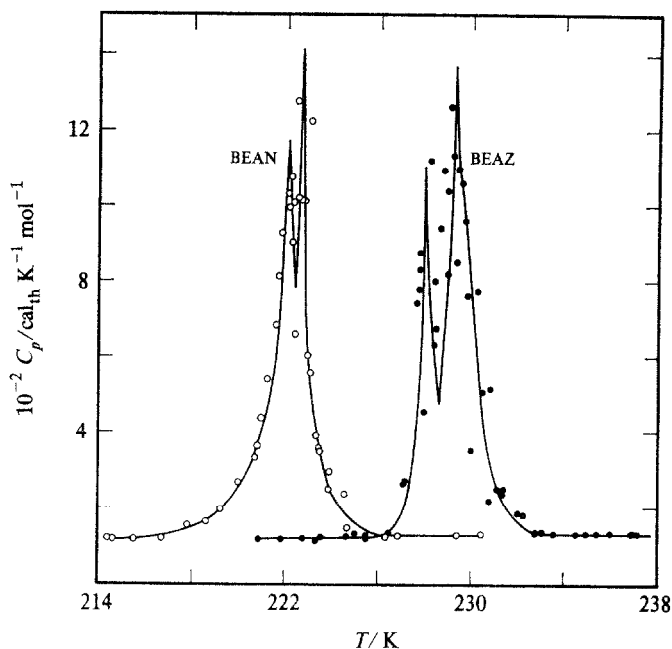
FIGURE 2. Experimental heat capacities in the transition regions. $\bigcirc$, BEAN; $\bullet$, BEAZ. Many points have been omitted (compare footnote a, table 2).

TABLE 3. Enthalpy increments of $[(CH_3CH_2)_4N]_2MCl_4$ compounds
(cal_{th} = 4.184 J)

Source of results	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{H°(T_2) - H°(T_1)}{cal_{th}\ mol^{-1}}$	$\dfrac{H°(233\ K) - H°(206\ K)}{cal_{th}\ mol^{-1}}$
		bis-Tetraethylammonium tetrachloronickelate (BEAN)		
ΔH_t Detn. B	206.18	233.44	5325.9	5289.1
ΔH_t Detn. C	209.66	236.98	5390.3	5287.2
ΔH_t Detn. D	205.54	232.15	5227.3	5285.6
ΔH_t Detns. E, F, G, H	207.71	235.74	5454.3	5290.4
ΔH_t Detns. I, J	206.13	232.83	5247.1	5284.0

Mean value: $\qquad\qquad\qquad\qquad\qquad$ $H°(233\ K) - H°(206\ K) = 5287 \quad \pm\ 3$
Graphical integration: $\qquad\qquad\qquad$ $H°(233\ K) - H°(206\ K) = 5288$
Lattice enthalpy increment: $\qquad\qquad$ $H°(233\ K) - H°(206\ K) = 3221 \quad \pm\ 6$
Additional ΔH_t from 186 to 206 K: $\qquad\qquad\qquad\qquad\quad = \ \ 21.1$
Enthalpy of transition: ΔH_t $\qquad\qquad\qquad\qquad\qquad\qquad = 2087 \quad \pm\ 7$
Entropy of transition: $\Delta S_t/cal_{th}\ K^{-1}\ mol^{-1} = 9.16 \pm 0.03$

TABLE 3—*continued*

Source of results	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{H°(T_2) - H°(T_1)}{cal_{th} \ mol^{-1}}$	$\dfrac{H°(240 \ K) - H°(205 \ K)}{cal_{th} \ mol^{-1}}$
			bis-Tetraethylammonium tetrachlorozincate (BEAZ)	
Detn. A	205.86	240.72	6449.7	6449.2
Detns. B, C	203.54	241.59	6829.8	6454.7
Detn. D	205.77	243.72	6857.4	6444.9
Series II (11 detn.)	204.37	242.37	6670.9	6450.3
Series IV (16 detn.)	205.47	237.94	6119.1	6446.6
Series VII (37 detn.)	200.78	237.66	6608	6450

Mean value: $\qquad\qquad\qquad\qquad\qquad\qquad\ H°(240 \ K) - H°(205 \ K) = 6449 \pm 4$
Graphical integration: $\qquad\qquad\qquad\qquad\ \ H°(240 \ K) - H°(205 \ K) = 6451$
Lattice enthalpy increment: $\qquad\qquad\quad H°(240 \ K) - H°(205 \ K) = 4165 \pm 6$
Enthalpy of transition: $\Delta H_t \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 2284 \pm 8$
Entropy of transition: $\Delta S_t / cal_{th} \ K^{-1} \ mol^{-1} = 9.66 \pm 0.04$

The results in the transition regions are of lower precision than the others due to the long equilibration times (several days) in these temperature ranges (see below). Adjustments were necessary to compute heat capacities from experimental results when measurements of the drift of temperature against time were abandoned before the sample reached complete thermal equilibrium. (These adjustments are discussed more fully in the appendix.) The accuracy of these points is, however, considered to be better than 5 per cent near the top of the heat-capacity maxima and increases

TABLE 4. Thermodynamic properties of $[(CH_3CH_2)_4N]_2MCl_4$ compounds
($cal_{th} = 4.184$ J)

$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th} \ K^{-1} \ mol^{-1}}$	$\dfrac{S°(T) - S°(0)}{cal_{th} \ K^{-1} \ mol^{-1}}$	$\dfrac{H°(T) - H°(0)}{cal_{th} \ mol^{-1}}$	$\dfrac{-\{G°(T) - H°(0)\}/T}{cal_{th} \ K^{-1} \ mol^{-1}}$
		bis-Tetraethylammonium tetrachloronickelate (BEAN)		
		Crystal III		
5	0.229	(0.079)	(0.295)	(0.020)
10	1.751	0.609	4.547	0.155
15	4.984	1.875	20.694	0.495
20	9.646	3.920	56.79	1.080
25	15.09	6.649	118.46	1.911
30	20.54	9.888	207.71	2.965
35	25.71	13.446	323.44	4.205
40	30.51	17.20	464.14	5.593
45	34.96	21.05	627.9	7.096
50	39.10	24.95	813.2	8.686
60	46.58	32.75	1242.4	12.048
70	53.20	40.44	1741.9	15.56
80	59.17	47.94	2304.2	19.14
90	64.65	55.23	2923.6	22.75
100	69.76	62.31	3596.0	26.35

TABLE 4—continued

$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{S°(T) - S°(0)}{cal_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{H°(T) - H°(0)}{cal_{th}\ mol^{-1}}$	$\dfrac{-\{G°(T) - H°(0)\}/T}{cal_{th}\ K^{-1}\ mol^{-1}}$
110	74.58	69.19	4317.9	29.93
120	79.15	75.87	5087	33.48
130	83.48	82.38	5900	37.00
140	87.61	88.72	6756	40.47
150	91.52	94.90	7652	43.89
160	95.26	100.93	8586	47.27
170	98.89	106.81	9556	50.60
180	102.52	112.57	10563	53.88
190	106.27	118.21	11607	57.12
200	110.16	123.76	12689	60.31
222.1		C_p Maximum		
		Crystal II		
222.7		C_p Maximum		
		Crystal I		
240	131.80	154.74	19560	73.25
250	134.91	160.19	20893	76.62
260	138.11	165.54	22258	79.93
270	141.45	170.82	23656	83.20
280	144.94	176.02	25087	86.42
290	148.57	181.17	26555	89.60
300	152.3	186.27	28059	92.74
310	156.1	191.33	29601	95.84
320	160.1	196.35	31182	98.90
330	164.1	201.33	32803	101.93
340	168.3	206.29	34465	104.93
273.15	142.53	172.46	24103	84.22
298.15	151.6	185.33	27778	92.16

<div align="center">bis-Tetraethylammonium tetrachlorozincate (BEAZ)</div>
<div align="center">Crystal III</div>

T	C_p	$S°(T) - S°(0)$	$H°(T) - H°(0)$	$-\{G°(T) - H°(0)\}/T$
5	0.225	0.079	0.295	0.020
10	1.663	0.593	4.413	0.152
15	4.472	1.750	19.149	0.474
20	8.683	3.586	51.57	1.008
25	13.464	6.034	106.86	1.760
30	18.59	8.941	186.97	2.709
35	23.48	12.177	292.23	3.827
40	28.10	15.62	421.28	5.084
45	32.42	19.18	572.7	6.451
50	36.45	22.80	745.0	7.905
60	43.82	30.11	1147.0	10.997
70	50.49	37.38	1619.0	14.248
80	56.69	44.53	2155.3	17.59
90	62.48	51.54	2751.4	20.97
100	67.90	58.41	3403.6	24.37

TABLE 4—*continued*

$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{S°(T) - S°(0)}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{H°(T) - H°(0)}{\text{cal}_{th}\ mol^{-1}}$	$\dfrac{-\{G°(T) - H°(0)\}/T}{\text{cal}_{th}\ K^{-1}\ mol^{-1}}$
110	72.95	65.12	4108.1	27.77
120	77.69	71.67	4861.6	31.16
130	82.17	78.07	5661	34.52
140	86.46	84.32	6504	37.86
150	90.58	90.42	7390	41.16
160	94.55	96.40	8316	44.43
170	98.37	102.25	9280	47.66
180	102.08	107.97	10283	50.85
190	105.77	113.59	11322	54.00
200	109.58	119.11	12398	57.12
210	113.67	124.56	13514	60.20
220	118.10	129.95	14673	63.25
227.9		C_p Maximum		
		Crystal II		
228.9		C_p Maximum		
		Crystal III		
240	133.51	150.56	19407	69.70
250	136.78	156.08	20759	73.04
260	139.99	161.50	22143	76.34
270	143.25	166.85	23559	79.59
280	146.64	172.12	25008	82.80
290	150.1	177.32	26492	85.97
300	153.6	182.47	28011	89.10
310	157.1	187.57	29564	92.20
320	160.4	192.61	31152	95.26
330	163.6	197.59	32772	98.28
340	166.8	202.53	34425	101.28
350	170.0	207.41	36109	104.24
273.15	144.31	168.52	24012	80.61
298.15	153.0	181.52	27727	88.53

quickly as the heat capacity decreases to that of the lattice. Outside the transition regions, the accuracy is estimated to be within ± 0.1 per cent.

A further impression of the accuracy may be gained from figure 3 showing the deviations of the experimental points from the smoothed results. The Schottky-like deviation of the heat capacities between the compounds themselves is discussed elsewhere.[6]
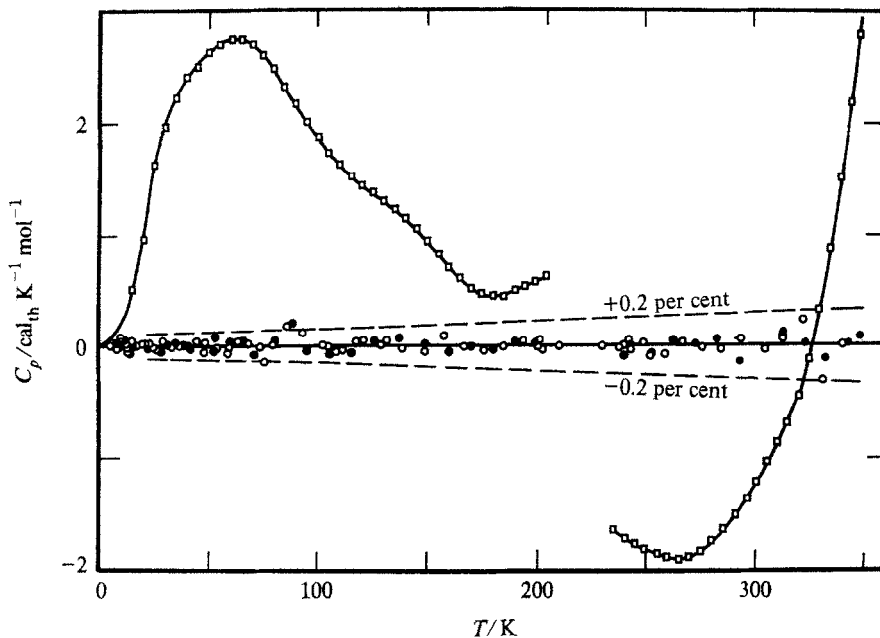
FIGURE 3. Deviation plot for BEAN and BEAZ.
□, C_p (BEAN, smoothed)—C_p (BEAZ, smoothed); ○, C_p (BEAN, exptl)—C_p (BEAN, smoothed);
●, C_p (BEAZ, exptl)—C_p (BEAZ, smoothed).
The dashed lines indicate deviations of ±0.2 from the smoothed curves.

BIFURCATION OF THE TRANSITIONS

Although only one series of quasi-equilibrium points has been taken through the transition region of BEAN, the existence of the bifurcation is indicated in other ways. A series of rapidly collected points (which involved heating for 10 min, waiting 60 min, and repeating) also showed a drop in the heat capacity at 222.3 K. In addition, the rate of equilibration is distinctly different on the two peaks, and is much slower on the low-temperature peak. Finally, the integrated enthalpy from the C_p curve agrees with the value of ΔH_t provided the minimum produced by bifurcation is included in the curve.

The long equilibration times in the transition regions of both compounds require discussion. Following an energy input (usually sufficiently large to raise the sample temperature by several K in the non-transition region) the sample would require more than several days to reach internal thermal equilibrium. In contrast, outside the transitions, equilibrium was usually reached within 20 min following energy inputs which were five times as intensive.

Such slow equilibrium times and hysteresis have previously been reported[10, 11] for other ammonium salts. Sorai and coworkers[11] as well as Alles et al.[12] found the equilibrium times for NH_4Br increased from 10 min to several hours near the first-order phase transition near 108 K.

Due to the long equilibrium times no enthalpy measurements could be made between the peaks. When energy sufficient to raise the temperature from an initial value well below the transitions to in between the peaks was added, the sample nearest the heater would heat through both transitions and then undercool as it came into equilibrium with the rest of the sample. The resulting temperature would be lower than that of the lower peak. Further addition of energy would reveal a heat capacity very nearly that of the lattice. Enthalpy measurements of the transitions were thus made only across the entire transition regions for both compounds.

The very high values of the transitional heat capacities are indicative of a first-order transition. This first-order nature is confirmed by other evidence: hysteresis effects have been observed near the transitions, and substantial volumetric changes occurred within the samples during the measurements. One example of hysteresis has been mentioned above. Another occurred when the nickel compound was cooled slowly from above the transitions to 207 K, 15 K below the transitions. Subsequent heating of the sample revealed less than 10 per cent of the transitional enthalpy indicating the sample had undercooled.

For both compounds, the small crystals which had been loosely loaded into the calorimeter were found to be tightly packed fine powders during unloading. Such shattering must have taken place at the transitions and is characteristic of first-order transitions.

COMPARISON WITH OTHER COMPOUNDS

The thermal properties of the series of compounds $[(CH_3CH_2)_4N]_2MCl_4$, where M = Mn, Fe, Ni, Co, Cu, and Zn, have been previously studied by Melia and Merrifield[13] who used differential scanning calorimetry (d.s.c.). They found two distinct transitions in the manganese compound and shoulders on the main peaks of the cobalt and zinc compounds. The nickel, iron, and copper compounds revealed only a single anomaly. A comparison of their results with the present work is shown in table 5. It is found that the transition in BEAN observed with d.s.c. was several K

TABLE 5. Temperatures, enthalpies, and entropies of transition[a]
(cal_{th} = 4.184 J)

Compound[b]	$\dfrac{T_t}{K}$	$\dfrac{\Delta H_t}{cal_{th}\ mol^{-1}}$	$\dfrac{\Delta S_t}{cal_{th}\ K^{-1}\ mol^{-1}}$	References
R_2NiCl_4	222.1 222.7	2087	9.16	This work
	[218]	[1760]	[8.1]	(13)
R_2ZnCl_4	227.9 228.9	2284	9.96	This work
(heating)	[227]	[2120]	[9.3]	(13)
R_2MnCl_4	218	1120	5.1	
	224	780	3.5	(13)
		1900	8.6	

[a] Results in [ ] are d.s.c. determinations.
[b] R = $(CH_3CH_2)_4N$.

lower in temperature than the present work and that the entropy of transition was lower; presumably the long equilibration time and rapid heating rate (4 K/min) were the causes of these discrepancies. Had the sample been cooled through the transitions too rapidly, some of the material would have undercooled, remaining in the high-temperature phase. When the sample was then heated, not all of the normal transitional enthalpy would be required; hence, a low value for the entropy would be found.

The two studies are in closer agreement for the zinc compound. This is expected since both the equilibration times for the BEAZ are shorter than those of BEAN and the two-phase transitions occur 1 K apart, rather than only 0.6 K apart in BEAN. Consequently, the d.s.c. was able to detect two peaks (at about 213 K and 218 K) during cooling. This separation may mean that one of the processes occurring within BEAZ is more susceptible to undercooling. During heating a single peak was observed at 227 K.

MECHANISM OF THE TRANSITION

The 300 K X-ray diffractional determination of BEAN[2] structure revealed several types of disorder. The methylene carbon atoms are rotated approximately $\pi/4$ from the two mirror planes which intersect at the nitrogen position. As the methylene carbons flop from side to side the tetraethylammonium groups form motionally disordered right- and left-handed swastikas. Some disorder is also revealed in the $NiCl_4^{2-}$ groups by the abnormal thermal quantities.

The temperature dependence of the magnetic anisotropies of BEAN has been measured by Gerloch and Slade.[3] The anisotropies reveal a large discontinuous change near 220 K. Thermal hysteresis was observed during these measurements. As the authors note, it has been previously observed[14] that slight structural changes can cause large alterations of the magnetic anisotropies. Such structural changes were indicated by Gerloch and Slade's analysis of the prior magnetic susceptibilities of BEAN collected by Figgis and coworkers.[15] The data in the two regions above and below the transition were fitted to a three-parameter model, involving θ (the Cl–Ni–Cl angle), λ (the spin-orbit coupling parameter), and k (the electron-delocalization parameter). The low-temperature angle was fitted as $109\pi/180$, (i.e. almost perfectly tetrahedral) while above the transition θ was taken as $106\pi/180$, in good agreement with the crystallographic value.[2] The high-temperature value of λ was taken as 190 cm^{-1}, 25 per cent larger than the low-temperature value.

The specific causes of the twin transitions $[(CH_3CH_2)_4N]_2MCl_4$ are not presently understood. The several types of motional disorder as well as the volumetric changes are certainly all significant but the amount of entropy each process contributes cannot yet be determined. Temperature-dependent structural studies are obviously desirable. Since Melia and Merrifield[13] have found the peaks in the heat capacity of the manganese compound to be separated by 6 K, this substance would be the logical candidate with which to begin.

Some suggestions can be made on the basis of the present results. First-order transitions occur during reorientation of symmetric groups such as the ammonium group in NH_4Br,[11,12] and in NH_4ZnF_3 and NH_4CoF_3.[10] In the latter pair of compounds, reorientation accompanies a structural change, which expands the

lattice sufficiently to allow the reorientation. Since the tetraethylammonium groups would presumably require more space for their disorder, we assume this is the disorder which sets in at the structural change. The consequent motion of the ammonium groups may then allow the MCl_4^{2-} groups to disorder. The long equilibration times may be a consequence of the two types of tetrahedral groups interfering with one another's motion. An adiabatic thermophysical study of the manganese compound and its equilibrium time behavior may yield important information.

Several other people have also contributed to the present work. We wish to acknowledge Dr James Thirtle for the preparation and analyses of the samples and Mr Charles Galeas for his assistance with the collection of results for BEAZ and both him and Ms Laurel Harmon for the computer treatment and reduction of the results. We also wish to thank Professor T. M. Dunn for helpful discussion.

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Registry Nos.

$(Et_4N)_2NiCl_4$, 5964-71-6
$(Et_4N)_2ZnCl_4$, 5964-74-9

Appendix

The sluggish nature of the transitions in the two compounds made true equilibrium measurements difficult. The results detailing the shapes of the transitional heat-capacity peaks were obtained without waiting for ultimate equilibrium. Rather, as is explained below, use was made of the regularity of equilibration behavior to estimate the final equilibrium temperatures on most of the determinations.

   Preliminary studies of the transitions showed that following an energy input, the rate of change of temperature was almost linear with periods greater than 1 d. Such linearity was observed for both compounds even though, for times less than 1 d, the equilibration rates were different for each of the peaks. The transition results were

collected by establishing *zero* drift in regions adjacent to the transition where hysteresis did not occur, then making an energy input, and observing the rate of change of the temperature of the sample until this rate followed the "normal" curve. Since the "apparent drift" was then largely occasioned by relaxation processes, it is possible to predict the equilibrium temperature; no more observations were necessary on most of the determinations and the next energy input was initiated.

The refinement of results for each determination consisted of making a tentative estimate of the slight deviations from adiabaticity on the basis of an assumed heat capacity, then deducing the estimated equilibration time, and finally extrapolating the equilibration rate to calculate the additional temperature increment had the drift been carried to equilibrium. This increment was subtracted from the last temperature measured. Then the increments between fore- and after-drift temperatures were used to deduce an apparent heat capacity. A revised adjustment was made for deviations from adiabaticity, new final equilibrium times were estimated, and revised heat capacities deduced. Convergent values for the heat capacities were always produced by three iterations; most converged after two. The heat capacities were considered to have converged when further iteration changed the heat capacity by less than 5 per cent. The estimate of the additional temperature change required for equilibrium accounted for 80 per cent of the total correction with the other 20 per cent due to adjustments for nonadiabaticity.

The ultimate accuracy of these measurements depends on the validity of the assumption of a consistent equilibration behavior for all points as the basis for the extrapolation routine. One test of this assumption is the comparison between the integrated area under the curve specified by these points and the enthalpy derived from the enthalpy determinations. The agreement is within 2.5 per cent. Still, points on the transition curve must be considered to have an uncertainty of twice this value.