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Phase Transitions and Thermodynamic Properties of Rubidium and Cesium Cyanides[*1]

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Heat-capacity measurements were performed for rubidium and cesium cyanide crystals between 15 and 300°K. It is found that each crystal has only one anomalous peak in its heat capacity curve, being located at 110.3°K and 193.1°K for rubidium and cesium cyanides, respectively. By the comparison of the present data with those for potassium and sodium cyanides, it was shown that these anomalous heat capacities can be interpreted in terms of the orientational ordering processes of cyanide ions in the crystals. It was suggested that there should exist the residual entropy due to the frozen-in state in their orientational configuration and they were estimated as $\boldsymbol{R}\ln 4$ for rubidium cyanide and $\boldsymbol{R}\ln 2$ for cesium cyanide.

In the two previous papers,[1,2] we have reported the results of our investigation on potassium and sodium cyanide crystals. In each salt we have found two kinds of phase transition which were interpreted as the orientational order-disorder phenomenon with respect to the distinction of carbon and nitrogen atoms in cyanide ion as well as to the random orientation of the carbon to nitrogen bonds. As a series of our study concerning the orientational motion of cyanide ion, we have studied the phase transition phenomenon of rubidium and cesium cyanides with paying special attention to the effect of the difference of their size of cation on the orientational motion of cyanide ion.

According to the X-ray analysis by Lely,[3] rubidium cyanide is of NaCl-type, while cesium cyanide is reported to have CsCl-type at room temperature. This is in contrast to the fact that both potassium and sodium salts have the same NaCl-type.

Thus, it seems interesting to study the effect of the difference of size of cation in rubidium salt and further of the difference in crystal structure for cesium cyanide on an appearance of phase transition.

We have measured heat capacity of these salts between 13 and 300°K and found only one anomalous peak of the heat capacity in each salt. This remarkable difference in the behavior of the temperature dependence of their heat capacities was attempted to interpret in connection with the thermal motion and ordering process of cyanide ion in the crystalline field.

Experimental

Samples. a) Rubidium Cyanide.[4] Commercial rubidium hydroxide (Nakarai Chemicals Co., Ltd.) was dissolved in the absolute ethyl alcohol and the insoluble substances supposed to be mainly of rubidium carbonate were removed by filtration. Liquid hydrogen cyanide was then poured slowly to the phase separated solution which consisted with liquid benzene over the ethanol solutions mentioned above. Rubidium cyanide crystal was first produced at the interfacial layer and then it was deposited to the bottom of the container with a solution of absolute methyl alcohol and absolute diethylether. After the product was filtrated, the sample was recrystallized twice from the solution of water and methyl alcohol. The final product thus obtained was dried *in vacuo* (about 10^{-3} mmHg) carefully for several hours at 120°C to remove the solvents completely.

b) Cesium Cyanide. The crystal was prepared by the same method as mentioned above. The cesium hydroxide used for preparation is the product of Nakarai Chemicals Co. Ltd.

By a spectroscopic analysis, all the impurity contents of carbonate ion were confirmed to be less than 0.1 mole percent, and the traces of metallic ions (Na^+, K^+, Si^{2+}, Mg^{2+}, and Ca^{2+}) were also found.

[*1] Read before the 17th and the 18th Annual Meetings of the Chemical Society of Japan at Tokyo (1964) and at Osaka (1965).

1) H. Suga, T. Matsuo and S. Seki, This Bulletin, **38**, 1115 (1965).

2) T. Matsuo, H. Suga and S. Seki, *ibid.*, **41**, 583 (1968).

3) J. A. Lely, **1942**, *Dissertation*, Utrecht, pp. 84.

4) J. Meyer, *Z. anorg. Chem.*, **115**, 207 (1921).

Heat-Capacity Measurement. Measurements of heat capacities were made on the sample of 0.2899 mol of rubidium cyanide and 0.2357 mol of cesium cyanide, sealed in a gold calorimeter cell (18 K) with a small amount of helium gas. The low-temperature adiabatic type calorimeter, the details of which were described in the previous paper,[5] was used between 15°K and 300°K.

The reported values are based on a formula weight of 111.49 for rubidium cyanide and 158.92 for cesium cyanide, and also on the basic relations 0°C=273.15°K and 1 cal=4.1840 abs. joules. Temperature measurements were carried out with platinum resistance thermometer calibrated in terms of the International Temperature Scale between 90 and 500°K and the provisional scale of the National Bureau of Standards between 11 and 90°K.

Experimental Results

Heat Capacities. The heat capacities obtained from 15 to 300°K are listed in Table 1 for rubidium cyanide and in Table 2 for cesium cyanide. The heat-capacity curves are given in Figs. 1 and 2 for rubidium and cesium cyanides, each of which shows only one phase transition, respectively.

Thermodynamic Properties. Thermal data on phase transition are listed in Table 3, and the thermodynamic functions are given in Table 4 for rubidium cyanide and Table 5 for cesium cyanide. The values below 15°K are obtained by extrapolation on the assumption of the Debye T^3-law. As is shown in the previous paper,[5] the error in the values of the heat capacity is within ±0.3% above liquid nitrogen and ±1% in liquid hydrogen temperature regions, respectively.

TABLE 1. HEAT CAPACITIES OF RUBIDIUM CYANIDE

$T_{av.}$ °K	Approx. ΔT	$\Delta H/\Delta T$ cal/(mol degK)
	Series 1	
80.83	1.912	13.534
82.72	1.882	13.781
84.59	1.855	14.001
86.43	1.829	14.237
88.25	1.805	14.460
90.05	1.784	14.657
91.82	1.761	14.896
93.57	1.741	15.109
95.30	1.721	15.340
97.01	1.699	15.640
98.70	1.677	15.890
100.36	1.652	16.253
102.00	1.622	16.734
103.60	1.577	17.581
105.14	1.500	19.098
106.57	1.361	22.487
107.86	1.229	26.428
109.00	1.037	34.072
109.93	0.825	46.655
110.79	0.909	40.897
111.84	1.175	28.151
113.18	1.504	18.584
114.74	1.619	16.113
116.36	1.616	16.068
117.97	1.614	16.052
119.59	1.611	16.020
121.19	1.607	16.031
	Series 2	
22.09	2.510	3.059
24.41	2.098	3.630
26.66	2.364	4.204
28.89	2.077	4.765
31.05	2.215	5.321
33.31	2.284	5.873
35.50	2.090	6.405
37.61	2.109	6.882
39.81	2.280	7.307
42.03	2.143	7.718
44.11	2.029	8.120
46.25	2.257	8.485
48.45	2.151	8.853
50.55	2.058	9.222
52.75	2.338	9.598
55.04	2.248	9.974
57.25	1.085	10.340
59.39	2.101	10.686
61.46	2.042	11.031
	Series 3	
14.90	1.871	1.529
16.66	1.500	1.881
18.06	1.282	2.176
19.57	1.653	2.491
21.13	1.435	2.849
	Series 4	
62.10	2.213	11.154
64.26	2.100	11.459
66.34	2.050	11.732
68.36	2.006	11.985
70.35	1.965	12.243
72.30	1.929	12.471
74.21	1.895	12.708
76.09	1.862	12.950
78.03	1.833	13.153
79.75	1.804	13.398
	Series 5	
120.84	1.750	16.107
122.58	1.744	16.073
124.33	1.748	16.064
126.07	1.738	16.082
127.81	1.735	16.085
129.54	1.731	16.072
131.27	1.727	16.075

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

(Table 1 continued)

$T_{av.}$ °K	Approx. ΔT	$\Delta H/\Delta T$ cal/(mol degK)
133.00	1.722	16.082
134.72	1.719	16.075
136.54	1.929	16.066
138.49	1.926	16.058
140.39	1.921	16.081
142.31	1.917	16.070
144.23	1.925	16.083
146.15	1.910	16.092
148.08	1.907	16.088
149.96	1.904	16.078
151.86	1.904	16.042
157.73	1.901	16.054
	Series 6	
155.64	1.928	16.113
157.56	1.933	16.067
159.48	1.918	16.124
161.40	1.916	16.112
163.31	1.911	16.122
165.22	1.909	16.116
167.13	1.906	16.111
169.04	1.905	16.094
170.94	1.903	16.082
172.83	1.901	16.079
174.74	1.898	16.099
176.64	1.897	16.090
178.55	1.930	16.093
180.48	1.928	16.087
182.41	1.926	16.098
184.33	1.926	16.084
186.26	1.924	16.076
188.18	1.921	16.104
190.10	1.922	16.068
192.03	1.921	16.062
193.92	2.175	16.122
196.08	2.278	16.050
198.35	2.276	16.035
200.62	2.271	16.060
202.89	2.266	16.093
205.16	2.264	16.089
207.42	2.263	16.056
209.68	2.259	16.079
211.94	2.257	16.077
214.19	2.254	16.084
216.44	2.252	16.087
218.69	2.250	16.079
220.94	2.249	16.062
223.18	2.247	16.058
225.42	2.245	16.047
227.66	2.243	16.059
229.89	2.237	16.110
232.12	2.233	16.127
234.35	2.231	16.107
236.57	2.228	16.124
	Series 7	
238.44	2.223	16.048
240.65	2.217	16.115
242.86	2.212	16.144
245.07	2.209	16.150
247.27	2.205	16.174
249.47	2.206	16.117
251.67	2.204	16.124
253.87	2.202	16.115
256.07	2.200	16.111
258.27	2.197	16.132
260.46	2.195	16.132
262.65	2.192	16.146
264.84	2.190	16.151
267.04	2.186	16.152
269.21	2.184	16.156
271.40	2.178	16.215
237.57	2.177	16.191
275.75	2.178	16.146
	Series 8	
277.61	2.623	16.146
280.22	2.617	16.180
282.83	2.613	16.193
285.44	2.610	16.189
288.04	2.605	16.210
290.64	2.600	16.226
293.24	2.598	16.206
295.82	2.592	16.252
298.41	2.589	16.243
300.98	2.581	16.298
303.55	2.581	16.253

TABLE 2. HEAT CAPACITIES OF CESIUM CYANIDE

$T_{av.}$ °K	Approx. ΔT	$\Delta H/\Delta T$ cal/(mol degK)
	Series 1	
15.16	2.0484	1.473
17.09	1.7586	1.928
18.73	1.4853	2.235
20.42	1.8802	2.650
22.18	1.6196	3.062
	Series 2	
14.20	2.0124	1.213
16.23	1.9808	1.699
18.02	1.5974	2.103
19.50	1.3684	2.434
21.07	1.7785	2.792
22.73	1.5521	3.177
24.19	1.3927	3.525
26.90	1.9134	4.095
28.72	1.7335	4.497
30.50	1.8392	4.926
32.24	1.6986	5.306
33.85	1.5915	5.637
35.37	1.4969	5.977
36.81	1.4165	6.313
38.29	1.5535	6.572
39.80	1.4837	6.834

(Table 2 continued)

$T_{av.}$ °K	Approx. $\varDelta T$	$\varDelta H/\varDelta T$ cal/(mol degK)
41.24	1.4179	7.131
42.61	1.3530	7.520
43.92	1.3060	7.785
45.25	1.3808	8.022
46.60	1.3391	8.253
48.10	1.7014	8.493
49.76	1.6447	8.769
51.37	1.5939	9.044
53.06	1.8182	9.323
54.85	1.7711	9.526
56.58	1.7234	9.781
58.26	1.6789	10.040
59.91	1.6406	10.259
	Series 3	
60.02	1.8373	10.263
61.84	1.7944	10.493
63.61	1.7534	10.744
65.35	1.7164	10.991
67.15	1.8954	11.198
69.03	1.8612	11.394
70.87	1.8279	11.597
72.76	1.9691	11.758
74.71	1.9392	11.919
76.63	1.9045	12.152
78.51	1.8751	12.345
80.38	1.9606	12.467
82.33	1.9297	12.665
84.24	1.9027	12.840
86.13	1.8770	13.024
87.99	1.8543	13.196
89.83	1.8369	13.307
91.66	1.8175	13.458
93.47	1.8007	13.590
95.26	1.7857	13.703
97.11	1.9280	13.827
99.03	1.9120	13.959
100.90	1.8982	14.053
102.81	1.8849	14.144
104.68	1.8693	14.275
106.44	1.8556	14.370
108.38	1.8456	14.432
110.21	1.8325	14.548
112.03	1.8202	14.666
113.83	1.8060	14.818
115.62	1.7947	14.928
	Series 4	
115.71	1.7931	14.911
117.70	2.1834	15.048
119.87	2.1658	15.198
122.03	2.1514	15.319
124.17	2.1351	15.469
126.30	2.1185	15.626
128.41	2.1038	15.762
130.61	2.2949	15.844
132.89	2.2760	16.020
135.16	2.2588	16.181
137.41	2.2426	16.335
139.64	2.2282	16.475
141.86	2.2161	16.581
144.06	2.1981	16.765
146.25	2.1811	16.949
148.42	2.1691	17.066
150.58	2.1552	17.215
152.72	2.1398	17.392
154.84	2.1209	17.623
156.95	2.1050	17.821
	Series 5	
159.10	2.2396	18.007
161.33	2.2207	18.237
163.54	2.1997	18.503
165.73	2.1786	18.765
167.89	2.1591	19.044
170.04	2.1363	19.359
172.16	2.1120	19.711
174.26	2.0851	20.122
176.23	2.0590	20.522
178.37	2.0296	20.997
180.39	1.9961	21.564
182.37	1.9640	22.142
184.30	1.9224	22.892
186.19	1.8681	23.952
188.03	1.8066	25.237
189.79	1.7035	27.626
191.28	1.2847	38.347
192.18	0.5290	121.366
192.57	0.2516	271.700
192.78	0.1924	359.788
193.39	1.0437	54.074
195.08	2.3388	16.045
197.32	2.3397	16.038
199.76	2.3391	15.869
202.10	2.3401	15.924
204.44	2.3421	15.773
206.78	2.3397	15.881
209.12	2.3408	15.833
211.46	2.3403	15.808
213.80	2.3401	15.784
216.43	2.3414	15.799
218.78	2.3472	15.761
	Series 6	
216.10	2.3484	15.719
218.44	2.3429	15.728
220.78	2.3382	15.737
223.12	2.3356	15.729
225.45	2.3339	15.720
227.79	2.3319	15.732
230.11	2.3297	15.713
232.44	2.3265	15.726
234.77	2.3231	15.744
237.09	2.3219	15.732
239.41	2.3200	15.727
241.73	2.3207	15.687
244.05	2.3195	15.672
246.36	2.3167	15.678
248.67	2.3129	15.716
	Series 7	
251.01	2.4101	15.698
253.42	2.4072	15.706
255.82	2.4036	15.718

(Table 2 continued)

$T_{\text{av.}}$ °K	Approx. ΔT	$\Delta H/\Delta T$ cal/(mol degK)
258.23	2.4019	15.713
260.63	2.3985	15.763
263.02	2.3965	15.714
265.42	2.3911	15.754
267.81	2.3875	15.769
270.21	2.3894	15.710
	Series 8	
261.92	2.3830	15.676
264.30	2.3813	15.666
266.68	2.3780	15.681
269.06	2.3747	15.691
271.43	2.3736	15.681
273.80	2.3715	15.674
276.17	2.3674	15.700
278.54	2.3639	15.723
280.22	2.3625	15.673
282.12	2.3604	15.703
	Series 9	
285.52	2.3508	15.704
287.82	2.3503	15.682
290.22	2.3468	15.697
292.57	2.3443	15.700
294.91	2.3415	15.709
298.42	2.3367	15.725
300.75	2.3321	15.754
303.08	2.3799	15.771

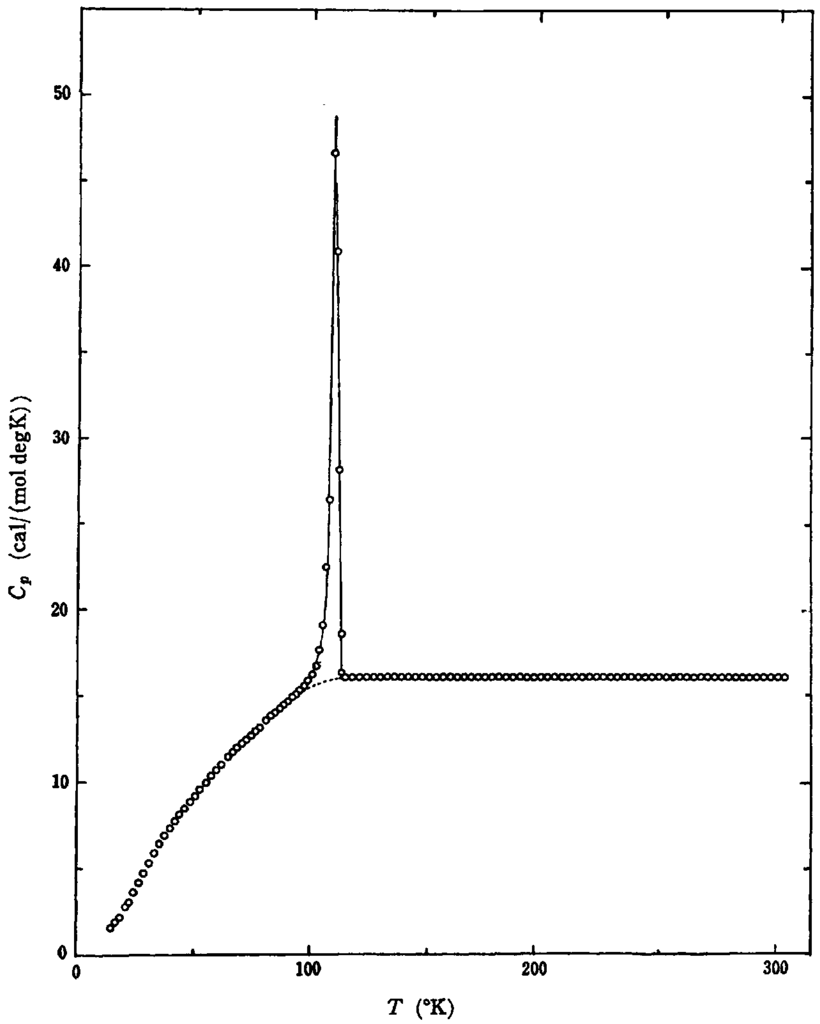

Fig. 1. Heat capacity curve of rubidium cyanide.

TABLE 3. THERMODYNAMIC PROPERTIES OF PHASE TRANSITIONS FOR RUBIDIUM AND CESIUM CYANIDES

	RbCN	CsCN
Transition temperature (degK)	110.3±0.1	193.1±0.1
Entropy change (cal/(mol degK))	1.38±0.04	2.60±0.05
Enthalpy change (cal/mol)	177±4	461±10

TABLE 4. THERMODYNAMIC PROPERTIES OF RUBIDIUM CYANIDE IN cal/(mol degK)

T (°K)	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
10	(0.714)	(0.386)	(0.240)	(0.146)
15	1.555	0.830	0.533	0.297
20	2.595	1.421	0.916	0.505
30	5.048	2.926	1.875	1.051
40	7.362	4.709	2.968	1.741
50	9.108	6.542	4.030	2.512
60	10.807	8.354	5.013	3.341
70	12.200	10.130	5.946	4.184
80	13.408	11.838	6.803	5.035
90	14.655	13.492	7.608	5.884
100	16.166	15.106	8.380	6.726
110.3	Transition temperature			
120	16.100	19.079	10.613	8.466
130	16.080	20.364	11.034	9.330
140	16.080	21.555	11.394	10.161
150	16.080	22.665	11.707	10.958
160	16.080	23.702	11.980	11.722
170	16.080	24.677	12.221	12.456
180	16.080	25.597	12.435	13.162
190	16.080	26.467	12.627	13.840
200	16.080	27.292	12.800	14.492
210	16.080	28.076	12.956	15.120

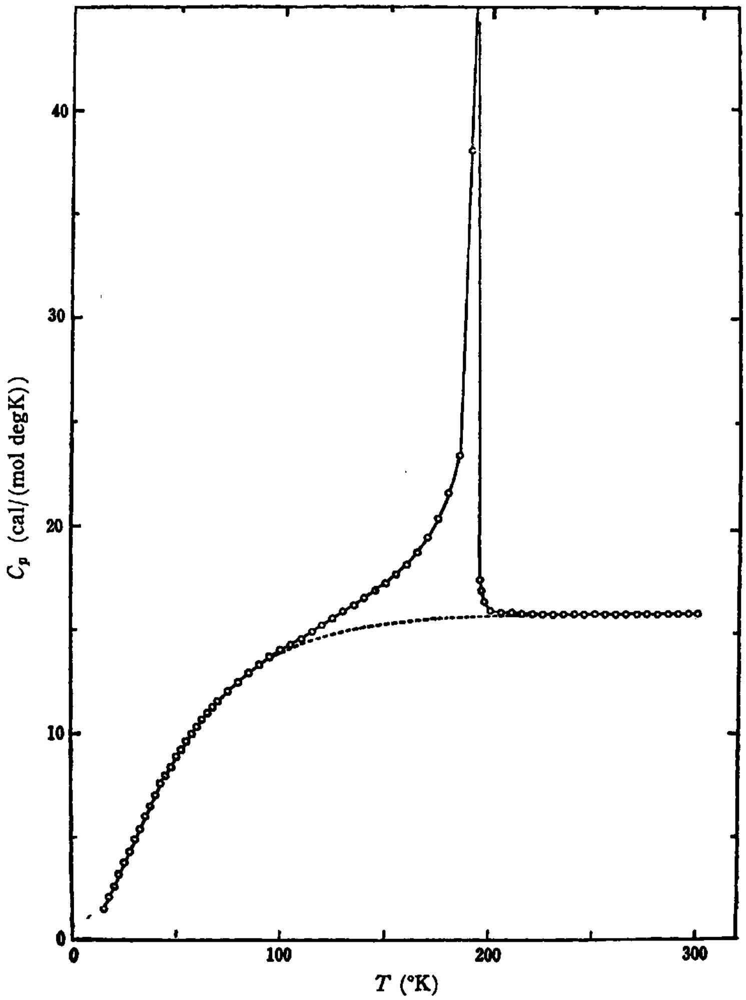

Fig. 2. Heat capacity curve of cesium cyanide.

(Table 4 continued)

T(°K)	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
220	16.080	28.824	13.098	15.726
230	16.100	29.540	13.228	16.312
240	16.130	30.226	13.348	16.878
250	16.130	30.885	13.460	17.425
260	16.150	31.517	13.563	17.945
270	16.160	32.127	13.659	18.468
280	16.180	32.715	13.749	18.966
290	16.200	33.284	13.834	19.450
298.15	16.200	33.673	13.949	19.724

TABLE 5. THERMODYNAMIC PROPERTIES OF CESIUM CYANIDE IN cal/(mol degK)

T(°K)	C_p°	S°	$(H^\circ-H_0^\circ)/T$	$-(G^\circ-H_0^\circ)/T$
10	(0.456)	(0.161)	(0.113)	(0.048)
15	1.425	0.509	0.373	0.136
20	2.554	1.074	0.772	0.302
30	4.812	2.538	1.742	0.796
40	6.954	4.220	2.782	1.438
50	8.803	5.976	3.808	2.168
60	10.280	7.716	4.768	2.948
70	11.501	9.398	5.646	3.752
80	12.467	10.998	6.440	4.558
90	13.338	12.518	7.160	5.358
100	14.010	13.960	7.813	6.147
110	14.563	15.321	8.401	6.920
120	15.210	16.616	8.941	7.675
130	15.852	17.858	9.448	8.410
140	16.496	19.056	9.928	9.128
150	17.231	20.219	10.390	9.829
160	18.121	21.358	10.844	10.514
170	19.371	22.036	11.306	10.730
180	21.452	23.650	11.805	11.845
193.1	Transition temperature			
200	15.940	27.117	13.925	13.192
210	15.822	27.893	14.019	13.874
220	15.743	28.627	14.099	14.528
230	15.728	29.326	14.170	15.156
240	15.715	30.636	14.294	16.342
260	15.713	31.253	14.348	16.905
270	15.712	31.846	14.399	17.447
280	15.710	32.417	14.446	17.971
290	15.704	32.968	14.489	18.479
298.15	15.701	33.404	14.523	18.881

Discussion

Behavior of Thermal Motion of Cyanide-groups. In order to investigate the mode of motion of the cyanide-group in these cyanide crystals, the torsional heat capacity was sorted out from the total heat capacity by following the same procedure taken in the previous papers.[1,2] By assuming the simple harmonic oscillation model for each cyanide group and also by making a flat portion in the Debye-temperature curve with suitable estimation of their oscillator frequencies, we have obtained the wave numbers of 185 cm^{-1} and 160 cm^{-1} for rubidium and cesium salts, respectively. Further, we have estimated the contributions of torsional motion of the cyanide-groups to the heat capacities which are given in Fig. 3. The potential barrier heights for the torsional motion at higher temperature, *i.e.* for the hindered rotational motion derived from these curves based on the Pitzer-Gwinn method[6] are 8.0 and 7.4 kcal/mol for the low temperature phases of rubidium and cesium cyanides, respectively. Finally this motion approaches the state of the free rotation where the heat capacity amounts to 2 cal/mol degK per two degrees of freedom. The fact that the heat capacity at room temperature is about 3 cal/mol degK in the range of relevant temperature shows that the rotation of the cyanide-group is still hindered considerably. The potential barrier heights of this hindered rotational motion are 1.7 and 1.1 kcal/mol for rubidium and cesium cyanides, respectively. It may be noted here that the potential barriers hindering the rotation of the cyanide-group estimated above are comparable with those for sodium and potassium cyanides.

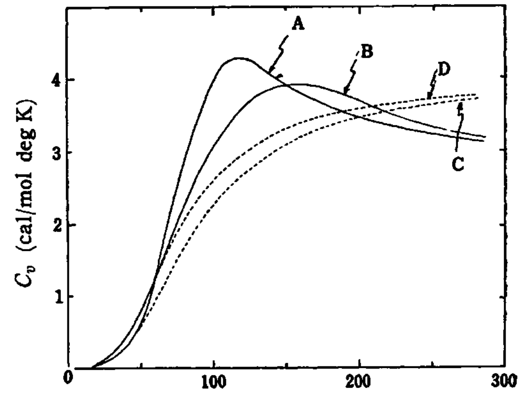

Fig. 3. Torsional heat capacity curves of cyanide-groups.
A: rubidium cyanide.
B: cesium cyanide.
C: assumed harmonic oscillator with its wave number ω=185 cm^{-1}.
D: assumed harmonic oscillator with its wave number ω=160 cm^{-1}.

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[6] K.S. Pitzer and W.D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

Possible Existence of the Residual Entropy. *a) Rubidium Cyanide.* In this compound we can observe only one peak of anomalous heat capacity at about 110°K. The value of entropy associated with amounts to be 1.38 e.u. which is corresponding to $\boldsymbol{R}\ln 2$. This circumstance is markedly different from those of sodium and potassium cyanides in which two anomalous heat capacities are observed. They have been interpreted in terms of the stepwise cooperative phenomena concerning the reorientational motion of the cyanide-group in the crystalline phase. The cubic symmetry of the rubidium cyanide crystal at room temperature suggests that all cyanide-groups may orientate themselves equally at random in the directions of four body-diagonals of its unit cell as in the case of the highest temperature phases of sodium and patassium cyanides. In this case, the configurational entropy with respect to the possible orientations of the cyanide-groups comes out to be $\boldsymbol{R}\ln 8$ if we can distinguish the individuality of carbon and nitrogen atoms. The amount of observed entropy change of $\boldsymbol{R}\ln 2$ at the transition point leads us to expect that the configurational entropy in the low-temperature phase might be $\boldsymbol{R}\ln(8/2)=\boldsymbol{R}\ln 4$. As one of the explanation of such a value of entropy change as $\boldsymbol{R}\ln 2$, we may refer to Parry's model[7] for the low temperature phase of rubidium cyanide. Based on the detailed X-ray analysis of the metastable monoclinic phase of potassium cyanide, he proposed that the crystal structure of the low temperature phase of rubidium cyanide is closely similar to the disordered structure of the metastable monoclinic phase of potassium cyanide. In this metastable phase, all cyanide-groups are at rest with their principal axis approximately parallel to the one direction of body-diagonals of the original cubic phase, the potassium ions being displaced alternately vertical to (110) plane by about 1/4 Å, as is shown in Fig. 4.

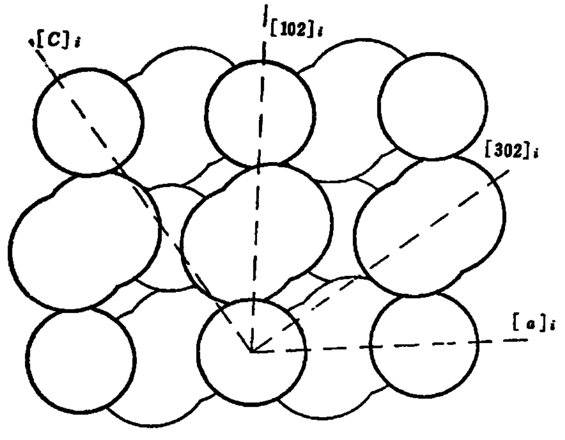
If the two kinds of y-parameter of the potassium ions are assumed te be zero and the new axis is taken as,

$$a = 1/2[a]_i, \qquad c = 1/2[102]_i,$$

here, $[a]_i$ and $[102]_i$ represent the a-axis and direction of [102] of the original monoclinic cell, respectively. Then, the dimension of new unit cell becomes as follows;

$$a=4.45,\ b=4.53,\ c=6.36\ \text{Å},\ \beta=94.6°.$$

Comparing these dimensions with those of rubidium cyanide, the differences in the axial lenghts a, b and c of the two unit cells are found to be 0.28, 0.35 and 0.31 Å, respectively. Taking into account of the difference in ionic radii between the potassium and the rubidium ions, it gets clear that this unit cell seems to correspond to the unit cell of the low temperature phase of rubidium cyanide, its dimensions being $a=4.78$, $b=4.88$, $c=6.67$ Å and $\beta=94.5°$.



[G. S. Parry, *Acta Cryst.*, **15**, 601 (1962)]

Fig. 4. Proposed structure for the monoclinic low-temperature form of potassium cyanide projected on to $[010]_i$ which corresponds to [110] of the original cubic cell. The displacement $y(K^+)$ is perpendicular to the plane of this figure and has been established experimentally to be of the order of 1/4 Å. The orientation of the cyanide-group has not yet been experimentally confirmed, but is based on a self-consistent interpretation of the cell dimensions.[7]

Therefore it may not be so unreasonable to suppose that the cyanide ions are in the disordered state with two kinds of their orientation. If the carbon and the nitrogen atoms of the cyanide-groups are distinguished in this phase, the entropy change of $\boldsymbol{R}\ln 2$ may be explained on this model.

Furthermore, the behavior of the rest of configurational entropy in low temperature region below 13°K will be an interesting problem. In our present measurement of the heat capacity from 13 to 320°K, no further anomalous heat capacity in addition to the anomaly at 110°K was observed. This implies that the degree of orientational freedom of the cyanide-group in low temperature phase will freeze and this frozen-in state will persist down to the lowest temperatures. Comparing the potential barrier (8 kcal/mol) hindering the rotation of the cyanide ions with the thermal excitation energy, it seems reasonable to suppose that there may persist the residual entropy of $\boldsymbol{R}\ln 4$ at the absolute zero.

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[7] G. S. Parry, *Acta Cryst.*, **15**, 596, 601 (1962).

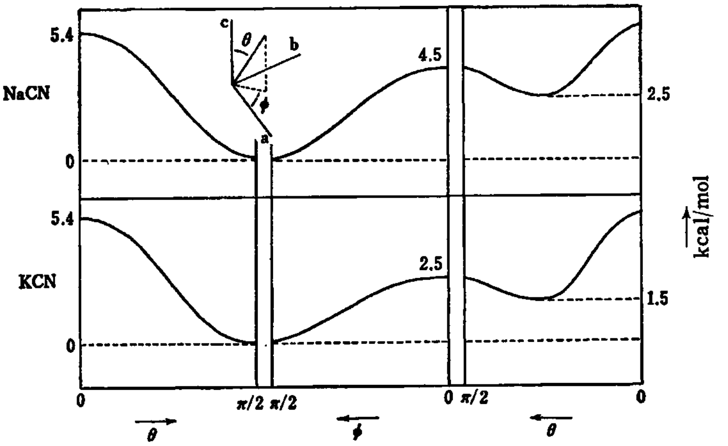

Fig. 5. The potential curves hindering the reorientation of cyanide groups of low temperature forms of potassium and sodium cyanide crystals.[8]

b) Cesium Cyanide. The entropy change of the phase transition of cesium cyanide at 193°K amounts to 2.6 e.u., nearly equal to $R \ln 4$, which is equivalent to those of the upper phase transitions of sodium and potassium cyanides at 288.1 and 168.3°K, respectively.

It is also shown that behavior of temperature dependence of torsional heat capacity of cesium cyanide is quite similar to those of both sodium and potassium salt, *i.e.*, in each case there appears hump of heat capacity near the phase transition. Thus, it is concluded that cyanide-groups are at rest along the three fold axis of the unit cell below the transition point, whereas they are in hindered rotational state above the transition point. This conclusion is consistent with the crystal structure determined by X-ray analysis.

The fact that the lower phase transitions of sodium and potassium cyanides are reasonably interpreted in terms of order-disorder phase transition with respect to the distinction of carbon and nitrogen atoms of cyanide-groups suggests that there is also the possibility of appearance of another phase transition of this kind for cesium cyanide. As a matter of fact, however, we can not find any further anomalous effect in its heat-capacity curve.

Consequently, the situation of cyanide-group in the low-teperature form of cesium cyanide crystal is such that the cyanide-groups are at rest along the three fold axis with no distinction of their heads and tails. This implies that a temperature region exists where the cyanide-groups are frozen in its fixed orientation and can no longer reorientate themselves.

The Appearance of the "Frozen-in" State and the Potential Barrier Hindering the Reorientation of Cyanide-groups. It is not definitely clear as to the reason why the cyanide-groups of rubidium and cesium cyanides behave differently from those of sodium and potassium cyanides in spite of the fact that they have nearly equal amount of potential barriers. It must be mentioned, however, that the potential barrier-height obtained from the analysis of the calorimetric data is such an averaged one over all possible directions, and it seems possible that a symmetry difference of the unit cell of potassium and sodium salts from the others may give rise to a somewhat lower barrier-height favourable to reorientation of cyanide-group in particular direction.

According to Nagamiya and Matsubara's calculation[8] for the case of the low temperature modification of sodium and potassium cyanides, the potential curve hindering the reorientation of cyanide-group has an anisotropy, *i.e.*, the potential barrier-height in the direction of c-axis is larger than that in the direction of a-axis. In the case of sodium cyanide this anisotropy is not so large, but in the case of potassium cyanide the anisotropy is so much larger that barrier-height along c-axis is larger by twice than that along a-axis (see Fig. 5). Moreover, it is characteristic to sodium or potassium cyanides that there exists a saddle point in the respective potential curves. Therefore, this saddle point provides a high transition probability concerning the reorientational motion of cyanide-group. Following the method used by Naga-

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[8] T. Matsuhara and T. Nagamiya, *Scientific Papers from the Osaka University*, No. 14, 17 (1949).

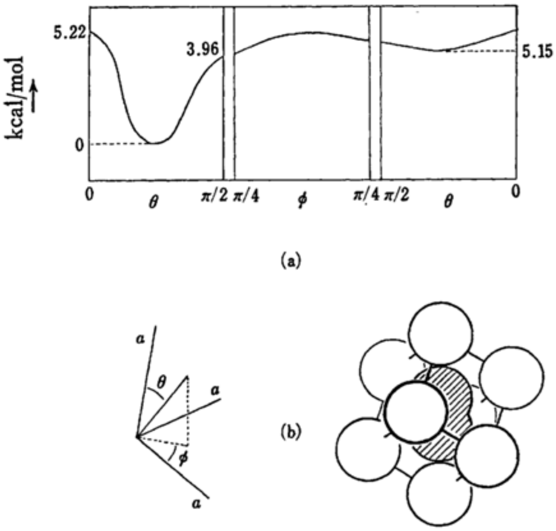

Fig. 6. (a) The potential curve hindering the reorientation of cyanide group of the low temperature form of cesium cyanide crystal.
(b) The unit cell of low temperature form of cesium cyanide crystal. This crystal structure is of a deformed *CsCl*-type. Hollow circles represent cesium ions, and a shaded deformed circle stands for cyanide group.

miya and Matsubara we have calculated the potential curve hindering the reorientation of cyanide-group of cesium cyanide. In this case the interaction due to a quadrupole effect will be neglected for approximate estimation of an anisotropy of the potential curve. The results obtained is given in Table 6. In the table W_{--} stands for the repulsive potential due to interaction between cyanide-groups, W_{+-} the repulsive potential for the interaction between cesium and cyanide-groups.

The potential form obtained is depicted in Fig. 6. As is seen there is no distinct anisotropy and the possibility of saddle point with appreciable low value is not expected.

TABLE 6. THE REPULSIVE LARTS OF THE HINDERING POTENTIAL FOR THE ROW-TEMPERATURE FORM OF CESIUM CYANIDE CRYSTAL (in kcal/mol)

(θ, ϕ)	W_{--}	W_{+-}	$W = W_{--} + W_{+-}$
$\pi/4$ $\pi/4$	1.47	7.43	8.90
0 0	5.04	8.91	13.95
$3\pi/4$ $\pi/4$	2.39	11.74	14.12
$\pi/4$ 0	1.79	11.07	12.86
$3\pi/4$ $3\pi/4$	2.82	11.56	14.39
0 $3\pi/4$	2.46	11.59	14.05

Accordingly it may be said that the realization of orientational frozen-in state of rubidium and cesium cyanides is closely related with the nonexistence of the appreciable anisotropy or a saddle point in their potential curves.

Finally, based on the same viewpoint we should like to infer the occurrence of a metastable phase of potassium cyanide. The saddle point of potassium cyanide is lower than that of sodium cyanide, so that the state probability on the saddle point, which corresponds to the [111] direction of the high temperature form, is larger for potassium cyande. In that case all cyanide-groups are frozen in the [111] direction of the original cubic form, and this structure is really corresponding to the monoclinic metastable phase. The correspnding one of sodium cyanide has not been found. This fact is certainly connected with the difference of the height of the saddle point in these two salts.

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