BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 583—593 (1968)

Thermodynamic Properties and Phase Transitions of Sodium Cyanide Crystal*[1]

Takasuke MATSUO, Hiroshi SUGA and Syûzô SEKI

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received October 6, 1967)

The heat capacities of the sodium cyanide crystal were measured from 14 to 310°K by an adiabatic calorimeter. The two anomalous regions reported by Ziegler *et al.* are confirmed. The entropy changes associated with these anomalies is explained by proposing structural changes at the transition points. Analysis of the lattice heat capacity gives the average librational frequency of the cyanide ion at the lowest temperatures as $210\ \mathrm{cm}^{-1}$ in the Einstein approximation. For the higher temperature range, the cyanide ions may be described as undergoing a hindered rotation, with a barrier height of approximately 2 kcal/mol. The upper-phase transition is discussed in terms of a model based on the coexistence of the two crystalline phases. The lower transition and the analogous one reported previously for potassium cyanide are interpreted together as order-disorder phenomena with respect to the behavior of the cyanide ions. The thermodynamic functions of the crystal are also calculated by the graphical integration of the heat capacity data.

In a previous paper we reported the results of a thermal study of the potassium cyanide crystal.[1] Investigations of the sodium cyanide crystal along the same line of study will be presented in this paper. The present crystal has the same rod-like shaped anion as potassium cyanide as its constituent, so that in order to simulate the rock-salt structure observed at room temperature, the cyanide ion must be either rotating or randomly-orientated along one of the eight body-diagonal directions of the rock-salt-type lattice. Verweel and Bijvoet[2] investigated the structure by the X-ray diffraction method and interpreted their results in terms of the spherical rotation model of the cyanide ion. By the use of the same technique, Siegel[3] attempted to settle whether the dynamical or the statical model was more realistic. He could not, however, arrive at any definite conclusion, although he succeeded in detecting the presence of a new crystal phase of sodium cyanide. Verweel and Bijvoet found that, on cooling, the crystal is transformed into an orthorhombic modification at about 290°K. Messer and Ziegler[4] measured the heat capacity of the salt from 100°K to 350°K and observed an anomalous heat capacity at the corresponding temperature, 287°K, associated with an entropy change of approximately $R\ln4$. They also concluded, by estimating the oscillation-rotation heat capacity of the cyanide ions, that their motion is rather restricted in the cubic phase and highly hindered in the orthorhombic phase.

For the potassium salt, Elliot and Hastings[5] suggested a free rotation model on the basis of their neutron diffraction data. More recently, after the completion of our study, Sequeira[6] published a short note in which he showed that even with the neutron diffraction, the dynamical and the statical states are indistinguishable as long as one employs a powdered sample. NMR[7] and infrared[8] studies have also been reported on these problems.

A theoretical treatment of the phase changes of these salts was carried out by Matsubara and Nagamiya[9]; they found that the potential barrier hindering the rotation of the cyanide ion is about 1.2 kcal/mol in the cubic phase and 6 kcal/mol in the orthorhombic phase for the sodium salt.

Besides the phase transition mentioned above, Messer and Ziegler observed another anomalous region in the heat capacity with its maximum value

---

*[1] Read before the 17th Annual Meeting of the Chemical Society of Japan, 1964, Tokyo, and presented partially at The International Symposium on the Reactivity of Solids, 1966, Aberdeen, Scotland.

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

2) H. J. Verweel and J. M. Bijvoet, *Z. Krist.*, **100**, 201 (1939).

3) L. A. Siegel, *J. Chem. Phys.*, **17**, 1146 (1949;) Y. Shin'naka, *J. Phys. Soc. Japan*, **22**, 669 (1967).

4) C. E. Messer and W. T. Ziegler, *J. Am. Chem. Soc.*, **63**, 2610 (1941).

5) N. Elliot and J. Hastings, *Acta Cryst.*, **14**, 1018 (1961).

6) A. Sequeira, *ibid.*, **18**, 291 (1965).

7) C. K. Coogan and H. S. Gutowsky, *J. Chem. Phys.*, **40**, 3419 (1964).

8) Y. Sato, *J. Phys. Soc. Japan*, **20**, 275 (1965).

9) T. Matsubara and T. Nagamiya, *Sci. Papers from Osaka Univ.*, No. **14** (1949).

at 172°K. The estimated entropy change is approximately $R\ln 2$, so they inferred that this anomaly is associated with a kind of ordering process with respect to the end-for-end rearrangement of the cyanide ions.

The present investigation aims at: (1) the extension of the temperature region of the heat capacity measurement down to the temperature of liquid hydrogen, (2) the analysis of the thermal motion of the cyanide ion using the low temperature heat capacity data and (3) the interpretation of the heat capacity anomalies in comparison with the analogous phenomena in the potassium cyanide crystal reported on previously.

Experimental

The sample employed was purified by the recrystallization of commercial sodium cyanide (Kantoh Kagaku, an extra pure reagent) twice from an absolute methyl alcohol, following the method by Thompson.10) The dominant impurity detected by infrared absorption was found to be carbonate ions, which amounted to 0.3 percent. The weight of the specimen used for the measurement was 19.375 g, or 0.4027 mol, taking NaCN=49.008 g/mol. The buoyancy correction was not made. The apparatus and the procedure used for the measurement were the same as have been reported previously.1,11)

Experimental Results

The observed heat capacity values are listed in Table 1 in chronological order; they are illustrated in Fig. 1. They are expressed in terms of the thermochemical calorie, equal to 4.1840 absolute joules. The ice point is taken as 273.15°K. The heat capacity values listed in the table are the ratios of the increase in enthalpy, ΔH, to the rise in temperature ΔT. The temperature given for each point is the arithmetic mean of the initial and the final temperatures.

As is shown in the figure, the lower anomaly was found to start at 70°K. The transition temperatures given by Messer and Ziegler4) coincide very well with the present data. Their heat capacity values above 100°K are, however, lower by about 1 percent.

In Table 2 the heat capacity, the entropy, the enthalpy, and the Gibbs energy functions are given for the rounded temperatures. They were obtained by fitting a smooth curve on the observed values of the heat capacity, extrapolating it to 0°K, and integrating it graphically. The contribution from the extrapolated region below 15°K to the entropy amounts to 0.050 cal/mol degK. Around the upper phase transition, a direct summation of the input energy was carried out. The estimated error in

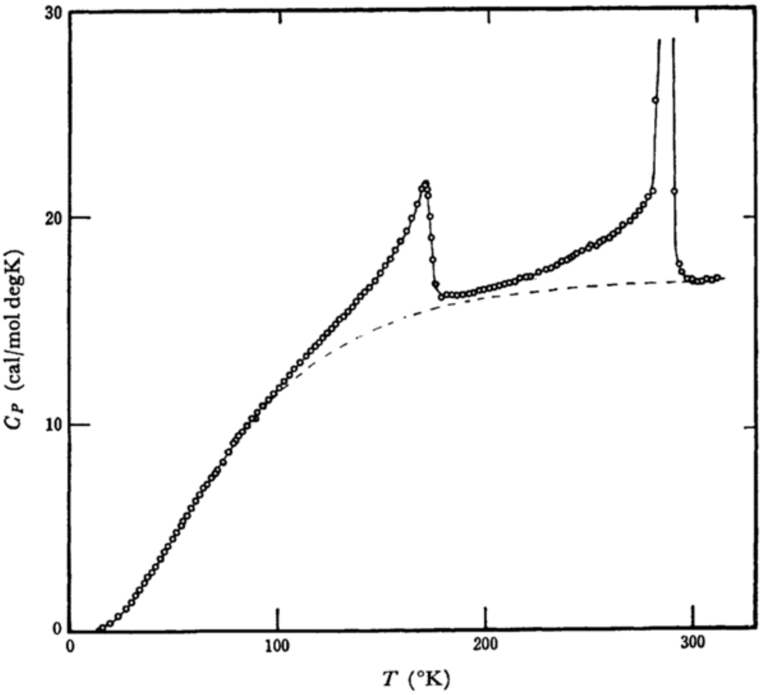

Fig. 1. Heat capacity *versus* temperature curve of NaCN crystal.

---

10) M. R. Thompson, *J. Res. Natl. Bur. Std.*, **6**, 1051 (1931).

11) H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

Table 1. Selected values of heat capacity for NaCN crystal

$T_{av.}$ (°K)	$\Delta H/\Delta T$ (cal/mol degK)	ΔT	$T_{av.}$ (°K)	$\Delta H/\Delta T$ (cal/mol degK)	ΔT
116.61	13.51	2.070	175.01	17.88	1.375
118.67	13.71	2.040	176.84	16.70	2.299
122.69	14.15	1.992	179.14	16.04	2.331
128.70	14.80	1.976	181.60	16.16	2.603
134.52	15.40	1.919	184.19	16.16	2.599
140.34	16.10	1.968	189.54	16.19	2.911
			192.06	16.21	2.901
15.53	0.180	3.428	194.72	16.24	2.895
16.02	0.202	3.872	197.36	16.39	2.648
20.42	0.461	1.753	202.15	16.47	2.576
23.15	0.700	1.569	207.26	16.60	2.558
27.10	1.081	2.390	212.34	16.72	2.540
33.83	1.970	2.168	217.37	16.91	2.516
37.75	2.559	1.768	222.36	17.05	2.499
41.37	3.076	1.734	226.31	17.25	2.476
44.76	3.662	1.812	232.25	17.42	2.447
48.47	4.289	1.709	237.11	17.71	2.418
52.58	4.973	1.925	241.84	17.90	2.394
56.53	5.595	2.060	244.20	18.14	2.372
60.81	6.281	2.087	247.29	18.24	2.369
66.33	7.090	1.957	251.98	18.35	2.333
70.24	7.560	2.081	255.69	18.72	2.313
74.11	8.158	2.777	260.25	18.86	2.298
79.38	9.079	2.564	264.74	19.20	2.267
83.21	9.612	2.447	270.27	19.64	2.228
88.28	10.26	2.525	274.61	20.14	2.162
93.47	10.87	2.576	278.96	20.86	2.130
98.58	11.45	2.586	281.05	21.09	2.111
103.67	12.01	2.491	282.98	25.51	1.840
108.91	12.65	2.626	284.49	40.32	1.289
116.55	13.16	2.101	286.57	59.47	0.927
120.69	13.93	2.016	287.21	127.9	0.464
124.70	14.36	2.022	287.55	189.4	0.320
128.70	14.80	1.976	287.72	300.3	0.206
132.61	15.20	1.937	287.78	245.0	0.250
136.42	15.63	1.898	288.09	220.3	0.277
140.34	16.11	1.968	288.31	205.2	0.297
144.88	16.55	2.562	288.62	136.7	0.436
147.43	16.89	2.537	289.05	108.2	0.542
152.39	17.59	2.449	289.79	58.74	1.058
157.20	18.35	2.373	289.93	40.52	1.281
162.06	19.23	2.639	291.32	21.68	2.064
164.89	19.85	2.579	293.39	17.59	2.379
167.51	20.60	2.509	294.84	17.15	2.420
169.98	21.34	2.444	297.24	16.90	2.441
170.02	21.32	1.224	299.67	16.84	2.444
170.24	21.49	1.215	302.12	16.70	2.456
171.80	21.61	1.210	304.56	16.74	2.450
172.45	21.29	1.220	306.99	16.84	2.440
173.02	21.00	1.235	309.41	16.80	2.441
173.69	19.93	1.277	311.83	16.88	2.431
174.30	18.93	1.328			

TABLE 2. THERMODYNAMIC PROPERTIES OF NaCN CRYSTAL*

T(°K)	$C°_P$	$S°$	$(H°-H°_0)/T$	$-(G°_0-H°_0)/T$
5	(0.005)**	(0.002)	(0.001)	(0.001)
10	(0.043)	(0.014)	(0.010)	(0.004)
15	0.166	0.050	0.038	0.012
20	0.433	0.129	0.099	0.030
30	1.443	0.477	0.363	0.114
40	2.903	1.085	0.809	0.276
50	4.540	1.908	1.391	0.517
60	6.156	2.878	2.049	0.829
70	7.587	3.938	2.741	1.197
80	9.135	5.048	3.440	1.608
90	10.469	6.205	4.151	2.054
100	11.621	7.368	4.840	2.528
120	13.853	9.686	6.159	3.527
140	16.037	12.100	7.413	4.687
160	18.819	14.409	8.646	5.763
171.9±0.2	Lower transition			
190	16.208	17.428	10.028	7.400
210	16.666	19.071	10.637	8.434
230	17.353	20.616	11.189	9.427
250	18.302	22.100	11.718	10.282
270	19.636	23.554	12.239	11.315
288.1±0.1	Upper transition			
289.15	16.831	27.654	15.039	12.615
305	16.704	28.018	15.042	12.976

* All values in units of cal/mol degK.

** Values in the parentheses were obtained by extrapolation of the C_p curve to 0°K.

the C_p is about 1 percent at the temperature of liquid hydrogen and 0.4 percent at room temperature.

Discussion

Thermal Motion of the Cyanide Ion. The method of analyzing the heat capacity data is essentially the same as that used for the potassium cyanide crystal in the previous paper.1) The observed heat capacity was transformed into the apparent Debye temperature, as shown in Fig. 2. We can see here that the presence of the transitions is more conspicuous than in the C_P-T curve itself. By a rather arbitrary interpolation of the normal Debye temperature below and above the transition regions, the anomalous heat capacities were estimated. This procedure is a convenient means of minimizing the ambiguity in separating the effect of the transition from the total heat capacity. In the present case of sodium cyanide, however, the anomalous effect due to the phase transitions contributes to the total heat capacities over considerably wide ranges of temperature, so we assumed three reasonable kinds of normal Debye temperature, as shown in Fig. 2 by A, B, and C. From these normal Debye temperatures, the normal heat capacity was calculated. This procedure may be convenient but not rigorous, since we are assuming a continuous temperature dependence of the normal heat capacity, even at the upper transition, where the crystalline field symmetry surrounding the cyanide ion changes abruptly from orthorhombic to octahedral. At the present stage of our knowledge, however, we have to content ourselves with the approximate procedure adopted here.

The normal heat capacity thus obtained comes from 6 N translational degrees of freedom of both the kinds of ions, and from $2N$ torsional degrees of freedom and N internal degrees of freedom of the cyanide ions (N, Avogadro constant).

In order to get more detailed knowledge about the motion of the ion, we first tried to estimated the torsional frequency of the cyanide ion. For this purpose, we adopted the following procedure. First, we subtracted the contribution of the internal vibration of the cyanide ion from the total heat capacity by using the Einstein function of the wave number, 2085 cm^{-1}.12) Then, by taking a rather arbitrary value of the parameter, the C_P values were transformed to C_V by applying the approximate relation, $C_P-C_V=1.1\times10^{-5}C_P{}^2T$.4) These C_V values yielded the Debye temperature, which is plotted in Fig. 3 (curve a), where only 6 N degrees of freedom are taken into account. The decline

---

12) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

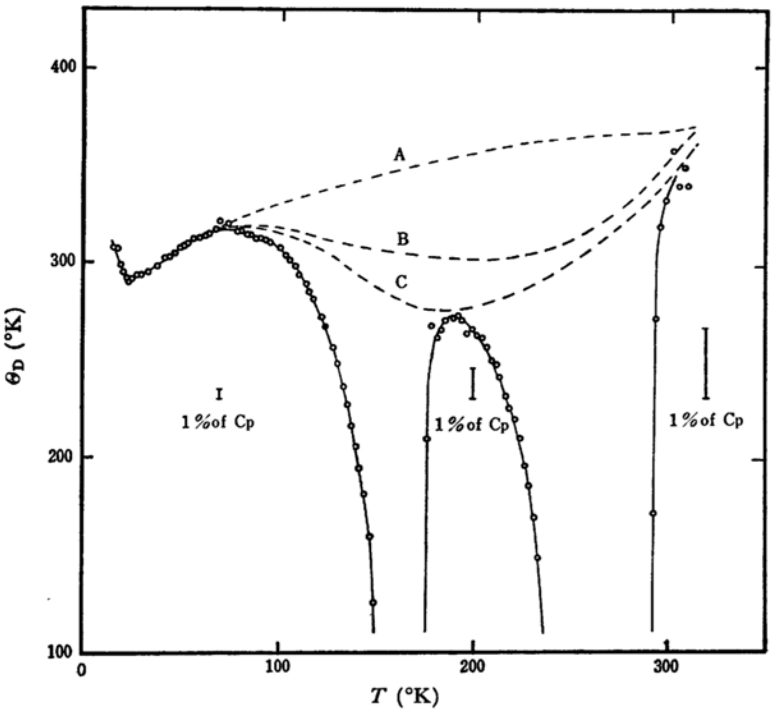

Fig. 2. Apparent Debye temperature of NaCN crystal.
-○-: observed, - - -: A, B and C: assumed.

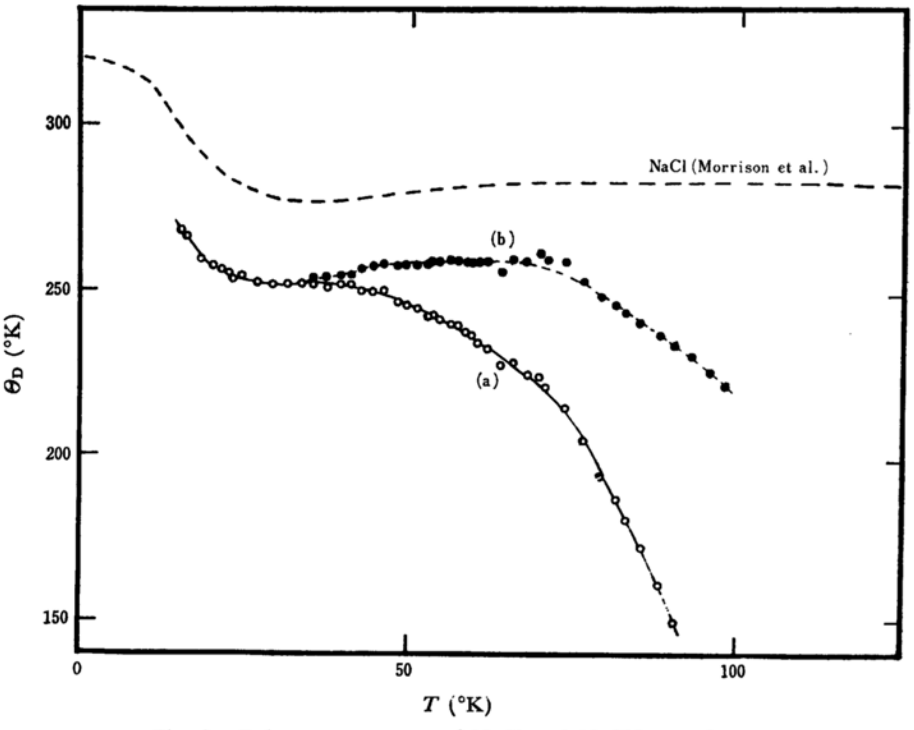

Fig. 3. Debye temperatures of NaCl and NaCN crystals.
- - -: NaCl, -○-: NaCN, assuming 6N degrees of freedom
-●-: NaCN, allowing for the two Einstein oscillators

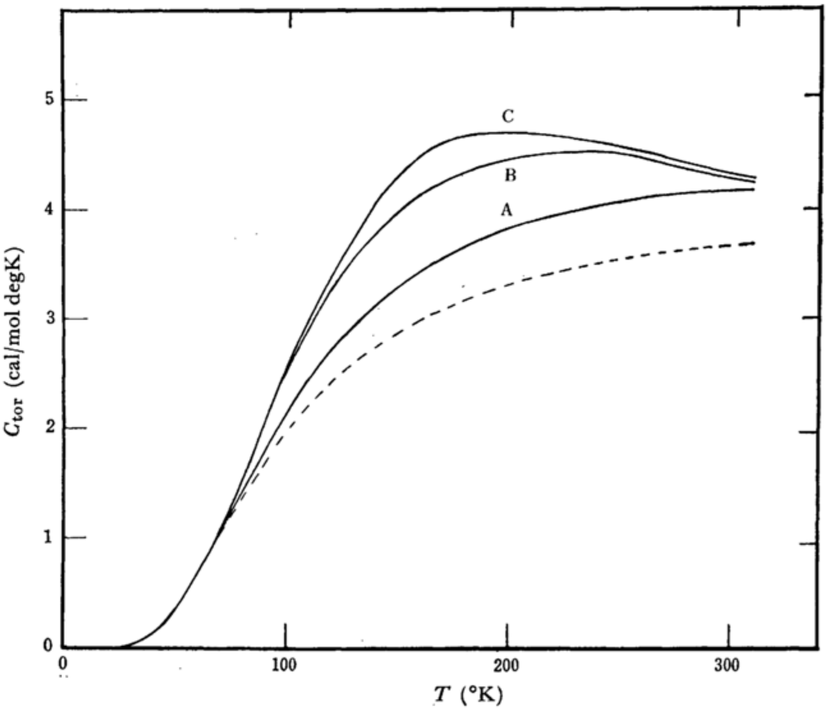

Fig. 4. Torsional heat capacity of CN^- ion in NaCN crystal.

——: A, B and C corresponding to the three estimations of the normal heat capacity
- - -: to two simple harmoic oscillators of wave number 210 cm^{-1}

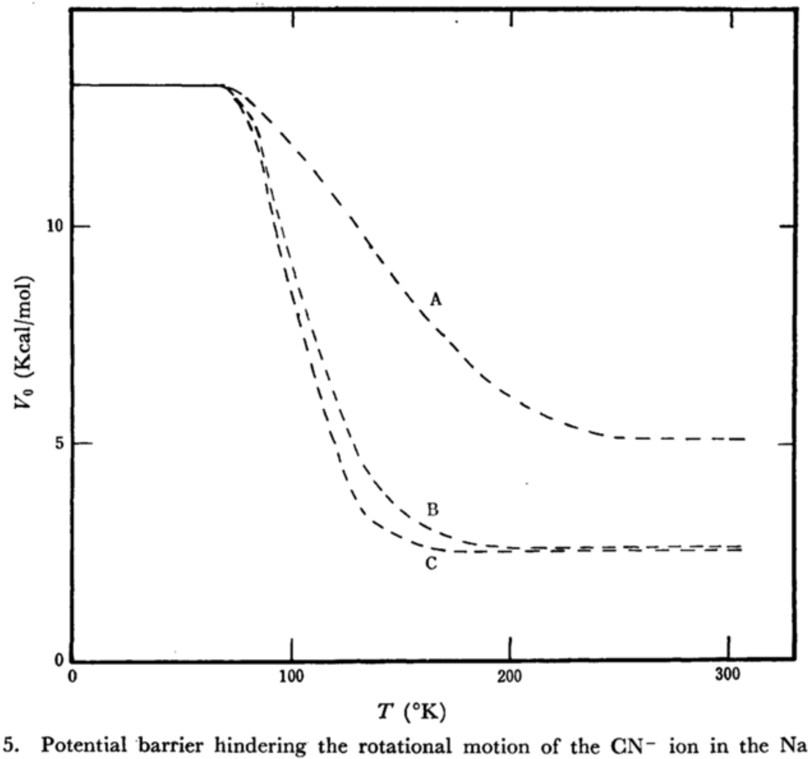

Fig. 5. Potential barrier hindering the rotational motion of the CN^- ion in the NaCN crystal as derived from the heat capacity analysis. The meaning of A, B and C is the same as in Fig. 4.

of the curve above 40°K comes from the neglect of the $2N$ degrees of torsional freedom. Therefore, if we assume further that the temperature dependence of the translational Debye temperature is similar to that of the sodium chloride crystal,[13] we can estimate the torsional frequency by a trial-and-error calculation. With one and the same wave number of 210 cm¹⁻ for the two degrees of freedom of the torsional motion, we obtained the most reasonable variation of the translational Debye temperature, as is shown in Fig. 3, curve b. This wave number may be looked upon as a kind of average value of two frequencies of an anisotropic, two-dimensional oscillator. Although the angular dependence of the potential energy of the cyanide ion in the crystal may be very complicated, for simplicity, we assume it to be $V=(1/2)V_0(1-\cos 2\theta)$, where θ is the polar angle from the equilibrium direction of the cyanide ion. Then V_0, which yields the torsional frequency of 210 cm^{-1} in the harmonic approximation, is calculated to be 13 kcal/mol. Extending the Debye temperature of the translational modes to higher temperatures, meanwhile keeping it parallel with that of NaCl, we can estimate the torsional heat capacity for all the temperature range (see Fig. 3) The results are plotted in Fig. 4. Above 70°K, no combination of two harmonic oscillators can produce the torsional heat capacity. This implies that the harmonic approximation fails around that temperature. Pitzer and Gwinn's treatment extend to two-dimensional motion by Stepakoff and Coulter[14] shows that the heat capacity of a hindered rotator can be larger than R per degree of freedom. Following this method, we can evaluated the V_0 from the experimental torsional heat capacity. The values of V_0 thus obtained are plotted in Fig. 5, in which the curves A, B and C correspond, respectively, to the three variations of the normal Debye temperature assumed in Fig. 2. The estimated V_0 value changes from 13 kcal/mol at the lowest temperatures to 2—3 kcal/mol at the higher temperatures. This is remarkable in view of the fact that there occurs no significant change in the crystal structure at the lower transition; it deserves further investigations, both theroetical and experimental. The high-temperature value may be compared with that of 1.8 kcal/mol derived by Sato[8] with combination of infrared data and Coogan and Gutowsky's result obtained by NMR.[7] (In passing, it might also be mentioned that the theoretical values of the barrier height given by Matsubara and Nagamiya are 6 kcal/mol in the orthorhombic and 1.2 kcal/mol in the cubic phases. These values represent the difference between the maximum and the minimum values of the hindering potentials, whose functional forms are different from those adopted here.)

Mechanism of the Phase Transitions. The temperatures, enthalpies, and entropy changes of the transitions are summarized in Table 3. Here, a "case B" estimation of the normal heat capacity was made. The entropy change of the upper transition amounts to approximately $R\ln 4$.

TABLE 3. TEMPERATURES, ENTHALPIES AND ENTROPIES OF TRANSITIONS IN NaCN CRYSTAL

	T °K	ΔH (cal/mol)	ΔS (cal/mol degK)
Lower transition	171.9±0.2	177.2±3.0	1.21±0.02
Upper transition	287.7±0.1	783.7±8.0	2.80±0.02

This implies that a kind of randomization in the alignment of the cyanide ions takes place at this transition point. Matsubara and Nagamiya treated this transition as a first order one. This treatment might be supported by the hysteresis phenomenon in the heat-capacity measurement found by Messer and Ziegler, and by the results of differential thermal analysis made in this laboratory. The heat-capacity peak is so sharp that 80 percent of the whole enthalpy change occurs in rather narrow range of 5°C for both the Na- and K-salts, although no latent heat effects were detected experimentally.

In principle, a first-order phase transition takes place at a definite temperature which is determined by the equality of the free energies of the two phases involved. Consequently, the heat capacity would behave normally at all but one temperature, where it would go on to infiinity. Experimentally, however, a number of phase transitions are known to occur over a finite temperature range. In some cases, *e. g.*, where the Ising model is an adequate picture, the phase transition is intrinsically diffused. In others, structurally different crystalline phases have to be in equilibrium with each other at the transition point, as is the present case; this gives rise to interfacial and strain energies in the crystal. As a result, the two phases can coexist over a finite range of temperature, since these variables provide extra degrees of freedom in the sense of the Phase Rule.[15] These ideas were used in quantitative calculations by Tobolsky, Kozak, and Canter.[16]

As has been mentioned above, the heat-capacity anomaly at the upper transition is over a temperature range of about 5°C for NaCN. For KCN also, the anomaly around 168°K takes place with a comparable diffuseness, as has been reported previously.[1] Seeking an explanation of this behavior,

---

[13] J. A. Morrison and D. Patterson, *Trans. Faraday Soc.*, **52**, 764 (1956).

[14] G. L. Stepakoff and L. V. Coulter, *J. Phys. and Chem. of Solids*, **24**, 1435 (1963).

[15] A. Ubbelohde, *Quart. Rev.*, **11**, 246 (1957).

[16] A. V. Tobolsky, J. J. Kozak and N. H. Canter, *Phys. Rev.*, **138**, A651 (1965).

we tried to apply the Tobolsky model of diffuse phase transitions to the present cases. The relevant parameters involved in the theory were determined with the experimental values of the transition temperature, the entropy of transition, and the maximum value of the heat capacity at the transition temperature. The last quantity was quite difficult to evaluate precisely, since at the critical temperature the thermal equilibrium in the calorimeter was achieved very slowly. To minimize the uncertainty due to the sluggishness of the transition in the experimental heat capacity, an extrapolation method was applied to the temperature change of the calorimeter after heating it, assuming an exponential decrease in the temperature.

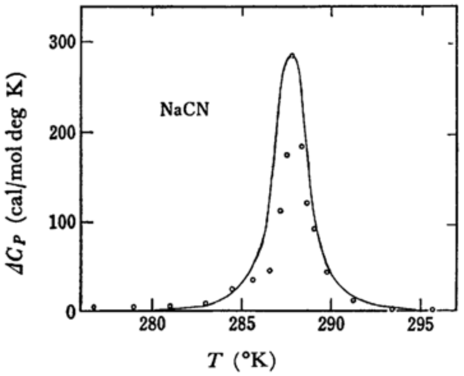

Fig. 6. Anomalous heat capacity at the upper transition of NaCN crystal.
○: observed, —: theoretical

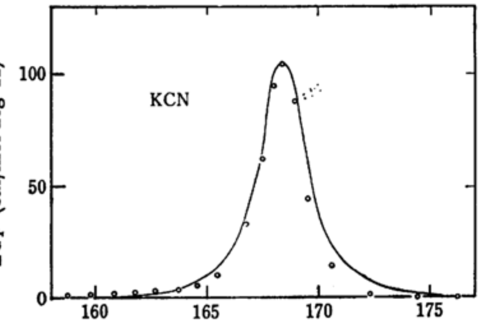

Fig. 7. Anomalous heat capacity at the upper transition of KCN crystal.
○: observed, —: theoretical

In Figs. 6 and 7, the calculated heat capacity is shown for NaCN and for KCN respectively, together with the experimental points. As may be seen in the figures, the heat-capacity anomalies are reproduced with reasonable success. The interfacial energy parameters are $\Delta G_K=6.33$ kcal/mol and 3.07 kcal/mol for NaCN and KCN respectively. Here, ΔG_K indicates the molar Gibbs energy difference of the domain boundary from that of the bulk crystal in the orthorhombic modification.

One important point to be added is that the two crystalline phases co-exist in both these salts over the corresponding temperature ranges. Cimino, Parry, and Ubbelohde[17] showed by the X-ray Laue photographic method that orthorhombic and cubic phases can coexist in KCN at around 168°K. The symmetry relation of the coexisting domains was later discussed in detail by Cimino and Parry.[18] For NaCN, the coexistence of the two phases was observed at around 285°K by Nitta and Oda[19] by the use of the X-ray powder method. In concluding the discussion of the upper phase transition of the two salts, it might be said that if one disregards the difficulty arising from the hysteresis phenomenon, the coexistence model provides a reasonably satisfactory picture of the upper phase transition of NaCN and KCN crystals. For the hysteresis phenomena, however, one would have to take into account nucleation and other aspects of the transition. This is a problem still to be investigated.

Let us now proceed to the discussion of the lower phase transition. Figure 8 shows the anomalous part of the heat capacity at the lower transition as a function of T/T_c (T_c: temperature corresponding to the heat capacity maximum), together with that of KCN. A theoretical curve is also plotted; it will be explained later.

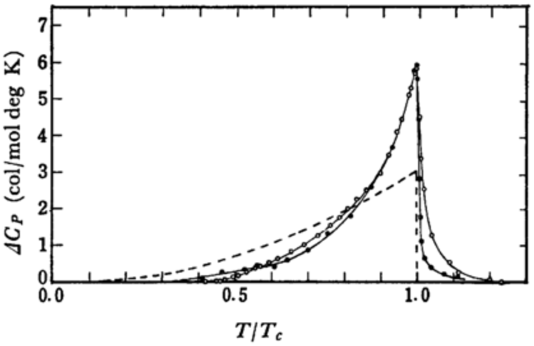

Fig. 8. Anomalous heat capacity at the lower transition of NaCN and KCN crystals.
-●-: NaCN, -○-: KCN, - - -: theoretical

Now we should like to treat these lower transitions of both the salts from the same point of view. Nagamiya presented a molecular field theory of order-disorder transition which includes Pauling's, Frenkel's and Weiss' treatments as extreme cases. In this theory the potential curve described in

---

[17] A. Cimino, G. S. Parry and A. R. Ubbelohde, *Proc. Roy., Soc.*, **A252**, 445 (1959).

[18] A. Cimino and G. S. Parry, *Nuov. Cim.*, **19**, 971 (1961).

[19] I. Nitta and T. Oda, unpublished work read before the 63th Annual Meeting of the Chemical Society of Japan (1941).

TABLE 4. THERMAL EFFECTS AT THE LOWER TRANSITION OF NaCN and KCN CRYSTALS COMPARED WITH THE WEISS APPROXIMATION VALUES

		ΔH (cal/mol)	ΔS (cal/mol degK)	ΔC (cal/mol degK)
NaCN (T_c=171.9°K)	Obs.	177	1.21	5.9
	Calc.	171	1.38	3.0
KCN (T_c=82.9°K)	Obs.	95	1.32	5.8
	Calc.	83	1.38	3.0

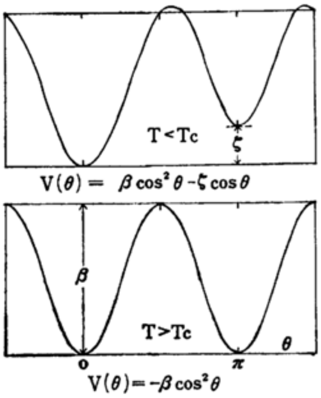

Fig. 9. Hindering potential in Nagamiya's theory of phase transition.

Fig. 9 is assumed for the molecular field, where β is a parameter related to the potential barrier height, and where ζ is an order paramater proportional to the population difference between the two potential minima. Equating β to the V_0 determined by the heat capacity analysis, $\zeta_0(=\zeta$ at 0°K) can be evaluated by using the observed transition temperature. This treatment gives $\zeta_0=400$ cal/mol for NaCN and 180 cal/mol for KCN. Thus, in either crystal $\beta/\zeta_0=30$; this essentially corresponds to the Weiss case. Hereafter, therefore, we will adopt the Weiss model throughout. Another reason for using the Weiss model, which is less realistic than Nagamiya's, is that the latter gives 2 cal/mol degK per degree of freedom for the heat capacity, even at the temperature of absolute zero, since the treatment is classical. The Weiss model is originally a static one, but actually the ions oscillate even at the lowest temperature. This difference can be shown to be negligible for the present cases, because of the strong force constant and the large moment of inertia of the oscillator. The enthalpy, the entropy, and the heat capacity jump based on the Weiss model are listed in Table 4. The theoretical curve in Fig. 8 is also calculated by the Weiss approximation. If we keep in mind the fact that the observed value is C_P while the theoretical one is C_V, the agreement seems to be rather satisfactory, since the volume effect usually sharpens transitions.

Finally, we should like to proceed to a discussion of the ionic interaction in relation to the crystal structure at the lowest temperature. According to Verweel and Bijvoet,(2) no significant change in structure occurs at the lower transition for NaCN, even though they observed an unusual contraction of the b-axis around 170°K without being aware of any transition effect. This effect was later shown by Messer and Ziegler(4) to correspond to the lower phase transition. In KCN also, as has been described in a previous paper, no change was detected by the powder X-ray photographs. In view of these results and the small difference in the atomic-scattering factors of carbon and nitrogen atoms, it may be that the transition is of a order-disorder type with respect to the sense of the cyanide ions. If we assume some specific interactions between the ions as the origin of the energy difference between the two orientations of the anions at 0°K, we may obtain the lowest energy configuration as the plausible structure in the lowest temperature phase. The possible types of interaction may be dipolar interaction and steric effect. Considering the fairly spheroidal shape of the cyanide ion and its short range nature, we can neglect the steric effect and retain only the dipolar term as we consider the mechanism of the phase transition.

The energy difference between the two orientations of the cyanide ion at 0°K, 2ζ, arises, then, from the interaction of the electric dipole of the ion with the local electric field, E, produced at the position of the ion by the array of all other dipoles in the crystal. The local field in a dipole array may be written as:

$$E=\sum_i \frac{3(\vec{\mu}_i\cdot\vec{r}_i)\vec{r}_i-r_i^2\vec{\mu}_i}{r_i^5},$$

where r_i and μ_i are the position vector and the moment of the ith dipole respectively. The summation can be extended over all the dipoles present. For the explicit calculation, let us resort to the approximate method of Lorentz.

Let E be written as:

$$E=E_1+E_2+E_3$$

Here, E_1 is the electric field due to the dipoles within a certain spherical region in the crystal; E_2,

TABLE 5. LOCAL ELECTRIC FIELD IN NaCN AND KCN CRYSTALS*

Configuration		E_1	E_2	E_1+E_2	E'
NaCN	Polar	-0.95×10^{22}	8.87	7.92	6.77
	Antipolar (A)**	−1.61	0	−16.1	−0.66
	Antipolar (B)	5.46	0	5.46	5.79
KCN	Polar	0.28	6.03	6.31	5.62
	Antipolar (A)	0.35	0	0.35	0.02
	Antipolar (B)	4.61	0	4.61	4.61

* In units of the dipole moment in cgs esu.

** The antipolar configurations (A) and (B) are the typical ones for the body centered orthorhombic cell as shown in Fig. 10. For detailed discussion of dipolar lattice, see Luttinger and Tisza, *Phys. Rev.*, **70**, 954 (1947); **72**, 257 (1947).

the cavity field produced by the charges which appear on the inside surface of the cavity left by the sphere, and E_3, the contribution from the charge on the outer surface of the crystal. If the crystal has not net polarization as a whole, then $E_2=E_3=0$ and only the contribution from the dipoles within the sphere is operative. On the other hand, if it has a net polarization, P, E_2 is equal to $(4/3)\pi P$ for a cubic crystal and E_3 is $-(4/3)\pi P$ for a spherical specimen and zero for a long, cylindrical specimen. E_1 was calculated by summing up the contribution from about 50 dipoles within a sphere. For three representative configurations, the results of calculation are summarized in Table 5. In the table E' represents the local field at the center of a long specimen ($12\times15\times250$ Å^3) polarized along the longest axis, calculated for the sake of comparison. If, as is usually assumed, there were some mechanisms supplying charges to the outer surface of the specimen, then $E_3=0$ for any shape of the crystal and the polar configuration would have the lowest energy. Or, following the discussion by Kittel,⁽20⁾ the polar structure would be the most stable by forming long domains.

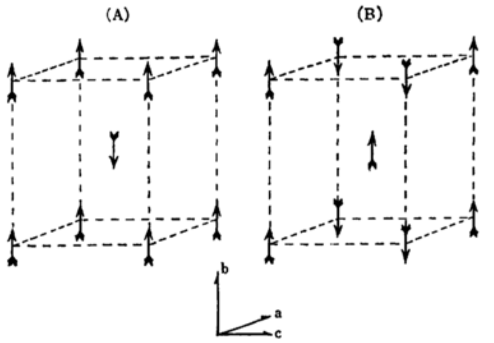

Fig. 10. Typical antipolar configurations of the CN⁻ dipoles in the lowest temperature phase of NaCN and KCN crystals.

If we assume that this polar configuration is realized in the lowest temperature, we can estimate the dipole moment of the cyanide ion in the crystal as follows. By equating the interaction energy to kT_c, we get $\mu=0.55$D for NaCN and 0.42D for KCN. Although, at present, we unfortunately have no experimental data to compare with these values, their order of magnitude seems quite reasonable. We may mention here a recent calculation of the electronic structure of some cyanide compounds by Yonezawa, Kato and Konishi,⁽21⁾ who used a semiempirical self-consistent field method. Their result was 0.49D for the dipole moment of the cyanide ion, a value which compares favorably with our experimental values, although their calculation refers to the free ion.

The difference between the two values derived from Na- and K-salt, however, seems to point to the approximate nautre of our treatment; we can not expect the electronic structure in the two salts to be really different. We observed little difference in the infrared fundamental bands of the cyanide ion in the Na- and K-salts, while for thallium cyanide,⁽22⁾ which is believed to be in electronically-different state, the C–N stretching band is greatly shifted. Accordingly, the difference between the two values may be accounted for more reasonably as a consequence of neglecting the steric, induced polarization and other effects. As may be seen in Table 5, the antipolar configuration, B, must be taken into consideration if the above-mentioned condition favoring the polar structure is in competition with other factors. Therefore, our results are not conclusive. In order to determine the structure of the lowest-temperature phase of the two salts, further experiments, such as neutron diffraction, far-infrared absorption, or dielectric measurements using single crystals, together with a more precise theoretical treatment of molecular interactions in crystals, are much desired.

---

20) C. Kittel, *Phys. Rev.*, **82**, 965 (1951).

21) H. Kato and T. Yonezawa, Proceedings of a Symposium on Molecular Structures, Osaka (1966) 53; T. Yonezawa, H. Kato and H. Konishi, This Bulletin, **40**, 1071 (1967).

22) Unpublished.

Summary

The heat capacity of the NaCN crystal was measured from 14 to 310°K by using an adiabatic calorimeter. Two anomalous regions were confirmed, at 171.9±0.2°K and 287.7±0.1°K. The estimated entropy changes of these anomalies were approximately equal to $R\ln2$ and $R\ln4$, respectively. These values may be interpreted in terms of a step-by-step randomization process of the orientation of the cyanide ions.

By analyzing the observed heat capacities, the contribution from the torsional motion of the cyanide ion was derived on several assumptions. It was shown that, below 70°K, the separated torsional heat capacity can be reproduced by a two-dimensional harmonic oscillator with the average wave number of 210 cm^{-1}, a value which corresponds to a barrier height of 13 kcal/mol. At higher temperatures it may be compared to those of a hindered rotator with a barrier height of 2—3 kcal/mol. This behavior is quite similar to that of KCN.

By integrating the heat capacity data, $S°$, $(H°-H°_0)/T$, and $-(G°-H°_0)/T$ were calculated.

The upper phase transitions of NaCN and KCN conform rather well to the coexistence model of diffuse phase transition proposed by Tobolsky and others.

As to the relative orientation of the cyanide ions in the lowest-temperature phase, the lattice energy was evaluated for both NaCN and KCN, and the most stable configuration was inferred to be polar. These considerations, coupled with the observed transition temperatures, yield estimates of the magnitude of the dipole moment of the anion in the crystal, 0.55D for NaCN and 0.42D for KCN.