# Thermodynamic Properties and Order-Disorder Phase Transitions of the Potassium Cyanide Crystal

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Potassium cyanide, though it consists of spherical $K^+$ and spheroidal $CN^-$ ions, has a cubic symmetry[1] ($O_h^5$; NaCl-type) at room temperature. When the crystal is cooled, it undergoes a phase transition[2] at 168.3°K, with an entropy change approximately equal to $\boldsymbol{R}\ln 4$. According to Bijvoet and his collaborators,[1] the cyanide ions either rotate freely or are orientated randomly in eight body-diagonal directions in the cubic phase, while they are all parallel to the b-axis of the orthorhombic lattice of the low temperature phase. Matsubara and Nagamiya[3] have calculated the lattice energies for both phases and have determined the transition point between them from the theoretical point of view. They have also calculated the potential barrier hindering the rotation of cyanide ions in both phases and concluded that the cyanide ions are subjected to hindered rotation with a barrier height of approximately 1.4 kcal. $\mathrm{mol}^{-1}$ in the cubic phase. These results imply that the cyanide ions have an orientational entropy of $\boldsymbol{R}\ln 8$ in the cubic phase. If one takes the difference between the carbon and the nitrogen atoms of the cyanide ion into consideration also, it may be expected that, when the crystal is cooled further, it will undergo another phase transition, one which corresponds to the orientational order-disorder rearrangement of the cyanide ion with respect to its head and tail. Otherwise, the crystal would have a residual entropy of $\boldsymbol{R}\ln 2$ at the lowest temperature, as in the case of carbon monoxide[4] and nitrogen suboxide[5] crystals.

On the other hand, in the course of the X-ray structural analysis of the potassium cyanide crystal at the transition temperature range, Ubbelohde and his collaborators[6] have recently observed the occurrence of an intermediate phase which appears when the crystal is subjected to a composite temperature cycle around 168°K. The new phase has been reported to belong to the monoclinic system, which was eventually transformed into the stable orthorhombic system at about 158°K when the crystal was cooled and to the stable cubic system at 166°K when it was heated. They also found the co-existence of various domains of the low temperature form in " hybrid " single crystals, as well as of domains of the low and high temperature forms over a range of temperatures.

The object of the present research was to study the thermal properties of the stable potassium cyanide crystal at lower temperatures and also those of the above-mentioned new phase around the transition region.

## Experimental

" Pro analysi " potassium cyanide (Merck reagent) was recrystallized twice from an absolute methyl alcohol solution by evaporating it under a stream of nitrogen gas.[7] The purity of the sample was assured by the method of purification.[7] The specimen was dried in a vacuum ($10^{-5}$ mmHg) at 110—130°C for several hours. In a spectrochemical analysis of the specimen, the only metallic impurities found were traces of silicon, manganese and iron, all less than 0.05 per cent. The predominant impurity was the $CO_3^{2-}$ ion, since a fairly intensive C=O stretching vibration appeared on the infrared absorption spectra. The amount was analyzed by a comparison

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[1] J. M. Bijvoet and J. A. Lery, *Rec. trav. chim.*, **59**, 908 (1940); Structure Reports 1942—44, 9, Utrecht: N. V. A. Oosthoek's Vitgevers Mij.

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

[3] T. Matsubara and T. Nagamiya, *Sci. Papers Osaka Univ.*, **No. 14** (1949).

[4] J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.*, **54**, 2610 (1932).

[5] R. W. Blue and W. F. Giauque, ibid., **57**, 991 (1935).

[6] A. Cimino, G. S. Parry and A. R. Ubbelohde, *Proc. Roy. Soc.*, **A252**, 445 (1959); G. S. Parry, *Acta Cryst.*, **15**, 596 (1962).

[7] M. R. Thompson, *J. Research Natl. Bur. Standards*, **6**, 1051 (1931).

of the intensity of the spectra with those involving a given amount of carbonate ions; it was thus revealed that the specimen used for heat capacity measurement contained 0.3 per cent of $CO_3^{2-}$ ions. In order to avoid possible contamination by humidity and carbon dioxide in the air, the procedure of transferring the sample was carried out in a vacuum-type dry-box under an atmosphere of nitrogen gas.

All measurements were made on a single loading of 20.5785 g. or 0.31596 mol., taking 65.120 as the molecular weight of potassium cyanide. The heat capacity was measured in the temperature range from 15 to 310°K by means of a low-temperature adiabatic calorimeter, the details of which have been reported previously.(8)

The occurrence of the intermediate, monoclinic phase was re-examined by a differential thermal analysis (DTA) apparatus(9) that operates automatically at low temperatures.

In order to follow the appearance and disappearance of the domains around the transition temperature, the intensity of natural light with a wavelength in the neighborhood of 5000 Å transmitted through the crystal was measured by means of a photo-tube. A schematic diagram of the apparatus is given in Fig. 1. Specimen B in the disk form is placed inside the hole fitted in a copper block, A, which is connected with the inside of a modified Dewar vessel by means of a "Housekeeper" seal so as to make vacuum tight. A fairly transparent disk specimen is obtained by compressing the powdered specimen, as in making infrared measurements of the KBr disk. In order to obtain better thermal contact, a thin film of "silicon" grease is coated over the edge of the specimen and the cap, C. In order to cool the crystal, cold gas from the storage vessel, N, containing liquid nitrogen was run through the transfer siphon, S. The temperature of the specimen was measured with a Chromel-P constantan thermocouple; it could be maintained for a long period of time within ±0.1°C at any temperature by adjusting the flow rate of cold gas. The photocurrent from a PL 50 V phototube was recorded on a voltage recorder.

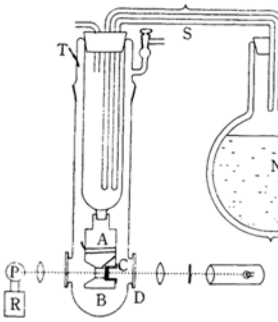

Fig. 1. Schematic diagram of apparatus for investigating transmission of natural light.

## Experimental Results

**Heat Capacity.**—The observed heat capacity data are listed in Table I in chronological order. These values are expressed in terms of the defined thermochemical calorie, equal to 4.1840 absolute joules. The ice point is taken to be 273.15°K. The heat capacities listed in the table are the ratios of the increase in enthalpy, $\Delta H$, to the rise in temperature, $\Delta T$. Also listed in Table I are the values of the approximate temperature rise in each measurement. The temperature given for each point is the arithmetic mean of the initial and the final temperatures. These results are plotted graphically in Fig. 2.

Series I comprises several exploratory measurements after the initial cooling of the calorimeter to liquid nitrogen temperatures. The calorimeter was then cooled to 12°K and the data of series II taken. In this measurement a new heat capacity anomaly was found at about 83°K. In order to define more closely the shape and the reproducibility of the curve in the anomalous region, measurements of series III were made. No evidence was found from the measurements for checking the dependence of the observed heat capacity on the thermal history of the sample, and the points obtained from all the series coincide with each other within the expected range of error. In the neighborhood of the maximum heat capacity, there was no evidence of sluggishness in the attainment of thermal equilibrium.

Series III also involves the upper thermal anomaly, corresponding to the orthorhombic-cubic phase transition reported previously by Bijvoet et al.(1) and Ziegler et al.(2)

Parallel to the heat capacity measurements, the occurrence of the intermediate, monoclinic phase around the upper transition temperature was re-examined by the DTA method. The results are reproduced in Fig. 3. Run 1 shows a heating curve up to about 30°C higher than the transition temperature, and run 2 is for the subsequent cooling curve. Runs 3, 4 and 5 all give heating curves which follow just after runs 2, 3 and 4 respectively are over. In this process, a new upheaval appears a few degrees below the orthorhombic-cubic transition temperature. As the temperature cycles are repeated further, this lower component of thermal anomaly increases with the consumption of the upper component, which eventually disappears (see run 5). Run 6 corresponds to the cooling curve just after the repeated temperature cycles; this is same procedure as that adopted by Ubbelohde et al.(6) Accordingly, the broad thermal anomaly located at about

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

9) H. Suga, H. Chihara and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 82, 24 (1961).

TABLE I. SELECTED VALUES FOR HEAT CAPACITY OF KCN

| $T_{av}$ °K | $\Delta H/\Delta T$ cal. mol$^{-1}$ deg$^{-1}$ | Approx. $\Delta T$ |
|---|---|---|
| | Series I | |
| 89.02 | 12.84 | 2.123 |
| 91.16 | 12.71 | 2.127 |
| 94.43 | 12.96 | 2.088 |
| 98.57 | 13.17 | 2.054 |
| 103.09 | 13.46 | 2.306 |
| 107.43 | 13.76 | 2.266 |
| 116.33 | 14.43 | 2.178 |
| 120.78 | 14.62 | 2.155 |
| 125.06 | 14.85 | 2.126 |
| 129.28 | 15.11 | 2.096 |
| 135.57 | 15.58 | 2.237 |
| | Series II | |
| 14.23 | 0.579 | 2.510 |
| 15.63 | 0.661 | 2.935 |
| 17.42 | 0.837 | 2.533 |
| 18.13 | 0.928 | 2.103 |
| 20.04 | 1.197 | 1.683 |
| 21.61 | 1.424 | 1.438 |
| 24.02 | 1.806 | 3.041 |
| 26.93 | 2.274 | 2.841 |
| 29.53 | 2.713 | 2.123 |
| 32.66 | 3.250 | 2.014 |
| 35.78 | 3.879 | 1.982 |
| 37.70 | 4.241 | 1.827 |
| 39.63 | 4.649 | 1.986 |
| 42.03 | 5.187 | 2.043 |
| 44.53 | 5.901 | 1.965 |
| 46.95 | 6.513 | 1.887 |
| 49.21 | 7.078 | 2.311 |
| 51.76 | 7.662 | 2.474 |
| 54.35 | 8.258 | 2.670 |
| 56.95 | 8.874 | 1.984 |
| 59.39 | 9.474 | 1.970 |
| 61.94 | 10.12 | 1.894 |
| 64.61 | 10.82 | 2.580 |
| 67.89 | 11.65 | 2.204 |
| 70.05 | 12.22 | 2.121 |
| 72.18 | 12.83 | 2.119 |
| 74.35 | 13.49 | 2.145 |
| 76.45 | 14.28 | 2.058 |
| 78.46 | 15.16 | 1.968 |
| 80.39 | 16.16 | 1.878 |
| 82.32 | 17.15 | 1.977 |
| 84.37 | 15.42 | 2.112 |
| 86.49 | 13.05 | 2.123 |
| | Series III | |
| 77.29 | 14.63 | 2.015 |
| 79.26 | 15.56 | 1.925 |
| 80.69 | 16.32 | 1.814 |
| 81.61 | 16.86 | 2.145 |
| 82.51 | 17.25 | 2.063 |
| 83.40 | 17.20 | 1.982 |
| 84.32 | 15.47 | 1.908 |
| 85.32 | 13.58 | 2.069 |
| 86.90 | 13.00 | 2.117 |
| 92.23 | 12.87 | 2.106 |
| 96.51 | 13.05 | 2.071 |
| 100.77 | 13.31 | 2.330 |
| 105.39 | 13.59 | 2.285 |
| 137.32 | 15.65 | 2.228 |
| 143.93 | 16.08 | 2.160 |
| 148.26 | 16.46 | 2.142 |
| 152.51 | 16.84 | 2.121 |
| 156.66 | 17.45 | 2.056 |
| 160.72 | 18.25 | 1.995 |
| 164.56 | 21.20 | 1.806 |
| 166.74 | 49.23 | 0.962 |
| 167.48 | 87.79 | 0.585 |
| 168.41 | 119.86 | 0.468 |
| 168.88 | 103.42 | 0.568 |
| 169.51 | 60.17 | 0.816 |
| 172.31 | 17.04 | 2.078 |
| 176.56 | 16.11 | 2.141 |
| 182.97 | 16.03 | 3.221 |
| 187.89 | 16.09 | 3.198 |
| 191.07 | 16.30 | 3.170 |
| 194.25 | 15.99 | 3.203 |
| 200.65 | 15.97 | 3.199 |
| 205.79 | 15.95 | 3.104 |
| 210.04 | 15.95 | 3.051 |
| 214.28 | 15.93 | 3.004 |
| 227.30 | 15.94 | 2.122 |
| 236.81 | 15.94 | 4.239 |
| 241.04 | 15.89 | 4.233 |
| 249.31 | 15.90 | 4.634 |
| 253.95 | 15.93 | 4.622 |
| 258.60 | 15.93 | 4.615 |
| 263.18 | 15.91 | 4.603 |
| 272.38 | 15.91 | 4.598 |
| 276.54 | 15.85 | 4.594 |
| 285.73 | 15.82 | 4.591 |
| 290.30 | 15.87 | 4.571 |
| 303.94 | 15.86 | 4.566 |
| 308.50 | 15.85 | 4.556 |
| | Series IV | |
| 160.05 | 19.24 | 0.966 |
| 161.01 | 19.65 | 0.953 |
| 162.41 | 20.39 | 1.858 |
| 164.19 | 23.11 | 1.707 |
| 165.48 | 55.29 | 0.872 |
| 166.50 | 189.99 | 0.287 |
| 166.29 | 248.01 | 0.222 |
| 166.50 | 265.12 | 0.208 |
| 167.07 | 51.01 | 2.022 |
| 168.53 | 17.82 | 2.311 |
| 170.60 | 16.48 | 2.120 |
| 172.72 | 16.16 | 2.143 |
| 177.02 | 16.11 | 2.143 |
| 179.16 | 16.08 | 2.144 |

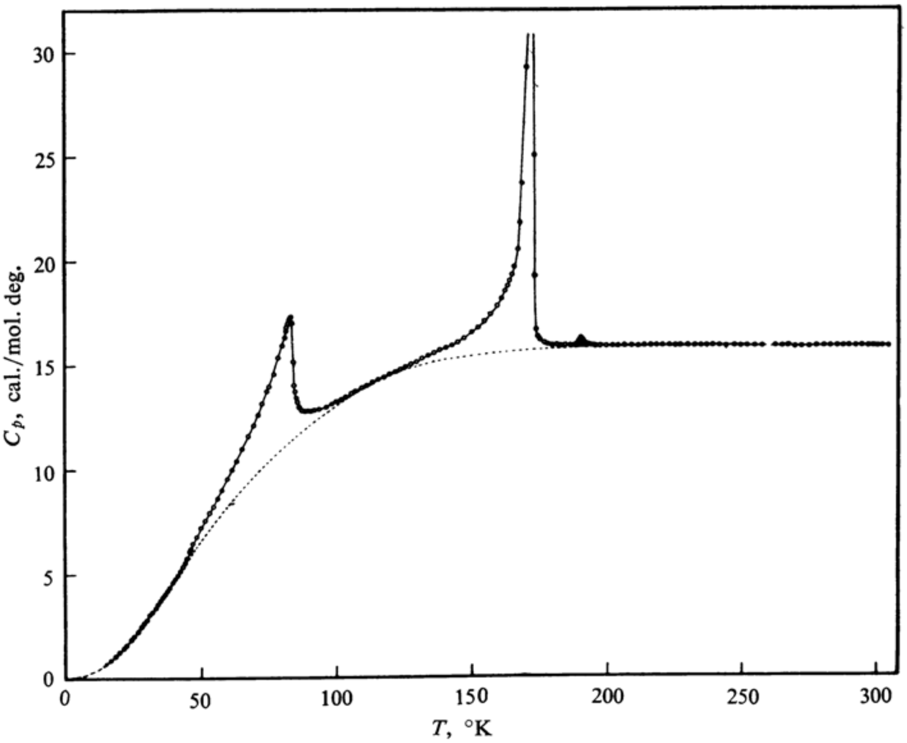

Fig. 2. Heat capacity versus temperature curve of KCN crystal.

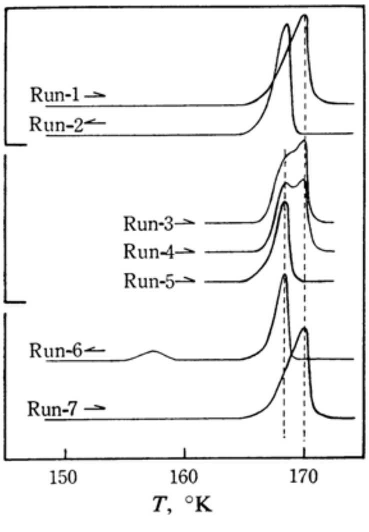

Fig. 3. DTA curves of KCN crystal undergoing various temperature cycles.

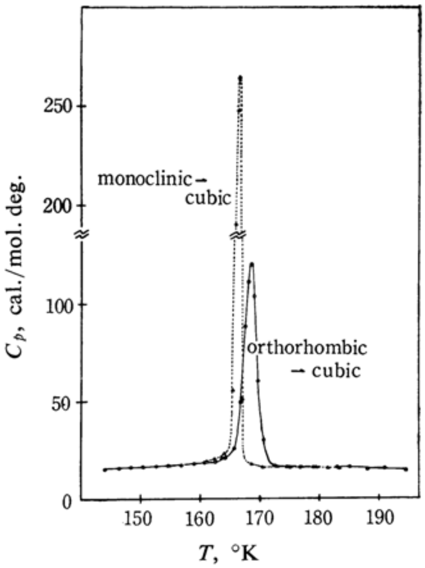

Fig. 4. Heat capacity versus temperature curves of KCN crystal around upper transition regions.

158°K corresponds to the monoclinic-orthorhombic transformation. These results agree well with the X-ray findings by Ubbelohde et al.

The monoclinic-cubic transformation was then studied more precisely by the calorimetric method. The results are grouped as series IV. The heat capacity anomaly corresponding to this transformation is plotted in Fig. 4, together with those for the orthorhombic-cubic transformation. In the neighborhood of both heat capacity maxima, the rate of attainment to the equilibrium was too slow for the final

TABLE II. TEMPERATURES, ENTHALPIES AND ENTROPIES OF TRANSITIONS OF KCN CRYSTAL

| | $T$ °K | $\Delta H$ cal. mol$^{-1}$ | $\Delta S$ cal. mol$^{-1}$ deg$^{-1}$ |
|---|---|---|---|
| Lower transition | 82.9±0.2 | 95.1±1.0 | 1.32±0.01 |
| Upper transition | 168.3±0.1 | 339 ±5 | 2.01±0.03 |
| Monoclinic-cubic transition | 166.5±0.1 | 291 ±5 | |

state to be reached in a reasonable period of time. The heat capacity values in these regions are, therefore, inferior in accuracy to the other results.

The heat capacity in the cubic phase keeps essentially a constant value. Such temperature-independent behavior of the heat capacity in the cubic phase has also been found by us in other alkali cyanides;[10] for example, sodium cyanide, rubidium cyanide, cesium cyanide and thallium cyanide. These results will be reported in the near future.

The only data available for comparison with these results are the measurements by Ziegler and Messer[2] on potassium cyanide from 100 to 340°K. Their data deviate 1.5 per cent at 100°K and are 2 per cent lower at 300°K than ours.

The lower anomaly in heat capacity, which has not been observed hitherto, has the lambda shape characteristic of processes where a co-operative ordering is taking place. The question as to whether the curve near the maximum is continuous, or cusped, can not be unambiguously decided on the basis of the present data. Because of the finite temperature increment in an individual measurement, it appears that a cusped curve would be smoothed out. It appears from a magnified scale plot of the data in the immediate neighborhood of the maximum that the data are better represented by a smooth curve, taking into account the finite resolution and precision of the measurement. The heat capacity reaches a maximum value of 17.25 cal. mol$^{-1}$ deg$^{-1}$ at 82.9±0.2°K.

The temperatures, enthalpies, and entropies of the phase transition are summarized in Table II. The transition temperature was taken as the one where the heat capacity reached a maximum value. The enthalpy of the transition was evaluated by integrating the excess heat capacity over the normal heat capacity, represented by the dotted line in Fig. 2. The method of estimating the normal heat capacity will be described later. The enthalpy of the transition, corresponding to the monoclinic-cubic transformation, was evaluated by assuming that the heat capacity of the monoclinic crystal had the same value as that of the orthorhombic crystal. It follows immediately that the enthalpy of the intermediate, monoclinic form is higher than that of the orthorhombic form by 53.9±0.5 cal. mol$^{-1}$ at 159.6°K.

A short comment should be added here about the small hump in the heat capacity observed around 190°K. This anomaly is very broad and so small as to make it almost invisible in Fig. 2. Six series of heat capacity measurements were made to ascertain its reality on specimens having different thermal history. These results are omitted from Table I, since they are reproduced in Fig. 5 on a magnified scale. It is of interest to point out that this thermal anomaly appears only for the cubic crystal which has been brought into the orthorhombic or the monoclinic phase prior to the measurement. This endothermic anomaly is presumable associated with some higher-order structural defect created by the phase transition.

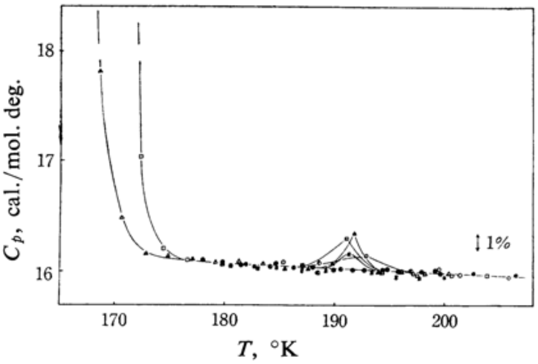

Fig. 5. Heat capacity versus temperature curves of KCN around 190°K.

-⊡- Series II -△- Series III
-✱- Series IV -⊗- Series V
-⊙- Series VI -●- Series VII

**The Thermal Transition of the Transparency around 168°K.**—Successive temperature cycles for the transmission of the disk specimen are recorded in Fig. 6. The transmission is plotted on an arbitrary scale, taking the room temperature form value as 100. The curve also affords a sensitive way of following the progress of the transformation. By taking readings at intervals and at a constant temperature, it was found that an equilibrium was attained for a considerably long time in the neighborhood of the transition point. There is a wide

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[10] H. Suga, T. Matsuo, M. Sugizaki and S. Seki, to be published.

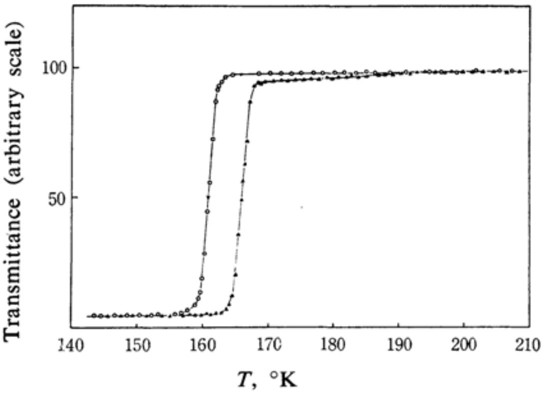

Fig. 6. Thermal transition of transparency in KCN crystal.
○ Temp. falling △ Temp. rising

hysteresis loop in the thermal transition of the transparency. Similar results were also obtained for the monoclinic-cubic transformation. The transition point on heating, taken as the maximum slope temperature of the transmission curve, does not agree exactly with the results of heat capacity measurement. The difference seems to be due to the less accurate temperature measurement resulting from the poorer thermal contact in this apparatus. The difference seems also to be due to the disk specimen employed, which may presumably not be free from the strain sustained when it is pressurized to form the disk. The width of this hysteresis loop is, however, consistent with those of the X-ray results obtained by Ubbelohde et al. and of the thermal findings by DTA.

## Thermodynamic Properties of Potassium Cyanide

The values of the heat capacity, the entropy and the enthalpy and Gibbs energy functions of the potassium cyanide crystal at selected temperatures are listed in Table III. The values of $C_p^\circ$ were determined at round temperatures on the smoothed curve drawn through the measured heat capacity data. These values may well be regarded as the true differential heat capacity, except for the anomalous regions, where they change very rapidly and require correction for curvature. In order to make the extrapolation to the absolute zero of temperature, plots were made of $C_p/T^3$ against the temperature in the range from 13 to 40°K. The extrapolated contribution to the entropy below 15°K is merely 0.307 cal. mol$^{-1}$ deg$^{-1}$.

The error of the smoothed heat capacity data is estimated as 2 per cent at 20°K and 0.3 per cent above 50°K. Although the inaccuracy of the functions $S^\circ$, $(H^\circ - H_0^\circ)/T$ and $-(G^\circ - H_0^\circ)/T$ is about 0.3 per cent above 50°K, the numbers in Table III are given to a higher precision than this so that they will be internally consistent.

TABLE III. THERMODYNAMIC PROPERTIES OF KCN CRYSTAL
(in cal./deg. mol.)

| $T$, °K | $C_p^\circ$ | $S^\circ$ | $\dfrac{(H^\circ - H_0^\circ)}{T}$ | $-\dfrac{(G^\circ - H_0^\circ)}{T}$ |
|---|---|---|---|---|
| 5 | (0.074) | (0.037) | (0.002) | (0.035) |
| 10 | (0.266) | (0.140) | (0.092) | (0.048) |
| 15 | 0.609 | 0.307 | 0.202 | 0.104 |
| 20 | 1.182 | 0.554 | 0.370 | 0.185 |
| 30 | 2.794 | 1.324 | 0.898 | 0.426 |
| 40 | 4.794 | 2.366 | 1.593 | 0.772 |
| 50 | 7.266 | 3.695 | 2.475 | 1.219 |
| 60 | 9.639 | 5.228 | 3.470 | 1.757 |
| 70 | 12.190 | 6.902 | 4.531 | 2.372 |
| 80 | 15.956 | 8.745 | 5.695 | 3.051 |
| 82.9±0.2 | Lower transition | | | |
| 90 | 12.795 | 10.487 | 6.699 | 3.778 |
| 110 | 13.934 | 13.144 | 7.894 | 5.249 |
| 130 | 15.169 | 15.574 | 8.921 | 6.654 |
| 150 | 16.624 | 17.840 | 9.844 | 7.995 |
| 168.3±0.1 | Upper transition | | | |
| 190 | 16.186 | 23.545 | 12.817 | 10.728 |
| 210 | 15.949 | 25.139 | 13.121 | 12.018 |
| 230 | 15.930 | 26.590 | 13.366 | 13.224 |
| 250 | 15.910 | 27.916 | 13.570 | 14.346 |
| 270 | 15.887 | 29.141 | 13.743 | 15.398 |
| 290 | 15.844 | 30.283 | 13.887 | 16.396 |
| 298.15 | 15.843 | 30.712 | 13.942 | 16.770 |
| 310 | 15.850 | 31.330 | 14.015 | 17.315 |

## Discussion

**Thermal Anomaly around 190°K.**—Concerning the nature of the upper phase transition at 168.3°K, Matsubara and Nagamiya³⁾ have proposed a suitable model, one upon which they calculated its transition point and obtained fairly satisfactory results. On this topic, therefore, there is further comment to be added. Here, however, a brief account may be given of the nature of the heat capacity anomaly around 190°K.

Ubbelohde and his collaborators⁶⁾ have found that the intermediate, monoclinic form was always produced by applying a particular, composite temperature cycle. This involved the direct cooling of a crystal from room temperature to below the transition temperature, then warming it to about 3°C above the transition onset temperature, and subsequently recooling it through the transition range. The intermediate form was never observed during any direct cooling. They also found that various domains of the orthorhombic form co-exist when the crystal is directly cooled through the transition point. These observations led them to the conclusion that "scars," resulting from the effects of strain within the domains, exist in the cubic phase just above the transition point.

The "critical temperature," 3°C higher than the transition onset temperature, seems to depend markedly on the physical states of the crystal, as well as on the heating rate employed and on the period of time spent at that temperature. In fact, we have found from another series of DTA measurements that in the specimen raised even above 25°C higher than the transition temperature, followed by immediate recooling, the monoclinic form was formed, though the heating rate employed in this case, 0.5—0.8°C $\mathrm{min}^{-1}$, is much higher than that of the heat capacity measurement, 0.03—0.1°C $\mathrm{min}^{-1}$.

The heat capacity anomaly around 190°K seems to correspond exactly to the "critical temperature." The reasons are as follows. In the first place, this thermal anomaly appears only for the cubic crystal brought into the orthorhombic or the monoclinic crystal prior to the measurement. Two series of measurements made on a specimen cooled to just above the transition temperature showed no sign of heat capacity anomaly. Additional evidence is offered by the experimental findings on the thermal transition of the transparency. The transparency of the scarred cubic crystal is somewhat lower than one directly cooled from room temperature. The scarred cubic crystal seems, therefore, to be a state in which the inter-domain walls produced by the formation of the orthorhombic form are not perfectly recovered. This state persists to higher temperature but ultimately changes into the cubic crystal, losing its scars around the "critical temperature."

The free energy of a crystal can by no means be expressed fully by only its volume, temperature and pressure. It may be also a functions of the strain and of the internal surface energy[11] when the crystal is composed of "sub-structure" or domains. The excess free energy assumed in the scarred cubic crystal seems to be responsible for the preferential formation of the intermediate phase on subsequent recooling.

A simple calculation was made on the average size of domains, based on the assumption that the cyanide ion located at the domain surfaces had less configurational entropy by the amount of $k \ln 2$ than that of the bulk phase, and also on the assumption that the entropy increment at the "critical temperature" was caused by a gain in the entropy of such ionic groups. The total entropy change around 190°K, merely about 0.005 cal. $\mathrm{mol}^{-1}\,\mathrm{deg}^{-1}$, combined with the above assumption, leads to the value of 4000 Å for the average domain size. Although this rough estimation, neglecting entirely the contribution from vibrational aspects of the ions, has no significance other than as an order of magnitude, the derived value is well in the range estimated by the X-ray method.[6] In order to obtain more quantitative knowledge on the average size as well as on its distribution, single crystal and monochromatized light should be used.[12] Such an experiment is being planned in our laboratory.

**The Nature of the Phase Transition at 83°K.** —The heat capacity anomaly takes place over a wide temperature range, with a maximum at 82.9°K, and has the lambda shape characteristic of processes where co-operative ordering is taking place. This phase transition resembles in thermal properties the lower phase transition at 172°K in the sodium cyanide crystal.[2] In the orthorhombic phase ($D_{2h}^{25}$ Immm) of both crystal,[1,13] all the C–N bonds in cyanide ions are arrayed along the b-axis of the unit cell. The orientations of the cyanide ions with respect to its head and tail have not, however, been clarified in the present stage of X-ray structural analysis. Preliminary Debye-Scherrer photographs* taken below and above the lambda point of the potassium cyanide crystal indicate only that there is no appreciable change in the atomic arrangement of either phase. Similar results have been reported also for the sodium cyanide crystal.[14]

Such a minor change in structure may be explained by assuming that the co-operative rearrangement with respect to the head and tail of the cyanide ion takes place over the anomalous heat capacity region, since there is no appreciable difference in the atomic scattering factor between the carbon and nitrogen atoms. Thus, we may picture the temperature effect as follows. At the lowest temperatures, all the cyanide ions are arranged along the b-axis with a uniquely defined orientation (a completely ordered state), and as the temperature is raised, the flipping motion between the two orientations with respect to the head and tail of the cyanide ion is excited progressively;

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[11] A. R. Ubbelohde, *Brit. J. Appl. Phys.*, **7**, 313 (1956); *Quart. Rev.*, **11**, 246 (1957).

[12] T. Horie, K. Kawabe and T. Iwai, *Ann. Rep. Scient. Works, Fac. Sci. Osaka Univ.*, **4**, 45 (1956).

[13] H. J. Verweel and J. M. Bijvoet, *Z. Krist.*, **100**, 201 (1939); Structure Reports, loc. cit.

* We are greatly indebted to Mr. Yasuo Yamaguchi of our University for his kind arrangements for taking the X-ray photographs.

at the transition point these two orientations of the cyanide ion become exactly equal energetically (a completely disordered state). The magnitude of the entropy change associated with this phase transition, which is nearly equal to $\boldsymbol{R}\ln 2$ $(=1.38\,\text{cal. mol}^{-1}\,\text{deg}^{-1})$, affords strong support for such an explanation of the mechanism of the phase transition.

The mode of the relative arrangement of cyanide ions in the completely ordered state is, however, not exactly clear at the present stage. Preliminary calculations involving the dipole-dipole interaction among the cyanide ions of the potassium cyanide crystal suggest strongly that the polar structure of the cyanide ions along the b-axis (space group; $C_{2v}^{20}$ Imm2) seems to be the most stable.** This polar structure was also suggested by Siegel[14] for the lowest modification of the sodium cyanide crystal.

**The Torsion-Rotational Motion of Cyanide Ions.**—In order to get more detailed knowldge about the thermal motion of cyanide ions in the crystalline state, the Eucken-Morrison type of analysis was applied to the present case. In the first place, the heat capacity at a constant volume, $C_v$, was computed from the observed $C_p$ value by the usual procedure. Here, the correction was made by use of the relation $C_p-C_v=1.1\times10^{-5}\,C_pT^2$, the numerical factor being estimated rather arbitrarily.[2] It may easily be seen that this crystal has 6 $N$ degrees of the translational freedom, 2 $N$ degrees of the torsional or the rotational freedom, and $N$ degrees of the internal-vibrational freedom of cyanide ions. The contribution from the last freedom to the heat capacity was evaluated by the Einstein function, using the wave number of 2085 cm$^{-1}$, obtained by the infrared spectroscopic method.[15] This vibrational heat capacity does not contribute in any significant degree within the temperature range measured. After subtracting this contribution from the total, the apparent Debye temperature $\Theta_D$ was calculated on the assumption that the other 8 $N$ degrees of freedom could be represented by a single Debye temperature. The $\Theta_D$ value thus obtained is given in Fig. 7 as a function of the temperature. The influence of the phase transition on this $\Theta_D$ - $T$ curve is much more sensitive than that on the heat capacity curve itself, so the ambiguities in the estimation of the " normal " lattice part of the heat capacity are considerably reduced when we utilize $\Theta_D$ - $T$ relationship for this purpose. The assumed dotted line in this figure is for the temperature variation of the normal heat capacity. The procedure adopted above for estimating the normal heat capacity is, of course, not severely rigorous, but it may be nevertheless looked upon as a convenient method for determining the effect of phase transitions on the total heat capacity.

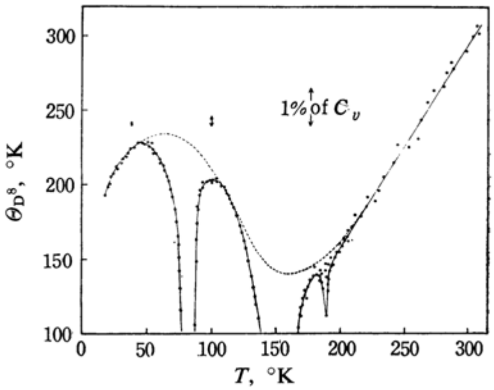

Fig. 7. Debye temperature versus temperature curve of KCN crystal, taking degree of freedom as 8.

Having excluded the effect of the phase transition, we shall now try to separate the torsion-rotational heat capacity. The principal difficulty encountered in an analysis of a heat capacity curve in an effort to determine frequencies other than those of the lattice vibration arises from the necessity for an accurate representation of the heat capacity of the lattice itself. This difficulty is minimized by assuming that the contribution from the translational degree of freedom to the heat capacity of the present crystal is well represented by the heat capacity of a suitable alkali halide crystal. The $\Theta_D$-$T$ curves of potassium chloride and potassium bromide[16] were selected as references since they are crystals of a similar nature with no torsional degree of freedom. Figure 8 summarized the variations of the Debye temperatures for potassium chloride, potassium bromide and potassium cyanide crystals. In this figure, the wide temperature variations of $\Theta_D$ for potassium chloride and potassium bromide crystals are a consequence of the procedure in which the heat capacity of the alkali halide crystal, with 6 $N$ degrees of freedom, is expressed by a single Debye temperature. It is presumably possible to describe the total heat capacity by a combination of the Einstein function with a single value of the Einstein temperature for the 3 $N$ degrees

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** The results of our calculations will be given in a later paper. At any rate, it is desirable to determine the ordered arrangement of cyanide ions by an experimental method such as the neutron diffraction technique.

[14] L. A. Siegel, *J. Chem. Phys.*, **11**, 1146 (1949).

[15] A. Maki and J. C. Decius, ibid., **31**, 772 (1959); F. A. Miller and C. H. Wilkens, *Anal. Chem.*, **24**, 1253 (1952).

[16] W. T. Berg and J. A. Morrison, *Proc. Roy. Soc.*, **A242**, 467, 478 (1957).

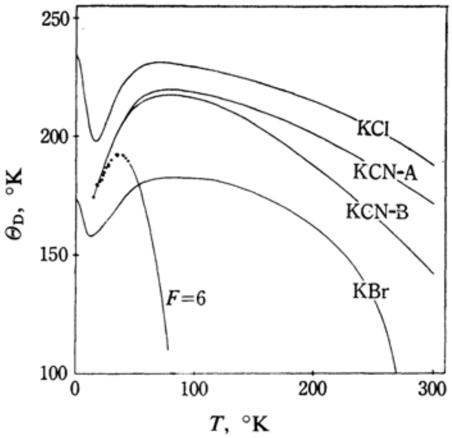

Fig. 8. Debye temperatures of KCl, KBr and KCN crystals as functions of temperature, A and B indicating the assumed upper and lower limits for KCN.

of freedom (optical modes), and the Debye function with a single value of the Debye temperature for the other 3 $\boldsymbol{N}$ degrees of freedom (accoustic modes), both characteristic temperatures being temperature-insensitive. If one assumes only 6 $\boldsymbol{N}$ translational degrees of freedom in the computation of the $\Theta_D$ of the potassium cyanide crystal, one obtains a steeply declining curve (the $F=6$ curve in Fig. 8). This decrease can be regarded as the result of a progressively-increasing torsional contribution of the cyanide ions. The hypothetical $\Theta_D$ curve of potssium cyanide, if there were no torsional modes, would go somewhere between the $\Theta_D$ curves of potassium chloride and potassium bromide. Two curves (KCN-A and KCN-B) in Fig. 8 are such hypothetical extrapolations from the low temperature region; this seemed to be a reasonable spread. Actually, the choice of either of the two does not make any significant difference in the evaluation of the torsion-rotational contribution, since $\Theta_D$ is far more sensitive than the heat capacity itself.

In Fig. 9 we compare the calculated and the observed torsion-rotational heat capacities. In the low temperature region, the observed torsional heat capacity values lie well on the calculated curve based on the model of two independent harmonic oscillators with the wave number of 160 cm$^{-1}$. For the harmonic oscillator approximation, this torsional frequency corresponds to 7.5 kcal. mol$^{-1}$ of barrier height if we employ the usual cosine-type hindering potential. As the temperature is raised, the difference between them becomes progressively more conspicuous; there can never be any model which explains the difference as long as we retain a simple harmonic oscillator

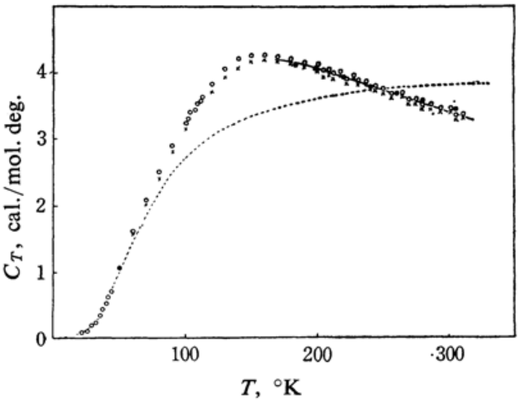

Fig. 9. Torsion-rotational heat capacity of cyanide ions in KCN crystal.
○ Observed values (case A)
× Observed values (case B)
---- $\omega=160$ cm$^{-1}$ two simple harmonic oscillators
—— $V=1300$ cal./mol. two-dimensional
● $V=1350$ cal./mol. hindered rotator

model. One satisfactory explanation of the torsion-rotational heat capacity may, however, be given by a hindered rotator model. It is well known by Pitzer's treatment[17] that the heat capacity of a hindered rotator can rise to a maximum value greater than $\boldsymbol{R}$ cal. deg$^{-1}$ per rotational degree of freedom and then falls off with an increase in the temperature, approaching the $1/2\,\boldsymbol{R}$ cal. deg$^{-1}$ per degree of freedom, the value for a classical free rotator.

This treatment was recently extended to the two-dimensional hindered rotator by Stepakoff and Coulter[18] with adequate approximations. The application of their results to the present case shows that the rotational heat capacity in the cubic phase may be well represented by the contribution from the two-dimensional hindered rotator with a barrier height of 1.30—1.35 cal. mol$^{-1}$ over a wide temperature range. This barrier height agrees well with the theoretical calculation by Matsubara and Nagamiya.[3] (In passing, we should like to point out that a recent study of the potassium cyanide crystal by Elliott and Hastings,[19] using neutron diffraction techniques, led them to the conclusion that the free rotational model is satisfactory for the cubic phase. Their analysis, however, has entirely neglected the Debye-Waller temperature factor in calculating the intensity data. Accordingly, we may say that their model may not be looked upon as conclusive.)

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

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

[19] N. Elliott and J. Hastings, *Acta Cryst.*, **14**, 1018 (1961).

The rotational heat capacity data in the intermediate temperature region, however, can never be represented by a single value of barrier height, even with the two-dimensional hindered rotator model. It varies continuously from 7.5 kcal. mol$^{-1}$ at 60°K to 1.40 kcal.mol$^{-1}$ at 168°K. This continuous variation in barrier height merely reflects the continuously varying estimated " normal " heat capacity. Actually, the barrier height would change abruptly with the phase transition phenomenon accompanying an abrupt volume change. Although such variation in the barrier height can not be clarified quantitatively and in detail by an analysis of the heat capacity data alone, and although the present model is merely a very simple one, a variation in barrier height with the temperature does not seem to be at all improbable. Actually, the crystal is subject to thermal expansion in a single phase, and the lattice parameter changes abruptly at the transition point. A simple calculation of the hindering potential demonstrates easily that a slight decrease in the lattice constant causes a marked change in the barrier height, since the repulsive part of the hindering potential varies with the inter-atomic distance, $r$, in the $r^{-9}$ form.[20] Such situations differ distinctly from the case of the internal hindered rotation of methyl groups in ethane, for example, where the hindering potential arises from its intramolecular interaction and is, therefore, very insensitive to the temperature variation.

These results may be summarized as follows. In the lowest temperature region, the cyanide ions undergo torsional oscillation with the wave number of 160 cm$^{-1}$. As the temperature is raised, this torsional motion is gradually excited, the barrier height diminishing gradually in a single phase or abruptly via the transition points; the torsional motion changes into a hindered rotational motion with a barrier height of approximately 1.35 kcal. mol$^{-1}$ in the cubic phase, and eventually into the state of free rotation at much higher temperatures.

## Summary

The heat capacities of the potassium cyanide crystal have been measured over the temperature range from 13 to 310°K by using a low temperature adiabatic calorimeter. It has been found that there are two regions of anomalous heat capacity, with maxima at 82.9±0.2°K and 168.3±0.1°K respectively. The heats and entropies of transition have been evaluated by utilizing a $\Theta_D$-versus-temperature plot. The entropy of the lower transition amounts to about $\boldsymbol{R}\ln 2$, which means that the transition is due to the orientational order-disorder rearrangement of the cyanide ion with respect to its head and tail. A perfectly-ordered structure for the orientation of the cyanide ions has been suggested. A certain small anomaly in heat capacity has been found around 190°K, one which seems to be associated with some change in higher-order structural defects created by the upper transition phenomenon.

The torsion-rotational heat capacity of the cyanide ions has been separated from the total on some reasonable assumptions. The results show that the cyanide ions below the lower transition point are subjected to torsional oscillation with the wave number of about 160 cm$^{-1}$, a value which corresponds to the barrier height of 7.5 kcal. mol$^{-1}$ based on a simple harmonic oscillator model. On the other hand, they are in a hindered rotational state with a barrier height of approximately 1.35 kcal. mol$^{-1}$ in the cubic phase, the barrier height diminishing from 7.5 kcal. mol$^{-1}$, gradually in a single phase or abruptly via the transition points.

The thermodynamic functions for this crystal have been evaluated by integrating the heat capacity data. The values at 298.15°K are, in units of cal. mol$^{-1}$ deg$^{-1}$: $C_p^\circ=15.84$, $S^\circ=30.71$, $(H^\circ-H_0^\circ)/T=13.94$ and $-(G^\circ-H_0^\circ)/T=16.77$ respectively.

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[20] L. Pauling "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1940), p. 355.