Neutron diffraction study of KCN III and KCN IV at high pressure*

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The high-pressure polymorphs of KCN, KCN III, and KCN IV, have been investigated by neutron diffraction using a polycrystalline sample. High-resolution intensity data have been obtained which confirm the structural description of KCN III but contradict the description of KCN IV suggested by previous high-pressure x-ray work. At a pressure of 25 kbar and at room temperature, KCN IV has a monoclinic structure with the $Cm(C_s^3)$ space group in which the C and N nuclei lie nearly along the body diagonal of a slightly distorted cube of K^+ ions. The conclusion from the x-ray work that KCN IV is rhombohedral is contradicted both by our intensity data and by the fact that several of the diffraction lines are displaced slightly from rhombohedral positions. Increase of the temperature from 66 to 74 °C at a pressure of 22 kbar results in the transformation from phase IV into the cubic phase KCN III with the space group $Pm3m(O_h^1)$ in which the CN^- molecules are ordered randomly along the eight equivalent [111] directions. The temperature factors in KCN III are unusually large indicating a high probability of a CN^- ion jumping between equilibrium positions along the eight diagonal configurations.

I. INTRODUCTION

The pressure-temperature phase diagram of KCN has been reported[1-3] and is shown over a restricted P-T range in Fig. 1. Recent neutron-diffraction measurements[4] confirm that the I-V phase line shown by Pistorius *et al.*[2] is in error as suggested in the note added in proof in that paper and thus it is not shown here. The high-pressure polymorphs KCN III and KCN IV, have been examined by means of x-ray powder techniques[5,6] in an opposed anvil type apparatus, but the limitations of the data left some uncertainty in the structure assignments. Richter and Pistorius[6] report KCN III as cubic, probably space group $Pm3m(O_h)$ but their intensity data could not be used to confirm this space-group assignment which was based on analogy arguments from measurements on CsCN and TlCN. They also suggested that the CN^- ions are disordered in KCN III, undergoing either a hindered rotation within the cubes of K^+ ions or a rapid reorientation among the eight equivalent positions along the four body diagonals. This latter structure could lead to a configuration entropy of $R \ln 8$. Neutron-diffraction measurements[4,7] in KCN I strongly suggest that the rotation model is incorrect. Pistorius[5] reported the KCN IV structure to be rhombohedral with the space group $R\bar{3}m(D_{3d}^5)$ and suggested that the linear CN^- ions are oriented but not ordered along the body diagonal. Again the intensities of the x-ray lines could not be used to help determine the space group. The space-group assignment was made using arguments from measurements on CsCN and a possible orientation entropy of $R \ln 2$.[8]

In order to clarify some of the uncertainties in the understanding of these high-pressure phases of KCN, we felt it of interest to measure the diffrac-

tion patterns of KCN III and KCN IV (Ref. 9) with the high-pressure neutron-diffraction apparatus[10] now at the CP-5 facility at Argonne. Our measurements confirm the structural description of KCN III but contradict the description of KCN IV suggested by previous high-pressure x-ray work. KCN III is cubic with the space group $Pm3m(O_h^1)$, while KCN IV is monoclinic with the space group $Cm(C_s^3)$ rather than rhombohedral.

Measurements at different pressures and temperatures in phase IV yield a value of $\alpha = (0.22 \pm 0.06) \times 10^{-3} \, °C^{-1}$ for the volume thermal expansion and $\kappa = (1.43 \pm 0.33) \times 10^{-3} \, kbar^{-1}$ for the isothermal volume compressibility in this phase. The volume change between KCN III and KCN IV is $0.38 \pm 0.07 \, cm^3/mole$ at 22 kbar. This may be compared to Bridgman's value[1] of $0.22 \, cm^3/mole$ at 23 kbar from a piston-displacement measurement and Richter and Pistorius's value[6] of $0.49 \, cm^3/mole$ at 30 kbar from high-pressure x-ray-diffraction work. From our measurement and the slope of the III-IV phase line (0.21 kbar deg^{-1}),[2] the entropy change between these two phases is calculated as $R \ln 2.62$.

The measurement at 22 kbar and 66 °C falls in the region previously reported as KCN III (Ref. 2) and, indeed, we found that the KCN IV → III transition had begun at this temperature and pressure. The most intense KCN III peak, (110), was resolved although barely perceptible in the predominantly KCN IV diffraction pattern.

II. EXPERIMENTAL

A high-purity KCN single crystal which was obtained from Susman and Hinks[11] was crushed with a mortar and pestle, loaded into a die inside a glove box, and pressed into pellets of 0.63-cm
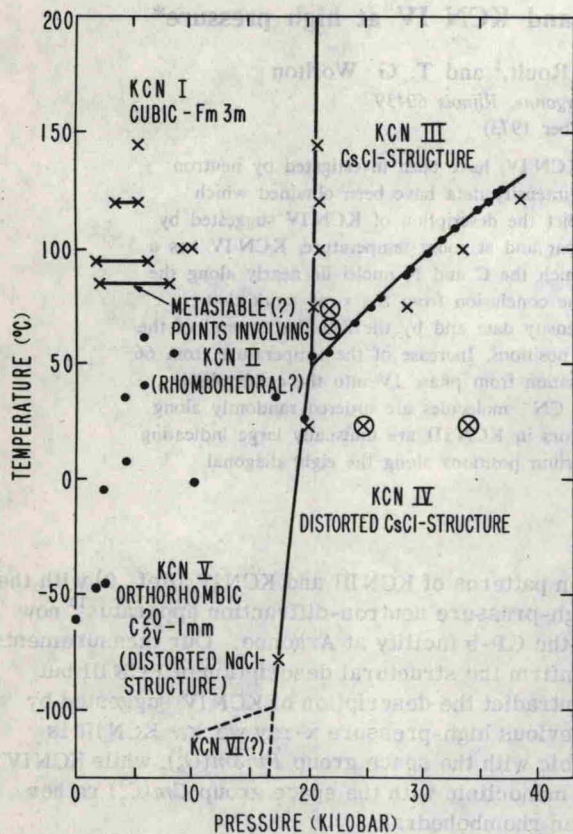
FIG. 1. Phase diagram of KCN for a restricted pressure-temperature range. The ⊗'s mark the P-T points corresponding to the measurements reported here. All other symbols are associated with phase boundary determinations as reported in Ref. 2.

diameter. The pressure apparatus, a double acting piston in cylinder, has been described previously.[9,12] The only new feature was the method of heating the pressure chamber and sample and the temperature control. Water from a large heated bath was pumped through channels in an aluminum jacket around the binding ring. A thermocouple in contact with the outside of the Al_2O_3 pressure chamber was used in a feedback circuit to control an auxiliary heater that kept the thermocouple reading constant to within ± 2 °C.

The pressure at the sample was determined from a calibration of the pressure cell. This was accomplished by making several diffraction measurements of either pure NaCl in the sample chamber or mixtures of materials containing NaCl. The pressure was determined from the NaCl lattice spacing using Decker's equation of state.[13] In all cases the pressure versus load was repeatable to within ± 0.5 to 30 kbar.

The neutron beam time-of-flight techniques have also been described.[12,14] The time-of-flight spectrometer was calibrated by taking diffraction pat-

terns of Si and Ge (Ref. 15) in the same position as the KCN sample. Diffraction spectra of KCN were taken at the P-T points indicated in Fig. 1. The collection time for the KCN measurements ranged from 28 to 88 h.

The phase changes in our pressure system were clean and sharp with complete disappearance of phase I at 25 kbar and room temperature and complete disappearance of phase IV at 74 °C and 22 kbar. The IV → III transition had barely begun at 66 °C and 22 kbar. These are indications of a good quasihydrostatic environment which is necessary in order to get meaningful intensity data from a powder sample for which one requires there be no preferential orientation of the crystallites.

III. RESULTS AND ANALYSES OF THE DIFFRACTION PATTERNS

Time-of-flight (TOF) neutron-diffraction patterns with scattering angles of 60° are compared in Figs. 2 and 3 for KCN III and KCN IV. The data were initially analyzed by fitting the peaks individually by a least-squares analysis to determine peak position and intensity. Tables I and II show that the positions of the diffraction peaks observed for KCN III are accurately indexed in terms of a simple cubic lattice, while some of the peak positions for KCN IV are displaced slightly from their exact rhombohedral values. This indicates that the actual structure of KCN IV is distorted from rhombohedral symmetry.

To further analyze the TOF data we wrote a computer program that yielded a least-squares fit to the entire spectrum assuming the diffraction peaks are superimposed on a Maxwellian background plus a time-independent background. The count rate, y_i, in the ith time channel is then

$$y_i = b + M(\lambda_i)$$
$$+ \sum_h \alpha_{\vec{h}} \exp \frac{(-4\ln2)(d_i - d_{\vec{h}})^2}{S_i^2}$$
$$+ v \sum_{\vec{h}} f_{\vec{h}'} \exp \frac{(-4\ln2)(d_i - d_{\vec{h}'})^2}{S_i^2}, \quad (1)$$

where b is the time-independent background; λ_i is the neutron wavelength scattered into channel i; $M(\lambda_i) = \beta d_i^{-\lambda} e^{-\delta/\lambda_i^2}$ is a Maxwellian intensity function with three variable parameters β, γ, and δ used to fit the time-dependent background; d_i is the wavelength scattered into channel i divided by the factor $2\sin\theta$, where 2θ is the scattering angle (30° or 60°); and S_i is the instrumental linewidth at half-peak height for each channel. The symbols $\vec{h}$ and $\vec{h}'$ stand for the Miller indices (hkl) for the KCN peaks and for the Al_2O_3 peaks, respectively, which might be present in the pattern. The calculated plane spacings for KCN and Al_2O_3, $d_{\vec{h}}$ and $d_{\vec{h}'}$, respectively, are determined from the lattice param-