gested by the argument that KCN III is similar to KCN I in which the large motional amplitude for the K^+ ions appears to be associated with the local dilatations accompanying the rotational motions of the CN^- ion.[4] In KCN IV the ordering of the CN^- molecules is more complete, and it is likely that these rotational motions are largely absent. Consequently, the local dilatations of the K^+ ions should be absent also.

Results for the computer fit to a third diffraction pattern for KNC IV (22 kbar, 66 °C) are also summarized in Table IV. The value obtained for the monoclinic cell angle, $\cos\beta = 0.0596 \pm 0.0007$, when compared with the corresponding value from the measurement at 25 kbar 23 °C, $\cos\beta = 0.0771 \pm 0.0003$, shows that the distortion from the cubic KCN III structure decreases as the IV-III phase boundary is approached. The small value for the C–N bond length, 1.02 ± 0.08 Å has a large uncertainty associated with it and is suspect due to the presence of weak KCN III peaks in the KCN IV diffraction pattern.

An attempt was also made to fit the KCN IV data (25 kbar 23 °C) using the rhombohedral space group $R3m(C_{3v}^5)$. This introduces an additional positional parameter in comparison with the fit to $R\bar{3}m(D_{3d}^5)$ since the C and N positions are now allowed to vary independently. However, the fit was different from that described for the space group $R\bar{3}m$ insofar as the fitting program was modified to include the effect of preferential line broadening due to a domain size effect following an analysis procedure for domain line broadening for single-crystal x-ray diffraction carried out by Evenson and Barnett.[21] Although the resultant fit reproduced the observed line shapes very well it could not account for the displacement of observed peak positions discussed above. This fit also could not account for the observed intensity of the diffraction line with rhombohedral indices (221). This is the discrepancy already pointed out in the monoclinic analysis, since the monoclinic pair (401), (312) corresponds to the rhombohedral (221) line in the undistorted cell. The goodness-of-fit ratio for this analysis (5.3) was significantly worse than the corresponding ratio for the monoclinic analysis (3.7).

V. DISCUSSION AND CONCLUSION

The KCN III phase seems to be understood reasonably well. The crystal structure is cubic with the space group $Pm3m(O_h^1)$. The diffraction peak intensities are well represented assuming a disordered crystal with the CN^- ion randomly distributed over the eight diagonal configurations. The temperature factors are unusually large indicating a high probability of the CN^- ion jumping between equilibrium positions. The large motional amplitude for the K^+ ions may be caused by local dilatations accompanying the rotational motions of the CN^- ion. This dynamical picture is very similar to that proposed for KCN I.[4]

The KCN IV phase is more difficult to interpret definitively. There is some displacement of the (100) and (200) peaks from their exact rhombohedral positions (~0.014 and 0.007 Å, respectively) which, although small, is well outside the accuracy of the experiment. This indicates some distortion of the rhombohedral structure. A centered monoclinic lattice with the space group $Cm(C_s^3)$ gives a good fit to the diffraction pattern.

Two features of the monoclinic analysis of the KCN IV phase stand out. First, the C and N atoms are ordered in the $Cm(C_s^3)$ space group, in which ferroelectricity is allowed. Possible evidence for this is the fact that the (200), (111) monoclinic pair shows line broadening in excess of the instrumental line width (Fig. 5), which may be due to the presence of domains in the monoclinic structure, with the implication of ferroelectric behavior. Second, the temperature factors for the K^+ and CN^- ions B_K and B_{CN}, are smaller in KCN IV than KNC III. The large temperature factors in KCN III are probably due in large part to the molecular libration which is present in this disordered system, so it is not surprising that the value for B_{CN} decreases upon passing to KCN IV where the CN molecules are much more ordered. It seems likely that the rotational motions of the rod-shaped CN molecules are largely absent in KCN IV. This would imply the absence of the local dilatations of the K^+ lattice present in a disordered system as KCN I.[4] This picture is consistent with our result that $B_K \approx 0$ in KCN IV.

Some intensity discrepancies remain. For the two orders of the (001), (110) monoclinic pair which were observed, the observed intensity for the (001) line is lower than allowed by the fit using the space group $Cm(C_s^3)$. The calculated intensities for the monoclinic pairs (401), (312) and (200), (111) which are not in particularly good agreement with the diffraction pattern collected at 25 kbar and 23 °C (Fig. 5) give a very poor fit to the diffraction pattern collected at 34 kbar, which also shows a similar discrepancy for the second-order reflection of the (200), (111) pair. These discrepancies may indicate the presence of preferred orientation in KCN IV or may be due to an inadequacy in the assumed model.

Results for measurements in phase IV at two different temperatures (Table IV) indicate that the C–N bond length may contract as the temperature is increased in phase IV. However, the value for the bond length obtained from the measurement at higher temperature (1.02 ± 0.08 Å) has a large uncertainty associated with it and is suspect due to the presence of weak KCN III peaks in the KCN IV

diffraction pattern. Further increase of the temperature results in the transformation into the cubic phase III in which the C–N bond length has lengthened to 1.23 ± 0.02 Å, a value which is slightly higher than the original value for the bond length 1.14 ± 0.06 Å in phase IV at room temperature. This result could be independently checked by infrared spectroscopy. It is also apparent from Table IV that the C and N nuclei lie nearly along the body diagonal of a slightly distorted cube of K^+ ions in the C_s^3 structure. This is exactly the case if $x_N = z_N$ and $x_C = z_C$ and even though the ratio of x/z in these analyses was completely free the best fit to that data gives a value close to unity.

ACKNOWLEDGMENTS

We wish to thank W. E. Evenson and J. D. Barnett for providing us with a copy of their domain-broadening theory prior to publication and we wish to thank Sherman Susman for the KCN sample material. One of us (D. L. D) wishes to express thanks to the Office of Educational Affairs at Argonne for the fellowship which allowed him to work on this project at Argonne. One of us (G. R.) would like to express his appreciation to Argonne National Laboratory for the opportunity to stay at Argonne while this project was carried out.

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*Based on work performed under the auspices of U. S. Atomic Energy Commission.

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