Neutron powder diffraction study of phase transitions and structures of $(KCN)_x(KBr)_{1-x}$ mixed crystals

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The structures of $(\text{KCN})_x(\text{KBr})_{1-x}$ mixed crystals for x=0.95, 0.90, and 0.80 have been determined as a function of temperature. As the temperature is decreased from 295 K, where all of the samples are cubic (as are pure KCN and KBr), all samples measured transform to a monoclinic structure (space group Cc). For x=0.95 and 0.90, at a lower temperature there is a further transition to an orthorhombic structure similar to that found for pure KCN below 168 K. However, the samples do not transform completely, and the monoclinic and orthorhombic structures coexist down to 6 K. More of the sample transforms for x=0.95 than for x=0.90. In both cases, that part of the sample which goes into the orthorhombic phase orders completely at the lowest temperatures, in a structure similar to that found for pure KCN at 6 K.

INTRODUCTION

Pure KCN has a cubic structure¹⁻⁵ (NaCl type) for temperatures between its melting point and 168 K, with the linear $(CN)^{-}$ ions achieving the required symmetry by rapid reorientation⁶ in the site of octahedral symmetry. At 168 K, there is a first-order phase transition⁷ to a body-centered orthorhombic structure⁸ (space group Immm) in which the molecular axes align along the b axis, but the small dipole moments of the $(CN)^{-}$ ion remain disordered. At 83 K there is an order-disorder transition,⁷ in which the $(CN)^{-1}$ ions begin to order completely, so that the lowest temperature structure⁹ is "antiferroelectric" (space group Pmnm). In addition, a monoclinic structure has been observed^{10,11} in a limited temperature range for pure KCN subjected to repeated thermal cycles. At 295 K, KCN and KBr have very similar lattice parameters (6.523 and 6.578 Å, respectively), and solid solutions can be formed over the entire concentration range of KBr in KCN. It has been observed¹² that as KBr is added to KCN the temperature of the upper phase transition is lowered, reaching about 85 K for x = 0.6. For x < 0.6, however, no transition is observed, and the crystal remains cubic down to the lowest temperatures. It has been assumed that for x > 0.6, the lowtemperature structure was the same as that observed for pure KCN.

In the present paper we present the results of an investigation of the crystal structure and phase transitions of $(KCN)_x(KBr)_{1-x}$ for x=0.8, 0.9, and 0.95, using the technique of neutron powder diffraction and Rietveld refinement.¹³ The results and analysis are presented in the next section, and a discussion of their interpretation is given in the final section.

RESULTS AND ANALYSIS

The samples of $(KCN)_x(KBr)_{1-x}$ were prepared by grinding solid boules of the appropriate concentration in a

mortar and pestle in a controlled atmosphere. The concentrations prepared were x = 0.80, 0.90, and 0.95. The samples were then loaded into aluminum cans in a helium atmosphere and sealed with indium O rings. The temperature-dependent measurements were performed using both controlled-temperature cryostats and closed-cycle helium refrigerators. Temperature control and calibration in all cases was to ± 1 K. The neutron-diffraction patterns were recorded on the high-resolution five-detector diffractometer at the National Bureau of Standards (NBS) research reactor using collimations of 20'-20'-10' before and after the monochromator and after the sample, respectively. Estimates of the phase-transition temperatures were taken from Ref. 12, and measurements were performed in the cubic phase just above the transition temperature and then at lower temperatures, first to check the transition temperatures and then to determine the structure as a function of temperature.

The results can be summarized by the following.

(1) For each concentration, the transition temperature observed was consistent with those given in Ref. 12 within the uncertainties (~ 3 K) of the present measurement ($T_c = 123$, 142, and 156 K for x = 0.8, 0.9, and 0.95).

(2) The structure observed just below (2-5 K) the transition temperatures was monoclinic (space group C_c). The details of the structures are given below.

(3) For x = 0.8, the monoclinic structure persisted down to the lowest temperatures measured (~ 4 K).

(4) For x = 0.90, part (~5-10%) of the sample transformed between 135 and 140 K to an orthorhombic structure to that found for pure KCN. The fraction of sample transformed was essentially constant below 140 K, and both the monoclinic and orthorhombic phases were present down to 6 K.

(5) For x = 0.95, a large part ($\sim 60-70\%$) of the sample transformed to the orthorhombic structure starting at $T \approx 140$ K. Below 130 K, no further transformation was seen down to 9 K, and both phases were present.





FIG. 1. Observed neutron-diffraction pattern for $(KCN)_{0.95}(KBr)_{0.05}$ at 9 K. The line is only a guide to the eye. The labels on the first few peaks denote the dominant contributions from the orthorhombic (*o*) and monoclinic (*m*) phases. Note the small peak near 17.0 degrees which shows that the orthorhombic phase is fully ordered in an antiferroelectric structure. The apparent step in the background near an angle of 30° is the result of changing from detector 1 to detector 2.

(6) For both x = 0.90 and 0.95, that portion of the sample which transformed to the orthorhombic (*Immm*) structure ultimately transformed to the low-temperature *Pmnm* structure, as shown by the measured diffraction pattern at 9 K. No estimate of the temperature at which this last transition occurred could be made because of the weakness of the characteristic superlattice reflection.⁹

Because of the complexity of the patterns obtained when both monoclinic and orthorhombic structures were present (in these mixed-phase regions the peak shapes were badly distorted, presumably due to strain), the only analysis possible was to determine approximate lattice parameters for the orthorhombic structures. An example of the patterns observed is shown in Fig. 1. These lattice parameters were determined by fitting orthorhombic peaks well removed from any monoclinic peaks with the results shown in Table I. However, there is a reasonably large uncertainty in the absolute values obtained, especially for the x = 0.90 samples where the orthorhombic peaks are rather weak. As can be seen from the table, the lattice parameters are monotonic functions of Br concentration, with *a* and *c* increasing and *b* decreasing with Br concentration.

For all concentrations, we have analyzed the pure monoclinic phases using the Rietveld technique of refinement.¹³ The starting point for refinement of these patterns was the monoclinic structure reported for pure KCN (Ref. 10) after repeated thermal cycles around the 168-K phase transition. This structure was solved by Parry,¹¹ from an x-ray diffraction study of a single crystal with many domains, by relating the symmetry of the domains formed to the original cubic system. It was found to be stable for the thermally cycled KCN between 158 and 165 K. Below this temperature, the normal orthorhombic structure began to appear, but some of the monoclinic phase persisted down to 153 K. Since this behavior is very reminiscent of what is observed in the present study of $(KCN)_{x}(KBr)_{1-x}$, we indexed the observed monoclinic patterns on this same basis. Although the lattice parameters required to index the mixed crystal patterns were somewhat different from those reported by Parry, this structure allowed us to index all peaks. In order to apply the Rietveld refinement program, we have relabeled the structure in a standard setting, i.e., we have interchanged the a and c axes as reported by Parry. The space group is then Cc with two formula units per primitive unit cell. Parry was not able to assign the orientations of the (CN)⁻ ion from his results, but inferred from steric considerations that it must be near a [203] direction. (This direction corresponds to a [111] direction in the cubic unit cell.) Within the Cc space group, one can choose the x and z positions for potassium to be zero in order to define an origin. This leaves the monoclinic cell parameters (a, b, c, and β), the K y displacement and thermal factor, and the C, N, and Br x, y, and z displacements and thermal factors as crystallographic parameters. In order to reduce the of overall number parameters, we constrained

TABLE I. Lattice parameters of $(KCN)_x(KBr)_{1-x}$ in the orthorhombic phases. The numbers in parentheses are the estimated precisions, which should be good estimates of relative changes.

x	<i>T</i> (K)	a (Å)	b (Å)	c (Å)	Volume per formula unit (Å)
1.0ª	90	4.21(1)	5.20(1)	6.11(1)	66.3
	6	4.18(1)	5.24(1)	6.07(1)	66.5
0.95	77	4.236(2)	5.173(2)	6.154(2)	67.5
	9	4.210(2)	5.207(2)	6.113(2)	67.0
0.90	77	4.244(2)	5.144(7)	6.163(4)	67.3
	9	4.222(2)	5.197(4)	6.133(2)	67.2

^a Reference 9.

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	Т		a	b	с	β	r _{CN}
x	(K)	S°	(Å)	(Å)	(Å)	(deg)	(Å)
1.0	170	c ^g	7.96	4.59	9.18	125.3	1.19
	165	m^{h}	7.47	4.53	8.97	122.3	1.19
	90	oj	8.02	4.21	10.40	130.4	1.19
	6	oj	8.02	4.18	10.48	130.8	1.19
0.95	153	m	7.59	4.60	9.18	122.3	0.81 ^k
	77	0	8.04	4.34	10.34	130.1	
	6	0	8.03	4.21	10.41	130.4	
0.90	140	m	7.60	4.60	9.20	122.4	1.08 ^k
	77	0	7.48	4.24	10.29	129.9	
	9	0	7.45	4.22	10.39	130.3	
0.80	110	m	7.65	4.60	9.19	122.7	1.00 ^k
	77	m	7.58	4.59	9.19	122.3	1.10 ^k
	6	m	7.54	4.59	9 17	122.1	1 15 ^k

TABLE II. Structural parameters for low-temperature $(KCN)_x(KBr)_{1-x}$ in monoclinic cell. Note that for all parameters presented in this study, the precision is ± 1 in the last digit quoted.

^aCN position is the center of molecule.

 ${}^{b}R_{w} = \left[\sum_{i} w_{i}(I_{m} - I_{c})^{2} / \sum_{i} w_{i}I_{m}^{2}\right]$, where I_{m} (I_{c}) are measured (calculated) intensities and w_{i} is the statistical weight; R_{e} is the ex-

pected value of R_w ; R_B is the R factor for Bragg peaks only (no background).

^cS represents c (cubic), m (monoclinic), and o (orthorhombic).

 $^{d}x, y$, and z are fractional coordinates (some fixed by symmetry).

 ψ is the angle between the c axis and the projection of the CN axis on an a-c plane.

 ${}^{\mathrm{f}}\phi$ is the angle between the CN axis and the *a*-*c* plane.

^gReferences 4 and 5.

^hReference 13.

ⁱ[203] direction; would be [111] axis in cubic cell.

^jReference 9.

^kUncorrected for libration.

 $\vec{r}_{Br} = \frac{1}{2}(\vec{r}_C + \vec{r}_N)$, and the C, N, and Br thermal factors were set equal and constrained to be isotropic. In addition, since there is likely to be disorder in $(CN)^-$ orientations, we allowed for partial occupancy of sites by either C or N and refined the background (in five segments, corresponding to the five detectors). The line-shape parameters of the BT-1 diffractometer were fixed during the refinements to values determined by fitting to well-resolved peaks in standard samples.

The results of the refinement procedure are summarized in Table II, which also includes the results found for pure KCN (Refs. 10 and 11) and for the orthorhombic structures (Ref. 9 and this work, Table I) expressed in terms of a monoclinic structure. The relationship of the orthorhombic and cubic unit cells to the monoclinic cell is shown schematically in Fig. 2. Since no preferred orientation of $(CN)^{-}$ ions was indicated by the fitting procedure. the results for $(CN)^-$ positions are given in terms of the location of the center of the molecule, and its orientation with respect to the c axis and the a-c plane. No thermal factors are shown in the table since we do not believe that the results are reliable, mainly because of inadequate background determination, but also because of the neglect of anisotropy, which must be present in these parameters. The effect of libration can clearly be seen in the values of the C-N distances shown, which are consistently low, suggesting large rotational motions in this phase. This in turn implies that anisotropic temperature factors are required to correctly model this structure. However, use of such factors would greatly increase the number of parameters and so was not attempted. No strong correlation with the parameters given in the table were observed. Samples of the quality of fit obtained are shown in Fig. 3 for x = 0.95, 0.90, and 0.80, at temperatures slightly below the cubic-monoclinic phase boundary. This figure shows that there may be some line broadening (perhaps as a result of strain).

Finally, in Table III the cell volumes determined for the cubic and monoclinic phases at temperatures very near their phase boundary are given. As can be seen, the volume change near the transition decreases monotonically with increasing Br concentration, going nearly to zero at x = 0.80, in accord with the results for the pressure dependence of transition temperatures reported by Lüty¹² and with the predictions of the Clausius-Clapeyron equation.¹⁴

DISCUSSION

The results shown in Table I for the Br concentration dependence of the lattice parameters in the orthorhombic

3509

K	C	CN ^a or E	Br	CN ori	entation	Cell volume	R	factors ^b	(%)
y ^d	<i>x</i> ^d	y ^d	z ^d	ψ^{e} (deg)	$\phi^{\rm f}$ (deg)	(Å)	R_w	R _e	R_B
0.00	0.50	0.00	0.25			272.1			
0.05	0.50	0.00	0.25	33.7 ⁱ	0.0	256.6			
0.00	0.50	0.00	0.25	0.0	0.0	267.4			
0.00	0.50	0.00	0.25	0.0	0.0	266.0			
0.07	0.53	0.00	0.26	50.8	-16.7	270.3	15.2	9.0	22.7
0.00	0.50	0.00	0.25	0.0	0.0	269.7			
0.00	0.50	0.00	0.25	0.0	0.0	268.0			
0.03	0.52	0.00	0.26	39.7	-40.6	271.5	10.7	7.4	10.3
0.00	0.50	0.00	0.25	0.0	0.0	269.1			
0.00	0.50	0.00	0.25	0.0	0.0	269.1			
0.04	0.53	0.00	0.26	41.9	- 39.4	272.0	11.9	7.3	15.5
0.02	0.54	0.00	0.25	33.7	-40.6	270.3	12.0	6.3	15.9
0.04	0.49	0.00	0.25	31.8	-42.7	268.8	12.5	6.2	12.3

TABLE II. (Continued.)

phase can be readily interpreted in terms of the reported shape of the $(CN)^-$ ion,⁸ an ellipse of semiaxes 2.15 and 1.78 Å, and the ionic radius of Br⁻, 1.95 Å. The Br⁻ radius is thus less than one semiaxis of the $(CN)^-$ ion and larger than the other.

In order to estimate the magnitude of the effect of adding KBr to KCN, we consider pure KCN (in the orthorhombic phase) and pure KBr, both referred to orthorhombic axes, and calculate the rate of change of a, b, and c with BR concentration. The results of this estimate are $\Delta a / \Delta n_{\rm Br} = +0.4$ Å, $\Delta b / \Delta n_{\rm Br} = -0.6$ Å, and $\Delta c / \Delta n_{\rm Br} = +0.4$ Å, in satisfactory agreement with the results shown in Table I. Thus the changes in the orthorhombic lattice parameters observed for $(KCN)_x(KBr)_{1-x}$ can be readily understood by linear interpolation between pure KCN and pure KBr, i.e., by the difference in shape between (CN)⁻ and Br⁻ ions. In Fig. 1, which shows the observed pattern for x = 0.95 at 9 K,

FIG. 2. Schematic representation of monoclinic and orthorhombic unit cells referred to original cubic axes. Monoclinic cell is in solid lines; orthorhombic cell is in dashed lines.

the small peak at approximately 17° is the (010) superlattice line, showing that that part of the sample which transformed to an orthorhombic structure is completely ordered at low temperature, as was found⁹ for pure KCN.

The results for the monoclinic structures, as summarized in Tables II and III, cannot be interpreted as readily as those for the orthorhombic structures. However, several points can be noted. First, the structure proposed by Parry¹¹ for pure KCN subjected to thermal cycling is very similar to that found here for the mixed halidecyanide system. This suggests that strain is responsible for the stabilization of this structure relative to the orthorhombic structure. Second, since neutron diffraction is more sensitive to C and N in the presence of K and Br than is x-ray diffraction, we were able to determine the $(CN)^{-}$ orientations in this phase, and find that they are tipped out of the cubic [111] direction proposed by Parry by angles between 10° and 40° (ϕ in Table II). This result has important implications for the interpretation of other measurements on these systems. Third, we find no tendency for the dipole moment of the $(CN)^-$ ions to order down to 9 K, even though the space group is compatible with either ferroelectric or antiferroelectric ordering. This may be of relevance to the lack of dipole order¹² in RbCN, which also has the monoclinic structure in its lowtemperature phase. A calculation of the predicted ordering temperature in this phase would be very useful to illuminate this point, since an ordered structure would presumably be stable at low temperatures, but might be blocked by kinetic effects (the slowing down of reorientation times with decreasing temperature). Preliminary measurements on RbCN (Ref. 15) show that the structure is quite similar to those reported here.

The differences in volume at the cubic-monoclinic transition shown in Table III correlate qualitatively with the observed trends in $\partial T_c /\partial P$ reported by Lüty.¹² In particular we observe that $\Delta V = 0.03$ at x = 0.80, in accord with the near vanishing of $\partial T_c /\partial P$ observed for x = 0.79 and with the predictions of the Clausius-Clapeyron¹⁴ equation.



FIG. 3. Examples of the data and results of profile refinement (parameters in Table II) obtained for x = 0.95, 0.90, and 0.80 at temperatures just below the cubic \rightarrow monoclinic transitions. The apparent broadening of some peaks at higher angles may be the result of strain. The apparent step in the background near an angle of 30° is the result of changing from detector 1 to detector 2.

TABLE III. Volume per formula unit for $(KCN)_x(KBr)_{1-x}$ in monoclinic and cubic unit cells at the phase-transition temperatures.

	0.95	0.90	0.80
Cubic (Å ³)	68.28	68.30	68.13
Monoclinic (Å ³)	67.58	67.87	68.10
T_{c} (K)	155	145	122
ΔV (Å ³)	0.70	0.43	0.03

However, when this equation is used to estimate ΔS , the entropy change at the transition, the values obtained are larger by factors of 3–5 than those reported in either Ref. 12 or Ref. 7. The most probable origin of this effect is lattice strains introduced by the transformation, as discussed by Cimino, Parry, and Ubbelohde¹⁰ in connection with the normal transition from the cubic to the orthorhombic phase, and the appearance of the monoclinic phase in pure KCN. Indeed, they have pointed out the similarities of the transitions in pure KCN to martensitic

transformations, and the coexistence of the high- and low-temperature phases in thermally strained KCN. A similar mechanism is undoubtedly responsible for the coexistence of orthorhombic and monoclinic phases in the samples with x=0.95 and 0.90 at low temperatures. It might well be expected that the relative amounts of the two phases present would be related to sample size and shape (and thermal history), so that different samples would have different behavior. It is clear, however, that the samples enter the *monoclinic* phase first upon cooling

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from the cubic phase for $x \le 0.95$. In addition, we have observed that the samples always go completely monoclinic before transforming to the cubic phase as the temperature is raised. Our results suggest that *only* the monoclinic phase will be found for $x \le 0.80$.

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