

Neutron powder diffraction study in the mixed molecular system $(\text{NaCN})_{1-x}(\text{KCN})_x$

T. Schröder and A. Loidl

Institut für Physik, Universität Mainz, D-6500 Mainz, Federal Republic of Germany

T. Vogt

Institut Laue-Langevin, F-38042 Grenoble, France

(Received 29 August 1988)

A detailed structural analysis of $(\text{NaCN})_{1-x}(\text{KCN})_x$ mixed crystals with $x=0.02, 0.19, \text{ and } 0.95$ was performed by neutron powder diffraction. The structural parameters of the cubic phases were refined, applying a model of preferred orientations. Different noncubic low-temperature phases were observed for $x=0.02$ and 0.95 . For $x=0.02$ the antiferroelectric ordering of CN^- dipoles at low temperatures is accompanied by significant alkali-alkali and alkali- CN^- sublattice shifts. Structural data are presented together with previous results for mixed crystals with $x=0.59$ and 0.85 and well-known results for the pure cyanides NaCN and KCN .

I. INTRODUCTION

In the past years mixed molecular systems of the types $(\text{MH})_{1-x}(\text{MCN})_x$ and $(\text{ACN})_{1-x}(\text{BCN})_x$, where H is a halide, A and B are alkali-metal ions, have been established as subjects of intense interest in physics of disordered materials. The dominant features of these systems are due to the rotational degrees of freedom of the aspherical CN^- molecules which change the usual properties of familiar pure alkali-halide ionic systems in a radical way. At present the mixed cyanides are discussed as model systems as well for structural phase transitions as for orientational glass formation.¹⁻⁴ The high-temperature pseudocubic structures of the alkali cyanides are stabilized by fast reorientations of the CN^- molecules. While NaCN , KCN , and RbCN exhibit a rocksalt type of structure in the high-temperature plastic phase, CsCN shows a CsCl structure. Depending on the concentration x the low-temperature state is characterized either by a long-range orientational order of the CN^- molecules (causing noncubic crystalline phases) or by orientationally disordered frozen-in CN^- molecules. In the latter case, diffraction experiments^{5,6} suggested that the mean cubic structure is unchanged. However, depending on the strength of the coupling of the rotational degrees of freedom to the translational modes, the long-range cubic order is disturbed. At present it is unclear to what extent the low-temperature glass state is characterized by a breakdown of long range order. The concentration-dependent crossover from noncubic low-temperature phases to the orientational glass states of cubic symmetry defines the critical concentrations x_c .

In the past, the behavior of the mixed cyanides, especially the frequency-dependent glass transition, was treated analogous to a spin-glass transition, where the freezing-in is dominated by frustrated interactions.⁴ Discussing the orientational glass state and the polymorphism as featuring properties of mixed molecular systems, recently published theoretical and experimental work of Michel,⁷ Lewis *et al.*,⁸ Civera-Garcia *et al.*,⁹ and Galam¹⁰ favor a treatment of the dominating physical

mechanisms in terms of random-strain fields. The nature of the low-temperature state in mixed cyanides seems to be determined by the strength of two competing interactions: the competition of strain rotation coupling (SRC) and translation rotation coupling (TRC) depends both on the concentration x and on the temperature. The amplitude of the static random-strain fields is directly related to the volume difference of the substitutional ions in the mixed crystals.⁷

By experimental work in $(\text{NaCN})_{1-x}(\text{KCN})_x$ (Ref. 11) these theories are supported in particular because earlier concepts of frustration, due to random dilution of the CN^- sublattice and due to the anisotropic CN-CN interaction, are not applicable for this system. Random-strain fields are implanted by the substitution of K^+ ions ($r_{\text{K}^+} = 1.33 \text{ \AA}$) by the much smaller Na^+ ions ($r_{\text{Na}^+} = 0.98 \text{ \AA}$) on the alkali sites, while the CN^- sublattice is completely preserved. For an intermediate concentration range $x_{c1} \leq x \leq x_{c2}$ (with $x_{c1} = 0.15$ and $x_{c2} = 0.89$) this leads to an orientational glass state. No structural information exists for the concentration ranges where noncubic low-temperature states are supposed. To elucidate the effects of the interplay between SRC and TRC on the low-temperature structures we performed neutron-powder diffraction studies on mixed crystals with different concentrations.

II. EXPERIMENTAL

Single crystals of $(\text{NaCN})_{1-x}(\text{KCN})_x$ with $x = 0.02, 0.19, 0.95$ were grown from the melt using the Czochralski technique. They were supplied by J. Albers from the Fachbereich Physik of the Universität des Saarlandes. Due to the liquid-solid phase boundaries¹² the true concentration of the single crystals grown differs from the nominal composition of melt. The change of composition of melt during the process of crystal growth and the eventual separation of carbon create concentration gradients in the single crystal. In Ref. 13 the connection between the composition of melt and the composition of single crystals is published in more detail. As-

suming the validity of Vegard's rule^{14,15} for the concentration-dependent room-temperature lattice constant we determined the actual concentration of the mixed crystals. The values for NaCN and KCN were obtained by averaging over the room-temperature lattice constants published in literature. The concentrations determined are in reasonable agreement with the expected deviations from the composition of melt (Fig. 1). The absolute error in concentration should be in the order of 1%.

The powder samples were prepared by grinding pieces of the single crystals with mortar and pestle in a controlled rare-gas atmosphere. In the same atmosphere they were loaded into vanadium cans of 16-mm diameter which were sealed with indium. The temperature was controlled by a conventional He-flow cryostat with an accuracy of about 0.1 K. Neutron-powder diffraction measurements were recorded on the high-resolution multicolimator diffractometer D1A located on a thermal neutron guide at the Institut Laue Langevin (ILL) Grenoble.¹⁶ The incident neutron wavelength was 1.909 Å and the scattering angle 2θ ranged from 18° to 150°.

III. RESULTS AND ANALYSIS

The powder profiles have been analyzed using the Rietveld technique of structural refinement.^{17,18} Special efforts were made to analyze the cubic phases of the mixed crystals. It is necessary to assume that the linear CN⁻ ions achieve effective cubic symmetry either by rotation or by disorder of their angular orientation. In comparison to carbon and nitrogen, both sodium and potassium have small scattering lengths, so that the diffraction intensities are largely determined by the orientation and motion of the cyanide group. The correspond-

ing strong decrease of Bragg intensities at higher scattering angles reduces the information considerably. Single-crystal diffraction studies in the pure cyanides NaCN and KCN by Rowe *et al.*¹⁹ and in (KBr)_{1-x}(KCN)_x mixed crystals by Loidl *et al.*⁶ lead to a model of preferred orientations of the CN⁻ axis, in contrast to either complete (free) rotation²⁰ or exclusive orientation in a particular direction.²¹ To analyze our data of cubic phases in the (NaCN)_{1-x}(KCN)_x mixed crystals we tested two models. Refinements of a rather simple model with summed scattering lengths of C and N placed at the molecular center of mass of the CN⁻ ion yielded unphysical large mean-square displacements. It was necessary to treat carbon and nitrogen as discrete scattering centers. Furthermore, the model of preferred orientations was applied. Within this model the orientational probability is developed in linear combinations of spherical harmonics which are invariant against cubic symmetry operations. The so-called cubic harmonics are listed by Altmann and Cracknell.²² Considering the limited number of cubic reflections, the lack of information required the refineable parameters to be reduced. In all refinements performed, the isotropic temperature factors were assumed to be of equal size for the CN⁻ and the K⁺, Na⁺ ions, respectively. This ansatz is suitable, because anisotropic refined temperature factors did not increase the goodness of fits in a significant way and separately refined temperature factors agreed within the estimated deviations.^{6,19}

A. Results for (NaCN)_{0.81}(KCN)_{0.19}

Figure 2 shows the diffraction pattern of a mixed crystal with a concentration $x = 0.19$. The spectra of differences between the best fits of the Rietveld structural refinement and the experimental data points are also

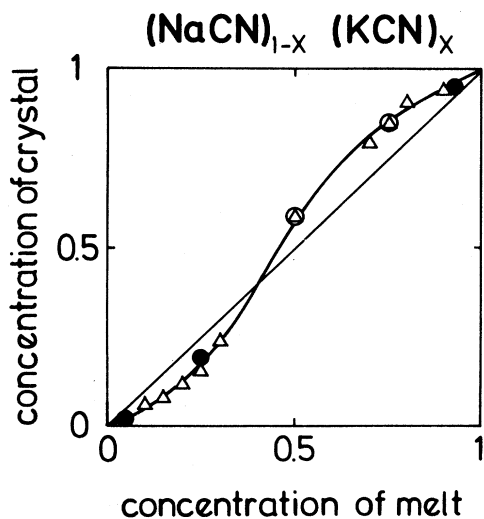


FIG. 1. Molar concentration x of mixed crystals (NaCN)_{1-x}(KCN)_x versus the molar concentration x of melt: crystals grown in Saarbrücken (●) and in Utah (Ref. 13) (△); concentrations determined by room-temperature lattice constant in this work (●) and in Ref. 5 (○) and atomic absorption spectrophotometry in Ref. 13 (△).

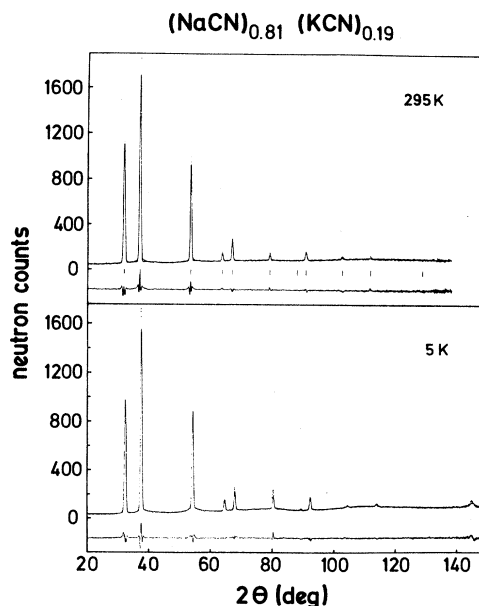


FIG. 2. Powder diffraction data of (NaCN)_{0.81}(KCN)_{0.19} recorded at high and low temperature. Calculated data and deviations from observed data are presented by solid lines.

shown. The structural parameters of all the samples investigated are listed in Table I together with the parameters derived in an earlier work.⁵ Results as obtained in the pure cyanides NaCN and KCN (Refs. 19 and 23–26) are also included in Table I. The agreement of fits is given by a weighed R factor: $R_w = \{\sum_i [w_i(I_{i\text{obs}} - I_{i\text{calc}})^2] / \sum_i w_i(I_{i\text{obs}}^2)\}^{1/2}$; w_i denotes the usual weight factor. All refinements were performed using Gaussian line shapes only. The measured profiles, however, show significant nonGaussian contributions centered around the Bragg positions, as can be seen from the difference pattern of the refinements. At high temperatures these contributions are due to thermal diffuse scattered intensities, while for low temperatures they arise from frozen-in strain fields. This results in R_w values which are conspicuously high. However, they are in the order of magnitude of R_w values given in Refs. 27 and 28 for structural refinements of other mixed cyanides.

As stated above, it was indispensable to treat C and N as discrete scattering centers, which reduced the isotropic B factors to reasonable values. In addition, we assumed not only an isotropic distribution of C and N around the center-of-mass position, but we too applied the model of preferred orientations of the CN^- molecule, as mentioned above. The orientational probability was developed in terms of cubic harmonics up to order 6. However, because of extremely large estimated deviations (twice as large as the value of the coefficient), the coefficient of the linear combination of spherical harmonics with $l=6$ was not significant. Moreover, the orientational probability of CN^- ions shows a sharp minimum along $\langle 111 \rangle$ direction. Limitation to the term of order 4 did not affect the results of refinement qualitatively. As illustrated in Fig. 3, the most probable orientation points along $\langle 100 \rangle$ followed by a relative maximum along $\langle 110 \rangle$ direction and a minimum but nonzero probability along $\langle 111 \rangle$. While a predominant orientational probability along $\langle 100 \rangle$ could also be determined from room-temperature measurements in pure NaCN,¹⁹ the minimum along $\langle 111 \rangle$ stands in contrast to the relative maxima in NaCN and absolute maxima along $\langle 111 \rangle$ found for pure KCN and $(\text{KBr})_{1-x}(\text{KCN})_x$ mixed crystals.⁶ However, one has to keep in mind that our results are determined from powder-diffraction profiles only, in comparison to the more reliable single-crystal data of Refs. 6 and 19. The CN^- bond length was determined to $l=1.189 \text{ \AA}$ and fits well with the room-temperature values for various mixed cyanides published in literature.^{6,19}

As expected from the phase diagram of Ref. 11, the sample with $x=0.19$ stays cubic down to the lowest temperature. The mean-cubic structure is no longer stabilized by fast reorientations of the CN^- molecules, but rather by CN^- molecules frozen-in without long-range orientational order, as already shown for $x=0.85$ and $x=0.59$.⁵ The parameters refined are listed in Table I. A stronger preference of the $\langle 100 \rangle$ orientations with decreasing temperatures is a significant result. The appearance of diffuse scattering intensities centered around the cubic Bragg reflections suggest that the freezing process is characterized by the freezing-in of long-wavelength lat-

tice strains coupled to the orientational degrees of freedom. This was studied by single-crystal neutron diffraction in more detail.²⁹

B. Results for $(\text{NaCN})_{0.05}(\text{KCN})_{0.95}$

For a mixed crystal close to pure KCN the powder profiles recorded at room temperature and 5 K are shown in Fig. 4. The actual concentration was determined to $x=0.95$.

Again the cubic high-temperature structure was refined using the model of preferred orientations. The parameters determined are listed in Table I. The coefficients of cubic harmonics obtained in the refinements give quite different orientational probabilities of the CN^- axis than do those observed for $x=0.19$. While for $x=0.19$ the CN^- axis shows preferred orientations, for $x=0.95$ the orientational probability is nearly isotropic (see Fig. 5). At room temperature the coefficient γ_4 of the cubic harmonic of order 4 is significantly smaller than those observed for $x=0.02$ and $x=0.19$. This is in qualitative agreement with the fact that the values of γ_4 were found to change sign from pure NaCN to pure KCN.¹⁹ For the pure cyanides γ_4 values, given in Table I, were taken from Ref. 19. Thus the most probable orientation of the CN^- axis changes from pointing along $\langle 100 \rangle$ directions for pure NaCN to $\langle 111 \rangle$ directions for pure KCN. However, the discrepancy in the absolute values between $x=0$ and $x=0.02$ given in Table I signals that our results are of qualitative character only.

The 5 K profile indicates that the crystal transformed into a noncubic low-temperature state that unequivocally could be identified as a pure orthorhombic phase generated by a uniform shear deformation of the previous cubic structure. At 5 K, the shear distortion caused by ferroelastic order of the CN^- molecules reaches $\Delta\beta=11.73^\circ$, where $\Delta\beta$ is the change in one of the cubic rectangles. The structural analysis showed that the ground state is of bc-orthorhombic symmetry (space group $Immm$) characterized by parallel-arranged CN^- molecules pointing along the previous cubic $\langle 110 \rangle$ directions. In analogy to the findings in $x=0.19$, the CN^- bond length showed a significant temperature dependence and decreased from 1.178 \AA at room temperature to 1.125 \AA at 5 K. Antiferroelectric order of CN^- dipoles as observed for the ground state of pure KCN (Refs. 6 and 30) should cause superlattice reflections, especially an additional (010) peak at smaller scattering angles arising from the appropriate cell doubling. But for $x=0.95$ no additional superlattice reflections are detectable. The CN^- molecules are ferroelastically ordered but remain dipolar disordered down to the lowest temperature. Obviously, even a small amount of 5% Na^+ ions randomly diluted in KCN is able to suppress the antiferroelectric phase transition of KCN. The suppression of the electric ordering process can be interpreted as a direct consequence of the presence of random-strain fields.

C. Results for $(\text{NaCN})_{0.98}(\text{KCN})_{0.02}$

The powder-diffraction patterns for a Na^+ -rich mixed crystal recorded at room temperature, at an intermediate

TABLE I. Structural parameters of $(\text{NaCN})_{1-x}(\text{KCN})_x$ -mixed crystals. Parameters from refinements of powder diffraction studies presented in this work are listed together with published results (see footnotes). $\Delta\beta$ denotes the shear angle of one of the cubic 90° angles caused either by ferroelastic or antiferroelectric order of the CN^- molecules along the previous cubic $\langle 110 \rangle$ directions. l denotes the CN bond length, γ_4 is the coefficient of the cubic harmonic of order 4 which is defined in spherical coordinates by $X_4 = (\frac{7}{12})^{1/2} Y_{40}(\theta, \phi) + (\frac{5}{12})^{1/2} [Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)] / \sqrt{2}$. The positions x, y, z are given in terms of the lattice parameters a, b, c . For the orthorhombic phases the volumes are given with respect to the previous cubic cells. The numbers in parentheses are the estimated standard deviations.

x	T (K)	Structure	a (Å)	b (Å)	c (Å)	Vol (Å ³)	$\Delta\beta$ (deg)	
0	295 ^a	fc-cubic	$Fm\ 3m$	5.88		203.30	0.0	
	5 ^b	p-ortho	$Pmnm$	3.6221(2)	4.8289(2)	5.4467(3)	190.58(4)	16.24(1)
0.02	295	fc-cubic	$Fm\ 3m$	5.891(1)			204.4(1)	0.0
	170	bc-ortho	$Immm$	3.7005(3)	4.7733(3)	5.5696(4)	196.76(4)	14.42(1)
	5	p-ortho	$Pmnm$	3.6448(2)	4.8254(2)	5.4822(2)	192.86(4)	15.86(1)
0.19	295	fc-cubic	$Fm\ 3m$	5.993(1)			215.26(7)	0.0
	5	fc-cubic	$Fm\ 3m$	5.916(1)			207.03(7)	0.0
0.59	280 ^c	fc-cubic	$Fm\ 3m$	6.234(6)			242.3(7)	0.0
	2 ^c	fc-cubic	$Fm\ 3m$	6.164(4)			234.2(5)	0.0
0.85	280 ^c	fc-cubic	$Fm\ 3m$	6.389(6)			260.8(7)	0.0
	2 ^c	fc-cubic	$Fm\ 3m$	6.300(4)			250.1(5)	0.0
0.95	295	fc-cubic	$Fm\ 3m$	6.472(1)			270.7(1)	0.0
	5	bc-ortho	$Immm$	4.1857(2)	5.1461(3)	6.0786(3)	261.86(4)	11.73(1)
1	295 ^d	fc-cubic	$Fm\ 3m$	6.523(1)			277.6(1)	0.0
	151 ^d	bc-ortho	$Immm$	4.2681(3)	5.1418(3)	6.1835(4)	271.33(4)	10.61(1)
	5 ^d	p-ortho	$Pmnm$	4.1916(2)	5.2573(2)	6.0832(3)	268.11(4)	12.86(1)

x	T (K)	γ_4	x	y	z	x	y	z	l (Å)	R_w (%)	
0	295	0.192(8) ^e	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.189 ^e	13.2	
	5		0	0.219(1)	0 (K,Na)	0.5	0.872(1)	0 (C)	1.159(5)		
							0.5	0.632(1)	0 (N)		
0.02	295	0.34(4)	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.198(4)	14.3	
	170		0	0	0 (K,Na)	0.5	0.620(1)	0 (C or N)	1.172(5)	11.9	
	5		0	0.221(1)	0 (K,Na)	0.5	0.380(1)	0 (C or N)			
						0.5	0.870(1)	0 (C)	1.162(6)	12.9	
						0.5	0.630(1)	0 (N)			
0.19	295	0.24(3)	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.189(4)	8.1	
	5	0.57(4)	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.150(4)	10.9	
0.59	280		0	0	0 (K,Na)	0.5	0.5	0 (CN)			
	2		0	0	0 (K,Na)	0.5	0.5	0 (CN)			
0.85	280		0	0	0 (K,Na)	0.5	0.5	0 (CN)			
	2		0	0	0 (K,Na)	0.5	0.5	0 (CN)			
0.95	295	0.07(3)	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.173(3)	8.7	
	5		0	0	0 (K,Na)	0.5	0.609(1)	0 (C or N)	1.125(5)	13.7	
							0.5	0.391(1)	0 (C or N)		
1	290	-0.132(22) ^e	0	0	0 (K,Na)	0.5	0.5	0 (CN)	1.177 ^f		
	151		0	0	0 (K,Na)	0.5	0.609(1)	0 (C or N)	1.121(5)	15.64	
							0.5	0.391(1)	0 (C or N)		
	5		0	0.273(1)	0 (K,Na)	0.5	0.860(1)	0 (C)	1.157(5)	14.98	
						0.5	0.640(1)	0 (N)			

^aAveraged values from References 23–26.

^bPreliminary results from Reference 31.

^cResults for mixed crystals from Reference 5.

^dResults from Reference 38.

^eReference 19.

^fReference 6.

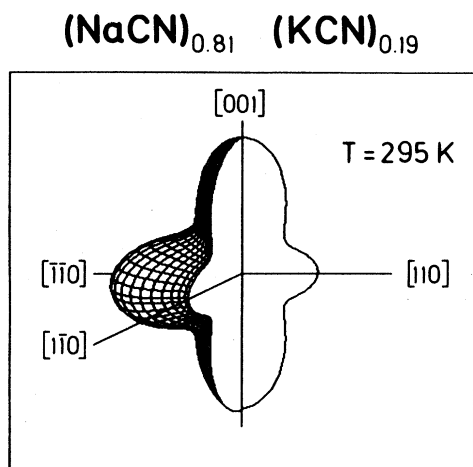


FIG. 3. Fraction of the three-dimensional orientational probability of CN^- axis in $(\text{NaCN})_{0.81}(\text{KCN})_{0.19}$ at 295 K. For a particular direction the density of C or N atoms at the sphere with the CN bond length in diameter is proportional to the radius vector of the corresponding point in the surface. The most probable orientation is represented by the maximum along the $[001]$ direction.

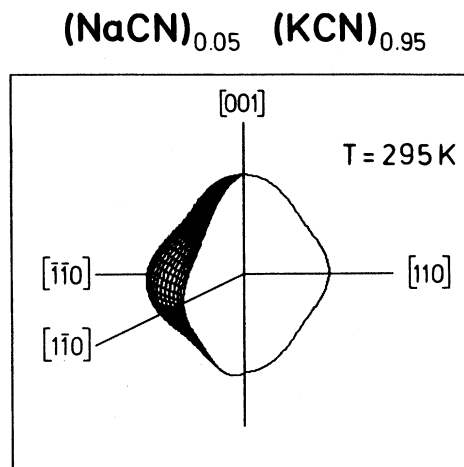


FIG. 5. Orientational probability of the CN^- molecule calculated from parameters for $(\text{NaCN})_{0.05}(\text{KCN})_{0.95}$ at 295 K. The figure demonstrates that the orientational distribution as determined from the powder diffraction data is nearly isotropic.

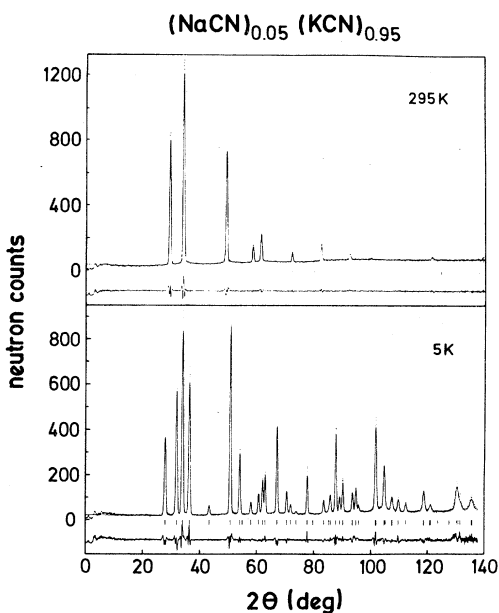


FIG. 4. Powder diffraction data for $(\text{NaCN})_{0.05}(\text{KCN})_{0.95}$ recorded at high and low temperature. At 5 K the profile is fitted with a pure bc orthorhombic structure only. The absence of a super lattice reflection at lower scattering angles indicates that the CN^- dipoles remain dipolar disordered down to the lowest temperatures. Calculated data and deviations from observed data are presented by solid lines.

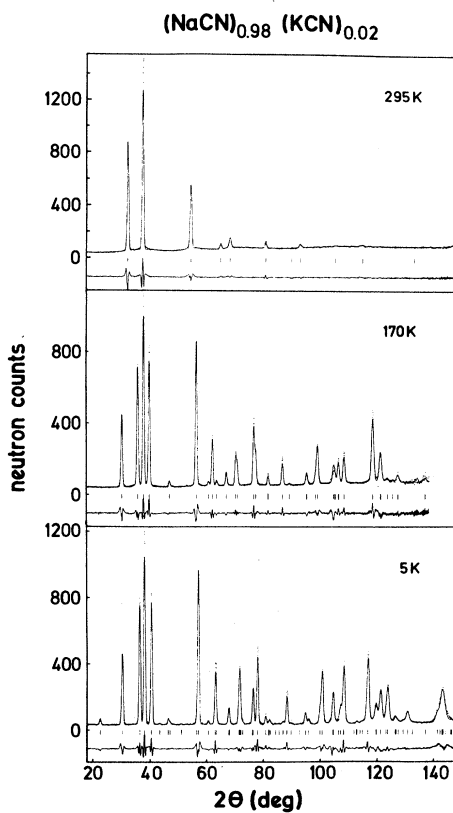


FIG. 6. Powder diffraction pattern compared with calculated intensities and deviations (solid lines) for $(\text{NaCN})_{0.98}(\text{KCN})_{0.02}$ recorded at three different temperatures. At 5 K the superlattice reflection appearing around 23° indicates that the CN^- dipoles are antiferroelectrically ordered.

temperature and at the lowest temperature are presented in Fig. 6. The analysis of the high-temperature phase gave an actual concentration of $x = 0.02$. However, the orientational behavior of the CN^- ion did not fit with the observations in NaCN ,¹⁹ but is nearly identical with the orientational distribution for $x = 0.19$ shown in Fig. 3.

Passing through an intermediate phase of orthorhombic symmetry (space group $Immm$) with ferroelastic ordered CN^- orientations, at lower temperatures this crystal transforms to a primitive orthorhombic structure (space group $Pmnm$). As indicated by the (010) superlattice reflection observed around $2\theta = 23^\circ$, the low-temperature ground state is characterized by antiferroelectrically ordered CN^- dipoles. Both of the orthorhombic phases are described by uniform shear distortions of the cubic high-temperature phase. The shear angle caused by parallel order of the CN^- molecules and by the additional antiferroelectric order is $\Delta\beta = 14.43^\circ$ at 170 K and $\Delta\beta = 15.87^\circ$ at 5 K, respectively. The appearance of these subsequent phase transitions is in agreement with the findings in the pure cyanides KCN (Refs. 6 and 27) and NaCN.³⁰

But furthermore, the refinement of the antiferroelectrically ordered phase shows a significant shift of the CN^- and alkali sublattices against one another. Figure 7 shows a Fourier projection down to the [100] direction using the observed structure factors F_{obs} measured at 5 K and the calculated phases. Taking into account that the transition from ferroelastic to antiferroelectric order is of second order, we suspected that the sublattice shift might be an artifact of incomplete electric order of the CN^- dipoles at 5 K. Therefore, we simulated gradual order by refining C and N occupation numbers, too. Although we started from different initial parameters for the atomic positions, every structural refinement led to a reproducible shift of sublattices and the initial disorder parameters shifted towards lower values. The observed cationic displacements along the [010] direction reach $\delta_1 = 0.14 \text{ \AA}$ (2.9% of the corresponding lattice constant) and are demonstrated in Fig. 7 by the solid and dotted-dashed lines. The off-center shift of alkali-alkali sublattices is indicated by $\delta_2 = 0.28 \text{ \AA}$. These results are in agreement with our previous experiments in NaCN (Ref. 31) but they are in contradiction to the findings of Fontaine for pure NaCN (Ref. 32) and of Rowe *et al.*²⁷ for pure KCN. Refining their data, Rowe *et al.* for KCN and Fontaine for NaCN claimed a y value of 0.25 for the $2a$ position in $Pmnm$, which implies a complete superposition of the two sublattices so that no shifts could be observed by these authors. For the low-temperature ground state of NaCN and KCN, static cationic displacements were implicated by atomic positions documented in the Ph.D thesis of Fontaine³³ but the author neither commented nor published these effects. The shift $\delta_1 = 0.15 \text{ \AA}$, derived from atomic positions given for NaCN, is in good agreement with the results for $(\text{NaCN})_{0.98}(\text{KCN})_{0.02}$ presented in this paper. To explain the antiferroelectrically ordered low- T phase in the pure cyanides NaCN and KCN, Pirc and Vilfan³⁴ developed a dynamic model based on the assumption of an interaction between permanent CN^- dipoles and dipoles induced by lattice vibrations. In this

context Koiller *et al.*³⁵ presented a simple model that includes collective static cationic displacements which predict the antiferroelectrically ordered dipolar configuration observed for the low-temperature ground states of NaCN and KCN. Within this model for increasing static cationic displacements, the electrostatic energy of the observed antiferroelectric arrangement decreases more strongly than the energy of alternative configurations, while simultaneously an increasing term of an (repulsive) elastic energy arises. The minimum of the sum over both of these energies defines an equilibrium displacement δ_1 .

IV. CONCLUSION

For the mixed molecular system $(\text{NaCN})_{1-x}(\text{KCN})_x$, a detailed structural analysis by Rietveld refinement of neutron-powder-diffraction data is presented for three different concentrations. Two other concentrations have been studied previously. In the case of cubic phases (especially the high-temperature plastic rotator phase) a model of preferred orientations was applied to refine the structural parameters. The angular orientation of the CN^- axis was expanded in a series of symmetry-adapted spherical harmonics. As a consequence of the limited number of observed cubic Bragg reflections, only the fourth-order term was considered. The orientational distribution of the Na-rich and the K-rich mixed crystals are quite different. For $x = 0.02$ and $x = 0.19$ at room temperature, the maximum orientational probability points along $\langle 100 \rangle$ followed by a relative maximum

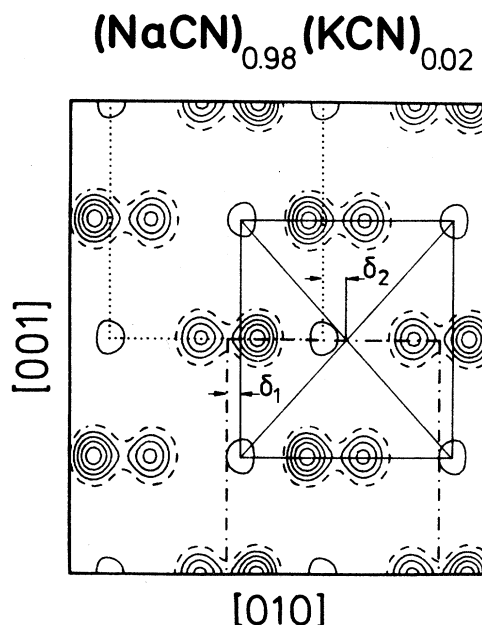


FIG. 7. Fourier projection down to (100) plane of the observed structure factor F_{obs} with the calculated phases for $(\text{NaCN})_{0.98}(\text{KCN})_{0.02}$ at 5 K. Considering the differences of scattering lengths ($b_{\text{N}} > b_{\text{C}} > b_{\text{Na}} \approx b_{\text{K}}$) the contours of the scattering densities allow one to distinguish between C, N, and K or Na. The different distances $d_{\text{alkali-N}} < d_{\text{alkali-C}}$ and the corresponding off-center shift of alkali-alkali sublattices are demonstrated.

along $\langle 110 \rangle$ and a minimum—with finite orientational probability—along $\langle 111 \rangle$. For $x = 0.95$ the orientational distribution of the CN^- axis is nearly isotropic. It was shown for pure KCN (Ref. 19) and $(\text{KBr})_{1-x}(\text{KCN})_x$ mixed⁶ cyanides that at room temperature the $\langle 111 \rangle$ orientations are most probable. The suppression of the $\langle 111 \rangle$ orientational probability is a striking feature of $(\text{NaCN})_{1-x}(\text{KCN})_x$ mixtures of low concentration. It must be understood as a consequence of the alkali sublattice disorder. The occupation of one of the eight nearest-neighbor sites in octahedral positions by a K^+ ion allows the CN^- molecule only to reorient in the remaining (100) plane, where the nearest neighbors are represented by smaller Na^+ ions only. Thus $\langle 111 \rangle$ orientations are improbable.

While the crystal with $x = 0.19$ stays cubic down to the lowest temperatures for $x = 0.02$ and $x = 0.95$, noncubic low-temperature states were identified. With a concentration close to pure NaCN the mixed crystal with $x = 0.02$ undergoes two subsequent phase transitions which are well known from pure NaCN and KCN, namely from the high-temperature cubic plastic phase ($Fm\bar{3}m$) via a ferroelastically ordered orthorhombic phase ($Immm$) into an antiferroelectrically ordered low-temperature phase ($Pmnm$). The latter one is characterized by CN^- dipoles which are ordered with respect to C and N. This antiferroelectric order-disorder transition is clearly demonstrated by the occurrence of the (010) superlattice reflection.

The refinement of structural parameters for the antiferroelectrically ordered low-temperature phase ($Pmnm$) showed that the dipolar order is accompanied by significant shifts of the alkali-alkali and CN^- -alkali sublattices. This is confirmed by closer inspection of structural parameters, assuming also gradual order during the refinements. Earlier publications of structural parameters of the antiferroelectrically ordered low-temperature phases in alkali cyanides^{30,32} did not mention those shifts, while in his thesis Fontaine³³ presented cationic displacements for the low- T phases of NaCN and KCN determined by neutron powder diffraction, too. The value given for NaCN is in good agreement with the displacements determined for $(\text{NaCN})_{0.98}(\text{KCN})_{0.02}$. The observed sublattice shifts are confirmed by calculations of Koiller *et al.*,³⁵ who showed within a simple model that in pure NaCN and KCN the transition to antiferroelectric order is enabled and accompanied by collective static cationic displacements.

In the case of $x = 0.95$ the CN^- molecules are ferroelastically ordered but remain dipolar-disordered down to the lowest temperatures. Obviously even a random dilution of 5% Na^+ atoms in KCN prevents the mixed crystal from antiferroelectric order caused by the implantation of large random-strain fields. Comparison with familiar mixed molecular systems such as $(\text{KBr})_{1-x}(\text{KCN})_x$ and $(\text{RbCN})_{1-x}(\text{KCN})_x$ with smaller size differences of substituents should demonstrate the influence of random-strain fields on the nature of the low-temperature glass state conclusively. According to this special aspect of dipolar order in mixed cyanides, only meager information is available. In spite of the dilution of the CN^- sublattice (but by Br^- substitutes of comparable size) in $(\text{KBr})_{1-x}(\text{KCN})_x$, the antiferroelectric phase transition survives down to around $x = 0.89$ (Ref. 36), which lies in a monoclinic-orthorhombic coexistence region where only the orthorhombic component is able to establish antiferroelectric order at low T . For $(\text{RbCN})_{1-x}(\text{KCN})_x$ at present no detailed structural information is published. However, the authors of Ref. 37 suggest in their schematic phase diagram a critical concentration of $x = 0.79$ for the antiferroelectric order in this mixed system; i.e., due to the small size difference of Rb^+ ions ($r_{\text{Rb}^+} = 1.48 \text{ \AA}$) and K^+ ions ($r_{\text{K}^+} = 1.33 \text{ \AA}$) a large concentration range with a dipolar-ordered low- T phase for Rb diluted in KCN. To understand the nature of the orientational glass state in mixed cyanides in the past, most attention was paid to the dynamical aspects of the related problems. But studying the concentration-dependent variation of noncubic low- T phases (especially in comparison between familiar mixed molecular systems which differ in the size difference of the substituents) a variety of information should be available to get more insight into the key role possibly played by random-strain fields in these systems.

ACKNOWLEDGMENTS

The authors would like to thank J. K. Cockcroft for making his Rietveld program PROFILE available for all data analysis. This work has been funded by the German Federal Minister for Research and Technology [Bundesminister für Forschung und Technologie (BMFT)] under Contract No. 03-L01MAI-0(C1-56).

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