Random-strain fields in $(KCl)_{1-x}$ $(KCN)_x$

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Powders of $(KCl)_{1-x}(KCN)_x$, $x = 0.9$, 0.8, 0.5, and 0.15, have been investigated by x-ray diffraction at temperatures from 20 to 300 K. The mixed crystal with $x = 0.9$ transforms from the cubic room-temperature phase into a monoclinic intermediate-temperature phase and finally enters a monoclinic-orthorhombic coexistence at low temperatures. For $x = 0.8$, 0.5, and 0.15 a broadening of the cubic lines is observed which is attributed to the formation of the orientational glass state. For $x = 0.8$ the orientational glass coexists with an orthorhombic phase. The results are discussed in terms of random-strain fields.

INTRODUCTION

The mixed alkali-metal cyanides $(KBr)_{1-x}(KCN)_x$, $(KCl)_{1-x}(KCN)_x$, and $(NaCl)_{1-x}(NaCN)_x$ have been the subject of intensive research in recent years, mainly because of the "quadrupolar" or "orientational glass" state[1,2] which has been observed in these compounds at low temperatures for CN concentrations below a crossover concentration x_c.[3] This "glass state" develops out of the crystalline room-temperature phase (NaCl structure with disorder of the CN orientations). It can be regarded as the continuation of the ordered noncubic low-temperature phases observed for $x > x_c$. Hence, the concept of a crystalline lattice is still a suitable and powerful reference and there is hope that the glass state of the mixed cyanides will eventually contribute to the understanding of conventional glasses.

Until recently the "glass" transition in the mixed cyanides has been interpreted as a purely relaxational effect, since both the dipolar and the quadrupolar susceptibilities show a distinct frequency dependence around the freezing temperature.[4] The experimental evidence for the relaxational behavior was particularly convincing for the dipolar response,[5] which, however—according to most recent results—is not involved in the primary freezing process, but rather constitutes what is called secondary or "β relaxation" in glass science.[6] For the quadrupolar, i.e., elastic and structural, behavior of the mixed cyanides, the concept of random stain fields has been propagated in the last months. Michel[7] postulates that these random fields originate from the size differences of the host and substitutionary species in the mixed crystals and achieves an excellent global understanding of the (x,T) phase diagram and the elastic properties. A strong support of Michel's ideas lies in the fact that the orientational glass state has been observed in $(NaCN)_{1-x}(KCN)_x$ too,[8,9] where the usual concept of frustrated CN-CN interactions in combination with the random dilution of the CN sublattice is not applicable. Furthermore we have shown recently that a sample of $(KBr)_{0.38}(KCN)_{0.62}$ can be driven from the noncubic or-

dered crystalline phase into the glass state by thermal cycling rather than by rapid cooling,[10] which we regard as further evidence that static random fields are more essential than relaxing strains. Finally, Lewis and Klein[11] have demonstrated, by computer simulations, that the various polymorphic phases of $(KBr)_{1-x}(KCN)_x$ depend on the Br:CN arrangement on the anion sublattice, i.e., on the pattern of random strains.

In the present article we will report x-ray diffraction experiments on $(KCl)_{1-x}(KCN)_x$, compare the results to those on $(KBr)_{1-x}(KCN)_x$ (Ref. 12) and $(NaCl)_{1-x}(NaCN)_x$,[13] and discuss the observations particularly with respect to the concept of random-strain fields. We recall that in the (x,T) phase diagrams of $(KBr)_{1-x}(KCN)_x$ and $(NaCl)_{1-x}(NaCN)_x$ several noncubic phases have been observed at low T and higher x, $x > x_c$; namely a rhombohedral and an orthorhombic modification for the NaCl-based compound, an orthorhombic, a monoclinic, a triclinic, and a rhombohedral one for the KBr-based compounds. A short report on neutron powder diffraction on $(KCl)_{1-x}(KCN)_x$ has been given by Rowe et al.[14] At low temperatures a triclinic-orthorhombic coexistence has been observed for $x = 0.9$. The cubic-noncubic phase boundary $T_c(x)$ of $(KCl)_{1-x}(KCN)_x$ has been determined by Lüty and co-workers from optical measurements.[3] At $T_c(x)$ the optical transmission decreases by several orders of magnitude due to the formation of the multidomain state of the noncubic phase. Garland et al. have studied the T dependence of the elastic constants of the cubic phase.[15] As in the other cyanides c_{44} softens when approaching $T_c(x)$, a fact which is explained by the linear coupling between the acoustic phonons and the orientational excitations of the CN molecule.[16]

RESULTS

The single crystals of $(KCl)_{1-x}(KCN)_x$, $x = 0.9$, 0.8, 0.5, and 0.15, have been grown from the melt using the Czrochalski technique. The room-temperature lattice parameters are listed in Table I. The experimental

TABLE I. The lattice parameters and the ferroelastic deformations of the noncubic phases.

Concentration	Structure	T (K)	Lattice parameters (Å or deg)	Deformations
0.9	cubic	300	$a = 6.50,$	
	monocl.	110	$a = 9.12,\ b = 4.61,\ c = 7.53$ $\beta = 122.62$	$\epsilon_{xx} = 0.0072$ $\epsilon_{xy} = -0.0057$ $\epsilon_{xz} = 0.0545$
		10	$a = 9.09,\ b = 4.63,\ c = 7.49$ $\beta = 122.44$	$\epsilon_{xx} = 0.0095$ $\epsilon_{xy} = -0.0088$ $\epsilon_{xz} = 0.0590$
	ortho.	80	$a = 5.05,\ b = 4.28,\ c = 6.16$	$\epsilon_{xx} = 0.0226$ $\epsilon_{xy} = -0.0850$
		10	$a = 5.09,\ b = 4.26,\ c = 6.13$	$\epsilon_{xx} = 0.0253$ $\epsilon_{xy} = -0.0910$
0.8	cubic	300	$a = 6.48$	
	ortho	60	$a = 4.77,\ b = 4.42,\ c = 6.24$	$\epsilon_{xx} = 0.0136$ $\epsilon_{xy} = -0.0390$
		20	$a = 4.83,\ b = 4.38,\ c = 6.20$	$\epsilon_{xx} = 0.0162$ $\epsilon_{xy} = -0.0493$
0.5	cubic	300	$a = 6.40$	
0.15	cubic	300	$a = 6.33$	

diffraction setup was the same as in our previous x-ray diffraction measurements on the other mixed cyanides.[12,13] We recall that the powder patterns have been recorded with a linear position-sensitive detector. In some of the following figures the scattering angle 2θ will be given in terms of channels. Twenty-six channels correspond to an arc of 1° in 2θ. Each sample has been investigated with at least three different 2θ settings of the detector. In each of these settings the diffracted intensity has been measured as a function of temperature, usually on cooling down.

x = 0.9

At lower temperatures a splitting of the cubic reflections indicates structural phase transitions. Figure 1 shows the (220) line of the cubic phase and its offsprings at lower temperatures. The corresponding positions of the lines are shown in Fig. 2(a). Two characteristic temperatures, T_{c1} and T_{c2}, can be defined. At T_{c1} the splitting sets in; at T_{c2} additional peaks appear. From the knowledge of the noncubic phases of the other series of mixed cyanides the identification of the low-temperature structures is straightforward. The peaks which develop at T_{c1} can be indexed in terms of the monoclinic structure C_s^4, which is well known as the intermediate phase of thermally cycled KCN,[17] as the low-temperature modification of RbCN,[18] and as the major noncubic phase of $(KBr)_{1-x}(KCN)_x$.[12,19] The monoclinic lattice can be derived from the cubic one by a ferroelastic distortion and an additional staggered displacement of the internal atomic positions.[19] This latter effect

gives rise to additional Bragg peaks at the L points of the formerly cubic Brillouin zone. The position of one of these peaks is included in Fig. 2(a).

The series of new peaks below T_{c2} belong to the orthorhombic structure (Immm or Pmmn), which is well established as the low-temperature phase of KCN, NaCN, and mixed cyanides with high KCN or NaCN content.[12,13,19] As x rays are practically insensitive to the CN orientation in the present system, the experiment cannot decide whether the orthorhombic phase is electrically ordered (Pmmn) or disordered (Immm). Between T_{c1} and T_{c2} the monoclinic phase exists in pure form; below T_{c2} it coexists with the orthorhombic phase. The volume fraction of the orthorhombic phase increases monotonically below T_{c2} and saturates at a value of about 60% at lowest temperatures [Fig. 3(a)]. As the intensities of the orthorhombic peaks are small in the temperature range where they appear first, T_{c2} is not well defined. A value of 100 K seems most appropriate from Fig. 3(a). At the upper characteristic temperature T_{c1}, a hysteresis of 3 K and shifts of the transition upon thermal cycling have been observed. These effects introduce an uncertainty of 5 K to the mean value $T_{c1} = 133$ K. The onset of the monoclinic and the orthorhombic peak positions [Fig. 2(a)] suggests that both transitions are of first order. Clearly the ferroelastic deformation with respect to the cubic parent phase is larger for the orthorhombic structure than for the monoclinic one. The cell parameters and the elements of the ferroelastic deformation tensor, as defined by Aizu,[20] are given in Table I. The cell volumes of the three phases are shown in Fig. 6.

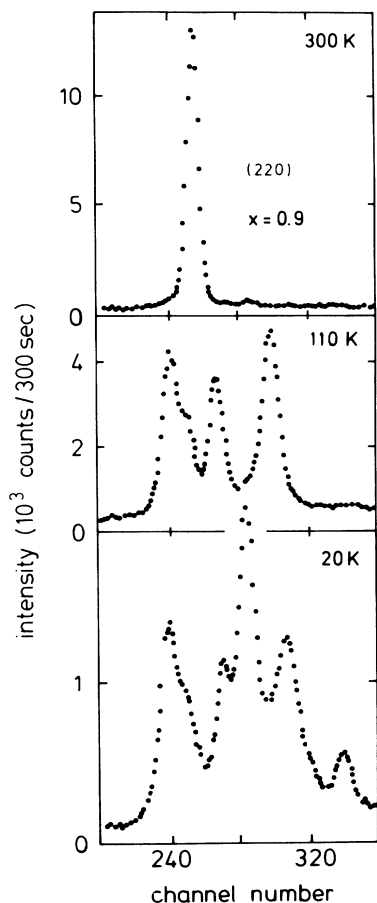RANDOM-STRAIN FIELDS IN $(KCl)_{1-x}$ $(KCN)_x$

FIG. 1. The powder profiles of the cubic (220) line and its products in the monoclinic phase (110 K) and in the monoclinic-orthorhombic coexistence region (20 K) for a CN concentration of $x=0.9$.
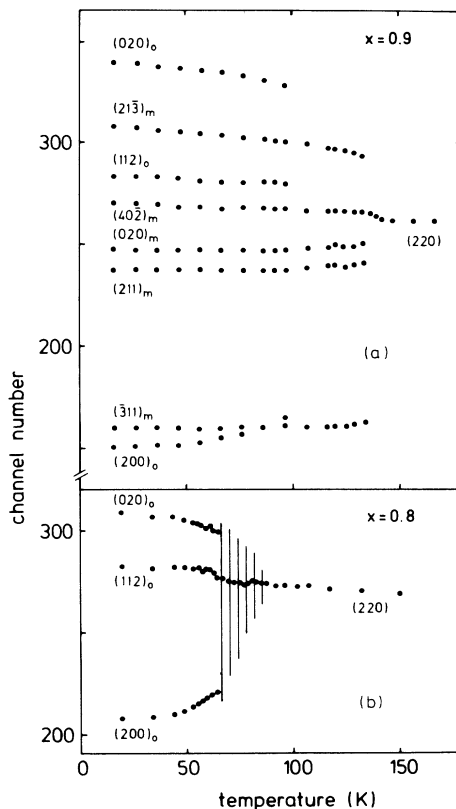

FIG. 2. The position of the cubic (220) line and its low-temperature products for $x=0.9$ and 0.8. The subscript "m" stands for monoclinic, "o" for orthorhombic. The hatched area indicates a strong broadening of the profile (see Fig. 5). Twenty-six channels correspond to 1° in the Bragg angle 2θ; the 2θ range covered is around $2\theta=40°$.

$x=0.8$

Powder profiles of this sample are shown in Fig. 4. The position of the (220) reflection and its products in the low-temperature phase are shown in Fig. 2(b). The width of the cubic lines starts to increase strongly below 100 K [Fig. 5(a)]. Below 65 K sharp and small additional lines develop, superimposed on the broad cubic profiles. These additional lines belong to the orthorhombic structure. The width of the cubic profiles is constant below 65 K. A qualitative analysis has been made for the (220) groups using the following peak shapes: A Gaussian G_c and a Lorentzian L_c with the same center representing the cubic (220) profile, three Gaussians G_0 representing the orthorhombic lines $(020)_o$, $(112)_o$, and $(200)_o$. The temperature dependence of the apparent width of the cubic component $(G_c + L_c)$ and of the width of the orthorhombic lines (G_o) is shown in Fig. 5. The width of the orthorhombic lines and of the cubic line above 200 K is resolution limited. Below 160 K the weight of L_c increases at the expense of G_c, as indicated be the dashed line in Fig. 3(b). Below about 75 K the
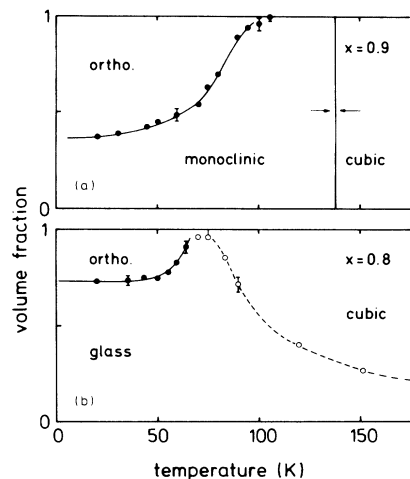

FIG. 3. The volume fraction of the various phases for $x=0.9$ and 0.8 as derived from the integrated peak intensities.
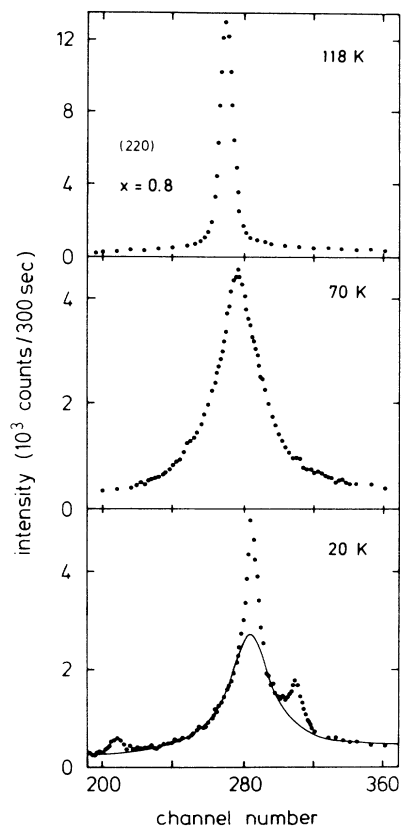
FIG. 4. The powder profiles of the cubic (220) line and its low-temperature products for $x=0.9$. The solid line of the 20-K profile is a Lorentzian profile which is understood as the contribution of the quasicubic "glass" state. The excess intensity above the Lorentzian are identified as orthorhombic lines.
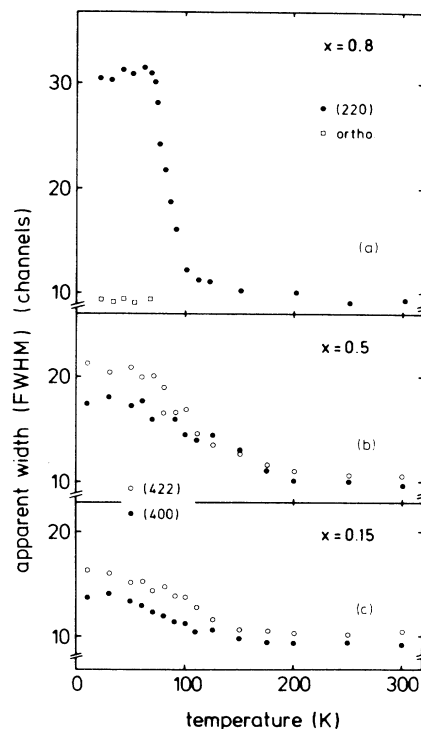
FIG. 5. The apparent linewidths of selected lines for $x=0.8$, 0.5, and 0.15. The residual width of 10 channels of the room-temperature cubic reflections and of the orthorhombic reflections is given by the instrumental resolution.

fraction of G_c is negligible, i.e., the cubic component is dominated by the Lorentzian L_c. Below 65 K the ortho-rhombic lines grow and finally reach about 25% of the total scattered intensity above background [Fig. 3(b)]. In analogy of the other mixed cyanides we regard the broadening of the cubic reflections at low temperatures as the signature of the glass state. In this sense the sample shows a coexistence of the orthorhombic phase with the glass state. The lattice parameters and the ferroelastic deformations of the orthorhombic phase are given in Table I. The T dependence of the cell volume is shown in Fig. 6.

$x=0.5$ and 0.15

These two mixed crystals stay cubic down to lowest temperatures. Below about 200 K the apparent widths of the cubic lines increase with decreasing temperature [Figs. 5(b) and 5(c)].

DISCUSSION

The structural behavior of $(KCl)_{1-x}(KCN)_x$ is in its basic features analogous to $(KBr)_{1-x}(KCN)_x$ and $(NaCl)_{1-x}(NaCN)_x$: Again the (x,T) phase diagram
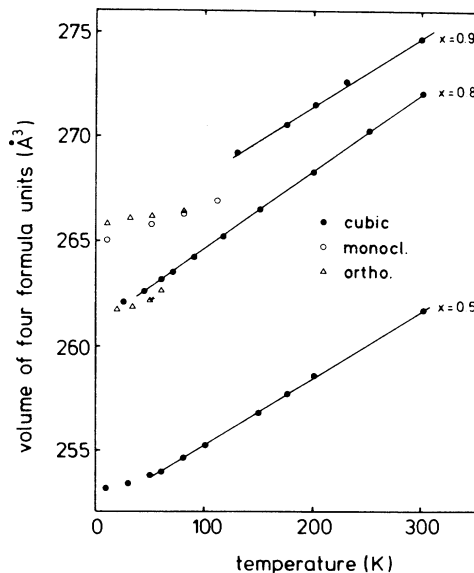
FIG. 6. The volume of four formula units as a function of temperature for $x=0.9$, 0.8, and 0.5.

shows the three principal regions, the orientationally disordered cubic phase, the ferroelastic phases, and the glasslike state. The substitution of the aspherical CN ions by spherical halide ions lowers the ferroelastic ordering temperature T_c, until finally at the crossover concentration x_c the ferroelastic ordering is suppressed in favor of the formation of the glasslike state. The glasslike state is characterized by a broadening of the cubic lines.

Before discussing the differences of the three series of mixed cyanides, some comments on the (x, T) phase diagram of $(KCl)_{1-x}(KCN)_x$ are in order. It is known from the experiment and from theoretical considerations that the ordered phases of the mixed cyanides are susceptible to history and shape effects.[10,11,21] Thus the experimental (x, T) phase diagrams need not necessarily represent the true equilibrium phase diagrams. Referring to $(KCl)_{1-x}(KCN)_x$ the following observations have been made: The values of the transition temperature vary slightly from run to run. For $x = 0.8$, the present powder sample enters a state of coexistence orthorhombic glass at 65 K. In a recent inelastic-neutron-scattering study on a large single crystal from the same charge an orthorhombic peak splitting at 103 K has been observed.[22] (Unfortunately the volume fraction of the orthorhombic and the glassy components has not been studied in this experiment.) X-ray diffraction on a small single crystal, again from the same charge, did not show any ferroelastic component.[23] It should be emphasized that the cubic room-temperature lattice constants of all these samples are identical, so that major differences of the overall chemical composition can be ruled out. We conclude that these samples have to be close to the crossover concentration x_c. For $x = 0.9$ the present measurements indicate a monoclinic phase at intermediate temperatures and a monoclinic-orthorhombic coexistence at low temperatures. Rowe et al.[14] report a coexistence 82% triclinic $P1$ and 18% orthorhombic $Immm$ at 120 K (where we observe a pure monoclinic phase) and the same type of coexistence with a ratio of 62%:38% at 17 K. Thus the agreement of their and our investigation is confined to the point that the weight of the orthorhombic fraction increases towards low temperatures, but there is diagreement on the nature of the second noncubic phase. The question remains whether a range of CN concentrations exists where there is a true monoclinic (or triclinic following Rowe et al.[14]) low-temperature phase. In this case the sample with $x = 0.9$ would just cross a miscibility gap between the orthorhombic and the monoclinic phase. To us this idea seems unlikely since it would require a sequence of low-temperature phases orthorhombic-monoclinic-orthorhombic-glass as a function of x. We rather think that the coexistence orthorhombic-monoclinic observed for $x = 0.9$ results from an incomplete transformation of the monoclinic intermediate-temperature phase to the orthorhombic low-temperature phase. Transformations of this type are well known in martensites.[24] The temperature dependence of the fraction of the parent and the product phase is usually explained by the migration of the transformation front across the sample where lat-

tice defects act as pinning centers. Following this idea we consider the orthorhombic phase as the "true" ground state for all $x_c < x \leq 1$.

As far as the relation between the orthorhombic and the monoclinic phases is concerned, the following observation can be made: The monoclinic phase occurs in RbCN as the stable low-temperature state,[18] in KCN as a metastable state,[17] but it is absent in NaCN. Obviously it is favored by cations having larger sizes. In KCN the transition from orthorhombic to monoclinic can be achieved either by applying hydrostatic pressure[25] or by the substitution of CN^- by Br^-.[19,12] Br^- is about 2% larger in volume than CN^-. The situation can be summarized by saying that positive pressure, external or "chemical," increases the existence range of the monoclinic phase at the expense of the orthorhombic phase. In that sense the relatively small existence range of the monoclinic phase in the present mixed crystals is not unexpected, since the substitution of CN^- by Cl^-, the latter being about 5% smaller, can be understood as a negative "chemical" pressure.

In the following we discuss some structural properties of the mixed cyanides in the light of the random-field concept. Following Michel[7] the origin of the random fields is the volume mismatch between Cl^- and CN^-, which is larger than that between Br^- and CN^-; random field effects are expected to be stronger in $(KCl)_{1-x}(KCN)_x$ than in $(KBr)_{1-x}(KCN)_x$.

There are several experimental indications that the influence of the random fields are in fact stronger in $(KCl)_{1-x}(KCN)_x$ than in $(KBr)_{1-x}(KCN)_x$. The crossover concentration x_c is 0.8 in the former system, but only 0.6 in the latter. The broadening of the cubic powder lines sets in at about 200 K in the mixed chlorides, but only at about 150 K in the mixed bromides. In $(KBr)_{1-x}(KCN)_x$ the line broadening dies out rapidly for CN concentrations $x < x_c$; already for $(KBr)_{0.4}(KCN)_{0.6}$ the line broadening is hardly detectable in powder diffraction experiments—whereas there is still significant broadening in $(KCl)_{0.85}(KCN)_{0.15}$.

In $(KBr)_{1-x}(KCN)_x$ the line broadening is strongly anisotropic and can be explained by assuming inhomogeneous T_{2g} strains only. In $(KCl)_{1-x}(KCN)_x$ the broadening is nearly isotropic. This statement is based on comparing the width of various (hkl) lines, particularly on the widths of (400) lines which are insensitive to T_{2g} strains. Thus the A_{1g} and E_g random strains cannot be ignored in $(KCl)_{1-x}(KCN)_x$.

In the discussion of MD computer simulations on $(KBr)_{1-x}(KCN)_x$ it was argued that the orthorhombic phase is characteristic for a situation with small random fields. (After all, the orthorhombic phase is the low-temperature state of pure KCN.) Thus it is surprising that the orthorhombic phase is the dominant ferroelastic plane of $(KCl)_{1-x}(KCN)_x$ which—from what is said above— is the system with the stronger random fields. On the other hand we have pointed out above that the average or "chemical" pressure introduced by the chemical substitution favors the monoclinic ground state. From a comparison of the (x, T) phase diagrams of

$(KCl)_{1-x}(KCN)_x$ we conclude that for the competition of the ferroelastic phases the "chemical" pressure is more important than the random fields.

Another point of interest is the behavior of the linewidth for $x=0.8$. In the other "glass"-forming cyanides the linewidth, which can be regarded as the glass order parameter, increases monotonically until it saturates at low temperatures. In the present case, the increase of the width is interrupted, even slightly reversed, by the appearance of the orthorhombic component. Obviously the formation of orthorhombic regions allows some relaxation of the inhomogeneous strains, which are characteristic of the glasslike state. This view strongly suggests that the coexistence of glasslike and orthorhombic regions occurs within the powder grains, which are typically of 10-μm size. The trivial case, namely that grains with a higher CN-concentration transform, whereas those with a lower concentration form the glasslike state, could not explain this behavior of the linewidth.

In the summary, the phase diagram of $(KCl)_{1-x}(KCN)_x$ has been investigated and two noncubic phases, monoclinic and orthorhombic, and a glasslike state have been identified and characterized by the order parameters. $(KCl)_{1-x}(KCN)_x$ shows essentially the same structural behavior as $(KBr)_{1-x}(KCN)_x$ and $(NaCl)_{1-x}(NaCN)_x$. The static random fields in the sense of Michel are stronger than in $(KBr)_{1-x}(KCN)_x$. At the crossover concentration $x_c = 0.8$ from the crystalline to the glasslike low-temperature state, a coexistence of these states on a rather local scale is observed.

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