PHYSICAL REVIEW B VOLUME 40, NUMBER 11 15 OCTOBER 1989-I

Structural transitions in the heavily strained cyanide crystal $(\mathrm{KCl})_{0.25}(\mathrm{KCN})_{0.75}$

Laurent J. Lewis
Département de Physique et Groupe de Recherche sur les Couches Minces, Université de Montréal, Case Postale 6128, Succursale A, Montréal, Québec, Canada H3C 3J7

Michael L. Klein
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 5 May 1989)

We use constant-pressure molecular dynamics to investigate the structure of the mixed cyanide $(\mathrm{KCl})_{0.25}(\mathrm{KCN})_{0.75}$. On cooling from the high-temperature cubic rotator phase, the system transforms to a ground-state monoclinic structure, with indications of a rhombohedral phase present at intermediate temperatures. At the same time, the CN^- molecular ions freeze into a state with disordered orientations, thus suggesting the formation of a *noncubic* quadrupolar glass phase. The orientational freezing is also accompanied by anomalous diffraction profiles. Both structural and quadrupolar transitions are examined in detail, and discussed in relation with our findings for the $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ system. Our results suggest that the experimentally observed, cubic orientational glass may in fact consist of large domains of noncubic symmetry.

I. INTRODUCTION

Mixed alkali-halide–alkali-cyanide crystals, such as $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$, $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$, and $(\mathrm{NaCl})_{1-x}(\mathrm{NaCN})_x$, exhibit a variety of structural transitions. There exists in these systems a critical concentration x_c above which a transition to a noncubic structure with long-range orientational order is induced by ferroelastic shear deformations.[1] For x less than x_c, however, the inhomogeneous strains of the heavily diluted anion sublattice now dominate the ferroelastic strains and, as a result, long-range orientational order is lost and the system freezes into an orientational glass state.[1–10]

The first-order ferroelastic transition in the *pure* cyanides is driven primarily by the coupling between orientational and translational degrees of freedom of the aspherical CN^- molecules.[10,11] As replacement of the CN^- by halide ions proceeds, the presence of random strains in the system increases. In an attempt to rationalize the effect of dilution on the resulting ground-state structure, we have performed an extensive series of molecular-dynamics (MD) simulations of the mixed cyanides.[12–14] In agreement with earlier theoretical work by Michel,[15] and also with recent neutron-diffraction[6] and ultrasonic[16] measurements, we find that the presence of random strain fields modifies the translation-rotation coupling constants, thus driving the system to a low-temperature phase which differs from orthorhombic. More precisely, the nature of the transition is determined by a *competition* between the translation-rotation and strain-rotation-mediated CN^--CN^- couplings. Random strains are presumably also present in the pure systems, however.[17,18] Repeated thermal cycling of KCN, for instance, leads to a low-temperature monoclinic—again rather than orthorhombic—structure.[8,17] It appears that in this case random strains are induced by the incomplete elimination of the low-temperature orthorhombic structure during the cycling process: traces of this phase have been observed to survive at temperatures well above the transition temperature.[8] Random strain fields are therefore critically important in determining the character of the ground-state structure.

In two previous papers[19,20] (hereafter referred to as I and II), we have given a full account of our investigation of the $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ mixed system. We have demonstrated that a simple model, consisting of effective two-body interactions plus a three-site approximation for the charge distribution of the CN^- molecular ion, gives a remarkably accurate account of the *whole* phase diagram for this material. Consistent with experiment, samples with $x > x_c$ transform to either orthorhombic, monoclinic, or rhombohedral at low temperature, and freeze into an orientational *crystal* state. Samples with $x < x_c$, on the other hand, remain cubic at all temperatures, but form an orientational *glass*.

The role played by random strains in these systems was for a large part inferred in I and II from a comparative study of site-*ordered* mixtures, which suggested that such effects should be maximal in heavily strained materials. To further test these ideas, we undertook an investigation of the chlorine-substituted cyanide $(\mathrm{KCl})_{0.25}(\mathrm{KCN})_{0.75}$, which lies close to the critical concentration $x_c = 0.8$ for this system,[2,3] and which is also characterized by a large anion-size disparity. A preliminary report of this study has already appeared.[14] Here, we present a more thorough account of our findings. First, however, a few additional remarks are in order.

As x approaches the critical concentration, numerous precursor signs announce the formation of the glass state in $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$ and other cyanides: polymorphism of the low-temperature phase,[9,21] anomalous diffraction patterns of the ground-state structure,[3,6] softening of the shear elastic constant c_{44},[22] etc. The latter is interpreted as evidence for the presence of critical fluctuations of T_{2g} symmetry, and leads to a diverging mean-square displacement at the transition.[22] Thus, the crystal exhibits characteristics of melting at a temperature which is an order of magnitude smaller than the real melting temperature.[6] At this point, it is usually argued that the system only has two options:[3] either (i) recrystallize ferroelastically into a phase of lower symmetry, or (ii) freeze its disorder into an orientational glass phase of overall cubic symmetry. The crossover from one to the other determines x_c. This implies that there is an abrupt ("discontinuous") change in the symmetry of the low-temperature structure at x_c, where the system passes from noncubic ($x \rightarrow x_c^+$) to cubic ($x \rightarrow x_c^-$).

Here we propose that this need not be the case. We suggest that the glass phase can actually evolve continuously out of the noncubic ferroelastic phases observed above x_c. There are in fact no *a priori* reasons why an orientational glass should exhibit overall cubic symmetry, at least at concentrations close to x_c. The actual definition of an "orientational glass" is crucial here. We recall that the quasispherical molecule CF_4 is known to exhibit rotational motion in a lattice which is noncubic.[23] Our simulations of $(KCl)_{1-x}(KCN)_x$ reveal that this system undergoes a complicated transition from the high-temperature cubic state to a low-temperature monoclinic structure, with indications of an intermediate rhombohedral phase. At the same time, the quadrupoles freeze into a state of disordered orientations. The ground-state structure therefore corresponds to a monoclinic orientational glass.

Table I summarizes the results of the simulations. For each temperature, we list the volume of the MD cell and the system's configurational energy. The simulations were performed in the isobaric-isoenthalpic (N,P,H) ensemble[24–26] and, as in our study of the $(KBr)_{1-x}(KCN)_x$ system, employed a neutral periodically replicated cell containing $N=512$ ions. Effective two-body interatomic potentials taken from previous studies of the alkali cyanides[27–32] were used. Further details of the model can be found in I.

We start in Sec. II with an investigation of the structural transformations in this system, i.e., of those transitions which involve a recrystallization of the underlying ordered lattice. Section III deals with the problem of quadrupolar freezing; the orientational glass is characterized in detail there. Discussions and conclusions are presented in Sec. IV.

II. STRUCTURAL TRANSITIONS

The temperature dependence of the cell parameters—angles and lengths—are displayed in Fig. 1. For reasons which will become clear shortly, these are plotted using a cubic-lattice reference frame (unlike the corresponding figures in I). At high temperature, the cell is indeed cubic (within the numerical accuracy of the calculation). As cooling proceeds below ~130 K, however, substantial

TABLE I. Temperature evolution of the simulation, in the isobaric-isoenthalpic (N,P,H) ensemble, for the $(KCl)_{0.25}(KCN)_{0.75}$ system. At each temperature, $\langle E_{\mathrm{conf}} \rangle$ is the run-averaged configurational energy of the system and $\langle V \rangle$ is the volume of the unit cell.

T (K)	$\langle E_{\mathrm{conf}} \rangle$ (kJ mol^{-1})	$\langle V \rangle$ (Å^3)
296	−695.10	268.34
202	−698.01	267.89
181	−698.81	266.95
160	−699.58	266.07
151	−699.86	265.68
143	−700.18	265.34
135	−700.54	264.96
130	−700.70	264.73
125	−700.87	264.58
121	−701.05	264.32
117	−701.21	264.18
115	−701.35	264.01
110	−701.51	263.85
104	−701.71	263.57
99	−701.93	263.37
89	−702.33	262.89
81	−702.68	262.50
72	−703.06	262.05
63	−703.41	261.69
51	−703.88	261.16
27	−704.72	260.31
21	−704.94	260.10

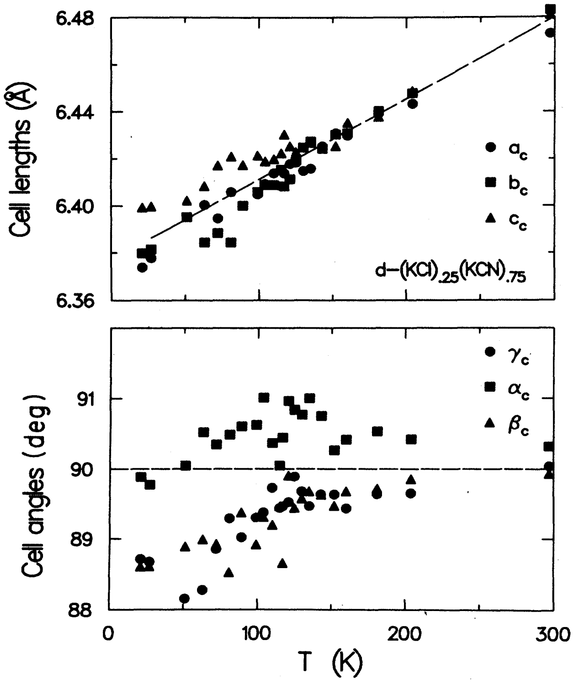

FIG. 1. Temperature dependence of the cell parameters (lengths and angles) expressed in terms of the high-temperature cubic reference frame.

scatter is revealed in the data points. The system is then evidently in metastable equilibrium, and attempting to decrease its energy by recrystallization into a phase of lower symmetry. The transitional sequence from the high-temperature cubic phase to the ground-state structure appears to be extremely complicated. The scatter in the values of the structural parameters is a clear signal of the presence of strong random strain fields in this system. Here, however, strains arise not only from the chemical disorder of the anion sublattice, but also from the large size disparity between the constituent ions Cl^- and CN^-. Random strains are therefore extremely important in this material and in fact explain the relatively high value of x_c ($=0.8$) for this system.[2,3]

The nature of the transition is best resolved by viewing the structure from a reciprocal-lattice viewpoint. Thus Fig. 2 shows the positions in **k** space of the $\{111\}$, $\{200\}$, and $\{220\}$ Bragg points as a function of temperature. In principle, these can be compared directly with corresponding neutron scattering profiles. Even though the dispersion effects discussed above are again apparent in this graph, the inherent structure of the transition now appears much more clearly. The low-temperature phase is monoclinic, with one of the shears zero and the other two equal (cf. also Fig. 1). Figure 2, however, also reveals significant structure at intermediate temperatures, around about 100 K. Though it exists for only a small temperature interval, we readily recognize this phase to be rhombohedral; as is clear from Fig. 2, it evolves from, and into, a phase which, because fluctuations are important, can at best be described as pseudocubic.

We therefore have here an explicit illustration of the competition between translation-rotation and strain-rotation couplings, first revealed by our studies of the $(KBr)_{1-x}(KCN)_x$ system: while the former tends to induce a structural transition, the latter strongly opposes it. Similar effects were also observed in the orientational-glass former $(KBr)_{0.5}(KCN)_{0.5}$; in this case, however, the sample remained cubic at all temperatures (Fig. 4 in I). Note that the system considered here lies in the presumed glass-forming range of concentrations ($x < x_c$). Though x_c is not known with great accuracy (owing to the relatively small number of experiments carried out on this system), it is clear from our simulation that $x=0.75$ lies *very* close to x_c. This is also confirmed by our findings for the low-temperature quadrupolar state which, as we will see in Sec. III, exhibits glasslike characteristics.

Phonons of T_{2g} symmetry soften at the transition, as they did in $(KBr)_{1-x}(KCN)_x$ samples. This can be seen from the temperature dependence of $\langle u^2 \rangle$, the mean-square displacement, and c_{44}, the shear elastic constant. Both quantities are displayed in Fig. 3. Just like the lattice parameters, $\langle u^2 \rangle$ exhibits a complicated behavior over a wide range of temperatures. The system in fact appears to undergo a number of transitions, though, because of the finite size of the MD cell, it is difficult to ascertain which features of this graph actually correspond to real transitions. On the other hand, while c_{44} does not soften completely at the transition, it does follow quite closely the ultrasonic data,[33] indicated by the

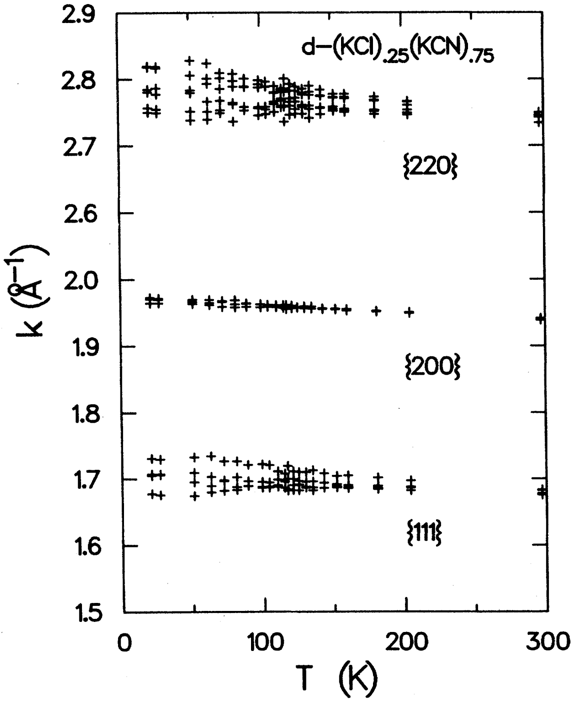

FIG. 2. Positions of the $\{111\}$, $\{200\}$, and $\{220\}$ Bragg peaks as a function of temperature.

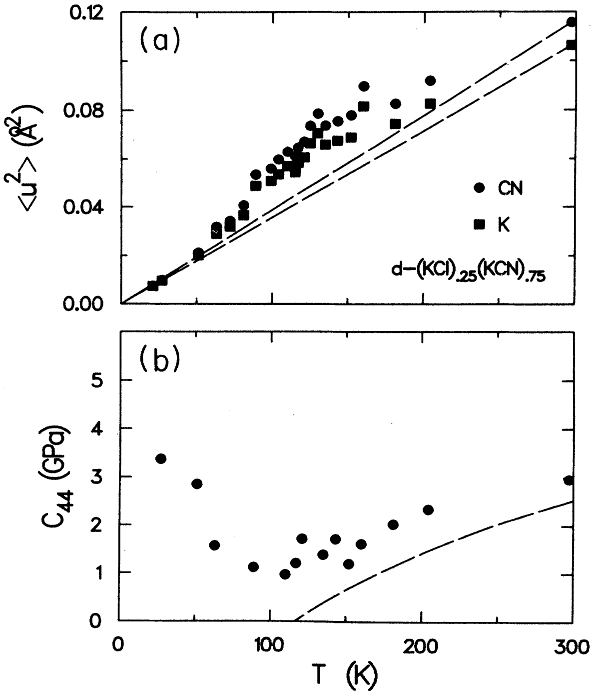

FIG. 3. Temperature dependence of (a) the mean-square displacement $\langle u^2 \rangle$, and (b) the shear elastic constant c_{44}. In (a), solid circles are for the CN^--molecule center of mass and solid squares are for the potassium ions, and the dashed curves indicate the expected "classical" linear behavior. In (b), the dashed curve is a mean-field fit to experimental data (Ref. 33).

corresponding mean-field fit in Fig. 3(b) (dashed curve). The discrepancies between experiment and simulation arise to a large extent from finite-size effects, as discussed in I. Thus, c_{44} is "measured" here with a probe whose frequency is comparable to that of neutron scattering experiments. Our results are therefore consistent with experiment, which show softening to decrease with increasing frequency.[34]

Strains also seem to be responsible for the interesting recent observation[3] by Knorr and Loidl of anomalous diffraction profiles in $(KCl)_{0.2}(KCN)_{0.8}$, i.e., exactly at the critical concentration. These authors have reported a highly unusual $\exp(-\alpha|\xi|)$ line shape (with $0<\xi<0.1$ the reduced wave vector and α a constant) which, they speculate, stems from a "yet unknown superposition of strains" arising from the size, shape, and domain structure of the sample, as well as from the chemical disorder. In order to assess this observation, we have calculated the $(2\xi 0)$ neutron profiles at several temperatures for our model system. Note here that because of the particular choice of MD cell length, only the points with $\xi=0$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ are accessible, and our conclusions can only be qualitative. Figure 4 shows the calculated diffraction intensity at four different temperatures (normalized at $\xi=0$). As temperature decreases, one sees a tendency for the diffraction profile to approach the shape reported by Knorr and Loidl, namely $I(\xi)\sim\exp(-\alpha|\xi|)$. When translated into real space, this signifies that $I(r)$ tends to a *constant* when $r\rightarrow 0$, which differs from the usual Ornstein-Zernike exponential decay law (i.e., Lorentzian in reciprocal space). We have calculated $I(r)$ directly in real space. Though it is difficult because of finite-size effects to draw definite conclusions, our results seem to be consistent with the interpretation of Knorr and Loidl.[3] When taken together with the reported experimental behavior,[3] therefore, our results confirm the highly strained nature of this system and in fact already suggest, in agreement with Knorr and Loidl, the presence of some sort of unresolved glasslike disorder in the low-temperature phase. The nature of this disorder will become clearer in the next section, where we discuss the orientational freezing transition.

III. ORIENTATIONAL FREEZING

The orientational freezing process in $(KBr)_{1-x}(KCN)_x$ was characterized in II by a number of parameters. We carry out a corresponding analysis here. The single-ion reorientation times relevant to NMR experiments, τ_{11}^s and τ_{33}^s, rapidly become very large—of the order of the length of the simulation—and it is therefore not possible to evaluate them accurately, except at room temperature or above. At 300 K, τ_{11}^s is of the order of 0.12 ps, which is comparable to the corresponding value in KCN as determined from NMR measurements, 0.16 ps.[35] At this temperature, the system is clearly in a state of rotational diffusion. As cooling proceeds, however, orientational freezing gradually sets in. The angular diffusion constant D_Ω is shown in Fig. 5. On the time scale of the simulation, $D_\Omega=0$ at $T\approx 60$ K.

In order to gain insight into the microscopic nature of the transition, we also examined the Michel-Rowe order

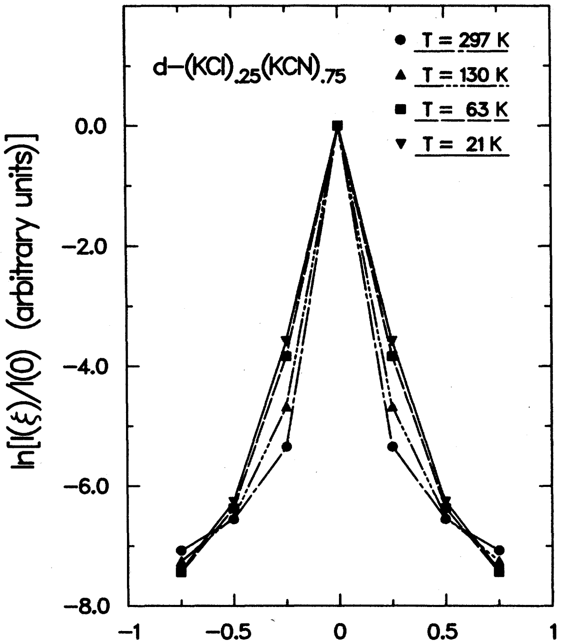

FIG. 4. Calculated neutron-diffraction profile $\ln I(\xi)$ (normalized at $\xi=0$) for the $(2\xi 0)$ line at four different temperatures. ξ is the reduced wave vector as measured from the Bragg point. Lines connecting the points are a guide to the eye; error bars are smaller than symbol size.

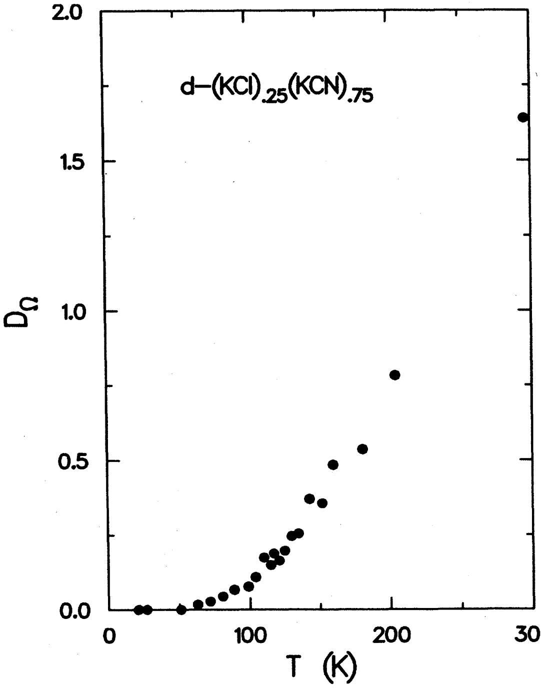

FIG. 5. Temperature dependence of the angular diffusion constant D_Ω.

parameters,[5] which are analogous to those introduced by Edwards and Anderson in the context of spin glasses.[36] Molecular orientations are thus described via functions of the form $[\langle Y(\hat{\mathbf{u}})\rangle]$ and their fluctuations $\{[\langle Y(\hat{\mathbf{u}})\rangle^2]\}^{1/2}$, where $\langle \cdots \rangle$ denotes the time average for an individual CN^- ion and $[\cdots]$ an average over all sites, and $\hat{\mathbf{u}} \equiv (x,y,z)$ is the unit vector along the C—N bond. Y is a function of symmetry appropriate to either dipolar (D) or quadrupolar (E_g or T_{2g}) order; details can be found in II.

Figure 6 shows the calculated temperature dependence of these parameters. From the behavior of the fluctuations, it is clear that the CN^- molecules have frozen-in orientations at low temperature. The quadrupoles order essentially along the $\{111\}$ directions of the parent cubic phase, as can be inferred from the D and T_{2g} fluctuations, which are close to their perfect $\{111\}$ values of 0.282 and 0.364, respectively. The E_g fluctuation, however, signals substantial departures from perfect $\{111\}$ alignment (which would yield $([\langle E_g\rangle^2])^{1/2}=0$). Though these departures can to some extent be attributed to residual librational motion, it must be concluded that dipoles align along $\{111\}$ only in an *average* sense. In fact, the order parameters for this sytem are strikingly similar to those for the $(\mathrm{KBr})_{0.5}(\mathrm{KCN})_{0.5}$ mixture (cf. Fig. 8 in II), which we found to form an orientational glass at low temperature. We therefore expect the same situation to hold here: though the sample exhibits a vanishingly small net dipole moment, a broad distribution of orientations is present at low temperatures. Similar conclusions are reached when examining the kubic-harmonic expansion coefficients C_4 and C_6 of the orientational distribution $F(\hat{\mathbf{u}})$ [cf. II, Eq. (4)], Fig. 7. Though both C_4 and C_6 become large at low temperature, they remain distinctly different from the corresponding values for perfect $\{111\}$ order, namely -1.53 and $+2.27$, respectively.

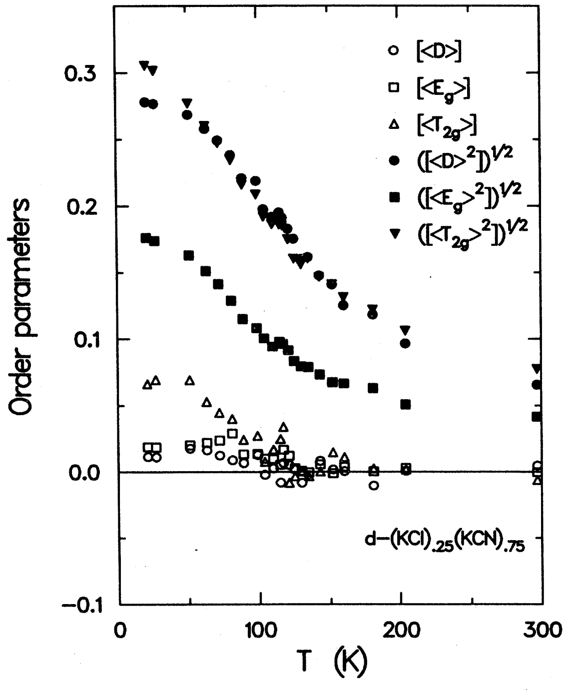

FIG. 6. Temperature dependence of the CN^- orientational order parameters (cf. text).

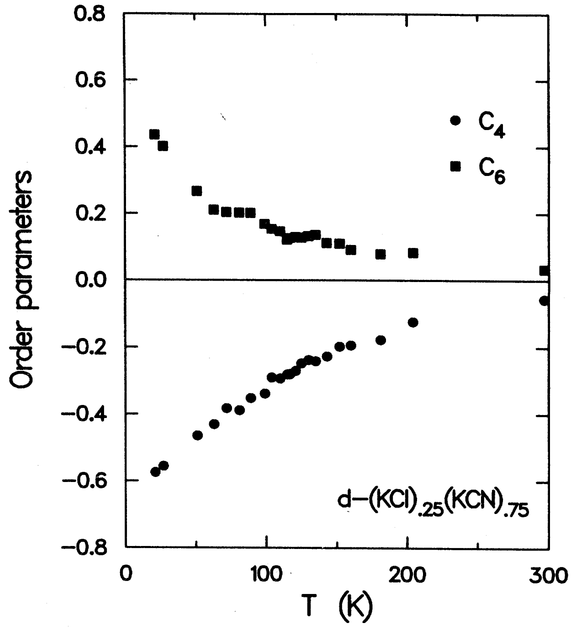

FIG. 7. Temperature dependence of the kubic-harmonics expansion coefficients of the orientational probability function $F(\hat{\mathbf{u}})$.

Information about the *relative* orientational distribution can be obtained by examining correlations between the orientations of the CN^- molecules. Such correlations are calculated here as a function of both temperature and distance. To this effect, we define the quantity $P_n(\cos\theta)$, which is the relative probability of finding a pair of nth-nearest-neighbor CN^- molecules such that θ is the angle between them.

First we monitor the freezing process in Fig. 8 in terms of the *first*-neighbor correlation function $P_1(\cos\theta)$. At high temperature, there is no preferred relative orientation and the distribution is flat; since we know from Fig. 4 that the molecules undergo rotational diffusion, we conclude that they actually behave essentially as independent rotors. As temperature is lowered, the tendency observed in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ mixtures for neighboring molecules to align with their axes parallel or antiparallel also develops here. As Fig. 8 shows, however, this behavior seems to saturate at intermediate temperatures, with a broad more or less diffuse background of relative orientations remaining at 21 K, the lowest temperature examined. Recall that, on the time scale of our MD experiment, the quadrupolar freezing transition occurs at about 60 K. Thus, further cooling is not likely to significantly affect the distribution. In fact, the lowest three panels are essentially identical, the small differences being due to decreased librational motion.

The existence of a glass state can be fully assessed by examining the *radial* dependence of the orientational correlation function. Thus, $P_n(\cos\theta)$ at the lowest temperature is shown in Fig. 9 for correlations between a

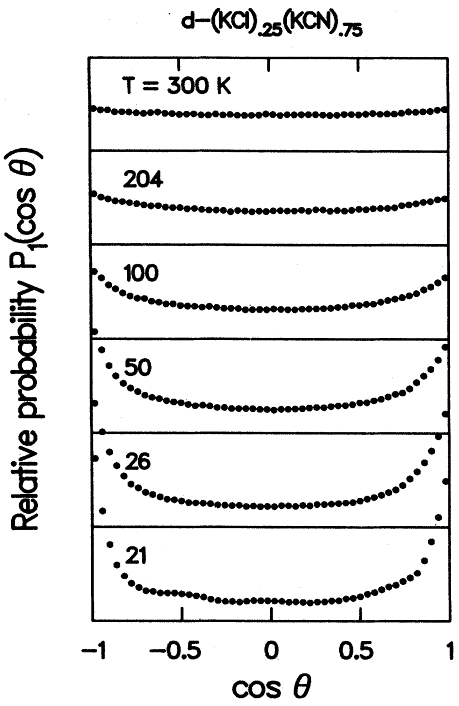

FIG. 8. The function $P_1(\cos\theta)$, which gives the relative probability of finding pairs of first-neighbor molecules such that θ is the angle between them, at various temperatures.

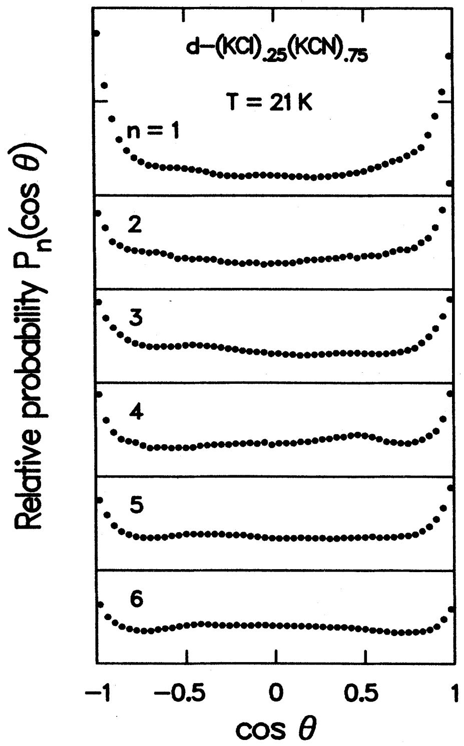

FIG. 9. Radial dependence of $P_n(\cos\theta)$, the probability of finding a pair of nth-nearest-neighbor molecules such that θ is the angle between them, for $n = 1-6$, at low temperature. The top panel of this figure is identical to the bottom panel of Fig. 8.

given CN^- ion and each of its first six neighboring shells of molecules (at distances of 4.6, 6.5, 8.0, 9.2, 10.3, and 11.3 Å, respectively). $P_n(\cos\theta)$ clearly exhibits some structure at short range (the top panel of Fig. 9 is identical to the bottom one of Fig. 8), which progressively fades out as distance increases. The distribution is in fact almost completely flat at a distance corresponding to the sixth nearest-neighbor shell. Such a state where correlations exist at short distances but not at large distances precisely coincides with the definition of a glass. Here, the "coherence length" appears to be of at most a few (i.e., 3 or 4) interatomic spacings. This can actually be seen *de visu* in Fig. 10, where we plot in-plane projections of the molecular bond vectors. Thus, again, as was the case in glass-forming $(KBr)_{1-x}(KCN)_x$ samples, there exist significant regions of local ferroelastic order where the molecules align with their axes parallel or antiparallel. It is, however, not possible, because of the small system size used, to describe this state in terms of domains and domain walls. These results therefore once more suggest a picture of the orientational glass phase in this and related systems as consisting of CN^- molecules loosely aligning along $\{111\}$ directions of the parent cubic phase, while exhibiting a definite preference for short-range ferroelastic ordering. ***Here, however, the overall structure of the glass is not cubic.*** We discuss next the validity of our findings in the light of the structural behavior observed in $(KCl)_{1-x}(KCN)_x$ and similar systems.

IV. DISCUSSION AND CONCLUSIONS

Though we know of no reported instance of a low-temperature noncubic orientational glass, several experimental observations appear to support our findings, when taken together with the results of our investigation of the $(KBr)_{1-x}(KCN)_x$ system.

First, both structural transitions observed here

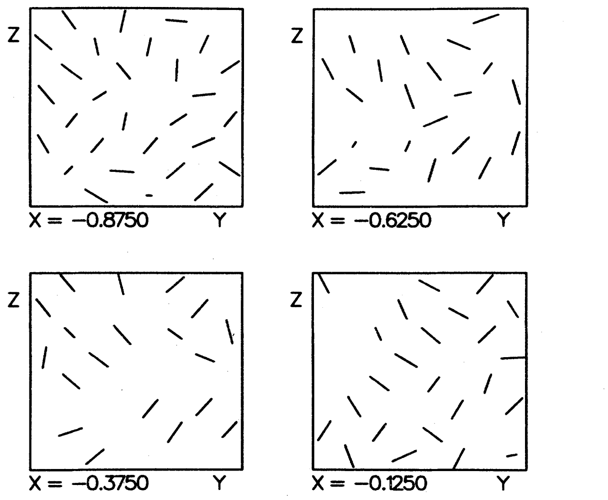

FIG. 10. Selected slices through the MD sample at low temperature, showing the orientations of individual CN^- molecules, projected onto the appropriate (100) plane. Br^- and K^+ ions are omitted for clarity.

(cubic→rhombohedral→monoclinic) are broad and ill defined, and appear to be continuous. A corresponding behavior in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ with $x<x_c$, which remain cubic at all temperatures, is believed to be intimately related to the formation of the glass state.[3,21] Further, though extremely subtle, the transition is unambiguously present [the lattice shears here are much smaller than those observed in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ mixtures with $x>x_c$]. Thus, random strain fields are quite effective at opposing the transition, though not enough to inhibit it completely.

The complicated transitional sequence observed in our simulation is also reminiscent of related phenomena in the other cyanides. In $(\mathrm{KBr})_{0.36}(\mathrm{KCN})_{0.64}$ (i.e., *exactly* at the critical concentration for this system) subjected to repeated thermal cycling, for instance, Knorr and Loidl[3] interpret the low-temperature phase diagram as arising from a competition between the parent cubic phase and two ferroelastic daughter phases, *precisely the same as we observe,* namely rhombohedral and monoclinic. Further, the sequence cubic→rhombohedral→monoclinic is identical to that observed in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ just above the critical concentration.[21] In addition, a monoclinic phase is also seen at intermediate temperatures in $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$, again just above x_c.[7,37] In $(\mathrm{NaCl})_{1-x}(\mathrm{NaCN})_x$, on the other hand, Elschner, Knorr, and Loidl[9] report the coexistence of a glass state together with noncubic components for $x=0.71$ and 0.76; they even suggest that these noncubic components are glasslike, the term "glass" being used to describe "a state of broadened powder diffraction lines." (Experimental limitations did not allow a definite identification of this phase.) Finally, in agreement with ultrasound measurements,[16,33] the shear elastic constant c_{44} here also softens dramatically at the transition. This is consistent with corresponding observations in other systems, and acts as a precursor signal to the formation of a glass state.

We therefore propose that for x close to the critical concentration x_c, highly strained mixed-cyanide crystals may very well freeze into a state of static disordered orientations *and* noncubic symmetry. This orientational glass phase would evolve *continuously* out of the noncubic components as concentration changes. Our findings seem to be consistent with the observed structural behavior of $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$ and similar systems. The fact that we observe an overall noncubic ground state may be related to the use of periodic boundary conditions and to a relatively small sample size. Our results nevertheless suggest that the experimentally observed cubic orientational glass phase may in fact consist of large domains of noncubic symmetry. In view of this possibility, a more detailed structural investigation of $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$—or other heavily strained compounds—close to the critical concentration appears worthwhile.

ACKNOWLEDGMENTS

We thank J.-F. Berret, M. S. Conradi, S. Galam, C. W. Garland, M. Grant, K. Knorr, A. Loidl, K. H. Michel, J. M. Rowe, and D. Walton for many enlightening discussions. The research described herein was supported by the National Research Council of Canada, by the Natural Sciences and Engineering Research Council of Canada, by the Fonds pour la Formation de Chercheurs et Aide à la Recherche (FCAR) and Actions Structurantes programs of the Government of Québec, and by the U.S. National Science Foundation.

---

[1] K. Knorr, E. Civera-Garcia, and A. Loidl, Phys. Rev. B **35**, 4998 (1987); K. Knorr, U. G. Volkmann, and A. Loidl, Phys. Rev. Lett. **57**, 2544 (1986).

[2] D. Durand and F. Lüty, Ferroelectrics **16**, 205 (1977); J. C. Castro and M. de Souza, Phys. Status Solidi B **86**, 137 (1978).

[3] K. Knorr and A. Loidl, Phys. Rev. Lett. **57**, 460 (1986).

[4] J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. **43**, 1158 (1979).

[5] K. H. Michel and J. M. Rowe, Phys. Rev. B **22**, 1417 (1980).

[6] A. Loidl, K. Knorr, J. M. Rowe, and G. J. McIntyre, Phys. Rev. B **37**, 389 (1988).

[7] J. Ortiz-Lopez and F. Lüty, Phys. Rev. B **37**, 5461 (1988).

[8] J. Ortiz-Lopez and F. Lüty, Phys. Rev. B **37**, 5452 (1988).

[9] S. Elschner, K. Knorr, and A. Loidl, Z. Phys. B **61**, 209 (1985).

[10] J. M. Rowe, J. J. Rush, N. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. **40**, 455 (1978).

[11] K. H. Michel and J. M. Rowe, Phys. Rev. B **32**, 5827 (1985).

[12] L. J. Lewis and M. L. Klein, Phys. Rev. Lett. **57**, 2698 (1986).

[13] L. J. Lewis and M. L. Klein, J. Phys. Chem. **91**, 4990 (1987).

[14] L. J. Lewis and M. L. Klein, Phys. Rev. Lett. **59**, 1837 (1987).

[15] K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986); see also Phys. Rev. B **35**, 1405 (1987); **35**, 1414 (1987).

[16] J. O. Fossum and C. W. Garland, Phys. Rev. Lett. **60**, 592 (1988).

[17] A. Cimino, G. S. Parry, and A. R. Ubbelohde, Proc. R. Soc. London, Ser. A **252**, 1445 (1959); G. S. Parry, Acta Crystallogr. **15**, 601 (1962).

[18] S. Galam, Phys. Lett. A **121**, 459 (1987).

[19] L. J. Lewis and M. L. Klein, Phys. Rev. B **40**, 4877 (1989), referred to hereafter as I.

[20] L. J. Lewis and M. L. Klein, Phys. Rev. B **40**, 7080 (1989), referred to hereafter as II.

[21] K. Knorr and A. Loidl, Phys. Rev. B **31**, 5387 (1985).

[22] K. Knorr, A. Loidl, and J. K. Kjems, Phys. Rev. Lett. **55**, 2445 (1985); see also Physica B+C **136B**, 311 (1986).

[23] S. Nosé and M. L. Klein, J. Chem. Phys. **78**, 6928 (1983).

[24] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).

[25] S. Nosé and M. L. Klein, J. Chem. Phys. **78**, 6928 (1983); Phys. Rev. Lett. **50**, 1207 (1983).

[26] R. W. Impey, S. Nosé, and M. L. Klein, Mol. Phys. **50**, 243 (1983).

[27] R. W. Impey, M. Sprik, and M. K. Klein, J. Chem. Phys. **83**, 3638 (1985).

[28] D. G. Bounds, M. L. Klein, I. R. McDonald, and Y. Ozaki, Mol. Phys. **47**, 629 (1982).

[29] D. G. Bounds, M. L. Klein, and I. R. McDonald, Phys. Rev. Lett. **46**, 1682 (1981).
[30] M. L. Klein and I. R. McDonald, J. Chem. Phys. **79**, 2333 (1983).
[31] M. Ferrario, I. R. McDonald, and M. L. Klein, J. Chem. Phys. **84**, 3975 (1986).
[32] P. W. Fowler and M. L. Klein, J. Chem. Phys. **85**, 3913 (1986).
[33] C. W. Garland, J. Z. Kwiecien, and J. C. Damien, Phys. Rev. B **25**, 5818 (1982); J. Z. Kwiecien, R. C. Leung, and C. W. Garland, *ibid.* **23**, 4419 (1981).
[34] U. G. Volkmann, B. Böhmer, A. Loidl, K. Knorr, U. T. Höchli, and S. Haussühl, Phys. Rev. Lett. **56**, 1716 (1986).
[35] R. E. Wasylishen, B. A. Pettitt, and K. R. Jeffrey, J. Chem. Phys. **74**, 6022 (1981); R. E. Wasylishen and K. R. Jeffrey, *ibid.* **78**, 1000 (1983).
[36] S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975).
[37] K. Knorr (private communication).