Is the Ground-State Structure of $(KCl)_{0.25}(KCN)_{0.75}$ a Noncubic Orientational Glass?

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Constant-pressure molecular dynamics has been used to study the mixed crystal $(KCl)_{0.25}(KCN)_{0.75}$. On cooling from the high-temperature cubic rotator phase, this system undergoes a transition to a ground-state monoclinic structure, with indication of an intermediate rhombohedral phase. At low temperature, the CN^- quadrupoles freeze into a state with disordered orientations, thus suggesting the formation of a *noncubic* orientational glass phase. The orientational freezing is accompanied by anomalous diffraction profiles.

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Orientational glass phases have been observed to develop at low temperature and in certain ranges of concentrations in a variety of mixed alkali cyanides, such as $(NaCN)_{1-x}(KCN)_x$,[1] and alkali-halide–alkali-cyanide mixtures, such as $(KBr)_{1-x}(KCN)_x$,[2,3] $(KCl)_{1-x}(KCN)_x$,[4,5] and $(NaCl)_{1-x}(NaCN)_x$.[6] In the latter group, there exists a critical concentration x_c above which a transition to a low-temperature noncubic structure with long-range orientational order is induced by ferroelastic shear deformations.[7] Below x_c, on the other hand, the inhomogeneous strains of the heavily diluted system now dominate the ferroelastic strains, thus causing the long-range orientational order to be lost and the system to freeze into an orientational glass state.[2,3] The nature of this state is not fully understood.[7,8]

In the pure cyanides, the (first order) transition is primarily driven by the coupling of the translational to the rotational degrees of freedom of the aspherical CN^- molecules.[9] As replacement of the CN^- by halide ions proceeds, the presence of random strains in the system increases. The coupling of these with the rotational motion of the cyanides plays a key role in establishing the ground-state structure of such systems.[10,11] In fact, it is believed that the nature of the transition is determined by a *competition* between translation-rotation and strain-rotation couplings.[10,11] Random strains are presumably also present in the pure systems,[12] though to a lesser extent: Indeed, repeated thermal cycling of *pure* KCN has been shown to lead to a low-temperature *monoclinic* (rather than orthorhombic) structure.[13]

As x_c is approached from above, numerous precursor signs announce the formation of the glass state: polymorphism of the low-temperature phases,[6,14] anomalous diffraction patterns of the ground-state structure,[3,5] complete softening of the shear elastic constant c_{44} at the (now continuous) transition,[15] etc. The latter is interpreted as evidence for the presence of critical fluctuations of T_{2g} symmetry, leading to a divergence of the mean square displacement at T_c.[15] Thus, the crystal "melts" at the transition,[3,10] i.e., long-range translational order is lost. It is usually argued[5] that, at this point, the system has two options: Either (i) for $x > x_c$, recrystallize ferroelastically into a phase of lower symmetry, or (ii) for $x < x_c$, freeze its disorder into an orientational glass phase of overall cubic symmetry. This implies that there is an abrupt (discontinuous) change in the symmetry of the lattice at x_c, where it passes from noncubic $(x \rightarrow x_c^+)$ to cubic $(x \rightarrow x_c^-)$.

We propose here that this is not necessarily the case. More precisely, we suggest that the glass phase could actually evolve continuously out of the noncubic ferroelastic phases observed above x_c. We note that there seems to be no *a priori* reason why the orientational glass phase should have cubic symmetry, at least for concentrations close to x_c. (In fact, the quasispherical molecule CF_4, for instance, is known to form a noncubic rotator phase.[16]) To establish this result, we have performed constant-pressure molecular dynamics (MD) on a sample $(KCl)_{1-x}(KCN)_x$ mixed crystal with $x = 0.75$, i.e., just below the critical concentration $x_c = 0.8$.[4] On cooling from the high-temperature cubic rotator phase, we find the system to undergo a very complicated transition to a low-temperature monoclinic structure, with indication of an intermediate rhombohedral phase. At the same time, the quadrupoles are unambiguously seen to freeze into a state of disordered orientations, with correlations present at short range but absent at long range. The ground-state structure for this system, therefore, appears to be a *monoclinic orientational glass*. The formation of this glass phase is accompanied by anomalous diffraction profiles.

The MD simulations were performed in the (N,P,H)

ensemble[17] on a neutral periodically replicated model of 512 ions. The room-temperature cubic rotator phase was set up with use of the known value of the lattice parameter,[5] and relaxed with interionic potentials taken from previous studies of the alkali cyanides[18]; this led to the correct zero-pressure experimental density. The effect of isobarically cooling the sample was then monitored. At each point in temperature, the equations of motion were integrated over 5000 time steps of 2 fs, the first 500 of which being used for equilibration. Over twenty such runs were carried out.

Figure 1 shows the temperature dependence of the positions of the {111}, {200}, and {220} reciprocal-lattice vectors (Bragg peaks). At high temperature, the cell is cubic since all lines of a given family are degenerate. As cooling proceeds, however, substantial dispersion is revealed. Though partly due to the finite size of our MD cell, such dispersion signals the presence of strong random strains in the system due, in particular, to the chemical disorder of the anion sublattice and to the large size difference of its components. (This explains the relatively high value of x_c for this system.) In fact, as also observed numerically[8,19] as well as experimentally[14,20] in other systems, this is a direct manifestation of the competition between transition-rotation coupling, which tends to induce a structural transition, and strain-rotation coupling, which opposes it.[10]

Random strains are therefore particularly effective in this material, as it undergoes an extremely complicated transition from the high-temperature cubic phase to a low-temperature structure readily identified to be monoclinic (with one of the shears zero and the other two equal). Figure 1 further reveals, at intermediate temperatures (around 100 K), a short-lived phase which we recognize to be rhombohedral.

Strains also seem to be responsible for the anomalous diffraction profiles recently observed by Knorr and Loidl[5] in $(KCl)_{0.2}(KCN)_{0.8}$, i.e., exactly at the critical concentration. These authors speculate that the highly unusual $\exp(-\alpha|\xi|)$ line shape (with ξ the reduced wave vector and α a constant) stems from a "yet unknown superposition of strains" arising from the size, shape, and domain structure of the sample, as well as from chemical disorder. In order to assess these observations, we have calculated the $(2\xi 0)$ neutron profiles at several temperatures for our model system. (Because of the finite size of the MD cell, only the points with $\xi=0$, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ were accessible.) Figure 2 shows the diffraction intensity of this line at four different temperatures (normalized at $\xi=0$). Indeed, as temperature decreases, one undisputably sees a tendency for the line shape to approach that reported by Knorr and Loidl,[5] namely $\ln I(\xi) \sim -\alpha|\xi|$, thereby confirming the highly strained nature of this system, and already suggesting the presence of some sort of glasslike disorder.

We now turn to a study of quadrupolar freezing. A

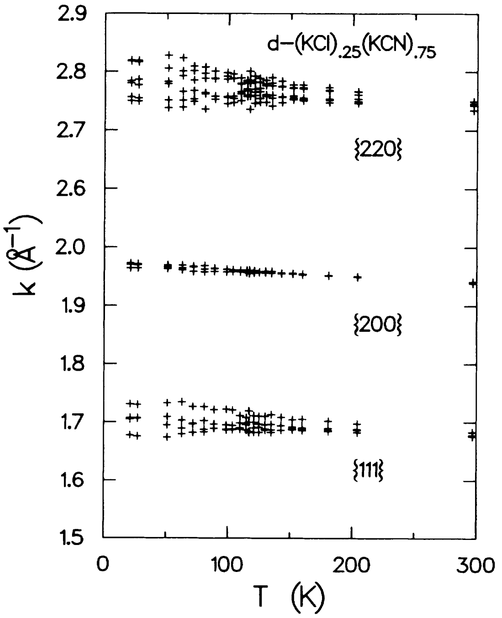

FIG. 1. Temperature dependence of the positions of the {111}, {200}, and {220} reciprocal-lattice vectors. At a given temperature, each cross represents a set of independent vectors. The prefix "*d*-" denotes a system with site-disordered anion sublattice—see also Ref. 10.

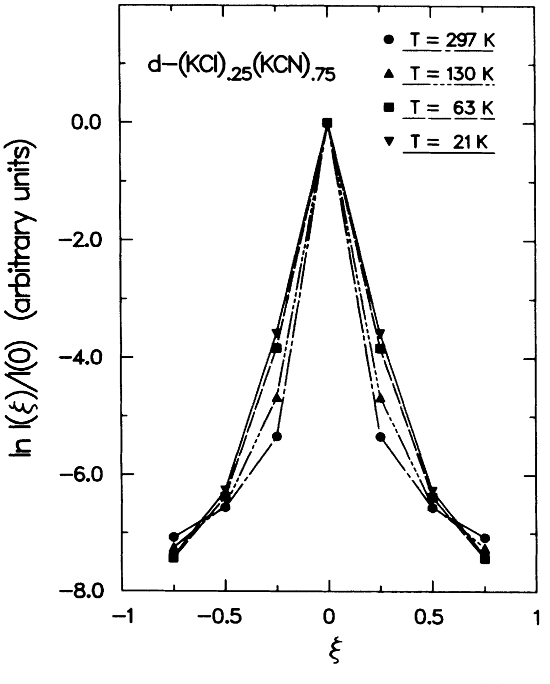

FIG. 2. Calculated neutron-diffraction profile $\ln I(\xi)/I(0)$ of the $(2\xi 0)$ line, where ξ is the reduced wave vector as measured from the Bragg point, at four different temperatures. Lines are a guide to the eye; error bars are smaller than symbol size.

preliminary analysis of orientational correlations in terms of Edwards-Anderson-type order parameters[8,10] indicates that, *on the average,* the CN^- molecular axes freeze into random {111} directions of the parent cubic phase. To get better insight into the distribution of these orientations, we examined correlations between them as functions of both temperature and distance; we define the quantity $P_n(\cos\theta)$, which gives the relative probability of finding a pair of *n*th-nearest-neighbor CN^- molecular ions such that θ is the angle between them.[8]

The freezing process is thus monitored in terms of first-nearest-neighbor correlations $P_1(\cos\theta)$.[8] At high temperature, where the molecules behave as quasi-independent rotors, there is no preferred relative orientation and the distribution is flat. As cooling proceeds, a tendency for neighboring molecules to align with their axes parallel or antiparallel develops. This behavior seems to saturate, and a more or less diffuse background distribution of orientations remains even at 21 K, the lowest temperature examined (see top panel of Fig. 3). On the time scale of our MD experiment, quadrupolar freezing was found to be complete at about 60 K.

The existence of a glass state can be fully assessed by the examination of the *radial* dependence of the orientational correlation function at low temperature. Thus, $P_n(\cos\theta)$ is shown in Fig. 3 for correlations between a given CN^- ion and each of its first six neighboring shells (arising at distances of 4.6, 6.5, 8.0, 9.2, 10.3, and 11.3 Å, respectively). Clearly, $P_n(\cos\theta)$ exhibits some structure at short range which becomes more and more featureless as distance increases. Such a state in which all correlations are lost at large distances precisely coincides with the definition of a glass. These results suggest a picture of the orientational glass phase in this and related systems[8] 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.

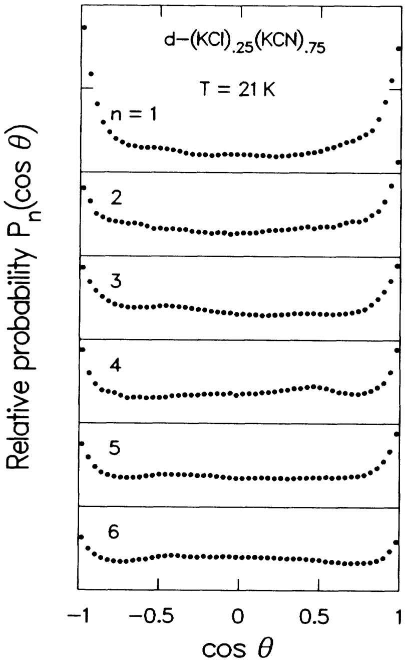

FIG. 3. Low-temperature radial dependence of $P_n(\cos\theta)$, the relative probability of finding a pair of *n*th-nearest-neighbor CN^- molecules such that θ is the angle between them, for $n=1$ to 6.

Here, however, the glass is not cubic, and we now discuss the validity of our findings in the light of the structural behavior observed in this and similar systems. Several points deserve mention. First, both structural transitions (cubic → rhombohedral → monoclinic) are broad and ill defined, and appear to be continuous; a corresponding behavior in $(KBr)_{1-x}(KCN)_x$ with $x<x_c$, *which remains cubic at all temperatures*, is believed to be intimately related to the formation of the glass state.[5,14] Next, the transitional behavior, though extremely weak, is unambiguously present. The shears of the lattice are in fact much smaller than those observed in $(KBr)_{1-x}(KCN)_x$ mixtures with $x>x_c$.[5,14] Thus, again, random strains are quite effective at opposing the transition, though not enough to inhibit it completely.

This complicated transition is also reminiscent of related phenomena in other alkali cyanides. In $(KBr)_{0.36}$-$(KCN)_{0.64}$ (i.e., at the critical concentration for this system) subjected to repeated thermal cycling, for instance, Knorr and Loidl[5] interpret the low-temperature phase diagram as resulting from a competition between the parent cubic phase and two ferroelastic phases, *precisely the same as observed here*, namely rhombohedral and monoclinic. In $(NaCl)_{1-x}(NaCN)_x$, Elschner, Knorr, and Loidl[6] report the coexistence of a glass state together with noncubic components for $x=0.71$ and 0.76, and even suggest that these noncubic components may be glasslike, the term "glass" being used to describe "a state of broadened powder lines." (Experimental limitations do not permit a more accurate determination of these phases.[6]) Next, the transitional sequence cubic → rhombohedral → monoclinic is precisely the one that is observed in $(KBr)_{1-x}(KCN)_x$ slightly above the critical concentration.[14] In addition, a monoclinic phase is also seen at intermediate temperatures in $(KCl)_{1-x}$-$(KCN)_x$ for $x>x_c$.[21] Finally, in agreement with ultrasonic measurements,[22] the shear elastic constant c_{44} was also seen here to soften dramatically.[19] Again, this is consistent with corresponding observations in related systems, and is a precursor sign to the formation of a glass state.

Based on the MD calculations cited above, we suggest that for x close to the critical concentration x_c, highly strained mixed cyanide crystals may very well freeze into a state of disordered orientations *and* noncubic symmetry. This orientational glass phase would evolve *continu-*

ously out of the noncubic components as concentration is varied. Our findings seem to be consistent with the observed structural behavior of $(\mathrm{KCl})_{0.2}(\mathrm{KCN})_{0.8}$ and similar systems. In view of this, a detailed structural investigation of $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$ just below the critical concentration would be worthwhile.

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[1] A. Loidl, T. Schräder, R. Böhmer, K. Knorr, J. K. Kjems, and R. Born, Phys. Rev. B **34**, 1238 (1986).

[2] J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. **43**, 1158 (1979); K. H. Michel and J. M. Rowe, Phys. Rev. B **22**, 1417 (1980).

[3] K. Knorr, A. Loidl, J. M. Rowe, and G. J. McIntyre, to be published.

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

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

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

[7] K. Knorr, E. Civera-Garcia, and A. Loidl, Phys. Rev. B **35**, 4998 (1987).

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

[9] J. M. Rowe, J. J. Rush, N. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. **40**, 455 (1978); K. H. Michel and J. M. Rowe, Phys. Rev. B **32**, 5827 (1985).

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

[11] K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986), and Phys. Rev. B **35**, 1405, 1414 (1987).

[12] S. Galam, Phys. Lett. A **121**, 459 (1987), and to be published.

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

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

[15] K. Knorr, A. Loidl, and J. K. Kjems, Phys. Rev. Lett. **55**, 2445 (1985).

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

[17] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980); S. Nosé and M. L. Klein, Phys. Rev. Lett. **50**, 1207 (1983).

[18] R. W. Impey, M. Sprik, and M. L. Klein, J. Chem. Phys. **83**, 3638 (1985); D. G. Bounds, M. L. Klein, and I. R. McDonald, Phys. Rev. Lett. **46**, 1682 (1981); M. L. Klein and I. R. McDonald, J. Chem. Phys. **79**, 2333 (1983); M. Ferrario, I. R. McDonald, and M. L. Klein, J. Chem. Phys. **84**, 3975 (1986); D. G. Bounds, M. L. Klein, I. R. McDonald, and Y. Ozaki, Mol. Phys. **47**, 629 (1982).

[19] L. J. Lewis and M. L. Klein, unpublished.

[20] J. M. Rowe, J. J. Rush, and S. Susman, Phys. Rev. B **28**, 3506 (1983); J. M. Rowe, J. Bouillot, J. J. Rush, and F. Luty, Physica (Amsterdam) **136B**, 498 (1986).

[21] K. Knorr, private communication.

[22] J. Z. Kwiecien, R. C. Leung, and C. W. Garland, Phys. Rev. B **23**, 4419 (1981); C. W. Garland, J. Z. Kwiecien, and J. C. Damien, Phys. Rev. B **25**, 5818 (1982).