

Two-part freezing in the orientational glass $(\text{KCN})_x(\text{NaCN})_{1-x}$

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^{15}N NMR line shapes of polycrystalline $(\text{KCN})_x(\text{NaCN})_{1-x}$ for $x=0.85$ and 0.59 are reported from 28 to 400 K. The $x=0.85$ spectra near 300 K reveal two components: a narrower line from orientationally mobile CN and a broader line from more nearly oriented CN. The distinction is enhanced by different relaxation times T_1 . The two fractions are identified by previous molecular-dynamics simulations as CN without and with Na nearest neighbors. The ratio of NMR intensities agrees well with this picture. The large random strain fields in these materials are indicated by large NMR linewidths at temperatures well above the freezing temperature. A maximum in T_2^{-1} near 70 K in both samples is due to slowing of the orientation fluctuations.

At high temperatures, NaCN and KCN have orientationally disordered, cubic structures¹ with CN-orientation correlation times in the picosecond range.² Thus, these structures may be described as "orientational liquids." At a first-order transition (at 168 K in KCN and 288 K in NaCN), the cyanide orientationally order approximately parallel to one of the cubic [110] axes^{3,4} and the lattice distorts to orthorhombic.¹ Even though the pure compounds exhibit the same phases and are fully miscible in the solid state, the phase transition is suppressed⁵ for remarkably small concentrations of NaCN in KCN (or KCN in NaCN). For $(\text{KCN})_x(\text{NaCN})_{1-x}$ with $0.15 \leq x \leq 0.90$, an orientational glass state appears below ~ 100 K, an apparently continuous freezing replacing the sharp phase transition.

Strong random strain fields are created by the random substitution of the differently sized cations Na and K (ionic radii of 0.98 and 1.33 Å).^{6,7} The importance of these static strains to the orientational freezing in $(\text{KCN})_x(\text{NaCN})_{1-x}$ [as well as similarly created strains to the freezing in $(\text{KCN})_x(\text{KBr})_{1-x}$] has been treated by Michel.⁸⁻¹¹ Loidl and co-workers reported¹² that freezing in $(\text{KCN})_x(\text{NaCN})_{1-x}$ with $x=0.59$ is a single-particle phenomenon. For $x=0.85$, cooperative effects also appear to be important.¹²

Cheng, Klein, and Lewis reported^{6,7} molecular-dynamics simulations of $(\text{KCN})_x(\text{NaCN})_{1-x}$ for $x=0.85$ and 0.50 . In the $x=0.85$ simulations, the orientational freezings of CN with and without any Na nearest neighbors were found to be quite different. In particular, those CN with any Na neighbors freeze at a high temperature (~ 200 K), generally along a [100] direction with the negative end of the CN (carbon atom) pointing towards a Na cation. The CN devoid of Na nearest neighbors are more orientationally mobile, freezing only at lower temperatures (~ 100 K). For $x=0.50$, nearly all CN have at least one Na neighbor and a two-part freezing was not reported.^{6,7} The present experiments are designed to test the simple picture advanced by the molecular-dynamics simulations.

Polycrystalline samples of $(\text{KCN})_x(\text{NaCN})_{1-x}$ were prepared in fused silica tubes at the University of Utah

Crystal Growth Laboratory by DeLong. The KCN was 99% enriched in ^{15}N ; the NaCN was natural-abundance, high-purity material. An approximately 1-g quantity of material was melted with a torch and was allowed to solidify in ~ 10 s. The entire sample so prepared was used for NMR, so the concentrations deduced from the starting masses of KCN and NaCN refer to averages across the NMR sample. The samples were maintained in a desiccator except for a few minutes during loading into the NMR apparatus.

The samples were cooled in an Oxford continuous-flow helium cryostat. The temperature was determined by a calibrated Lake Shore carbon-in-glass thermometer as well as with a thermocouple. Because no rapid temperature dependences were found, regulation to ± 0.5 K was adequate. Above room temperature, the sample was heated in a homemade oven arrangement.

The ^{15}N NMR experiments were performed at 34.52 MHz in an 8.0-T superconducting magnet. A superheterodyne pulsed spectrometer with an output power of ~ 200 W was used. The 90° pulse time was 12 μs ; composite pulses were not employed. Line shapes were obtained from the Fourier transforms of spin echoes ($90_x - \tau - 180_y$ pulse sequence). For T_1 measurements, the spins were saturated with a comb of fifteen 90° pulses, spaced by 0.03 s.

Briefly, ^{15}N NMR in the CN molecular anion is sensitive to molecular orientation because of the chemical-shift anisotropy. Currents induced in the molecule's electron cloud by the external field lead to a resonance frequency ω ,^{13,14}

$$\omega = \omega_0 \left[1 + \Delta\sigma (\cos^2\theta - \frac{1}{3}) \right]. \quad (1)$$

Here $\Delta\sigma$ is the anisotropic shift magnitude [about 520 ppm (Ref. 15)] and θ is the angle between the external field and the molecular axis; ω_0 is the isotropic average resonance frequency. For rigidly oriented CN in a powder, one obtains a Pake powder spectrum.^{13,14} For rapid isotropic reorientation of the CN, the average of $\cos^2\theta - \frac{1}{3}$ vanishes and a single sharp line at ω_0 results.

The spectrum of $x=0.85$ material at room temperature is presented in Fig. 1(a). Two components are clearly evident; a reasonable separation is indicated by the dashed curve. The narrower line is the signature of CN that are relatively orientationally mobile. Reorientational motions are sufficiently large in amplitude and sufficiently rapid ($\geq 10^5 \text{ s}^{-1}$, a scale dictated by the rigid lattice linewidth) to result in substantial averaging of the frequency ω in Eq. (1). The broader line is from less-mobile CN ions. Even this broader line, however, does not have the Pake pattern shape^{13,14} characteristic of completely nonrotating (aligned) molecules.

The two spectral components have different longitudinal relaxation times T_1 . In Figs. 1(a) and 1(b), a fully relaxed spectrum is presented for comparison with a partly relaxed spectrum. In detail, the average T_1 is $\sim 25 \text{ s}$, while the spectrum of Fig. 1(b) was obtained only 2 s after complete saturation. The broad line is relatively less intense, indicating it has a longer T_1 than the narrow line. The differential saturation supports the separation of the line into two components.

According to the molecular-dynamics work,^{6,7} the distinction between the two species of CN is the existence or absence of any Na nearest neighbors. Evidently, the strong crystal field of a Na aligns neighboring CN even at high temperatures. Assuming a totally random site selection by Na and K, the fraction of CN without any Na nearest neighbors (out of six nearest neighbors, the NaCl structure) is $(0.85)^6=0.38$. Using the partitioning shown in Fig. 1(a), the narrower line accounts for 0.33 of the NMR intensity (spectral area, proportional to numbers of spins). Of course, the separation of the NMR line into parts may be varied. But the reasonable separation shown yields an answer in surprisingly good agreement with the fraction of CN without any Na nearest neighbors.

Line shapes for $x=0.85$ and 0.59 are displayed in Fig. 2 for several temperatures. Although some structure is present for $x=0.59$, distinct components are not apparent. This is as expected, since only $(0.59)^6$ or 4% of the CN should be without any Na nearest neighbors. For both concentrations, the line shapes broaden continuous-

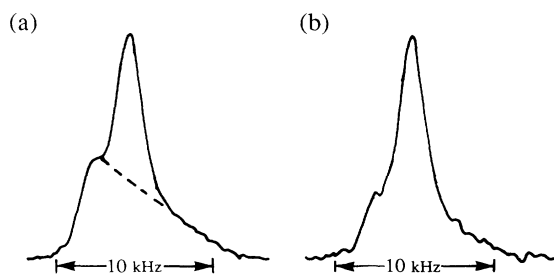


FIG. 1. ^{15}N NMR spectra at 293 K for $(\text{KCN})_x(\text{NaCN})_{1-x}$ with $x=0.85$. (a) Fully relaxed, (b) partly relaxed after saturation. A distinctly two-part line shape is observed; the dashed curve indicates a reasonable separation. Note the decrease in relative intensity of the broad feature in the partly relaxed spectrum.

ly with decreasing temperature, becoming Pake powder patterns characteristic of oriented CN (no longer rotating) by 70 K. The line shapes at higher temperatures may be understood as superpositions of Pake patterns of various widths, reflecting the various extents of orientational localization of the molecules.¹⁶⁻¹⁸

The random fields in $(\text{KCN})_x(\text{NaCN})_{1-x}$ from the random cation siting are much larger than the random fields in $(\text{KCN})_x(\text{KBr})_{1-x}$. This can be deduced by comparison of the high-temperature ^{15}N linewidths in the two systems, using widths expressed in ppm. That is, the dominant source of linewidth, the chemical shift anisotropy of Eq. (1), results in widths directly proportional to the external field. Thus, the $(\text{KCN})_x(\text{KBr})_{1-x}$ data¹⁵ for $x=0.50$, obtained at 2.0 T and analyzed in Ref. 19, have been multiplied by 4.0 for comparison with the present results (8.0 T). In both cases, the linewidth Δf is defined by

$$\Delta f \equiv \int |f|g(f)df / \int g(f)df, \quad (2)$$

where $g(f)$ is the NMR absorption spectrum (i.e., real part). This definition of linewidth is less sensitive to the resonance tails than the usual second moment.

The ^{15}N linewidths Δf from Eq. (2) are presented in Fig. 3. The scaling of linewidths yields agreement for the widths of the systems in the low-temperature, rigid limit, as expected. Clearly, the $(\text{KCN})_x(\text{NaCN})_{1-x}$ lines are much broader than the $(\text{KCN})_x(\text{KBr})_{1-x}$ line at high

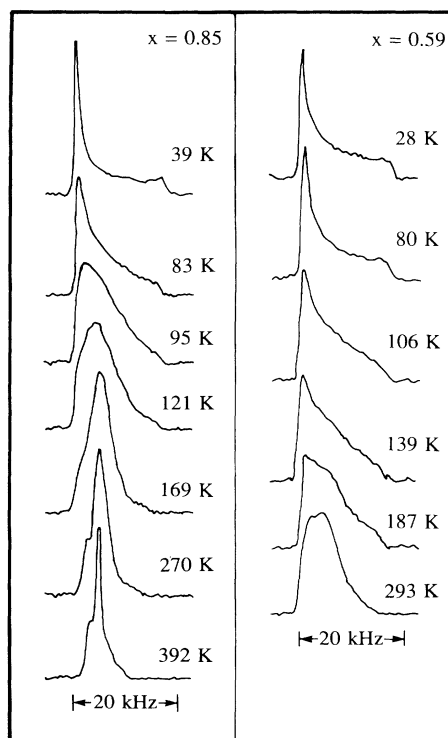


FIG. 2. Spectra of $(\text{KCN})_x(\text{NaCN})_{1-x}$ for $x=0.85$ and 0.59 at several temperatures, specified on each spectrum. With decreasing temperatures, the line shapes continuously evolve into Pake powder patterns.

temperatures. There are many ways to define the orientational freezing temperature T_F ; relevant data for $(\text{KCN})_x(\text{NaCN})_{1-x}$ ($x=0.85$ and 0.59 , Refs. 21, 22, and 12) and for $(\text{KCN})_x(\text{KBr})_{1-x}$ ($x=0.50$, Refs. 23–27) suggest 80 and 60 K, respectively. Scaling the experimental temperatures by T_F would not bring the $(\text{KCN})_x(\text{NaCN})_{1-x}$ and $(\text{KCN})_x(\text{KBr})_{1-x}$ data into agreement, unlike a previous comparison.¹⁹ Hence, the large random fields in $(\text{KCN})_x(\text{NaCN})_{1-x}$ are evident in the substantial CN alignment (specifically, $\langle 3 \cos^2\theta - 1 \rangle \neq 0$) at temperatures well above T_F . In the simplest picture of single CN ions interacting with fixed strain fields of rms strength V and in the high-temperature limit, the linewidth varies²⁰ as V/kT , as obtained from a high-temperature expansion of the Boltzmann factor. Here V refers to terms with $l=2$ symmetry. From Fig. 3, the random fields V are approximately three to five times larger in $(\text{KCN})_x(\text{NaCN})_{1-x}$ than in $(\text{KCN})_x(\text{KBr})_{1-x}$. Large random fields in $(\text{KCN})_x(\text{NaCN})_{1-x}$ are also evident from diffraction and scattering studies.^{12,28} In agreement with earlier work,¹² we find larger random fields in the $x=0.59$ material.

We note that the scaling of linewidths by the relative field strengths makes other sources of linewidth, such as dipole interaction, larger in the $(\text{KCN})_x(\text{KBr})_{1-x}$ data. Subtraction of this broadening would increase the differences in linewidths in Fig. 3.

T_2^{-1} data from the decay of spin-echo envelopes are presented in Fig. 4. Near 70 K, a strong maximum in T_2^{-1} is evident for both $x=0.85$ and 0.59 . The increased relaxation rate T_2^{-1} in this region indicates that the rate ω_c characterizing the orientation fluctuations (or at least some of the fluctuations) passes through the rigid-lattice linewidth $\Delta\omega$, about 10^5 s^{-1} here. This phenomenon is analogous to a conventional T_1^{-1} maximum,¹³ except that it occurs for $\omega_c \sim \omega_0$. Related treatments are provided by models of spins undergoing chemi-

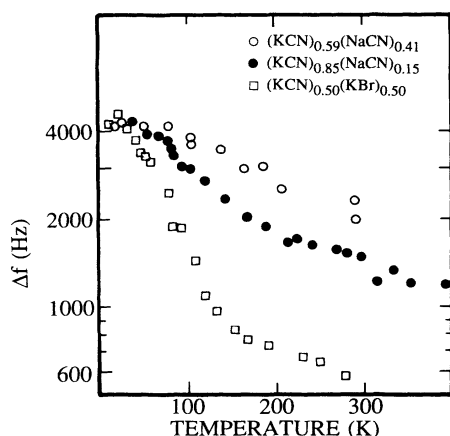


FIG. 3. Comparison of ^{15}N NMR linewidths of $(\text{KCN})_x(\text{NaCN})_{1-x}$ for $x=0.85$ and 0.59 (present results) and $(\text{KCN})_x(\text{KBr})_{1-x}$ for $x=0.50$ (Ref. 19). The latter linewidths have been scaled up by the ratio of external field strengths, 4.0. The NMR line of $(\text{KCN})_x(\text{NaCN})_{1-x}$ remains relatively broad even at temperatures well above the nominal freezing temperature, due to random strain fields.

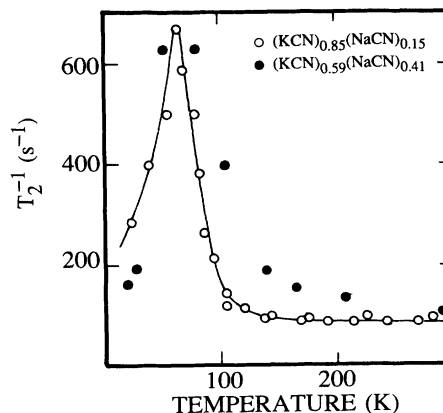


FIG. 4. Transverse relaxation rate T_2^{-1} for $(\text{KCN})_x(\text{NaCN})_{1-x}$ with $x=0.85$ and 0.59 . The maximum near 70 K demonstrates the slowing of the rate ω_c of orientation fluctuations through the rigid-lattice linewidth $\Delta\omega$, about 10^5 s^{-1} . The curve is only a guide for the eyes through the $x=0.85$ data.

cal exchange,¹³ the defeat of coherent averaging by stochastic motions,²⁹ and the maximum¹³ in T_{1D}^{-1} in dipolar systems for $\omega_c \sim \Delta\omega$. The T_2^{-1} maximum demonstrates that slowing of orientation fluctuations is an important aspect to the freezing in $(\text{KCN})_x(\text{NaCN})_{1-x}$. In the related $(\text{KCN})_x(\text{KBr})_{1-x}$, slowing is evident in the phase diagram (Fig. 1) of Ref. 23.

The theories^{13,29} explaining a maximum relaxation rate T_2^{-1} for $\omega_c \sim \Delta\omega$ all assume single values of the motion rate ω_c and all predict a maximum value for T_2^{-1} of order $\Delta\omega$. Specifically, the minimum T_2 will be approximately equal to the decay time of the rigid-lattice free-induction decay, about $40 \mu\text{s}$ here. The observed minimum T_2 is much longer ($\sim 1400 \mu\text{s}$), implying that only a fraction of the CN are involved in the motion or that the motion has a very wide distribution of rates ω_c , or both.

In conclusion, the observation of a two-part ^{15}N NMR line shape in $(\text{KCN})_x(\text{NaCN})_{1-x}$ for $x=0.85$ indicates two populations of CN, one more orientationally mobile than the other. The ratio of intensities agrees well with the statistical fractions of CN without and with Na nearest neighbors. Thus, these measurements confirm the picture advanced by molecular dynamics: CN with Na nearest neighbors freeze at a high temperature, with the other CN freezing at lower temperature by CN-CN interaction. As expected, the $x=0.59$ line shape does not have distinct components. Strong random fields in $(\text{KCN})_x(\text{NaCN})_{1-x}$ are evident from the large NMR linewidths at high temperatures, compared to NMR results from $(\text{KCN})_x(\text{KBr})_{1-x}$. A maximum in T_2^{-1} near 70 K demonstrates the slowing of orientation fluctuations.

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