PHYSICAL REVIEW B VOLUME 56, NUMBER 10 1 SEPTEMBER 1997-II

Discrete nature of the orientational glass ordering in $Na_{1-x}K_xCN$

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(Received 12 May 1997)

The local orientational ordering of the CN^- molecular ions in strongly substitutionally disordered $Na_{1-x}K_xCN$ crystals is investigated via ^{14}N quadrupole-perturbed NMR line-shape measurements. At low temperatures these systems represent order-disorder-type three-state orientational glasses with the CN^- molecular axes oriented essentially along the cubic crystal axes. The temperature dependence of the orientational glass order parameter is determined and shown to fit nicely to a recently developed three-state random-bond–random-field model of orientational glasses. [S0163-1829(97)52234-X]

NaCN-KCN solid solutions represent a model system for the study of orientational, or more specifically, quadrupolar glassy systems. In the $Na_{1-x}K_xCN$ system structural ferroelastic phase transitions of the first order from a cubic into an orthorhombic phase are observed only for compositions close to the pure compounds NaCN and KCN which undergo an identical sequence of phases with, of course, different transition temperatures. Random substitution of Na^+ ions in NaCN by K^+ ions and vice versa leads to a suppression of phase transitions in a broad region of concentrations x given by $x_c^{\mathrm{low}}=0.15\leqslant x\leqslant 0.9=x_c^{\mathrm{high}}$.[1–3] In this concentration range glassy ordering takes place and there is no long range order in the unit cell deformations and orientations of the CN^- molecules. Due to the substitutional disorder a random effective CN^--CN^- coupling and random local strain fields determining the single-particle behavior are present.[4,5]

Numerous orientational glass (OG) theoretical models were introduced,[4,6–8] most of them rather complex, but the agreement between the experimentally observed behavior and theoretical predictions falls far below the one found in pseudo-spin-glasses. Recently, however, a fairly simple model of OG (Refs. 9 and 10) was introduced, which extends the Ising spin-glass theory with random bonds and random fields[11] to a multiple-state cubic OG system. Within this model, molecular orientations are assumed to be restricted to a set of discrete directions in order to be able to explain the x-ray,[5] neutron diffraction,[5,12] and NMR (Refs. 13–15) experimental observations. These measurements revealed strong deviations from an isotropic orientational distribution of the CN^- molecules already at room temperature. At low temperatures, however, no conclusions on the degree of the orientational localization could be drawn due to the strong smearing-out of the diffraction patterns. The $1/T^2$ temperature dependence of the diffuse central peak intensities[4,5,12] demonstrated the influence of random local strains. ^{23}Na quadrupole perturbed NMR (Ref. 13) similarly did not allow for the exact determination of the angular distribution function of the CN^- dumbbells due to the nonlocal nature of the ^{23}Na probe, which senses at least the six nearest CN^- ions.

On the contrary, ^{14}N $(I=1)$ NMR in principle constitutes a powerful tool for investigating the distributions of orientations of the CN^- molecules in the systems under consideration since the local probe, i.e., the electric field gradient (EFG) at each ^{14}N nucleus, is determined for the respective molecule by the intramolecular charge distribution and its orientation in the crystal. On the other hand the applicability of this method is severely hampered by several facts: the ^{14}N nucleus has a low Larmor frequency, correspondingly a rather poor NMR sensitivity, and the large EFG at ^{14}N in the CN^- molecule[16] results in a broad distribution (about 6 MHz) of NMR frequencies. It is one purpose of this paper to demonstrate that we were able to overcome these difficulties and determine by ^{14}N NMR the detailed nature of the glassy ordering in the $Na_{1-x}K_xCN$ system. We did this by applying a frequency-stepped spin-echo technique resulting in very long measuring times (for one spectrum about several days at 20 K and up to weeks at room temperature). This disadvantage is not present if a ^{15}N nucleus is used as a local probe,[15] however, the samples have to be ^{15}N enriched. Our results demonstrate the significance of the ^{14}N NMR method. In particular, we show that the freezing process of the CN^- ions in substitutionally disordered $Na_{1-x}K_xCN$ crystals has a discrete character and that the low-temperature orientational distribution of the CN^- molecular directors in $Na_{1-x}K_xCN$ is strongly localized along the three cubic crystallographic axes. The method also allows for a determination of the components of the OG order-parameter matrix.

The CN^- molecule is cylindrically symmetric. The same is true for the EFG tensor at the ^{14}N site. The first-order quadrupole perturbed ^{14}N NMR frequency shift can be written as[17]

$$\Delta\nu_i=\nu_i-\nu_L=\pm 3/8K(3\cos^2\vartheta_i-1). \tag{1}$$

Here $K\approx 4$ MHz (Ref. 16) is the quadrupole coupling constant and ϑ_i denotes the angle between the direction of the external magnetic field $\mathbf{B}_0$ and the direction of the CN^- director. The head-tail CN^- ordering responsible for the establishment of the dipolar order cannot be detected by this method due to invariance of the quadrupole coupling with respect to the 180° flips of the CN^- groups. Relation (1) describes the ''rigid-lattice'' frequency shift, i.e., the shift at

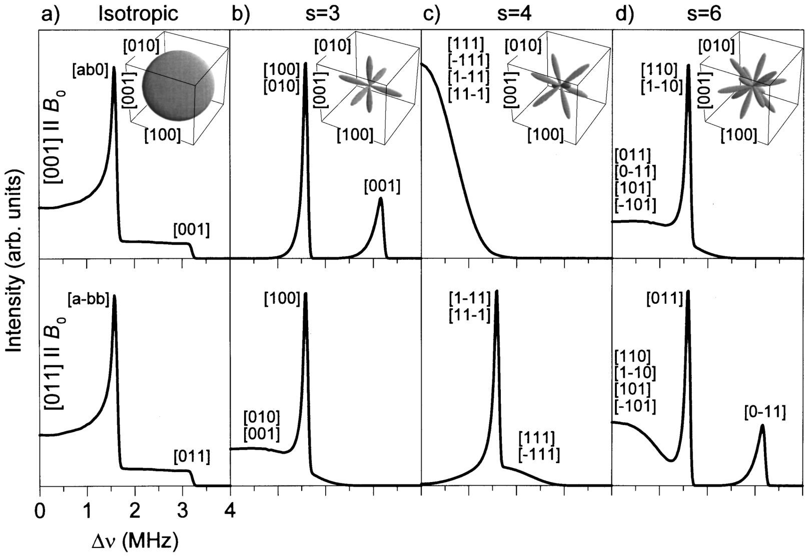

FIG. 1. Theoretical ^{14}N quadrupole-perturbed ''rigid-lattice'' NMR spectra of the CN$^-$ molecule at two different orientations $[001]\| B_0$ and $[011]\| B_0$. Line shapes are calculated with four different cubic averaged distributions $\psi(\Omega)$ (insets to the figures) for the following cases: isotropic orientational distribution (a) and localized orientational distributions with a smearing $\sigma=8°$ for $s=3$ (b), $s=4$ (c), and $s=6$ (d). Labels denote the orientations of the molecular axes of the cyanides giving rise to the associated peak.

low temperatures where the cyanide reorientational dynamics is slow on the NMR time scale $(2\pi K)^{-1}$. In this case each cyanide is found during the experiment to be apparently frozen in the solid angle $d\Omega = d \cos \vartheta d\varphi$ with the probability $\psi_i(\Omega)d\Omega$ where $\psi_i(\Omega)$ denotes the probability distribution function of orientational states, accessible to the ith cyanide. Because of the substitutional disorder the single-particle distribution function $\psi_i(\Omega)$ generally does not possess cubic symmetry. The average symmetry of the system, however, is cubic and this applies also to the average distribution $\psi(\Omega)=1/N\Sigma_i\psi_i(\Omega)$ of the mixed system. The shape of this distribution is mirrored into the ''rigid-lattice'' NMR line shape $F_{\mathrm{rl}}(\Delta\nu)$ through the relation $F_{\mathrm{rl}}(\Delta\nu)d\Delta\nu = \psi(\Omega)d\Omega$. Due to the $\pm$ sign in Eq. (1) $F_{\mathrm{rl}}(\Delta\nu)$ is symmetric with respect to $\Delta\nu=0$. An eventual deviation of $F_{\mathrm{rl}}(\Delta\nu)$ from the powder-pattern line shape [Fig. 1(a)] proves the isotropy of $\psi(\Omega)$ to be broken.

In order to describe the local orientational state of the CN$^-$ molecule one usually expresses $\psi_i(\Omega)$ as a linear superposition of the functions from an orthonormal basis set. In a most general case of a ''continuous'' OG a full set of spherical harmonics is needed.[4] However, if there are only a few allowed orientations for each CN$^-$ molecule, then the expansion in terms of spherical harmonics is inappropriate since a large number of terms would have to be included in order to reproduce distributions with sharp maxima around preferential directions. In such a case Gaussian-like localized distributions are more appropriate. Denoting the tilt and azimuth angles of a given preferential axis **n** in the laboratory frame as θ_n and ϕ_n, respectively, one can write the corresponding localized distribution as

$$Z_n(\Omega)=\Lambda(\sigma)\exp\left[-\frac{1-z^2(\theta_n,\phi_n;\Omega)}{2z^2(\theta_n,\phi_n;\Omega)\tan^2\sigma}\right], \tag{2a}$$

with

$$z(\theta_n,\phi_n;\Omega)=\sin\theta_n \sin(\phi_n+\varphi)\sin\vartheta+\cos\theta_n \cos\vartheta. \tag{2b}$$

$\Lambda(\sigma)$ is the normalization constant whereas σ measures the degree of the localization. Functions $Z_n(\Omega)$ do not possess cubic symmetry; however linear combinations $\psi(\Omega) = \Sigma_{n=1}^{s} Z_n(\Omega)$ can be constructed which do. It is straightforward to show that there are three basic possible arrangements with $s=3$, 4, and 6 with the CN$^-$ directors aligned along with the three cubic crystallographic axes, the four body diagonals, or along the six face diagonals, respectively. The resulting CN$^-$ probability distributions and theoretical ''rigid-lattice'' ^{14}N NMR spectra for different crystal orientations are shown in Figs. 1(b)–1(d).

The ^{14}N NMR spectra of Na$_{0.8}$K$_{0.19}$CN and Na$_{0.57}$K$_{0.43}$CN single crystals grown from the melt were measured in a 7 T superconducting magnet at $\nu_L = 21.674$ MHz. Measuring the distribution of ^{14}N resonance lines by the frequency-stepped spin-echo technique mentioned, the frequency was varied in small steps from ν_L to $\nu_L + 3.5$ MHz. At each step the intensity of the Fourier-transformed solid echo signal following a $90°_x$-τ-$90°_y$ pulse sequence was measured and plotted versus frequency. Only a narrow slice of approximately 20 kHz was irradiated by setting the pulse lengths correspondingly. $\tau=120$ μs was taken to be much smaller than T_2 in order to reduce the possibility of intensity modulations due to frequency-dependent T_2. For similar reasons T_1 (≈ 30 ms at 20 K) was checked regularly while modifying the irradiation frequency.

Spectra detected in the $x=0.19$ and $x=0.43$ samples at $T=20$ K and at an orientation $[001]\| B_0$ are presented in Figs. 2(a) and 2(b). The first sample was also measured at $[011]\| B_0$ [Fig. 2(c)]. The obtained spectra only match the theoretical predictions for the $s=3$ arrangement [Fig. 1(b)]. Peaks at $\Delta\nu \approx 1.65$ MHz in Figs. 2(a) and 2(b) that correspond to cyanides with $\vartheta \approx \pi/2$ are slightly shifted towards higher frequencies due to the higher-order contributions which have to be taken into account in addition to the shift in Eq. (1). Moreover, a tiny peak was detected at $\Delta\nu \approx 3$ MHz in Fig. 2(c) which can only arise from cyanides aligned along face diagonals of the cubic unit cell. Apart from this rather small discrepancy, the results clearly show that at low T, CN$^-$ molecules are predominantly aligned along the [100], [010], and [001] directions, with a rather weak dispersion $\sigma=8°$. The observed localization is much stronger than the one found in K(CN)$_x$Br$_{1-x}$ by ^{15}N anisotropic chemical shift-perturbed NMR.[15] This is clear evidence of the discrete

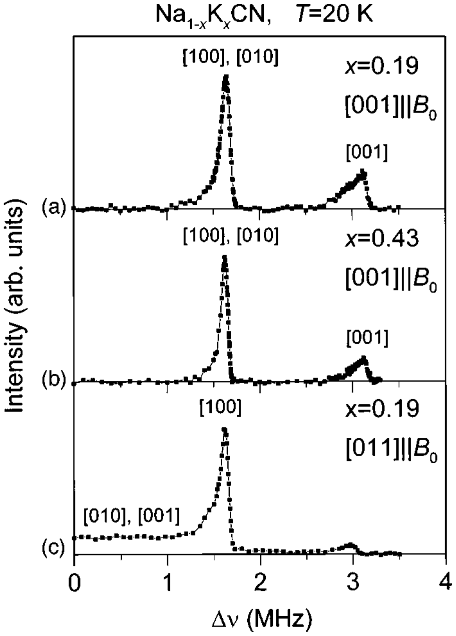

FIG. 2. Experimental ^{14}N quadrupole-perturbed ''rigid-lattice'' $Na_{1-x}K_xCN$ NMR spectra detected at $T=20$ K with the concentrations x and crystal orientations as indicated.

nature of the CN^- orientational ordering. A similar distribution profile has been observed at high temperatures by neutron- and x-ray-scattering techniques.[5,12] Combining these observations, we can definitively confirm the discrete three-state orientational model for strongly substitutionally disordered $Na_{1-x}K_xCN$. Each cyanide points towards one of the six surrounding alkali ions at any instant of time. In the undistorted cubic phase, these are found on cubic sites so that the CN^- molecular directions and cubic crystallographic axes match. This is no longer true if the symmetry is broken. Then, because of the presence of random local deformations, σ, representing a measure of the average mismatch, is nonzero. Thus, $\sigma \approx 8°$ clearly indicates the presence of frozen-in random local strains and the resulting deformations.

It should be stressed that the ''rigid-lattice'' line shape $F_{\mathrm{rl}}(\Delta\nu)$ is not sensitive to the breaking of the local cubic symmetry, i.e., to the appearance of noncubic distortions of $\psi_i(\Omega)$ which indicate the onset of the glasslike local breaking of the macroscopic cubic symmetry. The same is true for x-ray-scattering and elastic-neutron-scattering techniques where the average $\psi(\Omega)$ is determined from structure factors.[5,12] A local deviation from the cubic symmetry can, however, be detected at higher temperatures in the fast motion regime where motional narrowing[17] takes place. If $2\pi K\tau_{\mathrm{eff}}<1$ is satisfied with τ_{eff} representing the effective correlation time of the CN^- reorientational process among s localized states, then each individual cyanide contributes a single sharp resonance at

$$\Delta\overline{\nu_i}=\overline{\nu_i}-\nu_L=\pm 3/8K\sum_{n=1}^{s} p_{ni}(3\cos^2\vartheta_n-1). \qquad (3)$$

Here p_{ni} is the probability for the ith CN^- ion to be found in the state n in which the tilt angle of the molecular director with respect to the external magnetic field is ϑ_n. As we have shown above, our system compiles with $s=3$ so we have $p_{[100]i}$, $p_{[010]i}$, and $p_{[001]i}$. Of these three quantities only two are independent in view of $\Sigma_{n=1}^{s}p_{ni}=1$. By introducing symmetry-adapted local order parameters[10]

$$p_{1i}=\sqrt{3/2}(p_{[100]i}-p_{[010]i}),\quad p_{2i}=\sqrt{1/2}(3p_{[001]i}-1), \qquad (4)$$

one can rewrite Eq. (3) as

$$\Delta\overline{\nu_i}=\pm(A_1p_{1i}+A_2p_{2i}) \qquad (5a)$$

with

$$A_1=\sqrt{27/128}K(\cos^2\vartheta_{[100]}-\cos^2\vartheta_{[010]}),$$

$$A_2=3/\sqrt{128}K(3\cos^2\vartheta_{[001]}-1). \qquad (5b)$$

In the disordered glass state, there is a continuous distribution of parameters p_{1i} and p_{2i} resulting in an inhomogeneously broadened resonance line shape $F(\Delta\overline{\nu})=1/N\Sigma_i\delta(\Delta\overline{\nu}-\Delta\overline{\nu_i})$. Its second moment,

$$M_2=\int \Delta\overline{\nu^2}F(\Delta\overline{\nu})d\Delta\overline{\nu}=A_1^2q_1+A_2^2q_2+2A_1A_2q_\perp, \qquad (6)$$

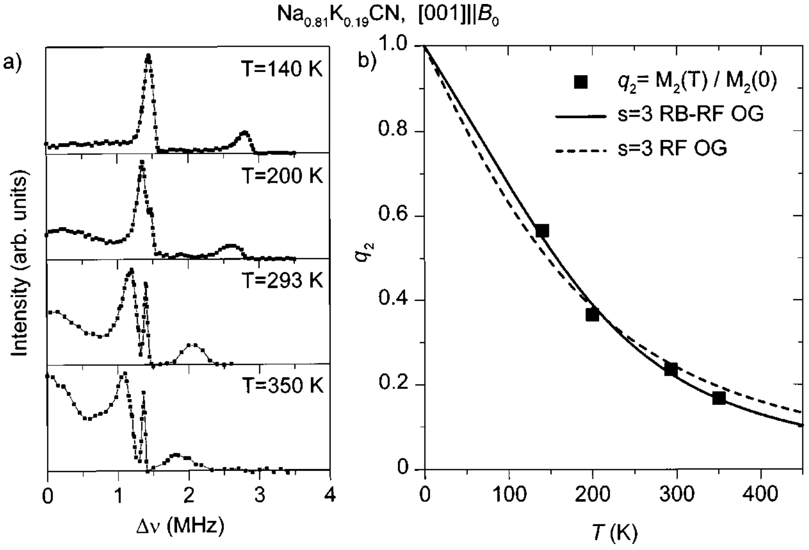

FIG. 3. (a) Temperature dependence of the ^{14}N NMR ''motionally narrowed'' $Na_{0.81}K_{0.19}CN$ line shapes. (b) Temperature dependence of the experimentally determined OG order-parameter component q_2 (squares). The solid line represents the random-bond–random-field (RB-RF) fits to the $s=3$ OG model ($T_J=188$ K, $T_\Delta=145$ K) whereas dashed lines show the pure random field (RF) fits to the $s=3$ OG model ($T_\Delta=183$ K).

depends linearly on the components of the $s=3$ symmetry-adapted[10] orientational glass order parameter

$$q=\left\{ q_1=1/N\sum_i p_{1i}^2,\; q_2=1/N\sum_i p_{2i}^2,\; q_\perp=1/N\sum_i p_{1i}p_{2i}\right\}. \tag{7}$$

According to Eq. (5b) for special orientations either A_1 or A_2 vanish and thus, because of Eq. (6) q_1 or q_2, respectively, are proportional to the measurable second moment M_2. If the static magnetic field is directed along one of the body diagonals $A_1=A_2=0$.

We measured $q_2(T)$ in $Na_{0.81}K_{0.19}CN$. In the temperature interval [60 K, 120 K] no resonance was detected. This indicates that here $2\pi K\tau_{\mathrm{eff}}\approx 1$ so that no response can be obtained by a frequency-stepped spin-echo technique.[13] Above $T=140$ K, ''motionally narrowed'' spectra $F(\Delta\overline{\nu})$ appear. These were measured at an orientation $\vartheta_{[001]}=0$ where $q_2=32/(9K^2)M_2$ and are shown in Fig. 3(a). The intensity around the Larmor frequency increases with temperature. Simultaneously, the intensity of the absorption peaks at the ''rigid-lattice'' positions decreases, whereas their position shifts continuously towards ν_L. An additional sharp peak with a constant intensity is observed around $\Delta\overline{\nu}=1.5$ MHz. It could be attributed to an ''in-plane'' motional averaging i.e., to the cyanides exhibiting a fast reorientational motion constrained to either the a-b, b-c, or a-c crystallographic plane. The contribution of this peak was disregarded in the second moments calculations. The resulting temperature dependence of the glass order-parameter component q_2 [Fig. 3(b)] qualitatively resembles the behavior found in previous studies with the ''nonlocal'' ^{23}N nucleus[13] and the ''local'' ^{15}N nucleus.[14] However, the values found in the present study are considerably higher. They should be taken as much more reliable than those of Ref. 13 due to the local nature of the ^{14}N NMR. Also, only a rough estimate of $q_2(T)$ can be made from the linewidth vs T data of Ref. 14 as no direct mapping $M_2(T)\rightarrow q_2(T)$ is possible in the polycrystalline sample.

The experimentally determined temperature dependence of q_2 should be compared with the predictions of the discrete three-state ($s=3$) random-bond–random-field model of OG transition recently proposed.[10] Within this model, $q_2(T)$ is given implicitly as

$$q_2(Q)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dx_1\int_{-\infty}^{\infty}dx_2\,\exp(-x_1^2/2-x_2^2/2)\times\left[\frac{\sqrt{6}\,\sinh(\sqrt{3/2}Qx_1)}{2\cosh(\sqrt{3/2}Qx_1)+\exp(3/\sqrt{2}Qx_2)}\right]^2, \tag{8}$$

where $Q=\sqrt{(T_J/T)^2q_2+(T_\Delta/T)^2}$. The characteristic temperatures T_J and T_Δ measuring the dispersion of the random interactions and random fields, respectively, can be determined by fitting $q_2(T;T_J,T_\Delta)$ to the experimental data. The best agreement is obtained for $T_J=188$ K and $T_\Delta=145$ K, showing that the collective glass transition in $Na_{0.81}K_{0.19}CN$ is smeared by strong random local fields.

In conclusion we have shown that strongly substitutionally disordered $Na_{1-x}K_xCN$ is a discrete, three-state OG system. We believe that this is a direct experimental confirmation of such a behavior. By applying the ^{14}N quadrupole-perturbed NMR technique, probing extremely sensitively the local behavior, the microscopical OG order parameter component q_2 was measured. Its temperature dependence reveals the random-band–random-field nature of the orientational freeze-out, compatible with the predictions of the $s=3$ model of the discrete OG. Furthermore, randomly frozen local deformations have been found to persist down to 20 K, showing that the onset of orientational disorder is closely related to the loss of translational order.

Financial support by the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, and the Ministry of Science and Technology of Slovenia is gratefully acknowledged.

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