Quadrupolar Glass State of $Ar_{1-x}(N_2)_x$

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Solid solutions of $Ar_{1-x}(N_2)_x$ $(0.5 < x < 1)$ have been investigated by x-ray powder diffraction and molecular-dynamics simulations. The boundaries between the dynamically disordered hcp phase, the ordered Pa3 phase, and the quadrupolar glass have been determined. The glass state is characterized by broadened diffraction lines. Indications for an elastic instability have been observed which suggest that the formation of the glass state is analogous to that for the mixed cyanides.

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For appropriate mixing ratios, $Ar_{1-x}(N_2)_x$ (Refs. 1-3) and the mixed cyanides like $(KBr)_{1-x}(KCN)_x$ (Refs. 4 and 5) form an orientational (or "quadrupolar") glass state at low temperatures. This state has attracted considerable interest since it plays the role of a conceptual link between the spin-glasses and the conventional glasses. The basic view of the glass state is that the aspherical units (N_2 or CN^-) are frozen in random orientations because of a frustration of their interactions. Within this view, which is borrowed from the spin-glasses, the glass states of the two systems appear to be analogous. The analogy of the two systems is further supported by the similarity of the x,T phase diagrams: N_2 and the concentrated cyanides show a phase transition from a high-T phase with dynamical orientational disorder into a low-T phase with long-range orientational order. When a sufficient fraction of the aspherical species is substituted by a spherical species (Ar or Br^-) the long-range order is suppressed in favor of the glass state.

However, there are differences between the two systems. In the cyanides the glass state is closely related to the ordered phase in the sense that the ferroelastic and ferroquadrupolar polarization of the ordered phase is replaced by a distribution of the same quantity in the glass state.[5] A preliminary understanding of the cyanides has been achieved in terms of a ferroelastic instability in the presence of random strain fields.[6-8] The random strains are introduced by the chemical substitution; the instability is brought forth by the coupling of the translational modes of the center-of-mass lattice to the orientational modes. For $Ar_{1-x}(N_2)_x$, this picture is not applicable since the ordered phase (Pa3) is not a ferroelastic variety of the high-T phase (hcp).[9,10] In fact, since there is no group-subgroup relation between the two phases, a Landau order parameter cannot be defined at all. Hence one wonders whether the glass states of the mixed cyanides and of $Ar_{1-x}(N_2)_x$ are really related and how the routes from the ordered phase into the glass state differ.

In order to answer these questions we have investigated $Ar_{1-x}(N_2)_x$, $0.5 < x < 1$, by x-ray powder diffraction and carried out molecular-dynamics (MD) simulations.

The phase diagram derived from the present experiments is shown in Fig. 1. Its gross features agree with those reported previously.[11,12] The high-T phase has a hcp structure for all x investigated. As for pure N_2, we assume that the N_2 molecules are orientationally disordered in the sense that they precess around the hexagonal axis,[10] a view which is supported by the observation that the intensities of the hcp lines die out rapidly at higher Bragg angles.

For $x > 0.8$ we observed the phase transition into the cubic (Pa3) low-T phase. The discontinuous character

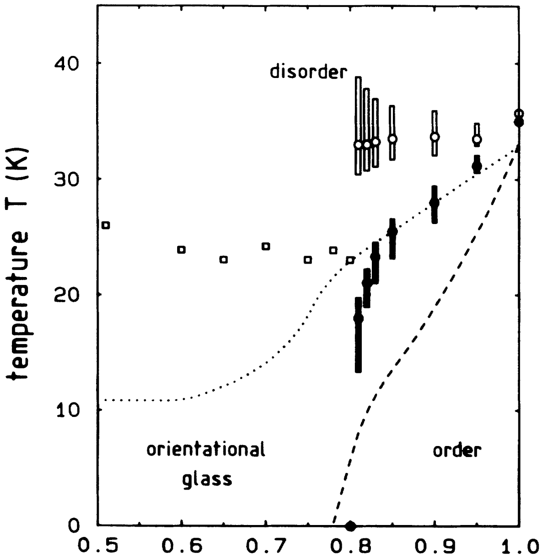

FIG. 1. The x,T phase diagram of $Ar_{1-x}(N_2)_x$. The broken lines are the phase boundaries of the MD simulation. The freezing temperatures (open squares) are derived from the T dependence of the width of the powder lines. The hcp-Pa3 transformation temperatures (open and filled circles) are defined as temperatures where the diffraction lines of the two phases are of comparable intensity. The bars indicate the width of the hcp-Pa3 two-phase region. Filled symbols refer to slow cooling, and open symbols to slow heating.

of the transition is apparent from two-phase regions where the hcp lines coexist with the cubic lines. Surprisingly, the two-phase region has not been observed in the diffraction study of Barrett and Meyer[11] whereas specific-heat data[13] do show this region. The temperature where the diffraction lines of the two phases are comparable are regarded as the transformation temperatures T_s. The transformation shows a strong hysteresis between heating and cooling. The width of the hysteresis is even larger than the width of the two-phase region, Fig. 1, a fact which suggests that kinetic effects are important.

The hcp-Pa3 transition involves an ordering of the N_2 orientations and a change of the fcc center-of-mass lattice which can be visualized as a change of the stacking of the $(111)_{\mathrm{cub}}/(001)_{\mathrm{hcp}}$ planes from the scheme *ABA*... to *ABCA*.... The change is presumably accomplished by dislocations (Shockley partial dislocations) moving in these planes. It is plausible that the substitution of N_2 by Ar introduces local strain fields which impede the motion of the dislocations, an effect known as solution hardening in metallurgy, and thus leads to the hysteresis of the transformation and eventually suppresses the transformation completely. Samples have been kept overnight at temperatures within the hysteresis region. A time dependence of the diffraction pattern has not been observed. The same statement applies to rudiments of cubic lines which could occasionally be traced up to 45 K on heating and relics of hcp lines at the lowest temperatures. Similar observations are known for other martensitic transformations.[14]

Mixtures with $0.5 < x < 0.7$ show a hcp diffraction pattern down to lowest temperatures. (The phase diagram of Ref. 11 shows a fcc rather than a hcp low-T phase for $x = 0.5$, but note that the fcc phase has been obtained after cold working only.) The hcp lines broaden strongly upon cooling (Fig. 2). In analogy to the mixed cyanides we interpret this broadening as the indication that the system enters the glass state. This view is based on the idea that the freezing-in of the N_2 orientations leads to inhomogeneous strains of the center-of-mass lattice, which in turn manifest themselves in broadened diffraction lines. The broadened line profiles represent distributions of the lattice parameters. The width of the distribution is the glass order parameter. The temperature where the width of the (110) reflection is halfway between the high-T value and the low-T value is regarded as the freezing temperature T_f. The T dependence of the c/a ratio suggests that the average angle between the hexagonal axis and the molecular axis decreases with decreasing temperature.

A peculiar behavior has been observed for $0.7 < x < 0.8$ below T_f. Here we found a simultaneous broadening and splitting of the hcp lines with decreasing temperature. The splitting is strongest for the $(hh0)$ reflections (Fig. 3). The changes of the line profiles suggest that inhomogeneous strains are superimposed on a homogeneous (ferroelastic) strain. The homogeneous component is consistent with a decrease of the cell angle from 120° to 119.3° (for $x = 0.75$ and $T = 8$ K). We regard the low-temperature state of these solid mixtures as a nonhexagonal glasslike state, which is the glassy version of a fictitious ferroelastic daughter phase of the hcp phase. Analogous effects indicating a second glasslike

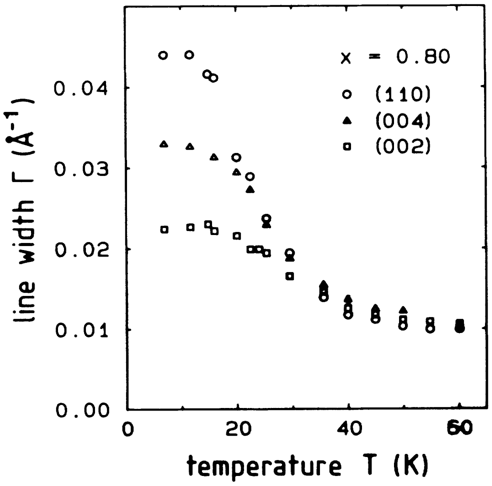

FIG. 2. The temperature dependence of the apparent width of powder lines.

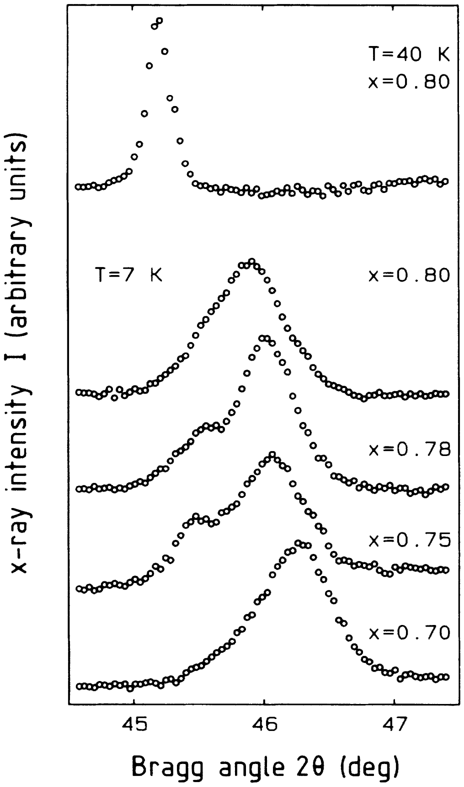

FIG. 3. Profiles of the (110) hcp powder line in the dynamically disordered phase and in the glass state.

state with a center-of-mass lattice different from the high-T phase have been observed in diffraction experiments in $(NaCl)_{1-x}(NaCN)_x$ (Ref. 15) and in pertinent MD calculations.[16]

In the mixed cyanides the glass state can be regarded as the successor of the ferroelastic phase (see above). Clearly this picture does not apply for the relation of the ordered phase (Pa3) and the glasslike phase of $Ar_{1-x}(N_2)_x$. In this context we want to emphasize that the broadening of the hcp lines is not consistent with the type of diffuse scattering which is expected for perturbed hcp stacking sequencies with local cubic . . . *ABC*. . . segments. Furthermore, unlike to the mixed cyanides,[5] $T_f(x)$ is not a linear extrapolation of the $T_s(x)$ phase boundary between the disordered and fully ordered phase. We rather suggest that in the N_2-rich mixtures there exists a metastable ferroelastic low-temperature modification which is screened by the appearance of the Pa3 phase. Only after the hcp-Pa3 transformation is blocked at smaller N_2 content is the glassy version of this modification detectable in the diffraction pattern. The glasslike state with the quasihexagonal center-of-mass lattice evolves out of this modification. The Pa3 phase has presumably no direct relevance for the glasslike state.

On the basis of these latter observations, a unified view of the glass state of $Ar_{1-x}(N_2)_x$ and of the mixed cyanides might be feasible in terms of the theory of an ferroelastic instability in the presence of random strain fields. On the other hand, there is no evidence so far for a planar ($m=2$) ferroelastic instability in $Ar_{1-x}(N_2)_x$, a point which is considered essential in the mixed cyanides.[5,7]

As far as the interatomic forces are concerned, $Ar_{1-x}(N_2)_x$ is definitely a simpler system than the mixed cyanides. Hence one hopes that a deeper understanding of the glasslike state will evolve from computer simulations on this system. In the following we present results of a MD simulation. The N_2 molecule is regarded as a rigid unit of two atoms, 0.545 Å apart. All interatomic forces are of the Lennard-Jones type with the parameters $\epsilon_{NN}=0.515$ and $\epsilon_{ArAr}=1.67$ in units of 10^{-21} J, $\epsilon_{ArN}=(\epsilon_{NN}\epsilon_{ArN})^{1/2}$, $\sigma_{NN}=3.31$ Å, $\sigma_{ArAr}=3.4$ Å, and $\sigma_{ArN}=(\sigma_{ArAr}\sigma_{NN})^{1/2}$. The ensemble consists of 256 molecules, held at constant temperature and pressure in a box of variable shape and size. The autocorrelation function

$$q(t_1,t)=N^{-1}\sum_{i=1}^{N}\tfrac{3}{2}\{[\mathbf{s}_i(t_1)\cdot\mathbf{s}_i(t)]^2-\tfrac{1}{3}\}$$

is calculated where $\mathbf{s}$ is a unit vector of the orientation of the N_2 molecule. In a first series of simulation runs the stability of the long-range-ordered Pa3 phase is examined in the x,T plane. The initial ($t_1=0$) configuration is that of the perfectly ordered Pa3 structure.

$$q^{\mathrm{lro}}=\lim_{t\to\infty}q(0,t)$$

is the parameter of long-range order; it describes the breaking of global symmetry. The Pa3 phase is considered stable if $q(0,t)$, taken at sufficiently large t, namely, $t'=40\,000$ MD steps or approximately 1.2 nsec in real time, settles at values greater than 0.5. The resulting phase boundary is included in Fig. 1.

After t' the relaxation of the initial configuration is nearly finished. For those x,T values where the Pa3 phase was found to be unstable, the autocorrelation function between t' and t, $q(t',t)$, is considered.

$$q^{\mathrm{EA}}=\lim_{t\to\infty}q(t',t)$$

plays the role of the glass order parameter[17]; it is a generalized Edwards-Anderson parameter. Nonzero values signal the break of local symmetry. The time evolution of $q(t',t)$ is shown in Fig. 4. We assume that the glass state is stable if $q(t', t'+0.29\ \mathrm{nsec})>0.5$. The corresponding boundary between the glass state and the dynamically disordered phase is included in Fig. 1. The time evolution of $q(0,t)$ and $q(t',t'+t)$ for $x=0.8$ is shown in Fig. 4.

For x around 0.6, the simulation gives a double-peaked distribution of the next-neighbor distance. Interestingly enough this is about the range of concentration where the diffraction experiment observes a homogeneous deformation of the lattice.

Clearly a more reliable determination of the two phase boundaries and of the center-of-mass correlations would require a larger MD ensemble and an extrapolation to longer relaxation times. Nevertheless, the general con-

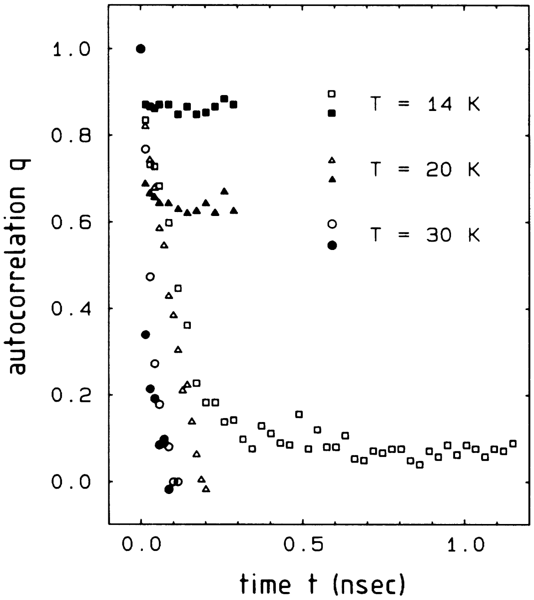

FIG. 4. The time dependence of the orientational autocorrelation starting from the Pa3 configuration [$q(0,t)$, open symbols] and from a relaxed configuration [$q(t'=1.2$ nsec, $t'+t)$, filled symbols]; for $x=0.8$.

clusions from the present MD simulations are supported by systematic theoretical investigations of lattice models of quadrupolar glasses.[17] These models condense the chemical substitution including displacements of the particles from their ideal lattice sites into a reduced Hamiltonian which is a function of the orientations only. For N_2, the effective coupling is of the quadrupolar type with anisotropic coupling parameters. The coupling constants are disordered, and hence they can be approximately described by distributions. The exact form of the distribution is unknown, but for the present system it is, e.g., plausible that the first moment of the distribution is negative since two neighboring N_2 molecules are expected to have a preference to be perpendicular with respect to each other. The details of the coupling, in particular, the structure of the center-of-mass lattice, are already considered in the distribution. (From this point we feel justified to refer to calculations on a cubic rather than on a hcp lattice.)

In the isotropic version of the quadrupolar glass the coupling constants are isotropic and obey a Gaussian distribution. Here the replica mean-field theory[18] yields a quadrupolar glass phase at intermediate T and a partially ordered phase at low T, whereas a Monte Carlo study shows that the isotropic quadrupolar glass is unstable at any finite T.[19] The glass state is stabilized, however, by the introduction of cubic anisotropic interactions, which are again assumed to follow a Gaussian distribution. Thus the lattice model suggests that the quadrupolar glass state can actually exist in a system with crystalline anisotropy, in agreement with the experiment and our conclusions from the MD calculations.

In summary, the present study suggests that the quadrupolar glass is actually the stable low-T phase in $Ar_{1-x}(N_2)_x$ for a wide range of N_2 concentrations. For $0.7 < x < 0.8$, the hexagonal center-of-mass lattice is slightly distorted. This ferroelastic distortion could be the basis for a unified view of the glass states of $Ar_{1-x}(N_2)_x$ and of the mixed cyanides in terms of a random-field model.

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