Orientational Ordering of Frustrated Molecular Quadrupoles: NMR Studies of N_2-Ar Solid Mixtures

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We report NMR studies of the effect of lattice geometry on the orientational ordering of $^{15}N_2$ molecules in solid N_2-Ar mixtures. The N_2 molecules interact through highly frustrated electrostatic quadrupole-quadrupole interactions and samples with 50% N_2 that form fcc lattices show evidence for long range order with a very small distribution of order parameters in contrast to the quadrupolar glass phase observed for the hcp lattice at higher concentrations (57%–77%).

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The phenomenon of frustration occurs in a wide variety of apparently disparate systems [1,2] and results from the presence of either strongly competing interactions (magnetic or elastic) or a fundamental geometrical incompatibility between the symmetry of the interactions and that of the underlying lattice structure, or a combination of both features. These systems include the spin glasses [1] (competing magnetic interactions), mixed dipolar crystals [$Rb_x(NH_4)_{1-x}H_2PO_4$ [3], $Rb_x(ND_4)_{1-x}D_2PO_4$ [4]] (competing ferroelectric and antiferroelectric interactions), mixed molecular crystals (ortho-para H_2 and D_2 mixtures [5], KCN-KBr [6], N_2-Ar [7–9], CH_4-Kr [10]) (frustrated anisotropic interactions), and pyrochlores ($Tb_2Mo_2O_7$ [11], $CsNiCrF_6$ [12]) with purely geometrically frustrated antiferromagnetic interactions of spins at vertices of corner-connected tetrahedra. All these systems exhibit a number of common features, notably a disordered glasslike low-temperature state with strong local correlations but no long range order and extremely slow polydispersive relaxation processes ("glassy" dynamics) below characteristic temperatures.

Systematic studies of prototype systems with strong frustrations are especially important as the insight gained from model systems is expected to have implications for other fields of physics such as neural networks, computing structures, and molecular diffusion on complex macromolecules. With this goal in mind we have studied simple molecular crystals (N_2-Ar mixtures) for which the interactions are well understood (electrostatic quadrupole-quadrupole), and the differing roles of geometrical frustration and substitutional disorder can be explored by varying the concentration of the noninteracting Ar atoms. There is also a clear distinction between quenched disorder [random occupation of lattice sites by the interacting quadrupole moments (N_2)] and the thermal disorder. Furthermore, the local order parameters (molecular alignments) can be measured directly by NMR techniques.

The frustration in the mixed molecular systems (N_2-Ar, ortho-para H_2 mixtures) arises from (i) the topological incompatibility of realizing the minimum possible energy configuration for all pairs of the neighboring quadrupoles on close packed 3D lattices, and (ii) the disorder from the replacement of a quadrupole by a noninteracting ("spherical") atom such as Ar in the N_2-Ar system. Despite the topological frustration, a long range periodic orientational order is observed for the cubic lattice that occurs at high N_2 concentrations [13].

Previous studies using NMR [5], neutron scattering techniques [8] and thermodynamic measurements [9], showed that orientational glass behavior with a random freezing of molecular alignments occurred in N_2-Ar mixtures for relatively high concentrations [$57 < x(N_2) < 77$ mol%], but systematic studies of dilute concentrations of N_2 have not been carried out. It might be expected that the introduction of more disorder by adding Ar atoms would lead to a completely disordered state, but the effect of the geometry of the lattice on the frustration must also be considered. The long range ordered phase has only been observed in the low disorder fcc structure [$x(N_2) > 77$ mol%], while the glassy phase has been seen in the relatively more highly disordered hcp crystal structure. It is therefore not clear whether the randomness introduced by Ar atoms alone is sufficient to destroy the long range order at $x(N_2) = 67.5\%$, or if the structural transition from fcc to hcp at $x(N_2) = 77\%$ also contributes to the transition to the glassy phase. The low temperature phase diagram [14] of N_2-Ar mixtures offers a unique opportunity to explore the role of the structural differences because there exists a second cubic phase at even higher disorder for $x(N_2) < 57\%$ (Fig. 1). A comparison of the orientational state of the cubic regime with that of the nearby hexagonal regime should show what role, if any, the crystal structure plays in the frustration of the orientational ordering. We chose a 50% N_2-Ar mixture that forms a fcc lattice but is sufficiently close to the fcc-hcp phase boundary that the effects of the quenched disorder should be comparable to that in the hcp phase for which one observes only glassy short range ordering.

The NMR line shape for a powder sample containing $^{15}N_2$ molecules consists of an asymmetric Pake doublet whose width as well as separation are proportional to the orientational order parameter, and can therefore be used

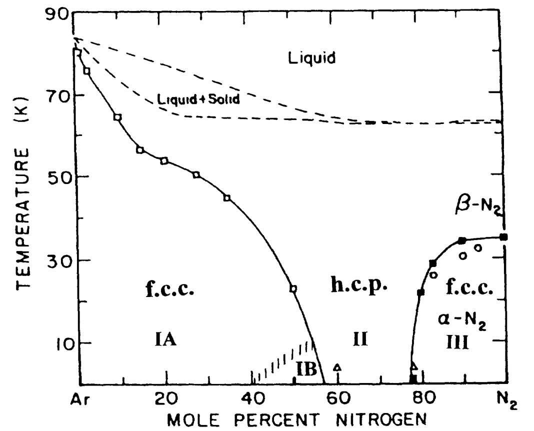

FIG. 1. Phase diagram for solid N_2-Ar mixtures. Phase I (fcc) and III (fcc) have negligible random fields compared to the glassy hcp phase II. Phase I can be considered as having large random bonds for low N_2 concentrations (phase IA) and negligible random bond effects in phase IB.

directly to determine the local order parameter and its distribution. If a magnetic field is applied along the $\hat{\mathbf{z}}$ axis, the intramolecular Hamiltonian for the ith ortho-N_2 molecule (total nuclear spin $I = 1$) whose molecular axis makes an angle θ_i with the $\hat{\mathbf{z}}$ axis is given by

$$H_i = P_2(\theta_i)[-D(I_{iz}^2 - 2/3) + KI_{iz}], \quad (1)$$

where $D/2\pi = 1.38$ kHz is the intramolecular dipole interaction strength, $P_2(\theta_i) = (3\cos^2\theta_i - 1)/2$, and $K = (4 \times 10^{-4})\omega_0$ is the asymmetric chemical shift which is proportional to the Larmor frequency ω_0. Averaging over the molecular fluctuations with respect to a fixed symmetry axis making an angle α_i with the $\hat{\mathbf{z}}$ axis, the NMR spectrum for the ith molecule is the superposition of two lines shifted from ω_0 by $\delta\omega_i^{\pm} = (K \pm D)P_2(\alpha_i)X_i$, where $P_2(\alpha_i)X_i = \langle P_2(\theta_i)\rangle$ and $X_i = \langle P_2(\gamma_i)\rangle$ are the orientational order parameter. γ_i is the angle between the instantaneous molecular axis and the local symmetry axis. For a powder sample, the α_i are uniformly distributed, and the angle averaged NMR absorption intensity for a given value of X consists of two branches Π_1, Π_2 of a Pake doublet given by

$$\Pi_a(X,\omega) = \frac{\Theta[(2K_aX - \omega)(K_aX + \omega)]}{\sqrt{K_aX(K_aX + \omega)}}, \quad (2)$$

with $a = 1,2$ and $K_1 = (K + D)/2$, $K_2 = (K - D)/2$, respectively. Θ is the step function. The observed spectrum $S(\omega)$ depends on the distribution $P(X)$ of the order parameter X and is given by

$$S(\omega) = \sum_a \int_0^1 dXP(X)\Pi_a(X,\omega)g(\omega), \quad (3)$$

where $g(\omega)$ is a broadening function that takes into account the intermolecular dipolar interactions.

Ideally one would like to extract the order parameter distribution $P(X)$ from the observed $S(\omega)$, but the inversion of Eq. (3) is not always possible. In particular, $P(X) = \delta(X - X_0)$ would imply that all molecules in the crystal would have the same degree of alignment with respect to their local symmetry axes, corresponding to long range orientational ordering. For a quadrupolar glass state, we expect a broad distribution of $P(X)$. The secondary peak of the NMR spectrum is very sensitive to $P(X)$. If there is a small distribution of $P(X)$, each peak occurs at a different value of X and therefore broadens the peak, and only when $P(X)$ is sharply peaked around a particular $X = X_0$ does the secondary peak survive. It is therefore possible to make preliminary judgements about the existence of long range order even before a fit with a distribution function is attempted. This is important because an actual fit involves certain adjustable broadening parameters that may always be questioned.

Figure 2 shows a theoretical Pake doublet (solid line) for an anisotropic chemical shift. The dashed line is the expected line shape $S(\omega)$ for a delta function distribution $P(X) = \delta(X - X_0)$ with an additional thermal broadening. Figure 3 is the experimentally observed line shape for the 50% (N_2-Ar) mixture for $\omega_0 = 3.3$ MHz. The existence of the sharp secondary peak for $T < 6.0$ K is a strong indication of long range orientational order. Above 6.0 K, the sharp peak broadens into a shoulder indicating a broad distribution of order parameters, and at much higher temperatures the secondary peak disappears completely corresponding to a fully disordered state. We used $P(X) = \delta(X - X_0)$ to obtain an actual fit. Note that X_0 need not be a free parameter. There are several possible criteria that can be used to extract the value of X_0 from the experimental line shape as long as the principal peaks of the doublet can be properly identified. For example,

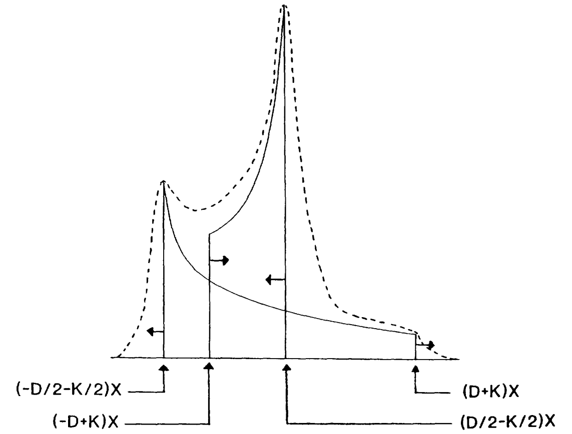

FIG. 2. Theoretical NMR line shape showing Pake doublet with asymmetric chemical shift (solid line), where D is the intramolecular dipolar interaction and K is the chemical shift. The dotted line is the expected line shape with thermal broadening.

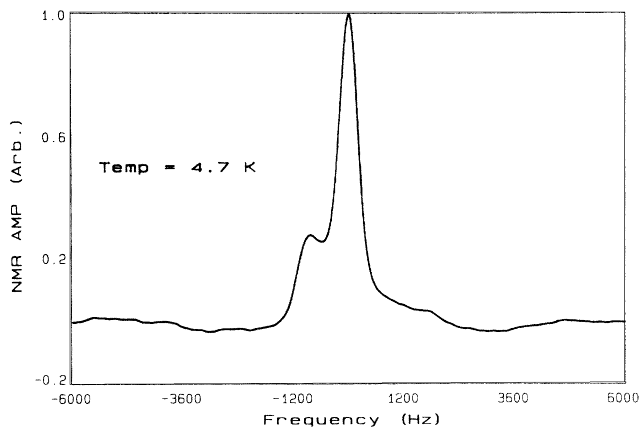

FIG. 3. Experimental line shape of 50% N_2-Ar mixtures recorded at a Larmor frequency of 3.3 MHz at 4.7 K.

the separation between the two square root divergences in the Pake doublet is given by DX, where the intramolecular dipolar interaction constant D is known for $^{15}N_2$. The broadening of the square root divergence of the secondary peak, however, introduces a large uncertainty in the correct determination of X_0. We chose the separation between the primary peak and the cutoff frequency at $(D + K)X$ to determine X_0 from the raw data. This has the advantage of being independent of the position of the secondary peak, which signals the long range order. We obtained $X_0 = 0.76$ for $T < 6.0$ K. This value of X_0 correctly reproduces the positions of the peaks and the cutoffs in the line shape. In order to obtain a better fit to the observed line shape we introduced three adjustable parameters to take into account the broadening of the Pake doublet. The procedure involved replacing the square root divergences $(K_1X + \omega)^{-1/2}$ and $(K_2X - \omega)^{-1/2}$ by $[(K_1X + \omega)^2 + C_1^2]^{-1/4}$ and $[(K_2X - \omega)^2 + C_2^2)]^{-1/4}$, respectively. The Θ function cutoffs are also replaced by a Fermi function of the form $\Theta(Y) = (1 + e^{-bY})^{-1}$, with a broadening parameter b. Figure 4 shows the best fit.

It is clear from the data that a delta function order parameter distribution function corresponding to long range order exists below 6.0 K. This is in contrast to the fact that long range order was absent for lower substitutional disorder (67.5% N_2 in the hcp phase). Our preliminary data at 40% N_2 show no evidence for long range order. It is therefore puzzling that long range order exists at 50% N_2 in between the two disordered phases.

We offer a possible explanation for this behavior based on the phase diagram, Fig. 1. Long range order occurs when the lattice structure is fcc, i.e., at both high (>77%) concentrations and at 50%, but there is no long range order in the hcp phase at intermediate concentrations. It is known that the introduction of Ar atoms not only makes the N_2 bonds random, but it also creates a strain in the local molecular field; this is a random local field in contrast to random bond disorder. Clearly which type of disorder dominates will depend on the strength of the random field, and that in turn depends on the crystal symmetry. To a first approximation, the random field disorder dominates for the hcp structure and it is much smaller for the fcc lattice. We therefore infer that the short range order in the hcp lattice is determined primarily by the random field scenario. Once we cross from the hcp phase to the fcc phase near 57% N_2, the long range order reappears. This occurs because the ordering of the molecular quadrupoles is accompanied by a change to a cubic structure for which the random fields are reduced.

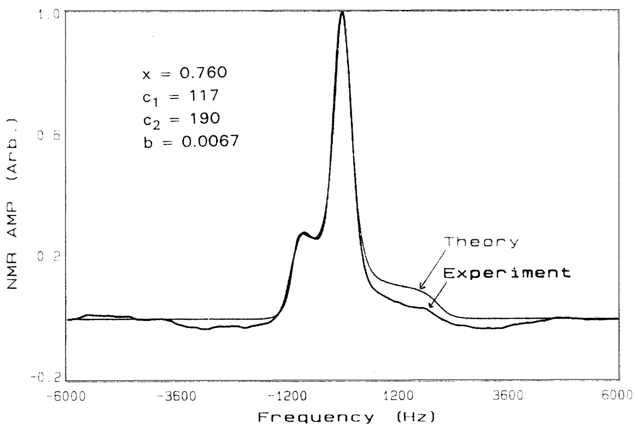

FIG. 4. Comparison of the experimental NMR line shape and the calculated shape for a delta-function distribution $P(X) = \delta(X - 0.76)$. C_1, C_2, and b are the three broadening parameters descibed in the text.

The NMR experiments measure only the local order parameters and their distribution. Further experiments using neutron scattering or x-ray techniques would be valuable to determine if the inferred long range order is periodic at 50% N_2 concentrations similar to that observed at very high N_2 concentrations. The results presented here show that the geometrical aspects of the frustration in molecular solids play a dominant role in the formation of the quadrupole glass similar to the behavior observed for the pyrochlores [11,12]. Further NMR studies are planned to explore the dynamics of the ordered phases at low concentrations and to complete the phase diagram for N_2-Ar mixtures below 40%.

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[1] D. Chowdhury, *Spin Glasses and Other Frustrated Systems* (Princeton Univ. Press, Princeton, NJ, 1986).
[2] *Disorder in Condensed Matter Systems,* edited by J. Blackman (Oxford University Press, New York, 1989).
[3] E. Courtens, Phys. Rev. Lett. **52**, 69 (1984).

[4] Z. Kutnjak, C. Filipic, A. Levstik, and R. Pirc, Phys. Rev. Lett. **70**, 4015 (1993).
[5] N. S. Sullivan, C. M. Edwards, Y. Lin, and D. Zhou, Can. J. Phys. **65**, 1463 (1987).
[6] J. Hessinger and K. Knorr, Phys. Rev. Lett. **65**, 2674 (1990); C. Bostoen and K. H. Michel, Phys. Rev. B **43**, 4415 (1991).
[7] D. Esteve, N. S. Sullivan, and M. Devoret, J. Phys. (Paris), Lett. **43**, 793 (1982).
[8] W. Press, B. Janik, and H. Grimm, Z. Phys. B **49**, 9 (1982).
[9] L. G. Ward, A. M. Solek, and D. G. Haase, Phys. Rev. B **27**, 1832 (1983).
[10] G. Grondley, M. Prager, W. Press, and A. Heideman, J. Chem. Phys. **85**, 2204 (1986).
[11] B. D. Gaulin, J. N. Reimers, T. E. Mason, J. E. Greedan, and Z. Tun, Phys. Rev. Lett. **69**, 3244 (1992).
[12] M. J. Harris, M. P. Zinkin, Z. Tun, B. M. Wanklyn, and I. P. Swainson, Phys. Rev. Lett. **73**, 189 (1994).
[13] T. A. Scott, Phy. Rep. **27**, 89 (1976).
[14] C. S. Barrett and L. Meyer, J. Chem. Phys. **42**, 107 (1965).