NMR Study of the Orientational Ordering of Monolayers of $^{15}N_2$ on Graphite

N. S. Sullivan[(a)] and J. M. Vaissiere
Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay,
F-91191 Gif-sur-Yvette Cedex, France

(Received 15 March 1983)

NMR pulse techniques have been used to study the orientational ordering of $^{15}N_2$ molecules physisorbed on graphite. A small hysteresis ($\sim 2.5\%$) and small discontinuity in the evolution of the NMR echo amplitudes which depend directly on the local order parameters indicates that the order-disorder transition is first order.

PACS numbers: 64.70.Kb, 61.50.-f, 76.60.Lz

We report results of an NMR study of the orientational ordering of monolayers of $^{15}N_2$ molecules physisorbed on exfoliated graphite. This system is a physical realization of the two-dimensional (2D) ordering of electric quadrupoles on a triangular lattice for which topological frustration and critical fluctuations are expected to play major roles.[1,2] The transition from the orientationally disordered phase has stimulated considerable interest since it is believed to belong to the same universality class as the $n=3$ component Heisenberg model with face-oriented anisotropy, and it is predicted that critical fluctuations will drive the transition first order.[1,3,4]

Although recent low-energy-electron diffraction measurements[5,6] have shown that the orientationally ordered phase is a (2×1) herringbone configuration, the nature of the phase transition has not been elucidated. In order to determine whether or not the transition is first order we have used NMR techniques to follow the evolution of the local order parameters. The results indicate that the transition is first order with a small discontinuity in the order parameter and a hysteresis $\simeq 2.5\%$ on thermal cycling. This agrees qualitatively with recent Monte Carlo simulations.[3]

Monolayers of N_2 form a commensurate 2D solid on graphite below 47 K with the molecules occupying the center of every third carbon ring, i.e., a $(\sqrt{3}\times\sqrt{3})R30°$ triangular net.[7] At high temperatures, the molecular axes are disordered as a result of thermal agitation, but at low temperatures this rotational symmetry is broken by anisotropic forces acting on the molecules. There are two contributions: (1) the strong anisotropic potential of the graphite substrate[8] for which the molecules tend to lie parallel to the graphite, and (2) the anisotropic interaction between the molecules (principally electric quadrupole-quadrupole) which leads to a collective orientational ordering of the axes.[9] The results of energy minimization,[10] Monte Carlo simulations,[11] and mean-field-approximation calculations[1] show that the ground state is a two-sublattice herringbone array.

The orientational ordering transition was first seen in heat-capacity studies[12] and later confirmed by neutron scattering.[13] The herringbone structure was identified by low-energy electron-diffraction measurements[5,6] which were able to detect several superlattice reflections. The intensity of the superlattice peaks varied continuously on warming with an apparently smooth transition at approximately 30 K although a weak intensity persisted up to 39 K. It was not possible to conclude from these studies whether the transition was smooth or first order.

More detailed information concerning the evolution of the local orientational order can be obtained from NMR studies since the intramolecular nuclear dipolar and electric quadrupole interactions, and anisotropic chemical shifts, do not average to zero if the molecular axes have a preferred orientation. [$^{15}N_2$ ($Q_{\text{nucl}}=0$) was chosen rather than $^{14}N_2$ ($Q_{\text{nucl}}\neq 0$) to avoid very broad lines which occur if there is a small distribution of order parameters.]

Since the nuclei of $^{15}N_2$ are identical fermions there are two molecular species: o-$^{15}N_2$ (total nuclear spin $I=1$, odd orbital symmetry) and p-$^{15}N_2$ ($I=0$, even orbital symmetry). For $T>4$ K the solid consists of a random mixture of 75% o- and 25% p-$^{15}N_2$. The NMR spectrum of the ortho molecules is determined by the perturbation of the nuclear Zeeman Hamiltonian by the dipolar and anisotropic chemical shift Hamiltonians whose secular components are given by[14,15]

$$\begin{aligned} H_{D_i}' &= -(\hbar D/3)P_2(\theta_i)(3I_{z_i}^{\,2}-2)\,, \\ H_{\chi_i}' &= \hbar\chi_{\text{ac}}P_2(\theta_i)I_{z_i}\,. \end{aligned} \tag{1}$$

θ_i specifies the orientation of the ith molecule with respect to the applied magnetic field (Z axis) and $P_2(\theta_i)$ is the Legendre polynomial. $D = 8710$ rad s^{-1} and $\chi_{ac} = 4\times10^{-6}\omega_0$. ω_0 is the Larmor frequency. If each molecule has a preferred orientation along an axis z_i we need to know the time scale of angular fluctuations with respect to z_i to determine the NMR spectrum. These deviations determined by the molecular interactions occur on a time scale $t_{mol} \ll D^{-1}$ (or χ^{-1}). For $t > t_{mol}$ the orientations are described by a probability distribution with principal axes x_i, y_i, z_i, and local quasistatic order parameters $p_i = \langle 3z_i^2 - 1\rangle/2$ and $n_i = \langle x_i^2 - y_i^2\rangle$ which define, respectively, the mean *alignment* along z_i and the *eccentricity* of the distribution. With this notation the angular dependence in Eqs. (1) becomes[16]

$$P_2(\theta_i) = p_i P_2(\alpha_i) + \tfrac{3}{4} n_i \sin^2\alpha_i \cos 2\beta_i, \qquad (2)$$

where the polar angles (α_i, β_i) specify the field direction with respect to the local reference triad (x_i, y_i, z_i). For the herringbone phase at low temperatures, $n_i \simeq 0$, and the simplified form of Eq. (2) can be used to follow the evolution of the order parameters p_i. The full form of Eq. (2) is kept at high temperatures to allow for nonzero n_i which can occur for thermal agitation out of the plane.

We used pulse techniques designed to eliminate the contributions of H_{χ_i} and local magnetic field gradients.[17] Sequences consisting of a 90° pulse, $R_y(90)$, followed at $t = \tau$ by a second pulse, $R_\varphi(\psi)$ (which rotates the spins by an angle ψ about an axis at angle φ to the y axis), produce a solid echo[15,18] at $t = 2\tau$ given by

$$\begin{aligned} A_\psi(2\tau) = {} & \tfrac{1}{2}e^{2i\varphi}[-\sin^2\psi + \cos\psi(1-\cos\psi)\langle\langle \cos 2D_i\tau\rangle\rangle] \\ & + \tfrac{1}{2}[\sin^2\psi + \cos\psi(1+\cos\psi)\langle\langle \exp[-2(\chi_i + \Delta\omega_i)\tau]\cos 2D_i\tau\rangle\rangle]. \end{aligned} \qquad (3)$$

$D_i = DP_2(\theta_i)$ and $\Delta\omega_i$ corresponds to a local field shift. Double angular brackets $\langle\langle\,\rangle\rangle$ indicate an average over different sites. By subtracting the amplitudes for sequences with $\varphi = 0$ and $\varphi = \pi/2$ we elminate the contributions of χ_i and $\Delta\omega_i$ and observe

$$S_\psi(2\tau) = -\sin^2\psi + \cos\psi(1-\cos\psi)\langle\langle \cos 2D_i\tau\rangle\rangle. \qquad (4)$$

Since the modulation term $\langle\langle \cos 2D_i\tau\rangle\rangle$ depends on the order parameters p_i and n_i *and* the orientations of the symmetry axes, one can follow the temperature dependence of the order parameters and the angular dependence as the magnetic field is rotated. We will assume for the moment that the p_i have the same value p_0 at each site and that $n_i = 0$. For ideal perfectly flat substrates there are two simple cases: (i) for the field B_0 perpendicular to the substrate, $P_2(\alpha_i) = -\frac{1}{2}$ at each site and $S_\pi^{\perp}(2\tau) = \cos p_0 D\tau$; (ii) for B_0 parallel to the substrate one must add the independent contributions from each 2D crystallite—for a 2D powder this gives

$$S_\pi^{\parallel}(2\tau) = \cos(\tfrac{1}{4}p_0 D\tau)J_0(\tfrac{3}{4}p_0 D\tau).$$

J_0 is the zero-order Bessel function.

The substrate was made from sheets of exfoliated graphite (Papyex-N)[19] separated by 0.015-mm Mylar sheets aligned parallel to the rf field. Cu wires linked each sheet of graphite to a regulated thermal plate whose temperature was monitored by a germanium resistance thermometer. Monolayer coverage ($x = 1.00 \pm 0.02$) was determined by observing the first knee in the 78-K isotherm.[12,20,22] The NMR echoes were obtained using a fast recovery 3-MHz pulse spectrometer.[23]

The results observed at 4.6 K for the orientationally ordered phase are shown in Fig. 1. Figure 1, curve *a*, shows the unmodulated T_2 decay for the 90°-τ-90° sequence and provides a necessary check on the value of T_2 used for the analy-

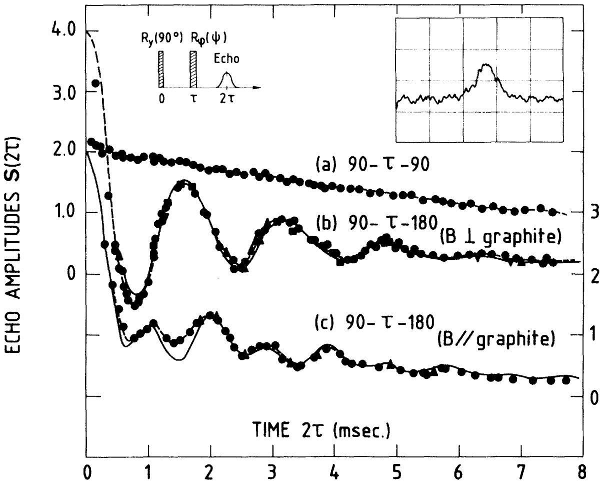

FIG. 1. Observed echo amplitudes for a monolayer of $^{15}N_2$ at 4.6 K for pulse sequences 90°-τ-90° (curve *a*), 90°-τ-180° with B perpendicular to the graphite sheets (curve *b*, left-hand scale), and 90°-τ-180° with B parallel to the sheets (curve *c*, right-hand scale). The solid lines represent fits described in the text. Inset: a typical signal for the average of 8-K echoes. The low signal-to-noise ratio is due to the poor effective filling factor ($\sim 10^{-3}$) compared with bulk material for the same sample chamber.

sis of the 90°-τ-180° sequences. The reduced depth of modulation of $S_{\pi}{}^{\perp}(2\tau)$ compared with the ideal case is due partly to the misorientation of the graphite platelets in the Papyex sheets which consist of a mixture of well-oriented platelets and dust (approximately 25%).[24] The best fit for *both* field orientations was obtained for a Gaussian spread $P(\Omega)$ of platelet orientations with a half-width at half maximum of 18° and a fraction $a = 0.31$ of sites with $p \simeq 0$. The value of the order parameter inferred from the fits is $p_0 = 0.83 \pm 0.05$, but the precise value depends on the assumptions made for $P(\Omega)$ and should be used with caution. [For the α phase of bulk N_2, $p_0 = 0.863 \pm 0.003$ (Ref. 9)].

A slightly better fit can be obtained if one allows for a small width in the distributions $P(p)$ of order parameters rather than the delta function form assumed above. Such a broadening may occur since the ordered phase is fragile with respect to defects, and boundary effects for graphite platelets ~100 Å would be significant.[25]

The analysis given above for low temperatures assumed *local* axial symmetry ($n_i = 0$). The excellent agreement between the calculated curve *b* in Fig. 1 and the experimental results justifies the assumption for $T \simeq 0$. This is expected for the herringbone phase at low temperatures, but the results for higher temperatures ($4.6 < T < 36$ K) indicate that n_i are small with an upper limit $|n_i| \lesssim 0.24$. A more precise analysis in terms of both parameters is hindered by uncertainties in graphite misorientations but this does not prevent testing for a first-order transition by following the thermal history of the echo amplitudes.

The temperature dependence of the order parameters was investigated using 90°-τ-180° pulse sequences with τ fixed (close to the first minimum of Fig. 1, curve *c*) and B_0 parallel to the graphite. Since the echo amplitudes $S(2\tau)$ increase as p_0 decreases, the observed variation of S with temperature can be used to deduce $p_0(T)$ if deviations from axial symmetry are not significant ($n_i \simeq 0$). The results [Fig. 2(a)] were reproducible on warming with a small discontinuity at 28.1 ± 0.1 K. Despite the difficulty with the determination of small n_i, the discontinuity in the signal amplitudes points to the first-order character of the transition. The upper limit $|n_i| < 0.24$ just above T_c was determined by comparing echo decays for B parallel and perpendicular to the graphite planes. A distinct jump in the height of the echo amplitudes $S^{\parallel}$ ($2\tau = 0.6$ msec) was observed at 28.1 K on warming at 25 mK/min.

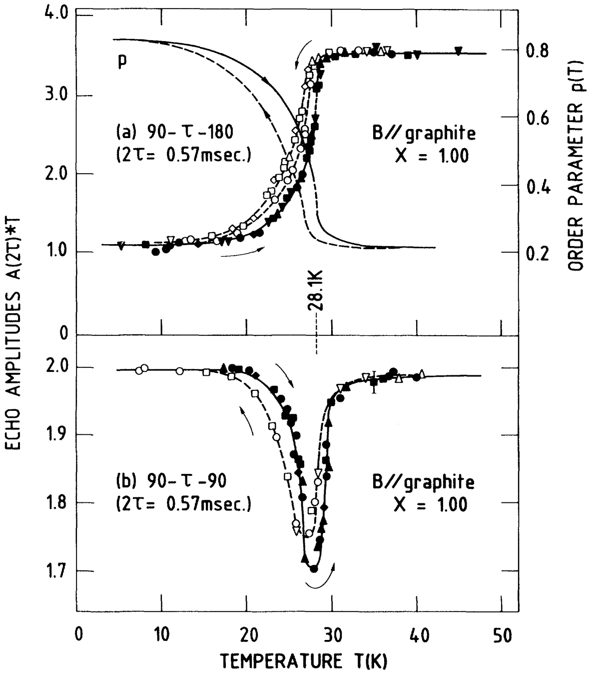

FIG. 2. Temperature dependence of the echo amplitudes $S(2\tau) = A^{\varphi=0} - A^{\varphi=\pi/2}$ for (a) 90°–180° and (b) 90°–90° sequences with τ fixed. There is a small discontinuity at $T = 28.1 \pm 0.1$ K. The hysteresis is reduced by annealing at 45 K for 38 h (open circles). Other samples were annealed for 8 h. Open (solid) symbols refer to cooling (warming) and different symbols indicate different samples.

The cooling curves vary with the thermal history of the sample. This irreproducibility is probably due to the problem of nucleation of the frustrated herringbone array which can be laid down in six different ways on a given lattice.

The above analysis of the 90°-τ-180° echo amplitudes is only valid if the order parameters are time independent for $0.1D^{-1} < t < 10D^{-1}$. This was checked by studying 90°-τ-90° amplitudes [Fig. 2(b)] which show only a small additional damping (~20%) just below T_c. This may be due to slow domain-wall motion rather than an intrinsic t dependence of the p_i.

The hysteresis of approximately 2.5% is observed for both types of echoes and for different samples. This is the best evidence so far obtained for the weak first-order character of the transition, and careful tests were made to exclude the effects of a possible thermal lag between the graphite and the N_2 layer by use of the NMR signals $S(\tau = 0)$ to measure the temperature. The thermal coupling of the N_2 to the substrate is poor with thermalization times ~45 min near 30 K. (The nuclear spin-lattice relaxation time is short, $T_1 \simeq 1$ sec, and attributed to magnetic impurities in the substrate.) The most convincing evidence that the hysteresis is real is the observation that if the warming cycle is stopped below T_c and the sample cooled, the solid "warming" curve (Fig. 2) is retraced. This is not true if the sample is warmed above T_c. The hysteresis appears to be associated with the first-order character of the transition.

In conclusion, the small hysteresis and discontinuity in the temperature dependence of the order parameters observed by NMR provide evidence for a first-order transition to the herringbone phase for monolayers of $^{15}N_2$ on graphite. Unusual effects possibly related to a second phase transition have been seen for coverages $X = 1.06$. Further work with use of improved techniques to enhance the signal-to-noise ratio and reduce the long data acquisition times should help elucidate these features.

Discussions with M. G. Richards, B. P. Cowan, A. J. Berlinsky, M. A. Klenin, J. R. Brookeman, M. Devoret, D. Estève, D. Glattli, and J. M. Delrieu are gratefully acknowledged, as is also S. Leibler's help with preliminary experiments.

Note added.—After submission of this Letter, our attention was drawn to recent heat-capacity mesurements by Migone *et al.*[26] The difficulty in determining T_c from the broad heat-capacity peaks of Migone *et al.* probably explains the difference between their T_c and ours.

---

[a] Present address: Department of Physics, University of Florida, Gainesville, Fla. 32611.

[1] A. B. Harris and A. J. Berlinsky, Can. J. Phys. 57, 1852 (1979).

[2] M. A. Klenin and S. F. Pate, Phys. Rev. B 26, 3969 (1982).

[3] O. G. Mouritsen and A. J. Berlinsky, Phys. Rev. Lett. 48, 181 (1982).

[4] A. Aharony, Phys. Rev. B 8, 4270 (1973); T. Natterman, J. Phys. C 9, 3337 (1976).

[5] R. D. Diehl, M. F. Toney, and S. C. Fain, Jr., Phys. Rev. Lett. 48, 177 (1982).

[6] R. D. Diehl and S. C. Fain, Jr., to be published.

[7] J. K. Kjems, L. Passell, H. Taub, and J. G. Dash, Phys. Rev. Lett. 32, 724 (1974).

[8] W. A. Steele, J. Phys. (Paris), Colloq. 38, C4-61 (1977).

[9] T. A. Scott, Phys. Rep. 27C, 89 (1976).

[10] C. R. Fuselier, N. S. Gillis, and J. C. Raich, Solid State Commun. 25, 757 (1978).

[11] S. F. O'Shea and M. L. Klein, Chem. Phys. Lett. 66, 381 (1979).

[12] T. T. Chung and J. G. Dash, Surf. Sci. 66, 559 (1977).

[13] J. Eckert, W. D. Ellenson, J. B. Hastings, and L. Passell, Phys. Rev. Lett. 43, 1329 (1979).

[14] I. M. Ishol and T. A. Scott, J. Magn. Reson. 27, 23 (1977).

[15] D. Estève and N. S. Sullivan, J. Phys. C 15, 4881 (1982).

[16] N. S. Sullivan, M. Devoret, B. P. Cowan, and C. Urbina, Phys. Rev. B 17, 5016 (1978).

[17] Magnetic impurities in the substrate contribute a large inhomogeneous linewidth and prevent the use of standard cw line-shape studies for determining the order parameters.

[18] D. S. Metzger and J. R. Gaines, Phys. Rev. 147, 644 (1966).

[19] LeCarbone Lorraine, B.P. 148, Sennevilliers, France 92231.

[20] S. Ross and W. Winkler, J. Colloid Sci. 10, 319 (1955).

[21] Y. Larher, J. Chem. Phys. 68, 2257 (1978).

[22] R. D. Diehl and S. C. Fain, Jr., to be published.

[23] N. S. Sullivan, P. Deschamps, P. Neel, and J. M. Vaissiere, Rev. Phys. Appl. 18, 253 (1983).

[24] J. P. Coulomb, M. Bienfait, and P. Thorel, J. Phys. (Paris) 42, 293 (1981).

[25] The electric quadrupole-quadrupole energy of nearest-neighbor pairs is higher than the minimum isolated pair energy, and molecules surrounding defects tend to reorient to lower their energy.

[26] A. D. Migone, H. K. Kim, M. H. W. Chan, J. Talbot, D. J. Tildesley, and W. A. Steele, Phys. Rev. Lett. 50, 192 (1983).