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Neutron Scattering as a Probe of the Orientational Ordering of Nitrogen Molecules on Graphite

J. Eckert

Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

and

W. D. Ellenson

Department of Chemistry, University of Maine, Orono, Maine 04473

and

J. B. Hastings and L. Passell

Brookhaven National Laboratory, Upton, New York 11973

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Orientational ordering of nitrogen-molecule overlayers on graphite has been investigated by neutron diffraction. The ordering transition is found to occur at 30 K in both the registered and dense-solid phases despite a 5% difference in the nearest-neighbor distance.

On substrates with uniform and homogeneous surfaces, physisorbed gas films are known to form surface states analogous to the solid, liquid, and vapor phases of bulk matter. In addition, when the films are composed of molecules rather than atoms, they also appear to undergo transitions from structurally ordered but orientationally disordered phases to phases in which the molecules assume preferred orientations. Such transitions, despite their fundamental interest, have thus far been virtually ignored in spectroscopic studies of physisorbed molecular systems. While efforts have been made to determine molecular arrangements in orientationally ordered surface states, little attention has been paid to the details of the actual ordering process.

Not long ago, we became interested in the possibilities of probing surface-ordering transitions in molecular films with neutrons. Our initial exploratory experiments, which we wish to describe here, involved nitrogen molecules on graphite, a system that has attracted considerable experimental and theoretical attention in the past and for which it has recently been predicted that orientational ordering would cause a doubling of the unit cell of the structurally ordered film.^{1,2} We will present evidence that the expected doubling does occur and can be detected by the appearance

of a superlattice peak in the neutron diffraction pattern. Moreover, the temperature range within which the peak is observed will be seen to coincide with a region in which a broad, ill-defined structure—conjectured to arise from the ordering process—appears in the heat capacity of the films.³

To place our experiments in their proper context, let us briefly review some of the salient features of the nitrogen-graphite system as it is presently understood. Heat-capacity^{3,4} and neutron-diffraction⁵ measurements have shown that, at temperatures below roughly 90 K, nitrogen-molecule monolayers form a two-dimensional, lattice-liquid film on graphite basal planes. Below 84 K the lattice-liquid solidifies into a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer, i.e., into an epitaxial solid in which one out of every three hexagons of the substrate basal plane is occupied. In this structure the molecular lattice is a triangular net with a nearest-neighbor spacing of 4.26 Å. When the coverage is further increased, the epitaxial solid is forced out of registry and converted to a denser, incommensurate-solid phase which is basically a self-defined, two-dimensional structure determined primarily by the interactions between molecules of the film rather than by their interactions with the atoms of the substrate. This can

be inferred from the fact that the dense-solid lattice is a triangular net with a nearest-neighbor distance of 4.04 \AA , a structure essentially isomorphous to the close-packed (111) plane of the low-temperature, α phase of bulk solid nitrogen. It should be noted, however, that the dense-solid overlayer is not a pure monolayer phase since a partial second layer is required to maintain its stability. The measurements to be described below involve both the registered and dense-solid phases of the nitrogen film.

In approaching the problem of orientational ordering experimentally, we were mindful of the possible ground-state configurations for the registered-solid overlayer suggested by Berlinsky and Harris's¹ mean-field theory of electric quadrupole-quadrupole coupled diatomic molecules in the orientation-dependent potential of the graphite substrate. Assuming, as Steele⁶ suggests, that the surface potential tends to align the nitrogen molecules with their axes parallel to the film plane; then, according to Berlinsky and Harris, the monolayer should form one or the other of the triangular configurations shown in the inset to Fig. 1—the two-sublattice case applying when the substrate interaction is stronger than the quadrupolar coupling and the four-sublattice case in the opposite limit when the quadrupolar coupling is dominant. In between these extremes, an intermediate phase is expected in which the molecules remain in the two-sublattice configuration but tilt their axes out of the plane. The two-sublattice, in-plane configuration of Fig. 1 was also independently proposed—specifically for nitrogen on graphite—by Fusilier, Gillis, and Raich.²

In the orientationally disordered, high-temperature phase, all lattice sites become equivalent. Thus, regardless of which configuration represents the low-temperature ordered phase, the ordering transition will have the effect of doubling the overlayer unit cell and new diffraction peaks can be expected to appear. Calculation of the relevant crystallographic structure factors showed that of the low-index diffraction peaks accessible to investigation with neutrons, the intensity of the (20) reflection (referring to the doubled unit cell of the ordered phase) ought to be relatively unaffected by the ordering process while the (21) reflection, which has a zero structure factor and therefore will not diffract in the disordered phase, becomes an allowed, low-intensity reflection when the molecules orientationally order. Hence in either the two- or four-sublattice case, the appearance of a (21) diffraction peak would signal

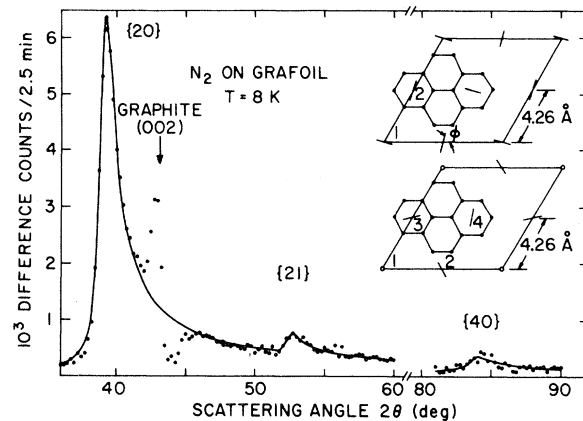


FIG. 1. Diffraction from a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adsorbed nitrogen-molecule overlayer in the orientationally ordered, registered-solid phase. The (21) peak is the superlattice reflection.

the onset of the orientational-ordering transition.

Our search for the ordered state of the nitrogen film involved the same basic experimental procedure as employed in the original neutron studies of Ref. 5. For the graphite substrate we used a stack of Grafoil⁷ sheets in a thin-walled, cylindrical aluminum container 5.1 cm high and 4.4 cm in diameter. The container was attached to the refrigeration block of a controlled-temperature, flow-type helium cryostat capable of maintaining any fixed temperature within the range 5–300 K. Monolayer coverage was determined from adsorption isotherm measurements; in our cell 357 cm^3 (STP) of nitrogen gas were required to obtain a complete registered-solid monolayer.

All diffraction scans were made with 2.47-\AA wavelength neutrons using a triple-axis neutron spectrometer set to accept only elastically scattered neutrons. Both the monochromating and analyzing crystals of spectrometer were pyrolytic graphite. In addition, a pyrolytic graphite filter was mounted in the incident monochromatic beam to remove unwanted higher-order (shorter-wavelength) neutrons reflected by the monochromator. For all scans, the sample cell was oriented so the scattering vector $\vec{Q} = \vec{k}_i - \vec{k}_f$ was aligned perpendicular to the most probable c -axis direction of the partially oriented substrate crystallites, i.e., \vec{Q} was nominally parallel to the graphite basal planes. (\vec{k}_i and \vec{k}_f represent, respectively, the incident- and scattered-neutron wave vectors.) As is usual in such experiments, the background from the substrate was measured with no gas in the cell and diffraction from the surface

nitrogen-molecule film taken as the difference between scattered intensities with and without gas in the cell.

Plotted in Fig. 1 is the difference diffraction pattern obtained from a complete monolayer of the registered-solid phase at a temperature of 8 K. Three peaks are evident, all with the asymmetric shape characteristic of powder diffraction from two-dimensional crystalline arrays; they index as the (20), (21), and (40) reflections from either of the orientationally ordered configurations shown in the inset to the figure. Increasing the temperature had only a slight effect on the (20) intensity but, as expected, the (21) intensity decreased rapidly, falling to zero at a temperature near 30 K. The same pattern emerged from a study of the dense-solid overlayer. Again, three peaks were observed and could be indexed as the (20), (21), and (40) reflections from the same basic unit cell, but in this case with a nearest-neighbor distance of 4.04 rather than 4.26 Å. As before, the (21) intensity was markedly temperature dependent, disappearing altogether at about 30 K, while the (20) intensity changed little over the same temperature range.

Figure 2 shows the observed variation of the (21) superlattice peak intensity at coverages of 0.8, 1.0, and 1.2 monolayers, the first two coverages corresponding to a partial and complete registered-phase monolayer and the third, to the dense, incommensurate-solid overlayer. It is important to note that the superlattice peak is superimposed on the trailing edge of the (20) reflection from the film. As a consequence, near the transition temperature the (20) scattering (which is temperature dependent) becomes a large fraction of the total observed intensity and is a significant source of systematic uncertainty in the difference count. For this reason, we are hesitant to attempt to parametrize the temperature dependence of the ordering process by fitting a power-law function to the data. Nevertheless, it is qualitatively if not quantitatively evident that at all three coverages the transition occurs very near 30 K. Aside from a marginally significant difference in the shape of the curves close to transition temperature, the registered and dense-solid superlattice reflections exhibit remarkably similar behavior. This is surprising in view of the fact that quadrupolar couplings, which vary as the fifth power of the distance, would be expected to be significantly stronger in the dense-solid phase unless, of course, some compensating orientational rearrangement takes place.

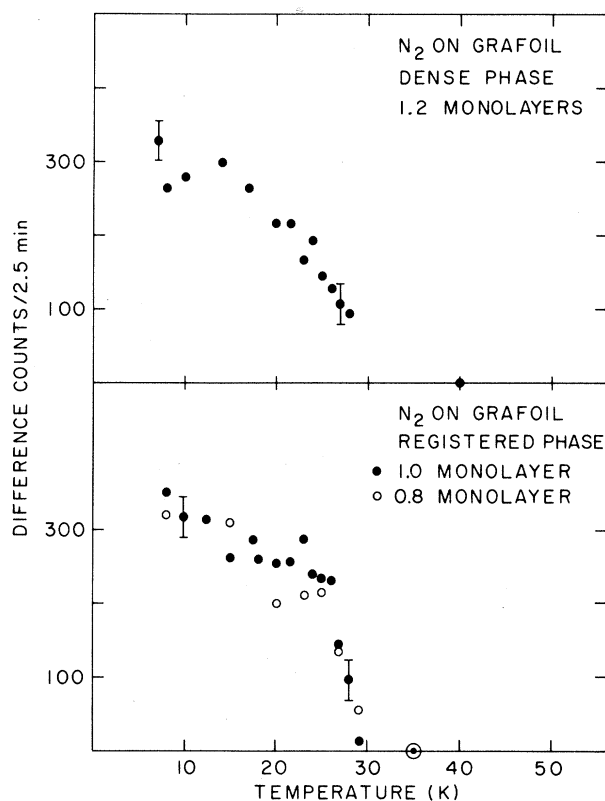


FIG. 2. Temperature dependence of the (21) superlattice reflection from the registered and dense-solid phases.

At this point, it is incumbent to ask if it is possible to interpret our observations in terms of a structural rather than orientational-ordering transition? In answer to this, we note that there are only five two-dimensional Bravais lattices and only the assumption of a doubled unit cell gives a fully satisfactory description of the low-temperature diffraction pattern. In every other case, either extra peaks are predicted—which are not observed—or lattice constants consistent with the data lead to intermolecular distances too small to be physically reasonable. Thus the conclusion that the transition at 30 K is an orientational-ordering transition seems well founded.

An interesting comparison can be made between our observations and O'Shea and Klein's⁸ Monte Carlo calculations of the orientational ordering of idealized, two-dimensional, quadrupolar-coupled, diatomic-molecular arrays. For nitrogen molecules on a triangular net with the same lattice constant as the registered-solid phase and with the additional constraint that the molecular axes lie in the film plane, O'Shea and Klein pre-

dict an ordering temperature of 28 ± 5 K. An equivalent calculation for a more compressed lattice with the same nearest-neighbor spacing as the dense-solid phase but with molecular axes allowed to tilt out of the film plane gave approximately the same ordering temperature,⁹ the closer spacing being compensated by the formation of a rickrack configuration of the molecular axes. That a model which treats the surface film as an idealized, two-dimensional structure gives results in good agreement with the experimental observations is testimony to the essentially two-dimensional character of the transition.

Finally, we have to address the question of what are the ordered-state molecular configurations of the registered and dense-solid films. This would be a difficult problem even if we were dealing with a three-dimensional solid. If that were the case, we would expect to be able to deduce the ordered configuration from the intensity profile of the diffraction pattern,¹⁰ assuming sufficient diffraction data could be collected. But there is too much background scattering from the substrate (particularly at larger scattering vectors) to make such an approach feasible with overlayer films. The only realistic alternative is to attempt to compare the observed intensities with those calculated assuming ordered configurations suggested by theory. We find, unfortunately, that either the two- or four-sublattice configuration can satisfactorily reproduce the observed diffraction profile of the registered-solid phase; the data available are not sufficient to allow us to choose between the two suggested alternatives. One other possibility remains, namely, to search for the extra superlattice reflections expected if

the ordered state is the four-sublattice rather than two-sublattice configuration. As it happens, this too appears to be impractical; a calculation of the relevant structure factors makes it clear that none of the extra reflections could be detected with neutrons. Thus we are forced to conclude that, while we can study the onset and development of orientational order in the nitrogen overlayer, we cannot, at least at this time, determine the ordered configuration.

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Critical Velocities in Superfluid ³He

J. M. Parpia and J. D. Reppy

Laboratory of Atomic and Solid State Physics, and The Materials Science Center, Cornell University, Ithaca, New York 14853

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The oscillatory flow of superfluid ³He through an 18- μ m-diam orifice has been studied. A clearly defined critical velocity is seen in both the *A* and *B* phases. For velocities greater than the critical value, the superflow involves an excess dissipation. The temperature dependence of the critical velocity is reported for temperatures near the superfluid transition ($T/T_c > 0.9$).

The possibility of dissipationless flow is one of the most dramatic aspects of the superfluid state. The study of the limits of stable superflow and

the mechanisms of critical velocities has proven a valuable test of our understanding of the nature of the superfluid state for both superconductors