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Orientational Ordering of Nitrogen Molecular Axes for a Commensurate Monolayer Physisorbed on Graphite

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Low-energy electron diffraction has been used to study the orientational ordering of the molecular axes of nitrogen molecules physisorbed on graphite single crystals. A 2 × 1 superlattice structure with in-plane orientations is inferred for the monolayer where the molecular centers have the commensurate $(\sqrt{3}\times\sqrt{3})\ 30°$ structure. The superlattice intensity decreases significantly near 30 K but persists up to 40 K, consistent with a first-order transition with finite-size effects.

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Previous structural studies of N_2 molecules physisorbed on graphite have shown that at submonolayer converages and $T < 47$ K, N_2 molecules have a commensurate structure in which the centers of mass of the molecules are in a $(\sqrt{3}\times\sqrt{3})\ 30°$ array.[1,2] With neutron scattering, Eckert *et al.* detected a new superlattice peak at $T < 30$ K due to ordering of the N_2 molecular axes, while the centers of mass remained in the $(\sqrt{3}\times\sqrt{3})\ 30°$ structure.[3] Because of intensity limitations, the neutron study was unable to distinguish between various proposed 2×1 and 2×2 superlattice structures,[4-6] nor could it detect any superlattice intensity above 30 K. In this study, low-energy electron diffraction (LEED) is used to show that the commensurate monolayer has a 2×1 superlattice herringbone structure essentially the same as that predicted from an energy-minimization calculation.[4] In addition, residual superlattice intensity is detected above 30 K, which indicates a persistence of some orientational order up to at least 40 K.

In this experiment we used a natural graphite single crystal about 5 mm in diameter and 0.2 mm in thickness. It was prepared by cleaving in air with Scotch tape and then baking at 1000 °C in flowing dry nitrogen gas. The crystal was then mounted on a sample holder which was installed in our ultrahigh-vacuum system. The entire system was baked at 110 °C for 24 h, after which the residual gas pressure was about 10^{-10} Torr. Typical beam parameters for these measurements were 5×10^{-10} A current, 25–200 eV energy, and a beam diameter of about 0.3 mm. LEED patterns were measured by taking photographs of the patterns or by measuring the intensity of a particular diffraction feature with the spot photometer described previously.[2] Spot profiles were measured by scanning the photometer aperture across the spot. The acceptance angle of the photometer when used in this mode was about 0.75°, or roughly the same size as a sharp diffraction spot at 15 K.

In the experiments described here, the temperature of the crystal was first lowered to about 30 K. Nitrogen gas was admitted to the vacuum system to a pressure of about 5×10^{-9} Torr, at which point it condensed on the crystal while the LEED pattern was observed. When one monolayer of N_2 was on the graphite, as evidenced by an intense ($\sqrt{3}\times\sqrt{3}$) 30° LEED pattern, the N_2 gas valve was closed and the pressure then dropped to less than 10^{-9} Torr. The coverage of N_2 on the graphite remained constant for measurements between 20 and at least 33 K. Above 33 K, the coverage may have changed, and these data will not be treated as quantitatively accurate.

Figure 1 shows a commensurate monolayer of N_2 on graphite at a low temperature in the structure inferred from our LEED measurements. The N_2 molecules are centered on the sites of a ($\sqrt{3}\times\sqrt{3}$) 30° lattice, and the molecular axes are in a two-sublattice herringbone arrangement which forms a 2×1 superlattice of the ($\sqrt{3}\times\sqrt{3}$) 30° structure. There are three equivalent orientations in which this superlattice can be placed on the graphite lattice at angles 120° apart. Figure 2 shows a schematic drawing of a diffraction pattern from one orientational domain of the superlattice. The systematic diffraction spot absences along the [10] and [11] directions indicate that the structure has two glide planes in these directions, indicated by dashed lines in Fig. 1. Absences due to glide planes arise from general symmetry arguments and are independent of multiple-scattering effects at normal incidence.[7] The condition that both of these glide planes exist rules out any structure except the two-sublattice in-plane arrangement shown in Fig. 1.[8] In addition, it puts a condition on the orientation angles of the N_2 molecules: the glide planes exist only if the angles θ_1 and θ_2 with respect to the [10] direction, shown in Fig. 1, are equal. In our LEED experiments, the electron beam samples an area large enough to contain domains of all three orientations. The resulting LEED pattern is an incoherent superposition of diffraction patterns from each of the three domains.

This herringbone structure with $\theta_1 \simeq \theta_2 \simeq 45°$ is essentially the same as the structure predicted by Fuselier, Gillis, and Raich[4] for this low-temperature phase. Their calculation assumed

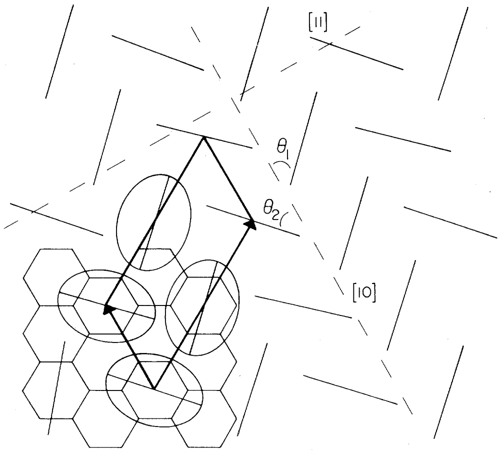

FIG. 1. N_2 molecules in a commensurate two-sublattice in-plane structure on the graphite basal plane (hexagons). The molecular axes of molecules in the two sublattices have angles θ_1 and θ_2 with respect to the [10] direction. Dashed lines denote glide planes in this structure. A real-space unit cell is shown.

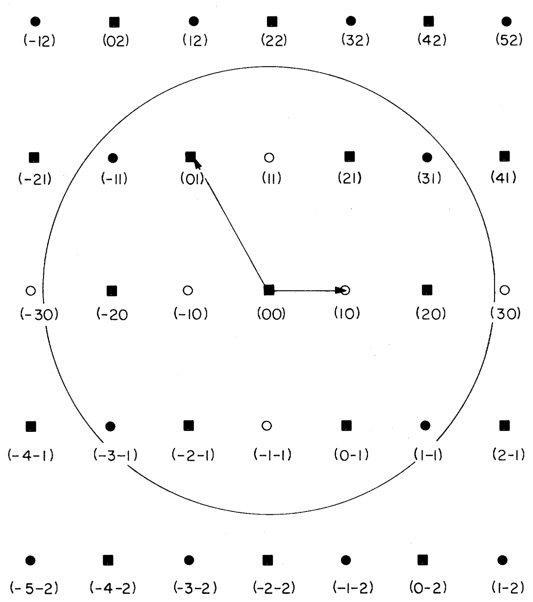

FIG. 2. Schematic diagram of diffraction pattern from one 2×1 domain. Reciprocal-space unit vectors are shown. Squares denote spots present from the ($\sqrt{3}\times\sqrt{3}$)30° structure seen at $T < 47$ K. Circles denote additional spots from the 2×1 superlattice. Open circles denote absences in the LEED pattern due to the glide-plane symmetries (see text). The actual LEED pattern is a superposition of three of these patterns, rotated 120° from each other. The large circle indicates the fraction of reciprocal space seen on our screen at 85 eV. The spots from the graphite substrate, equivalent to the (22) spots on this drawing, are outside the field of view at 85 eV.

graphite-nitrogen and nitrogen-nitrogen interaction potentials of the Lennard-Jones form, and quadrupole-quadrupole interactions between nearest-neighbor nitrogen molecules. The two-sublattice structure given by $\theta_1 = \theta_2 = 45°$ is identical to the two-sublattice in-plane phase predicted by Harris and Berlinsky[5] for large crystal fields and low temperatures. Structures closely resembling this configuration were also observed in the Monte Carlo simulations as the optimum structure for quadrupoles constrained to a plane in a triangular lattice.[6] The two-sublattice out-of-plane and the four-sublattice structures, which were also proposed as possible structures,[5,6] do not have the glide-plane symmetry of our LEED patterns.

The neutron-diffraction study[3] and an earlier heat-capacity study[9] observed a phase transition at about $T = 30$ K. The heat-capacity study was only sensitive enough to suggest a transition. The neutron-diffraction study was sensitive enough to show a large decrease in the superlattice peak intensity at about $T = 30$ K. The increased sensitivity of the LEED experiment enables us to measure the superlattice peak intensity with much higher precision. The integrated intensity of a (31) superlattice spot as a function of temperature is shown in Fig. 3(a). The LEED measurements show that the intensity does not simply decrease to zero at 30 K; instead, the intensity at the (31) positions persists until at least 40 K with no apparent broadening of the spot profiles within the accuracy of these measurements.[10]

Shown in Fig. 3(b) is the intensity of a (20) spot, which is present as long as the N_2 molecules are ordered in the $(\sqrt{3} \times \sqrt{3})$ 30° structure. The (20) scan was taken to determine the vibrational Debye-Waller contribution to the drop in intensity of the superlattice spots.[11] The ratio of the intensity scans 3(a) and 3(b), shown in Fig. 3(c), has a large drop in intensity over a fairly narrow temperature range and a more gradual decrease up to at least 40 K. Each of the scans shown in Figs. 3(a) and 3(b) was done at a local maximum of the intensity-energy curve for that particular spot. This was to minimize the effect of multiple scattering on the intensity changes of the spots. However, the possibility that multiple-scattering effects are present in these curves cannot be ruled out, and therefore the curve in Fig. 3(c) should not be interpreted as the exact decay of the square of the order parameter.

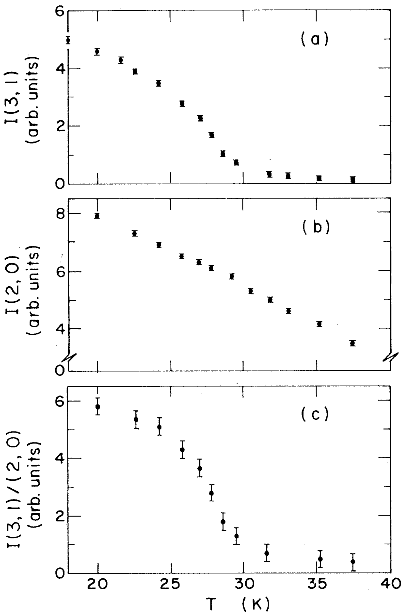

FIG. 3. (a) Integrated spot intensity (arbitrary units) as a function of temperature for the (31) spots at 85 eV. (b) Integrated spot intensity vs temperature for the (20) spots at 47 eV. (c) The ratio of the intensities in (a) and (b) showing a large drop in intensity between 25 and 39 K, followed by a more gradual decrease at $T > 30$ K. Scans (a) and (b) were taken with a normal-incidence beam and have the background intensities subtracted from them.

We believe that the $T > 30$ K tail on Fig. 3(c) is due to short-range order in the disordered phase. In a disordered phase, the diffraction spot profiles are expected to broaden due to the short range of correlations. However, the length over which our LEED apparatus can easily detect correlations is probably between 50 and 200 Å at these energies, and there is evidence that on high-quality substrates, these registered phases are coherent over thousands of angstroms.[12] Therefore, there could be an appreciable decrease in the range of correlations in the orientationally ordered phase before we would see a broadening of the spots.

The transition from the sixfold-degenerate two-sublattice structure determined by this study to the orientationally disordered phase is in the universality class of the Heisenberg model with face-oriented cubic anisotropy.[5] Renormalization-group results have determined that this transition is first order.[13] Monte Carlo calculations[14] for quadrupolar molecules constrained to a plane on a triangular lattice also indicate a first-order order-disorder transition for large systems. In addition, these calculations show a certain amount of finite-size rounding of the transition. The Monte Carlo data for a 400-spin system have a large tail that extends far beyond the transition temperature. A 400-spin system corresponds to a domain size on graphite of about 80 Å, which is approximately the size of our instrumental resolution and would therefore cause little broadening of the spots. In our LEED experiments, the diffraction pattern is a convolution with an instrument response function of the diffraction patterns of many different size domains. Below the transition the intensity of the large domains will dominate; above the transition there will be residual intensity from the small domains. Broadening of the $(\sqrt{3}\times\sqrt{3})$ 30° order-disorder transition because of finite particle size has already been seen in the case of krypton on graphite in an x-ray diffraction experiment.[12] In that case, the domain size is approximately 2300 Å. We expect domains in an orientationally ordered system to be much smaller because the orientational ordering energy is much smaller than the $(\sqrt{3}\times\sqrt{3})$ 30° ordering energy. Thus, finite-size effects can be much stronger in the orientational ordering transition.

The LEED study clearly shows that the orientationally ordered phase of N_2 molecules physisorbed on graphite for submonolayer coverages is the two-sublattice in-plane herringbone structure. There is a transition at about 30 K from this phase to a phase which has a small amount of order that persists until at least 40 K. We interpret this residual order as being caused by the finite size of the domains. This explanation is consistent with Monte Carlo calculations for different size systems.[14]

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