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Observation of a uniaxial incommensurate phase for orientationally ordered nitrogen molecules physisorbed on graphite and proposal of a phase diagram

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A previously unobserved uniaxial incommensurate phase of nitrogen molecules physisorbed on graphite occurs at 15 K for monolayer densities less than 1.05 times that of the commensurate phase. The orientational ordering superlattice is similar to that of the commensurate phase: a two-sublattice in-plane herringbone structure with two overlayer glide lines. The previously observed triangular incommensurate structure occurs only at higher densities at 15 K. A phase diagram is proposed for $10 < T < 40$ K.

Physically adsorbed films on graphite provide realizations of a number of phase transitions in two dimensions.[1] The transition from a commensurate (C) structure dominated by substrate-adsorbate forces to an incommensurate (IC) structure dominated by adsorbate-adsorbate forces has been extensively studied for Kr on graphite.[2–7] Previous studies of the commensurate-incommensurate (C-IC) transition of N_2 on graphite have been less detailed than for Kr and have observed only a triangular incommensurate (TIC) structure.[8–10] In this paper we describe results of low-energy electron diffraction (LEED) measurements that reveal a previously unobserved uniaxial incommensurate (UIC) phase in which the centers of mass of the N_2 molecules form a nontriangular structure. Such a UIC phase has been predicted for Kr on graphite,[5] but it has not been detected experimentally. The orientational ordering of the N_2 molecular axes in the C phase[11] creates anisotropic elastic constants which presumably lead to the UIC structure.[12] In the C-IC transition for Kr on graphite, a fluid phase is observed between the C and TIC phases.[4,7] In contrast, no fluid phase is expected between the C and UIC phases of N_2 on graphite[13] and the C-UIC transition can be a continuous transition of the Pokrovsky-Talapov type.[6,7,14]

These LEED measurements provide structural information about the UIC phase of N_2 on graphite, including an upper limit on the region of monolayer density in which this phase exists at 15 K. This temperature was chosen as being low enough to result in a high degree of orientational order but high enough to produce a reasonably short surface-equilibrium time. The principal experimental features are the same as described previously.[11] The density was increased above that of the C phase by admitting gas to the ultrahigh-vacuum system for a short time to produce small increases in coverage. The monolayer densities deduced from the LEED patterns are stated relative to the C phase monolayer density and do not include some adsorption in the second layer, which is certainly present in the IC phases.[8,15]

Figure 1(a) shows the structure inferred for the UIC phase. It is basically the same as that for the C phase at low temperatures,[11] a two-sublattice in-plane herringbone structure, except that the rectangular unit mesh shown[16] is compressed along the long side compared with the C phase. This compression preserves the two overlayer glide lines A and B that are present when the molecules remain in plane[17] and the angles θ_1 and θ_2 are equal. These angles are shown as equal to the 45° value obtained in an energy minimization calculation for the C phase,[18] but they probably change from their C value as the structure is compressed.

The LEED pattern expected for the rectangular structure shown in Fig. 1(a) can be explained with the aid of Fig. 1(b). The large circle indicates the area of the pattern that is visible in our apparatus for 85-eV normally incident electrons. The six hexagons represent the graphite LEED pattern. Open circles show the spot positions in the commensurate phase. The six open circles closest to the 00 beam, the {02} and {11} spots, are the $(\sqrt{3}\times\sqrt{3})30^\circ$ center-of-mass spots present even in the orientationally disordered C phase. As discussed in Ref. 11, certain spots from the orientational superlattice are absent in the C phase for normally incident electrons due to glide plane symmetries; they are indicated by pluses. The four open circles farthest from the 00 beam, the {12} spots, are the superlattice spots that are observed at 85 eV when the structure in Fig. 1(a) is in the C phase. Compression of the long side of the rectangular mesh shown in Fig. 1(a) causes the principal overlayer spots to move out to the positions shown by closed circles. The multiple-scattering spots indicated by the triangles move in the opposite direction from the {12} spots; these spots arise from one first-order graphite scattering plus one {01} overlayer scattering.[19] Thus the uniaxial compression can be detected in LEED when the spots indicated by triangles are present by looking for a splitting of the {12}

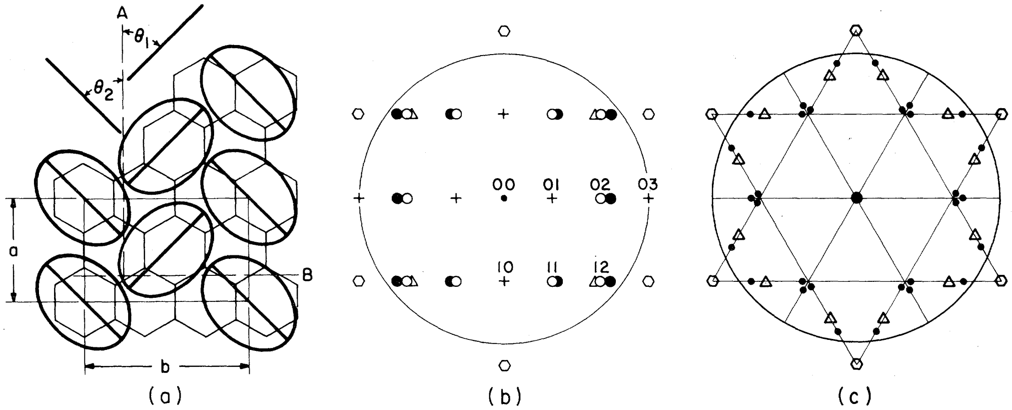

FIG. 1. Uniaxial incommensurate (UIC) structure and diffraction patterns drawn for a monolayer density of 1.10 (a maximum density of 1.05 is actually observed at 15 K). (a) The graphite basal plane is shown as hexagons and the adsorbed N_2 molecules as ellipses and thick lines. The rectangular unit mesh observed has $a = 4.26$ Å and $7.0 < b < 7.38$ Å (see Ref. 16). The two glide lines of the overlayer labeled *A* and *B* are present in both C and UIC phases. The directions of the molecular axes of the two sublattices are labeled θ_1 and θ_2 and are drawn to be 45°. (b) Schematic drawing of LEED pattern expected for a C domain (open circles). The triangles are multiple-scattering spots arising from one first-order graphite scattering plus one UIC overlayer{01} scattering (see Ref. 19). The pluses mark positions of spots absent in the C phase for normally incident electrons. The six hexagons indicate the first-order graphite spots, which are outside our field of view at 85 eV indicated by the large circle. (c) Schematic drawing of LEED pattern expected for three UIC domains rotated 120° apart. Spot movement in going from the C to the UIC phase occurs along the lines shown. The resolution of these LEED measurements is not sufficient to resolve the splitting into triplets in the UIC phase, but the motion of the unresolved center-of-mass spots is consistent with that inferred from the splitting of the orientational superlattice spots.

spots along the direction shown.

Since the lateral extent of the electron beam is larger than a typical domain, the actual LEED pattern includes three domains rotated 120° apart. Fig. 1(c) is a superposition of the patterns of three such domains. The movements of the {12} spots and the spots represented by triangles in Figs. 1(b) and 1(c) were used to measure the compression. The splitting of the {11} and {02} center-of-mass spots is not resolved, but the observed inner spots clearly become broader and their centers of intensity move out by an amount consistent with the compression measured from the {12} spots. At the particular energy used, the only multiple-scattering spots visible in the UIC phase are apparently those indicated by triangles. LEED photographs from the UIC phase will be presented elsewhere.[20]

The structure of the UIC phase can be expected to have density modulations (domain walls) due to the different periodicities of the substrate and overlayer.[5-7] Such modulations lead to diffraction satellites, which in the case of Kr on graphite are observed only for densities of the IC phase very close to those of the C phase.[3,4] The LEED apparatus used lacks the resolution to resolve such satellites, but they could contribute to spot broadening near the C-UIC transition.

Because the splitting of the {12} spots and the spots indicated by triangles in Figs. 1(b) and 1(c) cannot be resolved for densities of less than 1.02, it is possible that there is C-UIC coexistence with a density jump between the two phases of as much as 2%. Thus the LEED data cannot be used to determine whether the C-UIC transition is continuous or first order. However, the C-UIC transition is expected to be continuous, as mentioned above. Beyond this possible coexistence region, the layer compresses continuously from 2 to approximately 5% compression. It is not possible to measure directly the lattice constant versus chemical potential curve as for Kr,[2] due to the extremely low N_2 equilibrium vapor pressure at 15 K.[9] Another gas might be used to compress C monolayer islands, as was done for Kr.[3]

At higher densities at 15 K, the superlattice spots become broader and much less intense. The center-of-mass pattern changes to that of TIC Kr (Ref.2) with well-resolved triplets. The two inside spots of each triplet are located at a smaller reciprocal-lattice vector than that of the C phase and have intensity-energy characteristics that are very different from the outer spots, confirming that they are multiple-scattering spots just as for Kr.[2] The lattice constant of the N_2 TIC phase[10] at 15 K varies from 2.5 to 4% less than that of the C phase, representing a monolayer density range from 1.05 to 1.08 that of the C phase.

We were not able to determine whether the UIC-TIC transition is first order or continuous at 15 K. This is partly due to the lack of resolution of the inner spots, but primarily because the superlattice spots decrease in intensity rapidly. This decrease in intensity of the superlattice spots is probably a result of the N_2 molecules becoming more nearly parallel to each other during the uniaxial compression and tipping out of the plane to allow more compression room.

For $T > 30$ K, intensity of the superlattice spots drops due to the loss of long-range orientational order, and they cannot be used for structural determination. For densities from 1.04 to 1.08, only the TIC phase[10] is observed for $31 < T < 35$ K, with LEED patterns like those of TIC Kr.[2] At lower densities the resolution of the LEED patterns is not high enough to determine if the UIC phase exists at $T > 30$ K or to distinguish between the different C-TIC phase transition models.[3-7] These measurements are discussed in more detail elsewhere.[20]

Our measurements can be summarized by the proposed phase diagram shown in Fig. 2. The abbreviations for the different phases are the same as used above, except that the state of orientational long-range order of the N_2 molecular axes is indicated by ordered (O) or disordered (D). The coexistence regions identified with question marks are shown with the maximum density difference consistent with these measurements. These regions could well be smaller, and they will be absent for continuous transitions. The CO-CD phase transition is shown at 27 K, a value consistent with studies made so far.[11,21,22] The TICO-TICD transition temperature is not well known, but the 31-K value shown is consistent with studies done at higher than C coverages.[21,22] The upper density limits shown for the TIC phases are the limits of observed monolayer compression. The second-layer orientational order is discussed elsewhere.[20]

Higher-resolution diffraction studies for N_2 on graphite would be very useful and, if the example of Kr is any guide,[3,4] should provide more detailed information about the C-UIC and UIC-TIC phase transitions at low temperature, the domain of existence of the UIC phase, and the orientational order-disorder transitions of the various phases.

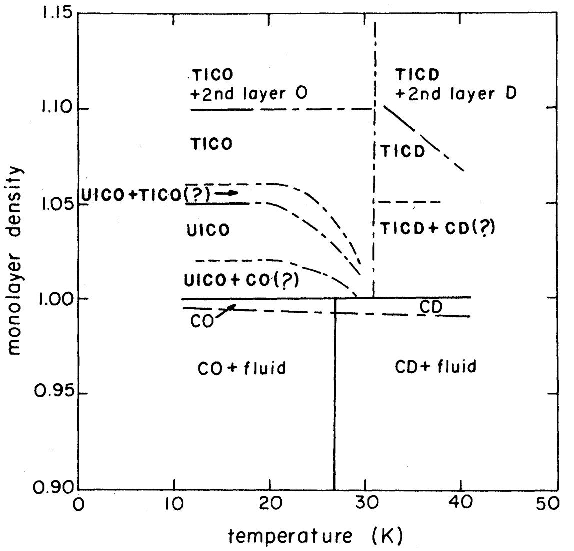

FIG. 2. Density-temperature phase diagram for monolayer densities between 0.90 and 1.15. The densities do not include adsorption in the second layer. The abbreviations C, UIC, TIC are defined in text; the O or D refers to orientationally ordered or disordered. Solid lines are phase boundaries determined by this study. Dashed lines show the maximum extent of possible coexistence regions (marked by question marks) discussed in the text. The dot-dashed curves are proposed phase boundaries.

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[10] Even in the absence of substrate-induced density modulations, the anisotropic N_2-N_2 forces will prevent an IC phase of N_2 on graphite from being perfectly triangular unless the molecular axes are perpendicular to the substrate or completely disordered.

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