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Growth mode and phase transitions of multilayer nitrogen on graphite

Q. M. Zhang, H. K. Kim, and M. H. W. Chan
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

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The nitrogen-on-graphite growth process above the monolayer was studied by ac heat-capacity technique. The evolution of the heat-capacity peaks due to the orientational-ordering transitions as a function of coverage indicates regions of coexistence of the single and bilayer films and of the bilayer and trilayer films. Between regions of coexistence pure bilayer and trilayer films are found. The data also show clear evidence that near 30 K, only a maximum of three layers can form on the graphite surface when the bulk clusters start to grow. In addition, a sharp heat-capacity peak at 23.4 K was found for coverages above two layers. This peak is related to structural transition in the three-layer system and is probably a layering transition from a two-layer—plus—bulk system for $T<23.4$ K to a three-layer—plus—bulk system for $T>23.4$ K.

I. INTRODUCTION

Recent experimental studies of the adsorption of multilayer molecular films on graphite and other attractive substrates reveal interesting film growth behavior including layering, wetting, and thin-film—thick-film transitions.[1-4] Some of these findings can be understood in terms of the simple lattice-gas model of Pandit, Schick, and Wortis.[5] In this model, the growth mode of multilayer film is thought to depend critically on the relative strengths and ranges of absorbate-adsorbate and adsorbate-substrate interactions. In the strong substrate case (when adsorbate-substrate interaction dominates), as the chemical potential is increased the film thickness increases and the excess surface density diverges as bulk coexistence is approached for all temperatures. This is the case of complete wetting. Substrates of intermediate strength are characterized by a wetting temperature, T_w. For $T>T_w$, the building up of the film is similar to the strong substrate case. For $T<T_w$, the film thickness remains finite even at bulk coexistence. This is the case of incomplete wetting. For still weaker substrate, wetting is thought to be incomplete at all temperatures.

The most striking experimental result not anticipated by this model is the phenomenon of reentrant wetting[1,2] where complete wetting is observed only for systems of moderate substrate strength. Incomplete wetting was observed for systems of both weak and strong substrates. One reasonable explanation for this phenomenon is that the strain induced by the mismatch between successive adsorbed layers and between the adsorbed film and the bulk structure may be too costly in energy for the continued film growth beyond the first few layers.[6,7]

The heat-capacity experiment to be presented in this paper provides detailed information on the growth process and phase transitions in the first three layers of N_2 on graphite from 20 to 40 K. The calorimeter used in this study is a piece of Graphite Foam of surface area 2 m^2 sandwiched between two sapphire disks that is suspended in the sample cell. Thin aluminum and Ge-Au films are evaporated respectively on each of the two sapphire disks to be used as the heater and thermometer of the calorimeter. The electrical leads to the Al heater and Ge-Au thermometer films also serve as thermal links from the calorimeter to the thermal bath for the sample cell.[8] In our experiment, heat capacity as a function of temperature is measured for successively higher N_2 coverages on the Graphite Foam. In this study heat-capacity scans of a total of 30 different N_2 coverages from $n=1.30$ to $n=24$ were made. A coverage of $n=1$ corresponds to the end point of the first-layer commensurate-solid and fluid coexistence region at 74 K.[9] This coverage scale, same as the one used in Ref. 9, is 2% larger than that used for earlier submonolayer studies[8] where $n=1$ is defined against a 70-K isotherm. ($n=1$ in the present 74-K scale correspond to $n=1.02$ in the 70-K scale.) We changed to the 74-K scale because it is easier to obtain reliable vapor-pressure isotherm data at the higher temperature. For this experiment a coverage of $n=1$ corresponds to 1.33×10^{19} molecules of N_2 or 2.2×10^{-5} moles. In Fig. 1, 17 of the 30 heat-capacity scans are shown. The background heat-capacity contribution due to the calorimeter is subtracted and the heat capacity is shown in reduced units, C/Nk_B, where N and k_B are, respectively, the total number of N_2 molecules on the graphite substrate and the Boltzmann's constant.

The proposed coverage-versus-temperature phase diagram of multilayer N_2 on graphite for $T=20$ K to $T=40$ K based on this study is shown in Fig. 2. In the experiment studying the commensurate-incommensurate transition of monolayer N_2 on graphite[9] the boundary separating the regions between the pure commensurate (C) solid phase and the coexistence region of commensurate (C) and uniaxially incommensurate (UI) solids was found at a coverage of $n=1.10$. The ($C+$UI) coexistence region extends up to $n=1.13$. Between $n=1.13$ and $n=1.19$ a pure uniaxially compressed incommensurate (UI) phase was found to exist below 30 K. Heat-capacity anomalies relating to the transition from an orientationally ordered to an orientationally disordered phase were found for both the commensurate solid (at 28.1 K) and the uniaxially compressed solid (at 29.4 K).

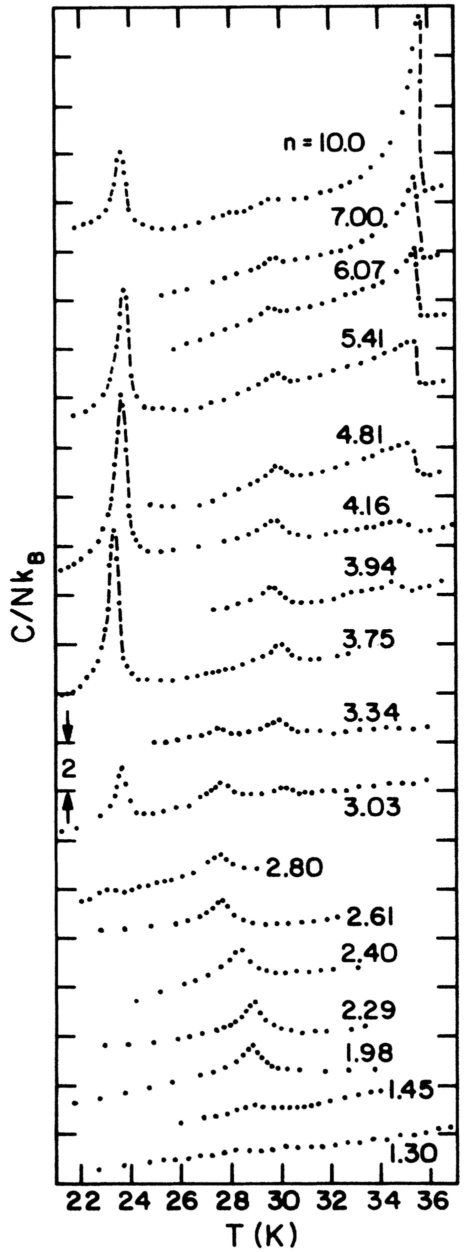

FIG. 1. Heat-capacity scans of multilayer nitrogen on graphite at 17 different surface coverages. Heat capacity is expressed in reduced units C/Nk_B; where N and k_B are, respectively, the total number of molecules on the graphite surface and the Boltzmann's constant. The N_2 film is expressed in units of n, the meaning of $n=1$ is defined in the text.

Above $n=1.20$, the N_2 overlayer was found to be in the triangular incommensurate (TI) phase where the molecular axes, according to low-energy electron diffraction [LEED (Ref. 10)] and neutron studies,[11] are no longer parallel to the graphite basal plane. A recent x-ray study[12] found that the N_2 overlayer in this phase does not go through an orientational transition as in the UI phase, but only gradually loses its orientational order with increasing temperature. This finding is consistent with the heat-capacity scan at $n=1.20$, where only a broad diffuse heat-capacity anomaly was found.[9]

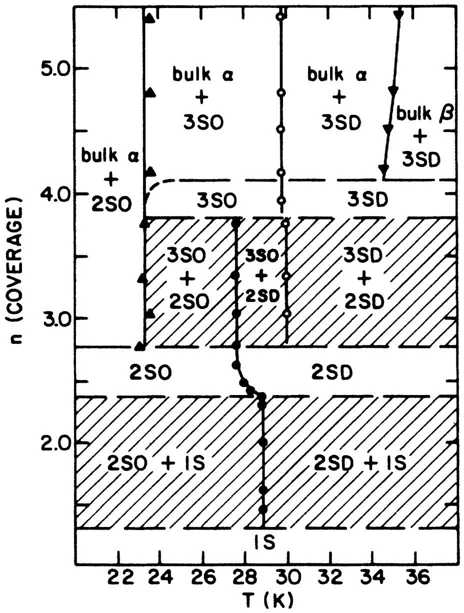

FIG. 2. Proposed phase diagram of multilayer nitrogen on graphite above the first layer. 1*S*, 2*S*, and 3*S* denote, respectively, single-layer, bilayer, and trilayer solidlike films. The detailed phase diagram in 1*S* region is shown in Refs. 8 and 9. Solid circles indicate the bilayer orientational-ordering transition; open circles, the trilayer orientational-ordering transition; triangles, the layering transition; inverted triangles, bulk α-β related transition. Hatched regions denote coexistence of (1*S* + 2*S*) and (2*S* + 3*S*). O and D denote orientationally ordered and disordered phases. See text for discussion in the offset of the peak positions from the proposed phase boundary for the layering transition and the apparent coverage-dependent α-β transition.

The heat-capacity scan at $n=1.30$ shown in Fig. 1 indicates that the N_2 overlayer is still in the TI phase since there is no detectable heat-capacity peak in the whole temperature range. Upon a slight increase in coverage to $n=1.45$, we found a small heat-capacity feature, signaling the beginning of the bilayer film.

In this paper we shall present evidence supporting the phase diagram shown in Fig. 2. Namely, between $n=1.30$ and $n=2.35$ there is a bilayer film coexisting with the dense single-layer film, between $n=2.75$ and $n=3.75$ there is a trilayer film coexisting with the bilayer. Between $n=2.35$ and $n=2.75$ the adsorbed nitrogen behaves as a pure bilayer film, and between $n=3.75$ and $n=4.10$ as a pure trilayer film. For all coverages above $n=4.10$ ($n=24$ is the highest coverage we studied) and temperature above $T=23.4$ K, the adsorbed nitrogen system consists of a trilayer film coexisting with bulk clusters at the bulk coexistence boundary. For temperature below 23.4 K there may only be a bilayer film coexisting with bulk. Our data suggest a layering transition at 23.4 K. In Sec. II of this paper results relating to the orientational-ordering transitions in the bilayer and trilayer film will be presented. By examining these results we are able to draw conclusions concerning the growth process in the adsorbed film. In Sec. III results regarding the bulk α-β related transition near 35.6 K and a possible layering transition at 23.4 K will be presented.

II. GROWTH PROCESS AND ORIENTATIONAL-ORDERING TRANSITIONS OF LAYERED FILMS

A heat-capacity anomaly that stays at 28.75 K is seen for coverages between $n = 1.45$ and $n = 2.35$. The area under the heat-capacity peak (C and not the reduced value, C/Nk_B versus T) as shown in Fig. 3 is found to increase linearly with coverage and develop to its full size at $n = 2.35$. The extrapolated zero-area coverage is found to be at $n = 1.30$. Since the shape, the peak position, and the peak size of the observed anomalies are similar to the observed heat-capacity anomalies related to the orientational-ordering transition in the monolayer commensurate and uniaxially compressed incommensurate phases, we are led to identify this peak to be related to orientational-ordering transition in the bilayer film. This observation is consistent with the LEED result of Diehl and Fain,[10] where an orientationally ordered bilayer system is seen at 15 K and an orientationally disordered bilayer is seen at 31 K. The linear increase in peak size and the coverage independence of the transition temperature in the range of $n = 1.30$ to $n = 2.35$ are clear signatures of bilayer condensation, and therefore this is the region of coexistence of the bilayer ($2S$) and the dense first-layer ($1S$) film.

In the coverage region between $n = 2.75$ and $n = 3.75$ two heat-capacity anomalies related to the orientational-ordering transition in the layered systems are seen. The most reasonable interpretation of this observation is that they are, respectively, the signatures of orientational-ordering transitions in the bilayer and trilayer films. The 27.50-K peak connects smoothly to the bilayer peak at 28.75 K at lower coverages, and the 29.95-K peak begins to appear for coverages above $n = 2.75$. (The $n = 2.75$ value is obtained from the extrapolation of the area of this peak versus coverage, see Fig. 3.) Between $n = 2.75$ and $n = 3.75$ a linear trade-off between these two peaks is seen: The linear increase with coverage of the trilayer heat-capacity peak (again total C and not C/Nk_B) occurs simultaneously with the linear decrease in the bilayer peak. This is also shown in Fig. 3. This linear trade-off, together with the coverage independence of the transition temperature in this coverage range, suggest that between $n = 2.75$ and $n = 3.75$, the adsorbed nitrogen system is in the coexistence region of the bilayer ($2S$) and trilayer ($3S$) films. It is noteworthy that the integrated area of the fully developed trilayer heat-capacity peak at $n = 3.75$ is 20% smaller than that of the fully developed bilayer peak, even though the trilayer peak occurs at a higher temperature than the bilayer.

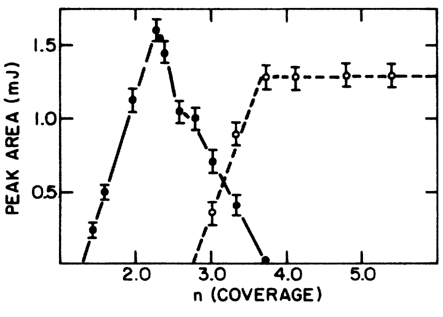

FIG. 3. Integrated area under the bilayer orientational-ordering transition peak (solid circle) and the trilayer orientational-ordering heat of transition (open circle) as a function of coverage. The solid and dashed lines are drawn to guide the eye.

It is interesting to note that both the ($1S + 2S$) and the ($2S + 3S$) coexistence regions discussed above extend over a coverage range of $n \leq 1.05$. This result suggests the reconstruction of the covered bottom layer [in the ($1S + 2S$) case] or layers [in the ($2S + 3S$) case] upon the condensation of the top layer. Our arguments go as follows: Since the graphite substrate is unlikely to be important in stabilizing the second or third layer into the $\sqrt{3} \times \sqrt{3}$ phase, the N_2 molecules in the second and third layers in the coexistence region should have a lattice spacing between the $\sqrt{3} \times \sqrt{3}$ value (at 4.26 Å) and that of the (111) face of bulk N_2 (at 4.00 Å).[13] LEED and neutron studies of N_2 bilayers on graphite[10,14] did find the lattice spacing of the bilayer film to be smaller than the $\sqrt{3} \times \sqrt{3}$ value. However, in our study, the amount of N_2 condensed during the coexistence region (at $n \leq 1.05$) is less than or at most equal to that needed ($n = 1.10$) to form a pure commensurate $\sqrt{3} \times \sqrt{3}$ layer on graphite.[9] Therefore, a reconstruction of the bilayer film [in the ($1S + 2S$) region] and the trilayer film [in the ($2S + 3S$) region] involving the depletion of the bottom layer(s) during the condensation of the top layer is very likely. Such a phenomenon was also observed in a synchrotron x-ray study of multilayer Xe on graphite.[15] On the other hand, in the ($2S + 3S$) coexistence region, the linear decrease of the heat-capacity peak size with coverage and the coverage-independent transition temperature of the bilayer film indicate that the structure of the bilayer film is not affected by the presence of the trilayer film.

In the coverage range between $n = 2.35$ and $n = 2.80$, where a total of nine heat-capacity scans were made, we found that the bilayer orientational-ordering transition signal moves continuously from 28.75 to 27.50 K. This is shown more clearly in Fig. 4. This is in striking contrast to the coverage-independent orientational transition observed in the ($1S + 2S$) and ($2S + 3S$) coexistence regions. We suggest that the adsorbed nitrogen in this coverage forms a pure bilayer film. Since the adsorbed system is not in the coexistence region, the chemical potential or the two-dimensional (2D) spreading pressure should rise with coverage which will cause a compression in the adsorbed bilayer film. The shift in the orientational-ordering transition temperature reflects the compression in the bilayer film. The shift to lower rather than higher temperature indicates that the effect of the compression is more than a uniform increase in the density in the bilayer film. An increase in the density should result in an increase in the electrostatic quadrupole-quadrupole interaction of the N_2 molecules which should stabilize the orientationally ordered structure. In addition to the shift to lower temperature, the size or the integrated area of the heat-capacity peak (from the C-versus-T plot rather than the C/Nk_B-versus-T scan as shown in Fig. 3) is observed to *decrease*

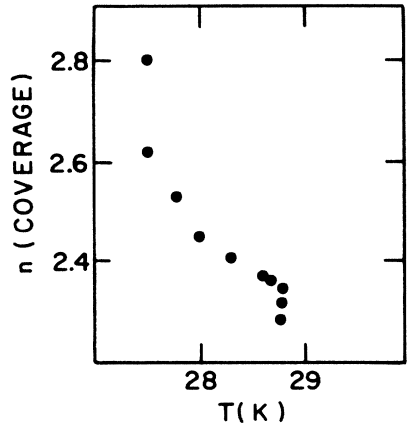

FIG. 4. The changes of the bilayer orientational-ordering transition position with coverage near $n = 2.35$. For $n > 2.35$, the transition temperature moves away from the constant value 28.75 K in the $(1S + 2S)$ coexistence region.

by 35% as the N_2 coverage is *increased* from $n = 2.35$ to $n = 2.75$. These two pieces of information suggest that in the $(1S + 2S)$ coexistence region the top and the bottom layers of the bilayer film in the orientationally ordered state are strongly coupled to each other. Such a strong coupling may and probably does involve substantial structural commensurability. A mutually commensurate N_2 bilayer was proposed in an earlier neutron scattering experiment.[14] As the coverage is increased in the pure bilayer region, both layers of N_2 on graphite are compressed and the axes of the nonspherical nitrogen molecules are pointing progressively more away from the in-plane direction. By in-plane we mean parallel to the graphite basal plane. Such a change in the tilting angle has been observed in the TI phase in the monolayer film.[10,11] The tilting angles of the N_2 molecules and the increases in the areal densities in the top and bottom layers are likely to be different since the effects of the substrate on these two layers should be very different. Therefore, as the coverage is increased from $n = 2.35$ to $n = 2.75$, the two layers of N_2 film will become increasing incommensurate both in terms of the molecular position and orientation. In the mutually incommensurate two-layer system the orientational-ordering transition is likely to be more localized within the top layer than that in a mutually commensurate two-layer film. The continued decrease in the size of the heat-capacity peak and the gradual shift of the transition temperature to lower value in the coverage range of $n = 2.35$ and $n = 2.75$ are consistent with this interpretation. The shift of the transition temperature to lower value upon increase in N_2 coverage, or the negative dT/dn of the phase boundary between the orientationally ordered and disordered phases, implies that the 2D density in the disordered phase is higher than that of the ordered phase. This can be seen from a Gedanken vapor-pressure isotherm experiment performed between 27.5 and 28.75 K, where the system can be brought from the orientationally ordered phase to the disordered phase by increasing the 2D spreading pressure (σ). This conclusion can also be drawn by considering the 2D Clausius-Claperon equation: Since $d\sigma/dn$ is always positive and dT/dn is negative, $d\sigma/dT$ and therefore the change in the surface area of the film is negative. In other words, the change in 2D density from ordered to disordered phase is positive. The most likely mechanism for the increase in the density is a discontinuous increase in the tilting angle of the molecular axes in crossing the boundary from the orientationally ordered to disordered phase.

A similar but much smaller shift in the orientational-ordering transition temperature of the trilayer film is seen for N_2 coverage just beyond the $(2S + 3S)$ coexistence region. At $n = 3.75$ when the remnant of the bilayer signal is barely visible, the trilayer orientational-ordering transition peak is at $T = 29.95 \pm 0.05$. At $n = 3.94$, where the bilayer signal is no longer visible, the trilayer peak is at 29.70 ± 0.10 K. This peak remains at the same temperature for higher coverages, where bulk clusters are coexisting with the trilayer film. The mechanism of the shift in transition temperature is likely to be similar to that in the bilayer film; namely the compression of the pure trilayer film due to the increase of N_2 molecules and two-dimensional spreading pressure. In Table I we have tabulated the crucial characteristics of the peaks at 23 different N_2 coverages related to the bilayer orientational-ordering transition, trilayer orientational-ordering transition, and the structural transition of the three-layer system at 23.4 K to be discussed below. In addition to those listed, heat-capacity scans were also made at $n = 2.32$, 2.36, and 2.37 to locate the transition peak position of the bilayer orientational-ordering transition (shown in Fig. 4) and at $n = 5.7$, 8.0, and 15 to search for hysteresis effects of these transitions. Furthermore, the heat-capacity scan was repeated at $n = 2.61$ to check our coverage determination. We found that our coverage determination is consistent within $\Delta n = 0.005$ for low coverages ($n \leq 5$) where desorption is not important; at higher coverage, due to the temperature difference (1 K) between the calorimeter and the (colder) walls of the enclosing sample cell, desorption caused an uncertainty in coverage of about 2%. We have made heat-capacity scans both during warming and cooling, and found no detectable evidence of hysteresis related to the bilayer and trilayer orientational-ordering transition and the 23.4-K transition.

The much smaller shift in transition temperature at the end of the $(2S + 3S)$ coexistence region and the smaller size of the fully developed heat-capacity peak (C and not C/Nk_B) in the trilayer film (as compared to the bilayer film as shown in Fig. 3), are consequences consistent with the interpretation that the three-layer system in the $(2S + 3S)$ coexistence region is already mutually incommensurate. The smaller peak size may be due to the fact that in a mutually incommensurate three-layer film, the orientational-ordering transition is mainly localized in the top layer. If the trilayer film is already incommensurate in the coexistence region, further compression in the pure trilayer film region has relatively minor effects regarding the shift in transition temperature and possible decrease in the peak size. In contrast to the bilayer film case, no noticeable decrease in the trilayer heat-capacity peak size was observed beyond the $(2S + 3S)$ coexistence coverage.

Whereas the disappearance of the bilayer orientational-ordering transition indicates an end of the $(2S + 3S)$ coex-

TABLE I. Heat-capacity anomalies in the layered film. For each transition the three numbers represent the peak position (in K), peak height (in mJ/K) and FWHM (in K). NA (not available) means that either we did not study this transition at the specific coverage or the value is difficult to extract from the heat-capacity traces. An empty space at the specific coverage indicates the absence of the particular transition.

Coverage	Layering transition	Bilayer orientational transition	Trilayer orientational transition
1.30			
1.45		28.75,0.14,NA	
1.52		28.75,0.18,NA	
1.60		28.70,0.26,1.4	
1.98		28.70,0.52,1.4	
2.29		28.80,0.73,1.2	
2.35		28.80,0.72,1.2	
2.41		28.30,0.70,1.3	
2.45		28.00,NA,NA	
2.53		27.70,NA,NA	
2.61		27.50,0.60,1.2	
2.80	23.15,0.15,NA	27.50,0.54,1.3	
3.03	23.65,1.21,0.5	27.60,0.44,1.3	30.00,0.21,NA
3.34	23.15,2.64,0.4	27.50,0.28,1.1	29.95,0.46,1.2
3.75	23.40,4.39,0.4	barely visible	29.95,0.74,1.2
3.94	NA,NA,NA		29.60,NA,NA
4.16	23.65,5.33,0.5		29.70,0.74,1.2
4.50	NA,NA,NA		29.80,NA,NA
4.81	23.65,5.20,0.5		29.80,NA,NA
5.41	23.70,5.34,0.5		29.70,NA,NA
6.1	NA,NA,NA		29.60,NA,NA
7.0	NA,NA,NA		29.80,NA,NA
10.0	23.65,5.5,0.4		29.60,NA,NA

istence region near $n=3.75$, the signature of the structural transition in the three-layer system at 23.4 K, to be discussed below, suggests that the N_2 continues to grow onto the three-layer system, up to a coverage of about $n=4.10$. This result indicates the existence of a pure trilayer film between $n=3.75$ and $n=4.10$. This coverage range for the pure trilayer film is to be compared with the coverage range of the pure bilayer film from $n=2.35$ to $n=2.75$. It is remarkable that both the pure bilayer and trilayer films extend over such a substantial coverage range. The high compressibility of the pure bilayer and trilayer film may be related to the nonspherical shape of the N_2 molecule. As we have suggested above, for the bilayer film, upon increase in the 2D spreading pressure, the N_2 molecules may be pointing more away from the in-plane direction and accommodate more N_2 molecules.

III. BULK α-β RELATED TRANSITION AND POSSIBLE LAYERING TRANSITION

The orientational-ordering transition signal at $T=29.70$ K of the trilayer film remains unchanged for all subsequent increases of N_2 coverages beyond $n\sim4$. No change in the size (C and not C/Nk_B) and position of the heat-capacity peak was observed for coverages as high as $n=10$. It is expected that if there is any more layer formed on the top of the trilayer it will probably result in a change in either the transition temperature or the size of the heat-capacity signal for this trilayer orientational transition. We also observed a rapid increase and sharpening of a heat-capacity peak around $T=35.6$ K as the coverage is increased beyond $n=4.16$. For coverages between $n=3.03$ and $n=4.16$ a barely resolvable rounded heat-capacity anomaly exists below and near 35.6 K. These results suggest that N_2 can form a maximum of three layers on graphite in this temperature range, and that upon further increase of coverage bulk clusters appear. The 35.6-K heat-capacity peak is a signature of the α-β transition of the bulk cluster.[13] The rapid sharpening of this peak with coverages for $n>4.16$ is related to the increase of the cluster sizes. The broad and weak anomaly observed near 35.6 K for coverage below $n=4.16$ is likely related to the condensation of small clusters due to capillary effects.

It is natural to consider the possibility of a wetting transition or a change in the layer growth behavior induced by the bulk α-β transition.[16] As discussed in the Introduction, the wetting behavior of an adsorbed film is determined by the ratio of the effective adsorbate-adsorbate and adsorbate-substrate interaction strengths and the difference between the bulk solid adsorbate structure and the structure preferred by the substrate. A structural transition in the bulk may therefore induce a change in the wetting behavior in the adsorbed system.[16] The heat-capacity signature near 35.6 K, however, evolves smoothly to be bulklike as the coverage is increased from $n=4.16$ to $n=24$. This evolution includes both a sharpening of the heat-capacity peak and a shift of the peak position from a lower value to the bulk value at 35.6 K as the nitrogen coverage is increased. The evolution of the bulk α-β related transition signal changes with increasing amount of nitrogen on graphite is summarized in Table II. As mentioned above, scans were also made at $n=4.5$ and 5.7 during both warming and cooling and at $n=8.0$ and 15 during cooling. Substantial hysteresis effect for this transition was found.[17] The data shown in Table II and in Fig. 5 are due to scans made upon warming the calorimeter. The heat-capacity signals upon warming were found to be reproducible. From Table II, we see that when the total coverage is at $n=7.0$, where the amount of nitrogen in the bulk cluster is equivalent to a coverage $n=3.0$, the full width at half maximum is 0.9 K, whereas at $n=24$, this value is about 0.25 K. This is clearly related to the finite-size effect.

The finite-size effect on a first-order phase transition has been considered by Fisher and Berker.[18] They found that for finite three-dimensional (3D) systems with linear dimension L, the rounding of the transition is proportional to L^{-3} and the shift in the transition temperature goes as L^{-1}. A careful inspection of Table II indicates that below a coverage of about $n=5.4$, the shift in transition temperature is significant (this is also shown in Fig. 2) but the half-width of the peak exhibits no noticeable change. For coverages above $n\sim5.4$, the behavior is quite different. Between $n=5.4$ and $n\sim24$, the total shift in peak position is only 0.2 K but the half-width narrows from 2.3 to 0.25 K. One possible explanation is that at low coverages ($n\leq5.4$) there is a broad distribution in the sizes of the bulk clusters. This distribution in sizes causes additional broadening of the transition peak. Upon further increases in the coverage, in addition to the increase in the average size of the clusters, the coalescing of small clusters sharpens the size distribution. The observed sharpening of the transition peak for coverages above $n=5.4$ is consistent with this interpretation. We wish to point out that the heat-capacity peak for the $n=24$ coverage is the most-detailed trace of the α-β transition of bulk N_2.[13]

TABLE II. Bulk α-β related transition. The size of this peak is too small for coverages between $n=3.03$ and $n=4.16$ for the accurate determination of the half-width. We found no evidence for this peak for coverage less than $n=3.03$.

Coverage	Peak position (K)	Peak height (mJ/K)	FWHM (K)
3.03	34.0±0.6	≤0.1	~2.5
3.34	34.0±0.6	≤0.15	~2.5
3.94	34.4±0.5	≤0.3	~2.5
4.16	34.6±0.5	0.36	~2.5
4.50	34.9±0.4	0.6	2.3
4.81	35.0±0.2	1.2	2.4
5.41	35.4±0.1	1.7	2.3
5.70	35.4±0.1	2.0	1.2
6.1	35.4±0.1	3.0	1.3
7.0	35.4±0.05	4.5	0.9
10.0	35.6±0.05	13.2	0.6
24	35.6±0.05	61	0.25

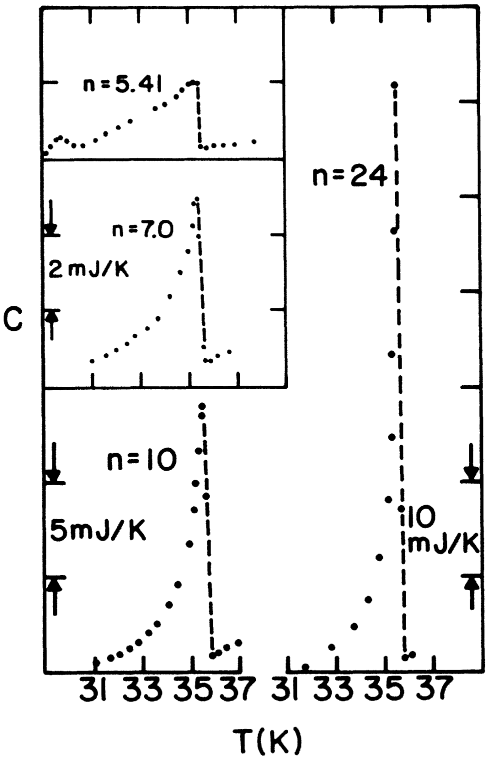

FIG. 5. The heat-capacity traces near the bulk α-β transition temperature. For the scans at $n=10$ and $n=24$, due to possible desorption, the coverage is less well defined. The small peak at 29.7 K for $n=5.41$ coverage is the trilayer orientational-ordering transition signal. The dashed lines are drawn to guide the eye. For clarity, different scales for heat capacity are used. Table II tabulates the peak position, peak height, and the half-widths of the heat-capacity anomaly of the α-β transition as a function of coverage.

Our heat-capacity scans were not continued beyond 40 K because desorption of the N_2 molecules from the graphite substrate becomes increasing severe. Heat-capacity measurement of multilayer N_2 film adsorbed on graphite in the temperature range between 40 and 75 K was made by Chung and Dash.[19] In addition to a broad heat-capacity anomaly near and below the bulk triple point, another anomaly near 53 K was observed for coverages near and above three layers. Chung and Dash interpreted the 53-K anomaly to be related to the melting of the adsorbed film, and the one below but near the triple point to be due to the melting from bulk clusters. They concluded from these results that N_2 forms bulk clusters at that temperature on top of a film three layers thick. Although this conclusion is consistent with our results discussed above, it should be noted that a number of recent experiments found that the melting temperatures of layered films only a few layers thick of various adsorbates, such as O_2 (Ref. 20), C_2D_4 (Ref. 21), and CF_4 (Ref. 17) on graphite, are very close to the bulk triple point.

In Fig. 6 results of the heat-capacity scans of several intermediate coverages in the vicinity of 33 K are presented. In addition to the main α-β related peak, a broad anomaly that appears as a shoulder on the low-temperature side of the α-β related peak is visible in these traces. The size of

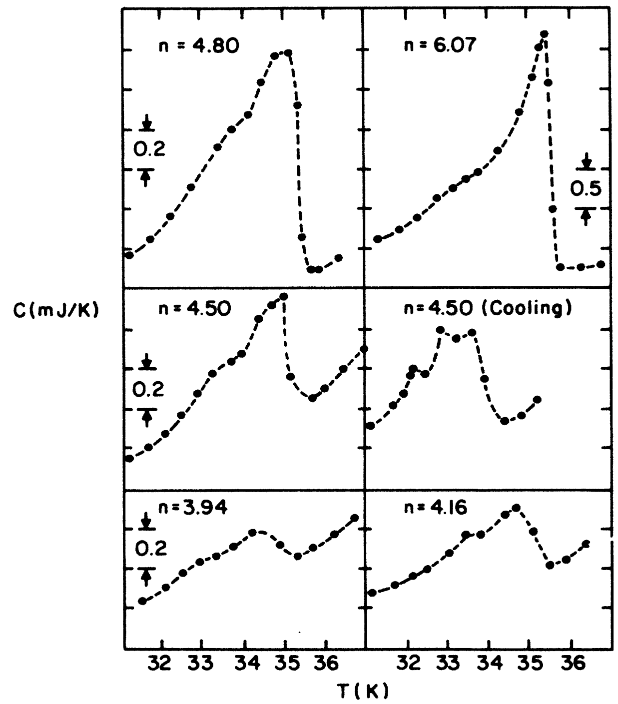

FIG. 6. The heat-capacity traces which show the weak heat-capacity anomaly near 33 K. For the scans below $n = 3.94$, this anomaly is not visible. for the $n = 4.50$ scan both the data taken upon warming and cooling are shown. Thermal hysteresis is clearly visible in these traces. Dashed lines are drawn to guide the eye.

this anomaly (with a peak height on the order of 0.2 to 0.4 mJ/K), is small in comparison to the peaks due to orientational-ordering transition, α-β related transition, and the 23.4-K heat-capacity peak to be discussed below. This broad anomaly begins to appear for a coverage near trilayer completion ($n = 3.94$) and appears to grow with coverage up to $n = 5$.[17] Beyond $n = 5$, the steep rise in the α-β related peak makes it difficult to separate out this broad shoulder. Thermal hysteresis of the α-β related transition and this broad peak were found in data taken during cool down of the sample cell[17] (almost all heat-capacity scans in this study were made during warming of the sample cell). As shown in one of the panels in Fig. 6, this broad anomaly was found to sharpen during cool down. It is not clear to us whether this weak anomaly is a signature of a true phase transition. If it is, there are a number of possibilities: Since the size of this anomaly is comparable to (but smaller than) the orientational-ordering peak of the bilayer and trilayer films, this transition may also be related to orientational-ordering transition either in trilayer film or, as a precursor to the α-β transition, in the bulk clusters. This anomaly may also be the signature of a layering transition that changes the adsorbed film from three to four layers. Recent preliminary neutron scattering results also suggest this possibility.[22] However, there appears to be some inconsistencies with the layering interpretation: the observed thermal hysteresis implies that this is a first-order transition. Therefore in the coverage between $n \sim 4$ and 5 and for $T \geq 33$ K the adsorbed film system should be in the three-layer and four-layer coexistence region. In this case the observed α-β related transition signal in this coverage range should be that of the four-layer system. It is then difficult to understand the significant changes of the α-β related peak observed within this coverage range of three- and four-layer coexistence, since the chemical potential in a coexistence region is constant. Another more speculative explanation is that a wetting transition is induced by the α-β transition and both the 33-K shoulder and the main peak near 35.6 K are associated with this wetting transition. In the absence of other firm information, we are hesitant to interpret this weak anomaly to be a signature of a wetting or other genuine transition. The most simple and consistent interpretation of our data is that in this temperature range, as shown in Fig. 2, the N_2 film adsorbed on graphite is limited to a maximum thickness of three layers.

The heat-capacity peak observed around 23.4 K appears to be different from that due to orientational-ordering transitions in the layer systems. The peak is sharper and more prominent. This peak begins to appear for the $n = 2.80$ scan and its size (C not C/Nk_b) increases linearly with coverage until saturation near $n = 4.10$. Since the heat-capacity scans in Fig. 1 are shown in reduced value, C/Nk_B, the scans need to be scaled with the number of nitrogen molecules to show the constancy in size. The evolution of the peak size (area under the peak) of this transition as a function of coverage is shown in Fig. 7. Since the coverage range between $n = 2.75$ and $n = 4.10$ correspond to the third layer, this peak should be related to a phase transition in the third layer or three-layer system. Since our data, as discussed above, indicate that the adsorbed N_2 film consists of a three-layer film coexisting with bulk cluster near 30 K and the recent reflection high-energy electron diffraction (RHEED) experiment[1] found the adsorbed N_2 system below 20 K to be a two-layer—plus—bulk system ($2S$ + bulk) at saturated vapor pressure, it is natural to interpret that the 23.4-K heat-capacity peak is a signature of layering transition. The saturation of the size of this peak at $n = 4.10$ indicates that no more nitrogen molecules can be accommodated in the trilayer film system. This result also lends support to the conclusion that the adsorbed film on graphite is limited to a maximum thickness of three layers above 23.4 K.

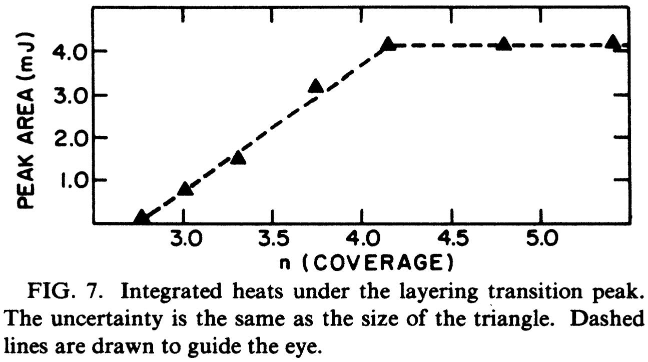

FIG. 7. Integrated heats under the layering transition peak. The uncertainty is the same as the size of the triangle. Dashed lines are drawn to guide the eye.

This coverage is different from the value of $n = 3.75$ where we observed saturation of the size and the shift in temperature of the trilayer orientational-ordering transition peak. As we have discussed above, $n = 3.75$ corresponds to the upper boundary for the $(2S+3S)$ coexistence region and a pure trilayer film is present on graphite above 23.4 K in the coverage range of $n = 3.75$ to $n = 4.10$. Whereas we found considerable hysteresis in the measured heat-capacity signature of the layering transitions of multilayer ethylene on graphite upon warming and cooling of the calorimeter,[21] no observable hysteresis effects were found in this 23.4-K layering transition of N_2. The reason for the difference in these two systems is unclear. Although there is no observable hysteresis, we found small variations in the "layering" transition temperature around 23.4 K for film coverages between $n = 2.75$ and $n = 3.75$. Above $n = 4.16$, the transition temperature always stays at 23.65 ± 0.05 K for all coverages studied. The small increase in the peak temperature above $n = 4.16$ may be related to the formation of the trilayer film after the layering transition. When the system is in the $(2S+3S)$ coexistence region at high temperature, lowering the temperature causes the system to cross the layering transition at 23.4 K, which is a triple point. At coverages above the coexistence region, a pure trilayer film, more compressed than the trilayer in the $(2S+3S)$ coexistence region, exists above 23.4 K, the layering temperature. If the temperature of such a system (at coverages above the coexistence region) is raised beyond 23.4 K, in addition to the layering transition, additional N_2 molecules will be "transferring" from the bulk clusters to form the more compressed pure trilayer film for $T > 23.4$ K. Such an effect should broaden the heat-capacity anomaly and shift peak positions relative to that at coverages in the $(2S+3S)$ coexistence region. The size of the broadening and the shift are dependent on the boundary of the pure trilayer film near the layering temperature. In the phase diagram shown in Fig. 2, we have adopted the interpretation that 23.4 K is the layering transition temperature even though the peak position for coverages above the $(2S+3S)$ coexistence region is found at 23.65 K. Since the shift in peak position is small compared with the half-width, no broadening of the peak was found. Based on the shift in the peak position, a blunt termination of the pure trilayer phase near the layering temperature is proposed in the phase diagram shown in Fig. 2. Our data indicate that this layering transition involves much larger energy and entropy change compared with the orientational-ordering transitions in the layered system. A simple calculation gives the energy change for this transition as $\Delta u = 16 k_B K$ per molecule if we assume the transition involves only the molecules in the third layer. If we convert this Δu to change in the entropy ΔS, we find it is almost equal to half of the entropy change involved in the melting of bulk N_2 at the triple point. Since Δu is related to conversion of the bulk nitrogen to the layered system, the large magnitude indicates the crystal structures or the lattice spacings between these two systems are quite different.

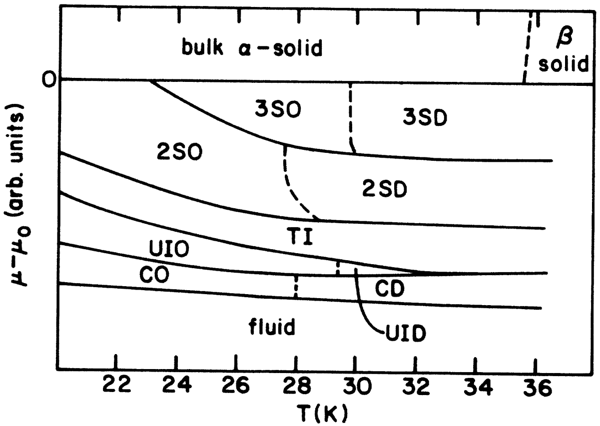

FIG. 8. Schematic N_2 on graphite phase diagram in the chemical potential-temperature plane where μ_0 is the bulk chemical potential. In this phase diagram, both the monolayer (Refs. 8 and 9) and the multilayer phases are included. The dashed lines indicate the orientational-ordering transitions. The boundary separating the uniaxially compressed incommensurate disordered (UID) and the triangular incommensurate (TI) phases is speculative. It is possible that UID is not a distinct phase.

IV. CONCLUSIONS

In conclusion, we have presented data showing the evolution of the heat-capacity peaks as a function of N_2 coverages in the low-temperature region. We found fascinating growth modes and phase transitions of the multilayer N_2 on graphite system. As a function of increasing coverage, the nitrogen molecules adsorbed on graphite evolve sequentially as a single-layer film, a region of coexisting single and bilayer films, and a pure bilayer film. For temperature above 23.4 K, the sequence continues with a region of coexisting bilayer and trilayer film, pure trilayer film, and a region of coexisting trilayer film and bulk clusters. For temperatures below 23.4 K, bulk clusters appear after the bilayer film is completed. These findings confirm earlier studies that nitrogen does not wet graphite at low temperature. It should be emphasized that a layering transition is not the only possible interpretation for the observed heat-capacity anomaly at 23.4 K. The absence of hysteresis at a first-order layering transition is unexpected. What can be concluded without ambiguity is that the observed anomaly at 23.4 K is related to a structural transition within the three-layer system. A schematic nitrogen-on-graphite phase diagram in the chemical potential-temperature plane is shown in Fig. 8. This diagram should be compared with Fig. 2 and the monolayer-coverage—versus—temperature phase diagrams shown in Refs. 8 and 9.

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