Synchrotron X-Ray Diffraction Studies of Multilayer Nitrogen Physisorbed Porous on Graphite Foam

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Abstract

We use synchrotron x-ray diffraction for structural analysis of the behavior of multilayer nitrogen films physisorbed on graphite foam. We provide structural information and concentrations of 2D and 3D solid

phases at a coverage of $\Theta = 8$ ML (Θ ⁄ 1 ML for a %3 x %3 structure) for temperatures from below the bulk α-ß transition temperature [$T_{\alpha\text{-}ß} = 34$ " 0.5 K] to above the bulk triple point [$T_{tp} = 63$ K].   Our data indicate layering begins near $T_{\alpha\text{-}ß}$, with subsequent layering occurring as the temperature is raised; all bulk nitrogen forms disordered film layers by 48 K at $\Theta = 8$ ML.   Our results are consistent with ellipsometry studies of nitrogen on HOPG which found multilayer nitrogen on single crystal graphite to undergo a series of layering transitions above the bulk nitrogen α-ß structural transition.[U.G. Volkmann, and K. Knorr, *Phys. Rev. Lett.* **1991**, *66*, 473.]   The effect of adsorption on a graphite foam substrate, which results in capillary condensation and finite size effects, is limited to a broadening and overlap   of the discrete transition temperatures observed on a single crystal substrate. A phase diagram for coverages above 2 ML is proposed, summarizing this and previous work.

Introduction

As a material physisorbs to a surface, three different classes of film growth can occur.[1] Class I multilayer growth (complete wetting) is characterized by an infinite number of two-dimensional layers condensing on a substrate. Class II growth (incomplete wetting) is characterized by a finite number of layers grown before bulk nucleation. Class III (non-wetting) films grow no layers. The type of growth mode a substrate-adsorbate system exhibits depends on the total surface tension in the system and the temperature.[2] Many adsorbate-substrate systems exhibit wetting transitions, which are usually driven by bulk structural transitions.[3] An example is triple point wetting, where the number of layers grown approaches infinity as the adsorbate temperature reaches the bulk triple point temperature.[3] Similarly, one might expect transitions in a physisorbed system to be driven by other types of bulk structural transitions, such as the α-ß phase transition observed in N_2 and CO. The number of film layers stabilized by a substrate can increase as the temperature changes;[4] this is called layering.

The multilayer structure of nitrogen physisorbed on graphite at low temperatures has been studied extensively[5] using neutron diffraction,[6,7] heat capacity measurements,[8] adsorption isotherms,[9,10] ir spectroscopy,[11] and computer simulation.[12] Monolayer nitrogen is commensurate (%3 x %3) and has herringbone molecular orientations; the monolayer compresses ~10% to form an incommensurate structure at higher coverage.[7,13] The bilayer structure is also compressed incommensurate. The two layers in the N_2 bilayer are commensurate with each other. The exact molecular orientations are still uncertain.[6] Nitrogen has been found to incompletely wet graphite at still higher coverages.[6,14]

At coverages above the bilayer nitrogen films on a single surface HOPG substrate were measured with ellipsometry isotherms to undergo a series of layering transitions.[15] At temperatures below $T_{\alpha-\text{ß}}$ [$T_{\alpha-\text{ß}}$ = 34 " 0.5 K, where bulk nitrogen undergoes a solid-solid phase transition. This is depressed 1 K for small crystallites[8] compared to large bulk nitrogen samples, where $T_{\alpha-\text{ß}}$ = 35 K.[16] A similar depression is seen for the γ-β transition of O_2.[17]], a maximum of two to four film layers formed before bulk nucleation began (incomplete wetting), in agreement with neutron diffraction.[6] Bulk nitrogen condensed in an optically-smooth epitaxial alpha phase (α-N_2). Bulk nucleation was inferred from stabilization of the equilibrium vapor pressure. The existence of one to two amorphous layers above the ordered bilayer, which would allow for lattice mismatch between the bilayer and the epitaxial α-N_2, was also inferred. This agrees with neutron studies of this system.[6] Significant hysteresis between adsorption isotherms and desorption isotherms was seen.

At temperatures above $T_{\alpha-\text{ß}}$, the number of layers formed before bulk nucleation increased as the temperature increased. At T = 35 K " 0.5 K, five layers formed on HOPG before beta phase bulk (ß-N_2) nucleation; subsequent layers formed near 38 K, 40 K, 44 K, 46 K and 50 K. A maximum of ten layers of film was observed before bulk nucleation began. The ß-N_2 was not epitaxial, and hence not optically smooth. There was little hysteresis observed in the isotherms above $T_{\alpha-\text{ß}}$.[15]

The objective of this research is to study with direct x-ray diffraction structural analysis the layering transitions observed from ellipsometry, since it is not possible to determine the structure of the adsorbed layers from ellipsometric measurements. We also examine the effects of using a porous graphite foam sample, which alters the behavior of the system due to, for example, finite bulk particle size and capillary condensation. Use of powdered substrates have often been dismissed for multilayer adsorption studies due to the possibility of capillary condensation of the adsorbate in the pores naturally found in such samples. These capillary effects do indeed complicate analysis of multilayers systems on powdered substrates, but do not preclude such techniques from providing important structural information as shown below.

Experimental Section

Standard x-ray diffraction in a transmission geometry was done at the MATRIX PRT beam line (X18A) at the National Synchrotron Light Source at Brookhaven National Laboratory. We used a double crystal Si(111) monochromator (λ = 1.550 Å), with both horizontal and vertical x ray focusing using a bent, cylindrical, platinum-coated mirror. A resolution of 0.02 Å^{-1} FWHM was achieved using Soller slits between the sample and a NaI scintillation detector. The sample, 0.68 " 0.02 g of graphite foam with a specific surface area of 33.8 " 0.1 m^2-g^{-1} and a density of 0.24 g-cm^{-3}, was contained in a copper cell 1.2 cm thick fitted with Be windows. The cell was mounted on a closed cycle He refrigerator with a temperature stability of " 0.1 K.

A vapor pressure isotherm at 76 K determined our monolayer coverage (Θ = 1 ML), defined as the amount of nitrogen adsorbed at the completion of a substep in the isotherm resulting from formation of a

commensurate %3 x %3 solid monolayer.[6,15] The sample cell was filled with Θ = 8.00 " 0.05 ML of nitrogen, sealed, annealed at 80 K for ~1 hr, and slowly cooled to 32 K at a rate of 30 K-hr^{-1} to minimize condensation in sample cell cold spots.[9] A sample coverage of 8 ML was selected because Volkmann and Knorr predicted three distinct layering transitions should be observed above $T_{\alpha\text{-ß}}$ and before complete disappearance of the bulk peaks.[15] This coverage was also studied by neutron diffraction at lower temperature.[6]

A Rietveld analysis[18] of diffraction scans taken below $T_{\alpha\text{-ß}}$ confirmed that a 2D compressed incommensurate film coexisted with α-N$_2$ [Fig. 1(a)]. Diffraction scans were taken at approximately 2 K intervals up through the ß-N$_2$ triple point temperature (T_{tp} = 63 K). The temperature of the sample was then monotonically decreased in approximately 2 K increments to 30 K, well below $T_{\alpha\text{-ß}}$. The scans typically took one hour to complete.

Results

To monitor the relative amounts of the different species of nitrogen present in our sample cell, we assume that the intensities of the diffraction peaks for a given phase are proportional to the amount of the phase in the cell. This method was used successfully in previous studies.[6,19-21] Specifically, layering transitions for iron pentacarbonyl[19] and ethylene[20] were inferred from a decrease in bulk phase Bragg peak intensity. Figure 1 shows typical diffraction scans both above and below $T_{\alpha\text{-ß}}$ after background scattering was subtracted.[22]

This report focuses on detailed results for one peak for each solid crystalline phase of nitrogen; similar analysis of several other bulk peaks are used to corroborate trends in these monitored peaks.[23] We identified the α-N$_2$ (111), the α-N$_2$ (200), the α-N$_2$ (201) & (210), and the α-N$_2$ (211) peaks in Figs. 1(a) and 1(b). Based on proximity to other peaks and intensity, we chose to monitor α-N$_2$ (200). The α(200) peak does overlap a very weak (21) film peak; however, the (21) intensity is nearly zero above the orientational disordering transitions at 28 K and 30 K.[6,24] The ß-N$_2$ (100), (101), and (102) peaks are evident Fig 1(b). We monitored the ß-N$_2$ (101) peak. There is only one monolayer film peak which is intense enough to monitor, the (20) peak at q = 1.78 Å^{-1}.[24] Unfortunately, the (20) peak coincides with the ß-N$_2$ (100) peak and is adjacent to the graphite (002) peak. Thus, accurate determination of the relative amount of film in coexistence with ß-N$_2$ is difficult; this is discussed further below.

Figure 2 is a plot of the integrated peak intensities of selected peaks as the temperature was monotonically increased. The intensity and width of the film peak [Fig. 2(c)] remain constant within error for 22 K # T # 48 K. At 54 K the peak has broadened 50% but the integrated intensity has remained approximately constant. By 64 K (just above T_{tp}), the (20) film peak has broadened to where it cannot be clearly distinguished from the background. This behavior could be attributed to a loss of long range order in the monolayer or to film melting. A similar decrease in intensity and increase in width was observed previously for incommensurate compressed nitrogen films above 50 K for coverages 0.5 # Θ # 1.2 ML and was

attributed to a gradual decrease in long range order of the film.[7,24] Film melting for these lower coverages occurred in the range 60 K to 85 K, increasing with increasing coverage.[6,13,24] No structural information is available for melting at higher coverages.   Statistical uncertainty in the film peak and the estimated systematic error due to contamination of the (20) peak by the ß (100) are reflected in the error bars in Fig. 2(c).   The latter is based on the peak intensity of the measured ß (101) peak, and the theoretical relative intensities of these two peaks for an isotropic powder.[25]

The α-N_2 (200) peak intensity for increasing temperature is plotted in Fig. 2(a).   At temperatures below $T_{\alpha-\beta}$ (22 K to 32 K) this peak is most intense and is constant within error.   At 36 K (above $T_{\alpha-\beta}$), the intensity drops by half, and continues to decrease monotonically to zero at 48 K, as the temperature increases.   This same behavior is also seen in the α-N_2 (211) peak, albeit with poorer statistics.   Thus all α-N_2 disappears by 48 K.

In Fig. 2(b) the intensity of the ß-N_2 (101) peak is plotted versus temperature.   Below $T_{\alpha-\beta}$, there is no evidence for ß nitrogen.   As the temperature is increased above $T_{\alpha-\beta}$, there is an abrupt increase in ß-N_2 peak intensity.   The intensity then decreases monotonically to zero as T is increased further.   Thus all ß-N_2 disappears by 48 K.

Figure 3(a) shows the intensity of the α-N_2 (200) peak as the temperature was monotonically *decreased* from 64 K to 30 K.   The first evidence of α-N_2 is at T = 33 K (below $T_{\alpha-\beta}$).   At T = 30 K, this   amount has increased substantially.   This corresponds to the bulk nitrogen undergoing the α-ß phase transition.

Figure 3(b) is a plot of the ß-N_2 (101) peak intensity.   For all scans between T_{tp} and $T_{\alpha-\beta}$, ß-N_2 is observed.   This contrasts to the situation where the temperature was monotonically increased; there all of the bulk material is gone above 48 K.   As the temperature is decreased, the amount of bulk beta nitrogen increases, until $T_{\alpha-\beta}$.   Below $T_{\alpha-\beta}$, the amount of beta nitrogen drops drastically, which corresponds to bulk material undergoing the α-ß phase transition.   The ß-N_2 (101) also shifts to higher momentum transfer as the temperature decreases.   This shift corresponds to an average linear coefficient of thermal expansion of 2.2 x 10^{-3} Å-EC^{-1}, which   agrees well with previously published values.[16]

Comparison of Figs. 3(b) and 3(c) shows that the film peak intensity plot has similar temperature behavior to the ß-N_2 peak.   We first see evidence of a weak film peak at T = 62 K.   The intensity of the film peak grows in the same manner as the ß-N_2.   This continues until $T_{\alpha-\beta}$, where the behavior for these two peak intensity plots diverges.   At T = 30 K, the film peak has dropped intensity once again, but is still evident, while the ß-N_2 is absent.   This data implies that there is significant contamination of the film peak by the ß-N_2 (100) peak for decreasing temperature when much ß-N_2 is present.

Discussion

In order to compare our data more directly with Ref. 15, we plotted the total amount of crystalline 3D solid   as a function of temperature in units of coverage (ML) in Fig. 4.[26]   Figure 4 shows that the amount of crystalline 3D solid in our cell is constant (within error) up to 32 K, begins decreasing near $T_{\alpha-\beta}$, and disappears entirely by 48 K (15 K below the ß-N_2 triple point at 63 K).   A comparison of these results to the layering behavior predicted by Volkmann and Knorr (stepwise line in Fig. 4) shows that our data is consistent with their predicted *temperature range,* but not necessarily the stepwise behavior resulting from discrete layering transitions.   Therefore, we cannot confirm the layering transition temperatures observed by Volkmann and Knorr.   A linear decrease in the amount of 3D solid over this temperature range in our data does not preclude layering, given the uncertainty in our data.   However, due to the difference between our foam and Volkmann

and Knorr's HOPG substrates, pore size distributions and capillary effects may broaden the layering transitions; the layering transitions also may not be abrupt because the film layers formed may not be crystalline or may not be complete.

There is no corresponding increase in the amount of translationally-ordered film evident in Fig. 2(c). Incomplete, amorphous layers above a crystalline monolayer have been observed previously at lower coverages.[6,13,24] From this, we conclude that the bulk solid nitrogen is probably layering as a 2D amorphous solid or fluid which does not contribute to the crystalline film peak intensity. One must be cautious, however, when estimating film coverage from peak intensity; destructive interference between layers produces very limited increase in the (20) integrated peak intensity from the nitrogen monolayer to the bilayer.[6,13]

There are a number of possible alternate explanations for the disappearance of the bulk peaks, other than layering. These are due to either migration of nitrogen from the scattering volume, the 3D bulk peaks becoming unobservable, or transitions to other 3D phases. We discuss each of these alternatives, and show that they do not reasonably explain the observed data.

Nitrogen could migrate out of the x-ray scattering volume due, for example, to a cold spot on the cell walls or in the fill line.[9] Significant migration can be ruled out by monitoring the large (15%) attenuation of the graphite (002) peak due to x-ray absorption by the nitrogen in the cell. No marked changes were observed over the entire temperature range of our experiment. Further, two scans at 36 K (immediately above $T_{\alpha\text{-}\beta}$) taken one hour apart show no change (< 2%) in any of the monitored bulk peaks. However, instabilities in the x-ray intensity of the synchrotron source prohibit ruling out some small migration.

Orientational effects did not cause the disappearance of the bulk peaks in Fig. 2. Specific peaks can change intensity, or disappear, due to changes of orientation of the crystallites. However, such orientational effects are minimized for powdered substrates. Further, the intensities of several peaks for both α and ß phases exhibit the same temperature dependence.

Given that the nitrogen remains in the scattering volume and is not in the α or ß phase above 48 K, there must be a transition to a 2D phase (implying layering) or another 3D phase. There are no other 3D solid nitrogen phases below 4 kbar.[16] At the saturation vapor pressure of 3D liquid at our highest temperature, desorption can contribute at most . 0.1 ML 3D gas in the sample cell dead volume. Transition to a 3D liquid cannot occur below T_{tp} for increasing T under normal conditions. However, two effects associated with porous substrates, finite bulk particle size effects and capillary condensation in the substrate pores, are known to suppress the 3D melting temperature in, *e.g.*, N_2,[11] as well as Ar, H_2 and O_2.[27]

Neither of these mechanisms, however, can reasonably explain the decrease in crystalline bulk intensity for temperatures ~15 K to ~28 K below T_{tp}. The change in the melting temperature due to finite size effects, δT, is given by $\delta T/T_M = 2\sigma_{SL}/rL$, where T_M is the large sample melting temperature, σ_{SL} is the interfacial energy between the solid and liquid, r is the radius of a spherical particle, and L is the latent heat of fusion per volume.[28] [σ_{SL} is estimated[29] as one tenth of the liquid-vapor interfacial energy ($\sigma_{LV} = 10.5$ mJ m^{-2}),[30] L = 24.19 MJ $^{-3}$,[16] and $T_M = T_{tp}$.] Chung and Dash have measured a 1.7 K depression in T_M attributed to finite size effects for multilayer nitrogen films adsorbed on Grafoil, with an estimated particle radius of 60 Å.[29] Based on our diffraction peak widths, we estimate coherence lengths of 40-100 Å for the ß phase and >300 Å (resolution limited) for the α phase, corresponding to temperature shifts of only ~0.3 K to 3 K. This shift is similar and comparable to the temperature shift of $T_{\alpha\text{-}\beta}$ for small crystallites[8] mentioned above. Typical pore size distributions for graphite foams are 40-60 Å.[28] For capillary condensation in a porous medium, $\delta T/T_M = 2\sigma_{SL}\cos\Theta/rL$, where Θ is the contact angle between liquid-solid interface, and the pore wall.[31] Again, we estimate δT # 3 K. Studies of similar adsorption systems exhibiting capillary condensation, reviewed in Ref.

19, found 2 K # δT # 4 K when supercooled; δT was considerably less when warming.[32-34] Based on the work of Morishige *et al.*[10], using peak height analysis, we are able to conclude that no more than 3% of the total nitrogen in the sample cell is capillary condensed as solid.[23]   This is supported by comparison of the coherence length of the crystalline solid (40 Å to >300 Å) to the typical pore size distribution (40-60 Å)

Comparison of Figs. 2 and 3 demonstrate that there is very different behavior in the system where the temperature was monotonically increased versus monotonically decreased.   As the temperature is decreased from above T_{tp}, bulk nucleation occurs at temperatures just below T_{tp}.   When the temperature was monotonically increased, the bulk material was evident only for T < 48 K.   This hysteresis implies that growth mode is also important in this system, as has been found for other studies of bulk nitrogen crystal growth near $T_{\alpha\text{-}\beta}$.[16]   Temperature dependent hysteresis would not be observed in the ellipsometry experiments as the coverage was varied while the temperature was held constant.[15]

We also see an α-ß coexistence over a 14 K temperature range which Volkmann and Knorr did not see. We attribute the coexistence to a difference in experimental technique, and possibly to differences in substrates. In the ellipsometry experiments, the temperature was fixed, and the coverage was varied.   Therefore, they would condense only the bulk nitrogen phase which was appropriate to the fixed temperature.   We fixed the coverage (approximately), and varied the temperature from below $T_{\alpha\text{-}\beta}$ to above.   This mode of experiment may allow a metastable state to exist, where the bulk nitrogen does not fully undergo the α-ß transition.   Such coexistence is not surprising because the α-ß transition is a martensitic type, involving a change in stacking sequence from ABC to AB.   Indeed, Huber, *et al.* proposed that the α-β transition in suppressed, although affected by finite size and extensive stacking faults, for N_2 adsorbed in porous glass.[11]   Such transformations may be influenced by crystallite size and shape.[12d]   Two of our scans taken just above $T_{\alpha\text{-}\beta}$ at 36 K, one hour apart, showed no indication of changes (<2%) in the 3D crystalline bulk peak intensities.   Our data in this 14 K coexistence temperature region were collected for over 8 hrs, which suggests any metastable state exists for times greater than 8 hrs.

How, then, do capillary condensation and finite size effects   manifest themselves in this system?   As mentioned above, a typical pore size distribution for graphite foam is 40 - 60 Å.[10]   This would lead to temperature shifts of 1 - 1.5 K for the melting transition according to our analysis above.   We might expect similar shifts to occur for other phase transitions in this system, specifically, the discrete layering transitions observed by Volkmann and Knorr.   In our experiment, we expect then that capillary condensation and finite size effects would broaden the discrete layering transition temperatures observed by ellipsometry.   Including errors bars in Fig. (4) to represent a worst case temperature broadening of approximately 1.5 K, it is clear that our data are consistent with the ellipsometry data; almost every point falls on the measured transition curve within error.   However, as stated above, we cannot definitively confirm discrete layering transition temperatures.

Conclusions

We interpret our data for the scans where the temperature was monotonically increased to be indicative of layering transitions, beginning near $T_{\alpha\text{-}\beta}$ and completing at T # 48 K.   Disappearance of the bulk peaks 15 K below the bulk triple point, with no indication of the nitrogen migrating out of the cell, is strong evidence for layering.   The lack of an increase is the intensity from translationally ordered 2D film suggests that any 2D layers grown are disordered or fluid layers.   As suggested by Volkmann and Knorr,[15] the 2D layering observed in a physical manifestation of a 3D structural α-ß phase transition driving a 2D phase transition similar to triple

point wetting.

The primary effect of capillary condensation in this system seems to be the smearing out of the discrete layering transitions observed on a single surface HOPG substrate. We believe layering is responsible for the gradual decrease of the bulk peaks in our diffraction scans, and that capillary effects broaden the transitions so that we do not observe discrete layering transitions. Capillary condensation of 3D bulk solid does not preclude layering; indeed, as is evident from our results, layering does occur. We estimate that the depression of the melting temperature due to capillary condensation in porous graphite foam and to finite bulk crystallite size as < 3 K.

The results of Volkmann and Knorr,[15] other previous work,[6-8,13,24] and our results (BDE) may be integrated into a proposed phase diagram (Fig. 5) for coverages above 2 ML. This phase diagram extends the phase diagram found in Ref. 7 to coverages above 5 ML and to temperatures above $T_{\alpha-\beta}$ and the composite phase diagram found in Ref. 6 to coverages above 2.5 ML; it is largely based on the combined results of the previous studies cited. It is proposed above 24 K, one ordered layer and amorphous or fluid film coexist;[6,13] above 3.7 ML, these coexist with bulk solid.[6,15] At coverages greater than 3.7 ML and temperatures ranging from just below $T_{\alpha-\beta}$ and above, the nitrogen on graphite system undergoes a series of layering transitions.[15,BDE] At temperatures just below $T_{\alpha-\beta}$, there is one compressed monolayer of nitrogen solid, several amorphous or liquid film layers, and α-N_2 condensate.[6,15,BDE] As the temperature is increased above $T_{\alpha-\beta}$, the number of film layers increases to five.[15,BDE] As the temperature is increased further, the system undergoes additional layering transitions until all the nitrogen in the system exists as a compressed crystalline solid film layer and as amorphous or liquid film layers.[15,BDE] This solid monolayer begins to lose long range order in the 50 K to 65 K range, from submonolayer coverage up to at least 8 ML.[6,7,13,24,BDE] From submonolayer coverage to . 1.2 ML melting of the solid monolayer increases from . 60 K to 85 K.[7,13,23] Above 1.2 ML the melting temperature of the film has not been determined.

More extensive structural and thermodynamic studies of multilayer nitrogen on both graphite foams and HOPG at temperatures above $T_{\alpha-\beta}$ are essential to the complete understanding of this system and its dependence on substrate. Detailed high coverage vapor pressure isotherm work is needed and would provide insight into the hysteresis seen in this system and the effects of capillary condensation and finite size effects.

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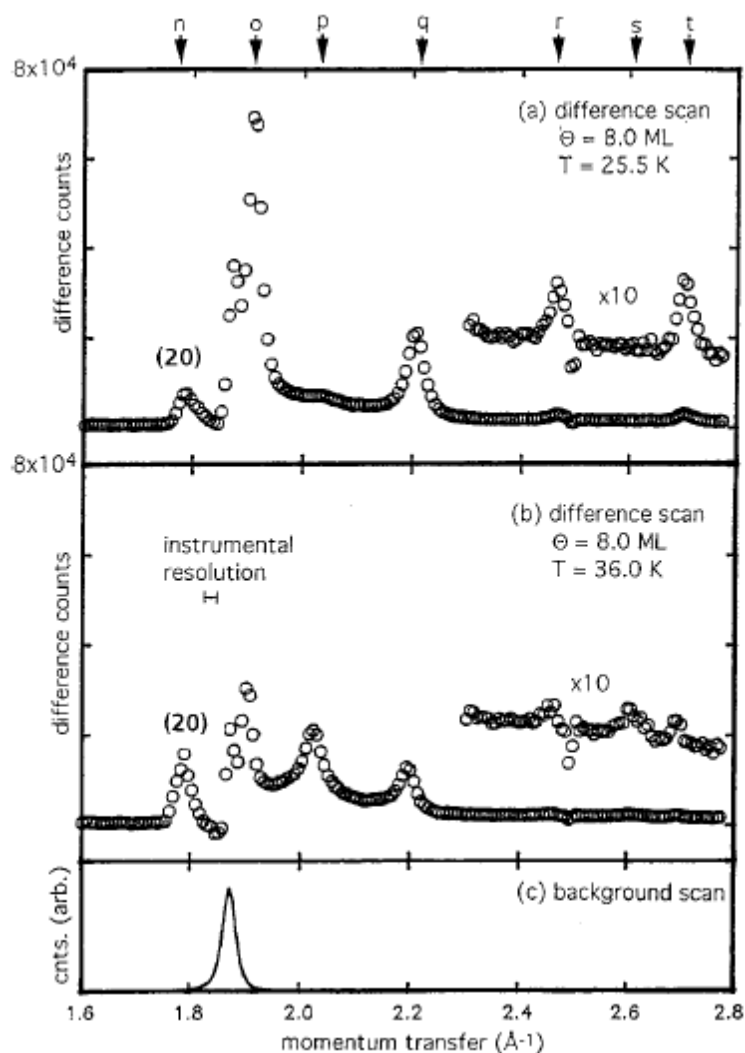[34] Tell, J.L. and Maris, H.J. *Phys. Rev. B* **1983,** *28*, 5122.

FIG. 1 (a) Typical diffraction scan of 8.0 ML nitrogen physisorbed on graphite foam at 25.5 K after subtraction of a scaled substrate background. The compressed monolayer N_2 (20) peak is labeled at q = 1.78 Å^{-1}. All the possible bulk diffraction peaks which occur in the measured momentum transfer range are indexed as follows: n = ß-N_2 (100), o = α-N_2 (111), p = ß-N_2 (101), q = α-N_2 (200), r= α-N_2 (201) & (210), s = ß-N_2 (102), and t = α-N_2 (211). (b) Typical diffraction scan of 8.0 ML nitrogen physisorbed on graphite foam at 36 K after subtraction of a scaled substrate background. The high momentum transfer scattering in (a) and (b) is presented on an expanded vertical scale. (c) Diffraction pattern of bare graphite foam.
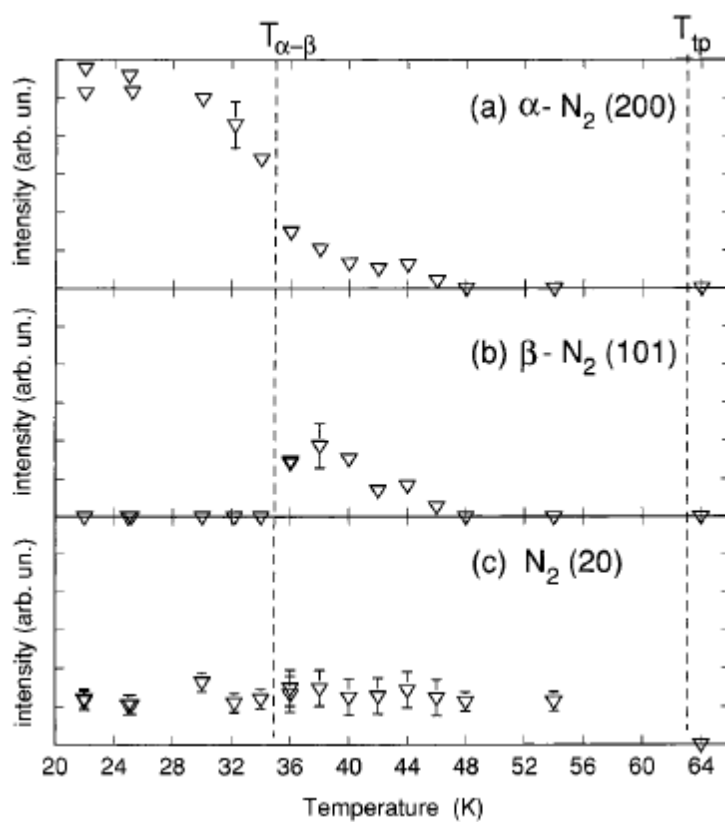
FIG. 2   Peak intensity as a function of increasing temperature: (a) α-N$_2$ (200) peak; (b) ß-N$_2$ (101) peak; and (c) N$_2$ (20) film peak.   Normalization to obtain coverage units is described in the text.
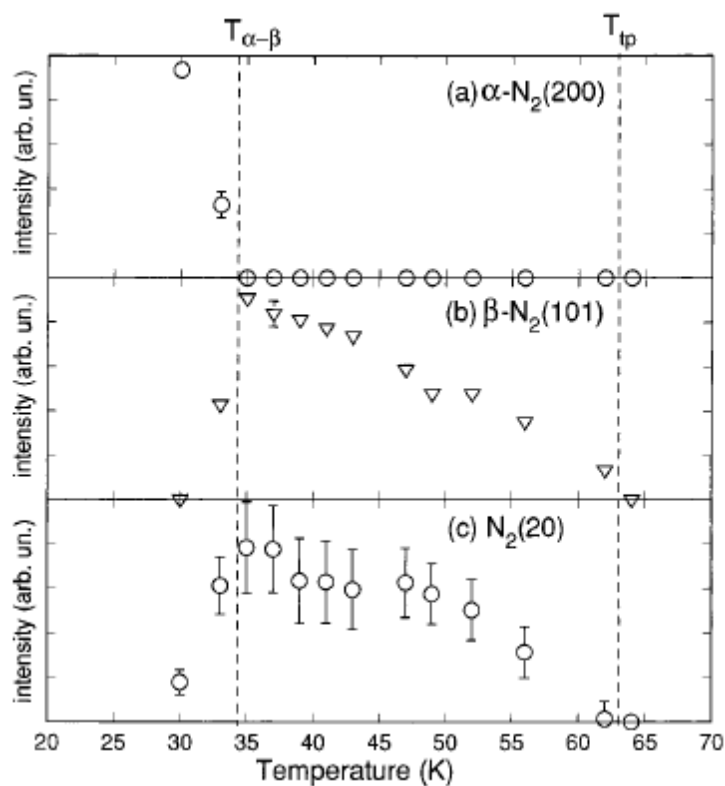
FIG. 3   Peak intensity as a function of decreasing temperature: (a) α-N$_2$ (200) peak; (b) ß-N$_2$ (101) peak; and (c) N$_2$ (20) film peak.
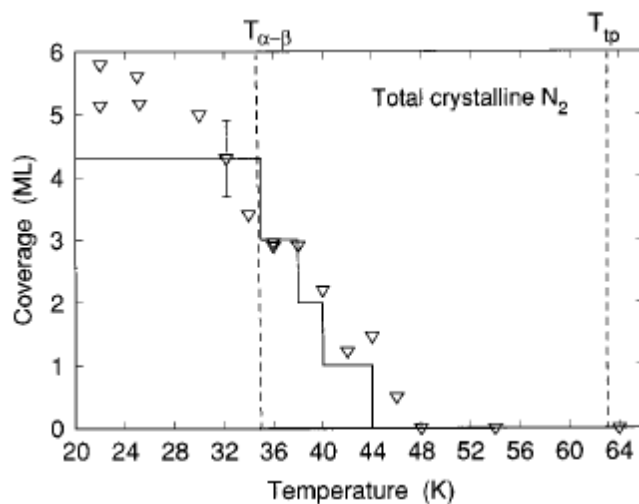

FIG. 4 Amount of 3D solid («) as a function of increasing temperature.   The stepwise curve (solid line) is based on the measured layering transitions by Volkmann and Knorr[15], as discussed in the text.
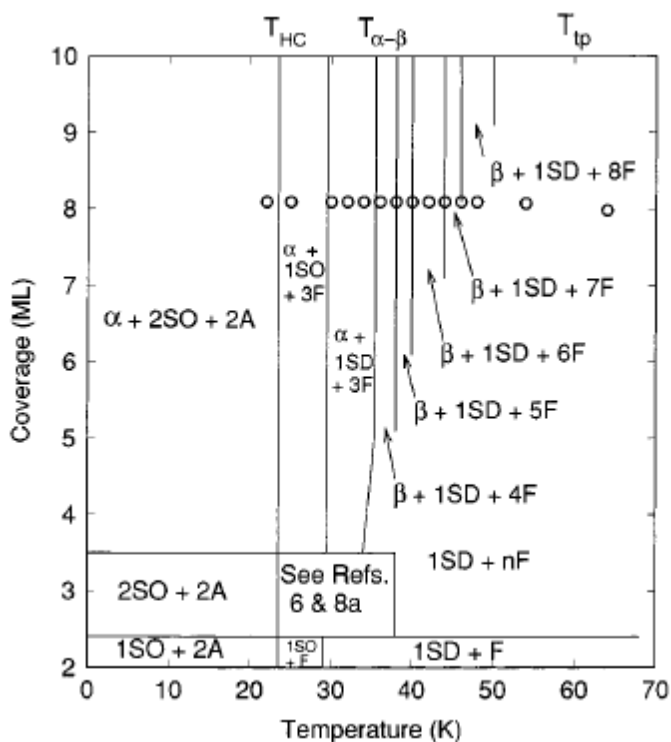
FIG. 5 Proposed phase diagram of multilayer nitrogen above 2 ML coverage physisorbed on the graphite basal plane summarizing this and previous work.[6-8, 13,15,24]   The notation follows Wang *et al.*[6]   1S, 1S', and 2S denote the fully compressed monolayer solid (TI) phase, expanded monolayer solid phase, and bilayer solid phase, respectively.   α, ß, A, and F denote the α-N_2 bulk phase, ß-N_2 bulk phase, amorphous or disordered 2D film, and 2D fluid, respectively.   The numerical prefix indicates the number of completed or partially completed layers of that phase.   O and D indicate orientationally ordered and disordered phases, respectively.   The circles (•) correspond to our diffraction scans.   The reader is referred to other articles for details of the complicated phase diagrams proposed for low temperature monolayer formation,[8b,13] and melting of the second layer.[6,8a]