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Commensurate-uniaxial-incommensurate transition of monolayer nitrogen on graphite

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Heat-capacity measurements were made to study the orientational-ordering transition of N_2 on graphite in commensurate and incommensurate phases. Whereas a sharp heat-capacity peak was observed in the commensurate (C) and striped or uniaxial-incommensurate (UI) phases, only a broad and weak anomaly was found in the triangular-incommensurate phase. These heat-capacity traces show regions of coexistence indicating the C-UI transition to be first order.

Depending on the relative importance of the adsorbate-adsorbate and adsorbate-substrate interactions, an adsorbed layer can be in phases either commensurate or incommensurate with respect to the modulation periodicity of the substrate. When these interactions are comparable a slight change in the spreading pressure or density of the adsorbed layer may induce a commensurate-incommensurate (C-I) transition. The nature of this transition is of considerable theoretical and experimental interest.[1] Just at the start of the incommensurate phase, according to current theories based on the ideas of Frank and Van der Merwe,[2] the adsorbed layer is composed of locally commensurate regions separated by periodic arrays of discommensurations or domain walls.[1] The structure of the domain wall is thought to be controlled by the wall energy per unit length and the sign of the wall-crossing energy. If the crossing energy is positive, then a uniaxial-incommensurate (UI) or striped-incommensurate phase with parallel domain walls should be favored for the adsorbed layer.[1,3] At higher incommensuration, the UI phase can transform to a triangular-incommensurate (TI) phase with hexagonal domain-wall structure. The TI phase is often called the hexagonal incommensurate phase in the theoretical literature. (We are assuming the commensurate (C) phase to have triangular symmetry such as the $(\sqrt{3}\times\sqrt{3})$ phase of Kr and N_2 on graphite.) If the crossing energy is negative, the UI phase is not stable and the C-I transition takes the adsorbate directly into the TI phase.[1,3]

The C-I transition of Kr on graphite appears to be one that leads to the TI phase. Despite the extensive studies made on this system important questions concerning the nature of this transition remain.[4–6] It is also not clear which theoretical model correctly describes this transition.[1,7,8]

In contrast, there is no important disagreement among the various theoretical models that deal with the C-I transition to the UI phase. A continuous transition in this case is thought to be likely,[1,3,8,9] and in some models a narrow fluidlike region has been proposed to exist between the C and the UI phases.[7,8,10] The C-I transition in bromine-intercalated graphite system is found to be consistent with theoretical predictions.[11] In this paper we shall present the results of a careful heat-capacity study of the orientational-ordering transition of N_2 molecules adsorbed on graphite near the monolayer completion region. In addition to other results, these heat-capacity traces show that the C-UI transition is clearly first order.

The experimental arrangement used in this study is similar to earlier studies from our laboratory.[12,13] A new sample cell and calorimeter were made with a fresh piece of graphite-foam substrate. The surface area of the calorimeter is approximately $2M^2$. In Fig. 1 heat-capacity traces of 16 surface coverages with the background contribution subtracted are shown between 20 and 35 K. A $n=1$ coverage is defined as the coverage at the top of the vertical substep [corresponding to the solid boundary of the commensurate $(\sqrt{3}\times\sqrt{3})$ solid-fluid coexistence region] in N_2 vapor-pressure isotherms taken at 74 K.[12] Owing to the presence of temperature-dependent vacancies and interstitial sites, this solid boundary does not stay constant at $n=1$. There is some evidence suggesting that this boundary rises above $n=1$ at low temperatures.[5,12] The coverage scale used here is 2% larger than that used in earlier publications[12,13] from our laboratory where $n=1$ is defined against the 70 K isotherm ($n=1$ in the 74 K scale corresponds 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 data at the higher temperature. These heat-capacity traces show signatures of orientational-ordering transitions in C (from $n=0.619$ to 1.101), UI (from $n=1.142$ to 1.178), and TI ($n=1.200$ and 1.302) phases. The heat-capacity traces at coverages between the three pure phases show signs of coexistence. It should be pointed out that two separate sets of data were taken, each by increasing the N_2 coverage in small steps. Upon the completion of the first data set the sample cell was evacuated and another set with N_2 coverages filling in the important gaps was taken. The consistency of these two sets of data, as indicated in Fig. 1, indicates that the *relative*-coverage determination is reliable to 0.2% or $\Delta n=0.002$.

The four heat-capacity traces in the C phase and C-fluid coexistence region are in excellent agreement[14] with those found in the earlier heat-capacity study from our laboratory.[12,13] Namely, there is a coverage-independent narrow first-order-like heat-capacity peak [full width at half maximum (FWHM) = 0.6 K] centered at 28.1 K with a reduced height of about $4k_B$ per molecule. This transition also has been observed in neutron,[15] low-energy electron diffraction (LEED),[16] NMR,[17] and x-ray[18] studies. The orientationally ordered phase was identified by LEED[16] to have a two-sublattice in-plane herringbone structure. Although we are not able to locate precisely the upper boundary of the C-fluid coexistence region, the fact that the orientational-peak at 28.1 K persists up to $n=1.101$ indicates a narrow strip of $(\Delta n \leq 0.1)$ of pure-C phase.

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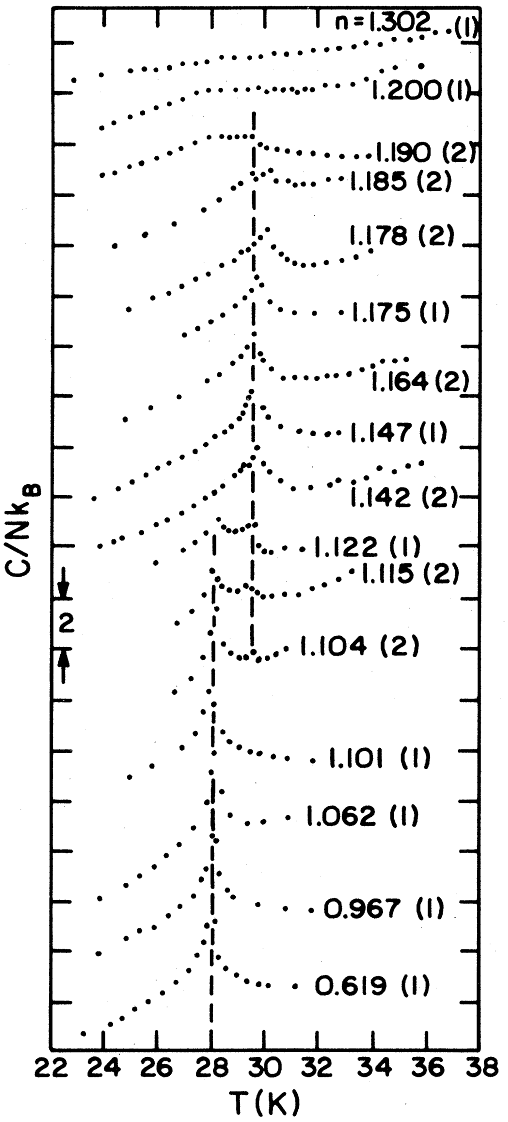

FIG. 1. Heat-capacity scans of N_2 films adsorbed on graphite at 16 different surface coverages. Heat capacity is expressed in reduced units; N and k_B are, respectively, the total number of molecules adsorbed and Boltzmann's constant. Two separate runs were made, and they are identified after each coverage. The vertical dashed lines at 28.1 and 29.4 K are drawn to highlight the orientational-ordering transition temperature of the C and UI phases.

The peaks of the heat-capacity traces for coverages between $n=1.142$ and 1.178 are wider and shifted by 1.3 K (to 29.4 K) in comparison to those in the C phase. The integrated areas under the peaks, however, are comparable (to 10%) to those in the C phase. At $n=1.200$ only a broad diffuse heat-capacity anomaly near 27 K is seen and at $n=1.302$ only the high-temperature end of the anomaly is apparent in the temperature range studied.

In two related LEED studies[19,20] an orientationally ordered UI (also with two-sublattice herringbone in-plane structure) was observed at 15 K with densities 2–5% above the $\sqrt{3}\times\sqrt{3}$ density. At density more than 8% above the C value a TI orientationally ordered phase was found. In the TI phase, the molecules are tilted with respect to the surface.[20,22] Since our $n=1.1$ corresponds to the C density, the reported densities in the LEED studies[19,20] naturally allow us to identify the traces between $n=1.142$ and 1.178 to be made in the UI phase and those at $n=1.200$ and 1.302 in the TI phase. The existence of the TI phase has been confirmed by an x-ray study performed by Morishige, Mowforth, and Thomas,[18] a synchrotron x-ray study[21] performed by Nielsen, Kjaer, and Bohr and a recent neutron-diffraction study.[22] The synchrotron and the neutron studies also found evidence for the UI phase. The UI phase in the synchrotron study was found to persist to at least 35 K, clearly above the orientational-ordering transition temperature. A different coverage scale was used in the synchrotron study but the relative coverages of the C, UI, and TI phases are consistent with the present and the LEED results.[19,20] The persistence of the UI phase to the orientationally disordered region is an interesting result and deserves further scattering study.

The fact that the orientational-ordering transition occurred at a higher temperature in the UI phase can be attributed to the reduced distance between the nitrogen molecules. This is the case because the orientationally ordered phase is stabilized by increased electroquadrupole-quadrupole interaction. The broadening of the heat-capacity peak may be due to the increase in density modulation during uniaxial compression. The nearly coverage-independent shape and temperature of the heat-capacity anomaly over the entire UI phase (the peak position at $n=1.178$ is only 0.3 K higher than those at lower coverage) may seem inconsistent with the LEED result,[19] where a continuous compression of 3% in density is seen. However, in the UI phase during further compression, the orientations of the molecular axes can change and this will compensate the possible increase in electroquadrupole-quadrupole interaction due to the reduction in lattice spacing. A recent computer result[23] shows this in fact is the case: They found the change in the interaction energy and transition temperature during the compression can be greatly reduced because of the change in the orientation of the nitrogen-molecular axes. Such a change in the molecular orientations has not been carefully investigated but cannot be ruled out by currently available scattering results.[24] A power-law analysis of the heat-capacity peaks, similar to that performed for the study in C phase,[12] indicates that the orientational-ordering transition in this phase is more likely to be first order than continuous. This finding is consistent with theoretical predictions of Cardy, den Nijs, and Shick[25] that the orientational-ordering transition in the incommensurate herringbone phase belongs to the same universality class as that in the C phase.

The broad anomaly extending between approximately 22 and 32 K observed for the $n=1.200$ scan can be interpreted as a signature of continuous orientational-ordering transition. The more likely interpretation, however, is that the orientation of the nitrogen-molecular axes (tilted with respect to the substrate) is gradually becoming more random as the temperature is raised from 0 K. The integrated area under the broad anomaly for the $n=1.200$ scan is about 20%–30% smaller than those in the C and UI phases. In the TI phase, when the nitrogen-molecular axes are tilting out of the graphite surface the density modulation is likely to be larger. A recent x-ray experiment[18] found substantial distortion in the center-of-mass lattice of the TI overlayer. The orientational-dependent substrate field and the corrugation of the surface may also randomize molecular orientation even at very low temperatures. These effects may broaden or even eliminate the orientational-ordering transition in the TI phase. Our finding of a broad heat-capacity anomaly is consistent with the recent x-ray result[18] that the orientational order in the TI phase was found to decrease gradually from 10 to 30 K. In contrast, an abrupt drop in the orientational order was seen near 30 K signifying a genuine transition in the C phase in this same x-ray study.

The heat-capacity traces between $n = 1.104$ and 1.122 show two orientational-ordering peaks: one at the C-phase position and the other the UI-phase position. The most direct explanation of this result is that this is a coexistence region of C and UI phases. The relative sizes (i.e., the areas under the peaks) of the two peaks obey, qualitatively, the lever rule if $n = 1.102$ and 1.130 are chosen as the boundaries of this region. The presence of this coexistence region and the abrupt jump in the orientational-ordering transition temperature in the two phases are clear signatures of a first-order C-UI transition. Since the 3% jump in density observed here is close to the instrumental limit of the LEED study (2%), it is not surprising that the LEED study did not detect this coexistence region. The $n = 1.101$ scan shows a C-phase orientational-ordering peak that is wider (FWHM=0.8 rather than 0.6 K) and located at a temperature 0.3 K below those at neighboring coverages. These differences are probably due to the fact that $n = 1.101$ is very close to the boundary between the C and the coexistence region. A recent computer simulation study[26] by Peters and Klein appears to confirm the presence of this coexistence region.

The heat-capacity traces at $n = 1.185$ and 1.190 similarly indicate the presence of a narrow ($\Delta n \sim 0.01$) region of coexistence between the UI and TI phases. The heat-capacity trace at $n = 1.185$ shows considerably more fluctuations near the peak region than other coverages. Upon close examination of this scan (Fig. 1) the peak region at this coverage shows more structure; these minor structures (not the peak) show variation upon temperature cycling. This indicates to us this coverage is close to a phase boundary. The heat-capacity trace at $n = 1.190$ can be interpreted as a sum of broad anomaly at low temperature similar to that observed in the TI phase at $n = 1.200$ and 1.302 and a sharp peak near 29 K similar to the orientational-ordering peak in the UI phase.

In Fig. 6 of Ref. 21, diffraction scans at 11 K of three different coverages ($\rho = 1.29$, 1.33, and 1.39) of the synchrotron study are shown. Despite the weak signal-to-noise ratio, these scans are consistent with the interpretation that $\rho = 1.29$, 1.33, and 1.39 are, respectively, in the C-UI, UI, and UI-TI coexistence regions. (As stated earlier, a coverage scale different from ours is used in the synchrotron study.)

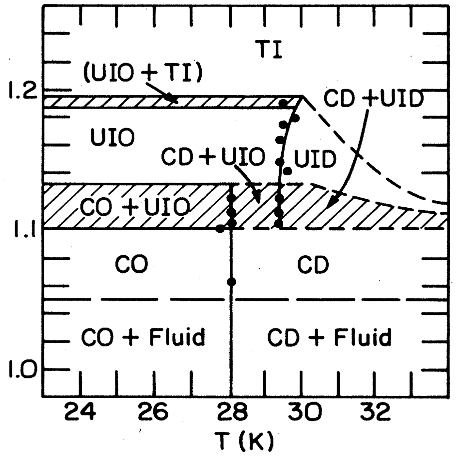

FIG 2. Proposed phase diagram of N_2 on graphite near $n = 1$ near 30 K. See text for definition of $n = 1$. Filled circles represent positions of heat-capacity peaks. The abbreviations are defined in the text, with O and D distinguishing orientationally ordered and disordered phases, respectively. The orientational-ordering transition in both C and UI phases are first order. Hatched regions denote coexistence. The lower boundary of the pure-C phase, the boundaries separating UIO + TI, UID and TI phases, and other dashed lines, are speculative. It is possible that UID is not a distinct phase.

A phase diagram of N_2 on graphite near $n = 1$ and near the orientational-transition region, consistent with the present and other experimental studies,[15–22] is shown in Fig. 2. The phase boundaries above 29.4 K, the UI-phase orientational-ordering transition temperature, are more speculative.

In conclusion, we have found evidence in support of a first-order-like orientational-ordering transition for monolayer N_2 adsorbed on graphite in the C and UI phases. In the TI phase, a broad heat-capacity anomaly is found. This is consistent with the x-ray result of Morishige *et al.*[18] suggesting a gradual loss of orientational order with increasing temperature without going through a distinct phase transition. We also found evidence in support of a first-order C-I transition between the UI-TI and C-UI phases. Whereas a first-order UI-TI transition is consistent with current theoretical models,[1,7,10] our result for the C-UI transition is unexpected from current theoretical models.

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[1] Per Bak, Rep. Prog. Phys. **45**, 587 (1982); J. Villian, in *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, New York, 1980), p. 123.

[2] F. C. Frank and J. H. Van der Merwe, Proc. R. Soc. London, Ser. A **198**, 205 (1949); **198**, 216 (1949).

[3] P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B **19**, 1610 (1979).

[4] M. D. Chinn and S. C. Fain, Jr., Phys. Rev. Lett. **39**, 146 (1977); S. C. Fain, Jr., M. D. Chinn, and R. D. Diehl, Phys. Rev. B **21**, 4170 (1980).

[5] P. W. Stephens, P. Heiney, R. J. Birgeneau, and P. M. Horn, Phys. Rev. Lett. **43**, 47 (1979); P. W. Stephens, P. A. Heiney, R. J. Birgeneau, P. M. Horn, D. E. Moncton, and G. S. Brown, Phys. Rev. B **29**, 3512 (1984); E. D. Specht, M. Sutton, R. J. Birgeneau, D. E. Moncton, and P. M. Horn, *ibid.* **30**, 1589 (1984); K. L. D'Amico, D. E. Moncton, E. D. Specht, R. J. Birgeneau, S. E. Nagler, and P. M. Horn, Phys. Rev. Lett. **53**, 2250 (1984).

[6] M. Nielsen, J. Als-Nielsen, J. Bohr, and J. P. McTague, Phys. Rev. Lett. **47**, 582 (1981).

[7] S. N. Coppersmith, D. S. Fisher, B. I. Halperin, P. A. Lee, and W. F. Brinkman, Phys. Rev. Lett. **46**, 549 (1981); **46**, 869(E) (1981); Phys. Rev. B **25**, 349 (1982); M. Kardar and A. N. Berker, Phys. Rev. Lett. **48**, 1552 (1982).

[8] D. A. Huse and M. E. Fisher, Phys. Rev. Lett. **49**, 793 (1982); Phys. Rev. B **29**, 239 (1984).

[9] V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. **42**, 65 (1979).

[10] P. Bak and T. Bohr, Phys. Rev. B **27**, 591 (1983).

[11] A. R. Kortan, A. Erbil, R. J. Birgeneau, and M. S. Dresselhaus, Phys Rev. Lett. **49**, 1427 (1982).

[12] A. D. Migone, H. K. Kim, M. H. W. Chan, J. Talbot, D. J. Tildesley, and W. A. Steele, Phys. Rev. Lett. **51**, 192 (1983).

[13] M. H. W. Chan, A. D. Migone, K. D. Miner, and Z. R. Li, Phys. Rev. B **30**, 2681 (1984).

[14] The orientational-transition temperature found in the C phase in the present study at 28.1 K is 1 K higher than that reported earlier (Refs. 12,13). The present temperature scale is calibrated against the bulk α-β transition of N_2 [T. A. Scott, Phys. Rep. **27**, 89 (1976)]. In our study, an amount of N_2 equivalent to $n \sim 24$ is plated onto the graphite-foam surface to approximate a bulk system. The transition temperature reported earlier may suffer from an incorrect extrapolation (to lower temperatures) of the thermometer's calibration. In contrast with the heat-capacity traces in the C phase, the traces at higher coverages as shown in Fig. 1 are not consistent with some of the preliminary results presented as the last six entries in Table I of Ref. 13. We do not completely understand the inconsistency; it appears that there is a relative shift in coverage of $\Delta n \sim 0.24$ between the present study and the earlier results. The consistency in the heat-capacity traces of the two separate runs, the consistency in surface area of the substrate as determined in the vapor-pressure isotherm study before and after the heat-capacity measurements, as well as the consistency of the results presented here with the other experiments, ensure our confidence in the present experiment. The present study, however, does not contradict any of the conclusions contained in Refs. 12 and 13, since these earlier studies deal primarily with coverages below commensurate completion. It should be pointed out that the $n = 1.37$ heat-capacity scan in the earlier study [shown in A. D. Migone, Ph.D. thesis, Pennsylvania State University, 1984 (unpublished)] does suggest the existence of two heat-capacity peaks, consistent with the scans between $n = 1.104$ and 1.122 in the present study.

[15] J. Eckert, W. D. Ellenson, J. B. Hastings, and L. Passell, Phys. Rev. Lett. **43**, 1329 (1979).

[16] R. D. Diehl, M. F. Toney, and S. C. Fain, Jr., Phys. Rev. Lett. **48**, 177 (1982).

[17] N. S. Sullivan and M. Vaissiere, Phys. Rev. Lett. **51**, 658 (1983).

[18] K. Morishige, C. Mowforth, and R. K. Thomas, Surf. Sci. **151**, 289 (1985).

[19] R. D. Diehl and S. C. Fain, Jr., Surf. Sci. **125**, 116 (1983); Phys. Rev. B **26**, 4785 (1982).

[20] H. You and S. C. Fain, Jr. (unpublished).

[21] M. Nielsen, K. Kjaer, and J. Bohr, J. Electron Spectrosc. Relat. Phenom. **30**, 111 (1983); and (unpublished).

[22] R. Wang, H. Taub, J. Newton, and H. Shechter (unpublished).

[23] W. A. Steele (private communication); and (unpublished).

[24] S. C. Fain, Jr. (private communication).

[25] J. L. Cardy, M. P. M. den Nijs, and M. Schick, Phys. Rev. B **27**, 4251 (1983).

[26] C. Peters and M. L. Klein (private communication); and (unpublished).