Vapor-pressure-isotherm study of monolayer CO films adsorbed on BN

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We have measured detailed adsorption isotherms for CO films on BN at 18 temperatures between 50 and 75 K, for coverages in the first layer. The isotherms and isothermal compressibilities are very similar to those reported for CO on graphite (the corresponding features, however, appear approximately 20 K lower on BN). We use the similarity between the characteristics of the thermodynamic features of CO on these two substrates to tentatively identify the phases present, and to propose a phase diagram for CO on BN. Our adsorption results are also compared with data reported for Kr and for N_2 films on BN; a possible explanation for why Kr behaves differently from either N_2 or CO on BN is discussed.

A great deal of the attention devoted to the study of physisorbed systems has been concentrated on monolayer films forming commensurate solids on graphite. In particular, films of Kr, N_2, CO, H_2, and ^{4}He on graphite have been extensively investigated.[1,2] H_2 and ^{4}He have phase diagrams that are quite similar to each other.[1,2] Similarly, for Kr, CO, and N_2 on graphite, the shape of the phase diagrams near melting and the sequence of phases present in the melting region are essentially identical to each other and are substantially different from those of other films adsorbed on graphite.[1,2] At low temperatures the phase diagrams of Kr, N_2, and CO differ from each other because of the presence (or absence) of different orientationally ordered solid phases.[3]

Since the results which we will present below for CO on BN will be extensively compared with those for CO on graphite in its melting region, we summarize below the information available for this system. The phases and phase transitions of monolayer films of CO on graphite have been studied with adsorption isotherms,[4,5] low-energy electron diffraction,[3,6] x-ray scattering,[7] and heat capacity;[5,8] end-to-end ordering of CO and CO and N_2 mixture films adsorbed on graphite has been studied with heat capacity.[9] From combining the results of these studies with structural[10,11] and thermodynamic[12] information for Kr on graphite, a phase diagram for CO on graphite has been put forth[5,8] which possesses the following features: There is a wide fluid-commensurate solid coexistence region which extends from low coverages up to the vicinity of $n = 1$.[3,6,7] For coverages below approximately $n = 0.8$, melting occurs from this fluid-commensurate solid coexistence region to a fluid at nearly constant temperature (approximately 49 K).[5] For coverages above $n = 0.8$ the melting temperature increases rapidly with coverage[4,5] while the coexistence region narrows considerably, ending at a tricritical point near a coverage $n = 1.25$ and a temperature of about 95 K.[5] For coverages above the commensurate solid-fluid coexistence region, a single-phase commensurate solid exists. Different identifications have been proposed for the phase(s) present immediately above the single-phase commensurate region: (i) In a phase diagram proposed by Feng and Chan,[5] as the coverage is increased above the

pure commensurate phase, the solid melts to a reentrant fluid phase which extends to below 55 K. This melting transition is first order up to 85 K, where the system exhibits another tricritical point; between 85 and 95 K the melting transition from the commensurate solid to the reentrant fluid is continuous.[5] (ii) In a more recent work by these same authors,[8] the region immediately above the pure commensurate solid is identified as an incommensurate-commensurate coexistence region which extends from 35 to at least 70 K (no upper boundary for this region was shown).[8] In either version of the phase diagram, at sufficiently low temperature the incommensurate solid phase is the densest monolayer phase present.

Below we report the results of adsorption isotherm measurements for CO films on BN performed at 18 different temperatures between 50 and 75 K. The data were taken primarily in the monolayer (and extended monolayer) regime, but for a few temperatures second-layer coverages were also explored.

BN is a nonconducting substrate which has the same structure as graphite, but has an in-plane lattice parameter which is 1.8% larger than that for graphite.[13] The well depths of the adsorption potentials of noble gases and N_2 on BN are smaller than those for the same adsorbates and graphite.[14] Calculations suggest that the values of the corrugation are also smaller than for graphite.[14]

The substrate used in our studies was hexagonal BN (grade HCP manufactured by Union Carbide). The reported specific area of the BN powder used was 5 m^2/g. The apparatus and measurement technique, as well as the cleaning treatment for the BN powder, have been described in some detail elsewhere.[15] The setup is the same one used in a recent study of N_2 films on BN.[16]

Some of our adsorption isotherm results are shown in Figs. 1 and 3. They correspond, respectively, to the higher and lower portions of the temperature range studied. Figures 2 and 4 display isothermal compressibility data obtained from the isotherms. We will present our results in order of decreasing temperature.

For temperatures above 70 K (see the data for the 71-K isotherm shown in Fig. 1), the isotherms do not have any substeps or kinks present in them. The corresponding isothermal compressibilities in this temperature re-

gion (see the data for 71 K shown in Fig. 2) are also featureless. Substeps and kinks in an isotherm, as well as isothermal compressibility peaks, are associated with phase transitions occurring in the film. We conclude, hence, that there is no evidence of any monolayer phase transitions taking place in the CO films on BN at and above 71 K.

For 69 and 70 K the isotherms have a single substep present in them (see Fig. 1). This feature decreases in size and appears at increasingly higher coverages as the temperature increases. An isothermal compressibility peak which corresponds to the isotherm substep is displayed in
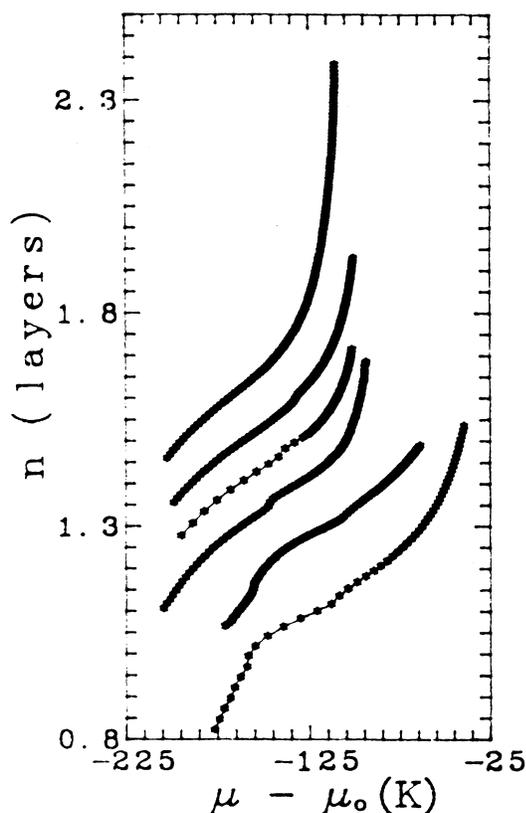
Fig. 2. For the data taken at 70 K the height of this peak is approximately 15 m/N.

The same isotherm substep which is present for the data at 69 and 70 K is also present at all lower temperatures studied. This feature appears in the isothermal compressibility as a sharp peak. Heights for this peak range from 50 to 120 m/N for temperatures below 68 K (see Fig. 2). Between 62 and 68 K an additional feature is present in the isotherms. As can be seen in Fig. 1, for the three lower temperatures shown, at coverages slightly higher than those for the substep, a kink or change in slope in the isotherm is present. This feature can be more easily resolved in the isothermal compressibility data of Fig. 2, where the isotherm kink appears as a markedly asymmetric peak (the low coverage rise toward the peak is much sharper than the decline at coverages above the maximum).

The isotherms in the region between 62 and 68 K are

FIG. 1. Adsorption isotherms corresponding to the upper half of the temperature range studied. The coverages in units of layers (Y axis), are plotted as a function of the difference between the chemical potential of the film and the condensed bulk chemical potential, in units of K (X axis). The definition of coverage $n=1$ is provided in the text. Shown from top to bottom are data measured at 71, 70, 69, 68, 65.5, and 62 K. Except for the lowest temperature shown, all other isotherms have been shifted along the Y axis for compactness in the presentation (the shifts, from top to bottom, are 0.6, 0.5, 0.4, 0.3, and 0.2 layers, respectively). The highest-temperature curve is smooth, indicating no phase transitions present in the monolayer at this temperature. There are clear substeps present in all lower-temperature curves (these substeps correspond to the commensurate solid plus fluid coexistence region). The three lower temperatures have a kink present in addition to the substep; the kink corresponds to the melting from the commensurate solid to a reentrant fluid.
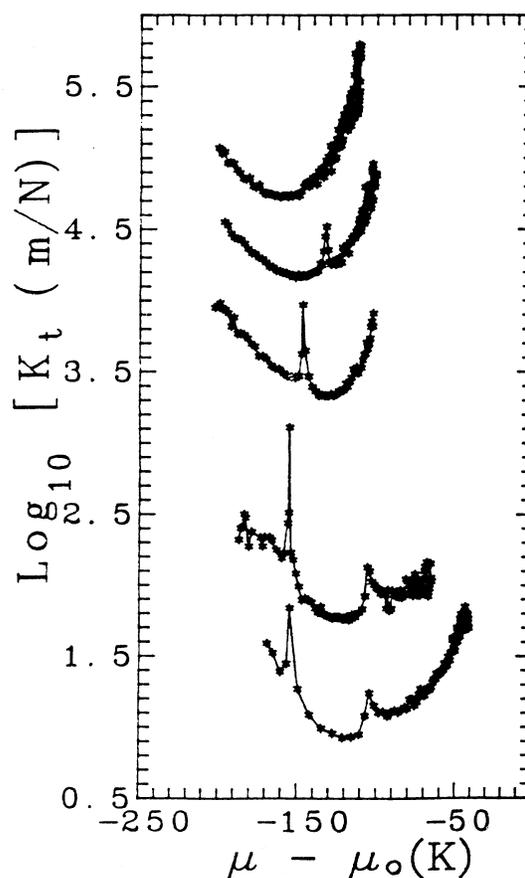

FIG. 2. Logarithm of the isothermal compressibility values (in m/N), plotted as a function of the difference between the chemical potential of the film and the condensed bulk chemical potential, in units of K (X axis). Shown, from top to bottom, are data for 71, 70, 68, 66, and 65 K. Except for the lowest temperature, the compressibility curves have been shifted for the sake of clarity (the logarithms have been shifted, from top to bottom, by 3.5, 3.0, 2.3, and 0.9). The two lowest temperatures shown also have an asymmetric cusp present at higher pressures (this feature corresponds to the kink in Fig. 1).

remarkably similar to those reported in the literature for Kr,[12] N$_2$,[17] and CO (Ref. 5) on graphite [and also quite similar to those recently reported for N$_2$ films on BN (Ref. 16)] in their respective high coverage melting regions. Structural studies for Kr on graphite[10,11] permit the unambiguous identification of the phases associated with the different isotherm and isothermal compressibility features:[5,12] the sharp substep corresponds to the fluid-commensurate solid coexistence region, and the isothermal compressibility cusp corresponds to the melting from the pure commensurate phase to the reentrant fluid as the coverage is increased. The reentrant fluid is a domain-wall fluid;[11] this condensed phase is made up of commensurate patches separated by domain walls (of a different density). These domain walls move about as a fluid. (In the incommensurate solid phase, which is present at lower temperatures and higher coverages, the domain walls are fixed.[11])

The complete lack of structural studies of BN restricts us to identifying the phases present for CO on BN only by comparing the thermodynamic features present for this system to those found for CO, Kr, and N$_2$ on graphite. This identification is aided by the fact that the isotherm and isothermal compressibility features exhibited by N$_2$, CO, and Kr near the fluid-commensurate solid region and the commensurate solid to reentrant fluid melting transition are only exhibited by these three systems on graphite[1,2] [and by N$_2$ on BN (Ref. 16)]. Proceeding in the manner described above, we identify the isotherm substep with the fluid-commensurate solid coexistence region and the kink in the isotherm with the melting from the pure commensurate phase to a reentrant fluid.

The coverage units in Figs. 1 and 3 have been chosen with the above phase identification in mind. Coverage $n=1$ is determined by the amount of CO adsorbed on the BN at the top of the fluid-commensurate solid substep, for isotherms measured below 62 K. This coverage should correspond to one complete commensurate layer at low temperatures.

Our phase identification together with the fact that the substep decreases in size and is no longer present at 71 K further suggests that the tricritical point for the fluid-commensurate solid coexistence region for CO on BN is located between 70 and 71 K. This is approximately 25 K lower than the temperature at which the corresponding feature is present for CO on graphite.[5]

It appears from our data that there is also a change in the nature of the melting transition from the pure commensurate to the reentrant fluid. The isothermal compressibility cusp becomes weaker with increasing temperature, decreasing from a maximum height of about 10 m/N at 65 K (and lower temperatures) to about 3 m/N at 68 K (see the curves for the three lower temperatures in Fig. 2). The cusp can no longer be resolved at and above 69 K, suggesting that this melting transition has become continuous in the vicinity of this temperature. This places the tricritical point for the melting from the pure commensurate phase between 68 and 69 K. This feature is approximately 17 K below that for the corresponding feature for CO on graphite.[5]

An approach identical to the one described above for

phase identification was recently used by our group for N$_2$ films on BN.[16] A sequence of phases similar to that proposed here for CO on BN has been proposed for N$_2$ on BN.[16] The similarity between N$_2$ and CO on BN is reinforced by the fact that we found an agreement to better than 2% in monolayer capacities determined using CO and N$_2$ on the same substrate.

It is interesting to note that while the isotherm characteristics and isothermal compressibility features exhibited by CO on BN are completely analogous to those for CO on graphite, the temperatures at which these features appear are substantially lower on BN than on graphite. This behavior is analogous to that observed for N$_2$ on BN relative to N$_2$ on graphite; in that case the corresponding features appeared approximately 20 K lower.[16] We be-
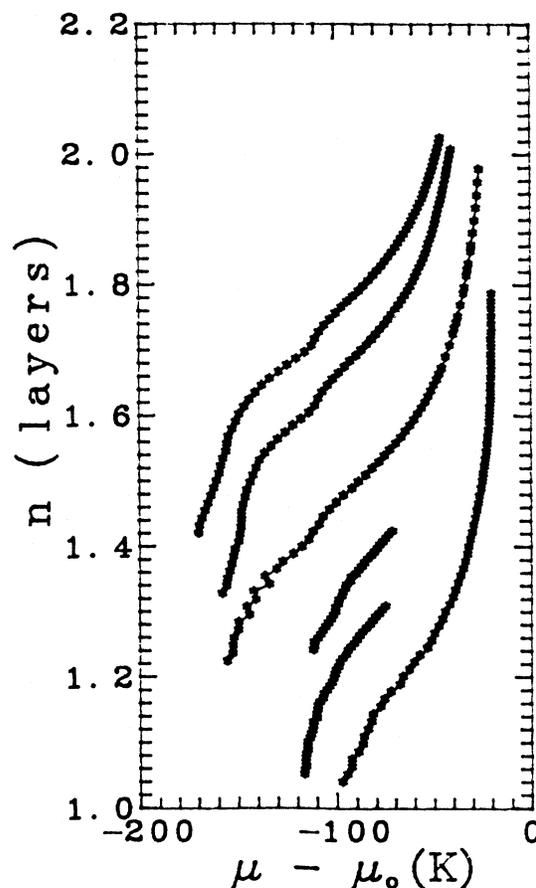

FIG. 3. Adsorption isotherms in the lower half of the temperature region studied. The units are the same as those used in Fig. 1. Presented from top to bottom are data for 59, 58.5, 56, 55, 54, and 50 K. Except for the lowest temperature displayed, all other curves have been shifted (the shifts, from top to bottom, are 0.6, 0.5, 0.3, 0.2, and 0.1 layers). The data for the two highest temperatures shown here start below the commensurate plus fluid coexistence region (substep in Fig. 1); for the four lower temperatures shown the data start above this coexistence region. The isotherm feature present in the four lower temperatures shown corresponds to a commensurate plus incommensurate coexistence region.

lieve that for both systems the explanation of this result is the same: the features appear at lower temperatures on BN because the depth of the adsorption potential and the strength of the substrate corrugation is smaller on BN than on graphite.[14]

Next we consider the region between 57 and 59 K. Three isotherms measured in this region are displayed in Fig. 3, and their corresponding isothermal compressibilities are shown in Fig. 4. There are now three features resolvable in the isothermal compressibility at these temperatures. Note that only the two peaks present at higher coverages are shown in Fig. 4: the cusp, corresponding to the melting from the pure commensurate solid to the reentrant fluid; and, a small, weak peak present at higher coverages (the sharp isothermal compressibility peak, corresponding to the fluid-commensurate solid coexistence region, is not shown). We identify the small, highest coverage peak as corresponding to the solidification from the reentrant fluid to an incommensurate solid phase. The densities for the reentrant fluid and the incommensurate solid are very similar; thus we expect this solidification transition to occur over a rather narrow coverage interval, and to have associated with it a rather small isothermal compressibility peak. Such expectations are in good agreement with our observed result: the coverage interval associated with the entire isothermal compressibility peak region for this transition is smaller than 5% of a monolayer (the actual coverage change associated with this transition is difficult to estimate accurately because this feature occurs at the beginning of the second-layer step, in a region where the coverage increases rapidly with pressure).

In an isotherm study of CO on graphite,[5] a very broad isothermal compressibility feature, with a coverage width of about one layer, was identified as corresponding to the reentrant fluid to incommensurate solid transition. However, it has recently been argued [in a study of N_2 films on BN (Ref. 16)] that the broad isothermal compressibility feature observed in the study of CO on graphite had probably been misidentified. It was suggested that the broad compressibility peak was more likely due to a second layer in an isotherm measured well above the second-layer critical temperature for CO on graphite.[16] This reinterpretation of the broad isothermal compressibility feature is strengthened here by our finding of an additional small isothermal compressibility peak, which has been tentatively identified as the solidification of the reentrant fluid to an incommensurate solid. We note that the study of CO on graphite had coverage spacings between data points on the order of 5% of a layer in the region corresponding to the one in which we found this peak;[5] thus this transition, which itself is of the order of 5% of a layer, would have gone unnoticed. Our data for the small isothermal compressibility peak seen between 56 and 59 K above the compressibility cusp displayed in Fig. 4 constitutes, to our knowledge, the first time that the solidification transition of the reentrant fluid has been observed in an adsorption isotherm experiment.

The solidification isothermal compressibility peak moves very rapidly to higher coverages as the temperature is increased. A steep boundary between the incom-

mensurate solid and the reentrant fluid is in good agreement with the steep phase boundary observed for this same region in x-ray studies on Kr on graphite.[10,11]

The isotherms measured below 56 K are shown in Fig. 3, starting at coverages above those corresponding to the fluid-commensurate solid substep. There are important changes observed in the isothermal compressibility cusp relative to the behavior found at higher temperatures: (i) For all temperatures above 56 K the isothermal compressibility cusp is markedly asymmetric, while starting at 56 K the cusp becomes symmetric (compare the data for the cusp at 56 and 54 K in Fig. 4 to those for the cusp at higher temperatures shown in Figs. 2 and 4). (ii) The isotherm feature corresponding to the isothermal compressibilty cusp grows in width as the temperature is reduced
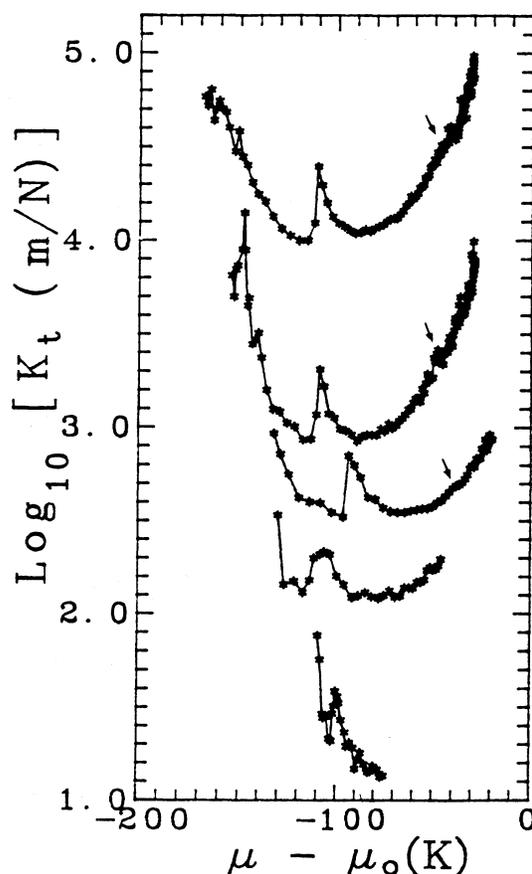

FIG. 4. Logarithm of the isothermal compressibility for data taken in the lower half of the temperature range studied. The units are the same as those for Fig. 2. The temperatures for the curves, from top to bottom, are 59, 58.5, 58, 56, and 54 K. The data displayed for all curves starts above the commensurate plus fluid coexistence region. The three highest-temperature curves shown have an asymmetric cusp and a weaker, broader peak at higher pressures; this latter feature is marked by the arrows. As before, except for the lowest-temperature curve, all others have been shifted (the shifts in the logarithms, from top to bottom, are 3.0, 1.9, 1.5, and 1.0). Note that the cusp is asymmetric for the higher temperatures shown (see also Fig. 2), while it is more symmetric for the lower two temperatures.

below 56 K, becoming a substep at these temperatures. In addition, there is also a dramatic change at 56 K in the slope of the chemical potential (measured relative to the equilibrium bulk phase) vs temperature curve corresponding to the cusp. This change in slope can be seen in Fig. 5, where the phase diagram for this system is displayed in the chemical potential (relative to bulk) vs temperature plane.

The most natural interpretation for the observed changes is that the higher coverage compressibility feature below 56 K corresponds to a different transition than above this temperature. We tentatively identify the isothermal compressibility cusp below 56 K as corresponding to a commensurate-incommensurate coexistence region, analogous to that proposed for CO on graphite.[7] Our data, hence, clearly suggest that the termination of the reentrant fluid region occurs slightly above 56 K (see Fig. 6). We believe this is the first time that changes in the thermodynamic behavior of a system associated with the end of the reentrant fluid region have been reported; other studies have covered regions above or below the end of the reentrant fluid.

It is of interest to contrast the behavior observed here for CO on BN with that of N_2 and Kr on BN. The most detailed study of Kr on BN was performed by Dupont-Pavlovsky, Bockel, and Thomy.[18] Quite unexpectedly, no features of any kind were observed in adsorption isotherms measured between 100 and 77.3 K; this indicates that there are no phase transitions taking place in the monolayer film in this temperature range.[18] Other stud-

FIG. 6. CO on BN phase diagram in the coverage vs T plane; the letters denote the same phases as in Fig. 5. Dashed lines correspond to expected phase boundaries not found in the data, while the solid lines correspond to isotherm and compressibility features.
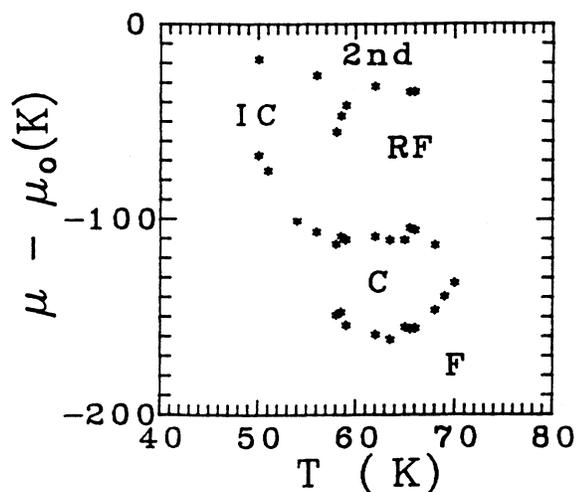

FIG. 5. CO on BN phase diagram in the chemical potential vs temperature plane. The chemical potentials are measured relative to the bulk chemical potential. F, fluid; C, commensurate solid; IC, incommensurate solid; RF, reentrant fluid; and 2nd, second layer. The C-F curve corresponds to the commensurate solid plus fluid coexistence region; it ends at a tricritical point near 71 K. The RF-C curve corresponds to the isotherm kink; there is an expected tricritical point at approximately 68 K for this curve. The IC-C curve corresponds to the commensurate-incommensurate coexistence region. The IC-RF curve corresponds to the solidification curve of the reentrant fluid.
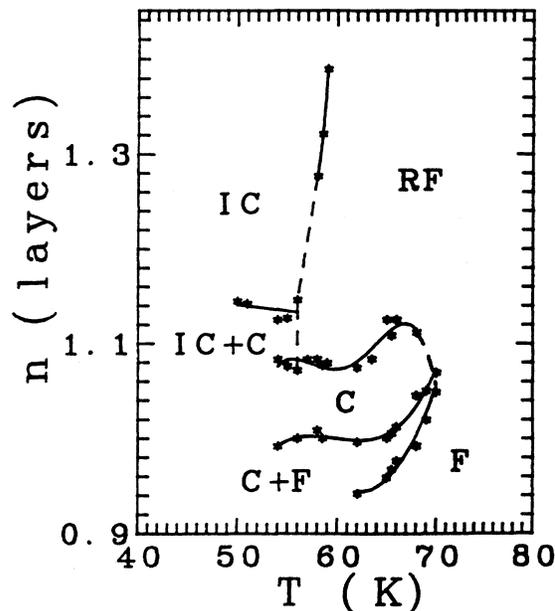
ies of this system have also found the same lack of features[19] (there is one exception, however, which will be discussed in more detail below). This result is surprising for at least two reasons: (i) First, the tricritical temperature for the fluid-commensurate solid coexistence region for Kr on graphite is somewhere between 120 and 129 K, between 40 and 50 K higher than the lower bound of the region studied on BN. (ii) Second, if the data for Ar (Ref. 14) or Xe (Refs. 18 and 19) on BN were to be scaled to Kr in a usual fashion (such as by dividing the temperature scale by the respective bulk triple or critical point temperatures), we would fully expect to find some coexistence region present in the Kr on BN films. We recall that in Ar isotherms measured at 77.3 K there is a substep in the isotherm.[14]

N_2 on BN,[16] as mentioned above, has a behavior entirely analogous to that of N_2 on graphite, except for having the corresponding features of the phase diagram shifted to lower temperatures by approximately 20 K. So, on BN, CO and N_2 exhibit closely similar behaviors, and are quite different from that of Kr on BN. It is possible that the similarity between CO and N_2 on BN and its difference from Kr on BN be related to electrostatic effects. We note that BN is an insulator, that N_2 has a quadrupole moment, and that CO has both a small dipole as well as a quadrupole moment (which is larger than that of N_2), while Kr has neither a dipole nor a quadrupole moment. Reports of studies of N_2 and CO on a more polar substrate than BN [specifically, MgO (Ref. 20)] have found that there are measurable differences between these two adsorbates and the noble gases due to electrostatic effects. These differences have been

confirmed by theoretical calculations as well.[21]

Interestingly, the only experimental report of a substep in adsorption isotherm data for Kr on BN came from a study in which adsorption isotherms were measured simultaneously with dielectric constant measurements.[22] The isotherms were measured while the electric field between the plates of the capacitor used to determine the dielectric constant was nonzero. It is possible that the presence or absence of an external electrical field may be related to the presence or absence of substeps for Kr on BN. However, the presence of impurities (especially soluble borates) in the BN substrates used in the Kr experiments cannot be ruled out as the explanation for the observed differences.[15] The question of why, in zero external electrical field, there is a complete lack of features in Kr isotherms down to 77.3 K (while some transition is to be expected for this region from the scaled data of Ar and Xe on BN) remains intriguing and unexplained.

Our results for CO on BN are summarized in Figs. 5 and 6, which present phase diagrams for this system in the chemical potential vs temperature and the coverage vs temperature planes, respectively. By comparing the observed thermodynamic features in the data for CO on BN to the rather unique features observed for CO, N_2, and Kr on graphite, we are able to propose a tentative identification of the phases present in the former system. A fluid-commensurate coexistence region which terminates at a tricritical point near 71 K has been identified. A purely commensurate solid region which ends at a melting transition to a reentrant fluid as the coverage is increased has been proposed between 56 and 70 K. Between 56 and 59 K we have identified a compressibility peak as corresponding to the transition from the reentrant fluid to an incommensurate solid as the coverage is increased. The reentrant fluid region has as its lower-temperature boundary 56 K; for temperatures at and below this the pure commensurate solid goes to a commensurate-incommensurate coexistence region as the coverage is increased. It would be very desirable to have structural information about CO on BN, because while the identification of the phases given here is highly plausible, structural studies would be able to establish on a much firmer footing which solid phases are present in the monolayer phase diagram of CO on BN.

[1]A review of experimental results for many adsorbed films is found in M. H. W. Chan, in *Phase Transitions in Surface Films 2*, Vol. 267 of *NATO Advanced Study Institute, Series B: Physics*, edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum, New York, 1991), p. 1.

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