PHYSICAL REVIEW B VOLUME 60, NUMBER 23 15 DECEMBER 1999-I

Multilayer Kr films adsorbed on BN

A. Diama and A. D. Migone
Department of Physics, Southern Illinois University, Carbondale, Illinois 62901

(Received 30 April 1999; revised manuscript received 2 July 1999)

We report on the results of an adsorption isotherm study of multilayer Kr films adsorbed on BN. Measurements were conducted on a computer-controlled adsorption apparatus at 22 temperatures in the vicinity of the bulk-triple point of Kr. The data are compared with those available for Kr on graphite. The phase diagrams for both systems are topologically identical in the region between two and five layers. The layer critical temperatures for the second and third layers are essentially identical for Kr on both substrates; the high-temperature solidification transition of the second layer, on the other hand, is shifted on BN relative to where it occurs on graphite. The implications of our results for the current understanding of re-entrant layering are discussed. [S0163-1829(99)01747-6]

I. INTRODUCTION

The growth of multilayer wetting films on homogeneous substrates, at low temperatures, occurs in layer-by-layer fashion.[1–3] In an adsorption isotherm the formation of a layer is marked by a sharp step (i.e., by a coverage increase occurring at nearly constant pressure).[4,5] The commonly held view was that a sharp step would persist as the temperature increased until the critical temperature for the layer was reached. At the layer critical temperature the step would cease being vertical, and beyond this point it would become increasingly rounded. The behavior was expected to be analogous to that for bulk isotherms near the liquid-vapor critical point.

Hess and coworkers, in an ellipsometric isotherm study of Ar on graphite,[6] showed that this picture was not correct. They discovered that there was a re-sharpening in some of the isotherm steps (4th, 5th, and 6th) at temperatures above the layer critical point.[6,7] This step resharpening has no analog in the bulk; Hess called this ''re-entrant layering.''[6] He and others[6–12] found that resharpened steps occur at lower values of the relative chemical potential, and, at lower values of the coverage than those corresponding to the low-temperature sharp steps. In addition, at the initial temperature at which they appear, the resharpened steps are smaller than their low-temperature counterparts. Step resharpening is not a universal phenomenon: some systems exhibit it (Ar,[6–9] Kr,[7,10] and Xe (Refs. 7, and 11) on graphite and Ar (Ref. 12) on BN), while others do not (CH_4 (Refs. 11, and 13) on graphite, and, N_2 (Ref. 14) on BN, and, on graphite[7]).

Arriving at a theoretical explanation for step-resharpening has been the source of some controversy.[8,15–17] After Hess' report,[6] den Nijs suggested that the resharpening could be a film manifestation of a preroughening transition.[18] Preroughening is a surface phase transition which den Nijs had found in studies of restricted solid-on-solid models.[18,19] This approach was elaborated upon by Weichmann and Goodstein,[15,17] Weichmann and Prasad,[20] and Pristipino and Tossati.[21] In this view, step resharpening is associated with the appearance in the film of a disordered-flat-phase. Step resharpening is a transition taking place in the topmost layer of the film, at the solid-vapor interface. The re-sharpening is a film version of a bulk-surface phase transition. The substrate does not play a very important role in this explanation.[18]

A competing explanation was put forward by Phillips and Larese.[8,11,16] Combining Monte Carlo simulations, adsorption isotherms, and, neutron scattering results for multilayer films, they constructed a picture in which the resharpened steps in the isotherm are the result of a solidification transition taking place in an underlying layer of the film, not in the topmost layer. A resharpened *fourth step* corresponds to a transition taking place in the *third layer* of the film.[8,11] (Note that this difference in interpretation leads to a different identification between layers in a film and steps in an isotherm). Because the re-solidification of an underlying layer is dictated by the subtle balance between substrate attraction, adsorbate forces, pressure exerted by the liquid overlayer, and entropy in the layer undergoing the transition, the substrate plays more of a central role in the Phillips-Larese explanation.

We have conducted an adsorption study of multilayer Kr films on BN. Kr exhibits ''re-entrant layering'' on graphite.[7,10] Our motivation in investigating Kr on BN was the hope that by studying this very well characterized adsorbate on a weaker substrate than graphite,[22] we would be in a position to shed some light on the relative explanatory powers of the two different proposals which have been put forth to understand this phenomenon.

II. EXPERIMENT

We measured isotherms at 22 temperatures between 90.65 and 109.13 K (from 0.77 to 0.95 of the bulk triple temperature). The measurements were performed in a computer-controlled adsorption setup. Details on the apparatus have been provided elsewhere.[23]

The BN used was purchased from Johnson Matthey. Prior to its utilization, the BN was subjected to a vigorous cleaning process consisting of heating it to 1700 °C for three hours in a nitrogen-saturated atmosphere. Measurements conducted in our laboratory show that this process yields BN substrates suitable for use in adsorption. Routinely up to six steps can

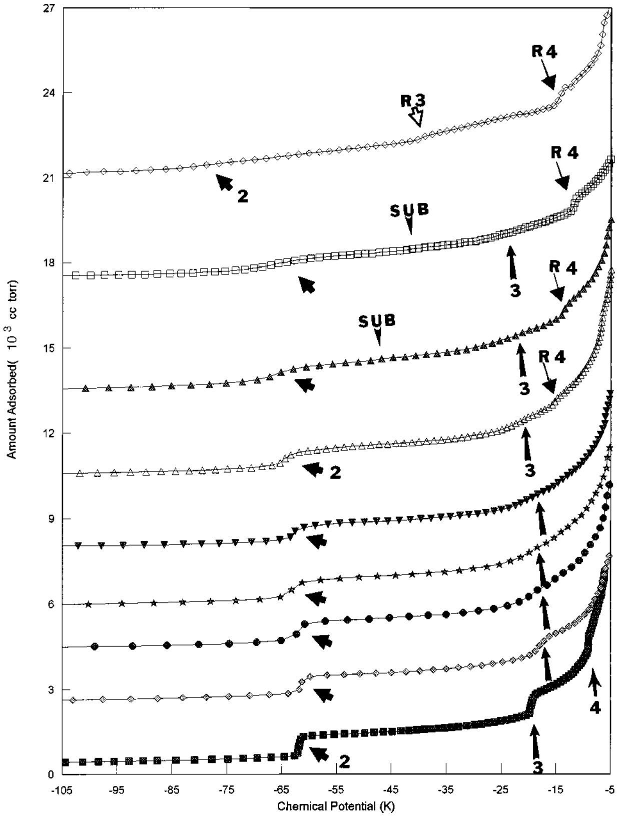

FIG. 1. Adsorption isotherms for a variety of the temperatures studied. The amount adsorbed (Y axis) is plotted as a function of the chemical potential relative to the bulk solid vapor chemical potential for the corresponding temperature. All data have been displaced vertically. Shown from top to bottom are isotherms at: 109.13, 104.07, 102.11, 100.13, 99.22, 99.04, 98.05, 97.17, and 93.24 K. Features marked by a thick arrow and labeled 2 (roughly between −60 and −80 in relative chemical potential) correspond to the second layer. The featured denoted by the arrowhead labeled ''SUB'' in the 104.07 and 102.11 isotherms corresponds to the substep present between the second and third layers at high temperatures. The hollow thick arrow labeled ''*R*3'' for the highest temperature shown corresponds to the ''re-entrant'' third step. The small arrow labeled ''3'' denotes the third layer. The italic arrow on the lowest temperature isotherm labeled ''4'' corresponds to the low temperature sharp fourth layer. The big arrowhead with a thin body labeled ''*R*4'' corresponds to the ''re-entrant'' fourth step.

be resolved in the adsorption data, indicating that the BN used is a high quality substrate.

III. RESULTS

A. Second step

The second steps in the isotherms do not exhibit resharpening in the range of temperatures studied here. Their behavior is the classical one: the steps are sharp until the layer critical temperature is reached; beyond this point the steps become increasingly broader. Such behavior can be seen in Fig. 1, for relative chemical potential values between −60 and −80 K. The second step is denoted by the arrow labeled ''2'' in this figure. For the lowest two temperatures shown (93.24 and 97.17 K) the second step is quasivertical, for all the other temperatures shown the second step is rounded and becomes increasingly more rounded as the temperature increases.

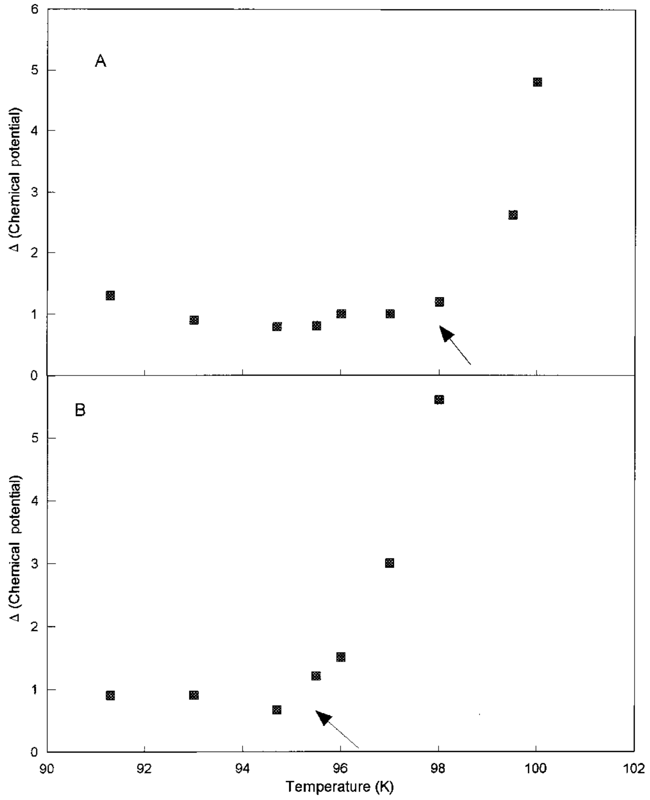

FIG. 2. (a) Horizontal width of the second-layer steps (i.e., range of chemical potential corresponding to the second layer) plotted as a function of temperature. The increase in step width marks the location of the critical temperature for this layer (denoted by the arrow). (b) Same plot as in (a) but for the third layer.

We obtain an estimate for the layering critical temperature for the second layer by plotting the horizontal width of the step (i.e., the range of chemical potential values corresponding to the quasivertical portion of the step) as a function of temperature, see Fig. 2(a). The temperature where the step widths start increasing determines the second layer critical temperature for Kr on BN; it is between 97.5 and 98.5 K. We do not have a sufficiently fine grid of temperatures to justify a more sophisticated analysis, however, our estimate should be valid to within one degree Kelvin or better.

The behavior of the isotherms for the second layer of Kr on BN is qualitatively identical to that of Kr on graphite:[7] for Kr on graphite there is no re-sharpening of the second step over the of range of temperatures studied here. Additionally, the second layer critical temperature for Kr on graphite is 97.4 K,[7] essentially the same value that we have determined on BN. The only difference between data measured on these two substrates is that the relative chemical potential at which the second layer appears is near −60 K on BN, while it is near −80 K on graphite.[7] This difference directly reflects the fact that BN is a weaker substrate than graphite[22] (higher layers also appear at lower relative chemical potential on BN than on graphite).

B. Region between the second and third steps

The region between the second and third steps has been carefully investigated for Kr on graphite, with thermody-

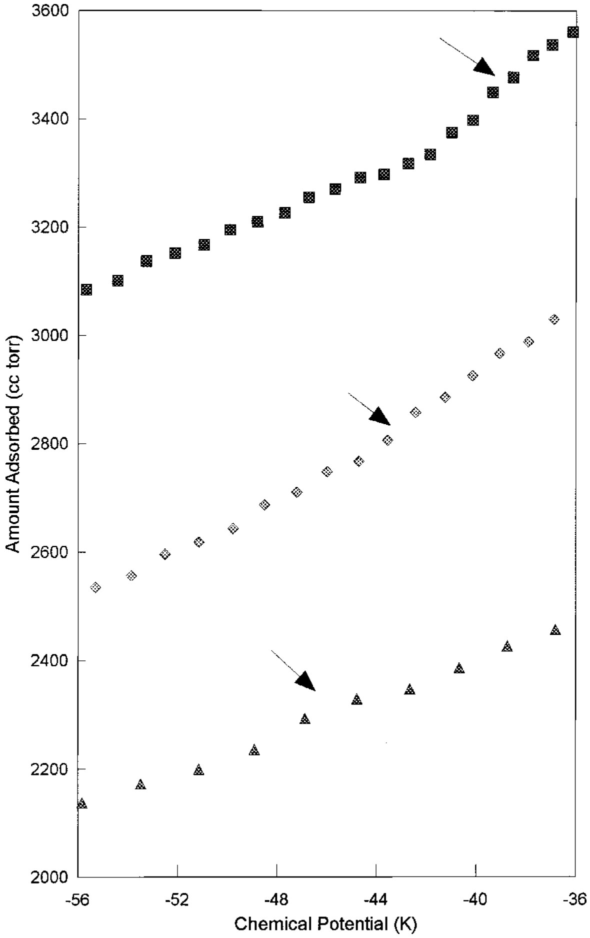

FIG. 3. Substep marking a solidification transition, between the second and third layers. The data has been displaced vertically for the sake of clarity. Shown from top to bottom are the substeps at 106.14, 104.07, and 102.11 K, respectively.

namic and structural probes, by Suter and coworkers.[24,25] A small isothermal compressibility peak was found between the second and third steps for temperatures between 96 and 103 K (the highest temperature reported).[24] This feature was found to move steadily to higher values in relative chemical potential as the temperature increased. The x-ray study determined that this small compressibility peak corresponded to a bilayer solidification transition, which occurs as the chemical potential (or pressure) is increased.[25]

We conducted a rather careful search for the small isothermal compressibility peak for Kr on BN between 93 and 100 K for coverages between the second and third steps; we found no corresponding feature for Kr on BN in this range. However, we found a feature between the second and third layers which appears first as a small sub-step in the isotherm at 102.11 K, and which becomes increasingly sharper for the 104.07, 106.14 K, and 107.07 isotherms. Data displaying this feature are labeled ''SUB'' in Fig. 1 and are shown in greater detail in Fig. 3.

Figure 4 displays a partial phase diagram for Kr on BN, between the second and third layers and temperatures between 90 and 109 K. This figure also reproduces the phase boundaries reported for Kr on graphite. (We performed a least squares fit to the Kr/graphite data to extend it beyond 100 K, since it do not overlap the temperature range over which we found the substep on BN.)

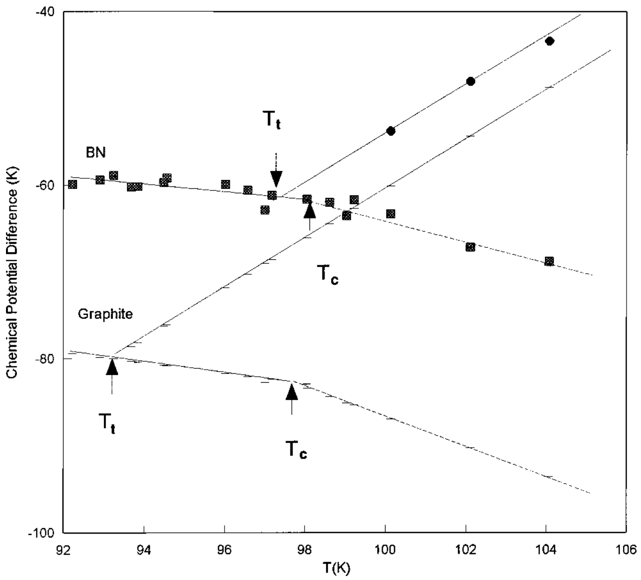

FIG. 4. Partial phase diagram for Kr on BN in the region between the second and third layer. Filled symbols correspond to our data. The positive-slope line starting at 97 K is the solidification transition which was presented in Fig. 3. Dashed lines correspond not to a true phase boundary, but mark the location of broad isotherm steps beyond the second-layer critical point. This figure also reproduces the bilayer solidification phase boundary for Kr on graphite (from Refs. 24 and 25). For temperatures above 100 K the Kr on graphite data was extended using a least squares fit to the low-temperature data. The temperature difference between the solidification lines on the two substrates is about 2.5 K (the two solidification lines are essentially parallel). The location of the critical and triple points on BN and on graphite for the second layer are marked by arrows.

To identify the nature of the phase transition corresponding to the small isotherm substep we note two characteristics: (i) The substep is located between the second and third steps in the adsorption data, i.e., the same coverages as for the feature present for Kr on graphite.[24,25] (ii) The slope of the chemical potential vs temperature plot is substantially similar in value, and of the same sign, for Kr on BN as it is for Kr on graphite[24,25] (this slope is proportional to the entropy difference between the phases undergoing the transition, as dictated by Maxwell's relations). We identify the small isotherm sub-step between the second and third steps for Kr on BN as corresponding to a solidification transition, just as for Kr on graphite.

We find that, for a given value of the relative chemical potential difference with the bulk, the resolidification step appears at a higher temperature on graphite than it does on BN. The difference for each relative chemical potential value is about 2.5 K. Thus, there is a measurable reduction in the temperature for the second layer solidification transition of Kr on BN.

For Kr on BN the line corresponding to solidification intersects the second-layer chemical potential (which, in fact is a second layer solid second-layer vapor coexistence region) very close to the second-layer critical temperature (see Fig. 4). This intersection determines the triple point for the second layer. The separation between critical and triple temperatures in adsorbed films becomes increasingly smaller as distance to the substrate (i.e. layer number) increases.[8,11,16] This is also observed on graphite;[8,9,10,11,16] however, owing to the higher strength of that substrate, the two temperatures remain distinguishable until higher layers.

C. Third step and higher coverages

The data corresponding to the third and fourth steps of the Kr films on BN exhibit a behavior, which in other systems has been identified as ''re-entrant layering.''[6,7,9,10,15] This behavior can be seen in Fig. 1, where we present data for nine temperatures between 93.24 and 109.13 K and coverages from just below two layers up to coverages above four layers.

The third layer at low temperatures occurs at a relative chemical potential of about -20 (see arrow denoted by ''3'' in the lowest curve in Fig. 1, for $T=93.24$ K). As the temperature is increased, this step becomes rounded. Rounding is already visible in the second to last curve, for 97.17 K, and becomes increasingly more marked as the temperature increases. Together with the rounding, the step gradually moves towards lower values of the relative chemical potential. At the highest temperature shown (109.13 K), however, there is a clear re-sharpening in the third step, this is the ''re-entrant'' behavior (feature denoted by ''$R3$'' in the Fig. 1, which appears at a relative chemical potential of approximately -42). The ''re-entrant'' step is clearly sharper than the third step at intermediate temperatures, and it involves a smaller coverage interval than the low-temperature sharp step.

The solidification substep between the second and third layers which was discussed in detail in the previous subsection, is denoted by the arrow labeled ''SUB'' in Fig. 1. This feature is shown 102.11 and 104.07 K in Fig. 1. We note that the ''re-entrant'' third step ($R3$) appears at a value of the relative chemical potential, which is at the upper end of the solidification substep region.

If we were to follow Hess' labeling[6,7] we would call the resharpened step at 109.13 K ($R3$) the ''re-entrant third layer,'' because it is a sharp, half-layer-like step, in the isotherm which occurs above the broad second step, at a temperature above the third-layer critical point. According to the Phillips-Larese picture,[8,11] the sharp step $R3$ corresponds to the formation of a solid second layer underneath more than one layer of fluid.

We can identify the critical temperature for the third layer by plotting the third step chemical potential width as a function of temperature, just as for the second layer. Such graph is presented in Fig. 2(b). We determine the third-layer critical temperature to be 95 K. Our value is in excellent agreement with the 94.9 K third layer critical temperature reported for Kr on graphite.[7]

The fourth step also displays a behavior which can also be identified with ''re-entrant layering.'' There is a sharp fourth step at 93.24 K (denoted by ''4'' in Fig. 1). The fourth step becomes so rounded that, on the scale of Fig. 1, it defies distinguishability for intermediate temperatures (between 97.17 and 100 K); finally at 100.13 K and above there is a re-sharpened fourth step present (which is labeled ''$R4$'' in Fig. 1). Note that the $R4$ step at 100.13 K is at a lower value of the chemical potential and involves a smaller interval of coverages than that for the 93.17 K, low-temperature sharp step (4).

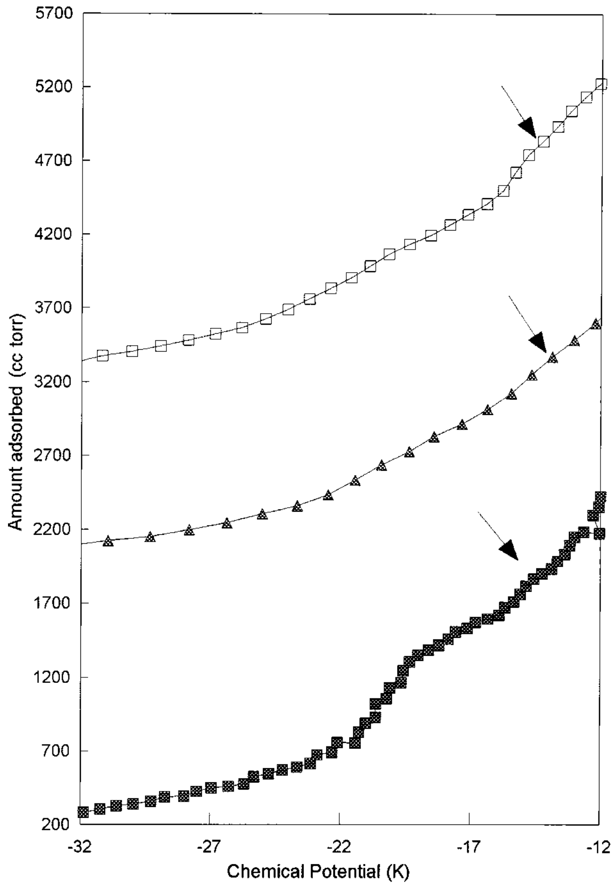

FIG. 5. Small substep present between the third and fourth steps. The temperature interval over which this feature is present is narrower than that at which the corresponding feature is found in Kr on graphite. The substep corresponds to a solidification transition of the underlying trilayer. The data shown, from top to bottom, correspond to 100.13, 99.22 and 97.17 K.

Interestingly, we note that also in this case, there is a small substep present just above the broad third step (look, in particular, at the isotherms at 99.04, 99.22 Fig. 1; this feature is not marked by any symbol in Fig. 1). This substep is displayed for three temperatures in Fig. 5. This feature is analogous to that present between the second and third steps. The temperature interval over which this small feature is present is, however, much narrower than that for the feature between the second and third steps: it occurs only between 97.71 and 100.13 K. Though we do not have the corresponding structural data, it is reasonable to argue on thermodynamic grounds that this feature also corresponds to a solidification (in this case, of the underlying trilayer).

IV. DISCUSSION

A concise summary of our results is presented in the chemical potential vs. temperature phase diagram given in Fig. 6. The values of the chemical potential (relative to the bulk) correspond to the sharpest point in the isotherm step. Following all the recent literature on this subject, we have plotted data points for the second, third, and fourth layers beyond their respective critical points, that is, in a region where these data points signify the presence of just a broad isotherm step (for example, the step labeled 2 in Fig. 1 for

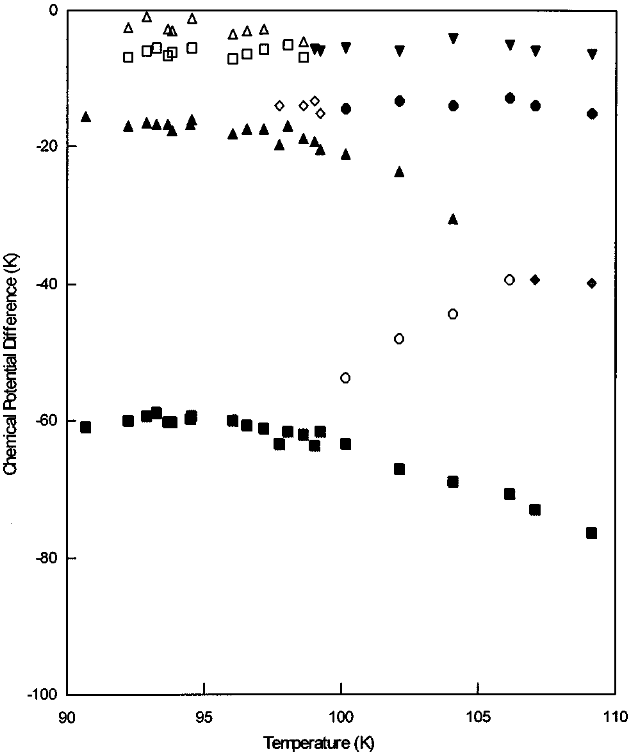

FIG. 6. Phase diagram for Kr on BN in the region between the second and sixth steps in the isotherm. Filled squares correspond to the second layer; for temperatures above 98 K the second-layer steps are very broad, and this feature no longer corresponds to a true phase boundary (these points have negative slope in the phase diagram). The open circles correspond to the solidification feature between the second and third layers. The filled diamonds (at about -40 and for temperature above 106 K) correspond to the ''re-entrant'' third step. Closed triangles denote the third layer; again in the region where these points have negative slope in the graph they correspond to the third layer above its critical temperature, and hence, they no longer mark a phase boundary. The filled circles correspond to the ''re-entrant'' fourth step. Open squares are for the fourth layer, open triangles are for the fifth layer, and inverted filled triangle are for the ''re-entrant'' fifth step.

temperatures above 97.5 K). Points corresponding to these broad features do not represent true phase boundaries.

Consider the region involving the second layer in Fig. 6: i.e., the two horizontal lines (at -60 and -40, respectively, in relative chemical potential) which are connected by the solidification line (positive slope line between 97 and 106.14 K). The horizontal line below 97 K corresponds to a region of coexistence between a solid second layer and a second layer vapor. At chemical potentials just above this coexistence line, there is a full solid bilayer and vapor grows above it in the third layer. Between 97 and 106.14 K, the positive-slope line corresponds to a solidification transition: a second layer solid in coexistence with a second-layer liquid. For chemical potentials slightly above this positive slope coexistence line there is a full solid bilayer and fluid grows in the third layer. In the horizontal portion that follows at higher temperatures, above 106.14 K, there is no further increase in chemical potential, so the number of solid layers in this region is the same as for 106.14 K (namely, two). The high-temperature horizontal line in the phase diagram is parallel to that of the bulk solid-vapor coexistence, indicating that the coexistence region in the film corresponds to the same entropy change as for the bulk. The changes in slope in the phase diagram of Fig. 6 between the regions of: low temperature to 97, 97 to 106 K, and, 106 to 109 K are due to the fact that up to 97 K there is a solid-vapor coexistence in the second layer, between 97 and 106 K the second layer of solid is in coexistence with a liquid in the second layer, while above 106 the second layer of solid is in coexistence with a third layer fluid. In interpreting the isotherm data, it is important to remember that the isotherm reflects changes in the compressibility of the system, whether those changes are happening principally in the topmost layer of the film (the situation at low temperatures) or in an underlying layer (the situation above 106 K).

The portions of the phase diagram for Kr on BN in the second and the third layer regions are topologically identical with the corresponding boundaries determined by Suter for Kr on graphite.[24,25] The most significant difference between the data for Kr on these two substrates is in the location of the solidification features. At the same value of the relative chemical potential, melting takes place at a lower temperature on BN, by about 2.5 K, than it does on graphite. This temperature decrease is due to the difference in substrate potentials.

It is interesting to contrast the temperature decrease for the second-layer solidification feature on BN relative to graphite (Fig. 4), with the values found on these two substrates for the layer critical points for the second and third layers. For Kr on BN the layering critical temperature of the second layer is 98 K and that for the third layer is 95.0 K; the values determined by Hess[7] for the second-and third-layer critical points for Kr on graphite were 97.4 and 94.9 K. That is, the critical temperatures are nearly identical.

As noted above, the ''re-entrant'' third step ($R3$ in Fig. 1) begins at the end of the region where the solidification substep between the second-and third-layer ends. Thus, a shift in the solidification temperature results in a shift in the temperature at which the ''re-entrant'' feature appears. Noting that the competition between adsorbate-adsorbate and adsorbate substrate forces lies at the core of the resolidification explanation of step-re-sharpening, we conclude that it is easier to account for shifts in the temperature at which the ''re-entrant'' feature appears on different substrates within the context of the Phillips-Larese explanation. On the other hand, the layering critical points are connected to the roughening transition: the roughening temperature is the thick-film limit of the layering critical temperatures. The almost identical values which we have found for the layering critical temperatures on the two substrates tend to complicate the preroughening explanation of Goodstein and Weichmann[15] for step resharpening. The critical temperature values for the second and third layers indicate that intrinsic adsorbate behavior associated with the critical point is not affected by the difference in substrate strength between BN and graphite. It is difficult to compatibilize substrate-independent layering critical temperatures with a substrate-dependent shift in the resharpening substeps temperature within the context of the Weichmann-Goodstein explanation.

The region between the second and third layer is completely analogous to the region between the third and fourth layers. This observation, is in agreement with the data of

Hess on Ar, Kr, and Xe, and that of Larese and Phillips on Ar and Xe. It differs, however, from what has been reported by Day *et al.* for Kr on graphite.[10] We note that the report by Day *et al.* does not include all the boundaries determined by Suter[24,25] for Kr on graphite.

Unlike what happens in the first four or five layers, with increasing film thicknesses the differences between films of the same adsorbate on different substrates will tend to disappear (because of the inverse cube nature of the effect of the substrate potential). Thus, for sufficiently thick films the preroughening scenario of den Nijs will be fully applicable. These thicker films will be indistinguishable from the surface of the bulk adsorbate.

V. CONCLUSIONS

We have determined that the phase diagram of Kr on BN is topologically identical to that of Kr on graphite. We have found that there are some important differences in the values of the temperatures and chemical potential differences at which the corresponding features appear on the two substrates. The measured shifts in the temperatures which we have determined (relative to their values on graphite) are more easily understood in terms of the Larese-Phillips explanation of re-entrant layering, i.e., in terms of a resolidification of an underlying layer.

ACKNOWLEDGMENTS

Acknowledgment is made to the Petroleum Research Fund, administered by the ACS for support of this research. Both of us are grateful to Professor J. M. Phillips for helpful and insightful comments on our results and their interpretation.

---

[1] See, for example, the articles by G. B. Hess and M. H. W. Chan, in *Phase Transitions in Surface Films 2*, edited by H. Taub *et al.* (Plenum, New York, 1991).

[2] A. Thomy and X. Duval, J. Chim. Phys. (Paris) **67**, 1101 (1970).

[3] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 7534 (1982).

[4] W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974).

[5] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[6] H. S. Youn and G. B. Hess, Phys. Rev. Lett. **67**, 918 (1990).

[7] H. S. Youn, X. F. Meng, and G. B. Hess, Phys. Rev. B **48**, 14 556 (1993).

[8] J. M. Phillips, Q. M. Zhang, and J. Z. Larese, Phys. Rev. Lett. **71**, 2971 (1993).

[9] P. Day, M. Lysek, M. LaMadrid, and D. Goodstein, Phys. Rev. B **47**, 10 716 (1993).

[10] P. Day, M. LaMadrid, M. Lysek, and D. Goodstein, Phys. Rev. B **47**, 7501 (1993).

[11] J. M. Phillips and J. Z. Larese, Phys. Rev. B **56**, 15 938 (1997).

[12] M. T. Alkhafaji and A. D. Migone, Phys. Rev. B **45**, 8767 (1992).

[13] M. J. Lysek, M. A. LaMadrid, P. K. Day, and D. Goodstein, Phys. Rev. B **47**, 7389 (1993).

[14] P. Shrestha and A. D. Migone, Phys. Rev. B **54**, 17 102 (1996).

[15] P. B. Weichman, P. Day, and D. Goodstein, Phys. Rev. Lett. **74**, 418 (1995).

[16] J. M. Phillips and J. Z. Larese, Phys. Rev. Lett. **75**, 4330 (1995).

[17] P. Weichman and D. Goodstein, Phys. Rev. Lett. **75**, 4331 (1995).

[18] M. den Nijs, in *Phase Transitions in Surface Films 2* (Ref. 1).

[19] K. Rommelse and M. den Nijs, Phys. Rev. Lett. **59**, 2578 (1987).

[20] P. B. Weichman and A. Prasad, Phys. Rev. Lett. **76**, 2322 (1996).

[21] S. Pristipino and E. Tosatti, Phys. Rev. B **59**, 3108 (1999).

[22] A. Migone, M. T. Alkhafaji, G. Vidali, and M. Karimi, Phys. Rev. B **47**, 6685 (1993).

[23] P. Shrestha, M. T. Alkhafaji, M. M. Lukowitz, G. Yang, and A. D. Migone, Langmuir **10**, 3244 (1994).

[24] R. Gangwar and R. M. Suter, Phys. Rev. B **42**, 2711 (1990).

[25] R. F. Hainey, R. Gangwar, J. D. Shindler, and R. M. Suter, Phys. Rev. B **44**, 3365 (1991).