[3]B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. 41, 121, 519(E) (1978).
[4]D. R. Nelson and B. I. Halperin, Phys. Rev. B 19, 2457 (1979).
[5]J. G. Dash, Phys. Rep. 38C, 177 (1978).
[6]D. Frenkel and J. P. McTague, Phys. Rev. Lett. 42, 1632 (1979).
[7]W. W. Wood, in *Physics of Simple Fluids*, edited by H. N. V. Temperley, G. S. Rushbrooke, and J. S. Rowlinson (North-Holland, Amsterdam, 1968), Chap. 5.
[8]I. R. McDonald, Mol. Phys. 23, 41 (1972).
[9]B. J. Alder and T. E. Wainwright, Phys. Rev. 127, 359 (1962).
[10]F. Tsien and J. P. Valleau, Mol. Phys. 27, 177 (1974).
[11]S. Toxværd, Mol. Phys. 29, 373 (1975).
[12]The critical constants for the 2-D L-J system have been estimated by Tsien and Valleau (Ref. 10) to be $P_c^* \simeq 0.11$ and $T_c^* \gtrsim 0.625$. The triple point is more difficult to ascertain, but a "best estimate" by this author indicates that the triple-point constants are $P_t^* \approx 0.01$ and $T_t^* \approx 0.4$.
[13]R. E. Peierls, Ann. Inst. Henri Poincaré 5, 1771 (1935).
[14]L. D. Landau, in *Collected Papers of L. D. Landau*, edited by D. ter Haar (Pergamon, Oxford, 1965), Chap. 29.
[15]See Dash, Ref. 5, pp. 179–183.
[16]W. G. Hoover, W. T. Ashurst, and R. J. Olness, J. Chem. Phys. 60, 4043 (1974).

Completion of the Phase Diagram for the Monolayer Regime of the Krypton-Graphite Adsorption System

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The results of a heat-capacity study of the region between one and two layers in the Kr/graphite (Grafoil) system are presented. Heat-capacity anomalies corresponding to the commensurable-incommensurable transition, the commensurable-fluid transition, and a previously unobserved incommensurable-fluid transition delimit the high-coverage extent of the registered phase. A phase diagram proposed on the basis of the heat-capacity data suggests the possibility of a new type of multicritical point.

Krypton physisorbed onto graphite has been the subject of a number of recent studies. Isotherm, low-energy electron diffraction, x-ray, and heat-capacity studies[1] have been used to map phase boundaries in the submonolayer and monolayer regimes. In particular, for coverages near one registered monolayer two higher-order transitions have been observed, a commensurable-incommensurable transition (CIT) at lower temperatures and a commensurable (registered) solid to a dense fluid transition (CFT). The phase diagram for the monolayer regime of the Kr/graphite system remains incomplete, however, since no transition delimiting the high-coverage extent of the registered solid has been observed. It has been conjectured[2] that the CIT and CFT join, enclosing the registered phase in a line of higher-order transitions and raising the interesting question of how the incommensurable solid melts. We have conducted a comprehensive heat-capacity survey of the regime between one and two layers. The results reported here map the boundaries of the registered phase and show that the CIT and CFT intersect at approximately 127 K and 1.5 layers. From this intersection a third line of heat-capacity anomalies emerges with increasing coverage. These anomalies constitute the first observation for the Kr/graphite system of the incommensurable-solid–dense-fluid transition (IFT), which appears to be higher order. The intersection of the CIT, CFT, and IFT suggests the possibility of a new type of multicrtical point.

In order to establish a detailed map of the phase boundaries, sixteen coverages (i.e., fixed total amount in the calorimeter) between 1.0 and 2.4 registered monolayers were studied. The results are summarized in Fig. 1, which shows the loci of heat-capacity anomalies in the temperature-coverage plane. For all coverages above the monolayer, desorption is significant and the amount adsorbed becomes a function of temperature. The heating paths for several representative coverages are also shown in Fig. 1. For coverages just above the monolayer, the heat capacity displays two anomalies [Figs. 2(a) and 2(b)]. With increasing coverage the lower temperature anomaly, at first (A_1, Fig. 1) broad and barely discernible, becomes larger and sharper, moving rapidly to higher temperature ($A_1A_2C_1$).

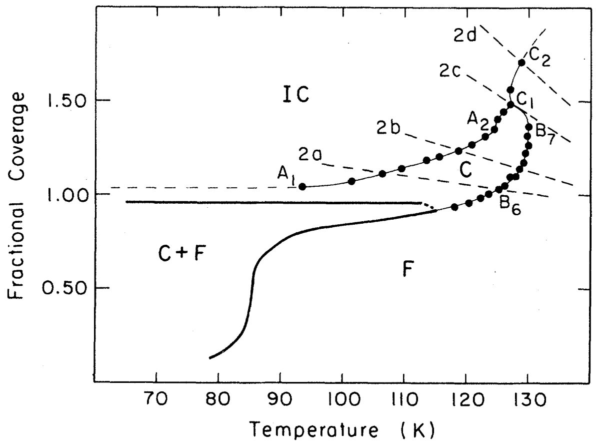

FIG. 1. Completion of the temperature-coverage phase diagram for the Kr/graphite system in the extended monolayer regime. Fractional coverages have been corrected for desorption. Observed heat-capacity anomalies are indicated by solid circles and connected by light solid lines. Dashed lines indicate extrapolated features. Heavy solid lines indicate submonolayer phase boundaries as given in Ref. 1. Dashed lines indicate approximate heating paths for coverages shown in Fig. 2.

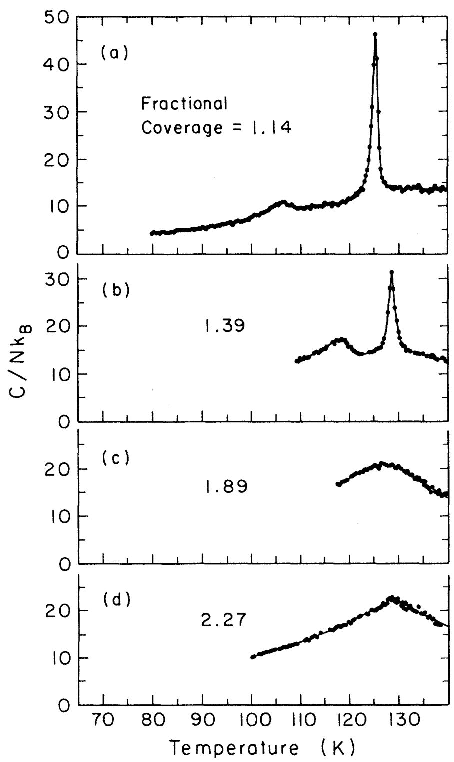

FIG. 2. Heat capacity vs temperature for several representative coverages. Listed coverages indicate total amounts in calorimeter. No corrections for desorption have been made. Solid circles, data points; solid lines, smoothing function fitted to data.

The higher temperature anomaly [Fig. 2(a)], a sharp peak at the monolayer (B_6), decreases slowly in magnitude [Fig. 2(b)] with increasing coverage, while also moving to higher temperature (B_6B_7). At 1.5 layers and 127 K (C_1) the two lines of anomalies merge. At this coverage [Fig. 2(c)], the heating path runs parallel to the phase boundary, and the heat capacity anomaly is consequently broad and rounded. Above this coverage the anomaly sharpens with increasing coverage (C_1C_2) and the heat capacity exhibits a cusp, or break in slope [Fig. 2(d)].

The anomalies along $B_6B_7C_1$ may be immediately identified as the registered-solid-fluid boundary since they evolve smoothly and continuously from the CFT anomalies in the submonolayer.[1] Along $A_1A_2C_1$ the pressure as a function of temperature (Fig. 3) both overlaps and forms a smooth extension of previous observations of the CIT and $A_1A_2C_1$ may be identified as the incommensurate-solid-registered-solid phase boundary. While this identification is unambiguous near the monolayer, it is possible that the bend in $A_1A_2C_1$ at A_2 represents nonsmooth behavior of the boundary, a "kink" rather than a bend. Such a kink would indicate the existence of another boundary which intersects $A_1A_2C_1$ at A_2. However, no other evi-

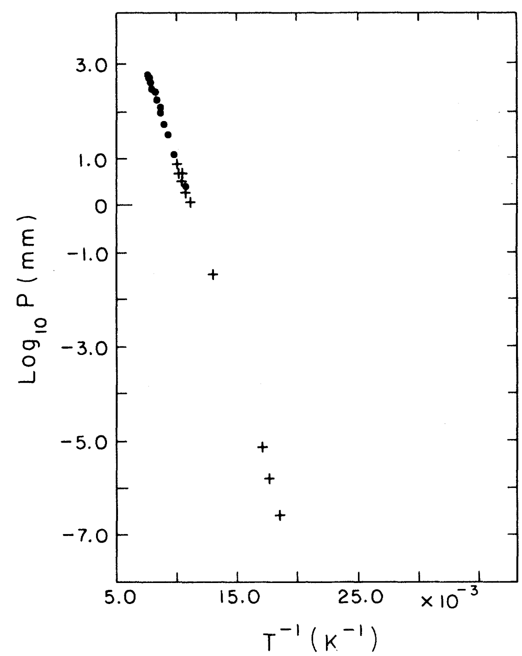

FIG. 3. Krypton vapor pressure vs inverse temperature at the CIT. Solid circles indicate values from the present work along locus $A_1A_2C_1$ in Fig. 1. Crosses indicate values from previous work taken from Ref. 5.

dence of another boundary was found and it is consistent with the data to assume that $A_1A_2C_1$ is smooth. The smooth behavior of $A_1A_2C_1$ and $B_6B_7C_1$ and the absence of any heat-capacity anomalies other than those shown indicate that the phases present near the monolayer extend to significantly higher coverages. In particular, the line of anomalies C_1C_2 is apparently associated with an incommensurable solid to fluid transition (IFT). The intersection of the CIT, CFT, and the anomalies C_1C_2 at C_1 delimits the extent of the registered phase and Fig. 1 constitutes a proposed completion for the monolayer-regime phase diagram.

Several explanatory comments should be made regarding this proposed phase diagram. First, the "monolayer regime" extends well above the monolayer proper. The extension of the two solid phases to 1.5 layers and above stands in contrast to the common picture which separates the first and second layers and views the solids as monolayer phases. This intuitive picture is useful at lower temperatures where a first-order transition between a surface phase (the incomensurable solid) with an areal density just over a monolayer and a surface phase with a density just under two layers is often interpreted as a transition between a gas and a solid or fluid *in the second layer*. Thermodynamics alone, however, does not provide this distinction between layers and, in the temperature range of the present work, the results show that a separation on intuitive grounds is not convenient. The incommensurable solid, the registered solid, and the fluid all can have significant second-layer components in their structure.

Second, if the theory of dislocation-mediated melting[3] describes the IFT the actual transition occurs as a temperature below the cusp in the heat capacity at C_1C_2 [Fig. 2(d)] and its precise location would be impractical, if not impossible, to determine from the heat-capacity data. The cusp itself is a somewhat sharper anomaly than predicted by this theory but could be due to desorption effects, as is suggested by results for the melting anomalies in the ^{3}He/graphite system.[4]

Third, the heat-capacity signatures at coverages of this study suggest qualitatively that the CFT (in contrast to the submonolayer regime), CIT, and IFT are all higher-order transitions. The effects of substrate inhomogeneity and desorption preclude detailed quantitative analysis of the present data but the qualitative conclusions agree with recent observations of the CIT[5,6] and CFT,[7] theoretical results for the CFT[8] and IFT,[3,9] and theoretical results for the CIT showing a higher-order transition.[10-12] On the basis of the previous and current results, C_1 appears to be the intersection of three lines of higher-order transitions, each belonging to a separate universality class, and if so C_1 corresponds to a type of multicritical point previously unobserved.

Last, we emphasize that the present heat-capacity study maps the phase boundaries. The proposed phase diagram indicates that this regime of the Kr/graphite system should be an interesting subject for more detailed studies in the future.

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[1]D. M. Butler, J. A. Litzinger, G. A. Stewart, and R. B. Griffiths, Phys. Rev. Lett. 42, 1289 (1979), and references contained therein.

[2]F. A. Putnam, T. Fort, Jr., and R. B. Griffiths, J. Phys. Chem. 81, 2171 (1977).

[3]B. I. Halpern and D. R. Nelson, Phys. Rev. B 19, 2457 (1979).

[4]R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[5]S. C. Fain and M. D. Chinn, J. Phys. (Paris), Colloq. 38, C4-99 (1977).

[6]P. N. Stephens, P. Heiney, R. J. Birgeneau, and P. M. Horn, Phys. Rev. Lett. 43, 47 (1979).

[7]P. M. Horn, R. J. Birgeneau, P. Heiney, and E. M. Hammonds, Phys. Rev. Lett. 41, 961 (1978).

[8]A. N. Berker, S. Ostlund, and F. A. Putnam, Phys. Rev. B 17, 3650 (1978); A. N. Berker and S. Ostlund, to be published.

[9]D. Frenkel and J. P. McTague, Phys. Rev. Lett. 42, 1632 (1979).

[10]P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B 19, 1610 (1979), and references cited therein.

[11]H. Shiba, to be published, and references cited therein.

[12]A. Luther, in Proceedings of the International School on Low Temperature Physics, Erice, Sicily, 1979 (to be published).