Heat Capacity of Krypton Physisorbed on Graphite

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The results of an exhaustive high-precision heat-capacity study of the submonolayer regime of the krypton-graphite(Grafoil) adsorption system are presented. A phase diagram exhibiting a single two-phase coexistence region is proposed as an alternative to the previously proposed triple-point phase diagram. A quantitive correspondence between the locus of heat capacity anomalies in the Kr-graphite system and that for the N_2-graphite system suggests the proposed phase diagram may apply to the N_2 system as well.

Previous experimental[1-5] and theoretical[6,7] work indicates that the krypton-graphite adsorption system exhibits several interesting phase transition phenomena. Near monolayer capacity, isotherm studies[1-3] have located phase boundaries at nearly constant density. At lower coverages isotherm studies suggest boundaries at nearly constant temperature, making it difficult for this probe to determine the entire phase diagram. The heat capacity at fixed coverage, however, is most sensitive to boundaries at fixed temperature and therefore is an appropriate probe to complete the experimental determination of the submonolayer phase diagram. In this Letter, we present the first heat capacity measurements of the krypton-Grafoil system. We show that the submonolayer heat capacity data is consistent with a phase diagram displaying a single two-phase coexistence region of unusual shape. This interpretation differs from that proposed by Thomy and Duval[1] and Lahrer,[2] who interpreted their isotherm results as indicating the presence of a triple point. In addition, our data establish experimentally a quantitative correspondence between the krypton-graphite and nitrogen-graphite[8-11] systems, suggesting the same interpretation can be extended to the N_2 case.

We have measured the heat capacity of 24 coverages between 0.1 registered monolayers (N_m) and $1.1N_mk$ and in the temperature range between 65 and 140 K. The loci of heat-capacity anomalies in the N-T plane are plotted in Fig. 1. The heat capacity at fixed coverage (C_n) versus temperature (T) is plotted for several coverages (N) in Figs. 2 and 3. Between $0.134N_m$ and $0.580N_m$ the heat capacity exhibits a single anomaly. The locus of the maximum is given by line B_1B_2 in Fig. 1. In C_n versus T, the low-temperature side of the anomaly has a rise to a peak, followed by a much sharper drop on the high-temperature side [Fig. 2(a)] suggesting a slightly smeared discontinuity. At the lowest coverage studied ($0.134N_m$) the peak height is $17.0k_B$. With increasing coverage, the peak height increases dramatically in size and sharpness reaching a maximum height of $53.6k_B$ at both $0.536N_m$ and $0.580N_m$ [Fig. 2(b)].

Above $0.580N_m$ the anomaly begins to decrease in height. The sharp drop on the high-temperature side becomes separated from the maximum

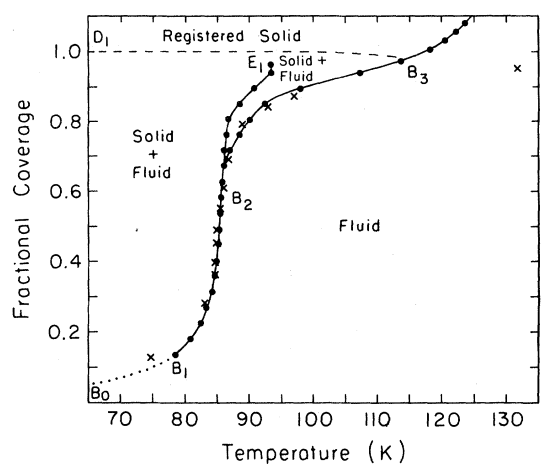

FIG. 1. Loci of heat-capacity anomalies in the N-T plane for the Kr-graphite system. Positions of observed anomalies are indicated by solid circles and connected by solid lines. Dashed line (D_1B_3) indicates break in slope of C_n vs N. Dotted line (B_0B_1) is extrapolation of $B_1B_2B_3$ to coverages below those studied. Crosses indicate anomalies in N_2-graphite system with temperatures rescaled by Lennard-Jones parameters as discussed in text.

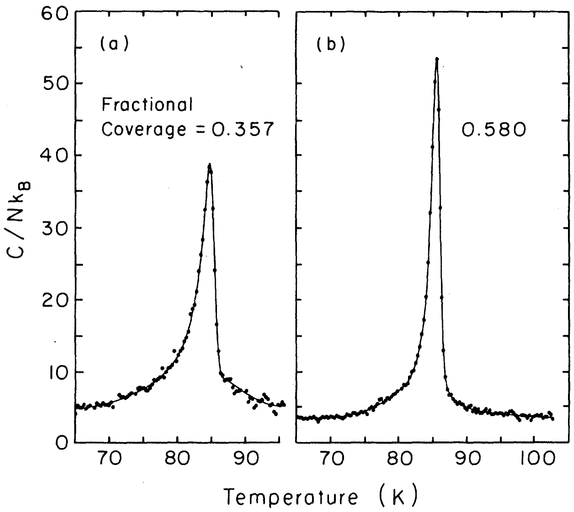

FIG. 2. Heat capacity of Kr film for two coverages. Solid circles, data points; solid line, piecewise-continuous cubic-spline smoothing function fitted to data.

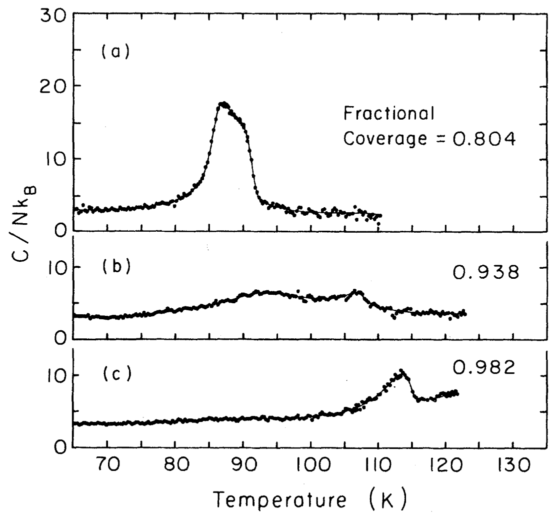

FIG. 3. Heat capacity of Kr film for three additional coverages.

by a region of much smaller slope [Fig. 3(a)]. As the coverage is increased the maximum moves to higher temperature (B_2E_1), decreasing in magnitude. The sharp drop moves more rapidly to higher temperature (B_2B_3) making the region of shallow slope wider and more concave. The peak continues to broaden and decrease in height leaving the region of the drop as a second local maximum [Fig. 3(b)]. Just below the monolayer the lower-temperature maximum disappears entirely (E_1), leaving a single anomaly in the heat capacity at the monolayer [Fig. 3(c)].

C_n versus N at fixed T shows a single linear region bounded by a break in slope on the high-density side. This break occurs at approximately $1.0N_m$ independent of temperature, and is indicated by D_1B_3 in Fig. 1. The linear region terminates at $B_1B_2B_3$ on the low-density side. It is most pronounced for temperatures between 80 and 84 K. For lower temperatures the break in slope is less distinct, while for higher temperatures the region becomes much narrower and the rounding at the edges proportionately more important.

It is well established that there is a first-order transition between the registered solid and a low-density fluid phase (gas) at sufficiently low temperatures.[1,2,4] Isotherm studies[1,2] have suggested that the solid-gas coexistence region terminates in a triple point. The triple-point hypothesis implies a fluid-fluid (liquid-gas) coexistence region and would require that the ideal-infinite-system heat-capacity signature at the critical density of the fluid show two anomalies: a δ function at the triple temperature (T_t) followed by a divergence at the critical temperature (T_c). Thomy and Duval place T_t near 77 K and T_c near 87 K. The absence of any anomaly in the heat capacity near 77 K rules out this possibility. Lahrer found no direct evidence of the fluid-fluid coexistence region and argued that the triple point and the critical point must therefore be very close, with $T_t = 84.8$ K and $T_c = 85.3$ K. Figure 2(b) shows that the heat capacity versus temperature near the critical density proposed by Lahrer has a single anomaly centered at 85.5 K. While it has been suggested[8] that in real systems inhomogeneities and finite-size effects could smear two close anomalies together, the data do not, of themselves, suggest this interpretation. Another interpretation is possible which does not assume the existence of the unobserved two-phase region.

The sharp drop in the heat capacity across $B_1B_2B_3$ suggests a discontinuity upon leaving a region of phase coexistence. The most straightforward interpretation of the data is to assume a single region of two-phase coexistence bounded by D_1B_3 for the registered and $B_1B_2B_3$ for the fluid phase.[9] The unusual shape of the latter can be explained by the following mechanism: It is plausible that if a triple point occurs, Fig. 4(a), the separation between the critical and triple temperatures might be a sensitive function of the inter-

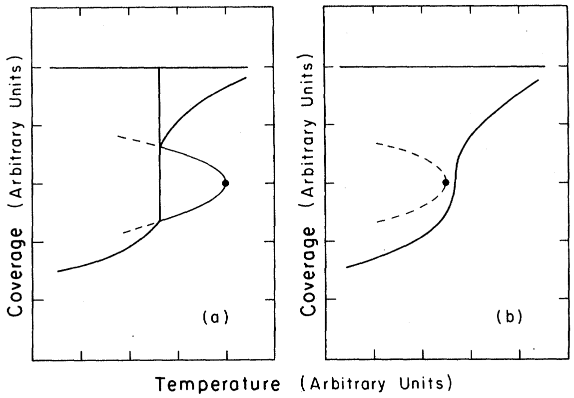

FIG. 4. (a) Triple point and (b) incipient triple point. The metastable extension of liquid-vapor coexistence is shown by the dashed curve.

action parameters (not accessible to experiment) which determine the relative free energies of the registered and fluid phases. It could be the case that for Kr on graphite these parameters result in a small negative value for T_c-T_t, with the critical point occurring only in a metastable extension of the fluid phase,[10] Fig. 4(b). Calculations on a simple thermodynamic model confirm intuitive expectations that for this "incipient triple point" the phase boundary can indeed have the shape indicated in Fig. 4(b), with the fluid near the center of the S curve in a near-critical state, in agreement with isotherms at 86 K and slightly higher temperatures.

The heat-capacity behavior expected for an incipient triple point is consistent with the observed heat capacity, and, in particular, explains the maxima along B_2E_1 without introducing an additional phase boundary. In any two-phase region, the heat capacity per unit area at constant average density (C_n) can be written

$$C_n = x_2\{C_{n2} + T(\partial\mu/\partial n)_{T2}(dn_2/dT)^2\} + (1-x_2)\{C_{n1} + T(\partial\mu/\partial n)_{T1}(dn_1/dT)^2\}, \quad (1)$$

where n_i ($i=1,2$) is the areal density of phase i, n is the average density, C_{ni} is the heat capacity per unit area at constant density in phase i, x_2 is the fractional area occupied by phase 2, $\mu(n,T)$ is the chemical potential, and the subscripts on $(\partial\mu/\partial n)_T$ indicate the phase in which the derivative is evaluated. Let phase 1 be the registered solid. The solid branch of the phase boundary lies roughly at constant density and, therefore, $dn_1/dT=0$ to first approximation. From Fig. 3(c), C_{n1} is small and essentially constant below 105 K. Thus we drop the second term in (1) and writing dn/dT in terms of derivatives of the chemical potential, we have

$$C_n \simeq x_2\{C_{n2} + T(\partial n/\partial\mu)_{T2}[(d\mu/dT)_{\text{coex}} - (\partial\mu/\partial T)_{n2}]^2\}, \quad (2)$$

where "coex" denotes the coexistence curve. The term in curly brackets, henceforth denoted by $f(T)$, is evaluated along the phase boundary and is thus a function of temperature only. Critical divergence of C_{n2} and $(\partial n/\partial\mu)_{T2}$ causes a sharp maximum in $f(T)$ at the temperature of point B_2 where the phase boundary passes close to the metastable critical point. For any given coverage below B_2, the heating path crosses the phase boundary before $f(T)$ reaches its maximum. The expected heat-capacity signature is thus an increase to a maximum immediately followed by a discontinuity, as observed. The magnitude of the maximum should increase with increasing coverage until the absolute maximum is reached at B_2. This behavior is also observed. For coverages above B_2, the heat capacity as a function of temperature should show a maximum at the temperature of B_2, due to the maximum in $f(T)$, but the discontinuity should occur at higher temperature, when the boundary is crossed. Because of the factor of x_2, the magnitude of the maximum should decrease to zero as the coverage is increased to the registered coverage. With the exception of the temperature dependence of the maximum, the expected behavior is observed and the incipient–triple-point interpretation is sufficient to explain the data.

We point out that if this interpretation is correct the maxima along B_2E_1 do not represent a phase boundary. Physically, they are caused by the near-critical state of the fluid near B_2 and the resultant steep section of the phase boundary forcing a rapid conversion of solid to fluid and a rapid increase in the density of the fluid as the temperature is increased. These maxima become the δ-function anomalies at an ordinary triple line as $T_c - T_t$ is increased to a positive value, another reason for the nomenclature "incipient." It has been shown[8] that finite-size effects and inhomogeneities can produce a temperature-dependent triple line and it seems likely that inhomogeneities can also produce a temperature dependence in the line of maxima for the incipient–triple-point case. Thus, although the triple-point interpretation is still a possibility, the incipient–triple-point interpretation provides an attractive alternative which does not assume the existence of the unobserved fluid-fluid coexistence region.

The triple-point interpretation suggested for the N_2-graphite phase diagram[8] also faces the problem of an unobserved fluid-fluid coexistence region. Although no isotherm studies have been made for N_2 in the temperature range of interest, heat-capacity studies[8,11] have shown anomalies similar to those presented here for krypton. It is known from diffraction probes that both the Kr-graphite system[4,5] and the N_2-graphite system[12,13] have a registered phase. Furthermore, from bulk virial-coefficient studies, the Lennard-Jones (LJ) hard-core parameters are very nearly the same with $\sigma(\mathrm{Kr}) = 3.60$ and $\sigma(N_2) = 3.698$. To the extent that Kr and N_2 behave like the ideal LJ adsorbate, one might expect the phase diagrams for these systems to have essentially identical coverage dependence with a temperature dependence that scales with the ratio of LJ potential strengths $\epsilon(\mathrm{Kr})/\epsilon(N_2) = 1.799$. In Fig. 1, the locus of heat-capacity anomalies in the submonolayer regime of the N_2-Grafoil system is plotted with the temperatures rescaled by $\epsilon(\mathrm{Kr})/\epsilon N_2)$. The identity of the scaled lines of anomalies establishes experimentally a quantitative correspondence between the Kr and N_2 submonolayer phase diagrams. Near the monolayer the temperature scaling breaks down (Fig. 1). The qualitative correspondence continues to higher coverage, however, and the Kr heat-capacity signature near the monolayer [Fig. 3(c)] is essentially identical to that previously observed for N_2 in the same coverage range.[11] This detailed correspondence between the N_2 and Kr systems suggests that the incipient–triple-point interpretation may also be applicable to the N_2 system.

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Virtual Bicritical Point in $CsMnF_3$

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The ordering temperature T_c of the easy-plane antiferromagnet $CsMnF_3$ was measured as a function of magnetic field H. When $\vec{H}$ is perpendicular to the easy plane, T_c decreases monotonically with increasing H, but the decrease is not proportional to H^2. The latter behavior is explained in terms of a virtual bicritical point which exists mathematically at a negative value of H^2.

In this Letter we introduce the concept of the virtual bicritical point in easy-plane antiferromagnets, and present experimental data in $CsMnF_3$ which support this concept.

The bicritical point (BP) of a low-anisotropy easy-axis antiferromagnet was discussed theoret-

