Melting Transition of Submonolayer Ar Adsorbed on Graphite

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Precision ac heat-capacity scans of submonolayer Ar on Graphite Foam exhibit a liquid-vapor anomaly near 55 K, a small, sharp, coverage-independent peak at 47.2 ±0.2 K, and a broad anomaly near 49.5 K. The 47.2-K peak suggests that the Ar overlayer melts via a "weak" first-order (rather than continuous) transition. The 49.5-K anomaly appears to be related to the gradual decrease of correlation (possibly substrate-induced orientational order) that exists in the liquid phase.

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The melting transition of a solid overlayer that is incommensurate with the substrate is of considerable theoretical and experimental interest. The dislocation-pair unbinding model of Kosterlitz and Thouless,[1] Halperin and Nelson,[2] and Young[3] (KTHNY) suggests that the melting of such a two-dimensional system could be continuous. The model of Chui of spontaneous generation of grain boundaries, on the other hand, predicts a first-order melting process.[4]

Experimental evidence for continuous melting of physisorbed systems has been reported for a high-coverage, incommensurate overlayer of Xe on graphite[5] and Kr on graphite.[6] It is not clear, however, whether the presence of the second layer in the above system plays an important role in determining the nature of the transition or not. The melting transition of high-coverage, compressed monolayer ^{4}He on graphite, however, was found to be probably first order.[7]

Experiments on spherical adsorbates that form an incommensurate solid on graphite in submonolayer coverages have always found the melting transition to be first order. Prominent two-dimensional triple-line melting signatures were found for submonolayer Xe on graphite,[8] Ne on graphite,[9,10] and CH_4 and CD_4 on graphite[11,12] systems. No such signature, however, has been previously found for submonolayer Ar on graphite. Recent experimental results of neutron scattering,[13,14] heat capacity,[15] and synchrotron x-ray scattering[16] studies were all interpreted as being consistent with a continuous melting process. We report in this Letter new heat-capacity results for Ar on graphite that clearly indicate that the melting transition is weakly first order occurring at a triple-line temperature.

In Fig. 1 heat-capacity traces of six of the twenty-four film coverages studied are shown. The coverages studied range from $n=0.175$ to $n=1.171$. $n=1$ in our experiment corresponds to a film coverage of one Ar atom for every three carbon hexagons. (The surface area of the Graphite Foam substrate in the calorimeter was determined via a 74-K N_2 vapor-pressure isotherm study.[17]) Below $n=0.783$ three heat-capacity anomalies are present. The highest-temperature peak appears to be related to the liquid-vapor transition: The heights, widths, and the coverage dependence of the peak temperature are consistent with this interpretation.[12] The critical temperature that we found at 55.1 ±0.3 K is lower than the 58.0- and 59.0-K values determined for vapor-pressure isotherm studies.[18] Above $n=0.783$, the liquid-vapor anomaly is no longer discernible.

The two peaks at lower temperatures can best be described as a small but sharp peak at 47.2 K with a

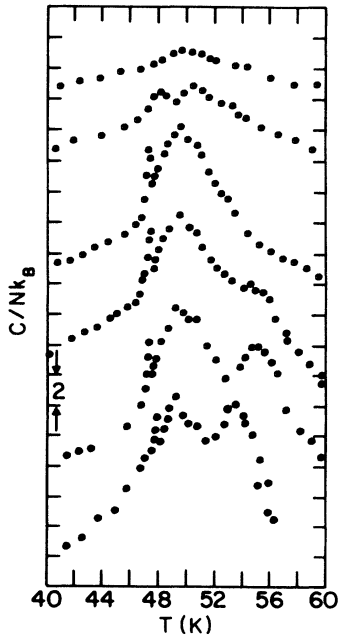

FIG. 1. Heat-capacity scans of Ar on graphite at coverages (from bottom to top) $n=0.175$, $n=0.572$, $n=0.717$, $n=0.872$, $n=1.043$, and $n=1.068$. For the sake of clarity, not all data points are shown.

full width at half maximum (FWHM) of less than 0.3 K, situated on the low-temperature side of a broad anomaly (FWHM = 6 K) centering near 49.5 K. Over the coverage range between $n = 0.232$ and $n = 1.034$ this sharp peak remains at 47.20 ± 0.2 K with the same reduced height ($C/Nk_B = 2.3 \pm 0.5$, with N the number of adsorbed Ar atoms) and width. The heat-capacity scans in this coverage range are represented in Fig. 1 by the three scans at $n = 0.572$, $n = 0.717$, and $n = 0.872$. At $n = 0.175$, the peak temperature is at 47.85 K. This sharp peak for $n = 0.717$ is shown more clearly in Fig. 2. For $n > 1.034$, as shown in the top two scans in Fig. 1, this sharp peak broadens and merges into the broad 49.5-K anomaly.

In the earlier heat-capacity study of Ar on graphite,[15] a single unresolved broad anomaly between 36 and 64 K with a half width (FWHM) of larger than 14 K was found at comparable submonolayer Ar coverages. This broad heat-capacity anomaly (or rather the absence of a sharp peak) had been cited by previous studies as being consistent with a continuous melting process.[14-16] The superior surface homogeneity[19] of Graphite Foam (the substrate used in our study) over Grafoil (used in the earlier heat-capacity study[15] and the neutron studies[13,14]) and the advantages of our ac calorimetric technique[17] are responsible for the much higher resolutions in our study. ZYX graphite, a substrate with slightly higher surface homogeneity[19] than Graphite Foam, was used in the synchrotron x-ray study.[16]

While performing these measurements we calibrated the silicon-diode thermometer used in the recent synchrotron x-ray study[16] against our Pt thermometer. Upon eight separate cyclings in temperature, the thermometer used in the x-ray study was found to read a temperature between 0.3 and 0.5 K higher than our thermometer. This shift, together with the uncertainties of both experiments, suggests that the melting temperature of submonolayer Ar on graphite as reported in the x-ray experiment (47.9 ± 0.2 K) is the same as our sharp-peak temperature at 47.2 ± 0.2 K. The melting temperature was defined in the x-ray study as the onset temperature of the broadening of the diffraction peak. The existence of this sharp heat-capacity peak at the x-ray melting temperature is inconsistent with the standard interpretation of the KTHNY continuous model of melting[2] for submonolayer Ar on graphite.

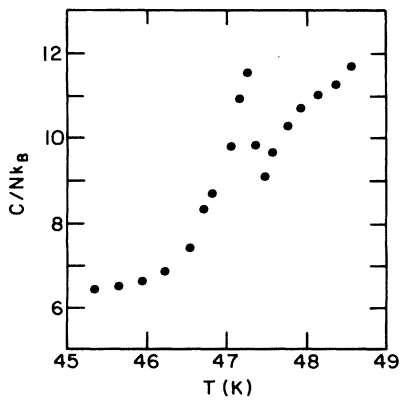

FIG. 2. Expanded view of the sharp heat-capacity peak at $n = 0.717$.

The fact that this 47.2-K peak is sharp and the peak temperature is coverage independent over a large coverage range is evidence in favor of melting at a two-dimensional triple-line temperature, similar to the melting transition of other incommensurate submonolayer systems. But why is the peak so small? The entropy change associated with the Ar melting peak, $\Delta S/Nk_B = 0.02$, is a factor of 15 to 20 smaller than that found under the triple-line peaks of CH_4, Ne, and Xe on graphite.[8,9,11,12] And what is the origin of the broad heat-capacity anomaly at 49.5 K that is observed only for the Ar-on-graphite system?

We suggest that both of these results are related to the strong orientational effects on the Ar overlayer induced by the graphite substrate. This orientational effect is expected to be strong for Ar overlayers because the lattice constant of Ar overlayer at 4.0 Å just before melting[16] is only slightly smaller than the commensurate value of 4.26 Å. Substrate effects on submonolayer Xe and CH_4 overlayers, with lattice constants larger than 4.26 Å,[8,11,16] are expected to be less important than on Ar since it is much more difficult for the graphite to compress than to pull apart the adsorbed molecules.[16] This is demonstrated in a recent simulation study[20] of the melting of Xe and Ar overlayers on graphite. Near melting the lattice constant of Ne overlayer on graphite is also larger (2%) than the $\sqrt{7} \times \sqrt{7}$ commensurate value.[10]

The effect of external orientational ordering field on an overlayer has been considered by Chui.[4,21] It was found that stronger orientational field results in larger core energy of the dislocations in the overlayer. Chui's calculation suggested that the melting transition goes from strongly first order to weakly first order if the core energy is larger than a critical value. Similar results were found in simulation studies by Saito[22] and Swendsen,[23] who found that the melting transition can change from first-order-like with small core energy to KTHNY or

continuous-like for sufficiently large core energy. The observed small (but sharp) heat-capacity peak at 47.2 K for Ar on graphite appears to be a signature of weakly first-order melting transition. In the context of the above discussion, such a weakly first-order transition is consistent with the grain-boundaries model with strong orientational ordering field.[4] We wish to point out that our results, in particular the observed broad 49.5-K anomaly to be discussed below, certainly are also consistent with the KTHNY continuous dislocation-pair unbinding mechanism preempted by a first-order transition.

A simple calculation based on the Clausius-Clapeyron equation indicates that the entropy change under our 47.2-K peak corresponds to an areal density change between the liquid and solid phase at melting of about 0.2%. Therefore it is not surprising that such a "discontinuous" change was not observed in the diffraction experiments.[13,14,16]

The broad heat-capacity anomaly near 49.5 K can be interpreted as due to the gradual decrease of orientational order in the liquid phase as temperature is increased beyond the melting temperature. In a LEED isotherm study at submonolayer coverage, a dilute disordered phase and a dense phase with orientational order with respect to the graphite were found to coexist up to 55 K.[24] A simple interpretation of the LEED result, in view of our results, is that orientational order from the solid phase[25] persists into the coexisting dense (i.e., liquid) phase. The simulation of Abraham also found that the lateral mobility of the fluid phase is strongly influenced by the substrate.[20]

An alternative explanation for this broad anomaly, as mentioned above, is that this is a signature of the continuous dislocation-pair unbinding process[26] in spite of the preemption by a weak first-order transition. This alternative explanation is qualitatively consistent with the observed temperature dependence of the correlation length observed in the synchrotron x-ray experiment just above the melting temperature.[16]

As the Ar coverage is increased beyond $n = 1.034$ the sharp 47.2-K peak broadens, moves to higher temperature, and then merges into the broad anomaly. This indicates that near $n = 1.034$ the Ar solid patches become connected and further increases in coverage are increasing the areal density of the Ar solid layer. Upon further increase in coverage ($n > 1.08$) this single anomaly (presumably separating the solid and liquid phases) broadens to a half-width of over 10 K (FWHM) and moves rapidly to higher temperature,[17] in agreement with other studies.[15,16,27] Vapor-pressure isotherm studies in

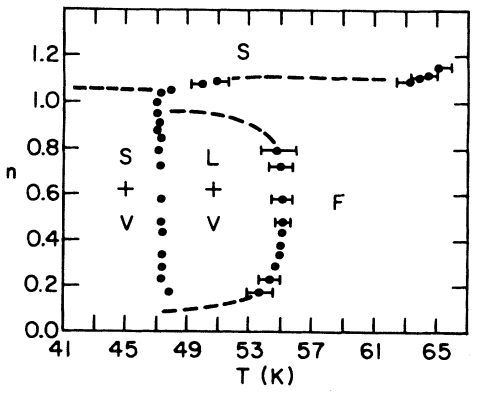

FIG. 3. Proposed phase diagram of Ar on graphite. S, L, V, and F represent respectively solid, liquid, vapor, and fluid phases. Solid circles near 55 K at submonolayer coverages correspond to positions of heat-capacity anomaly arising from liquid-vapor transition. Other circles are signatures of melting. Dashed lines are speculative. At submonolayer coverages, Ar solid melts via a weak first-order transition at a triple-point temperature (47.2 K) to a liquid-vapor coexistence region. The liquid phase appears to be orientationally ordered below 54 K. The positions of the broad anomalies centering near 49.5 K, due to the gradual decrease of this order, are not shown. Unless indicated otherwise, the uncertainty in the peak position of the heat-capacity anomalies is comparable to or smaller than the size of the circles.

this region suggest that the melting transition is continuous but not according to the KTHNY mechanism.[27] Our heat-capacity scans, being almost parallel to the phase boundary at these coverages, are not a sensitive probe of the melting transition. We cannot rule out (or confirm) the possibility that the weakly first-order transition at submonolayer coverages evolves to a continuous transition above the triple-point coverage. Synchrotron x-ray studies of Xe on graphite found that the melting transition changes from strongly first order to weakly first order and then continuous as the coverage is increased from the submonolayer to the supermonolayer regime.[5,28]

We do not understand why the melting temperature for the lowest-coverage film ($n = 0.175$) is slightly higher than the triple-line temperature (47.85 K instead of 47.2 ± 0.2 K). Similar behavior appears to be present in the Ne-on-graphite system. It could be related to the impurities that are present on the graphite surface.

In conclusion, our study together with earlier results shows that all known incommensurate submonolayer systems of spherical molecules on graphite melt via a first-order transition. Our data show that the melting of submonolayer argon is

weakly first order, which can be explained by a strong substrate-induced orientational field. The effect of this field may persist into the liquid phase above the melting transition. An alternative interpretation of our data is that submonolayer Ar on graphite melts according to the KTHNY mechanism preempted by a first-order transition. The submonolayer Ar on graphite phase diagram based on this heat-capacity study is shown in Fig. 3.

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