

Vapor-pressure study of the melting of two-dimensional argon adsorbed on BN

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(Received 26 December 1990; revised manuscript received 5 February 1991)

We have measured monolayer adsorption isotherms of Ar on BN and obtained the compressibility of the Ar films. A small substep in the isotherm is present at melting. Two peaks are present in the compressibility: a sharp one associated with the substep, and a broader one that occurs at lower pressures. We compare our results to those of a recent study of Ar on graphite.

The study of the melting behavior of two-dimensional (2D) solids has attracted attention for over a decade. Efforts in this area have largely been driven by the Kosterlitz-Thouless-Nelson-Halperin-Young theory,^{1,2} which makes the unusual prediction that melting can be a continuous transition in two dimensions. The majority of 2D solids, however, melt via first-order transitions.²

We report here on a vapor-pressure adsorption-isotherm study of Ar on BN. BN has the same structure as graphite; it has a longer basal-plane lattice parameter (2.50 Å for BN versus 2.46 Å for graphite³). Calculations of the interaction potential between rare gases and BN (Ref. 4) found well depths $\sim 10\%$ shallower than the corresponding ones for graphite.⁴ BN has been used in several physisorption studies.⁵⁻⁷ No structural data exists for Ar on BN. However, since Ar forms an incommensurate solid on graphite⁸ (graphite is too big for registry) and since BN and graphite have the same structure, Ar will also be incommensurate on BN.

In two previous studies of Ar on BN, adsorption isotherms at 77 and 90 K were obtained, together with calorimetric heat-of-adsorption measurements.^{6,7} A weak substep, identified as melting, was seen in the 77-K isotherm.⁷

We used HCP-grade BN powder manufactured by Union Carbide. Its specific area is 5 m²/g. We baked it under a vacuum of 1×10^{-6} Torr at 770 K for 8 h. The BN was briefly exposed to air during transfer to the copper cell in which the isotherms were performed. To test whether its quality deteriorated upon exposure to air, we built a stainless-steel cell in which we took the BN from 770 to 77 K without breaking the vacuum. Figure 1 shows Ar isotherms measured before [1(a)] and after [1(b)] air exposure. There is no measurable difference between them. The coverage scale was established by the point *B* method on a 77.4-K Ar isotherm. The homogeneity of the BN was determined from an 80.57-K CH₄ isotherm. CH₄ has a first-order melting transition on BN.⁵ The coexistence substep is $\sim 4\%$ of a layer. We measured a chemical-potential difference of ~ 2 K between the top and bottom of the CH₄ substep.

The pressures were measured using capacitance gauges in the dosing system. A correction was applied to account for thermal transpiration.⁹ The dosing system allowed the introduction of Ar to the cell in small doses; 0.0015% of a layer was easily achieved. A helium closed-cycle refrigerator produced the low temperatures. The cell tempera-

ture was controlled to better than 0.005 K.

Figure 2 shows four Ar adsorption isotherms taken between 67.94 and 76.93 K. The only feature evident in them is a small substep. A much expanded view of the substep is presented in Fig. 1, its size is $\sim 1.5\%$ of a layer. The substep corresponds to the solidification of the Ar film as the coverage is increased.

Data in the isotherms were taken at small intervals to enable us to obtain the 2D isothermal compressibility K_T

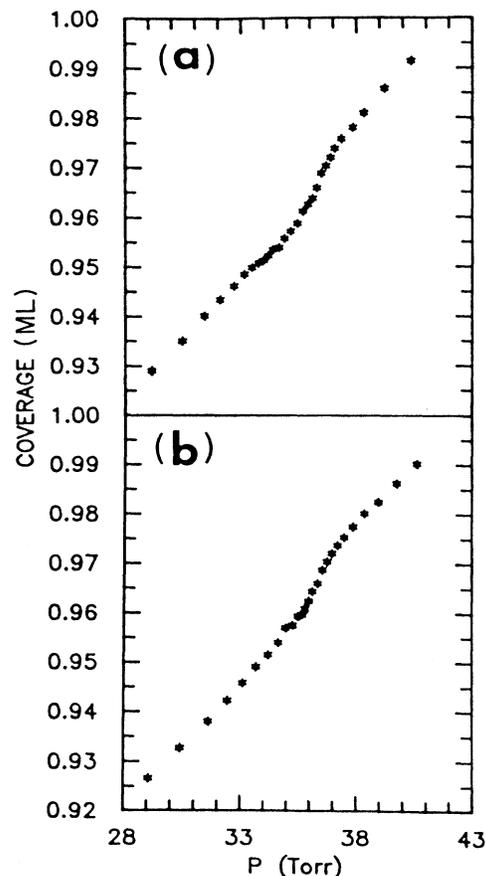


FIG. 1. Isotherm substep indicative of melting. (a) Data taken on the BN sample not exposed to air. (b) Data taken on the BN sample exposed briefly to air. Data were taken at 77.4 K. The coverage is given in monolayers.

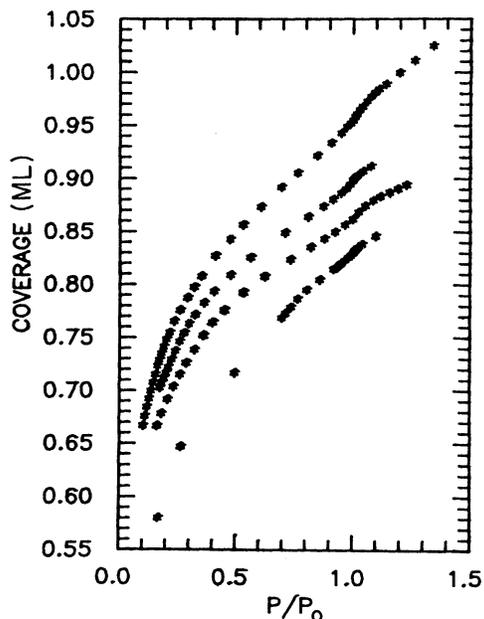


FIG. 2. Argon adsorption isotherms on BN. Shown from top to bottom are isotherms at: 76.93, 73.94, 71.97, and 67.94 K.

defined as

$$K_T = - (1/a) \frac{da}{d\phi}, \quad (1)$$

where a is the area per atom and ϕ is the 2D-spreading pressure. ϕ and a are connected to the measured quantities by the equilibrium condition between the 2D film and the 3D vapor: $ad\phi = vdP$. P is the pressure of the 3D vapor and v the volume per atom in the vapor. Equation (1) can be rewritten as

$$K_T = \frac{1}{n^2 v} \frac{dn}{dP}, \quad (2)$$

where n is the 2D density.

Figure 3 displays K_T for the 71.97 K isotherm. Two features are clearly visible in the data. At higher pressures there is a sharp compressibility peak. It corresponds to the small isotherm substep present at melting. At lower pressures there is a broad compressibility peak.

Shown in Fig. 4 are isothermal-compressibility data from which a smooth background contribution has been subtracted. The background was obtained by fitting the compressibility in the region away from the peaks with a polynomial. Two peaks can be seen for all temperatures. The sharp peak's height is 31 ± 5 m/N and its shape remains essentially unchanged. The broad peak becomes sharper and larger as the temperature decreases.

The pressure P_0 at the midpoint of the substep in the isotherm can be expressed as function of temperature as

$$\ln P_0 = - (A/T) + (B). \quad (3)$$

Fitting our data to (3) we get $A = 1958.6 \pm 7$ and $B = 28.83 \pm 0.1$; P_0 is in Torr and T in K. If the substep were occurring at constant coverage, we could directly relate A to the isosteric heat of adsorption and B to the en-

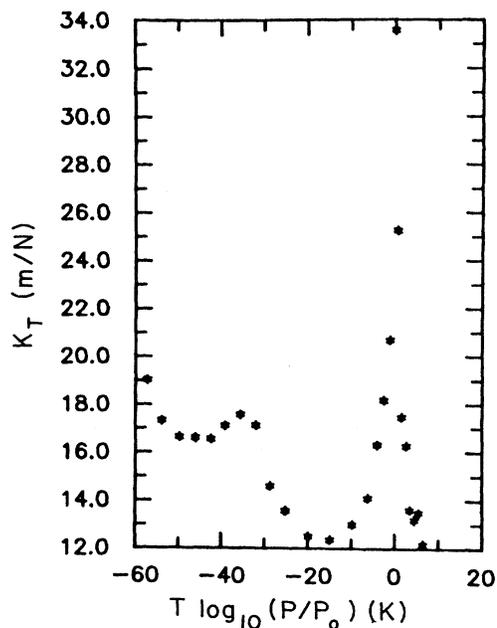


FIG. 3. Isothermal compressibility for $T=71.97$ K. The sharp peak is associated with the small substep in the isotherm.

tropy difference between the two adsorbed phases.¹⁰ Figure 2 shows that the substep occurs at higher coverages for higher temperatures so that the connection between these quantities is less direct.

The above characteristics of the compressibilities and the isotherms correspond closely to the isotherm and

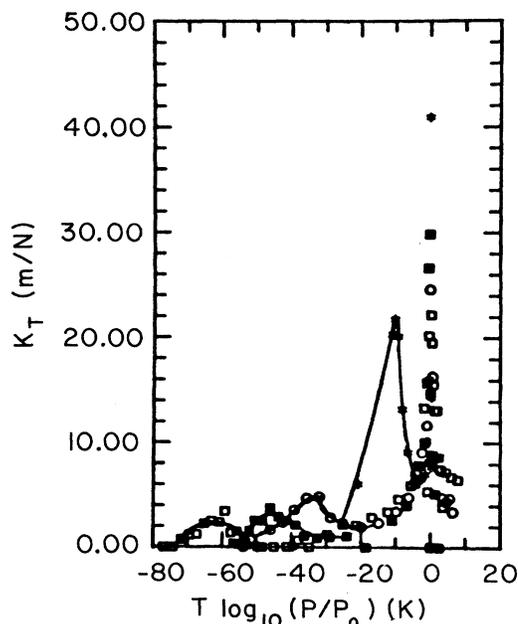


FIG. 4. Isothermal compressibility; 67.94 (asterisks), 71.97 (open circles), 73.94 (full squares), and 76.93 K (open squares). A smooth background has been subtracted. Lines drawn through the data in the broad peak region are guides to the eye.

compressibility behavior which has recently been reported for Ar on graphite.¹¹ Both systems have only a small isotherm substep at melting (for Ar on graphite it is about 1.2% of a layer). Both systems have a broad peak followed by a sharper one in the compressibility [for graphite the height of the sharp peak is ~ 30 m/N (Ref. 11)]. The value reported for B in (3) is 27.426 for Ar on graphite, close to the 28.8 we found for Ar on BN (to be expected if the coexisting phases present at the transition are similar for Ar on graphite and on BN).

Only one qualitative difference was observed in the behavior of the compressibilities of these two systems. For Ar on BN the broad peak moves away from the sharp peak with increasing temperature while for Ar on graphite the two peaks get closer.¹¹ This difference may be caused by different corrugation in the potentials for graphite and for BN.

The isotherm study of Ar on graphite¹¹ has gone a considerable distance towards eliminating an existing controversy. Heat-capacity studies¹² first indicated the presence of two peaks near the melting of Ar on graphite, a sharp one followed by broad one at higher temperature. X-ray,¹³ neutron scattering,⁸ heat capacity,¹⁴ and adsorption isotherms,¹⁵ on the other hand, found only continuous behavior at melting. A recent isotherm study¹¹ not only showed that a broad peak followed by a sharp one exists in the compressibility, but it also reanalyzed the x-ray-diffraction data¹³ and found that the temperature derivative of the inverse correlation length also has two peaks. This showed that all existing high-resolution data were consistent. Disagreement remains regarding the order of the melting transition. The heat-capacity study¹² concluded that it was weakly first order while the isotherm study¹¹ concluded that it probably was continuous. Correspondingly, the isotherm study¹¹ identified the broad compressibility peak as the disappearance of an intermediate regime of short-ranged solidlike domains, while the broad heat-capacity peak¹² was identified as gradual loss of order with increasing temperature in a liquid phase strongly

influenced by the substrate.

We can interpret our results for Ar on BN in similar terms. The presence of a substep in the isotherm is an indication of a discontinuity (albeit a small one) at melting between the densities of the 2D liquid and 2D solid. This argues in favor of a weakly first-order transition. Reasonable arguments can also be made in favor of interpreting the results in terms of continuous melting, however. The step size is quite small. 1.5% of a layer for a substep at solidification is smaller than what is found at a typical first-order phase transition (for CH₄ on BN the step is of order 4%). The value of the sharp compressibility peak is small. It is at least a factor of 2.5 smaller than that which we have measured for the first-order melting of CH₄ on BN.

The above discussion underscores the difficulty in discerning experimentally a weakly first-order transition from a continuous one. It would be highly desirable to have more information for Ar on BN (heat capacity as well as structural data) in the hope that it could, perhaps, enable us to resolve the question of the order of the melting transition. Given the similarities between Ar on graphite and on BN it is clear that the solution to this remaining question would apply equally to both systems.

In summary, we have measured adsorption isotherms of Ar on BN. They show only a small substep, corresponding to 1.5% of a layer, at the melting transition. The isothermal compressibility has two peaks: a sharp peak corresponding to melting and a broader one which occurs at lower pressures. The behavior observed for Ar on BN is very similar to that recently reported for Ar on graphite.¹¹ The two systems are very likely to have the same melting mechanisms.

We thank Dr. J. Z. Larese for helpful discussions regarding the melting of Ar on graphite. We thank Professor M. H. W. Chan and Professor H. Taub for suggestions on this manuscript.

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