Layer-by-Layer Melting of Argon Films on Graphite: A Neutron-Diffraction Study

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Elastic neutron diffraction is used to study the melting of multilayer argon films physisorbed on a graphite substrate. The layers are found to disorder sequentially from the outermost layer of the film toward the graphite surface with the melting of individual layers occurring gradually over a temperature range of about 10°. For films initially two or more layers thick the melting of the layer closest to the substrate occurs near 100 K. Comparisons are made with recent computer simulations and with thermodynamic measurements.

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During the past decade considerable progress has been made toward characterizing the melting of two-dimensional (2D) systems, especially with regard to monolayer films physisorbed on graphite.[1] However, a renewed interest in the melting properties of multilayer films and in bulk surface melting[2] underscores the fact that from a microscopic perspective a complete understanding of the melting process in three dimensions (3D) or quasi 3D is still far from being realized. Computer simulations,[3-5] diffraction studies of the premelting of metal surfaces,[6,7] and thermodynamic studies of the melting of multilayer films on graphite[8,9] have raised a number of questions concerning the role played by the outermost layers of a solid in this phase transition. In fact, evidence of atomic mobility in surface layers of solids at temperatures below the bulk melting point has been reported.[7,10] These results are particularly intriguing because it is widely recognized that the melting of 3D systems is always an abrupt first-order process whereas in some 2D studies evidence of continuous melting has been reported.[1,11] This suggests that a microscopic examination of surface melting could provide important insights into the basic mechanism by which bulk solids disorder.

In this Letter, detailed microscopic evidence for the layer-by-layer melting of multilayer argon films physisorbed on graphite is presented. The same powder neutron-diffraction techniques used in earlier investigations of the structure and stacking arrangements of one-to-four-layer methane and argon films[12] on graphite have been employed. These experiments exploit the changes which occur in the diffraction profiles as the system proceeds from 2D to 3D. The changes can be qualitatively understood by recognizing that the Bragg rod (which is the characteristic feature of a 2D reciprocal lattice) is modulated along its axis as additional layers of material are added. Ultimately the modulations coalesce into Bragg spots as the system becomes three dimensional. Therefore by monitoring the diffraction profiles as a function of initial film thickness and temperature a microscopic picture of the multilayer melting process can be derived. Restricting the measurements to films of finite thickness (i.e., ≤ 4 layers), which were characterized previously by detailed profile analysis,[12] circumvents the complications associated with capillary condensed bulk particles which appear to form at coverages beyond four or five layers.[11,13] It also avoids the difficulties encountered in premelting studies of bulk solids which require the detection of a surface signal several orders of magnitude smaller than the bulk background.

Our experiments were performed on the H5 triple-axis spectrometer at the High Flux Beam Reactor at Brookhaven National Laboratory. The spectrometer was operated in the elastic mode at an incident wavelength of 2.43 Å with a Q resolution of 0.02 Å^{-1}. Our film preparation and annealing techniques have been described previously.[12] Sample temperatures were controlled to better than 0.1 K. Our coverage scale is such that $X = 1.00$ represents a $\sqrt{3}\times\sqrt{3}$ solid phase.[11] As usual, background scattering from the sample cell and the graphite substrate was subtracted from the observed diffraction profiles.

Perhaps the greatest experimental difficulty associated with the study of multilayer melting arises when trying to separate the contribution of the liquid or disordered component of the scattering from that associated with the solid. As noted above, when there is no significant liquid contribution to the scattering a well-defined method of establishing the stacking sequence and structure of a multilayer solid already exists. To improve our sensitivity to the liquid signal in these experiments we simultaneously performed the usual powder-diffraction scans and monitored the total scattered intensity within a fixed-Q window as a function of temperature. Intuition tells us that the best place for the Q window is on the low-Q side of the leading edge of the argon (10) surface peak since the first and most intense peak of the liquid structure factor will appear there. In a separate experiment, scans of the liquid structure factor of monolayer argon films at several different densities were made. In these scans, in which the *monolayer* melting temperature varied from ≈ 50 K (at low density) to above 80 K near monolayer completion ($X \sim 1.3$), it was seen that the region 1.30 Å$^{-1} \leq Q \leq 1.70$ Å^{-1} was indeed the optimum window location.

But before proceeding further, let us make a few general comments concerning the type of information that can be obtained by monitoring the temperature dependence of the intensity in a fixed-Q window. At temperatures well below the melting temperature of an individual layer, sharp diffraction lines characteristic of well ordered solids will appear. A fixed-Q window located close to, ***but not at***, the leading edge of the first diffraction peak will yield only a small constant signal in this regime. As the temperature of the system is increased toward the melting point, however, the diffraction peak will broaden as the long-range order within the solid starts to decay. This means that for an *appropriately positioned* Q window, the recorded intensity will rise steadily until it ultimately saturates when the atomic arrangement, either within an individual layer or within the system as a whole, reaches a state characteristic of the liquid phase. The location of the Q window is very critical. If it is positioned too close to the (10) surface peak, either thermal expansion or restructuring of the local atomic environment of the solid part of the film (or both) could change the diffraction profile enough to preclude a simple interpretation of the temperature dependence of the intensity. On the other hand, if the window is too far from the (10) peak, there will be a loss of intensity and sensitivity. Within the framework of the present discussion a layer-by-layer melting process viewed via a Q window would appear as a sequence of vertical risers (associated with the melting of individual layers) separated by a series of horizontal plateaus, i.e., it will have a staircaselike shape. Not considered in this description is thermal desorption which depletes the number of atoms in the surface phase at higher temperatures.

Figure 1 illustrates the thermal evolution of an idealized three-layer ($X=4.00$) solid-argon diffraction profile as the film undergoes a layer-by-layer disordering process. The line shape, which is characteristic of an *ABC* stacked three-layer solid at low temperature, changes progressively as the temperature is raised until at temperatures near 90 K it evolves into the characteristic "sawtooth" profile of a solid-argon monolayer. As we will discuss below, this disordering process can be shown to start at the layer furthest from the substrate and to move inward. (Several intermediate temperature profiles have been omitted for the sake of clarity.) Panel (a) of the figure shows three profiles calculated as in Ref. 12 for a one-, two-, and three-layer *ABC*-close-packed structure. The experimental profiles in panel (b) are recorded at progressively higher temperatures, i.e., for a decreasing number of solid layers. In addition, both the Debye-Waller factor and the near-neighbor distance are expected to increase for the thinner solid films owing, respectively, to increased thermal motion and expansion of the lattice. Both effects were taken into account in the model profiles of Fig. 1(a). In fact, detailed fits to the experimental data (to be presented in a future longer paper) show clear evidence of increases in both thermally dependent parameters. The thermal evolution of the diffraction patterns shown here is representative of behavior observed in both two- and four-layer films except that there is an overall shift upward in the temperature scale at higher coverage. In addition to the detailed structural information which the data of Fig. 1(b) provide, it also contains information relating to the disordered or liquid component of the film.

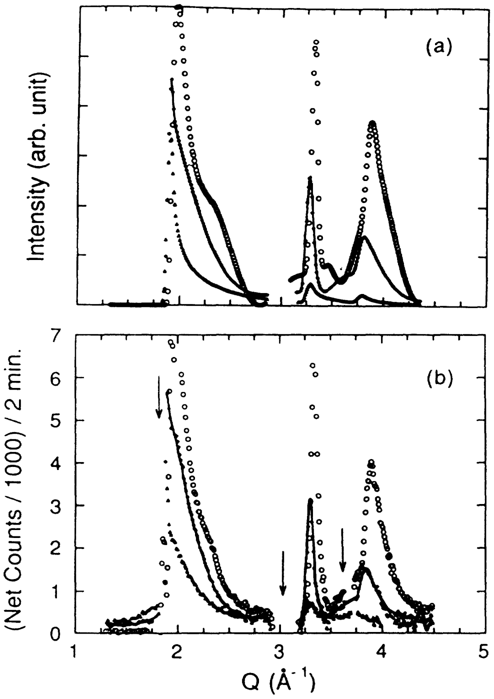

FIG. 1. (a) *Calculated* diffraction profiles for idealized *ABC* stacked three-layer (open circles) and *AB* bilayer (BL) (solid lines) close-packed solids, and a triangular monolayer (ML) (triangles). A near-neighbor distance (a_{nn}) of 3.76 Å and a 0.02-Å^2 Debye-Waller factor (DWF) was used for the trilayer, while an a_{nn} of 3.81 Å for both BL and ML solids was used with a DWF of 0.15 for the BL and 0.20 Å^2 for the ML. (b) *Experimental* diffraction profiles for an $X=4.00$ film recorded at 10 K (open circles), 77 K (solid lines), and 92 K (triangles) for, respectively, a three-layer solid, BL solid plus liquid, and a ML solid plus liquid. Notice the incremental increase in the scattering at low Q (~ 1.75 Å^{-1}). Arrows locate position of significant background diffraction peaks (Ref. 11). The solid line in (b) has been introduced for clarity and serves only as a guide to the readers eye.

Since all of our scattering experiments are performed in a closed cell (i.e., the total number of atoms is held constant), it is to be expected that as the system temperature is raised a signal with a structure factor characteristic of a liquid phase should appear if layer-by-layer melting occurs. As noted, the liquid-phase contribution to the scattering profile is most easily observed on the low-Q side of the first peak in the solid diffraction pattern. Examination of the scattered intensity in the region near $Q \sim 1.75$ Å^{-1} of Fig. 1(b) shows that this is exactly what occurs. As the thickness of the solid layer decreases, the signal at $Q \sim 1.75$ Å^{-1} rises proportionally, precisely the expected behavior if there is an increase in the disordered (liquid?) component. In fact, if the temperature of the three-layer system is raised beyond ~100 K, a diffraction pattern which strongly resembles that expected for a normal liquid appears.

Figure 2 displays the temperature dependence of the Q-window intensity recorded as a function of temperature for films which are nominally two and three layers thick at low temperatures. At each new temperature step (usually 0.5 K higher than the previous one) the system was equilibrated for approximately 1 h. Several general statements can be made concerning the Q-window data. First, we see that in both scans the scattering exhibits a staircaselike temperature dependence. The integers "3,2,1" indicate the number N of solid layers present at each temperature. The scans in Fig. 1(b) correspond to specific sections of the upper trace ($X = 4.00$) in Fig. 2. Except for a small decrease in magnitude as the temperature rises above 85 K, the individual steps represent increments of ~3800 counts. (The decrease in step height at elevated temperatures disappears when the data are corrected for thermal desorption.) Even though this correction was not applied to the data in the figure, they clearly indicate that a layer-by-layer melting process occurs. The uniformity of the steps also implies that the Q dependence of the liquid component of the scattering profile, as monitored by the Q window, does not change significantly. The rate of change of intensity as a function of temperature makes it clear that the progression from an N-solid-layer film to an $(N-1)$-solid-layer film is not an abrupt process but one that proceeds gradually (over a range of roughly 6° to 10° per step). This strongly suggests that layer disordering for thin argon films is not the discontinuous, first-order process that might have been expected.

Turning now to Fig. 3, we compare the solid structures that exist in the regions labeled "2" and "1" in the two traces of Fig. 2. It is remarkable how similar these two diffraction profiles are. Evidently the structure of a given layer depends only on N and is relatively independent of the initial thickness, X. In fact, the actual difference in the two monolayer traces of Fig. 3(b) shows up only in the region near 1.75 Å^{-1} and indicates, as would be expected, that the amount of liquid present is greater for the film with a larger initial thickness (i.e., for $X = 4.00$). In the bilayer solid profiles shown in Fig. 3(a) the $X = 4.00$ profile exhibits not only an enhanced liquidlike component but also a noticeable increase in the scattered intensity on the trailing edge of the first diffraction peak. Detailed fits to the data indicate that this extra intensity can be accounted for if one assumes a weak, residual correlation of the liquidlike third layer to the underlying solid layers. This suggests that although

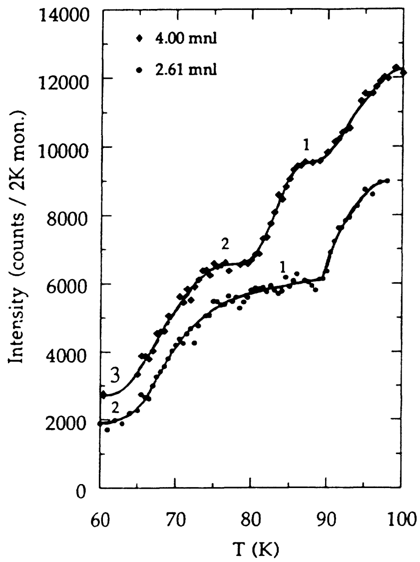

FIG. 2. Fixed Q-window scan (see text) displaying the layer-by-layer melting via the integrated intensity between 1.30 and 1.70 Å^{-1} as a function of temperature for argon films nominally two ($X = 2.61$) and three ($X = 4.00$) layers thick. The numbers 1, 2, and 3 on the horizontal portions of the traces indicate the nominal number of solid layers present at that temperature. The solid line has been introduced for clarity and serves only as a guide to the readers eye.

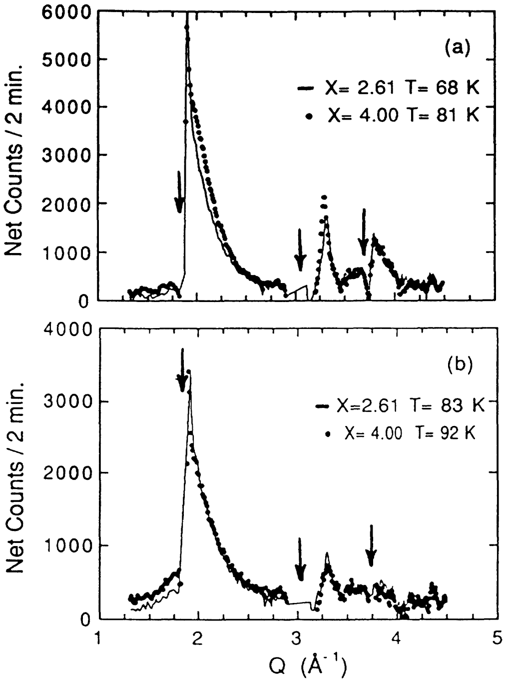

FIG. 3. Comparison of diffraction profiles for films initially two ($X = 2.61$, solid line) and three ($X = 4.00$, dots) layers thick. (a) Bilayer solid (BL) profile for $X = 2.61$ at 68 K and BL plus correlated liquid (L) for $X = 4.00$ at 81 K. (b) Monolayer solid (ML) profile plus L for $X = 2.61$ at 83 K with ML plus L for $X = 4.00$ at 92 K. Arrows locate position of significant background diffraction peaks (Ref. 11).

the atoms in the third layer possess only short-range order their atomic positions are influenced by the ordered layer below. Remarkably, the monolayer solid signal persists until we reach temperatures in excess of 100 K at which point the diffraction pattern becomes that of a typical liquid.

Cheng and Steele[4] and Phillips[5] have systematically modeled the melting of argon films several layers thick as a function of temperature. Their simulations of the argon multilayer melting process show an extended temperature range over which layer disordering and melting occurs. Furthermore, these simulations suggest that the melting process is initiated by the promotion of a few atoms to the layers above the solid layers of the film. This is then followed by a structural disordering within the outermost layer. First, a lattice liquid is formed due to the strong influence of the argon solid template below. Then, a more isotropic liquid phase develops as the melting process replicates itself within the layer below.

Our data can also be correlated with the recent heat-capacity studies of Zhu and Dash (ZD).[8] In particular, ZD find several heat-capacity anomalies which they interpret as evidence of the layer-by-layer melting of argon films on graphite. Although none of their measurements was made at exactly the coverages used in the present study, some general comparisons can nevertheless be made. First, a heat-capacity feature is present in the neighborhood of each vertical region of our Fig. 2. Further, ZD interpret their data as indicating the monolayer solid is stable at temperatures well above the bulk triple point of argon (83.8 K) for films ≥ 3 layers thick and that melting proceeds from the outermost layer towards the graphite substrate (although at films near five or six layers thick we believe that there are some inconsistencies which arise in this interpretation). Both features are consistent with our neutron findings. ZD regard the anomaly near 65 K in their higher coverage data to be the signal of film roughening. We observe a buildup of the Q-window intensity in precisely this region but we cannot say definitely that it is due to roughening. Attempts to pursue this question further by recording the scattering at small Q were frustrated by the large background from the graphite substrate in this angular range. There is one aspect of the ZD data interpretation that our measurements do not support, however. For argon coverages near four layers they see, in the neighborhood of the argon bulk triple point, sharp heat-capacity peaks with asymmetric shapes. These peaks become progressively more intense as the film thickness increases. ZD interpret this as evidence of surface melting. But at low temperatures in this coverage regime we find evidence of capillary-condensed particles of bulk argon coexisting with four or possibly five adsorbed solid layers. For these thicker films we also find a sizable increase in the Q-window intensity between 82 and 87 K. The magnitude of this signal increases proportionally with the number of effective layers added to the system in excess of five layers, a trend which continues to hold for gas dosages up to ten effective layers (the highest coverage studied). In our view this behavior is most simply explained as the melting of small, capillary-condensed particles, an interpretation consistent with the findings of a recent vapor pressure isotherm study.[13]

We noted above that our measurements support the view that melting proceeds from those portions of the film farthest from the substrate inward. The evidence we have for this is that the first disordering occurs in films nominally two layers thick (and greater) at a temperature *below* the onset of the melting transition of the compressed monolayer (~84 K). In fact, the melting of the layer closest to the substrate (in films initially thicker than two nominal layers) occurs at temperatures that approach 100 K. Presumably, these highly compressible, near-substrate solids are stabilized both by the presence of the atoms in the layer above and by the substrate holding potential. Finally, we want to emphasize that the melting of individual layers appears to be a gradual process extending over nearly 10° and that our results are remarkably consistent with both computer simulations[4,5] and heat-capacity measurements,[8] except in the latter case for certain details related—we believe—to capillary condensation.

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