Direct Observation of Layer-by-Layer Wetting of Graphite by Ethylene

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It has been demonstrated directly by use of x-ray diffraction that at temperatures below the triple point of bulk ethylene (103.8 K) adsorption of ethylene onto the basal planes of graphite only occurs up to a finite number of molecular layers. Further addition of molecules results in the formation of bulk crystallites. Reversible transitions between the total number of layers adsorbed and the coexisting bulk are observed.

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An important basic issue in surface science and in epitaxial film growth is the manner in which adsorbed materials evolve from monolayer coverage to thick films. Macroscopically, it is known that a liquid in coexistence with its vapor either may completely cover an adsorbing substrate or it may form droplets. The former case has been named complete wetting and the latter partial wetting. It has also been noted that both types of behavior may be observed in the same system depending on the temperature.[1] The transition from one type of behavior to the other occurs at the wetting temperature, T_w.

Recent theoretical work,[2] using a lattice-gas model to study adsorption, has predicted that there is a number of subclasses under the rubric *partial wetting* depending on the relative strengths of the adsorbate-adsorbate and the adsorbate-substrate interactions. For a certain range of relative interactions and temperatures these theories suggest that partial wetting consists of bulk particles coexisting with a finite number of adsorbed layers. For a given temperature, a well defined number of layers will coexist with the bulk; further this number of layers (n) should increase in discrete steps at successively increasing transition temperatures T_n. T_w corresponds to the temperature at which the T_n accumulate; above T_w an infinite number of layers form. On the basis of Menaucourt, Thomy, and Duval's[3] vapor-pressure isotherm measurements, Pandit, Schick, and Wortis[2] have suggested that ethylene on graphite may be a model system in which to study this novel behavior. Recent NMR measurements[4] also provide evidence for bulk-film coexistence in this system.

In this Letter we report the results of an x-ray–diffraction study in the region of one to four layers of ethylene adsorbed on graphite. The results provide direct structural evidence that with increasing temperature, one, two, and three layers of ethylene coexist with bulk ethylene particles. We also obtain interesting structural and thermodynamic information on the coexisting film and bulk phases.

The x-ray measurements were performed by utilizing a two-axis spectrometer with Cu-$K\alpha$ radiation in transmission through a sample of Union Carbide vermicular graphite.[5] This substrate has no preferred orientation, a large specific area, and a surface coherence length of ~1000 Å. Use of this loosely packed substrate is necessary to reduce the effect of capillary condensation. In addition, this substrate exhibits sharp vertical risers in multilayer-ethylene-adsorption isotherms—a clear prerequisite for these studies. The surface area is measured by a krypton-gas isotherm at 95 K and all coverages (f) are measured in units of a complete $\sqrt{3}\times\sqrt{3}$ monolayer. The experimental techniques are identical to those discussed by Heiney *et al.*[6]; the resolution was 0.012 Å^{-1}.

Concurrent with this work, neutron diffraction of C_2D_4 on graphite with emphasis on the monolayer region of the phase diagram has been carried out by Satija *et al.*[7] Indeed, preliminary communication of their results greatly facilitated this study. In general, our x-ray results in the monolayer-coverage region agree in detail with the neutron studies. We now discuss the results of our experiments.

The monolayer-coverage behavior is summarized below. Further details and a phase diagram are given in the accompanying Letter by Satija *et al.*[7] At low temperatures and for coverages below $f = 0.9$, ethylene forms a low-density (LD) triangular phase[7] characterized by a (1,0) peak at 1.56 Å^{-1}, incommensurate with respect to the graphite substrate. This peak position gives monolayer completion at $f = 0.84$. Between $f = 0.9$ and $f = 1.1$ this phase coexists with a high-density (HD) incommensurate phase with the primary Bragg peak at $Q_0 = 1.72$ Å^{-1}. Under the assumption of a triangular lattice, this corresponds to $f = 1.02$. This latter structure is observed for all $f \geq 1.1$ and $T \leq 73$ K. By analogy with oxygen on graphite,[6] lattice-constant and molecular-structure considerations suggest that this phase transition originates in a structural reorientation in which the ethylene molecule goes from having its C-C bond parallel to perpendicular to the surface.

The LD structure melts at a temperature of 68 K for coverages less than $f = 0.8$.[4,7] This melting temperature increases with increasing coverage above 0.8 until at $f = 1.10$ it reaches $T \simeq 90$ K. The HD phase transforms on heating at $T = 73$ K into a lower-density structure. This structure is characterized by a peak at 1.60 Å^{-1} and indeed, this phase probably connects continuously with the submonolayer LD phase. This lower-density phase which exists for high temperatures for coverages between one and two layers also melts at $\gtrsim 90$ K. As we shall discuss later, the solid two-dimensional (2D) peaks in the monolayer region are satisfactorily explained by standard 2D diffraction theory.

We now present our results for coverages beyond a monolayer. These, of course, constitute the principal results of this study. Figure 1 shows the evolution of the diffraction profile as the temperature is varied at a constant coverage of $f = 3.68$. For simplicity we discuss the behavior with increasing temperature. As is immediately evident from Fig. 1, the most striking feature of the profile at 56.7 K is the presence of several symmetric peaks. These peaks index with the known monoclinic crystal structure of solid bulk ethylene.[8] The small peak between the (110) and (011) bulk peaks is just the 2D peak seen in the HD phase at $f = 1.1$. Indeed as the amount of condensed ethylene in the cell is increased from $f = 1.1$ for temperatures $\leqslant 73$ K, the intensity and position of this peak remain unchanged while the bulk peaks grow linearly in intensity. This demonstrates conclusively the coexistence of one monolayer of ethylene with bulk particles in this temperature range.

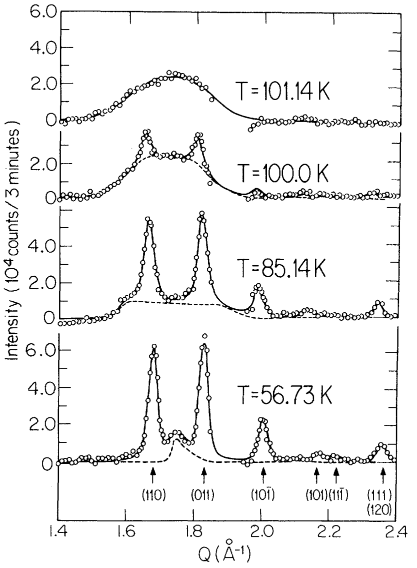

FIG. 1. X-ray scattering profiles at a coverage of $f = 3.68$ and several temperatures. Graphite backgrounds of ~10 000 counts/min have been subtracted and data from $Q = 1.85$ to 1.95 Å^{-1} are not plotted because of the graphite (002) reflection. To improve clarity not every data point is shown. The solid lines are fits to the data as discussed in the text. The arrows indicate the bulk ethylene Bragg peaks. The changes in their position reflect 2D expansion. The dashed lines show the empirical film line shapes used in the fits.

All bulk diffraction profiles may be fitted with the fixed peak intensity ratios and line shapes determined from data taken at $f = 10.5$. The intensity ratios agree to within 15% with the known structure of solid C_2H_4. The line shape for each peak is a Gaussian with Q^{-2} tails to account for a finite-size cutoff. The peak half-widths are all close to the spectrometer resolution of 0.012 Å^{-1}, requiring that the crystallites have linear dimensions of at least 300 Å in all directions.

As the temperature is increased for $f = 3.68$ the profile does not change until at $T \simeq 75$ K the bulk intensity drops while the 2D scattering changes to a profile characteristic of a bilayer of ethylene. The bilayer-plus-bulk profile is shown in Fig. 1 for $T = 85.14$ K. Above 98.4 K the bulk intensity again drops and the 2D scattering which is now fluidlike changes again. Finally, above 101 K all signs of bulk disappear. These transitions all occur well below the triple point of ethylene. Fits to the scattering profiles at 56.73, 85.14, 100.0, and 101.14 K at $f = 3.68$ are shown in Fig. 1. As we shall discuss below, fits to these spectra as well as those at many intermediate temperatures clearly show the coexistence of bulk with one layer, two layers, and three layers, as well as the existence of transitions between them.

Figure 2 shows the evolution of the diffraction profile with increasing coverage at a constant temperature of 83.3 K. From the results in Fig. 1 we expect that at 83.3 K up to two adsorbed layers will be stable. It is evident from Fig. 2 that a monolayer line shape provides a good, albeit not perfect, description of the lowest-coverage peak ($f = 0.918$). At a coverage $f = 1.55$, equaling 1.8 ethylene monolayers, the 2D line shape has changed significantly from that at 0.918 and there

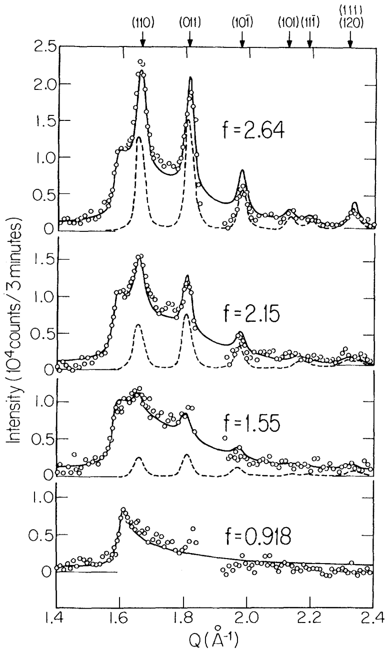

FIG. 2. X-ray scattering profiles at selected coverages for $T = 83.3$ K; the solid lines are the results of fits by 2D-plus-bulk scattering as discussed in the text. The arrows indicate the bulk peaks whose contribution is shown by the dashed line.

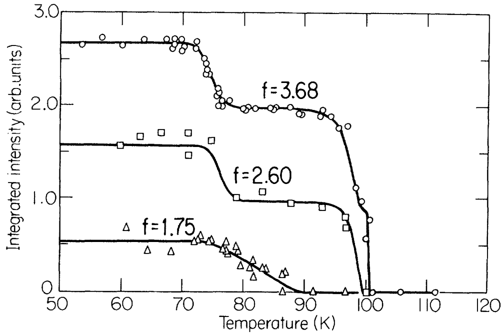

FIG. 3. Integrated intensity of the bulk ethylene peaks for several coverages as a function of temperature. Solid curves are drawn as a guide to the eye; the intensity scale is normalized to 2.7 for $f = 3.68$ at low temperatures. The knee for $f = 3.68$ near 100 K is inferred from the knowledge that $T_3 = 98$ K.

is evidence for a small amount of bulk scattering. The solid line in Fig. 2 for $f = 1.55$ corresponds to the line shape of a close-packed bilayer structure with $Q_0 = 1.58$ Å^{-1} together with a small bulk contribution. The figure shows that as the amount of condensed ethylene is increased above $f = 1.55$ the intensity of the bulk peaks increases, while the film scattering does not change. One of the curious features of the scans is that the bulk appears at vapor pressures well below the saturated vapor pressure of ethylene; indeed the vapor pressure increases continuously with increasing coverage for all of the scans shown in Fig. 2. The existence of solid below the saturated vapor pressure could be an intrinsic feature of this multicomponent system although it more likely originates in capillary condensation between graphite crystallites.

The two-layer line shape used in Fig. 2 overestimates the scattering around 2.0 Å^{-1}. As the temperature is increased this discrepancy worsens; we do not understand the details of the multilayer structure and indeed, additional single-crystal information will be required before the structure can be properly determined. In order to extract the bulk intensity properly we have used an empirical line shape for the film profile and then fitted the total scattering.

Our results for the bulk intensity so obtained at three different coverages are summarized in Fig. 3. We emphasize first that the bulk intensity scales linearly with the total amount of material added to the cell minus the amount in the layers. The size and position of the steps in the bulk intensity are conclusive evidence of discrete incomplete wetting[2] temperatures of $T_2 = 75$ K, $T_3 = 98$ K, and $T_4 = 101$ K; this is the principal result of this paper. We have also observed a slight hysteresis, of the order of 2 K, at T_2 and T_3.

We emphasize that the layering transitions are distinct from the structural and melting transitions in the film. For low values of f the high-density–low-density transition occurs at a temperature below that of the disappearance of the bulk. For high cell density the T_2 transition temperature decreases, overlapping that of the HD-LD transition. The melting transition of the bilayer film occurs at a lower temperature than T_3.

Two features of Fig. 3 require further explanation—the decrease of the monolayer-bilayer transition temperature with increasing cell density and the finite slope through the transition regions. Both of these features reflect a distribution of chemical potentials again possibly due to capillary condensation. On an ideal graphite surface the monolayer-bilayer transition temperature should be a triple point, thus occurring at a well defined temperature and pressure.

These experiments thus confirm some aspects of the novel behavior predicted by Pandit, Schick, and Wortis[2] for a "class-II system" in the layering subregion. Much work remains to be done in the still higher coverage region. Of ultimate interest is the wetting transition itself. Our preliminary high-layer data, supported by the isotherm measurements of Menaucourt, Thomy, and Duval,[3] indicate that the wetting temperature is very close, if not identical, to the bulk triple-point temperature T_t. This is a surprising result since T_w depends on the adsorbate-substrate interaction while T_t is purely a property of the bulk. If the wetting temperature is at or higher than the triple-point temperature ethylene should exhibit prewetting or possibly critical wetting transitions. We should also emphasize that it will be necessary to extend the lattice-gas theories to include bulk triple-point behavior in order to make quantitative contact with the ethylene-graphite system.

In all of our scans the bulk peaks are close to being resolution limited. Simple volume considerations show that at a layering (or rather incomplete drying) transition with decreasing temperature, ethylene molecules from many different surfaces must agglomerate to form a bulk crystallite. It is clearly important to study the size, shape, and orientation of the bulk crystallites and their evolution through the successive transitions. This should be possible with use of high-resolution synchrotron techniques; such experiments are planned in the near future. Finally, we note that the coexistence of layers with bulk crystallites is familiar in epitaxial film growth under the name "Stranski-Krastanov growth mode." The system of ethylene on graphite should provide a model equilibrium system to study this growth mechanism.

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