

## Multilayer adsorption of ethylene on graphite: Layering, prewetting, and wetting

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We report the results of a comprehensive x-ray-scattering study of multilayer ethylene physisorbed on graphite. At temperatures well below the triple point of bulk ethylene (103.8 K), adsorption only occurs up to a finite number of layers; any further addition of material results in the nucleation of bulk crystallites. The number of layers that coexist with bulk increases at successively increasing transition temperatures. Reversible, first-order transitions between the total number of layers adsorbed and the coexisting bulk are observed at  $T=75$  K (one to two layers) and at  $T=98$  K (two to three layers). Bulk particle-size information is obtained as a function of both temperature and the amount of material in the cell. We present evidence that suggests that ethylene undergoes a thin-film to thick-film transition immediately below the triple point and that the triple point is the wetting temperature of ethylene on graphite. Pronounced hysteresis effects are observed both at the layering transitions and in the neighborhood of the triple point.

### I. INTRODUCTION

Two-dimensional systems consisting of a single layer of atoms or molecules adsorbed on an attractive substrate have been extensively studied.<sup>1</sup> However, given a substrate and an adsorbate, it is also natural to pose the question of how the adsorption of material evolves from monolayer to macroscopic coverage. We present x-ray measurements for the case of multilayer ethylene physisorbed onto the basal planes of graphite in the region of one to eight layers. The results provide direct structural evidence that with increasing temperature, one, two, and three layers of ethylene coexist with particles of bulk ethylene. We also provide evidence that suggests ethylene adsorbed on graphite undergoes a thin-film (two layers) to thick-film (continuously variable from three to many layers) prewetting transition below its bulk triple point. Structural and thermodynamic information on the coexisting film and bulk phases is also presented.

In the context of gas-liquid coexistence in the presence of an attracting wall, two different types of behavior are possible.<sup>2</sup> Depending on the surface tensions between the three "phases," the liquid may either form droplets, with a finite angle of contact to the substrate, or it may completely cover the substrate, interposed between gas and wall. In this latter case the liquid is said to "wet" the substrate. In general, the three different surface tensions will vary differently with temperature. Therefore, it is possible to go from one type of behavior to the other at a temperature called the wetting temperature. In particular, as first noted by Cahn,<sup>2</sup> sufficiently close to, but below, the liquid-gas critical point, the liquid must wet the substrate. The importance of wetting concepts to multilayer absorp-

tion has been noted by Dash<sup>3</sup> and Ebner and Saam.<sup>4</sup>

Our interest in the phenomenon of wetting was initiated by the work of Pandit, Schick, and Wortis.<sup>5</sup> These authors introduced a simple lattice-gas model (see also Ref. 6) that contains the minimal ingredients necessary to describe the physics of multilayer adsorption. Based on a mean-field analysis of this model, together with certain known results, Pandit *et al.* suggested a variety of possible phase diagrams. The topology of a phase diagram depends crucially on the ratio of the adsorbate-substrate interaction ( $u$ ) to the adsorbate-adsorbate interaction ( $v$ ). Following Pandit *et al.*, we suppose that  $v$  fixes the energy scale, and then describe the three types of behavior as  $u$  varies.

For large  $u$  (the strong substrate regime) an infinite number of first-order layering transitions exist, each transition ending at a critical point. At any temperature, as the chemical potential is increased, the film thickness increases and the excess surface density ( $n_s$ ) diverges as bulk coexistence is approached (complete wetting). As the number of layers becomes large, the critical temperatures of the layers tend to a limiting temperature ( $T_R$ ). Pandit *et al.* identify this temperature with the roughening temperature for that particular bulk crystallographic face. Above  $T_R$  the growth is smooth and in this region layers cannot be distinguished.

The intermediate substrate regime, with  $u$  comparable to  $v$ , is characterized by a new temperature, the wetting temperature ( $T_W$ ). Above  $T_W$ ,  $n_s$  again diverges at bulk coexistence, but below  $T_W$  the film thickness is always finite (incomplete wetting). The relative values of  $T_W$  and  $T_R$  define three subregions. Below  $T_W < T_R$ , there is a finite, well-defined number of layers at coexistence; fur-

ther, this number of layers ( $n$ ) increases in discrete steps at successively increasing transition temperatures  $T_n$ . Throughout this paper, the term layering transitions refers specifically to the transitions at bulk coexistence.  $T_W$  corresponds to the temperature at which the  $T_n$  accumulate; above  $T_W$  the number of layers is infinite at coexistence and film growth then proceeds as in the case of a strong substrate. If  $T_R < T_W$ , since layers cannot be distinguished, the layering transitions collapse into a single thin-film to thick-film transition, which is termed "prewetting." This then is the prewetting subregion. If  $T_R \ll T_W$ , the prewetting line shrinks to a critical wetting transition at bulk coexistence. This identifies the critical wetting subregion. Finally, for yet weaker substrates the surface is always incompletely wet.

As recognized by these authors the lattice-gas theory is an oversimplification. Two major effects are not included: Firstly, there is only one dense phase, whereas in real systems there are both liquid and solid phases; secondly, since the structure of the film and the bulk are the same, the model cannot describe effects due to differences between film and bulk structure.

Pandit and Fisher<sup>7</sup> considered the effect of bulk triple points on wetting behavior. They remarked that different bulk phases, for example, liquid and solid, may have quite different interactions with the substrate; concomitantly there may be a discontinuous change in the wetting behavior induced by the bulk triple point. In the language of Ref. 5, this might correspond to a discontinuous change in  $u/v$  at the triple point. Equally, one can imagine that a phase transition in the film itself, such as two-dimensional (2D) melting or a 2D structural phase transition, would have a similar result.

There are two solid allotropes of bulk ethylene.<sup>8</sup> The high pressure modification forms a body-centered-cubic plastic crystal of the space group  $O_h^9$  ( $Im\bar{3}m$ ), with the molecules orientationally disordered. In this paper we will be solely concerned with the low-pressure phase. The structure of this phase is illustrated in Fig. 1. It is monoclinic of space group  $C_{2h}^5$  ( $P2_1/n$ ), with two molecules in the unit cell. The gas-liquid-solid triple point occurs at  $T_t = 103.8$  K and  $P_t = 0.876$  Torr.

The first investigation of ethylene adsorbed on graphite was that of Menaucourt, Thomy, and Duval.<sup>9</sup> Their vapor-pressure isotherm measurements reveal that instead of undergoing a large number of layering transitions at low temperatures, as do, for example, krypton and methane on graphite,<sup>10</sup> the number of ethylene layers is limited and depends on temperature. For temperatures below 80 K only a single layer adsorbs before the bulk vapor pressure is achieved. With the addition of more ethylene, bulk solid is therefore nucleated without further layer formation. Between 80 and 98 K there are two layering transitions, while above 98 K there are three. Above  $T_t$ ,  $n_s$  increases beyond three layers, but there is no evidence for further layering transitions. From their measurements Menaucourt *et al.* deduce the critical points for the layering transitions ( $T_{nc}$ ) to be  $T_c = 114.2$  K and  $T_{2c} = 119$  K, and they estimate  $T_{3c}$  to be around 116 K.

Laresse and Rollefson<sup>11</sup> performed an NMR study of ethylene adsorbed on Grafoil for temperatures between 55

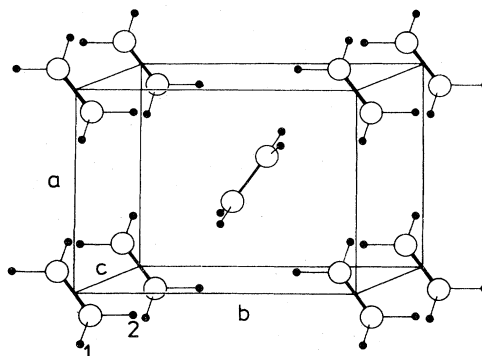


FIG. 1. Monoclinic structure of bulk solid ethylene, which has space group  $C_{2h}^5$  ( $P2_1/n$ ), with two molecules per unit cell. At 100 K the lattice parameters are  $a=4.669$  Å,  $b=6.628$  Å,  $c=4.101$  Å, and  $\beta=94.4^\circ$  (Ref. 6).

and 110 K and coverages between  $f=0.5$  and 2.0 ( $f=1$  corresponds to a complete  $\sqrt{3} \times \sqrt{3}$  monolayer coverage). Using the minimum of the nuclear magnetic spin-lattice relaxation time as a signature for melting, they deduced the melting line of two-dimensional solid ethylene. Below  $f=0.81$  the melting temperature was constant at  $T=69$  K. For coverages between  $f=0.81$  and 1.1 the melting temperature increased sharply with coverage to a final value of  $T=89$  K. The large spin-spin relaxation time observed demonstrated that the 2D solid is orientationally disordered at least down to temperatures of  $T=55$  K. Below  $f=1.3$  they found that the signal from the film increased with coverage. Beyond  $f=1.3$ , however, there was no further increase in the signal from the film. For very high coverages ( $f=10$ ) they saw a signal with a short decay time with the same temperature dependence as that of bulk ethylene. From this they inferred that above about  $f=1.3$  the excess ethylene formed bulk solid.

Concurrent with this work, neutron diffraction from deuterated ethylene on Grafoil, with emphasis on the monolayer region of the phase diagram, has been carried out by Satija *et al.*<sup>12</sup> Indeed, preliminary communication of their results greatly facilitated this study. Where our results overlap with theirs, we agree in detail.

There are several other systems in the literature which display incomplete wetting behavior. For example, oxygen,<sup>13-15</sup> ammonia,<sup>16</sup> and carbon tetrafluoride<sup>17</sup> on graphite all exhibit an increasing number of layering transitions as the temperature is increased. Recently Sequin *et al.*<sup>18</sup> have performed high-energy electron diffraction (HEED) studies at low temperatures on a number of systems, and have shown that while the low- (essentially zero) temperature behavior of xenon and argon is to wet graphite completely, both nitrogen and neon can only form two layers before bulk starts to form.

Considerations about wetting should have important implications for thin-film fabrication techniques. In the study of epitaxial film growth the coexistence of the bulk structure with layers, which are in this case chemically bonded to the substrate, is familiar under the name of "Stranski-Krastanov growth mode."<sup>19</sup> One of the most studied cases is the growth of a silver film on the  $7 \times 7$

reconstructed Si(111) surface. For temperatures greater than 200°C a single layer of silver may form. Upon exposure to more silver, bulk crystallites form. This is strikingly demonstrated by Venables *et al.*,<sup>20</sup> who provide beautiful scanning electron-microscope pictures that show faceted silver crystallites growing on the silicon surface. Most fabrication techniques use highly nonequilibrium processes and kinetic effects dominate. Here we only discuss effects that happen in thermodynamic equilibrium.

The format of this paper is as follows. The experimental details are given in Sec. II. The low-resolution data are presented in Sec. III. In Sec. IV we present the high-resolution data. Finally, in Sec. V we draw our conclusions. A preliminary report of the low-resolution experiments was given in Ref. 21.

## II. EXPERIMENTAL METHODS

Two experimental configurations were utilized. Firstly, at Massachusetts Institute of Technology (MIT), an extensive set of low-resolution measurements was performed using a 12-kW rotating-anode x-ray generator, operating at 10 kW, and, secondly, a more restricted series of high-resolution measurements was done using synchrotron radiation at the Stanford Synchrotron Radiation Laboratory (SSRL). In the low-resolution experiments, a two axis configuration was used. Bragg reflection from a 2 in. high  $\times$  1 in. wide vertically focusing pyrolytic graphite (002) monochromator selected copper  $K_\alpha$  radiation ( $\lambda = 1.54$  Å). The beam was collimated by slits before and after the monochromator and immediately before the sample and by Soller slits after the sample. The resultant longitudinal in-plane resolution was  $0.012$  Å<sup>-1</sup> half-width at half maximum (HWHM). For further details see Ref. 22. The high-resolution experiments utilized synchrotron radiation from the eight-pole wiggler on Beamline VII-2 at SSRL.<sup>23</sup> The x-rays were focused by glancing angle reflection from a platinum-coated mirror, and monochromated by a double Ge(111) asymmetrically cut monochromator tuned to the iron  $K$  adsorption edge ( $\lambda = 1.742$  Å). The analyzer was also Ge(111). This configuration provided a longitudinal resolution of  $0.0005$  Å<sup>-1</sup> HWHM.

Both experiments used similar volumetric equipment and techniques. The sample cells were cooled in Displex closed-cycle cryostats. The temperature was controlled and measured between 12 K and room temperature with platinum and germanium resistance thermometers at MIT and silicon diodes at SSRL. The pressure was measured with a 10-Torr Baratron pressure gauge. The cylindrical sample cells were made of beryllium.

The substrate used was Union Carbide vermicular graphite. This has no preferred orientation, a large specific area, and, as we shall demonstrate, a surface coherence length of 500 Å.<sup>24</sup> The use of such a loosely packed substrate is necessary to reduce the effects 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 was measured by a krypton adsorption isotherm at 95 K and, as is usual, all coverages ( $f$ ) are presented in units of a complete  $\sqrt{3} \times \sqrt{3}$  monolayer. In the present case, mono-

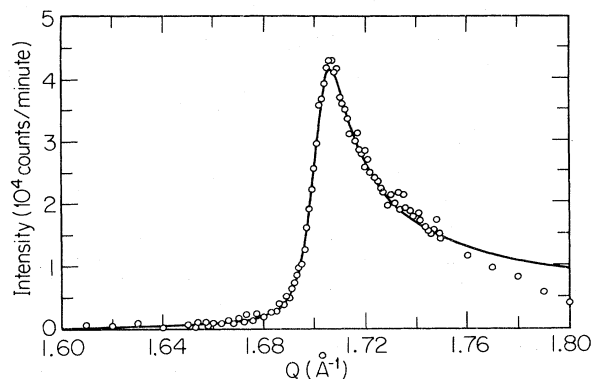


FIG. 2. X-ray scattering profile of a commensurate krypton monolayer measured at SSRL. A graphite background of  $\sim 9000$  counts per minute has been subtracted. The solid line is a fit to the data as described in the text. To improve clarity not every data point is shown in this and succeeding diffraction profiles.

layer coverage corresponded to  $2.4 \times 10^{20}$  molecules in the SSRL sample and somewhat more than half that at MIT. Before each experiment the graphite was prepared by baking at 900°C under a vacuum of better than  $10^{-5}$  Torr for several hours, and loading it into the cell in a clean nitrogen atmosphere.

The scattering from 2D crystals adsorbed on a randomly oriented substrate depends on both the intrinsic line shape and the powdered nature of the substrate.<sup>25</sup> Figure 2 shows the resultant scattering from the (10) Bragg rod of a monolayer of commensurate krypton measured at SSRL. The resolution of the spectrometer is smaller than the separation of neighboring experimental points. The solid line is fit to a powder-averaged, finite-size-limited, Gaussian line shape as is appropriate for a commensurate overlayer with a finite crystallite size of 500 Å. This line shape is commonly referred to as a Warren line shape.<sup>26</sup> This length may be contrasted to the surface coherence length of around 150 Å for Grafoil. The Warren line shape fits the krypton profile exceptionally well, except near  $Q = 1.80$  Å<sup>-1</sup>. We believe that the discrepancy at high  $Q$  is due to a modification of the graphite (002) peak by the overlayer of krypton.

## III. LOW-RESOLUTION RESULTS

The putative ethylene-graphite phase diagram is shown in Fig. 3. The solid lines indicate boundaries between two phases; the dashed lines correspond to triple points.

In the submonolayer regime adsorbed ethylene forms a triangular solid characterized by a (10) peak<sup>12</sup> at  $Q_0 = 1.56$  Å<sup>-1</sup>. Following the authors of Ref. 12, we label this phase the low-density (LD) phase. For coverages less than  $f = 0.8$  the LD phase melts<sup>11,12</sup> at a constant temperature of 68 K. This suggests that 68 K is a 2D gas-liquid-solid triple point as found, for example, for xenon on graphite.<sup>27,28</sup> This observation, together with the knowledge that  $T_{1c} = 114$  K, leads to the submonolayer phase diagram shown.

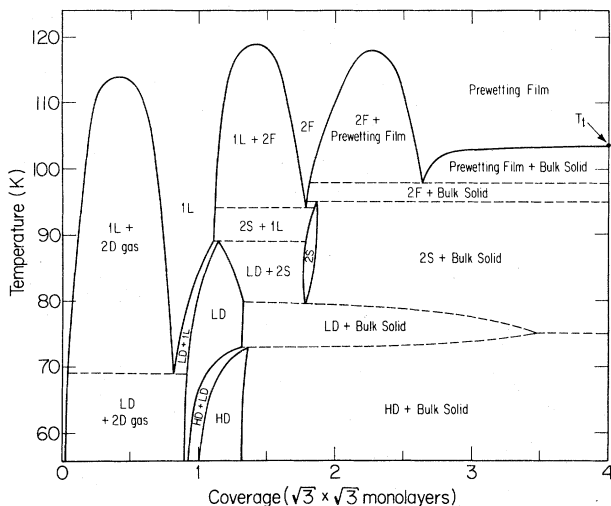


FIG. 3. Tentative ethylene-graphite phase diagram. The solid lines indicate boundaries between two phases; the dashed lines correspond to triple points. The precise location of phase boundaries is speculative. See the text for a discussion.

Beyond  $f=0.8$  the melting temperature of the LD phase increases sharply with coverage. At  $f=0.86$  the LD phase melts between 85 and 90 K. We have illustrated LD melting as a first-order transition for simplicity. For a range of coverages it could equally well become second order, as does, for example, xenon on graphite. At a coverage of  $f=0.93$  for low temperatures we observe coexistence between the LD phase and a high-density (HD) phase. The HD phase is incommensurate with the primary Bragg peak at  $Q_0=1.72 \text{ \AA}^{-1}$ . No further peaks from this phase have been observed, but were it to form a triangular lattice the (11) peak would be masked by the substrate's graphite(100) peak. Under the assumption of a triangular lattice, this wave vector gives monolayer completion at  $f=1.02$  (an areal density of  $f=1$  corresponds to a triangular lattice with  $Q_0=1.70 \text{ \AA}^{-1}$ ). As the temperature is raised the intensity of the LD peak grows relative to that of the HD phase; thus we infer that we are traversing a coexistence region. By  $\approx 67 \text{ K}$  only the LD peak remains, now with  $Q_0=1.60 \text{ \AA}^{-1}$ . Reference 12 suggested that this might be a new intermediate-density phase (ID), but in the absence of any evidence to the contrary we shall suppose that this does indeed evolve continuously from the lower-temperature LD phase. Evidence in support of this hypothesis is provided by the NMR measurements.<sup>11</sup> These show that throughout the region we have labeled LD on the phase diagram, the molecules retain complete rotational mobility.

For coverages greater than  $f=1.0$  only the HD phase remains and this phase is then stable for all  $T \leq 73 \text{ K}$ , as shown. Lattice constant and steric considerations suggest that this phase transition originates in a structural change in which the ethylene molecules transform from an orientationally disordered phase, but with the C—C bond parallel to the substrate, to one having the C—C bond perpendicular to the substrate. A similar lying-down to standing-up transition is observed<sup>13</sup> in adsorbed  $\text{O}_2$ , which

is also nonspherical. In the HD phase at higher temperatures the ethylene molecule is presumably rotating about its C—C axis. Therefore, both the LD and HD phases have orientational disorder. Consequently, at low temperatures, as pointed out by Satija *et al.*<sup>12</sup> for the LD phase, one would expect the molecules to order orientationally with a herringbone structure in both the LD and the HD phases. This was not observed down to a temperature of 12 K for the LD phase,<sup>10</sup> but the behavior of the HD phase was not investigated. Further NMR studies would be useful in this respect.

We now present our results for coverages in the multilayer regime. These form the principal focus of this study. One way to understand easily the nature of the adsorption isotherms of Ref. 9 is to measure the diffraction profiles at various positions along an isotherm. Figure 4 shows the evolution of the diffraction profile with increasing coverage at a constant temperature of 83.3 K. At this temperature we would expect up to two layers of ethylene to be stable. A monolayer line shape ( $Q_0=1.58 \text{ \AA}^{-1}$ ) provides a good, albeit not perfect, description of the lowest coverage peak ( $f=0.918$ ). In the case of adsorbed crystals incommensurate with the substrate the intrinsic line shape is a power-law decay about the positions of the zero-temperature Bragg peaks. As discussed by Heiney

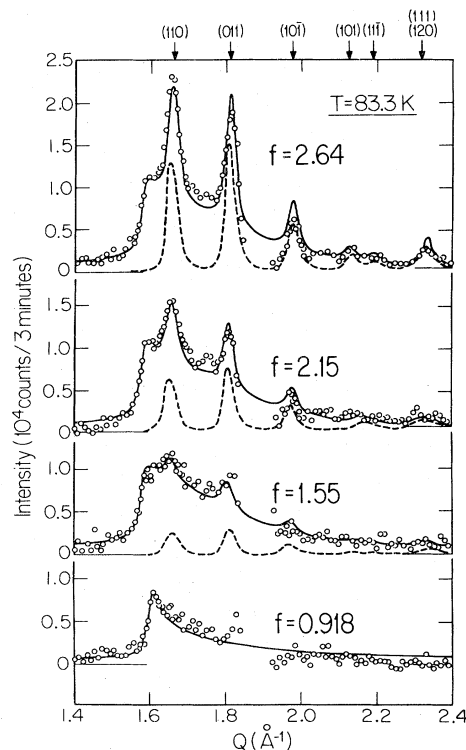


FIG. 4. X-ray scattering profiles measured at MIT at selected coverages for  $T=83.3 \text{ K}$ . The solid lines are the results of fits to 2D-plus-bulk scattering as discussed in the text. The arrows indicate the bulk peaks whose contribution is shown by the dashed line. Graphite backgrounds of  $\sim 10000$  counts per minute have been subtracted and data from  $Q=1.85$  to  $1.95 \text{ \AA}^{-1}$  are not plotted because of the strong graphite(002) reflection.

*et al.*,<sup>28</sup> this line shape, when convoluted with the instrumental resolution function, is very well approximated by a Lorentzian profile convoluted with the resolution function, and for computational simplicity this latter form was used to describe the scattering from solid monolayer ethylene. The half-width of the Lorentzian used was  $0.003 \text{ \AA}^{-1}$ , as was found appropriate for describing the scattering from a floating solid for data taken at comparable resolution in Ref. 28.

By a coverage of  $f=1.55$ , the film profile has changed to that characteristic of a solid bilayer of ethylene. We have labeled this the  $2S$  phase. It is also important to notice that there is a small amount of extra scattering indicated by the dashed line. The bilayer scattering was fit with a model of two close-packed triangular lattices. The quality of the fits shows consistency with this model, but certainly not uniqueness. In any case the primary wave vector of this phase appears at  $Q_0=1.58 \text{ \AA}^{-1}$ . If this is indeed the (10) peak of a close-packed triangular lattice, then bilayer completion is at  $f=1.73$ ; thus  $f=1.55$  corresponds to 0.9 ethylene bilayers.

It can be seen that our model overestimates the scattering around  $2.0 \text{ \AA}^{-1}$ . The discrepancy increases for higher temperatures and coverages where the film scattering is fluidlike. One possible explanation is a modification of the graphite(002) peak centered at  $Q_0=1.88 \text{ \AA}^{-1}$  by the ethylene overlayer. We do not understand the details of the film line shapes and believe that additional single-crystal information will be required before the line shape is completely solved.

For coverages above  $f=1.55$  the scattering acquires several sharper symmetric peaks which grow in intensity as the amount of condensed ethylene increases while the bilayer scattering remains constant. As the figure shows, the extra peaks can be indexed by the known monoclinic crystal structure of solid bulk ethylene. The relative intensities of these extra peaks also agree to better than 15% with those calculated from the crystal's structure factor. We can therefore conclude that these extra peaks are the scattering from a powder of bulk ethylene crystallites. This confirms the deductions made from the isotherm and NMR measurements, and shows the coexistence of bilayer and bulk ethylene.

The contribution to the scattering from bulk  $C_2H_4$  has been modeled by a line shape with seven peaks in the range of  $Q$  from  $1.4$  to  $2.4 \text{ \AA}^{-1}$ . The integrated intensity ratio of these peaks was fixed using the intensities from data taken at  $f=10.5$ . Each peak line shape is the sum of a Gaussian and a Lorentzian having the same half-width and a ratio of areas set to 1:1.3. The  $q^{-2}$  tails of the Lorentzian for the three-dimensional (3D) peaks arise from the finite-size cutoff of the Fourier sum. The positions of the seven peaks were determined by fitting the four lattice constants of the monoclinic structure. There is thus just one overall integrated intensity constant characterizing the bulk scattering. For all of the low-resolution data the half-width of the bulk peaks was fixed at  $0.016 \text{ \AA}^{-1}$ ; this appears to be somewhat larger than the resolution of  $0.012 \text{ \AA}^{-1}$ .

One curious feature of the scans is that the bulk first appears at a vapor pressure well below the saturated vapor

pressure of bulk ethylene; indeed, the pressure increases continuously with increasing coverage for all the scans shown in Fig. 4, from 0.011 Torr at  $f=1.55$  to 0.013 Torr at  $f=2.64$ . These values have not been corrected for thermal transpiration. As we discuss below, we believe that the existence of solid below the saturated vapor pressure of bulk ethylene is a result of capillary condensation.

Figure 5 shows the evolution of the integrated intensity of the bulk scattering versus coverage at a temperature  $T=97.5 \text{ K}$ . At this temperature the x-ray profile shows the film to be a fluid. We find coexistence of bulk solid with a 2D fluid commences at about  $f=1.8$ , and, as expected the bulk intensity grows linearly with "coverage." The zero intercept of  $f=1.8$  is close to the value 1.73 expected for  $Q_0=1.58 \text{ \AA}^{-1}$ .

An alternative way to cross the phase diagram is to change temperature while keeping the amount adsorbed constant. Figure 6 shows data taken at several temperatures and a constant coverage of  $f=3.68$ . The  $T=56.73\text{-K}$  profile again shows a superposition of film and bulk scattering. The dashed line in the figure corresponds to the scattering from a monolayer of ethylene with a peak position now at  $1.72 \text{ \AA}^{-1}$ , as expected for the HD phase.

As the temperature is raised the scattering remains unchanged until at  $T \approx 75 \text{ K}$  the bulk intensity drops precipitously while the film scattering changes to a profile characteristic of a solid bilayer of ethylene. For this coverage the two transitions appear coincident. A bilayer-plus-bulk profile is shown at  $T=85.14 \text{ K}$ . Lower coverages data clearly show that at this temperature the bilayer is solid. Above  $98.4 \text{ K}$  the bulk intensity again drops and the film scattering changes again. Finally, above  $101 \text{ K}$  all signs of bulk solid disappear. Our x-ray measurements cannot distinguish between a fluid film and a bulk liquid. However, from the isotherm measurements we infer that at this temperature the fluid adsorbate wets the surface.

As noted earlier the simple 2D line shape does not work when the film has more than two layers or is a bilayer fluid. Accordingly, in order to extract the bulk intensity properly throughout a whole range of temperatures we

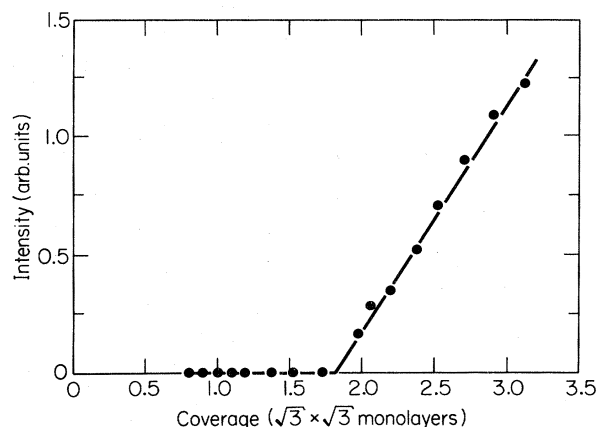


FIG. 5. Integrated intensity of the bulk ethylene peaks at  $T=97.5 \text{ K}$  as a function of coverage. The solid line is a guide to the eye; the intensity scale is normalized to unity at  $f=2.8$ .

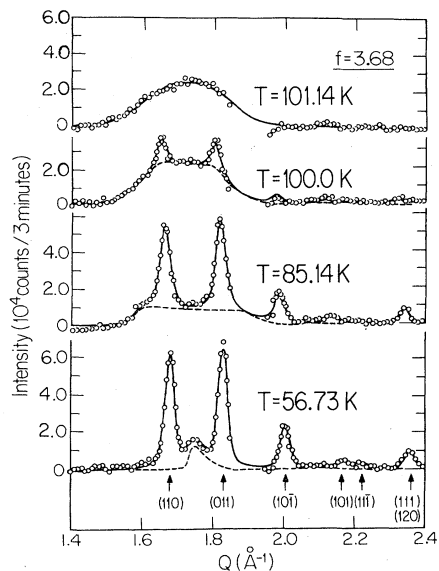


FIG. 6. X-ray scattering profiles at a coverage of  $f=3.68$  and several temperatures measured at MIT. The arrows indicate the bulk ethylene Bragg peaks. The changes in their positions reflect thermal expansion. The dashed lines show the empirical film line shapes used in these fits.

have used an empirical line shape for the film profile and then fitted the total scattering. The empirical line shape used for the fluid phase was a Gaussian with an adjustable width. At temperatures where the data are well described by a close-packed bilayer-plus-bulk line shape, fits using the empirical line shape gave essentially identical results for the parameters that describe the bulk. Fits that use this empirical line shape at  $T=56.7$ ,  $85.1$ ,  $100.0$ , and  $101.1$  K are shown in Fig. 6.

Our results, so-obtained for the bulk intensity at three separate coverages, are shown in Fig. 7. In this figure, we again see that the bulk intensity scales linearly with the amount of material in the cell minus the amount in the film. The steps in the data are direct evidence of a change in the number of layers of film in coexistence with the bulk. The size and position of the steps in the bulk intensity are conclusive evidence of discrete layering transition temperatures. We estimate  $T_2=75$  K and  $T_3=98$  K. The additional 0.7 layers of bulk left above 98 K at  $f=3.68$  have vanished by 101 K. The melting temperature of the 2S phase is lower than  $T_3$ . We should note that we have observed hysteresis at both  $T_2$  and  $T_3$ . This hysteresis is pronounced in the  $f=1.75$  data on the appearance and disappearance of bulk, but not evident in the  $f=3.68$  data, where only the amount of bulk changes.

We now describe in more detail the relationship between the transitions within the film and the monolayer-bilayer transition. Figure 8 shows the evolution at a constant coverage of  $f=1.67$ ; the model (shown by the solid line) is a sum of a Warren line shape (shown by the dashed line) and bulk. The profile at  $T=73.2$  K again shows the coexistence of HD and bulk. As the temperature is raised to 74.5 K the intensity of the bulk peaks remain unchanged within errors, while the film has

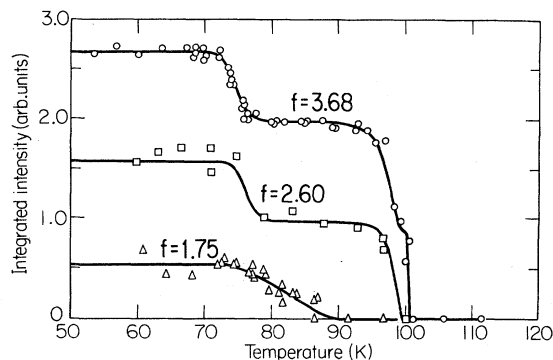


FIG. 7. Integrated intensity of the bulk ethylene peaks for several coverages as a function of temperature. The solid curves are drawn as a guide to the eye; the intensity scale is normalized to 2.7 for  $f=3.68$  at low temperatures. The knee for  $f=3.68$  is inferred from the knowledge that  $T_3=98$  K.

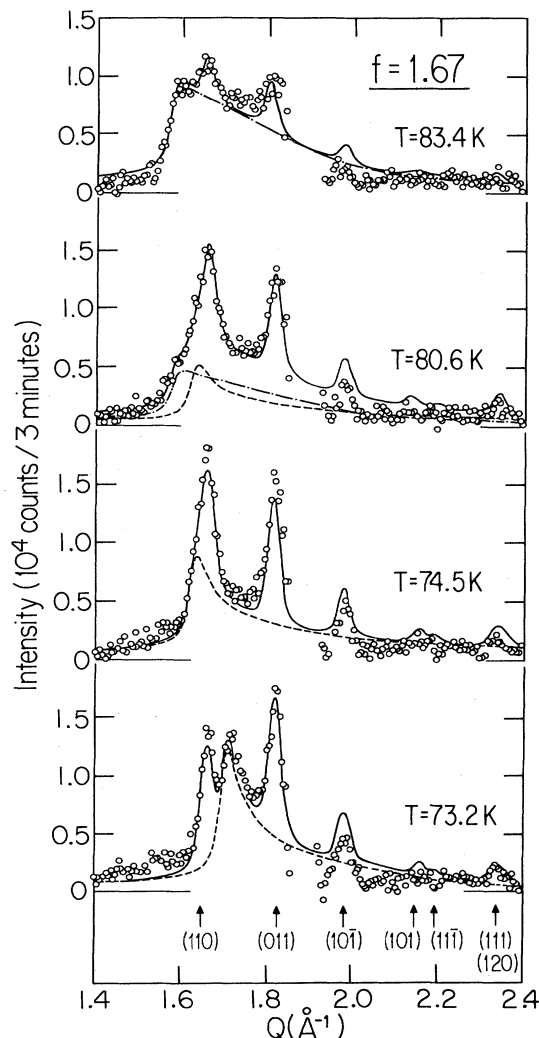


FIG. 8. X-ray scattering profiles at a coverage of  $f=1.67$  and several temperatures measured at MIT. The solid lines are fits to the data as described in the text. The dashed lines show the monolayer contribution to the scattering, while the dashed-dotted lines show the bilayer contribution.

transformed from the HD phase to the LD phase. This establishes the independence of the monolayer to bilayer transition temperature from the HD to LD transition temperature at low coverage. The profile at  $T=83.4$  K shows the profile characteristic of the 2S phase. Again, there is a small amount of bulk evident. At  $T=80.6$  K the scattering profile is well described by the sum of three contributions: LD phase, 2S phase, and bulk. Accordingly, this temperature should be a triple point and thus unique. However, this composite profile is seen over a small temperature range between 79.5 and 82.0 K at this coverage. The 2S phase melts between 93 and 97 K at this coverage. The results of the fits to the  $f=1.67$  data are shown in Fig. 9.

Each of the layering transitions should be a triple point with two films phases and the bulk solid coexisting. Therefore, two features of the data require further explanation: the decrease of the monolayer-bilayer transition temperature with increasing total cell density and the finite slope through the layering transition regions. The decrease in  $T_2$  might arise from an increase in bulk particle size. We know that bulk forms below the saturated

vapor pressure; presumably, these small particles are more stable and therefore can persist to higher temperatures. Capillary condensation onto concave surfaces allows bulk to form below the saturated vapor pressure.<sup>3</sup> A distribution of particle sizes would then lead to the finite slope through the transition region. In the data at  $f=1.67$  the HD to LD transition occurs below the layering transition, at higher coverages the layering transition moves to lower temperatures and preempts this, so that the HD phase transforms directly into the 2S phase along with the layering transition. It is not clear how to represent this behavior on the phase diagram of Fig. 3. We have shown the two triple-point temperatures changing with increasing coverage to reflect what is empirically observed.

#### IV. HIGH-RESOLUTION RESULTS

The low-resolution data presented above raise a number of interesting questions. In all of the diffraction scans the bulk peaks are close to being resolution limited. Simple volume and area considerations then require that when cooling through a layering transition, ethylene molecules from many different surfaces must agglomerate to form a bulk particle. More specifically, the 2D crystallite size is determined by the substrate and is 500 Å; therefore, there are of order  $10^4$  molecules in each 2D crystallite. Were these to form a single bulk crystallite, it would only be 100 Å in linear extent and would lead to bulk peaks much broader than observed. An incipient wetting transition could be signaled by the shape of the crystal changing from nearly isotropic to flat-disk-like. If, furthermore, bulk crystallites grow in some preferred orientation with respect to the graphite basal planes, the widths of peaks for planes perpendicular to the substrate would become broader than those for planes parallel to the substrate. We remark in passing that calculations would be useful on this aspect of wetting behavior. Clearly, therefore, it is important to study the size and shape of the bulk crystallites and their evolution through the layering transitions.

The details of the behavior at higher coverages and the transition from incomplete wetting below  $T_i$  to apparently complete wetting above  $T_i$  also remains to be elucidated. To address the above issues, we undertook a further set of measurements using the high intensity and resolution available at SSRL.

Figure 10 shows the evolution of the scattering profile, taken with the high-resolution configuration at SSRL, as a function of increasing coverage near  $T=70$  K. In each case the final coverage was reached starting from an empty cell, and then admitting the requisite amount of gas. We stress that for these data the spectrometer resolution is smaller than the spacing between data points, so the observed profiles represent the intrinsic scattering. It is found that purely Lorentzian line shapes give an excellent fit to the bulk diffraction profiles and that all the peaks observed have the same HWHM ( $\kappa$ ) to within errors. The integrated intensity ratios of the bulk peaks are fit using the results from a profile taken at  $\approx 70$  K at a nominal coverage of  $f=33$  and fixed for all further fits. As before, these intensities agree reasonably well with the known structure factors.

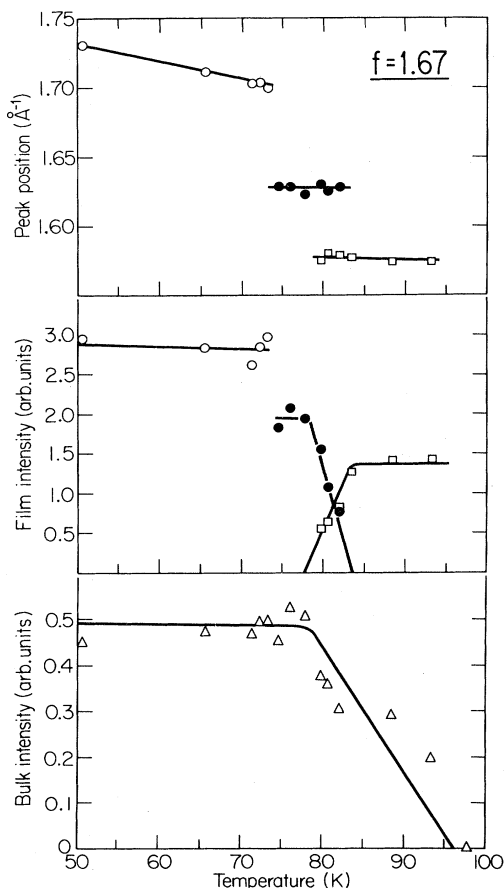


FIG. 9. Film-peak positions and intensities and bulk intensity as a function of temperature at  $f=1.67$ . The open circles correspond to the high-density monolayer phase, the solid circles to the low-density monolayer phase, and the open squares to the solid bilayer phase.

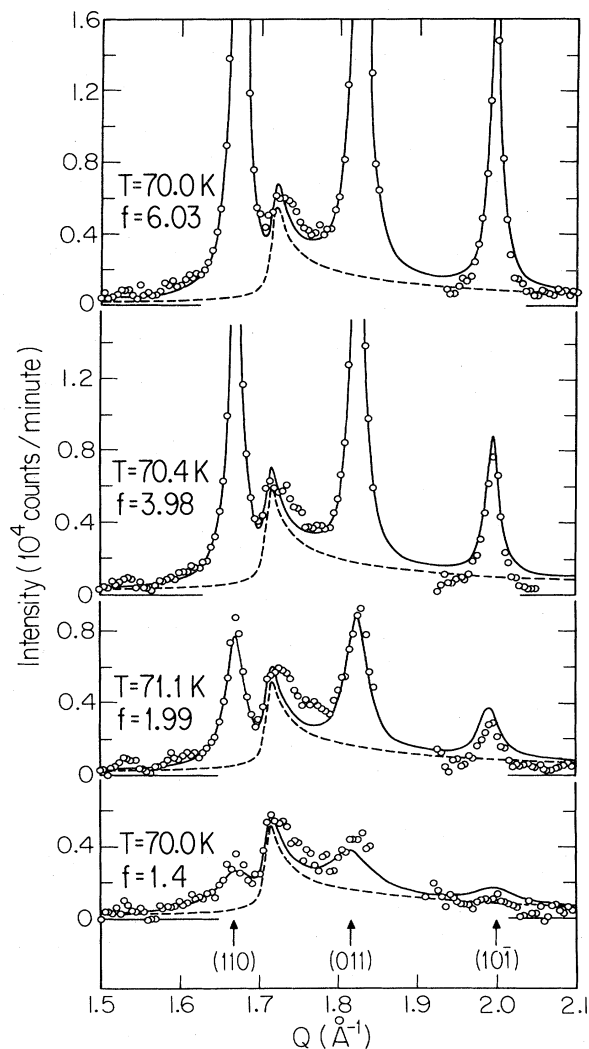


FIG. 10. X-ray scattering profiles measured at SSRL as a function of coverage at  $T \approx 70$  K. The solid lines are fits to the data as described in the text. The dashed lines show the contribution to the scattering from the high-density monolayer phase. Graphite backgrounds of  $\sim 9000$  counts per minute have been subtracted.

In Table I we show the fitted particle size ( $L$ ) defined by  $L = \pi/\kappa$ , where  $\kappa$  is the HWHM of the Lorentzian. The bulk crystallite size increases with increasing dosage. The equal half-widths of different Bragg peaks indicate

TABLE I. Estimated particle size at  $T \approx 70$  K as a function of coverage.

$f$ $\left[ \begin{array}{c} \sqrt{3} \times \sqrt{3} \\ \text{monolayers} \end{array} \right]$	$\pi/\kappa$ ( $\text{\AA}$ )
1.4	125
1.99	220
3.98	315
6.03	430

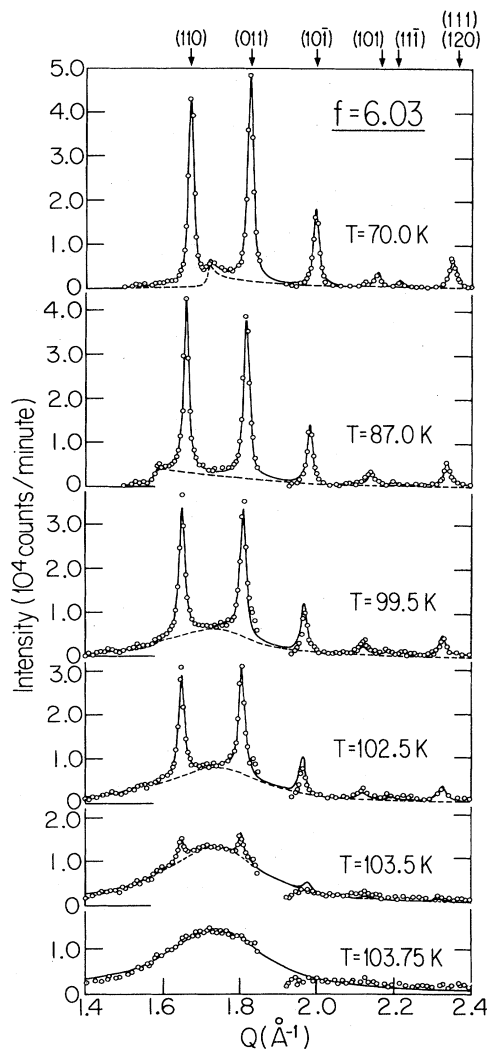


FIG. 11. X-ray scattering profiles at a coverage of  $f=6.03$  for selected temperatures measured at SSRL. The dashed lines show the film line shapes used in the fits.

that there is no particular crystal direction along which the crystallites have a much smaller dimension. Of course, individual crystallites could still be highly anisotropic in shape even though the anisotropy has no overall preferred axis.

Figure 11 shows diffraction profiles taken with increasing temperature at a coverage of  $f=6.03$ . As in the low-resolution data at  $f=3.68$ , and contrary to the low-resolution data at  $f=1.67$ , the disappearance of the HD phase appears coincident with the monolayer to bilayer transition. With increasing temperature the 2S phase is observed to melt at  $T=94$  K and the bilayer to three-layer transition appears at about  $T=98$  K. The model for the film scattering used in the fits shown is as follows. In the HD-plus-bulk region a monolayer Warren line shape was used. In the 2S-plus-bulk-region a bilayer Warren line shape was used. For all temperatures above the melting temperature of the film a simple Lorentzian was used to describe the film-fluid structure factor. We emphasize



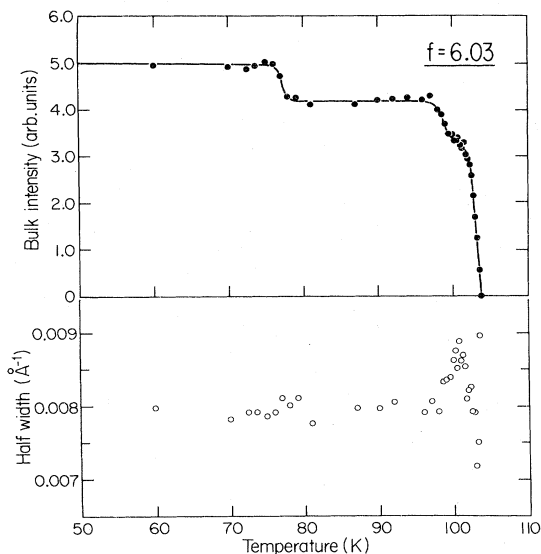


FIG. 12. Integrated intensity and half-width of the bulk ethylene peaks as a function of temperature at  $f=6.03$ . The solid line is a guide to the eye.

again that these fits give the same results for the bulk parameters as fits to the same data using the empirical line shape discussed previously.

In Fig. 12 we show the results for the bulk intensity and the bulk half-width. There are the same steps in the bulk intensity at  $T_2$  and  $T_3$  as seen in Fig. 7. There is no evidence for a distinct transition from a three-layer to a four-layer phase before the bulk intensity has vanished completely, which it does by 103.75 K. The half-widths do not appear to change at the incomplete wetting transitions, although the scatter in the data and possible sys-

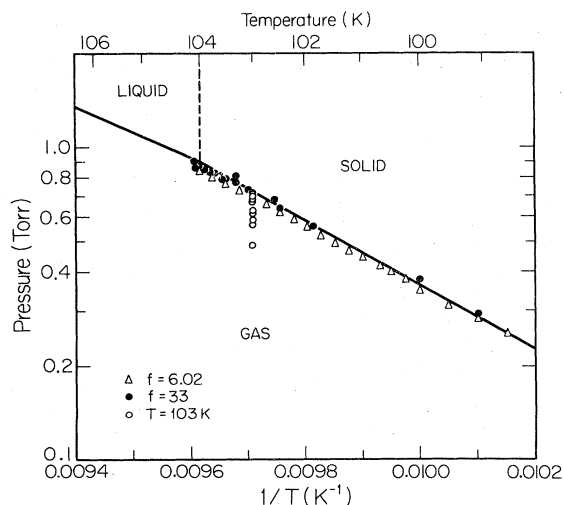


FIG. 13. Bulk ethylene phase diagram in the neighborhood of the triple point. The solid lines are phase boundaries taken from Ref. 7. Our measured experimental points, as discussed in the text, are shown as open circles, closed circles, and open triangles.

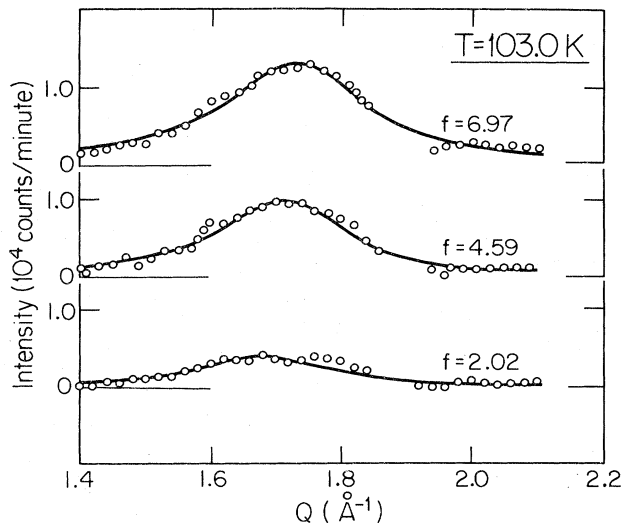


FIG. 14. Selected x-ray diffraction profiles as a function of coverage at  $T=103$  K measured at SSRL. The solid lines are fits to the data as discussed in the text.

tematic errors in separating the film and bulk scattering make it difficult to make a definitive statement.

To obtain an *in situ* check on the bulk ethylene coexistence curve, we measured the pressure-versus-temperature curve for a nominal  $f=33$  coverage. Comparison of our results with Ref. 9 is shown in Fig. 13. We regard the agreement to be good; the small systematic discrepancy could easily originate in a small difference between temperature calibrations. Also shown are the pressure measurements for the  $f=6.03$  data. Clearly, the pressure for  $f=6.03$  is indistinguishable from the coexistence pressure. To investigate further the behavior immediately below  $T_c$ , we carried out an isotherm at  $T=103$  K. This was chosen to be above the temperature at which the bulk intensity decreased precipitously (102 K) at  $f=6.03$ , and below the temperature at which bulk solid appeared on cooling (103.7 K) at  $f=33$ . Diffraction profiles are shown in Fig. 14 and the corresponding thermodynamic measurements are shown in Fig. 13. Remarkably, there are no bulk solid peaks in the scattering up to the highest coverage measured  $f=8$ . This lack of bulk, compared to its early formation seen in the isotherms at  $T=83.3$  and  $97.5$  K, indicates a fundamental change in behavior. Now, the ethylene no longer forms bulk crystallites; instead, the pressure measurements indicate that the data shown in Fig. 14 represent the scattering from a film containing up to at least eight layers of ethylene. The discrepancy between this scan and the temperature scan at  $f=6.03$  is another demonstration of the effect of hysteresis.

## V. CONCLUSIONS

These experiments confirm some aspects of the novel behavior predicted by Pandit, Schick, and Wortis for an intermediate substrate system. However, ethylene displays features beyond those contained within a lattice-gas picture.

We have shown that at low temperatures ethylene will

only adsorb onto graphite up to a finite thickness. Any further attempt to add material results in the spontaneous nucleation of bulk crystallites. A temperature  $T_2=75$  K exists at which this thickness changes discontinuously from one to two layers. A similar discontinuous change from two to three layers occurs at  $T_3=98$  K. We have also obtained interesting structural data on the nature of the film phases. In the monolayer regime there are two incommensurate phases: the LD and the HD phases. There is a first-order transition from the HD to the LD phase as the coverage is decreased or the temperature is raised. In the bilayer regime, we observe a single incommensurate solid phase, which we have labeled the 2S phase.

The structure of adsorbed ethylene bears no simple relationship to that of the bulk solid. Therefore, we would expect a large cost in energy in going continuously from the film to the bulk structure. Indeed, we may make the more general observation that if a strong substrate enforces a structure on the film, which is completely different from that of the bulk, the ensuing cost in healing energy might be expected to elevate the wetting temperature far above that predicted by a naive application of the lattice-gas model; indeed, it might eliminate  $T_W$  altogether.<sup>29</sup> Behavior consistent with this has been observed in a number of systems in recent HEED measurements.<sup>30</sup>

Since the film and bulk structures are so different we certainly cannot expect the critical points of the first few layering transitions to be related in any way to the roughening temperature of any bulk crystallographic face. Only the first three critical points have been observed. At these critical temperatures both the bulk and the film phases are fluids. The transitions probably persist to such high temperatures because of the substrate potential.

Of course, the outstanding issue for the ethylene-graphite system is the nature of the wetting transition and the role of the triple point. We believe that this experiment has shed considerable light on this question. The pertinent experimental data are illustrated in Fig. 12, which shows the evolution of the bulk intensity at  $f=6.03$ , and in Fig. 14, which shows data from the coverage scan at  $T=103$  K. For  $f=6.03$ , above 98 K the bulk intensity remains constant until approximately 102 K; at this point, it starts to fall precipitously, while the film intensity increases concomitantly. Finally, by  $T=103.75$  K all traces of bulk have disappeared. There is no evidence of any further layering transitions. The coverage scan at a temperature  $T=103$  K, well below the triple-point temperature and vapor pressure, shows no bulk scattering. Therefore, at this temperature, at least eight layers wet the substrate. Above the triple point, isotherm data indicate that there is complete wetting at coexistence.

Before trying to interpret these data, a word of caution is in order. At all of the transitions we have observed, hysteresis and rounding have been important. For example, the transition at 98 K is spread over  $\approx 2$  K. We are therefore insensitive to details that, in a perfect system, would be separated in temperature by less than about 2 K.

As noted in the Introduction, a simple mechanism which would give the triple point as the wetting temperature is the assumption that a discontinuous change occurs

in surface tensions at the triple point, such that the liquid phase wets the surface while the solid phase does not. As pointed out by Pandit and Fisher,<sup>7</sup> even below the triple point a film of liquid ethylene may be stabilized by its attraction to the substrate. The crossover from the layering behavior for the first few layers to lack of layering in the thick film near the liquid coexistence necessitates a line of first-order phase transitions. We designate this line of phase transitions as a *prewetting line*. Above this prewetting line the film thickness would increase continuously, both along and below gas-solid coexistence, as the triple point is approached.

Finally, at the triple point itself the thickness of the film would continuously diverge to infinity with the addition of more and more material. This continuous wetting transition is not related to the critical wetting theoretically investigated by many authors. The behavior along gas-solid coexistence may be thought of as simply a particular approach to coexistence for a system that wets. The intrinsic wetting temperature of the liquid phase is inaccessible because of the bulk solid. This behavior may be rather widespread; Krim, Dash, and Suzanne<sup>31</sup> have argued that the triple point is also the wetting temperature for several gases adsorbed on the Au(111) surface.

We now apply these considerations to the case of ethylene on graphite. Let us suppose that the transition at 98 K is the prewetting transition discussed above. Evidently, at this prewetting transition the jump in coverage is one layer. The model presented above then requires that as the temperature is raised above 98 K the film thickness, which coexists with bulk, increases continuously with increasing temperature. In fact, the thickness of the film at any given temperature is determined by the shape of the phase boundary between the region labeled "prewetting film" and that labeled "prewetting film + bulk solid" in the phase diagram of Fig. 3. Because the bulk solid intensity shown in Fig. 12 remains approximately constant until  $T=102$  K, this phase boundary must rise sharply with coverage until  $T=102$  K, if the model is correct. Beyond this temperature, the phase boundary must become flatter in a smooth fashion. Accordingly, this is the behavior we have illustrated in Fig. 3. This scenario is the simplest one that is consistent with the data; specifically, it does not require the introduction of any new phase transitions. The phase diagram corresponding to this possibility in the pressure-temperature plane is illustrated in Fig. 15. The lines show the known phase transitions.

However, we cannot by any means rule out other possibilities. For example, the data would be equally well explained by supposing that the transition at 98 K is into a phase that is strictly three layers thick. Then, to account for the isotherm at  $T=103$  K, we would postulate the existence of a new prewetting transition at approximately 102 K. At this transition the film thickness jumps to some large number of layers, which empirically must be greater than eight. At temperatures higher than 102 K the film thickness again evolves continuously as described above.

Because of the limitations due to our substrate, we are unable to rule out the possibility that wetting proceeds

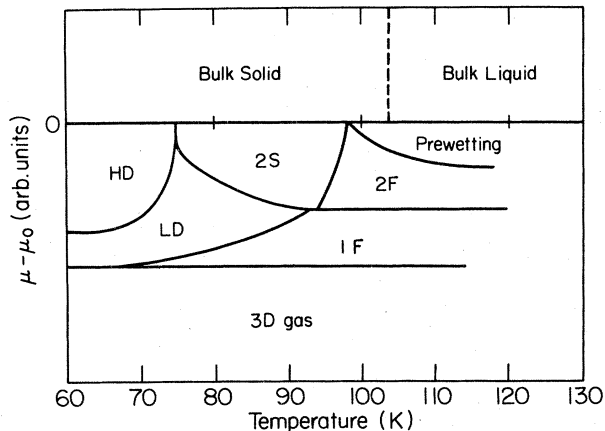


FIG. 15. Schematic ethylene-graphite phase diagram shown in the chemical potential-temperature plane. Chemical potential is plotted relative to that of the bulk. The phases and phase transitions are discussed in the text. This is the conjugate phase diagram to that of Fig. 3.

through a sequence of layering transitions, which are very closely spaced around 102 K. Nevertheless, we feel that this possibility is less likely than those presented above, because in a fluid phase there is no lattice structure to enforce discrete layering transitions far from the substrate.

This completes the discussion of the phase diagram that we have suggested for ethylene on graphite. Although it

appears complicated, we speculate that these are all possible film phases for ethylene adsorbed on graphite. Finally, we note that the use of single-crystal substrates may alleviate the effects of capillary condensation and thus allow more precise statements to be made about the details of the transition-to-wetting behavior in the vicinity of the triple point.

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