Observation of a metastable state in monolayers of carbon tetrafluoride on graphite

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We find that the two-peak diffraction patterns seen in slightly incommensurate monolayers of CF_4 adsorbed on graphite are metastable; the peak at the commensurate position shrinks, while the incommensurate peak grows, with time or with temperature cycling. Similar behavior is seen with *ZYX* and single-crystal exfoliated graphite substrates. Thus, there is no striped phase in this system, but rather a metastable coexistence of commensurate and incommensurate phases.

Phase transitions in physisorbed monolayers continue to be a subject of tremendous interest.[1] Among the most fascinating of these is the commensurate (*C*)–incommensurate (*I*) transition; it has been observed in many systems and in a number of different contexts, but has probably been elucidated in the most detail for the monolayer krypton on graphite system.[2–6] At the same time, progress in the theory of *C*-*I* transitions[7–13] has resulted in a simple physically appealing picture of the underlying mechanism. The *I* phase is thought of as a collection of *C* domains separated by walls (decommensurations). The detailed structure of the *I* phase depends on the form of the walls, wall energies, and interactions between the domain walls. In particular, for an incommensurate system on a substrate consisting of a hexagonal array of adsorption sites, negative wall-crossing energies result in hexagonally shaped domains, while positive wall-crossing energies are predicted to result in a striped phase.

The krypton-graphite system forms a $\sqrt{3}\times\sqrt{3}$ commensurate phase, and undergoes a transition to an incommensurate structure with hexagonally shaped domains. Between the *C* and *I* solid phases is an incommensurate phase characterized by broadened diffraction peaks;[2–6] this intermediate phase with short-range order is believed to be a domain-wall liquid.[9]

There has been much effort devoted to finding systems in which the *C*-*I* transition results in a striped phase.[14–17] One system with a particularly rich and unusual phase diagram is CF_4 on graphite;[18,19] the large size of the CF_4 molecule results in a 2×2 structure for the commensurate solid. It has been suggested[14,15,20] that in the commensurate structure the carbon atom of each CF_4 molecule is directly above a carbon atom in the graphite substrate, so that three fluorine atoms fit into the three hexagonal "wells" around the substrate atom while the fourth is above the carbon atom. (We call this a tripod configuration.) Although there is no experimental evidence, given the size and shape of the molecule it is reasonable to expect that this configuration will be energetically favored over the position favored by krypton and other rare-gas atoms (in which the center of the molecule is directly above a "well"). There are two substrate atoms to a graphite-surface unit cell; in the 2×2 tripod structure, therefore, an adsorbed molecule sits above one out of every eight atoms. In other words, the tripod structure is eightfold degenerate; in contrast, if the molecules were centered above the wells, the 2×2 structure would be only fourfold degenerate since there is only one well per graphite unit cell. It can be shown[21] that for the tripod configuration the incommensurate phase will have triangular domains. This involves six walls meeting at each crossing point and may, therefore, require a high wall-crossing energy, and thus, a striped phase may be favored in these systems.[22]

Kjaer and co-workers have studied CF_4 on *ZYX* graphite using x-ray diffraction.[14,15] One interesting feature of their results is the appearance of a phase, intermediate in coverage between a purely commensurate and a purely incommensurate phase, that is characterized by a diffraction peak at the commensurate position (1.475 Å^{-1}), and a second peak at slightly higher diffraction vector. They report that the position of the second peak varies with coverage (moving to higher diffraction vectors at higher coverage), and that the integrated peak intensity is twice that of the peak at the commensurate position. Ideally, a striped phase should give rise to satellite peaks, but if the density modulations are not sharp one might expect to observe only a broadened incommensurate rate peak; in fact, the peak at the commensurate position was found to be resolution-limited, while the second peak was approximately twice as broad as the resolution. Since *ZYX* graphite is a powder in the plane, both distorted (incommensurate) and undistorted (commensurate) peaks should be visible simultaneously, with a 2:1 intensity ratio (as reported).

We have undertaken a series of synchrotron x-ray-scattering investigations of the CF_4-graphite systems, both on *ZYX* graphite and on single-crystal exfoliated graphite[23] substrates. The basic experimental arrangements have been described numerous times[24,25] and will not be repeated here; our apparatus, in particular, has been described in Ref. 24. We used beam line VII-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Since the vapor pressure for CF_4 adsorbed on graphite at the coverages and temperatures of interest is extremely small, constant pressure experiments are impractical; we dosed the substrates with known quantities of gas and performed the experiments with a closed sample cell. This constitutes an almost ideal constant-density condition; the correction for the amount of CF_4 in three-dimensional-gas form within the cell is negligible because of the small vapor pressure. The amount of gas required for a one-monolayer coverage (3.2 torr cm^3) was determined from a CF_4 isotherm at a sufficiently high temperature (94.5 K).

Figure 1 shows the 2×2 commensurate (10) peak at a coverage of 0.72 monolayer (ML) on single-crystal exfoliated graphite and a temperature of 73 K. The data have been corrected for background and attenuation using the methods described in Ref. 24. The solid line is a two-dimensional Gaussian profile asymmetrized by the substrate mosaic spread.[24] The fitted width of the peak is a measure of the average domain size, found to be approximately 2200 Å.

Figure 2 shows a succession of scans at a coverage of 0.66 ML and at four temperatures as marked. At 73 K we see the 2×2 *C* peak, similar to Fig. 1. As the temperature is lowered one observes a two-peak line shape: one at the *C* location, and a broader peak at a slightly higher wave vector. The solid lines are combinations of a Gaussian profile constrained to the position and width independently measured for a *C* phase, and a broad Lorentzian with a temperature-dependent width and position.

The observed peak positions as a function of temperature are shown in Fig. 3. Our results at this and other coverages are consistent with those of Kjaer *et al.* to the

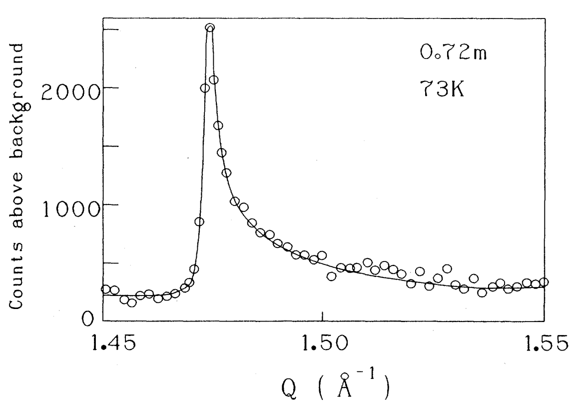

FIG. 1. Diffraction peak from a monolayer of carbon tetrafluoride on single-crystal exfoliated graphite at a coverage of 0.72 ML and a temperature of 73 K. The peak position is that expected for a 2×2 commensurate structure, and the fit (using a Gaussian structure factor) gives a domain size of 2200 Å.

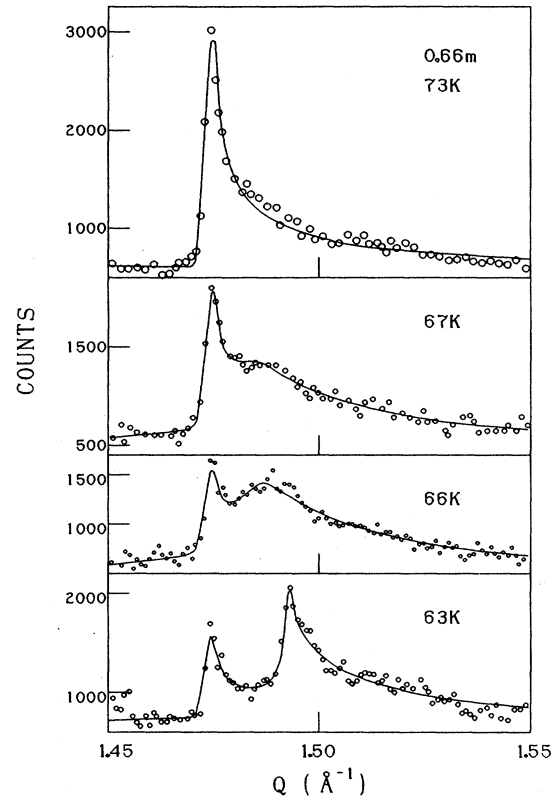

FIG. 2. Diffraction scans at a coverage of 0.66 ML on single-crystal exfoliated graphite, at four temperatures as marked. The lines are least-squares fits to a combination of a Gaussian at the commensurate position and a Lorentzian at the incommensurate position.

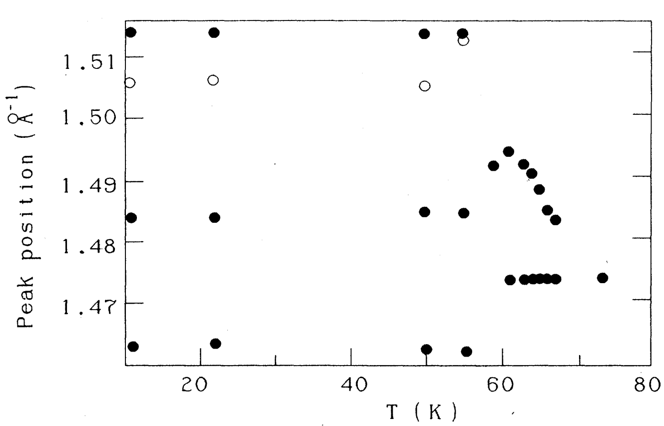

FIG. 3. Observed peak positions as a function of temperature at 0.66 ML coverage (compare Ref. 14).

extent that we do initially see both the three-peak low-temperature phase and a two-peak "phase." However, the intensity ratios in the two-peak phase are not 2:1, and the diffraction patterns are not stable. Figure 4 shows a typical set of scans at a coverage of 0.85 ML and a temperature of 75 K. Scan (a) was taken immediately after cooling to 75 K; scan (b) after waiting one half hour. Clearly the commensurate peak is dropping, while the incommensurate peak is growing. This cannot be reconciled with a striped domain model.

The evolution of the peak with temperature cycling is shown in Fig. 5 for a monolayer on *ZYX* graphite (coverage 0.8 ML). Panel (a) shows the line shape after initially cooling to 64 K; panel (b) shows the diffraction pattern after the system was heated to 80 K twice, cooling slowly to 64 K each time; (c) shows the final reproducible line shape achieved after five such cycles. The final line shape is entirely incommensurate. In this figure, the lines through the data are guides to the eye, not Lorentzian or Gaussian fits.

It seems clear, therefore, that there is no striped phase; the final, stable structure may be a hexagonal array of domain walls (as with krypton), or the triangular array predicted for this system.[21] The broad nature of the final incommensurate peak suggests that the monolayer is in the domain-wall liquid state associated with the transition from the *C* to the *I* phase. Figure 6 shows the half-width of the *I* peak on single-crystal exfoliated graphite as a function of temperature at a coverage of 0.66 ML; the behavior is reminiscent of the Kr-graphite system. Broadening of the *I* peak could also arise from a distribution of transition temperatures caused by inhomogeneities.[2,6] Simple estimates of the magnitude of this effect[6] suggest that inhomogeneities alone probably cannot fully explain

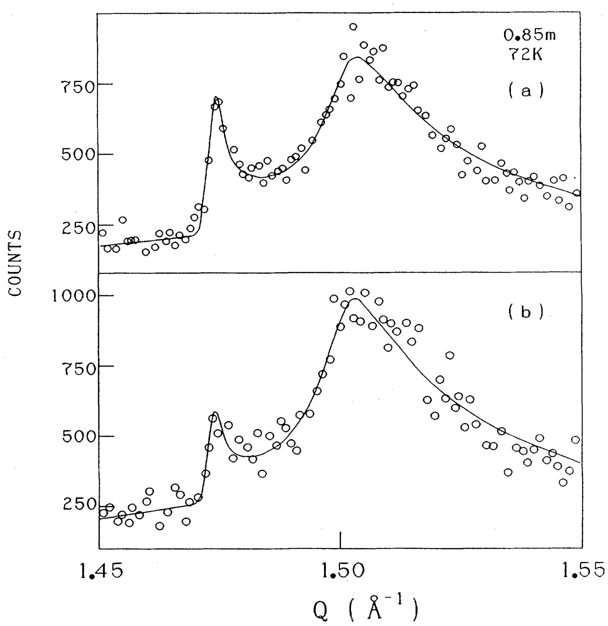

FIG. 4. Time evolution of a two-peak diffraction pattern at 0.85 ML coverage: (a) immediately after cooling to 72 K; (b) after 30 min.

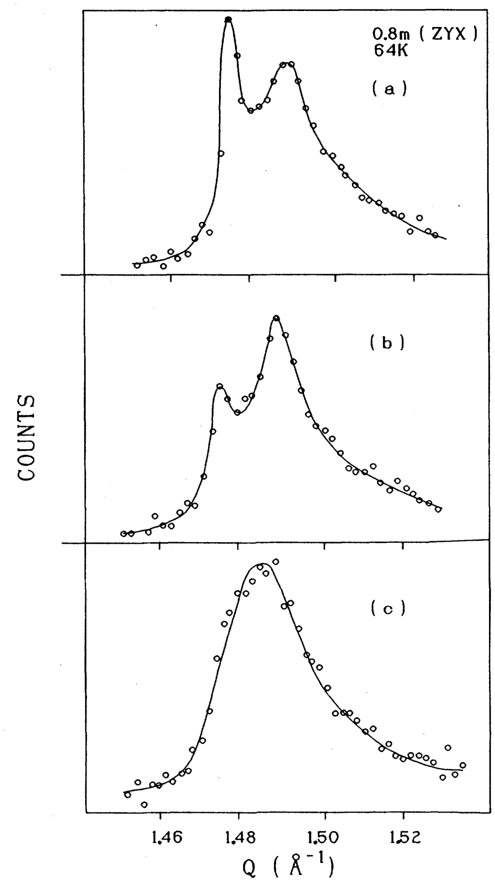

FIG. 5. Evolution of diffraction peak from 0.8 ML coverage on *ZYX* graphite with temperature cycling: (a) after first cooling to 64 K; (b) after being heated twice to 80 K and slowly cooled back to 64 K; (c) final reproducible line shape. The lines through the data are guides to the eye.

the observed peak width. On the other hand, the evidence does not definitively prove the domain-wall model.

We think that the two-peak diffraction patterns may in fact be due to a metastable coexistence of commensurate and incommensurate phases. Fluorine atoms are small

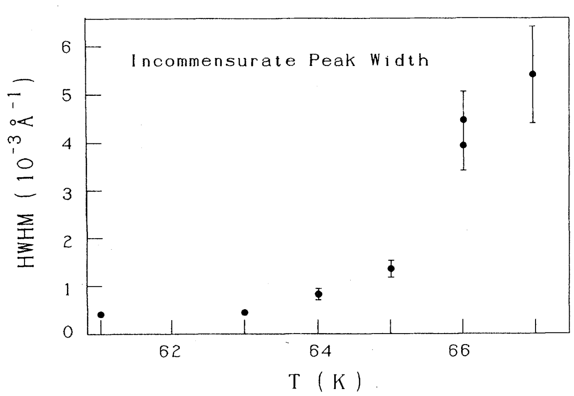

FIG. 6. Width [half width at half maximum (HWHM)] of the incommensurate peak vs temperature at 0.66 ML coverage.

(about the same size as carbon atoms) and it is possible for the three lower fluorine atoms in the "tripod" configuration of CF_4 to be quite deeply embedded in the graphite-surface "wells." Therefore, there may be a large activation barrier preventing the molecules from moving out into an incommensurate state. In this picture, temperature cycling is a way of accelerating the molecules' detachment from their commensurate positions. An alternative explanation is that equilibration between different regions of the surface does not occur through the vapor, since the vapor pressure is negligible, and is therefore slow; in this picture as well, it is reasonable that the process would be speeded up by heating. At 64 K this process appears to be extremely slow; at 72 K, visible but too slow for us to follow it to the final purely incommensurate line shape; and at 80 K, somewhat more rapid.

In conclusion, the long-time scales required for the equilibration of monolayers of large molecules such as CF_4 give rise to deceptive metastable diffraction patterns. When equilibrium is reached the slightly incommensurate phase shows one broad peak only, and may be a domain-wall liquid.

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