Higher-Order Commensurate Phase of CF₃Cl Physisorbed on Graphite

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X-ray diffraction experiments have been carried out on monolayers and submonolayers of the polar molecule CF_3Cl physisorbed on the (001) planes of exfoliated graphite. The coverage-temperature phase diagram shows three crystalline phases: an incommensurate phase, a commensurate 2×2 phase, and a higher-order commensurate phase. For the latter phase an arrangement of ferroelectric chains with a stacking sequence $ABCDA \ldots$ is proposed which belongs to the oblique plane group $p1$. Surprisingly the lattice parameters exhibit hexagonal relations $(\sqrt{73} \times \sqrt{73}R5.8°)$.

The solid phases of monolayers physisorbed on homogeneous substrates such as the (001) plane of graphite are regarded as a realization of two-dimensional (2D) crystalline arrays.[1] Though there are some problems connected with this view (strictly speaking, 2D crystals are unstable with respect to long-wavelength excitations[2]) the adsorbed layers have been successfully characterized and classified in reference to the 2D space groups (plane groups) of crystallography.[3]

In this Letter, we report x-ray diffraction results on the 2D solid phases of the polar molecule CF_3Cl adsorbed on graphite (001). Special attention will be paid to a higher-order commensurate hexagonal phase $(\sqrt{73} \times \sqrt{73}R5.8°)$ where the molecules are ordered in a ferroelectric chain pattern with a $ABCDA \ldots$ stacking sequence. The structure belongs to the oblique plane group $p1$ whereas the Bravais symmetry is hexagonal. We will comment on this point and on the higher-order commensurability in the discussion.

The experimental setup has been described in Ref. 4. The substrate is a sheet of exfoliated graphite, Papyex, obtained from Carbonne Lorraine. The CF_3Cl gas has a nominal purity of 99.8%. The raw x-ray diffraction counting rates have been corrected for background. The coverage ρ is quoted in terms of the number of molecules per four graphite hexagons.

In total, twenty different coverages have been studied as a function of temperature T. A full account of the results will be given elsewhere. The ρ, T phase diagram is shown in Fig. 1. At higher coverages the phase diagram resembles that of the nonpolar reference, CF_4 on graphite.[5] The commensurate (C) phase has a 2×2 structure where the molecules are thought to rest on the F_3 tripod. The incommensurate (IC) phase is triangular and presumably disordered with respect to the orientations of the molecules. We concentrate on phase E (E stands for electrically ordered as deduced below), a phase which has not been observed for CF_4. Within the wave-vector range examined in the diffraction study, $0.9 < Q < 2$ Å^{-1}, four diffraction peaks have been observed which are attributed to the E phase (Fig. 2). The peak shapes
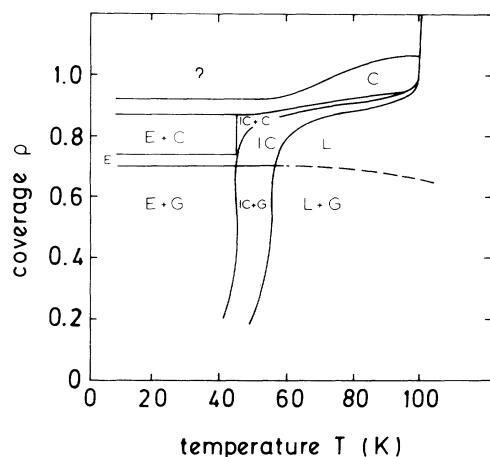

FIG. 1. The coverage-temperature phase diagram of CF₃Cl adsorbed on graphite. C: 2×2 commensurate; IC: triangular, incommensurate; E: electrically ordered, commensurate; L: 2D liquid; G: 2D gas. The phases at higher coverages are yet unknown.
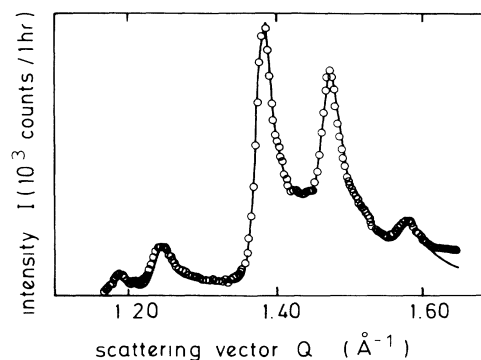

FIG. 2 A section of the diffraction pattern for $\rho = 0.75$, $T = 30$ K showing four peaks of the E phase ($Q = 1.195$, 1.245, 1.384, 1.582 Å^{-1}) in coexistence with the principal reflection of the 2×2 phase at $Q = 1.475$ Å^{-1}. The solid line is a best fit based on Gaussian line shapes.

have been analyzed in terms of 2D powder line shapes based on Lorentzian and Gaussian structure factors. For the E phase (and for the 2×2 phase) the Gaussian gives a better fit to the data. This is a first indication that the E phase is commensurate since the Gaussian profile is regarded as a good approximation to the Kummer-function-type structure factor which is expected theoretically for commensurate arrangements.[6] The peak parameters, namely the integrated intensity, the peak position, and the coherence length, are shown in Fig. 3; they are independent of ρ and T throughout the E phase. The peak width corresponds to a characteristic length of 230 ± 20 Å which is the average crystallite size of Papyex. The independence of the peak intensities and, in particular, of the peak positions on ρ and T is a further indication that the E phase is commensurate with the substrate lattice. The transitions from the E phase to the neighboring phases C and IC are first-order transitions.

The four peaks of the E phase can be indexed in terms of a 2D hexagonal lattice with $Q = 2\pi/a(4H/3)^{1/2}$ and $H = h^2 + hk + k^2$. The lattice parameter is $\sqrt{73}a_c$ where a_c is the lattice constant of the basal plane of graphite. Thus the E phase is a higher-order commensurate phase with a $\sqrt{73} \times \sqrt{73} R5.8°$ lattice. If we consider the size of the molecule, the value of the lattice parameter suggests that the adsorbed layer repeats a given phase relation to the substrate every four intermolecular distances. The four peaks correspond to the values 12, 13, 16, and 21 for the quadratic expression H. Peaks with $H = 7$, 9, 19, 25, 27, 28, and 31, though required by hexagonal symmetry, are absent. Their absence has to be explained by a special arrangement of the molecules in the cell.
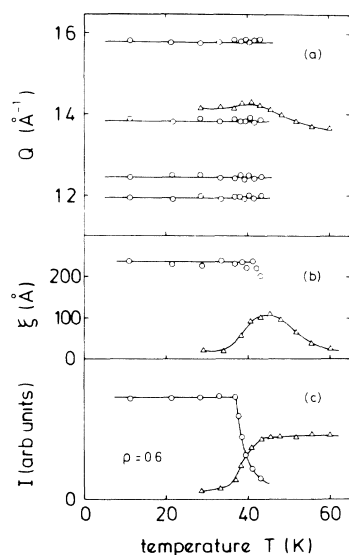
In our first attempts of constructing a structural model of the E phase, we strictly referred to the hexagonal plane groups and used steric considerations as a guide. By comparison of the coverages and the cell parameters of the C and the E phases, the hexagonal cell should host fifteen or sixteen molecules with a preference for the F_2Cl tripods down. In the most plausible hexagonal structure, three molecules are placed in special positions $0,0$; $\frac{1}{3},\frac{2}{3}$; $\frac{2}{3},\frac{1}{3}$ with the molecular axis, i.e., the dipole moment, perpendicular to the surface. Twelve additional molecules can be arranged with the F_2Cl tripods down in ring patterns around the three special molecules (plane group $p3$). This pinwheel arrangement is appealing, but it fails to explain the peak intensities even if a generous use is made of the freedom which remains for the positions and orientations of the molecules.

The absence of reflections is readily explained by indexing with a smaller rectangular cell with the parame-
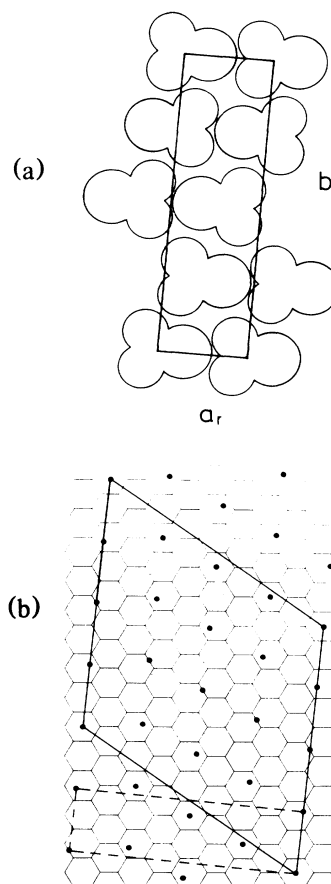

(a)

b_r

a_r

(b)

FIG. 3. The T dependence of the (a) positions, (b) the coherence length, and (c) the integrated intensity of the diffraction peaks of the E phase (O) and the IC phase (△) for $\rho = 0.6$.

FIG. 4. (a) The higher-order commensurate (hexagonal, $\sqrt{73} \times \sqrt{73} R5.8°$) cell and the relation to the smaller rectangular cell, (b) superimposed on the graphite surface. A special $+ + - -$ arrangement which places the Cl atoms (●) of four out of sixteen molecules in the centers of the graphite hexagons is shown in (b). Here the molecules are represented by the contour of the F_2Cl tripod in (a).

ters $a_r = a/4$, $b_r = a\sin(60°)$, Fig. 4. It is clear that the smaller cell is unphysical since it no longer reflects the commensurability. From the size of the rectangular cell and from the coverage where the E phase occurs, one concludes that this cell hosts four molecules. Further insight into the arrangement of the molecules can be obtained from the b_r/a_r ratio. Since this ratio is 13% short of four, we suggest that the molecules are stacked along b_r but that their longest linear dimension (which is parallel to the electric dipole moment and the C—Cl bond) coincides with the a_r direction. In a rectangular lattice the proper structural units are rows rather than rings. In fact, one notes from the size of the molecule that a row of molecules which have their dipole moments parallel to the direction of propagation has an intermolecular distance which matches the lattice parameter a_r. Hence, we think of the E phase as a structure which consists of ferroelectric chains propagating along a_r. As far as the stacking of these rows perpendicular to a_r is concerned, the repetition sequence $ABCDA...$ is required. This scheme can be realized with several structural arrangements where each row is characterized by a displacement x_i in the a_r direction and the polarity P_i (+ or −). We further suggest that the rows are equidistant in the b_r direction, i.e., $y_i = i/4$ in reduced units. This statement is supported by the absence of the $(03)_r$ and $(05)_r$ diffraction peaks. Up to this point we consider our analysis conclusive.

Several sets of parameters x_i, P_i yield acceptable fits to the observed peak intensities. For a selection among these sets further assumptions are necessary. Two different lines of reasoning are possible. (A) If the structure is mainly determined by the intermolecular interactions, one would impose restrictions on the parameters of the type that the relative displacements between neighboring rows, $|x_i - x_{i+1}|$, should be identical for ++ and − − pairs of rows on one hand and for + − and − + pairs on the other hand. Based on this assumption, only a + + − − pattern is consistent with the diffraction data. (B) For the case of strong adsorbate-substrate interaction, one would try to position as many molecules as possible into favorable adsorption sites. We consider the Cl atom in a graphite hexagon as most favorable. Making use of the freedom in the parameters x_i, one manages to place the Cl atoms of four out of the sixteen molecules of the hexagonal cell in these positions. Having fixed the displacements x_i in this way, one finds that the intensities of the diffraction experiment again favor a + + − − sequence. This structure is shown in Fig. 4. In summary, we suggest that the E phase consists of ferroelectric rows which are most likely stacked in a + + − − pattern.

The E phase requires some comments. The example of N_2 on graphite shows that the herringbone pattern is likely to occur in a 2D array of elongated molecules.[7] Considering the tetrahedral shape of the molecule, one

can imagine, however, that this pattern would be in conflict with the principle of minimizing the steric hindrance between neighboring molecules. In fact, it seems plausible that rows are favorable where the Cl ligand resides in the dimple formed by the F_3 group of the next molecule in the row. As far as the stacking sequence is concerned, we do not know whether the direct multipolar interactions and the hard-core repulsion between the molecules or the substrate corrugation are most important.

The first of the amazing aspects of the E phase is that its plane group ($p1$, oblique system) symmetry is different from its hexagonal Bravais symmetry. There is no fundamental reason why the lattice parameters of a low-symmetry structure cannot accidentally become degenerate and exhibit the relations of higher Bravais symmetry. In 3D, e.g., a monoclinic crystal may exhibit hexagonal lattice parameters at a special temperature due to thermal expansion. In the present case it is clearly the surface corrugation which is responsible for this accidental degeneracy. Nevertheless, the question for the physical origin of the disagreement between plane group and Bravais symmetry has to be posed. In the present case one would think that the row pattern of the E phase should automatically destroy the commensurability and thus lift the hexagonal relations between the lattice parameters. If, on the other hand, the corrugation of the surface is strong enough to impose the hexagonal Bravais symmetry on the adsorbed layer, the internal positions and orientations of the molecules should adapt to this symmetry, too.

Related problems have been encountered in low-energy electron diffraction studies on the reconstructed surface of tungsten. The W(001) surface shows a $\sqrt{2} \times \sqrt{2}R45°$ ($P4mm$) lattice which undergoes reversible transitions into the rectangular structures $p2mg$ and $c2mm$, depending on whether chemisorbed hydrogen is present or not.[8] In either case, however, the $\sqrt{2} \times \sqrt{2}$ translational symmetry is maintained. The phase transition of W(001) has been interpreted in terms of the condensation of a zone-boundary displacive mode.[9] The appearance of spontaneous strains, which usually couple in higher order to the soft zone-boundary mode, is suppressed by the commensurability, i.e., by the fact that the long-wavelength phonons of a commensurate structure exhibit a gap in the excitation spectrum. Unfortunately this picture is not applicable to the E phase of CF_3Cl since a disordered $\sqrt{73} \times \sqrt{73}$ phase, which would be analogous to the $P4mm$ phase of W, does not exist.

The example of the E phase shows that the plane group symmetry of an absorbed layer can be lower than the Bravais symmetry which is deduced from the positions of the diffraction peaks.

The second amazing aspect of the E phase is that its commensurability is of an unusually high order. Only one, or at maximum four, out of sixteen molecules can

be brought into registration with the substrate. A comparable situation has been observed for a submonolayer of Xe on the (111) surface of Pt (Ref. 10). These adatoms form a $(5\times5)R0°$ lattice where one out of six atoms is in registration with the Pt surface. A suggestion of a higher-order commensurability is open to the criticism that a small number of Bragg peaks can be always indexed within the error of the experiment by a large enough commensurate cell. Our claim that the E phase is commensurate is not only based on the peak positions, but additionally on the following observations: (i) There is practically no thermal expansion in the E phase (the same criterion has been used in the work on Xe/Pt). Note for comparison the strong thermal expansion of the IC phase (Fig. 3). (ii) The small width of the E phase with respect to the coverage (Fig. 1). (iii) The Gaussian shape of the diffraction peaks of the E phase.

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