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**Tetrafluoromethane monolayer physisorbed on graphite: its orientational walls and its complex phase diagram**

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**Abstract.** — Neutron diffraction results for a monolayer of CF₄ physisorbed on different graphites show the complexity of the system, mainly due to the non spherical shape of the admolecule. From our neutron data and LEED results [6] we recognize at least 6 different phases. These are, with decreasing temperature, liquid, plastic, commensurate solid, incommensurate solid, incommensurate tilted and a surprising triple-peaked incommensurate phase. This low temperature phase is especially studied and compared to previous models, of increasing sophistication, based on the concept of small domains with varying degrees of compression which alternate periodically and are limited by different types of walls. These different types of walls are due to the ability of the molecule to have different orientations relative to the substrate. These models give also a tentative explanation to the puzzling fact that diffraction patterns are different according to the graphite substrate used, Papyex or ZYX-Uncar. Finally a tentative phase diagram is given for this complex system.

The molecule of carbon tetrafluoride was chosen very early for neutron diffraction studies of a physisorbed monolayer on graphite. It was thought that CF₄, a very nearly spherical molecule, should give simple results like rare gases, but more easily due to a larger diffusion length than krypton, for example.

We want to show here that, even on one of the flattest known substrates, i.e. graphite, the small non sphericity leads to a great complexity. We give neutron diffraction results especially for a low temperature phase as found with better resolution on a substrate with larger coherence length (ZYX). We compare them to previous results on papyex [1, 2] which are strikingly different and we suggest a model for this low-temperature phase. We also propose a phase diagram based on previous results given by neutron and low-energy electron diffraction as well.

1. **Earlier neutron studies.** — We studied earlier the neutron diffraction by a layer of physisorbed CF₄ on papyex. Papyex is a recompressed exfoliated graphite from Carbone-Lorraine, the properties of which are very similar to grafoil from Union Carbide; a maximum coherence length of this substrate is between 250 and 350 Å as observed by X-ray diffraction with krypton [3]. The studies were done with the 2-axis powder diffractometers D2 and D1B at the Institut Laue-Langevin (ILL) [1, 2].

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Between 65 K and 75 K, a peak with the classical two-dimensional shape at 1.478 Å\(^{-1}\) corresponds clearly to a superstructure (2 \(\times\) 2) of graphite for coverages lower than about 0.9; it will be labelled (1, 0). Between 70 K and 75 K, even for small coverage, this peak decreases continuously and coexists with a liquid-like band. It disappears abruptly at 75 K (over less than 1 K) in favour of the liquid structure. We first thought that this line shape was attesting to the coexistence of liquid and commensurate solid and we drew an unusual phase diagram [2]. We discovered later that the intensity ratio of the narrow and wide peaks is constant with coverage. This fact cannot be explained by the coexistence of the solid and liquid phases. This type of behaviour was also found for xenon and argon on ZYX; the curves pertinent for comparison, i.e. at coverage less than the critical one, are given by [3]. For argon the intensity of the 2D-solid peak goes down to the liquid one without the break in the intensity curve seen for CF\(_4\). The facts are well explained by high order melting: the coexistence domain at coverage higher than 0.7 and \(T > 75\) K calls for a first order melting in the CF\(_4\) case, but for xenon there is a 50 % decrease of the solid peak over 5-7 K and below a clear critical point with first order melting. This decrease was considered by [4] as a roughening transition, but these authors remark that this effect should be less important for the melting of a commensurate solid. We then propose to consider that at 70 K some kind of spinning begins for the CF\(_4\) molecules, with correlation between neighbouring positions — i.e. a plastic phase occurs. This hypothesis should be checked by quasi-elastic neutron diffusion, currently under preparation. The triple point is then 75 K rather than 70 K; this value agrees with conclusions by S. Calisti [5] based on volumetric isotherms by P. Dolle [6], and his own Auger isotherms.

Below 65 K the (1, 0) peak moves to slightly larger angles and a peak near 2.55 Å\(^{-1}\) appears below 50 K and can be labelled (1,1). In this incommensurate structure satellites appear near the principal peaks, but are too far from them to be explained by a model with relaxed walls, i.e. Novaco-McTague distortion wave theory [7] or simple walls « à la Villain » [8]. Moreover, some structure seems to exist in the (1,0) peak, but the resolution was too poor to be sure of this fact and to ascertain positions and intensities.

2. New neutron diffraction results. — We therefore studied again CF\(_4\) on graphite with the triple axis spectrometer IN12 of ILL, and we used a better preferentially-oriented substrate (ZYX from Union Carbide).

We observed at 70 K, as before with papyex on D1B and D2, the (1,0) peak of the superstructure near 4.26 Å (1.478 Å\(^{-1}\) exactly), with a coherence length better than 600 Å (resolution limit of the instrument) (Fig. 1). The peak is not perfect; irregularities between

![Fig. 1.](image1)

1.54 Å\(^{-1}\) and 1.58 Å\(^{-1}\) correspond to a strong background from graphite, but the shoulder at 1.5 Å\(^{-1}\) may correspond to the beginning of the spinning of molecules with strong correlation.

At 18 K and 37 K (coverage about 0.6) we resolved the (1, 0) peak into three peaks at 1.465 Å, 1.493 Å, and 1.522 Å (Fig. 2). Their relative integrated intensities (fitted with a coherence length 400 Å) are 140, 330, 450 (A.U) for positions 1.465, 1.493, 1.522 Å\(^{-1}\).
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Fig. 3. — Spectrum from D1B on Papyex at K. The solid line a) is calculated with the three-peak positions of figure 2 and least squares fitted intensities: 560, 2500, 1640, i.e., enhancement of the central peak. A fit with one peak is not suitable: b).

Fig. 4. — IN12-ZYX spectrum at 62 K near the full monolayer. A single peak is observed at 1.544 Å⁻¹: incommensurate solid. A shoulder is hinted at on the high-Q edge. The signal-to-noise ratio does not enable us to observe small satellites as we did with D1B.

3. The low-temperature structure with three peaks excludes simple models. — 1) The positions of the three peaks could be assigned to a simple unit cell with three different lengths. If we consider CF₄ as sitting on the surface with three fluorines touching the surface (this is certainly the case at low temperatures) we note that the square of the structure factor of CF₄ varies with orientation only from 13.21 to 13.35 (in units of fluor diffusion cross-section). As a consequence the large differences between the amplitudes of the 3 peaks cannot be explained.

2) A larger cell can be searched for, with two atoms per cell for instance. If the three peaks at \( \chi = 1.465 \) Å⁻¹, 1.493 Å⁻¹ and 1.522 Å⁻¹ are indexed as 10, 01, 11 the simple cell is \( |a| = 4.782 \) Å, \( |b| = 4.863 \) Å, \( \gamma = 118.21° \).

Using the actual intensities of these three peaks, three different double cells with two molecules per cell can be built:

- the cell (I): \( 2a, b \) with two molecules at (0, 0) (0.33, 0.78);
- the cell (II): \( 2b, (a - b) \) with two molecules at (0, 0) (0.44, 0.22);
- the cell (III): \( 2(a - b), a \) with two molecules at (0, 0) (0.39, 0.12).

But:

- a) The molecules overlap.
- b) Other superstructure peaks should be observed, such as \( (\frac{1}{3}, 0) \) \( (\frac{1}{3}, 1) \) in our previous way of indexing, with noticeable intensities. If we only look for peaks with a structure factor larger than \( b_{CF_4} \) we should always observe peaks between the group near 1.49 Å⁻¹ and the group near 2.59 Å⁻¹ (see Table).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Structure factor in ( b_{CF_4} ) units</th>
<th>( \chi ) Å⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell I</td>
<td>1</td>
<td>1.76</td>
</tr>
<tr>
<td>3</td>
<td>1.21</td>
<td>1.99</td>
</tr>
<tr>
<td>3</td>
<td>1.99</td>
<td>2.2</td>
</tr>
<tr>
<td>Cell II</td>
<td>3</td>
<td>1.94</td>
</tr>
<tr>
<td>3</td>
<td>1.48</td>
<td>2.24</td>
</tr>
<tr>
<td>Cell III</td>
<td>3</td>
<td>1.79</td>
</tr>
</tbody>
</table>

are 140, 300 and 450 at 18 K; 121, 296 and 435 at 37 K. The results for papyex at 40 K can be fitted with three peaks at those very positions. The least-squares fit yields relative intensities of 1, 4.45 and 2.93. It should be noted that the middle peak is now stronger than the others (Fig. 3). We have then, for the first time, clear evidence of a difference in the apparent structure of a physisorbed layer on two very similar substrates. We shall try to explain this difference on the simple basis of the maximum coherence length observed on papyex (350 Å [9]) and on ZYX (2300 Å [10]). We note also that at 62 K and coverage near the full monolayer we observe a single peak at 1.544 Å⁻¹, with perhaps a shoulder on its high-Q edge (Fig. 4).
Yet it must be remembered that the DIB spectra on a wide angular domain show that there is no peak except near 1.5 Å⁻¹ and 2.59 Å⁻¹.

c) The peaks observed on DIB near 2.59 Å⁻¹ cannot be interpreted as coming from the peaks at 1.465; 1.493 and 1.522 Å⁻¹, even when we consider only their positions (experimental values 2.51, 2.62, 2.69 Å⁻¹; calculated values 2.53, 2.58, 2.63 Å⁻¹).

3) Larger cells with 3 or 4 molecules would give rise to the same contradictions.

4) The use of even larger cells means looking for relaxed walls.

Such a model would explain the absence of other peaks, but the difference of intensities of the three peaks can still not be accounted for. We also do not see any reason for not having ternary symmetries of the walls. Moreover the peak at 1.465 Å⁻¹ would correspond to a dilatation when the temperature is decreased below the (2 x 2) commensurate phase range. This is improbable. As this peak is noticeably weak one could suspect it to be a satellite, but in that case it is too high for a simple wall theory.

4. Double orientation wall model: a first approach. —

With a non spherical molecule such as CF₄, hindering of rotation at low temperature is to be expected, as

![Diagram](image)

Fig. 5. — Orientational walls on a commensurate CF₄ layer on graphite. Back-to-back walls save $a_0/6$ perpendicularly to the wall. Head-to-head walls save $a_0/3$.

But this structure is too much compressed in the walls because the molecules overlap. Triangles join the fluorine tripod of the molecule. $a_1 = 4.92$ Å; the cell $(a_1, a_2)$ accommodates $2M$ molecules; $a_2 = (2M - 1/2) a_0$.

The molecules drawn with full lines can build a structure in which the bistrip $A_1 + B_1$ is repeated ($\delta_1 = \delta_1$). But another position $B_2$ of the molecule (dotted drawing) is possible, which has the same relation to strip $A_1$ (the dotted arrow $\delta_1$ indicates how to go from $A_1$ positions to $B_2$ ones). These two positions have different neighbouring only at very long distances (the width of a bistrip); they are energetically very near and introduce disorder — i.e. the reflection not perpendicular to the wall can be diminished if the coherence width of the substrate is larger than the bistrip width.

The strong difference between spectra on papyex and ZYX cannot be described by a widening of the spectrum on a worse (in the sense of coherence length) substrate. This fact finds an explanation in our model: if the width of a bistrip is about the coherence length for papyex (as will be shown later) disorder cannot show up. Some kind of flexibility will remain in a better model, e.g. the ability to develop « two-dimensional stacking faults ».

5. Apparent molecular shape of CF₄ and compression. —

Further complications must be introduced because near the walls the molecules cannot sit on the drawn positions but must overlap. We do not know exactly the shape of CF₄ molecules. The C-F distance has been given as 1.52 Å [12], the projection of which on the graphite plane is

$$1.52 \AA \times \frac{2\sqrt{2}}{3} = 1.43 \AA,$$

i.e. approximately the distance between a carbon and the next centre of carbon hexagons of the graphite surface (1.42 Å). The radius of fluorine is between 1.1 and 1.25 Å whereas the radius of the inscribed circle in carbon hexagons is 1.23 Å. Calisti [5] drew the shape of CF₄ as the outline of three inscribed circles in adjacent carbon hexagons; it gives for the (2 x 2) superstructure whole free carbon hexagons, i.e. a much more compact structure could appear: CF₄ may change its orientation from one row to the next, and the coverage would be 4/3 of the known commensurate one, which is much larger than any
observed monolayer coverage even at low temperature and high pressure. The true shape may be that of Calisti or even smaller, but rotation of the molecule gives a much larger apparent shape. To account for this we shall use the following model for the apparent shape of CF₄: it is the outline shape of a figure with the three circles from Calisti but also the tangent between these circles (Fig. 5). Moreover we allow for a size reduction of 1 or 2 %.

Let \( a₀ = 4.26 \text{ Å} \) be the distance of two adjacent lines of CF₄ in the \((2 \times 2)\) structure. We previously used \( δ₂ = a₀/3 \) for head-to-head molecules and a compression component (perpendicular to the walls) of \( δ₁ = a₀/6 \) for back-to-back molecules. With the present shape these gains in the walls reduce to \( δₐ = 0.179 a₀ \) for the head-to-head molecules and \( δₐ = 0.089 a₀ \) for the back-to-back molecules (using no size reduction). This avoids the overlap. But the centre of gravity of CF₄ can no longer lie exactly over a graphite surface carbon and a small compression occurs in a CF₄ strip between two walls. Let us call \( b \) the distance between CF₄ rows with the same orientation (\( b ≤ a₀ \)).

Supposing that this distance is constant, that the walls are straight, and that \( M \) rows of CF₄ occur between two adjacent walls, we shall have (the periodicity of the structure is \( 2M \))

\[(2Mb) - dₐ - dₐ = (2M - \frac{1}{2})a₀ = a₂\]

the gain for two walls being still \( a₀/3 + a₀/6 = a₀/2 \) to keep the maximum degree of registry over long distances.

I.e. \( M(a₀ - b) = 0.116 a₀ \).

6. The diffraction pattern. — The scattering amplitude of a strip for a reflexion \((h, k)\)

\[\mathcal{A} = b_{\text{CF₄}} \frac{\sin \pi Nh}{\sin \pi h} \frac{\sin (\pi Mkb/a₂)}{\sin (\pi 2kb/a₂)} \times 2 \cos \pi \left(\frac{h}{2} + \frac{kb}{a₂}\right)\]

The scattering amplitude of the molecule \( b_{\text{CF₄}} \) is taken as constant for a given reflexion, the molecular orientation having small effects only. The indices \( h \) and \( k \) are relative to the cell \((a₁, a₂)\), with \( a₁ = 4.92 \text{ Å} \) and \( a₂ = (2M - \frac{1}{2})a₀ \); the number of molecules in this cell is \( 2M \). The first factor corresponds to a line with \( N \) molecules. The third factor accounts for a rectangular cell (useful in what follows) describing a triangular net. For the formula to be exact \( M \) must be even, but we can verify that \( M \) odd introduces nothing different in the following. The amplitude is calculated relative to the centre of the strip.

For the bistrip the scattering amplitude is

\[\mathcal{A}(A + B) = \mathcal{A} \cos \pi \frac{k}{a₂} \left(\frac{a₀}{4} + \frac{dₐ}{2} - \frac{dₐ}{2}\right)\]

\[= \mathcal{A} \cos \pi \frac{k}{a₂} \left(\frac{dₐ}{2} + \frac{dₐ}{2}\right)\]

relative to the centre of the cell \( a₁, a₂ \).

For \( \gamma \) bistrips a further factor occurs

\[\frac{\sin \pi kγ}{\sin \pi k} f(h, k)\]

The factor \( f(h, k) \) is introduced to account for the disorder previously described; for its calculation papers on three-dimensional stacking faults are useful, e.g. [13, 14]; it is equal to 1 for \( h = 0 \).

The factor \( \sin πkγ/\sin πk \) shows that \( k \) must be an integer. The second factor in \( A \) constrains \( k \) to be near \( M \) times an integer (the half-width at middle height is about 2). The third factor in \( A \) constrains \( \frac{k}{M} + h \) to be even.

Near \( χ₀ = 1.478 \text{ Å}^{-1} \) principal reflections occur for

\[h = 0, \ k = 2M \quad \text{at} \quad χ = χ₀ \left(1 + \frac{1}{4M}\right)\]

\[h = ± 1, \ k = M \quad \text{at} \quad χ = χ₀ \left(1 + \frac{1}{16M}\right)\]

(This last one is attenuated by stacking-fault disorder in \(ZYX\).) One expects a satellite near \((0, 2M)\)

\[h = 0, \ k = 2M - 1 \quad \text{at} \quad χ = χ₀ \left(1 - \frac{1}{4M}\right)\]

(The satellite \((0, 2M + 1)\) is too far from \( χ₀ \) to be observed.)

The ratio of its intensity to the intensity of the main peak is

\[\frac{\sin \pi N dₐ}{\sin \pi a₀} \sim \frac{\sin \pi N dₐ}{\sin \pi a₀}\]

modified by the second factor in \( A \). For our CF₄ model this intensity ratio is much too small (less than 1 %), and it may be that \( (dₐ - dₐ)/a₀ \) is larger than we think. In the limit of Calisti’s molecular shape (Fig. 5) this ratio is 0.33. In IN12 experiment it is 0.27 at 37 K, 0.31 at 18 K and about 0.34 at 0 K.

The worst feature is the bad position of the peaks. Peaks at 1.493 \text{ Å}^{-1} and 1.522 \text{ Å}^{-1} fit reasonably the position of the principal peaks relatively to the commensurate 1.478 \text{ Å}^{-1}, but the satellite is expected at 1.434 \text{ Å}^{-1} instead of the experimental value 1.465 \text{ Å}^{-1}.

We have to conclude that more compression is needed.

If the indices \((0, 2M)\) and \((0, 2M - 1)\) are nevertheless attributed to 1.522 \text{ Å}^{-1} and 1.465 \text{ Å}^{-1} \( M \sim 13\) and \( 2M a₀ ≈ 110 \text{ Å} \) which agrees with disorder weakly acting on the Papyex spectrum. The compression perpendicular to the wall, \( \frac{a₀ - b}{a₀} \), is less than 1 %.

7. More compression. — Back-to-back walls have been drawn, up to now, with fluorine atoms of neigh-
bour molecules on each side of the walls lying in adjacent rows of carbons hexagons. But with our model shape they are indeed able to sit on the same hexagon row. Figure 6 shows the use of this fact to get more compression without being too much out of registry. In this figure, to come back to the same place relative to the substrate, four walls are needed; two head-to-head (β and δ), two back-to-back but one with fluorines on the same row of carbon hexagons (γ) and the other with fluorines on adjacent rows as previously (α). The type of wall γ can be used one time over n and it yields an extra gain of $a_0/2$. n bistrips would extend over $n a_2 = [(2M - \frac{1}{2})n - \frac{1}{2}]a_0$ and positions would be:

\[
\begin{align*}
\text{for } h = 0, \quad k = 2M & \quad \chi = \chi_0 \left(1 + \frac{1}{4M} + \frac{1}{4Mn}\right); \\
\text{for } h = 1, \quad k = M & \quad \chi = \chi_0 \left(1 + \frac{1}{16M} + \frac{1}{16Mn}\right); \\
\text{for } h = 0, \quad k = 2M - 1 & \quad \chi = \chi_0 \left(1 - \frac{1}{4M} + \frac{1}{4Mn}\right).
\end{align*}
\]

They fit reasonably the positions on IN12 for $n = 2$ (case of figure 6).

The calculated intensities are not much changed.

As we cannot go to the compression of Calisti's molecular shape there is still a problem.

Finally we must admit that this model is somewhat unusual as compression occurs in a particular direction: in the perpendicular direction the commensurate distance between molecules is maintained, whereas on the whole many molecules sit out of registry.

8. Chevrons (herring-bones pattern). — We remarked that walls may geometrically have kinks; the shape of back-to-back walls would be more complicated and presumably less favourable energetically than the kinked head-to-head walls (Fig. 7).

Fig. 6. — In order to get more compression we can imagine a special position of a back-to-back wall «α»: 2 fluorine centres lie in the same graphite hexagon. Molecules relax inside each strip. Only bottom and top positions of the molecules are drawn in each strip. The displacement of CF₄ molecule with respect to the regular commensurate position is given for each row in unit of $a_0$. We can use one wall «α» over n bistrips made of 2M rows each. Walls β and δ are equivalent.

Fig. 7. — h) Kinks in head-to-head wall. The two head-to-head horizontal sections are connected with back-to-back oblique segments. b) Kinks in back-to-back wall. To get back to the original directions it is necessary to use a wall segment with different compression in the wall (-----).
Let us suppose now that these walls are wholly saw-toothed (Fig. 8) and undertake the task of calculating the diffraction amplitudes of such patterns.

An equilateral triangle with a basis of \( P \) molecules has an amplitude of scattering for a reflexion perpendicular to the basis of

\[
b_{\text{CF},x} \sum_{n=0}^{P-1} (P - n) e^{2i\pi nx} = b_{\text{CF},x} e^{i(P-1)x} \left\{ \frac{P + 1}{2} \sin \frac{Px}{\sin x} + \frac{id}{dx} \left( \frac{\sin Px}{\sin x} \right) \right\}
\]

with respect to its basis and with

\[ x = \pi kb/a_2. \]

The cell \((a_1, a_2)\) is analogous to the previous one, \( a_2 \) still being the distance between two back-to-back walls. Figure 8 shows that

\[ a_2 = (P + 1/4) a_0. \]

Two equivalent filled triangles, head-to-head and nearly adjacent (see Fig. 9) would give a scattering intensity

\[
b_{\text{CF},x}^2 \left\{ \cos^2 \delta (P + 1) \frac{\sin^2 \frac{Px}{\sin x}}{\sin^2 x} + 4 \sin^2 \delta \left[ \frac{d}{dx} \left( \frac{\sin Px}{\sin x} \right) \right]^2 \right\}
\]

where \( \delta = \pi k(b - d)/a_2. \)

This «bitriangle» motif is repeated \( N/P \) times along the basis (which generates a bistrip) and \( \gamma \) times perpendicularly.

\[
(P + 1) \text{ plays the same role as } 2M \text{ before, peaks have the same configuration and the width of a bistrip is the same. The intensity ratio between satellite and main peak is slightly enhanced.}
\]

Moreover we can now see that this pattern can support a compression parallel to the back-to-back walls indicated by arrows on figure 8. This compression along a second direction is likely to happen. In that case \( \delta \) may be greater. The figure is drawn with \( d = 0.27 a_0 \) and \( (a_0 - b) = 0.39 a_0/P \), i.e. still a compression of about 1 %. The ratio of satellite to main peak intensities is then about 0.3, which is about the experimental value.

The pattern appears now to be more symmetrical. Previously we had strips. Now we have triangular domains and walls are all back-to-back; head-to-head positions occur only at nodes. Straight walls could occur over two directions as can be seen in figure 9 (but not over three directions). But an \( a_1/2 \)
slip can occur along a straight wall (e.g. of $\delta_i$ became $\delta_i'$ at the beginning of the paper). There is then no straight wall left along another direction and another slip in another direction would need more complicated defects, certainly needing much more energy — i.e. the ternary symmetry is not broken at the molecular level, but at the wall level.

It can be remarked that this pattern is necessary for ZXY, i.e. with the coherence length of the substrate larger than a few times two widths of a bistrip. For papyex few walls occur, say about one single node, but nearly the same compression is expected for the same pressure — temperature conditions, which gives the same position of peaks even if their relative intensities are different.

On a substrate with larger coherence length the central peak would tell if there are correlations between the $a_i/2$ slips : on a perfect crystal the central peak would be replaced by a broad feature if there are no correlations, or have satellites describing correlations. High resolution LEED on a single crystal may be attempted.

The $\zeta$-phase of $O_2$ absorbed on ZYX [15] has also a three-peak structure with peaks at about the same positions (2.14, 2.21, 2.25 Å), but the intensities are not equal, their ratio depending upon coverage and temperature. Moreover one peak (at 2.14 Å$^{-1}$) is enhanced on grafoil [16, 17] and a fit with a distorted triangular simple structure is as bad as for CF$_4$. This phase is very far from registry; molecules are very probably perpendicular to the surface, the magnetic spins interacting without long-range order. The modulation by substrate added to magnetostrictive forces [16] could create walls and these walls may perhaps be treated as in the CF$_4$ case.

9. Phase diagram (Fig. 10). — Let us sum up now what we understand from the different phases of adsorbed CF$_4$.

For coverages around 0.5 the layer is liquid above 75 K, the critical point being at 99 K [5]. Between 65 K and 75 K the layer is commensurate, but above 70 or 72 K the commensurate phase (C) becomes plastic (P); we think that CF$_4$ then spins over all directions but with some correlation. The concept of plastic phase should be considered also for CH$_4$ on graphite at medium coverage between 46 K and 56 K; a spinning has been detected [18] without checking angular correlations. The plastic phase could be invoked to explain a tail in the diffraction spectra [19]. The triple point at 75 K is remarkably near the three-dimensional triple point (89.5 K) (for incommensurate adsorbate the ratio is:

$$T_c(2d)/T_c(3d) \sim 0.61 \ [20].$$

It is higher for commensurate krypton on graphite (0.73), but here it is still higher (0.84)). It may be thought that the binding on the substrate hinders the full rotation which is favourable to the liquid state. Below 65 K a quasi-commensurate phase (SC) occurs which from LEED studies [4] is not rotated from the substrate. It begins to rotate slightly (up to 3.5°) below 59 K; some kind of hysteresis is an indication of first order transition to such a phase T, without or with a very small change in distances. The compression can be as high as 4% relatively to phase C; it is higher than the compression in our 3-peak phase (III) which we therefore think different, with probably a first order transition. The phase T observed in LEED may correspond to the one- (or two- ?) peak structure we observed at 62 K near the full monolayer; at coverage larger than one the compression is 6%. (A triangular compressed phase, out of registry, would be compressed by 7 to 8% on the basis of our molecular shape model.) The question of this phase being different from T remains unanswered.

From the studies on D1B and D2 we still maintain that satellites prove that compression occurs together with orientation changes. For orientational static distortion waves ternary symmetry is likely to be disrupted and for that reason we called the intermediate phase SC, for semi-commensurate. The phase T may become more symmetric at high coverages, as it becomes more out of registry.

Finally we must mention that at coverage 1.9 the spectrum is the superposition of the compressed monolayer peaks plus peaks we called bulk-CF$_4$ [2]. However, this « bulk » spectrum was obtained with 6 monolayers of CF$_4$ on graphite and is different from the $\alpha$-phase of CF$_4$ observed at these temperatures [12] and should be studied for itself.

Fig. 10. — Tentative phase diagram of submonolayer CF$_4$ on graphite. This diagram is approximative for the coverage. Some coexistence domains are not shown because we have no experimental evidence for them. 7 different phases are shown: g = gas; L = liquid; P = plastic; C = commensurate; SC = incommensurate; T = tilted incommensurate; III triple-peak orientational wall phase. The III to T transition should be drawn at 56 K.
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Note added in proof: after submitting the manuscript we received a preprint of a synchrotron study [21]. It confirms the existence of the $2 \times 2$ commensurate phase, of the low-temperature 3-peak phase and of the compressed-regular-triangular incommensurate phase at high coverage (called I by them and T by us). They also see a semi-commensurate phase (which they call S for stripe phase) between 57 K and 65 K; they do not distinguish between the unrotated SC phase and the rotated T phase as seen by LEED. An error in the drawing of our figure 10 should be noted: the III to T transition should be at 56 K. A different analysis of synchrotron spectra near 58 K could perhaps reconcile them with LEED studies. Differences in coverage are due to different monolayer determination: we call 1 the B point of volumetric adsorption isotherm, [21] calls 1 the coverage for which a $2 \times 2$ structure would be complete; substrates are also different. On the whole the two phase diagrams agree well and are complementary.

References


