



HAL
open science

First-order wetting transition in CF₄ solid films adsorbed on the (0001) graphite surface

J.M. Gay, M. Bienfait, J. Suzanne

► **To cite this version:**

J.M. Gay, M. Bienfait, J. Suzanne. First-order wetting transition in CF₄ solid films adsorbed on the (0001) graphite surface. *Journal de Physique*, 1984, 45 (9), pp.1497-1504. 10.1051/jphys:019840045090149700 . jpa-00209889

HAL Id: jpa-00209889

<https://hal.science/jpa-00209889>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

68.10C — 68.40 — 61.14H — 68.55

First-order wetting transition in CF₄ solid films adsorbed on the (0001) graphite surface

J. M. Gay, M. Bienfait and J. Suzanne

Département de Physique (*), Faculté des Sciences de Luminy, 13288 Marseille Cedex 9, France

(Reçu le 20 février 1984, accepté le 7 mai 1984)

Résumé. — La configuration de films de CF₄ condensés sur la face de clivage d'un monocristal de graphite a été observée par diffraction d'électrons en incidence rasante et par diffraction d'électrons lents. Le dépôt subit une transition de mouillage du premier ordre à 37 K, une température bien en dessous du point triple de CF₄ tridimensionnel (89,5 K). La structure du film a été étudiée au voisinage de la température de mouillage. La double couche est instable dès qu'une couche supplémentaire est déposée ; elle perd alors son ordre à longue distance. L'ensemble du film se réorganise après le dépôt de plusieurs autres couches statistiques. On observe alors une condensation couche après couche au-dessus de 37 K et la formation de cristallites au-dessous. Des isothermes d'adsorption par diffraction d'électrons lents (DEL) sont obtenues et permettent de caractériser les propriétés thermodynamiques de la 2^e et de la 3^e couche entre 51 et 58 K. L'ensemble de nos résultats, ainsi que ceux publiés auparavant dans la littérature, sont reproduits sur un diagramme de phase « pression vs. 1/T » ($50 < T < 110$ K ; $5 \times 10^{-8} < p < 50$ torr). Enfin, des mesures de cinétique d'adsorption par DEL ont été effectuées entre 15 et 45 K. Les résultats obtenus sont commentés.

Abstract. — The configuration of CF₄ films condensed on a graphite single crystal (0001) surface has been observed by reflection high energy electrons diffraction (RHEED) and by low energy electron diffraction (LEED). The films exhibit a first order incomplete to complete wetting transition at 37 K, a temperature far below the CF₄ bulk triple point (89.5 K). The structure of the film has been studied around the wetting temperature. The double layer structure is unstable against deposition of a third layer and loses its long range order. Upon further condensation the structure of the film is reorganized and gives well defined RHEED diffraction patterns featuring layer by layer condensation above 37 K and clustering below. LEED adsorption isotherms measured on graphite spots are used to characterize the second- and third-layer condensation between 51 and 58 K. The equilibrium vapour pressure vs. inverse temperature phase diagram is constructed from data obtained in this work and in the literature for $50 < T < 110$ K and $5 \times 10^{-8} < p < 50$ torr. Finally, LEED kinetics adsorption measurements are also carried out between 15 and 45 K. The shapes of the recorded curves are discussed.

The mechanism of wetting phenomena on uniform substrates has been a topic of recent experimental [1-6] and theoretical [7-20] interest. The wetting is considered to be complete when layer by layer condensation is observed and continues up to coexistence with bulk. This phenomenon is also called Frank van der Merwe [21] or type 1 [23-25] mode of growth. On the other hand, the wetting is incomplete if a limited number of layers are formed before bulk crystallites are deposited. The coexistence of a few adsorbed layers and three-dimensional clusters is also known as Stranski-Krastanov [21-22] or type 2 mode of growth [23-25].

According to the first theoretical studies [11, 13] it was believed that the major physical parameter conditioning the mode of wetting at low temperature was the relative substrate interaction strength. It was suggested that complete wetting should occur for sufficiently attractive substrates. However recent experiments [3, 4] contradicted these predictions and showed that the type 2 mode of growth was reentrant [4]. In other words, incomplete wetting occurs at small and large substrate strength. Complete wetting is observed only in a narrow range of intermediate substrate strength. These experiments stimulated further theoretical investigations and since then, it has been shown that the mode of growth at low temperature is quite sensitive to the strain induced

(*) Equipe de Recherche Associée du CNRS 899.

in the film by crystal structure mismatch [26, 27, 29] or to the shape and magnitude of the adsorbate-adsorbate and adsorbate-substrate potentials [28]. Although much progress has been made on the understanding of the mode of wetting at low temperature, the problem is far from being completely understood.

Another related phenomenon is the modifications of the film configuration as the temperature is increased. Contact angle measurements of droplets condensed on solid surfaces have shown, since a long time [30], that the contact angle can become zero at some given temperature. This type 2-type 1 transformation is called a wetting transition. Such a transition can also occur in solid films adsorbed on uniform crystal surfaces [1, 2, 5, 6]. Theoreticians have analysed the conditions controlling the complete-to-incomplete wetting transition and have predicted that its nature is quite sensitive to the range dependence of the substrate potential. It was demonstrated within mean-field theory [12, 16, 31] or renormalization group [32] contexts that for short-range forces the transition can be either continuous or first order. As for long range van der Waals forces, the prediction is that wetting can only be first order [31-33].

In this paper, we describe an experimental contribution to the analysis of wetting phenomena and present strong evidence that a solid film can undergo a first-order wetting transition. The experiment has been carried out on CF_4 multilayers adsorbed on graphite. The CF_4 interaction is usually modelled by a Lennard-Jones potential [34]. Furthermore, given the value of the isosteric heat of adsorption of the CF_4 monolayer [39, 50], it is reasonable to assume that the graphite- CF_4 interaction is of the van der Waals type. As a consequence, it seems that our results confirm the theoretical predictions. The other solid films studied up to now [1, 2, 6] exhibit a wetting transition in the vicinity of the bulk triple point and the transition, when measured [6], is shown to be continuous. Hence, in that case, the spreading of the film can be related to melting. In our system the type 2-type 1 transition occurs at 37 K, a temperature far below the bulk triple point (89.5 K). It must be noted that first order wetting transitions have also been found in binary liquid mixtures [35, 36]. Our work extends the experimental study to multilayers adsorbed on single crystal surfaces in temperature ranges where the films are no longer fluid.

This work has been reported briefly in a letter [5]. Here, we want to develop and complete the previous results. The two major techniques of analysis were low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED). We first report on our experimental method and summarize the work already published. Next, we extend our investigation of the properties of the film at lower and higher temperature and analyse in more detail the wetting transition at 37 K.

1. Experimental

The experimental procedures have been reported, at length, in previous papers [3, 37, 38]. The experimental apparatus consists of two surface probes, i.e. a low current low energy electron diffractometer (LEED) [37], and a reflection high energy electron diffractometer (RHEED) adapted to physisorption studies by incorporating differential pumping. The cryogenic holder enables the temperature to be regulated to better than 0.1 K between 20 and 100 K and to better than 0.5 K between 8 and 15 K. The absolute uncertainty in T is estimated to be ± 1 K in all the attainable temperature range. The ultra high vacuum chamber also contains a mass spectrometer to monitor the gas purity and an ionization gauge to record the vapor pressure surrounding the crystal. A schematic diagram of the experimental apparatus can be found in reference [38].

The Bayard-Alpert gauge was calibrated at room temperature against a Baratron gauge. A \sqrt{T} thermomolecular correction has also been made to account for the temperature difference between the CF_4 gas and the graphite crystal.

Before starting an experiment, the cleanliness and the long-range order of the surface were checked by observing first the bare graphite LEED pattern and then the well-known structures of the CF_4 adsorbed monolayer quoted in the literature [39-41].

The thickness of the film was measured as follows [5]. Beginning with the bare substrate at constant temperature and a base pressure in the 10^{-11} torr range, the pressure was raised abruptly by introducing CF_4 gas through a leak valve to a constant value p . The time required to condense a monolayer was determined by observing the evolution of the LEED pattern. At around 40 K, the structure at monolayer completion is composed of doublets [39] in a position close to the 2×2 structure. The time $\Delta\tau$ needed to observe the doublets gives the exposure $p \Delta\tau$ required to condense a complete layer. This exposure is used to estimate the pressures and times necessary to deposit any desired quantity, assuming that the sticking coefficient is constant over the entire range.

The film structure can be observed successively by RHEED and LEED. Only a few seconds are needed to change the setting of the diffractometers. However, for the sake of clarity, we prefer to report the observations from both techniques one after the other.

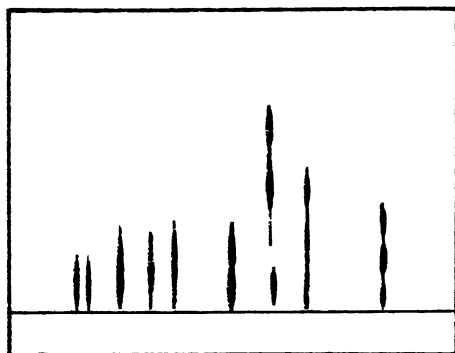
2. RHEED results.

RHEED can clearly differentiate the different modes of growth or the type of wetting of thin films [3, 4, 38, 42]. In the case of layer-by-layer condensation (type 1), the diffraction pattern is composed of parallel streaks, whereas sharp spots appear on the screen when the deposit forms crystallites of bulk material.

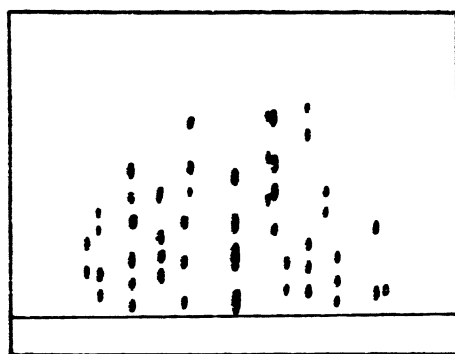
If the film consists of crystallites small enough for appreciable beam transmission and deposited on a few adsorbed layers, the pattern is a composite of spots and streaks.

The RHEED observations have been made under grazing incidence (about 2°) with electrons accelerated under ~ 30 kV. They have been partly reported in a letter [5] which we first summarize and then complete with new results.

2.1 SUMMARY OF PREVIOUS RHEED RESULTS [5]. — Between 15 and 37 K, parallel streaks are observed as soon as one or two statistical layers are deposited. Upon further deposition, sharp spots appear close to or on the former streaks. For thicker films (20-100 layers) the streaks disappear totally and the RHEED pattern is only made of sharp spots. A typical pattern obtained at 35 K is drawn in figure 1a.



b



a

Fig. 1. — RHEED patterns of CF_4 films drawn from photographs published in Ref. 5 and 38 (angle of incidence $\sim 2^\circ$, incident energy ~ 30 kV, azimuth ~ 13.0).

a) Incompletely wet surface at 35 K (~ 50 statistical layers). Sharp spots featuring bulk crystallites are seen.

b) The same film at 40 K. The modulated streaks indicate that the film completely wets the graphite surface. The wetting transition occurs at 37 K.

It corresponds to a photograph published in reference [5]. The succession of the different RHEED patterns means that a few ordered solid layers are first deposited, then that bulk crystallites coexist with the two-dimensional adsorbed structure and finally that the whole surface is covered by bulk crystals. These results clearly indicate that below 37 K thick films of CF_4 incompletely wet the graphite surface and that the mode of growth is of type 2.

Between 37 and 50 K, the evolution of the RHEED pattern is quite different. We first observe, as at the lowest temperature, the appearance of parallel streaks, then, upon further deposition, the streaks become modulated and keep the same modulation when the thickness is increased. Such a thick film pattern is drawn in figure 1b. It corresponds to a photograph displayed in reference [5]. This RHEED pattern is the signature of a layer by layer condensation. The modulation of the streaks is a well-known effect and results from the finite penetration of the grazing incidence beam [42].

Hence, a wetting temperature has been observed at $T_w = 37$ K. Above T_w , the mode of growth of CF_4 on graphite is of type 1; below T_w , wetting becomes incomplete and the mode of growth is of type 2. It must be pointed out that the wetting temperature occurs far below the triple point (89.5 K).

Furthermore, it has been shown that the bulk transition type 1-type 2 is first order. This result has been demonstrated as follows. A thick film (20-100 layers) is condensed and the gas introduction is stopped. Then, we cross the wetting temperature back and forth by changing the temperature between 40 and 30 K by steps of 0.5 K. We waited at each step to insure that a steady state was reached. We always obtained a hysteresis of about 2 K (transformation type 1 \rightarrow type 2 at 35 K) upon cooling down whereas we always observed the transition at 37 K upon rewarming. This hysteresis is a clear indication of a first-order transition.

Finally, other observations show that local equilibrium is achieved very rapidly by surface mobility. In the type 2 configuration, the sharp spots weaken and broaden gradually over a period of a few minutes. However the sharp spots can be restored by sweeping the electron beam over the surface. We believe that the beam carries enough energy to produce a slight local heating of the film, causing the distillation of bulk crystallites from the probed region to adjacent areas of the film.

2.2 NEW RHEED RESULTS. — We studied two important points more thoroughly. First, we analysed carefully the beginning of the growth of the incompletely wet film. That is, we looked for the thickness at which clusters are deposited on two-dimensional layers. Second, we studied the change in the structural properties of thick films at the wetting transition (37 K). Finally we extended our measurements down to 8 K.

As already reported, we observed streaks below 37 K as soon as one or two layers of CF_4 are condensed. If we now add at 35 K a third statistical layer, the RHEED pattern almost disappears and the background increases dramatically. The addition of a fourth statistical layer does not change the diffraction pattern. However condensing a 5th (and a 6th, 7th...) layer results in a restoration of a high contrast RHEED pattern with fine, modulated and bright streaks and tiny spots located close to the streaks. This means that the two-dimensional long range order of the double layer is almost destroyed when a third and a fourth statistical layer is condensed. The local strains probably become too large and relax into numerous defects. A new long range order occurs above five statistical layers. It can be concluded from these results that clustering appears at ~ 35 K on the top of a very thin film of 2 to 4 adsorbed layers and that the structure of the thick film is different from that of the double layer.

The second observation deals with the crystallography of thick films (20-100 layers) close to the wetting transition. A few pictures have been taken when the film was warmed up (or cooled down) around 37 K. The photograph exposure was ~ 2 minutes and, thus, results in the superimposition of the type 2 and type 1 structures. It can be seen on these RHEED patterns that some of the sharp spots (coming from bulk crystallites) lie slightly outside the streaks (diffracted by completely wet multilayers). The variation of the lattice parameters in that direction is about 2-3 % and close to the instrumental resolution. This discontinuity in the crystal structure at the transition is another argument in favour of the existence of a first-order wetting.

Finally we extended our observations down to 8 K, the lowest temperature possible with the cryogenic holder. We started with thick films (20-100 layers) in the type 2 configuration and cooled down the sample. At about ~ 10 K, the sharp spot RHEED pattern disappeared suddenly and was replaced by a very intense background on the screen. We waited for several minutes at these low temperatures (~ 8 K) and we never succeeded in restoring a new long-range order. The kinetics of reorganization of the film is probably too slow at these temperatures. However, rewarming the film to 15-20 K results in the reappearance of the classical type 2 RHEED pattern. Hence a new transition in the film has been detected around 10 K but its nature is still unknown.

2.3 RHEED PATTERN ANALYSIS. — Complete RHEED interpretation needs control over the azimuthal incidence angle [42]. However our apparatus was not equipped with this facility and our results have been obtained for a unique azimuth which was close to the $\bar{1}30$ graphite reciprocal direction [4, 38]. As a consequence, the crystallographic interpretation of the RHEED pattern must be considered as tentative. In figure 1a, the periodicity ($7 \text{ \AA} \pm 0.3$)

of the rows perpendicular to the graphite surface is close to the (001) lattice plane spacing (7.29 \AA) of the $\alpha\text{-CF}_4$ bulk crystal. The (001) plane exhibits a pseudo hexagonal symmetry and is one of the densest planes of the $\alpha\text{-CF}_4$ structure which is stable between 10 and 76 K [43]. Unfortunately the information gained from our RHEED pattern is not sufficient to determine unambiguously the orientation of the bulk crystallite with respect to the substrate. Further work with other azimuths is required to clarify this point.

3. LEED results.

3.1 DIFFRACTION PATTERN. — The LEED patterns in the submonolayer regime have been studied carefully. They correspond to those published elsewhere [39]. Around 40 K, an almost commensurate solid corresponding to the so-called « triple peaked » phase [40] is first observed. Then at higher coverage a rotated incommensurate solid [39-41] featuring LEED doublet occurs close to the monolayer completion. This structure persists, although less contrasted, up to second layer completion. As soon as the third layer is deposited the LEED pattern disappears totally and is replaced by a very intense background on the screen. The destruction of the long range order at three statistical layers is observed on both sides of the wetting temperature between 30 and 40 K. The deposition of a fourth layer is needed to reorganize slightly the structure. Then, six weak and very broad peaks are observed close to the 2×2 directions. These peaks become more intense after the condensation of a 5th, 6th, ... layers. It is impossible to differentiate the type 1 from the type 2 regime from the observation of the LEED patterns obtained for films below 10 statistical layers. However, for thicker films (10-100 layers), the diffraction pattern is quite different below or above 37 K. In the type 1 configuration, the six very broad peaks are not modified whereas they are resolved into six broad doublets below the wetting temperature. If the doublets are due to hexagonal domains slightly rotated with respect to the 2×2 structure, their corresponding lattice parameter is $\sim 4.5 \text{ \AA}$. It is comforting to note that this quantity is just the mean value between the two CF_4 nearest-neighbour distances (4.32 and 4.74 \AA) in the close-packed (001) $\alpha\text{-CF}_4$ plane. However this apparent agreement may be fortuitous.

It must also be emphasized that LEED measurements confirm the destruction of the long range order in the double layer around T_w when a statistical third layer is deposited. The deposition of a fourth and fifth layers is needed to initiate the reorganisation of the film. The instability of the double layer structure upon further condensation has already been noted for N_2 and O_2 films adsorbed on graphite [38]. These facts point out the importance of molecular reorientation and/or displacement in the mechanism of wetting phenomena.

LEED measurements also provide new information about the structure of the thick film in the type 1 and type 2 configurations. We have already said that doublets are observed for incompletely wet films even for thicknesses (~ 50 layers) where the whole surface is covered by bulk crystallites. The low energy beam penetration does not go beyond 3-4 layers and the LEED pattern cannot arise from the few two-dimensional layers stable below the bulk clusters. The only way to explain our LEED pattern observation when bulk crystals are deposited is to assume that these crystals have a tabular shape with a well developed face parallel to the substrate surface. As for the layer grown film above T_w , the very broad LEED pattern indicates that the multilayer contains numerous defects (domain walls, grain boundaries, dislocations...).

3.2 ADSORPTION ISOTHERM MEASUREMENTS. — The attenuation of a beam diffracted by the substrate *versus* the thickness of adsorbed layers can be used to record adsorption isotherms [39, 44-46]. In our study, the variation of the intensity of the 01 LEED graphite peak was measured at constant temperature by using a spot photometer. The aperture size was chosen to be large enough to cover the whole surface of the 01 spot, but to exclude most of the adjacent background. The CF_4 pressure and temperature were varied between 10^{-7} and a few 10^{-6} torr and between 51 and 58 K respectively in order to achieve an adsorption-desorption steady state between the adsorbed layers and the 3D vapour. The main purpose of

this experiment was to determine, by LEED, the configuration of CF_4 film in a temperature range where observation could be made under equilibrium conditions.

In that temperature range, according to the RHEED conclusions, a layer by layer condensation was expected to be observed. A typical LEED adsorption isotherm is displayed in figure 2. It is recorded as follows. The temperature of the graphite crystal is kept constant and CF_4 gas is admitted through a leak valve. The introduction of the gas is slow enough to be always in quasi-equilibrium conditions. The total recording time was about 10 minutes. A sudden drop of the graphite 01 beam intensity is observed as soon as the gas is admitted. It corresponds to the adsorption of the first layer for which the equilibrium pressure is too low to be measured. Then second and third steps occur at 9.7×10^{-7} and 1.17×10^{-6} torr respectively for $T = 55.7$ K. One can even guess a fourth step at 1.21×10^{-6} torr. Each step represents the condensation of a new layer. Above four layers, the attenuation of the graphite spot is too strong and the method is unable to distinguish any further layer condensation. The bulk vapour pressure is reached when the beam intensity remains constant. It must be noted that the pressures of the 2nd, 3rd and 4th layer obey a $\exp - \alpha/d^3$ law where d is the thickness and α a constant. However, it is impossible to infer any deviation from the d^{-3} law due to the difference between film and substrate interaction [47-49], given the limited number of experimental points.

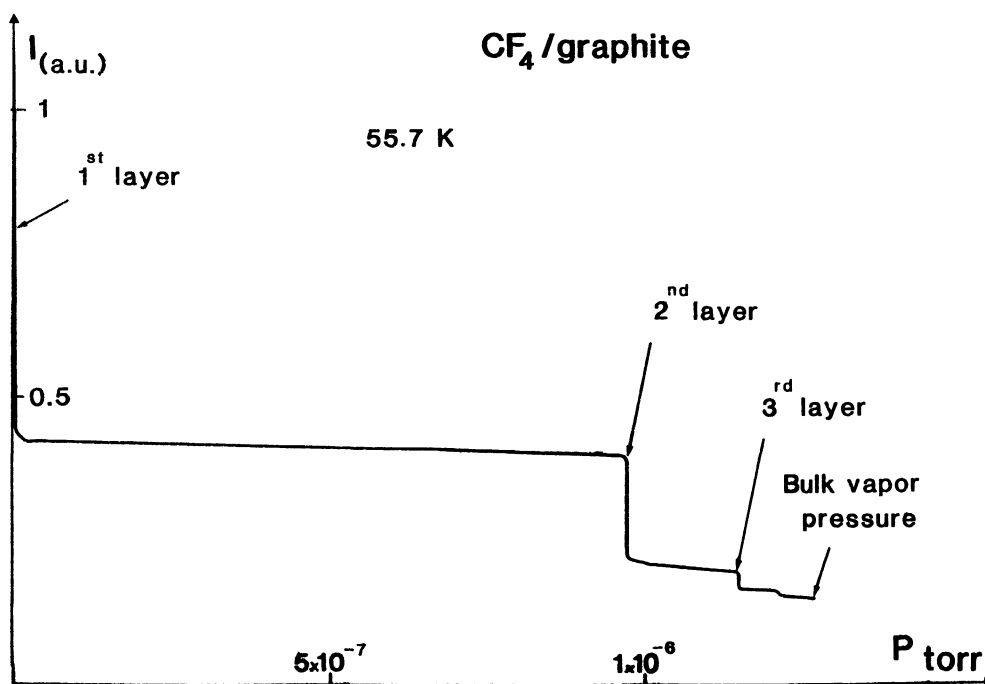


Fig. 2. — Variation of the intensity of the LEED 01 graphite spot *versus* CF_4 pressure at 55.7 K. Each step corresponds to the condensation of a CF_4 molecular layer (incident energy 140 eV).

All the LEED adsorption isotherm measurements recorded between 51 and 58 K look like the one displayed in figure 2. They are all consistent with complete wetting of the CF_4 film above 37 K. Unfortunately, it is impossible to measure adsorption isotherms below the wetting temperature because at low T the bulk equilibrium vapour pressure falls much below 10^{-10} torr. However adsorption kinetics measurements can be carried out. They will be reported in paragraph 3.3.

The position of the second and third vertical steps obtained at different temperatures are plotted on the vapour pressure-inverse temperature phase diagram in figure 3. The experimental points and their best-

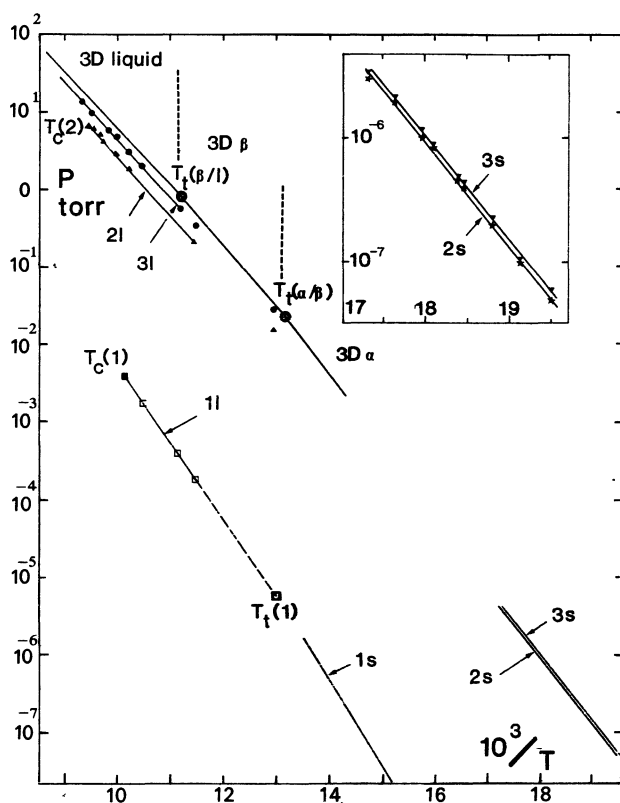


Fig. 3. — Vapour pressure vs. inverse temperature phase diagram for CF_4 on graphite (0001). The steps corresponding to the adsorption of the 2nd and 3rd layer obtained from our LEED graphite intensity isotherms are plotted in the box. Within the temperature range of the measurements, the complete layers are solid (s). The gas-solid transitions in the 2nd and 3rd layers are called 2s and 3s respectively. The figure represents all the available p vs. $1/T$ data. The gas-solid transition in the first layer (1s) is taken from reference [39]. The notations 1l, 2l, 3l correspond to the gas-liquid equilibrium in the first, second and third layers at higher T , obtained from reference [50]. The bulk vaporization and sublimation lines passing through the β solid-liquid triple point ($T_1(\beta/1) = 89.5$ K) and the β solid- α solid triple point ($T_1(\beta/\alpha) = 76.2$ K) are taken from Ref. 50 and 51. The critical temperature $T_c(1)$ and the triple point $T_1(1)$ of the first layer are 99 and ~ 77 K, respectively (Ref. [50] and [40, 41]).

fit lines are drawn in the insert. All the known phase diagram of CF_4 adsorbed on graphite is reported in the figure, except in the low temperature region where the pressure is too small to be measured. (A more detailed coverage-temperature phase diagram in the submonolayer range determined by X-ray and neutron diffraction measurements can be found in the literature [40, 41, 52]).

Adsorption isotherm measurements obtained by volumetry [50] were devoted to the study of the coexistence of the gas and liquid phases in the first, second and third layers condensed on graphite. They are plotted in the top left-hand part of the figure. The critical temperature of the first $T_c(1)$ and of the second $T_c(2)$ layers are 99 and 106 K respectively (let us recall that the bulk critical temperature $T_c(3D)$ is 227.5 K). The triple point temperature $T_1(1)$ of the first adsorbed layer has been estimated by neutron scattering (77 K) [40, 52] and by X-ray diffraction (75.5 K) [41]. We placed it on the extrapolation of the liquid-gas coexistence line of the monolayer. The triple points of the second and third layers are not known but they must be located between $T_1(1) = 77$ K and $T_1(3D) = 89.5$ K, the bulk triple point. The sublimation pressures of bulk liquid and solids plotted in figure 3 come from reference [51]. Below 76.2 K, the α - CF_4 structure is stable.

LEED measurements of the gas-solid coexistence in the monolayer range have also been obtained [39]. They are reported in the bottom of figure 3.

The best-fit lines through the LEED second and third layer points have the same slope within experimental uncertainty (3.9 ± 0.1 kcal mole $^{-1}$); this value is close to the bulk latent heat of sublimation (4.01 kcal mole $^{-1}$) measured at higher temperature in the α - CF_4 solid domain [50, 51]. We know, from our LEED measurements (see Fig. 2) that the bulk vapour pressure is only $\sim 10\%$ larger than the equilibrium pressure of the third layer. Hence, the third layer gas-solid coexistence line represents a good approximation of the bulk sublimation pressure in the same temperature range. Its extrapolation to higher pressure is in good agreement with the data of reference [51] for α - CF_4 , if we keep in mind that the absolute value of our temperature and pressure are known to within ± 1 K and $\sim 20\%$ respectively.

3.3 ADSORPTION KINETICS. — Our photometric setup can be used to record the adsorption kinetics in a temperature range (below 45 K) where the CF_4 bulk sublimation pressure is smaller than 10^{-10} torr. In these conditions, desorption can be considered as negligible. The experiment started with a residual pressure in the 10^{-11} torr range and a crystal at constant temperature, and the pressure was adjusted within one second to a new value, by means of the leak valve. The value of p (5×10^{-9} torr) was chosen so that the total recording time was a few minutes. The intensity of the 01 graphite spot

decreased continuously with time as represented in figure 3. All curves in this figure have been normalized to the same total intensity variation. It is obvious from the records that LEED is sensitive to the kinetics of condensation of the first two layers only and cannot be used to determine the mode of growth above that thickness. Still, we performed the following experiment. We first deposited 4 to 6 statistical layers at 35 K, that is, in the type 2 regime. Then, we slowly warmed up the film and observed, at around 37 K, a decrease of the graphite peak intensity by about 1 to 2 percent. This slight attenuation of the graphite LEED signal is consistent with a spreading of the bulk crystallites at the wetting temperature.

Nevertheless, we prefer to pay more attention to condensation of the first two layers. The inflexion points observed between 45 and 30 K, after the 1st and 2nd layer adsorption, indicate that layer by layer condensation occurs at least up to that thickness. This is in agreement with the results of paragraph 2.2 showing that at 35 K clustering occurs on top of 2 to 4 layers and that layer growth is present above 37 K up to coexistence with bulk phase. More interesting is the disappearance of the above inflexion points below 30 K. This could indicate a reduction of the number of stable adsorbed layers before bulk crystallite deposition. The linear part corresponding to the first 3/4 drop in the intensity seems to indicate that monolayer deposition still occurs at 25 and 15 K. The remaining rounded curve could be interpreted as due to the growth of bulk clusters. However, the inflexion points can also be blurred out at low temperature by a very slow rate of reorganization of the deposited material. Yet more work is needed to draw definite conclusions on this point.

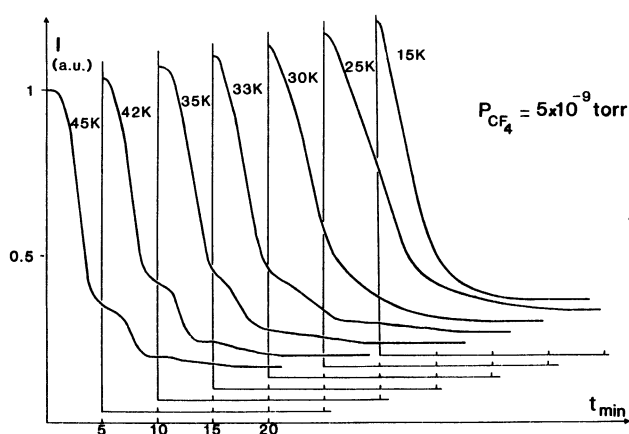


Fig. 4. — Adsorption kinetics measurements. The curves represent the variation of the intensity of the graphite 01 beam (incident energy 140 eV) versus time, under a constant flux of CF_4 vapour, at different temperatures. The discontinuities correspond to successive layer condensation. The curves are shifted by intervals of 5 min for the sake of clarity.

4. Discussion.

All the data reported here are consistent with the existence of a first order wetting transition at 37 K for CF_4 films adsorbed on graphite (0001) single crystals. This transition occurs far below the melting of the film (89.5 K) and is not related to any known structural transition in the adsorbed monolayer [39-41] or in the bulk solid [43]. Hence, the available information indicates that the layering-clustering phase change at 37 K is a genuine wetting transition. In this system, the crystalline cohesion mainly results from van der Waals interactions that are known to be long range forces. As recalled in the introduction, the latest theoretical works predict that for such forces the wetting transition must be first order. Our experimental observations confirm this prediction.

The above wetting transition was anticipated a few years ago [50] by extrapolating, to low T , multi-layer adsorption data. However the adsorption isotherm measurements were carried out in the liquid-gas coexistence domain of the 1st, 2nd and 3rd adsorbed layers. The extrapolation of the coexistence lines towards temperatures for which the layers were solidified, was obviously not correct and gave an expected wetting temperature which was much too high. Still, the proposed wetting transition was an interesting suggestion and partly motivated the present study.

Finally, we would like to stress the importance of the structural changes during the film growth. We unambiguously showed that, around the wetting temperature, the long range order of the double layer disappears as soon as a third statistical layer is deposited. Then, upon further condensation, the film reorganises itself and gives clear RHEED and LEED diffraction patterns. Furthermore, for thick films, we observe a slight structural change at the wetting transition. All this information points to the importance of molecular reorientation and displacement during the type 1-type 2 transition. Unfortunately, for technical reasons explained above, our structural study was just outlined. It should be developed and deepened in the near future.

Acknowledgments.

We are grateful to J. G. Dash, J. A. Venables and M. Schick for their permanent interest in this work and for their critical comments. We thank J. Y. Hoarau for designing the RHEED and LEED set-ups and G. Boato for providing us with graphite crystals.

Note added in proof. — After submission of this paper, we received several preprints and reprints dealing with wetting phenomena. Two were devoted to experimental studies of wetting transitions in the

vicinity of a bulk triple point (ethylene/graphite (0001) [53]; ethylene/boron nitride [54]). Another four articles examined the nature of the wetting transition with different statistical models [55-58]. The

basic results which were summarized in the introduction remain unchanged. According to the terminology of reference [58], the transition reported here corresponds to a thin film-thick film transition.

References

- [1] MENAUCOURT, J., THOMY, A. and DUVAL, X., *J. Physique Colloq.* **38** (1977) C4-195.
- [2] SUTTON, M., MOCHRIE, S. G. J. and BIRGENEAU, R. J., *Phys. Rev. Letters* **51** (1983) 407.
- [3] SEGUIN, J. L., SUZANNE, J., BIENFAIT, M., DASH, J. G. and VENABLES, J. A., *Phys. Rev. Lett.* **51** (1983) 122.
- [4] BIENFAIT, M., SEGUIN, J. L., SUZANNE, J., LERNER, E., KRIM, J. and DASH, J. G., *Phys. Rev. B* **29** (1984) 983.
- [5] SUZANNE, J., SEGUIN, J. L., BIENFAIT, M. and LERNER, E., *Phys. Rev. Lett.* **52** (1984) 637.
- [6] KRIM, J., DASH, J. G. and SUZANNE, J., *Phys. Rev. Lett.* **52** (1984) 640.
- [7] CAHN, J. W., *J. Chem. Phys.* **66** (1977) 3667.
- [8] EBNER, C. and SAAM, W. F., *Phys. Rev. Lett.* **38** (1977) 1486.
- [9] EBNER, C., *Phys. Rev. A* **22** (1980) 2776. *B* **28** (1983) 2890.
- [10] CHALUPA, J. and HUBERMAN, B. A., *J. Chem. Phys.* **72** (1980) 5276.
- [11] SULLIVAN, I., *Phys. Rev. B* **20** (1979) 3991; *J. Chem. Phys.* **74** (1981) 2604; *J. Am. Chem. Soc. Faraday Symp.* **16** (1981) 1.
- [12] PANDIT, R. and WORTIS, M., *Phys. Rev. B* **25** (1982) 3226.
- [13] PANDIT, R., SCHICK, M. and WORTIS, M., *Phys. Rev. B* **26** (1982) 5112.
- [14] SAAM, W. F., *Surf. Science* **125** (1983) 253.
- [15] TELETZKE, G. F., SCRIVEN, L. E. and DAVIS, H. T., *J. Chem. Phys.* **77** (1982) 5794; **78** (1983) 1431.
- [16] HAUGE, E. H. and SCHICK, M., *Phys. Rev. B* **27** (1983) 4288.
- [17] WEEKS, J. D., *Phys. Rev. B* **26** (1982) 3998.
- [18] BRÉZIN, E., HALPERIN, B. I. and LEIBLER, S., *J. Physique* **44** (1983) 775.
- [19] NAKANISHI, H. and FISHER, M. E., *Phys. Rev. Lett.* **49** (1982) 1565.
- [20] KROLL, D. M. and LIPOWSKY, R., *Phys. Rev. B* **28** (1983) 5273; **28** (1983) 6435.
- [21] VENABLES, J. A. and SPILLER, G. D. T., in *Surface Mobilities on Solid Materials*, vol. 86, edited by V. T. Binh, NATO Advanced Study Institute Series (Plenum) 1982.
- [22] BAUER, E., *Zeits. Krist.* **110** (1958) 372; *Thin Sol. Films* **12** (1972) 167.
- [23] DASH, J. G., *Phys. Rev. B* **15** (1977) 3136.
- [24] PEIERLS, R. E., *Phys. Rev. B* **18** (1978) 2013.
- [25] DASH, J. G. and PEIERLS, R. E., *Phys. Rev. B* **25** (1982) 5523.
- [26] HUSE, D. A., preprint.
- [27] EBNER, C., ROTTMAN, C. and WORTIS, M., *Phys. Rev. B* **28** (1983) 4186.
- [28] MUIRHEAD, R. J., DASH, J. G. and KRIM, J., *Phys. Rev. B* **29** (1984) 5074.
- [29] GITTES, F. and SCHICK, M., *Phys. Rev. B*, to be published.
- [30] ZISMAN, W. A., in *Ad. Chem. Ser.* **43** (1964) 1.
- [31] TARAZONA, P. and EVANS, R., *Mol. Phys.* **48** (1983) 799.
- [32] NIGHTINGALE, M. P., SAAM, W. F. and SCHICK, M., *Phys. Rev. Lett.* **51** (1983) 1275.
- [33] DE GENNES, P. G., *C.R. Hebd. Séan. Acad. Sci.* **297** (1983) 9.
- [34] TAKAKO SHINODA, *Mol. Cryst. Liq. Cryst.* **55** (1979) 101.
- [35] MOLDOVER, M. R. and CAHN, J. W., *Science* **207** (1980) 1073.
- [36] SCHMIDT, J. W. and MOLDOVER, M. R., *J. Chem. Phys.* **79** (1983) 379.
MOLDOVER, M. R. and SCHMIDT, J. W., Proceedings of Conf. on Fronts, Interfaces and Patterns (1984), to be published.
- [37] CALISTI, S., SUZANNE, J. and VENABLES, J. A., *Surf. Sci.* **115** (1982) 455.
- [38] VENABLES, J. A., SEGUIN, J. L., SUZANNE, J. and BIENFAIT, M., *Surf. Science* (to be published).
- [39] CALISTI, S., Thesis, Marseille 1981.
CALISTI, S. and SUZANNE, J., to be published.
- [40] CROSET, B., MARTI, C., THOREL, P. and LAUTER, H., *J. Physique* **43** (1982) 1659.
- [41] KJAER, K., NIELSEN, M., BOHR, J., LAUTER, H. J. and MCTAGUE, J. P., *Phys. Rev. B* **26** (1982) 5168.
- [42] BAUER, E., in *Techniques of Metal Research*, ed. R. F. Bunshah (Interscience, New York) 1969, Vol. 2, p. 501.
- [43] BOL'SHUTKIN, D. N., GASAN, V. M., PROKHVALITOV, A. and ERENBURG, A. I., *Acta Cryst. B* **28** (1972) 3542.
- [44] SUZANNE, J., Thesis, Marseille (1974).
- [45] UNGURIS, J., BRUCH, L. W., MOOG, E. R. and WEBB, M. B., *Surf. Sci.* **87** (1979) 415; **109** (1981) 522.
- [46] DIEHL, R. D. and FAIN, S. C., Jr., *J. Chem. Phys.* **77** (1982) 5065.
- [47] FRENKEL, J., *Kinetic Theory of Liquids* (Oxford University Press, London and New York) 1949.
- [48] HALSEY, G. D., *J. Chem. Phys.* **17** (1949) 520.
- [49] HILL, T. C., *J. Chem. Phys.* **17** (1949) 590.
- [50] DOLLE, P., MATECKI, M. and THOMY, A., *Surf. Science* **91** (1980) 271.
- [51] GENOT, B. and DUVAL, X., *J. Chimie Physique* **67** (1970) 1332.
- [52] CROSET, B., Thesis, Marseille (1983).
- [53] MOCHRIE, S. G. J., SUTTON, M., BIRGENEAU, R. J., MONCTON, D. E. and HORN, P. M. (preprint).
- [54] BOCKEL, C., MENAUCOURT, J. and THOMY, A., *J. Physique* (to be published).
- [55] CHIN, S. T. and MA, K. B., *Phys. Rev. B* **28** (1983) 2555.
- [56] EVANS, R. and TARAZONA, P., *J. Chem. Phys.* **80** (1984) 587.
- [57] BENNER, R. E., JR., TELETZKE, G. F., SCRIVEN, L. E. and DAVIS, H. T., *J. Chem. Phys.* **80**, 589 (1984).
- [58] NIGHTINGALE, M. P., SAAM, N. F. and SCHICK, M. (preprint).