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STM of $CrCl_3$-graphite intercalation compounds

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Résumé. — La microscopie à effet tunnel a été utilisée pour étudier les composés d'insertion graphite-$CrCl_3$ de stade-2. Les images obtenues de la surface après clivage sont caractéristiques de deux types de domaines. Le plus fréquent apparaît sous forme d'un plan de structure hexagonale dont tous les atomes de carbone sont équivalents, tandis que l'autre montre une structure hexagonale centrée proche de celle du graphite pur. Ces deux types de domaines peuvent être reliés aux domaines de Daumas-Herold avec un et deux plans de graphite, respectivement, recouvrant le plan intercalé le plus proche de la surface.

Abstract. — Scanning tunneling microscopy has been used to image stage-2 $CrCl_3$-graphite intercalation compounds with atomic resolution. Images obtained after cleaving the samples are characteristic of two types of domains. One (the most frequent) exhibits an hexagonal lattice where all carbon atoms are equivalent, whereas the other shows a centered hexagonal structure similar to that of pristine graphite. These two domains can be related to Daumas-Herold domains with one and two graphite layers, respectively, covering the guest layer closest to the surface.

Among all the surfaces studied by scanning tunneling microscopy (STM), graphite occupies a special place. Although its structure is quite simple (hexagonal layers of carbon atoms, in ABA stacking) the images obtained by STM still pose questions. These images show strong corrugations with deep 'holes' corresponding, according to Tersoff, to the center of hexagons [1] . One explanation is that in the constant-current mode, STM gives contour lines of local density of states at the Fermi energy. Thus the 'hole' corresponds to the Fermi electron wave function node at the center of hexagons. The images also display the inequivalency of the carbon atoms. The ABA stacking implies that one carbon atom site has a neighbour in the inferior plane whereas the adjacent site does not (α and β sites). As these two types of sites are not electronically equivalent, they give different tunneling profiles.

The above properties can be modified by the intercalation of chemical species into the graphite interplane galleries. Since intercalation always occurs with a charge transfer between the intercalate and the graphite, the intercalate is defined either as a donor or an acceptor according to the direction of the Fermi level displacement.

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Some donor graphite intercalation compounds (GIC's) have recently been studied by STM [2,3,4]. Images of stage-2 alkali metal GIC's exhibit the centered hexagonal structure typical of pristine graphite, but with significantly smaller vertical corrugation. However, images of the stage-1 complexes exhibit new superlattices, contrary to theoretical calculations [5,6] showing that all surface carbon atoms should be imaged equally, since intercalation removes the carbon-site asymmetry present in graphite. This may be due to the fact that theoretical calculations are based on simple tight-binding models, in the absence of a full knowledge of the GIC's band structure. The interpretation of the experimental results requires additional electronic structure calculations.

The band structure of GIC's with acceptors, such as metal chlorides, on the other hand, is not so complicated as for donor compounds : electronic properties may generally be described in the frame of the rigid-band model [7]. Therefore we can expect that the theoretical calculations will reproduce the STM images. Using the tight-binding model of Blinowski *et al.* [8], Qin and Kirczenov [6] calculated constant-current STM profiles for a typical acceptor GIC, stage-4 $SbCl_5$-graphite. The results show that corrugation amplitudes and carbon site asymmetry are sensitive to the number n of graphite layers covering the first intercalated layer (Fig. 1). For $n = 1$ and $n = 2$, the carbon atoms should all be equivalent, whereas the asymmetry of α and β site should reappear at $n = 3$. To our knowledge, only one STM investigation of acceptor GIC's has been published up to now [2]. The images given by a stage-1 $FeCl_3$-graphite sample and residual bromine-graphite sample were similar to that of pristine graphite, with the same range of corrugations. This result was interpreted by a surface-acceptor depletion [9].

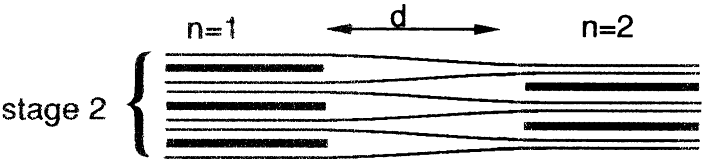


Fig. 1. — Representation of the surface of a second stage GIC, after it has been cleaved, according to the Daumas-Herold structure.

In this paper, we present new STM results obtained with another acceptor compound, stage-2 $CrCl_3$-graphite, which has very high air-stability. The stoichiometry of the second-stage sample is $C_{14}CrCl_{3.3}$ with a charge transfer coefficient $f = 0.3$ [10], similar to the case of $SbCl_5$ studied by Qin and Kirczenow. These samples were prepared from Kish graphite and $CrCl_3$ (> 99.99 %) in chlorine atmosphere at 800 °C. They were cleaved in situ before STM measurements. The possible existence of Daumas-Herold intercalation domains implies that the cleavage of such stage-2 compounds allows the number n of graphite layers covering the $CrCl_3$ layer closest to the surface to be $n = 1$ or $n = 2$ (Fig. 1). The two domains must give different constant-current mode profiles in STM. The experiments were carried out in a white-room with a commercial STM[12] installed on an anti-vibration system. Small bias voltage (≈ 30 mV) in the constant-current mode, with current between 2 and 5 nA, was used.

Contrary to previous authors [2], for these compounds, we have never obtained STM profiles similar to those of pristine graphite. A typical image of 16×16 Å^2 surface area is given in figure 2. All carbon sites appear equivalent in agreement with the theoretical calculations of Qin and Kirczenow. This result is better exemplified in figure 3 which is an enlarged image $\left(4 \times 4 \text{ Å}^2\right)$ of a part of figure 2. Here the six carbon atoms of a graphite hexagon are clearly seen.

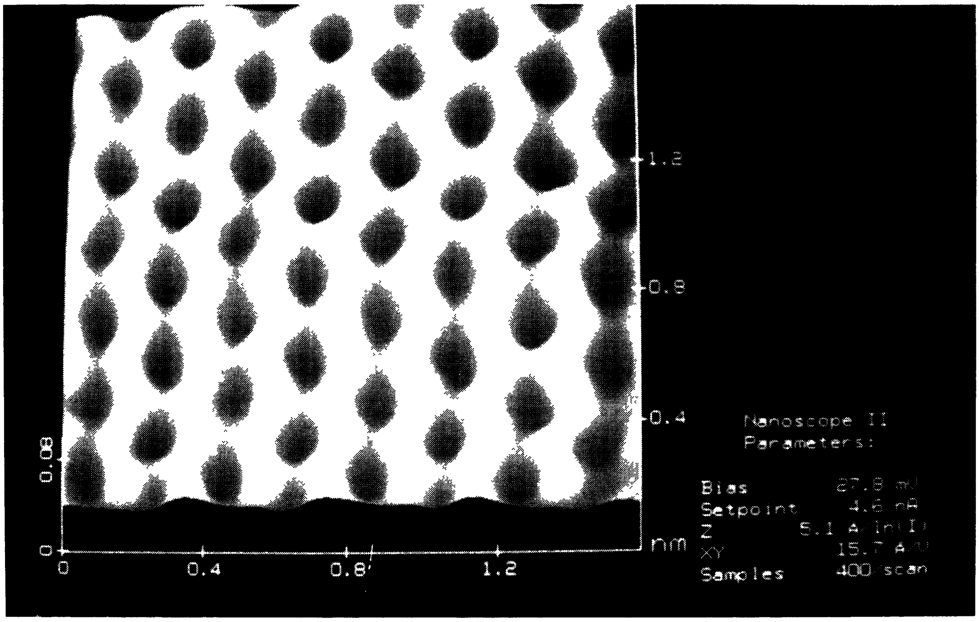


Fig. 2. — Image 16 × 16 Å of the surface graphite layer of cleaved stage-2 $CrCl_3$, which show all carbon atom sites equivalent. One can see the hexagonal arrangement of atoms. Experimental conditions : current 4.6 nA, bias voltage 27.8 mV, 8.7 Hz.

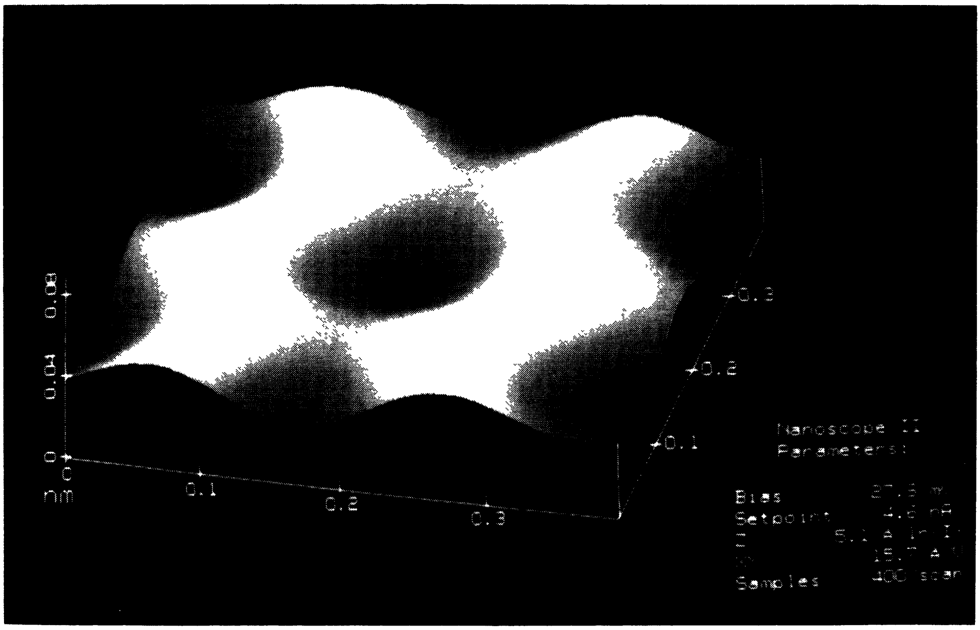


Fig. 3. — Close up on a part of image given in figure 2. The six atoms of the carbon hexagon appear clearly and are all identical.

In some images, two kinds of domains appeared (Fig. 4). The lower part of this figure corresponds to the same kind of surface as above, whereas the upper part resembles pristine graphite with non-equivalent α and β sites. It could correspond to the limit of an intercalation island in the Daumas-Herold model shown in figure 1, with $n = 1$ and $n = 2$ for the lower and the upper part of figure 4, respectively. The measured distance for the transition from one kind of surface to the other has been found to be $d \approx 8$ Å, which corresponds approximatively to that of five carbon-carbon bonds. Numerous images containing both kinds of domains have been obtained with different tips. Images are reproducible and all orientations were found for the domains separation excluding artefacts or multitip tunneling effects [13].

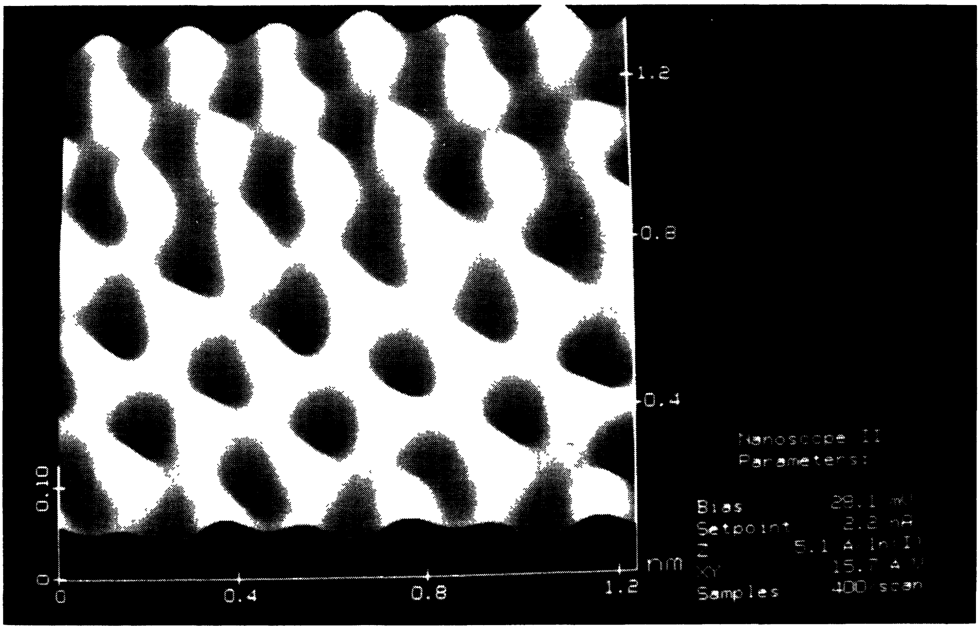
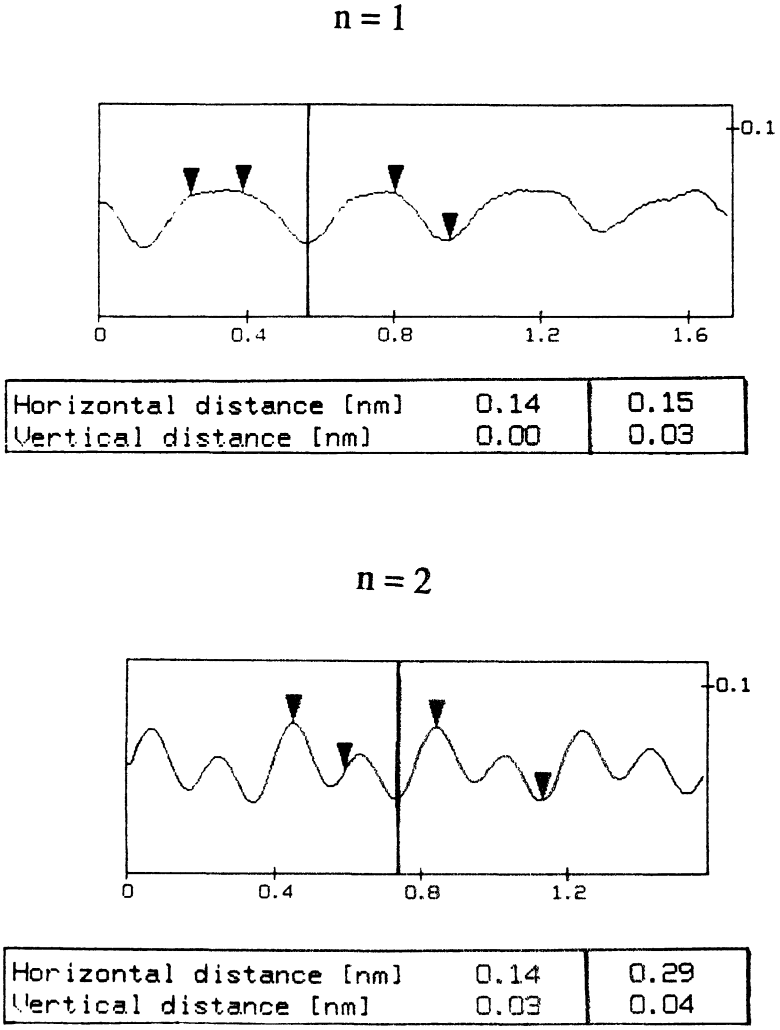


Fig. 4. — Transition zone between the two types of domains. One domain gives profiles similar to those of graphite (upper part), while the other (lower part) gives hexagonal arrangement as in figure 2. Experimental conditions : current 2.2 nA, bias voltage 28.1 mV, 8.7 Hz.

The corrugation amplitudes are given in figure 5. These are much smaller than in pristine graphite : 0.3 and 0.5 Å for $n = 1$ and $n = 2$ domains respectively, *versus* 1 to 3 Å for pristine graphite. This is in qualitative agreement with theoretical calculations, although Qin and Kirczenow predict that in the $n = 2$ case all carbon atoms should be equivalent. The reduced vertical corrugation is consistent with the fact that the wave functions of the Fermi electrons no longer have an exact node at the hexagon center.

In conclusion, we have studied stage-2 $CrCl_3$-graphite using STM. We have observed two different types of domains on the same carbon layer. Images of the stage $n = 2$ exhibit a structure close to the centered hexagonal structure of pristine graphite. The other type of domain exhibits a carbon layer, for the first time in STM, as an hexagonal layer of carbon atoms equivalent from one site to another. In both cases, the corrugations are substantially smaller than in pristine graphite.



Horizontal distance [nm]	0.14	0.15
Vertical distance [nm]	0.00	0.03

Horizontal distance [nm]	0.14	0.29
Vertical distance [nm]	0.03	0.04

Fig. 5. — Sections of the two types of domains along the carbon-carbon bonds. The $n = 1$ section shows all the carbon atoms to be equivalent, while the other ($n = 2$) shows the α and β sites. However, in both cases the corrugation amplitudes are smaller than in graphite. In both cases, the two markers on the left show the carbon atoms' positions, while the two right markers show the corrugation amplitudes.

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