

## STM Studies of Fluorine-Intercalated Graphite

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Samples of stage-2 fluorine graphite intercalation compounds (GIC) were studied by scanning tunneling microscope (STM) from submicrometer to atomic scale. From the STM view point, the most striking observation concerns the topographic modifications of the (*a*, *b*) sample surface induced by the intercalation process. Our STM images of a  $C_6F$  compound are the first direct visualization of the fluorine atoms organization in the van der Waals gap. © 1993 Academic Press, Inc.

### Introduction

Graphite intercalation compounds (GIC) have been in the last three years the subject of renewed attention from the "scanning tunneling community." This new interest originates from the observation that the surface analysis of graphite by this new technique does reveal, at the atomic scale, details on the nature and structure of the first inner layers. Thus the Daumas-Herold structure was experimentally confirmed in the case of acceptor GICs (1-3), as well as the modulation of the electronic charge of the carbon atoms by the intercalation layer was directly measured in the case of donor GICs (4).

Depending on the preparation procedure,  $C_xF$  compounds may exhibit drastically different behaviors (5). When the fluorination

is performed at high temperature, the corresponding graphite fluorides are insulators; C atoms have a  $sp^3$  hybridization and C-F bonds show a covalent character. On the other hand, when the treatment is carried out at low temperature (i.e., below 100°C) in the presence of traces of metal fluorides or HF as catalysts, the obtained intercalation compounds possess even higher electrical conductivities than the pristine graphite (6, 7), provided fluorine content is not too great (C/F ratio > 3.5, GIC with stage number  $n \geq 2$ ). Their transport properties and the binding energy of the C-F bonds have been shown to be dependent on the amount of fluorine intercalated in the structure (8, 9). Since fluorine atoms in these materials generally exhibit a higher electronic charge than in the covalent-type compounds, the nature of the C-F bond has been called "semi-ionic" after Mallouk and Bartlett (10).

However, many problems concerning

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these fluorine-intercalated GICs are still open. Among them we can quote the organization of the fluorine species in the van der Waals gap and the possible modifications (from *AB* to *AA*) of the graphene stacking induced by the intercalation process. This STM study was undertaken on two different fluorine-intercalated graphite samples with the aim of providing some light on these structural problems.

### Experimental

The fluorination experiments were performed on HOPG samples. The pellets were introduced in a nickel container adapted to a "fluorine line" as previously described (11). After vacuum degassing of the sample, the reactive atmosphere was introduced into the reactor. The first series of samples (hereafter noted F(HF)-GIC) was treated with a  $F_2/HF$  mixture in 3/1 ratio. In the experimental procedure, HF was first introduced and the pressure was completed to 1 bar with  $F_2$ . Due to consumption of fluorine during the first two hr, further  $F_2$  was added to maintain 1 bar pressure. The reaction was carried out at room temperature for 72 hr. After elimination of the excess of gaseous mixture, the sample was first characterized by its weight uptake. X-ray diffraction (XRD) patterns showed that the GIC was a stage-2 compound with clearly defined 001 peaks. The repeat distance was  $I_c = 0.95 \pm 0.01$  nm. These materials did not seem to be very sensitive to moist air since no change in the XRD pattern was observed over a several months period. Elemental analysis at Service Central d'Analyse, CNRS were in good agreement with the weight uptake and led to the  $C_4F(HF)_8$  composition with  $\delta < 0.1$ .

The second type of samples (hereafter noted F-GIC) was prepared under similar experimental conditions, but, in this case, the fluorination medium was gaseous  $F_2$  (COMURHEX) containing less than 0.1% HF. Powder XRD patterns were also consistent with a stage-2 compound with a repeat

distance  $I_c = 0.93 \pm 0.01$  nm. The mean  $C_6F$  composition was deduced from both weight uptake and elemental analyses. This second type of GIC is more sensitive to moisture than the former one and should be handled in a dry atmosphere.

STM studies were performed in Bordeaux (CRPP), ESCA in Japan, the former (from submicrometer to atomic scale) in a clean room using a commercial STM (12) installed on an antivibration system. The samples were cleaved with adhesive tape in the clean room immediately before their STM observation. Images were collected in either constant-current or constant-height modes with small bias voltages ( $\approx 3$ –30 mV) and currents in the range of 1 to 2.5 nA. Two different types of tunneling tips were used: commercial Pt/Ir tips from Digital Instrument or electrochemically etched tungsten tips prepared in our laboratory.

### Results and Discussion

#### (1) F(HF)-GIC

Whereas this sample is chemically stable over a long period of time, the stability of the STM images is relatively poor: after less than one hr of observation the image quality deteriorates and could only be recovered by a change of the tip and a cleavage of the sample. Because this degradation is not observed on the F-GIC sample we suppose that it comes from a pollution of the tip by residual HF molecules lying on the surface. It has been suggested that the presence of HF facilitates the fluorine intercalation because  $HF_2^-$  groups are at first very rapidly intercalated, then in a second step are exchanged with fluorine (10, 13). However, some  $HF_2^-$  or HF species remain in the final GIC because of strong hydrogen bonding which are formed within the intercalate or with the host lattice. Thus it is possible that HF molecules still remain on the surface of the sample after cleavage and progressively pollute the tip. The presence of HF on the surface could also be the origin of high noise areas of a few tenths of  $nm^2$  surface which

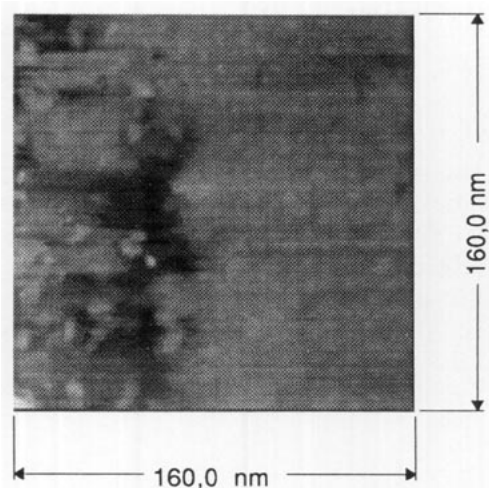


FIG. 1. STM image ( $160 \times 160 \text{ nm}^2$ ) of the surface of a stage-2 F(HF)-GIC which shows large terraces separated by a deep valley ( $\approx 2 \text{ nm}$ ). Full contrast is 2 nm. Experimental conditions: bias voltage 20.1 mV, current 1.5 nA, constant height mode, Pt/Ir tip.

are observed from time to time on 20–30  $\text{nm}^2$  images.

On freshly cleaved F(HF)-GIC, at large scan, we observe large terraces separated

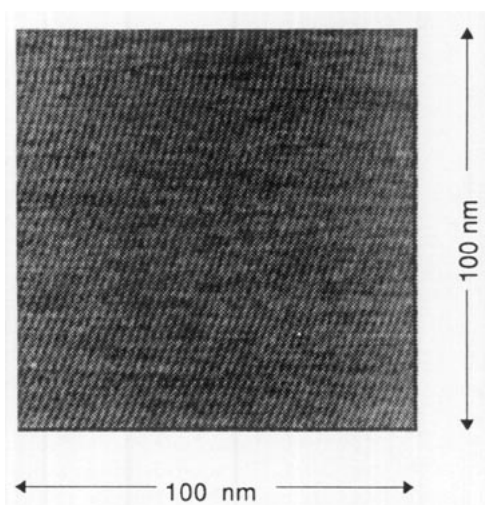


FIG. 2. STM image ( $100 \times 100 \text{ nm}^2$ ) of the surface of HOPG before intercalation: at this scale, no corrugation could be detected. Full contrast is 0.1 nm. Experimental conditions: bias voltage 15 mV, current 1.4 nA, constant height mode, Pt/Ir tip.

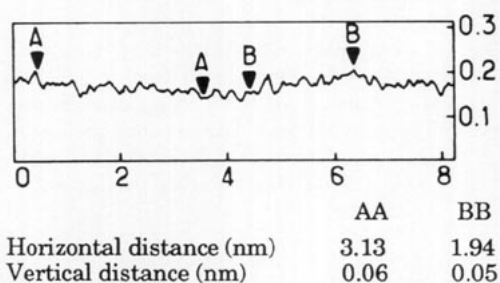
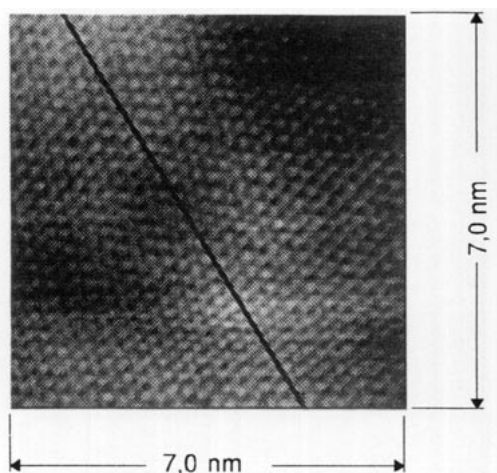


FIG. 3. Atomic resolution STM image ( $7 \times 7 \text{ nm}^2$ ) of the surface of the stage-2 F(HF)-GIC and cross section showing the absence of relief. Only one out of two carbon atoms could be observed resulting in the triangular lattice of carbon atoms. The interatomic distance is 0.246 nm. Full contrast is 0.15 nm. Experimental conditions: bias voltage 3.7 mV, current 2 nA, constant height mode, W electrochemically etched tunneling tip.

by deep (2–3 nm) valleys (Fig. 1). If we focus on these plateaus one can distinguish islands which are by no way homothetical of the plateaus seen at larger scan: the corrugation ( $\sim 0.2\text{--}0.6 \text{ nm}$ ) is smoother without any cracks, pits, or steps. For comparison, images of the surface of HOPG before intercalation do not show any corrugation at these scales (Fig. 2). In our opinion the large scale plateaus and valleys are the consequence of the intercalation process whereas the islands on the plateaus attest to the presence of fluorine atoms immediately below the surface and may be attributed to Daumas–Herold domains. At smaller scan,

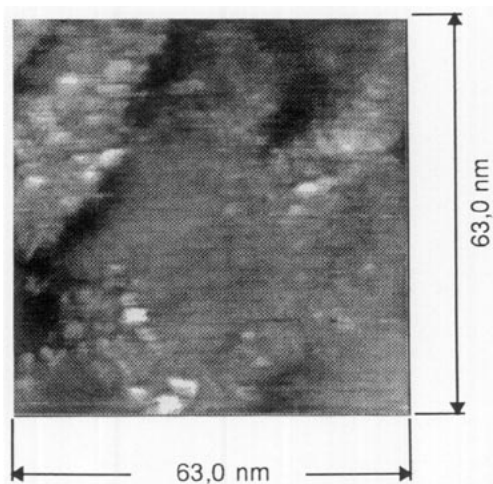


FIG. 4. STM image ( $63 \times 63 \text{ nm}^2$ ) of the surface of the stage-2 F-GIC. One can distinguish numerous cracks, faults, pits . . . on this strongly damaged surface. Full contrast is 1.5 nm. Experimental conditions: bias voltage 7 mV, current 2 nA, constant height mode, W electrochemically etched tunneling tip.

where one can reach atomic resolution, the usual image of pristine graphite with its trigonal symmetry can be distinguished above the islands as well as between them (Fig. 3). This result is surprising compared to the behavior of  $\text{CuCl}_2$ - and  $\text{CrCl}_3$ -acceptor GICs where, precisely, the signature of the Dumas–Herold domains is the change from trigonal to hexagonal symmetry (1, 2). However, this difference in behavior may simply arise from the difference in size of the intercalant. Actually, contrary to  $\text{CuCl}_2$ - and  $\text{CrCl}_3$ -GICs, the gap between two intercalated layers in fluorine-GICs (0.6 nm instead of 0.95 nm for the former GICs) is not high enough to suppress the carbon sites asymmetry for the STM observations. The STM images of fluorine-intercalated islands display the trigonal symmetry of pristine graphite and we can thus follow the continuity of carbon atoms rows at these islands borders: no discontinuities were ever observed. These images did not change when the bias between tip (commercial Pt–Ir or W electrochemically etched) and graphite was varied from +20 mV to –20 mV or when the tun-

nelling current was changed from 0.5 to 2.5 nA.

## (2) F-GIC

The surface images of these samples are drastically different from those of F(HF)-GIC. The surface is dramatically damaged, nearly destroyed, with numerous cracks, faults, pits, etc. (Figs. 4 and 5), a situation never observed in previous STM studies of GICs.

This difference observed between the two

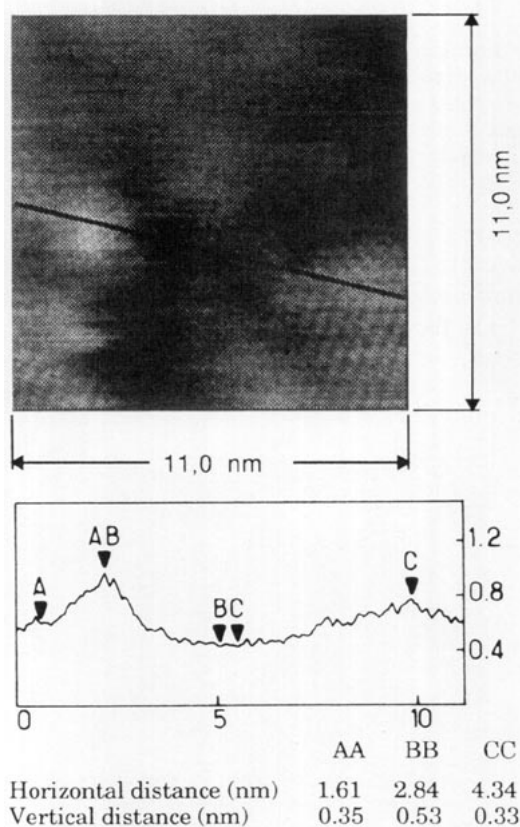


FIG. 5. STM top-view image of a  $11 \times 11 \text{ nm}^2$  surface area of the stage-2 F-GIC and cross-section showing numerous cracks even on such a small area. Full contrast is 0.7 nm. Note the typical vertical distances are distributed around 0.33 and  $\sim 0.6$  nm which correspond respectively to G–G and G–F–G stacking. Experimental conditions: bias voltage 10.1 mV, current 1.3 nA, constant height mode, W electrochemically etched tunneling tip.

types of fluorine-intercalated graphite clearly originates in the preparative methods. We know that the HF-treated graphite can later be intercalated with fluorine at room temperature whereas the direct intercalation of graphite by fluorine is only possible in the presence of traces of impurities. The nondestruction of the graphite network after the exposition to the HF + F<sub>2</sub> mixture gives a new hint on this mechanism: HF molecules first gently separate the graphite layers and later give room for the fluorine atoms which otherwise enter the graphite network with greater difficulties at the expense of the surface cohesion, thus inducing cracks, faults, etc.

STM images at atomic resolution of uncracked parts of the surface show the usual trigonal graphite network and, from time to time, in an irreproducible way, the hexagonal symmetry observed for the other acceptor GICs. More often, although not everywhere, we observed a new hexagonal superlattice with a periodicity of 0.25 nm, which is commensurate with the graphite lattice (Figs. 6 and 7). These structures

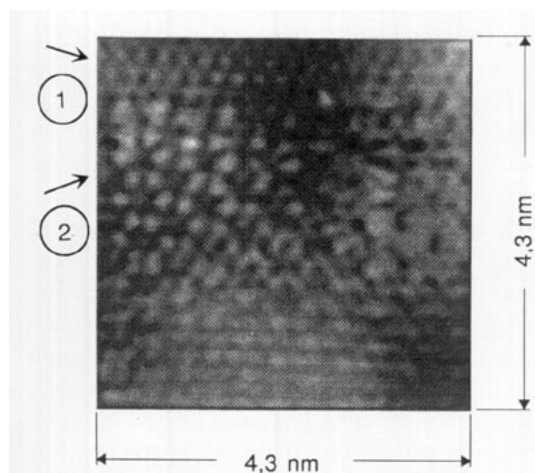


FIG. 6.  $4.3 \times 4.3 \text{ nm}^2$  surface area atomic resolution STM image of the stage-2 F-GIC showing, in the upper part (arrow 1), the triangular lattice of carbon atoms and, in the lower part (arrow 2), the new hexagonal lattice with a periodicity of 0.25 nm attributed to fluorine atoms. Full contrast is 0.42 nm. Experimental conditions: bias voltage 4.9 mV, current 2 nA, constant current mode, Pt/Ir tunneling tip.

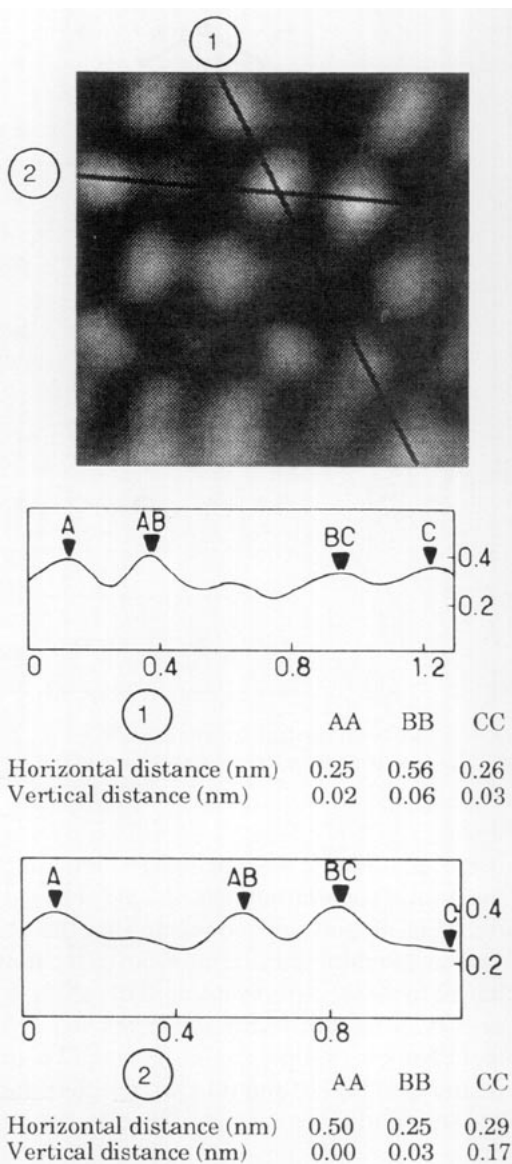


FIG. 7. Zoom ( $1.16 \times 1.16 \text{ nm}^2$ ) on three fluorine hexagons of the STM image of Fig. 6. The smaller F-F distance is 0.25 nm.

never extend over large domains, typically 10 to 100 nm<sup>2</sup>, are not very dense and are randomly distributed on the sample surface. Furthermore they can be observed either with Pt-Ir tips or W tips and, in any case, at low bias (3 to 8 mV) with a tunnelling current between 1.5 and 2.5 nA. Under

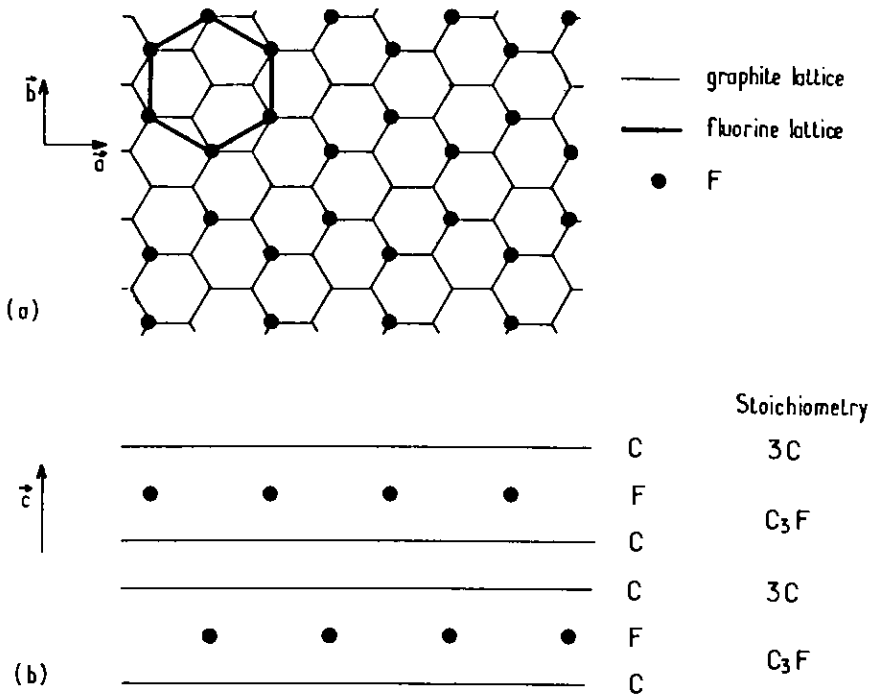


FIG. 8. (a) In-plane structural model for a  $C_3F$  sheet showing the hexagonal lattice of fluorine atoms commensurate with the graphite lattice; (b)  $c$ -axis structure of the stage-2  $C_6F$  compound.

these conditions we can image simultaneously this superlattice and the graphite lattice (Fig. 6) and thus conclude that the observed stoichiometry is one atom of the new lattice for three carbon atoms. This observation is consistent with the proposed  $C_6F$  stoichiometry supposed for this stage 2 compound (see Fig. 8) and thus we propose that the superlattice can be attributed to the fluorine atoms. Because the STM signals of these F atoms are unusually high and can be observed over a wide bias voltage range we are inclined to think that they lie above the surface. Since this lattice is stable for the time of an observation (1 to 3 hr), these fluorine atoms are certainly tightly bound to the surface.

As we never observed these atoms on the surface of F(HF)-GIC, this absence would suggest that in this case the F atoms were less strongly bound to the graphite network. This result leads us to the conclusion that, *at the surface*, the percentage of covalent

bonds between fluorine and graphene is greater for F-GIC than it is for F(HF)-GIC, a result in agreement with the fact that the latter samples seem to be better conductors than the former ones. Furthermore our results seem to indicate that in the F-GIC case the covalently bound F atoms (which are the only ones that remain on the surface after cleavage) form clusters of 10 to 100  $\text{nm}^2$ , randomly distributed so that they occupy only a small percentage of the global surface of the F-GIC sample. The amount of these covalent bonds is not high enough to be clearly detected by XPS and no convincing difference can be established by this technique between the two different compounds. In both cases, the binding energies of the  $F1s$  and  $C1s$  peaks are characteristic of semiionic bonds. A broad envelope (FWHM = 3.5 eV) is observed for  $F1s$  in the 685–686 eV range. The  $C1s$  peak is located at 284.2 eV.

But even in a small amount, these covalent

lent bonds seem to have a great influence on the topographic aspect of the sample surface. Their occurrence for F-GIC and not for F(HF)-GIC is also in agreement with the greater damage induced by the former type of intercalation: it can be suggested that the fluorine intercalation may destroy the *ABAB* stacking of graphite, a destruction that seems more probable when some covalent bonds are formed. Thus, for F-GIC, one may observe from time to time some *AFABFB* stacking when covalent bonds are involved, a situation never observed for F(HF)-GIC. Such a destruction of the graphite network must affect the surface and provoke cracks, faults, etc. The measured depth of the cracks on the surface are distributed around three values, namely: 0.33 nm, ~0.6 nm, ~0.93 nm, which correspond respectively to *G-G*, *G-F-G*, and *G-G-F-G* distances (with *G* for graphite layer) in good agreement with this hypothesis (Figs. 5 and 8).

### Conclusion

Our STM studies of two different fluorine-GICs emphasized the influence of the preparative methods on the topographic aspect of the surface sample. These surface modifications are correlated with the structural characteristics of the GICs and more precisely to the graphene layers stacking along the *c*-axis.

The intercalated fluorine atoms in the van der Waals gap were directly observed, thus giving some direct information about their organization between the graphene layers.

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