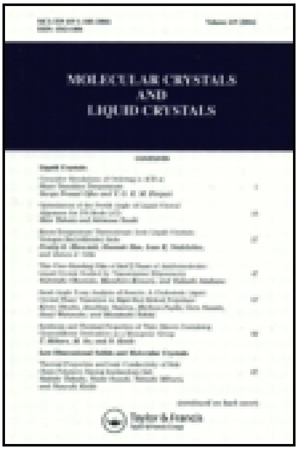

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CDW IN $FeCl_4^-$ - GRAPHITE INTERCALATION COMPOUNDS STUDIED BY STM.

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ABSTRACT Samples of graphite electrochemically intercalated with $FeCl_4^-$ in CH_3NO_2 solution are studied by scanning tunneling microscopy (STM) from a submicrometer to atomic scale. A new long range triangular modulation of the charge density is observed on the surface. This modulation is superimposed on the usual graphite periodicity. This new structure is tentatively attributed to a charge density wave (CDW) resulting from the charge transfer between the intercalated species and the graphite host.

INTRODUCTION

The Scanning Tunneling Microscopy (STM), developed by G. Binnig and H. Rohrer[1] at the beginning of the 1980s, allows us to image, in the direct space and on a large range of scales (from several micrometers to angströms), atomically flat surfaces, that are either electrically conductive or semi-conductive. Layered materials such as graphite or dichalcogenides have been largely studied by this recent technique. Atomic resolution STM images of graphite surfaces usually present a threefold symmetry instead of the hexagonal one, as could be expected: only one out of two carbon atom is observed.The usual explanation is that the AB stacking of graphene planes implies two structurally adjacent different carbon sites in an hexagon with a large asymmetry in their electronic properties near the Fermi level, which results in a large asymmetry in their tunneling current.

Numerous STM studies have shown that intercalation of acceptor or donor species in the graphite interlayer space has a great influence on STM atomic resolution images due to modification of the electronic properties of the graphite. 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-Hérold structure was experimentally confirmed in the case of acceptor GICs[2,3] 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].

This STM study on $FeCl_4^-$ - GICs was undertaken with the aim of completing our study on acceptor-GICs, more precisely for the case of the ionic intercalated species. The choice of $FeCl_4^-$ as intercalate was determined by the fact that these ions can be electrochemically intercalated into graphite[5,6] in a different medium (HCl, CH_3NO_2), and at ambient temperature in air.

EXPERIMENTAL

$FeCl_4^-$ - graphite intercalation compounds ($FeCl_4^-$ - GIC) have been electrochemically prepared using the four-electrode system of the Nanoscope II Electrochemical Scanning Tunneling Microscope (EC-STM). The ECSTM combines an STM with an electrochemical cell under control of a potentiostat which allows voltammogram (I versus V) measurements on either the STM tip or the working electrode. STM operation is possible while performing voltammogram measurements. In this case, the tunneling tip must be isolated in order to minimize non-tunneling currents while scanning in conducting solutions. A slab of highly oriented pyrolytic graphite (HOPG) or of PGCCL was used for the working electrode. The counter and reference electrodes were platinium wires. The STM tip constitutes the fourth electrode. This tip was made of either tungsten electrochemically etched (prepared in our laboratory) or mechanically cut Pt/Ir wire (commercial tips from Digital Instrument), and isolated by Apiezon Wax or polyethylene. The electrolyte solution consists of an equimolar amount of $FeCl_3$/LiCl salts dissolved in dry nitromethane. Working electrode voltammetry allows control of the intercalation of the $FeCl_4^-$ - CH_3NO_2 species. D. Billaud et al.[5] have shown that nitromethane molecules were co-intercalated during this process. In the electrochemical cell, the electrolyte is only in contact with part of the sample surface. The intercalation could thus only occur from surface steps or cracks. Thus, the intercalated regions were very thin and X-ray diffraction could not provide any useful information.

The ECSTM and the classical STM were installed on an antivibration system in a clean room. STM images were acquired immediately after intercalation and several days later on non-cleaved surfaces, mainly with the classical STM which is easier to use. Then, the samples were cleaved with adhesive tape in the clean room before new STM observations. Images were collected in either constant-current or constant-height modes with a large range of bias voltages ($\approx \pm$ 540 mV) and currents in the range of 0.5 to 3 nA.

RESULTS

A typical example of a voltammogram is given in figure 1.

The voltammogram could be stopped at any point and STM images of the intercalated sample surface acquired. We performed in this way scanning tunneling microscope studies from submicrometer to atomic scale. A new long range triangular modulation of the charge density is observed on parts of the surface (fig. 2). This modulation is superimposed on the usual graphite periodicity (fig. 3). Tunneling conditions (constant-current or constant-height mode), bias voltage and setpoint current, seem to have

FIGURE 1 Voltammogram (10 mV/s).Vertical units mA, horizontal units V.

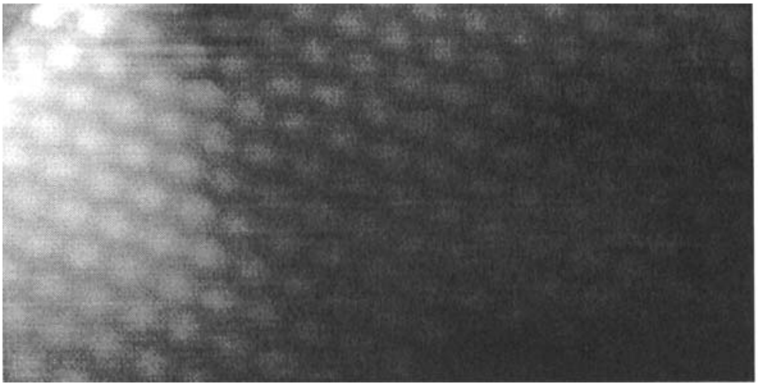

FIGURE 2 Large scale view (91.1x30.8 nm^2) showing the long range periodicity (5nm)

only a minor effect on the STM image. The parameter of this new periodicity depends on the intercalation level: it decreases while the intercalation level increases, but for a given sample (a given intercalation level) the large scale periodicity is constant: it is independent of the sample surface area where the periodicity is observed, whether images were taken before or after cleavage.

The superstructures are very stable and reproducible during many days with different tunneling tips and STM heads. They span large areas (more than several hundred nm wide) as well as more restricted ones. It was always possible to image simultaneously regions with and without superstructures, and to switch between these two kinds of regions.

DISCUSSION

At first glance, several explanations could account for these new periodicities.

A Moiré effect due to the rotation of the first graphene plane relative to the second one would produce similar superstructures, when not studied in detail. Moiré patterns were largely studied in our lab-

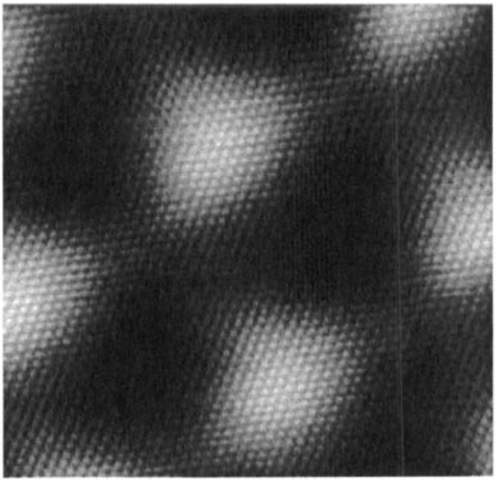

FIGURE 3 10.3x10.3 nm^2 view showing both graphite and long range periodicities.

oratory by STM in the case of pyrocarbons[7] and on polyimide films[8] during the graphitization process. In the case of our GIC, Moiré patterns appear unlikely for many reasons.

Large scale periodicities were only detected on intercalated compounds. STM images were free of this Moiré-like effect when taken on pure HOPG or PGCCL previous to the intercalation.

Furthermore, the observed angle between the axes of the new periodicity and the axes of the usual triangular periodicity of graphite (0,246 nm) measured on our STM images, Φ_{exp}, is not consistent with the theoretical angle calculated in the case of a Moiré effect, $\Phi_{Moiré}$, where $\Phi_{Moiré}$ is given by:

$$\Phi_{Moiré} = 30° - \Theta/2 \qquad (1)$$

where Θ is the rotation angle between the two top layers deduced from the long range periodicity, D, and the graphite lattice parameter, a_0, using the following relation :

$$\sin(\Theta/2) = a_0 / 2D . \qquad (2)$$

Results are summarized in the following table:

Sample	D [nm]	Φ_{exp} [degrees]	$\Phi_{Moiré}$ [degrees]	Θ [degrees]
A	5	26	28,6	2,8
B	3	-	27,7	4,7
C	1,3	26	24,6	10,8
D	1,1	21	23,7	12,5

But, considering the error in the determination of Φ_{exp} ($\approx$ 10%), no definitive conclusion can be drawn from these calculations.

It was also shown that, if the superstructure is due to the misorientation of two upper layers, an"odd-even" transition should be observed along the atomic rows between the areas presenting a higher corrugation[7]. In these zones, the layer stacking is close to that of graphite while, in the area in-between, the hexagons are almost superimposed, leading to a lower corrugation. H. Saadaoui et al.[7] have shown that the β atoms in a graphite-like area become the α atoms in the neighbouring one. In other words, if the hexagon atoms are labelled from 1 to 6, those playing the role of the β atoms will be for instance the 1-3-5 atoms in one area and the 2-4-6 atoms in the neighbouring one. This yields an "odd-even" transition along the lattice axes of the graphene layer and a wavy appearance of the atomic rows.A zoom performed on the superstructures on our $FeCl_4^-$-GIC did not reveal this usual "odd-even" transition along the atomic rows characteristic of Moiré superstructures[7,8].

Another argument arises from the fact that, for a given sample, the large scale periodicity occupies large domains separated by domains where the usual triangular symmetry of graphite is observed. But the parameter of the large periodicity is independent of the sample surface area where this periodicity is observed. This periodicity is also observed before and after cleavage of the sample. Thus, for a given sample, the superstructure always presents the same characteristics. This would not be the case for a Moiré pattern: the probability to find two areas presenting exactly the same misorientation angle between the two top layers and separated by several microns is certainly very small.

Artifacts due to the tip, such as multiple tips scanning simultaneously over two grains whose crystal axes are rotated with respect to one another[9] or contamination of the tip by a small graphite flake[10], can also give an STM image with a Moiré effect. The hypothesis of a tip contamination can be ruled out because, for a given sample, the superstructure periodicity does not depend on the tunneling tip. This would imply that, for each tip, the misorientation angle between the crystallographic axes of the small graphite flake at the end of the tip and those of the surface sample would be exactly the same. This hypothesis is also highly improbable. Furthermore, it was always possible to image simultaneously areas presenting the superperiodicity and areas without it or to switch several times between them.

Thus, Moiré patterns could reasonably be ruled out, whatever their origin, and we are inclined to think that these new periodicities are the direct STM manifestation of the intercalated species under the graphene surface layer and have an electronic origin. The wavy STM signal would be the result of a modification of the surface charge density repartition due to the intercalated anions just under the graphene surface plane. The superperiodicity could thus be attributed to charge density waves (CDW).

CDW have been revealed in the case of a few donor-GICs by ARPES of CsC_8[11] or STM of MC_8 (with M= K, Rb, Cs)[12] but, to our knowledge, have never been observed in the case of acceptor-GICs.

Previous STM observations of acceptor-GICs ($CrCl_3$[2], $CuCl_2$[3] or F-GIC[13]) did not reveal CDW contrary to the present work. This is not surprising if we consider the fact that $CrCl_3$ as well as $CuCl_2$ form a rigid 2D lattice in the graphite van der Waals space with well defined crystallographic parameters, while $FeCl_4^-$

ions, more or less solvated by nitromethane molecules, form a non-rigid 2D lattice whose parameters vary according to the inter-plane ionic concentration, i.e. the intercalation level, which depends directly on the electrochemical experimental conditions. The periodicity of the CDW is directly correlated to the charge transfer between the intercalated species and the graphite host and therefore reflects the ionic repartition in the graphite inter-layer space.

The long range superstructure observed at the surface of $FeCl_4^-$ -GICs has been tentatively attributed to CDW. This STM study revealed for the first time CDW in the case of an acceptor-GIC and additional experiments need to be performed to verify this proposal.

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