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## STM of CrCl<sub>3</sub>-graphite intercalation compounds: Islands, graphite in-plane defects

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**Résumé.** — La microscopie à effet tunnel (STM) a été utilisée pour étudier les composés d'insertion graphite-CrCl<sub>3</sub> de stade-2. Deux types de domaines, montrant des images différentes en STM, 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. Pour la première fois, l'existence d'îlots de petite taille est démontrée. Cette étude montre que la forme des îlot est très compliquée. Enfin, des défauts ont été observés dans les plans de carbone, et sont interprétés comme des atomes interstitiels dans les plans. Ceux-ci créent des cycles à sept et trois atomes dans les plans de symétrie hexagonale. Ces défauts pourraient être responsables des propriétés chimiques particulières bien connues du graphite Kish, et du déplacement de son niveau de Fermi par rapport au graphite pur, que mettent en évidence des mesures de susceptibilité magnétique.

**Abstract.** — Samples of stage-2 chromium chloride graphite intercalation compounds have been studied by Scanning Tunneling Microscopy (STM) with atomic resolution. Due to the existence of Daumas-Herold domains with one and two graphite layers on the guest layer closest to the surface, which exhibit different STM images, the first direct evidence is given for the existence of small intercalated islands. The island shape is shown to be very complicated. In addition, a new kind of defects has been observed in some images, where extra carbon atoms give rise to the presence of heptagons and triangles inside the hexagonal lattice of the carbon layers. These defects could be responsible for the well known particular chemical properties of Kish graphite and for the shift of its Fermi level relative to pristine graphite, as deduced from magnetic susceptibility experiments.

### 1. Introduction.

Graphite has been the subject of many theoretical and experimental studies by Scanning Tunneling Microscopy (STM). The main feature is the observation of one out of two carbon atoms, due to the non-equivalence of the atomic sites  $\alpha$  and  $\beta$  resulting from the ABAB stacking of the graphite layers. In a previous paper [1], we showed that intercalation of graphite with acceptor compounds wipes out the difference between  $\alpha$  and  $\beta$  sites of graphite, resulting in a sixfold symmetry of the STM pattern: all the carbon atoms of the layer covering the intercalated material become

equivalent and are equally imaged.

This result is in agreement with the theoretical calculations of Qin and Kirczenow [2]. Using the tight-binding model of Blinowski *et al.* [3], they have calculated constant-current STM profiles for a typical acceptor graphite intercalation compound (GIC): stage-4 SbCl<sub>5</sub>-graphite. They showed that corrugation amplitude and carbon site asymmetry are sensitive to the number  $n$  of graphite layers covering the first intercalated layer.

In addition, our results, obtained with cleaved samples of stage-2 CrCl<sub>3</sub>-graphite compounds, gave evidence for the presence of Daumas-Herold domains. The cleavage of stage-2 compounds allows the number  $n$  of graphite layers covering the CrCl<sub>3</sub> layer closest to the surface to be either  $n = 1$  or  $n = 2$  (Fig. 1).

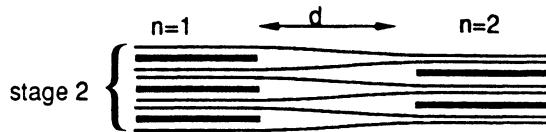


Fig. 1. — Representation of the surface of a second stage GIC, after it has been cleaved, according to the Daumas-Herold structure.

The two areas must give different STM constant-current mode profiles. Indeed, some images show the transition from hexagons to a triangular lattice, which should correspond to  $n = 1$  and  $n = 2$  regions respectively.

The ability of STM to distinguish intercalated domains led us to examine further their morphology. The islandic structure of intercalated layers was proposed ten years ago [4], however, up to now no direct evidence was given for such small islands. In this paper, we present the first direct evidence for the presence of small islands. Moreover, it will be shown that Kish graphite has certain in-plane defects which could be responsible for its particular chemical properties.

## 2. Experimental.

The samples were prepared as previously [1] from Kish graphite flakes and CrCl<sub>3</sub> (>99.99%) in chlorine atmosphere at 800°C. The composition and the stage were determined by magnetic susceptibility experiments and X-Ray diffraction of individual flakes. Second stage samples were selected for STM examination. The stoichiometry of the second-stage sample is C<sub>14</sub>CrCl<sub>3.3</sub> with a charge transfer coefficient  $f = 0.3$  [5], similar to the case of SbCl<sub>5</sub> studied by Qin and Kirczenow. The samples were cleaved with an adhesive tape in a white room and immediately observed with a commercial STM [6] installed on an antivibration system in the same white room. Small bias voltage ( $\approx 15\text{-}30$  mV) in the constant-current mode, with current between 0.89 and 4 nA, was used.

## 3. Results.

**3.1 ISLAND SHAPE.** — As shown previously, images with hexagonal symmetry or trigonal symmetry are obtained according to the number of carbon layers covering the first CrCl<sub>3</sub> intercalated layer (Hexagons:  $n = 1$ , triangles:  $n = 2$ ). Numerous images containing both kinds of domains have been obtained with different tips. Images are recurrent and all orientations were found for

the domains separation excluding artefacts or multi-tip tunneling effects [7]. Moreover, supposing continuity from the hexagonal domain to the triangular one, we are able to confirm that the holes in the triangular domain actually correspond to the centers of the hexagons as supposed by Tersoff [8]. The measured transition length between the two types of surfaces was found to be  $d \approx 6 - 8\text{\AA}$ , which corresponds approximatively to 4-5 carbon-carbon bonds.

The two kinds of domains are clearly seen figure 2 which calls for a few remarks. (i) There are no visible steps in this figure; thus we can assert that a single plane is scanned on this image. (ii) In some parts of the sample the two kinds of domains are very "closely mixed" with highly complicated border separating them. This complicated shape is reminiscent of fractal contour. Indeed, such a fractality of the domains in a bidimensional growth of interacting particules in high temperatures was calculated by Rosso [9]. He showed that the fractal dimension depends on the interaction strength and on the temperature. In our case, the synthesis of the  $\text{CrCl}_3$ -GIC meets the two most favourable conditions for fractal shape, that is to say, small interactions between particles and high temperature.

**3.2 IN-PLANE DEFECTS.** — Being able to observe the six carbon atoms of a graphite plane by STM allowed us to examine the in-plane organization of the carbon planes, its regularity and the occurrence of defects. In non-intercalated graphite, defects may be observed in STM images with trigonal asymmetry but with no possibility to assign them to a precise type of defect: missing atom(s), extra atom(s), dislocations or whatever. Since here all the atoms can be seen the defects may be checked and identified more easily.

We have observed in-plane defects in the carbon layers of Kish graphite. These defects appear to be of two different types: Seven-atom ring and three-atom ring. These two types of rings are always closely associated, a triangle having one base in common with an heptagon and the two others with distorted hexagons. These effects may be explained in the frame of an extra carbon atom in an hexagon, creating an heptagon plus a triangle. The  $z$ -corrugation displays no strong fundamental differences near the defects. Thus, we can assert that (i) the extra atom is a carbon atom and (ii) it is located in the scanned plane. Indeed, an extra atom of  $\text{Cr}^{3+}$  or  $\text{Cl}^-$  out of the plane could perhaps give rise to a similar image. However (i) in such a case no distortion of the surrounding hexagons should be observed and (ii) as we shall see later, the specific chemical properties of Kish graphite are understandable in the perspective of this extra atom being a carbon atom. Some defects are isolated in the planes (Fig. 3) while in other parts they appear in groups (Fig. 4). Figures 3bis and 4bis are schematic representations of the photographs 3 and 4 respectively. The triangles appear to have two long bonds which are each shared with one distorted hexagon and one short bond which is shared with the heptagon. The latter has three short bonds and four longer ones. If these extra atoms are in-plane carbon atoms they must modify the density of states at the Fermi level.

Indeed, it was often observed that when Kish graphite is used as the host for acceptor intercalation, it does not behave the same way as other graphite materials. That is to say in the case of acceptor intercalation compounds, Kish graphite leads to GIC's richer in intercalate, or at least to better crystals with diffraction lines narrower than those of compounds prepared from natural graphite of HOPG. In our case, Kish graphite allowed the synthesis of stage-1 and stage-2  $\text{CrCl}_3$ -GIC's whereas only stage-3 is obtained in natural graphite.

Pre-graphitic carbons have a lower Fermi level than graphite and can give donor-GIC's better intercalated than graphite itself. The symmetry of the charge transfer mechanism in graphite intercalation [4,10] suggests, by analogy, that graphite materials with higher Fermi level must lead to better intercalated acceptor compounds. In order to verify that Kish graphite has a different density of states at the Fermi level from HOPG, STM measurements were carried out on both pure Kish and HOPG with the same tip and experimental conditions. We observed that the corrugation

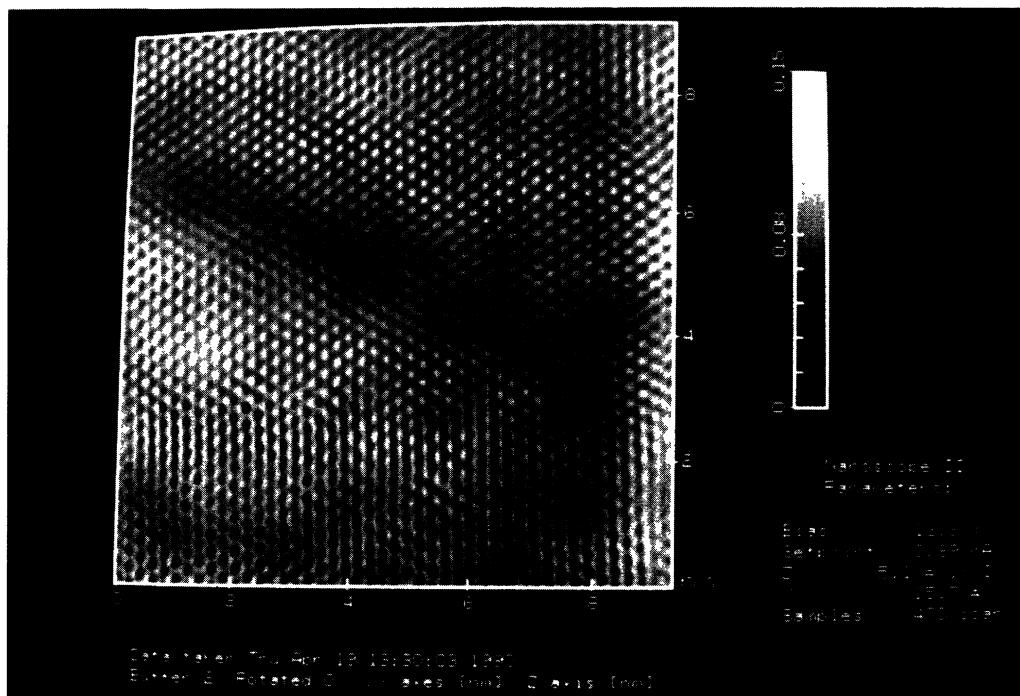


Fig. 2.

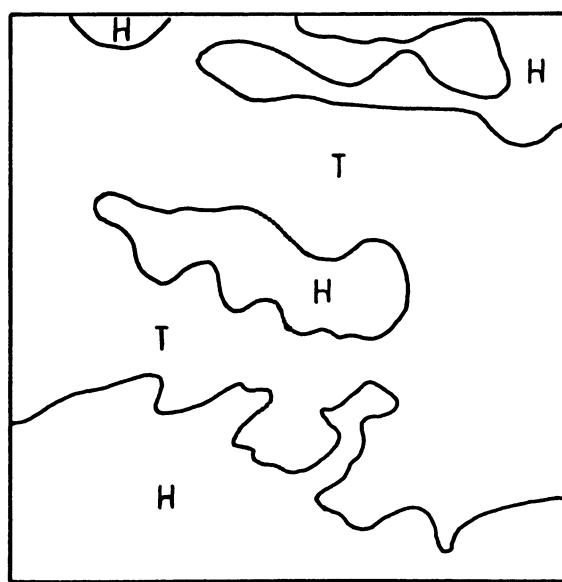


Fig. 2.bis.

Fig. 2. — Two kinds of domains appear closely mixed. Figure 2bis is a representation of the border between the different domains (H for hexagons, T for triangles). Experimental conditions: current 0.89 nA, bias voltage 16.8 mV, 8.7 Hz.

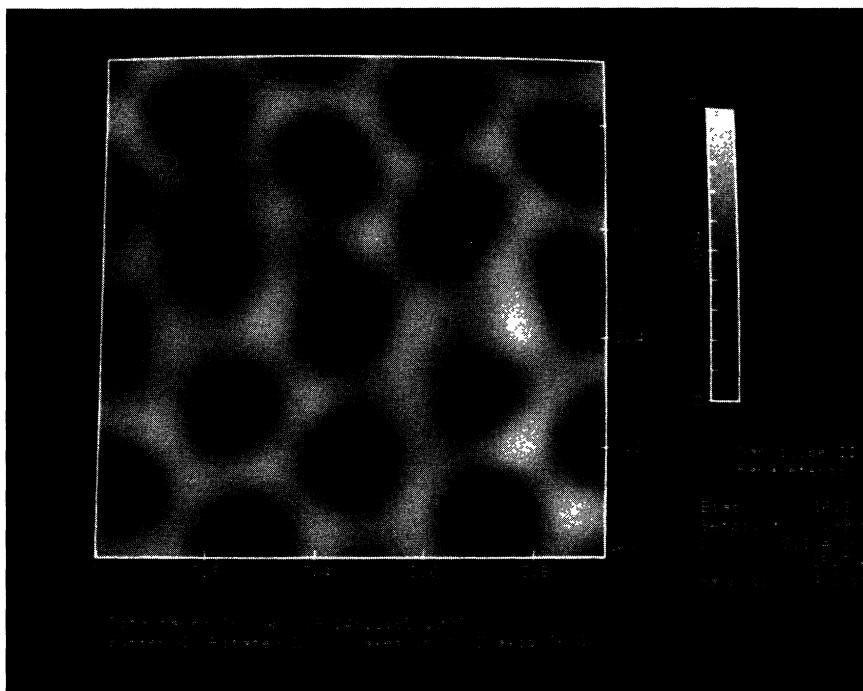


Fig. 3.

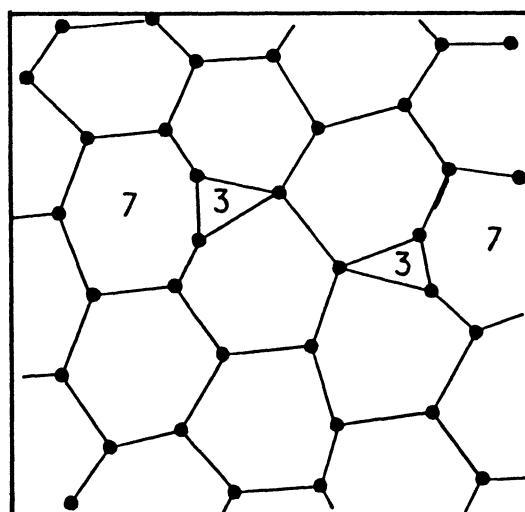


Fig. 3.bis.

Fig.3. — Two isolated defects. Figure 3bis clearly shows the extra atoms (7 for heptagons, 3 for triangles).

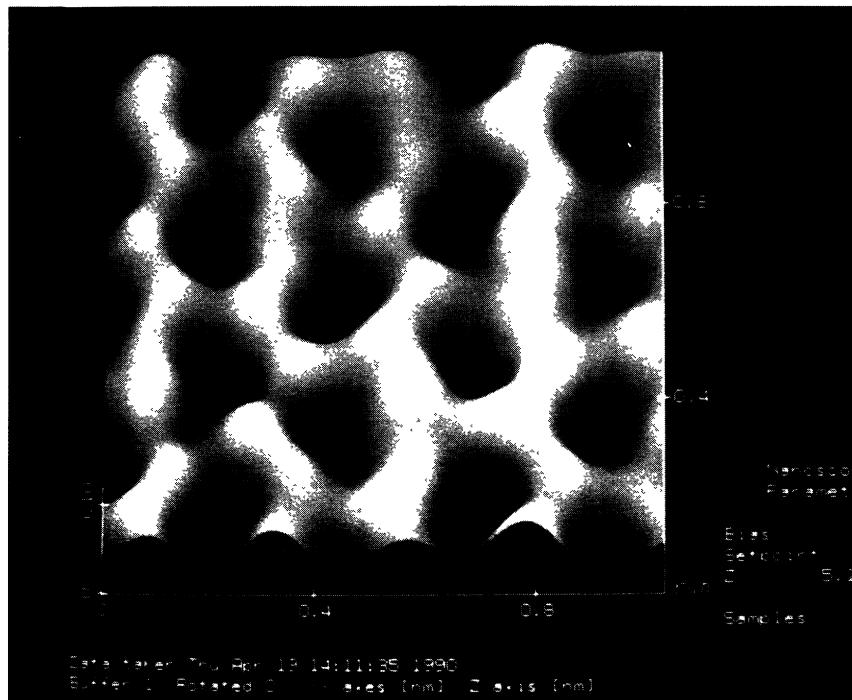


Fig. 4.

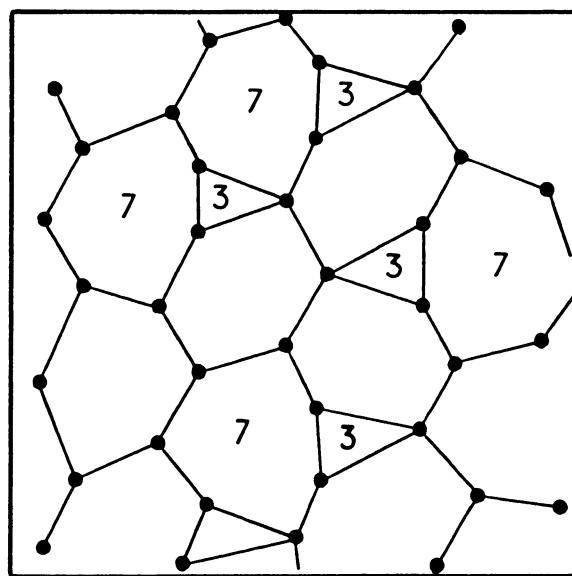


Fig. 4.bis.

Fig.4. — Two groups of defects; one at the top left, the other in the lower-middle of the image. In this image the extra atoms are closer to each other and the deformations are more important than in figure 3. (Fig. 4bis: schematic representation of Fig. 4).

amplitude of images obtained with Kish is about 40% lower than those of HOPG. Furthermore, this ratio does not depend at all on the tunneling conditions. Figure 5 gives an example of the corrugations obtained with  $I = 1 \text{ nA}$  and a bias = 40 mV : the corrugation amplitudes are about 0.2 nm and 0.32 nm for Kish and HOPG, respectively. If we suppose, which seems to be reasonable, that the elastic interactions between the tip and the surface does not depend on the precise nature of the graphite under study, then the observed differences in corrugation between HOPG and Kish graphite originated mainly from the differences in density of state at the Fermi level.

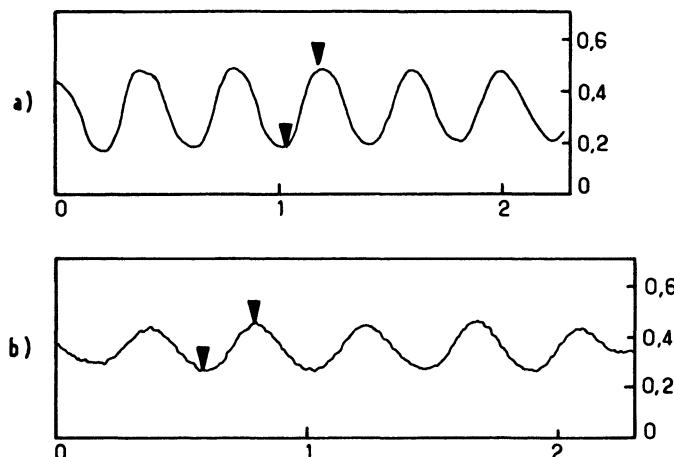


Fig. 5. — Corrugation amplitude of pure HOPG (a) and Kish (b) in the same tunneling conditions (same tip,  $I = 1 \text{ nA}$ , bias = 40 mV). Scales are in nanometer.

In order to get a quantitative estimate of the shift in Fermi level, we have measured the temperature dependence of the magnetic susceptibility of Kish graphite. As it is well known, the diamagnetic susceptibility of graphite, measured with the magnetic field applied parallel to the c-axis, has a strong orbital contribution, which is temperature dependent and sensitive to the Fermi level value. Using the Mc Clure's theory based on the Slonczewski-Weiss (S.W.) band model, a fit of the diamagnetic susceptibility gives the values of the band parameters [11]. The temperature dependence of the magnetic susceptibility of Kish graphite has been measured with a SQUID magnetometer on a Kish flake perpendicular to the applied magnetic field (1 Tesla). The results are shown in figure 6. The curve has the expected behavior, with a maximum of diamagnetism at low temperatures, as observed for HOPG [11]. However, the maximum occurs at a temperature (45 K) higher than for HOPG (32 K). The fit with Mc Clure's expression (Fig. 6) gives band parameters close to those of HOPG, with the exception of the Fermi level, which is higher ( $E_F = +0.006 \text{ eV}$ ) than for HOPG ( $E_F = -0.0248 \text{ eV}$ ) (Tab. I).

Thus the Fermi level seems to be strongly shifted, up to a value slightly above the top of the valence band. This shift corresponds to a gain in charge carriers (electrons), which can be calculated using the relationship between density of states and energy. Using the S.W. band model Dresselhaus *et al.* [12] (among others...) calculated, in the case of pristine graphite, the shift of the Fermi level as a function of the number of charge carriers. According to their results a Fermi level shift of + 0.031 eV corresponds to a gain of  $2 \times 10^{19}$  carriers per cubic centimeter. Assuming that each defect gives one extra electron, this gain corresponds to a ratio of one defect for about 6000

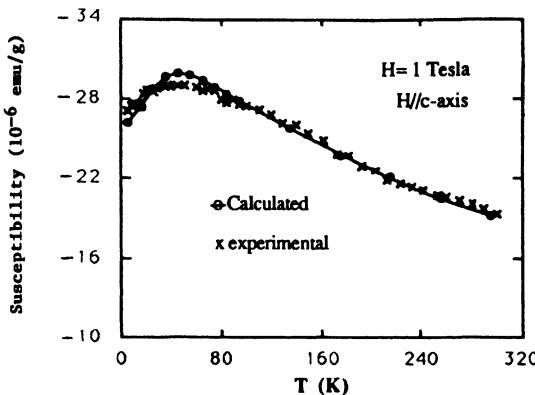


Fig. 6. — Temperature dependence of the magnetic susceptibility of kish graphite ( $H \parallel a$ -axis). The curve is the fit with Mc Clure's expression.

Table I. — *Band parameter values (eV) obtained from the fit of the temperature dependence of diamagnetism with Mc Clure's model.*

	$E_f$	$\gamma_0$	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\gamma_4$	$\gamma_5$	$\Delta$
Kish	0.006	3.17	0.45	-0.019	0.29	0.06	0.04	-0.005
HOPG	-0.0248	3.22	0.41	-0.019	0.32	0.06	0.04	-0.005

carbon atoms. Such a defect concentration seems quite reasonable, taking into account both the resulting non-modification of the graphite band structure and the frequency of defect appearance on STM images. Actually,  $25 \text{ nm}^2$  images, which is convenient to detect defects, contain about 1000 carbon atoms. As defects sometimes appear in groups on some images, one can estimate that on average one image out of ten will contain defects. This order of magnitude is in good agreement with our observations.

#### 4. Conclusions.

In conclusion, we have shown that whereas the STM allows the study of intercalation compounds down to the atomic scale, at intermediate scale it also allows the precise determination of the intercalation islands and of their complicated (fractal ?) borders. We have also shown that Kish graphite and HOPG have different density of state at the Fermi level. This difference may well arise from the observed defects of the graphite network which have been observed here on the intercalated compounds. In addition, magnetic susceptibility experiments corroborate the shift in Fermi level of Kish graphite relative to HOPG.

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**References**

- [1] BIENSAN P., ROUX J.C., SAADAOUI H., FLANDROIS S., *J. Microsc. Microanal. Microstruct.* **12** (1990) 103-108.
- [2] QIN X. and KIRCZENOW G., *Phys. rev. B* **39** (1989) 6245  
QIN X. and KIRCZENOW G., *Phys. Rev. B* **41** (1990) 4976.
- [3] BLINOWSKI J., HAU N.H., RIGAUX C., VIEREN J.P., TOULLEC L., FURDIN G., HEROLD A. and MELIN J., *J. Phys. France* **41** (1980) 47
- [4] FLANDROIS S., MASSON J.M., ROUILLON J.C., GAULTIER J. and HAUW C., *Synth. Met.* **3** (1981) 1-13.
- [5] BIENSAN P., Thesis, University of Bordeaux (1991).
- [6] Nanoscope II, Digital Instrument Inc, Santa Barbara.
- [7] MIZES H.A., PARK S. and HARRISON W.A., *Phys. Rev. B* **36** (1987) 4491.
- [8] TERSOFF J., *Phys. Rev. Lett.* **57** (1986) 440.
- [9] ROSSO M., Proc. of the G.F.E.C.I. 90, Grenoble (1990);  
SAPORAL B., ROSSO M. and GOUYET J.F., The fractal approach to the heterogeneous chemistry, D. Avnir Ed. (John Wiley, 1989) p.227.
- [10] PIETRONERO L. and STRÄSSLER S., *Phys. Rev. Lett.* **47** (1981) 593.
- [11] MAAROUFI A.; FLANDROIS S., COULON C. and ROUILLON J.C., *J. Phys. Chem. Solids* **43** (1982) 1103.
- [12] DRESSELHAUS M.S., DRESSELHAUS G. and FISCHER J.E., *Phys. Rev. B* **15** (1977) 3180.