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# Defects at the Carbon terminated SiC(001) surface

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## Abstract

We present first principle molecular dynamics simulations for selected point defects on the (001) stoichiometric carbon terminated surface of cubic Silicon Carbide. In particular we investigated missing units and coordination defects. The results of our calculations are compared with recent experiments, in particular we discuss simulated STM images, which are in good agreement with measured ones.

## I. INTRODUCTION

Silicon Carbide is a promising material for high power and high frequency applications [1]; in particular the cubic polytype ( $\beta$ -SiC) is expected to present higher mobilities and break-down voltages than the more stable hexagonal polytypes. Furthermore,  $\beta$ -SiC is a potential substrate for nitride growth, since its lattice mismatch with several nitrides is fairly small and it has elastic and thermal properties similar to those of nitride materials. However, the production of SiC based electronic devices is still bound to the difficulty of preparing large areas defect free substrates. A complete understanding of microscopic defect formation is mandatory in order to fully characterize SiC polytypes.

In particular, since most SiC samples are grown by CVD, the control of surface stoichiometry is a key issue: missing atoms and dimers are expected to be the most probable surface defects. While defects have to be avoided to build efficient devices, certain types of defects can be exploited to create surface nanostructures with tailored bonding and transport properties. A series of recent experiments on Si and C lines on cubic SiC suggests the possibility of building one and two dimensional structures with selected bonding properties. For example, Soukiassian et al. [2] have recently shown that stable Si atomic lines can be deposited on the Si-terminated  $\beta$ -SiC(001) surface by temperature assisted STM techniques. Other recent experiments [3] have shown that stable  $sp^3$ -like bonded carbon lines can be formed on the C-terminated  $\beta$ -SiC(001) surface, by inducing an irreversible  $sp \rightarrow sp^3$  phase transition in the substrate. These  $sp^3$  lines point at possible precursors for diamond growth on SiC surfaces.

Although bulk defects have been studied both theoretically [4] and experimentally [5], the analysis of surface defects in  $\beta$ -SiC is yet incomplete: to our knowledge, only one *ab-initio* calculation on defects on the (111) surface of  $\beta$ -SiC is available, which points at vacancies as responsible for one of the experimentally observed reconstructions [6]. A widely studied surface of  $\beta$ -SiC is the (001) plane. In spite of many theoretical [7–9] and experimental [10] results on the electronic and structural properties of the stable reconstructions for this

surface, a detailed characterization of point defects is still lacking. Only recently Soukiassian and coworkers [11] have presented a STM study of point and extended defects at the Carbon-terminated  $\beta$ -SiC(001) surface.

In the present paper we present a first principle study of point defects on the  $\beta$ -SiC(001) C-terminated stoichiometric surface [C-SiC(001)] and show how the presence of defects is crucial to understand the reconstruction geometry. For all of the studied defects, we discuss calculated STM images: STM has proven to be an important tool for the description of surface properties at the atomic level; however, theoretical calculations are usually needed in order to properly interpret measured images. Finally we discuss possible driving forces for the  $sp$  to  $sp^3$  transition observed experimentally, and we present results on the geometry of coexisting  $sp$  and  $sp^3$  dimers on  $\beta$ -SiC(001) [12].

## II. METHOD

Our calculations have been performed at  $T=0$ , within the Local Density Approximation (LDA) and Generalized Gradient correction (GGA) [13] approximations to the Density Functional Theory (DFT) scheme. The studied surfaces were simulated by a repeated supercell along (001). For most calculations, we used supercells with 11 layers slab,  $\simeq 8$  Å vacuum, and 8 atoms/layer; the defected surfaces were simulated with a 7 layers, 16 atoms/layer or with a 6 layers slab with 32 atoms/layer. All atoms in the slab were allowed to relax [14]; however, in the largest slabs only 4 layers were allowed to move. We used fully non-local pseudopotentials for Si ( $s$  and  $p$  nonlocality) and C ( $s$  nonlocality) [15]; the electronic wavefunctions and charge densities were expanded in plane waves up to an energy cutoff of 40 (80) and 160 (320) Ry, respectively in LDA (GGA) calculations. The integration over the Brillouin Zone (BZ) was performed with the  $\Gamma$  point only in the supercell, which corresponds to 3 (6) inequivalent  $k$ -points of a  $p(2 \times 1)$ , or  $c(2 \times 2)$ , unit cell, for the supercell with 8 (16) atoms/layer. This number of  $k$ -points was proven to be sufficient to satisfactorily describe the C-term [7,12] and Si-term [8,16] SiC(001) clean surfaces and to interpret the

available experimental data on surface reconstructions [17,18] and CLS [19]. STM images were calculated within the Tersoff-Hamman [20] approximation as indicated in Ref. [8].

### III. RESULTS AND DISCUSSION

*The clean C-term surface.* The experimentally determined reconstruction of the C-SiC(001) is a  $c(2 \times 2)$  pattern [10,17], with staggered, flat,  $sp$  bonded carbon dimers bridging Si atoms of the underlying plane; the Si atoms slightly dimerize, the Si-Si distance decreasing by  $\simeq 24\%$  with respect to the bulk Si-Si distance in SiC. A poorly resolved and not well studied  $p(1 \times 2)$  reconstruction (*i.e.*  $90^\circ$  rotated with respect to the Silicon terminated  $p(2 \times 1)$ ) was also observed [10]. Ab-initio LDA calculations yield the geometry and electronic properties of the *bridge* (B) reconstruction in very good agreement with experiment, however, they find that this B- $c(2 \times 2)$  reconstruction is metastable and 0.25 eV/dimer higher in energy than a  $p(1 \times 2)$  dimer row (DR) reconstruction [7,9], with  $sp^3$ -like carbon dimers.

Experimentally, the preparation conditions for the C-(001) SiC surface may play a crucial role in determining the stable reconstruction [7]. Theoretically, the LDA description of the small energy differences between  $sp$  bonded and  $sp^3$  bonded carbon dimers can be a source of inaccuracy. Indeed, when using a GGA approximation with the PBE functional [13], we found that the energy ordering of the *bridge* and the  $p(1 \times 2)$  reconstruction is reversed, at the bulk theoretical equilibrium volume, the B geometry being lower in energy by 0.065 eV/dimer [12]. While the LDA underestimates the SiC bulk lattice constant by 1 %, the GGA approximation overestimates it by 0.7 %: the LDA and GGA values are 4.30 and 4.39 Å respectively, to be compared with the experimental value of 4.36 Å. Correspondingly, small differences appear in the equilibrium geometry found for the B reconstruction within the PBE and LDA approximations: for example, the C-C and Si-Si dimer bond lengths are 1.25 (1.23) and 2.42 (2.37) Å, when using GGA (LDA). However, the main features of the reconstructions are very similar, both from the geometric and electronic point of view. The calculations described here [12] are the first GGA-PBE calculations for surface reconstruc-

tions of cubic SiC. An extensive comparison of different exchange correlation functionals for the description of SiC surface reconstructions is in progress.

STM calculated images [21] for the clean Carbon terminated stoichiometric (001) surfaces are shown in Fig. 1, together with the different atomic structures (Fig. 1-b). Filled and empty states are represented in top and bottom panels for the metastable reconstructions obtained via first-principle molecular dynamics [7]. In the figure, the left panels refer to the DR- $p(1 \times 2)$  reconstruction, and the central panels refer to the B- $c(2 \times 2)$  geometry. For the sake of completeness, a further reconstruction is presented in the right panels, although higher in energy than the other two (the LDA value for this geometry is higher than the  $p(1 \times 2)$  of  $\simeq 0.4$  eV/dimer): this is the so called "staggered dimers" SD- $c(2 \times 2)$  surface, which was addressed to in the past as a possible stable model for the C-SiC(001) surface [7,9,10]. While the  $p(1 \times 2)$  reconstruction gives STM images totally different from the other two  $c(2 \times 2)$  geometries, the SD- $c(2 \times 2)$  and the B- $c(2 \times 2)$  reconstruction give similar results. Indeed, only an analysis at different voltages can distinguish between the two geometries, and in particular empty states images may be used as a probe. The calculated STM images compare fairly well with recent experimental data [11], both for the filled and empty states of the B reconstruction. The authors of Ref. [11] however infer an asymmetric dimer geometry, from the empty states image: we do not have evidence of any asymmetry or buckling either in LDA or GGA results for this surface.

*Missing units.* For the most stable B reconstruction, we have also studied a missing dimer defect on the C-terminated SiC(001) surface [21], which should be one of the most frequently observed defect in experiments (see Fig. 2-a). Because of the strength of C-C *sp* bonds, the defect does not induce any perturbation to the surrounding dimers, at variance with what reported for missing dimers at the Si-term surface [8]. Instead, both the C and Si-dimers bond lengths remain the same as at the clean surface, also in the vicinity of the missing unit. The STM calculated image for filled states is shown in Fig. 2-b: the wide bright spot centered at the missing dimer is due to the charge spilling from the underlying Si dangling bonds. The same features appear in the empty states calculated images (not shown), were

the largest contribution comes from antibonding states localized at the Si-sites. A recent STM study for the B surface, performed in the vicinity of missing units [11], indeed reveals bright spots in the empty states images, always associated to missing dimers. A better agreement between theory and experiment may be probably obtained including the effect of the electric field applied between the tip and the sample in the calculations. Indeed, in this case where a large charge spilling from the Si-dangling bonds is observed, charging effects might play a crucial role.

*Coordination defects.* Motivated by recent experiments [3], we then simulated the appearance of coordination defects on the B- $c(2 \times 2)$  surface. Starting from the ideal geometry of this reconstruction we arbitrarily rotated some C-dimers by  $90^\circ$ , thus inducing a local  $sp \rightarrow sp^3$  transition. The calculations were performed at different defect densities ( $\rho_d$ : 1/8, 1/4, 1/2), at the equilibrium lattice parameter and  $T=0$ . The defect formation energy, which is  $\simeq 1.2$  eV/dimer at  $\rho_d=1/8$ , decreases rapidly when more defects are created at the surface, and is  $\simeq 0.05$  eV/dimer at  $\rho_d=1/2$ . This result is in good agreement with recent experimental findings, showing that  $sp^3$  dimers are more stable on the B reconstruction at high defect concentrations, obtained, e.g. by increasing the substrate temperature [3].

For all values of  $\rho_d$ , we found flat  $sp^3$  defects which always lie *below* the  $sp$  pattern, the difference in their respective  $z$  coordinates being about  $0.4 \text{ \AA}$ ; the C-C distance ( $d_{CC}$ ) of  $sp^3$  defects is  $1.36\text{-}1.38 \text{ \AA}$ , depending on defect concentration. While the  $d_{CC}$  of the  $sp$ -bonded chains is unaffected by the presence of the  $sp^3$  dimer, its overall geometry is modified: for example, for the smallest value of  $\rho_d$ ,  $sp$  dimers close to the defect rotate of  $\simeq 6^\circ$  and present a  $\simeq 0.3 \text{ \AA}$  buckling. Correspondingly, some Si-Si dimers are elongated to  $2.50 \text{ \AA}$ . This is an indication of the strain associated with the presence of these coordination defects.

The  $sp^3$  defect conformation which results from our calculation is in apparent disagreement with the experimental observation [3] of asymmetric  $sp^3$  dimers lying *above* the  $sp$  chains, as inferred from measured STM images. We have calculated both filled and empty states STM images of the defected surface with  $\rho_d=1/2$  [21], in order to make direct contact with experiment. From an analysis of the electronic states within a few eV around the

Fermi level, we have found two surface states localized on the defects, and separated by a gap of 0.2 eV: these states have the same symmetry and orbital character as the HOMO and LUMO surface states found in the DR reconstruction [7]. The STM images computed using the Tersoff-Hamman approximation [20] are shown in Fig. 3. In the filled state image (Fig. 3-a), bright spots originate from bonding states, and clearly reflect the different arrangements of  $sp^3$  and  $sp$  dimers. An apparent buckling may be assumed for the  $sp^3$  defects from simple inspection of the image; the ‘buckling effect’ comes instead from charge distribution in the neighborhood of  $sp^3$ -like bonded carbon atoms. In the empty state image (Fig. 3-b), the bright spots are localized on atoms, and originate from dangling bonds on the  $sp^3$  dimers. The charge spilling of the dangling bonds make the  $sp^3$  defect appear very bright and *higher* than the regular  $sp$  array, while it is instead lying  $\simeq 0.4 \text{ \AA}$  lower than the  $sp$  pattern. Both filled states and empty states images are in good agreement with their experimental counterparts.

Finally, we considered the effect of missing  $sp$  units on the appearance of coordination defects: to this aim, we studied a symmetric slab with a missing  $sp$  dimer at both surfaces. We then rotated an  $sp$  dimer close to the missing unit and optimized the atomic and electronic structures of the supercell. In this case the formation energy of the  $sp^3$  defect is about 7 times lower than on a clean surface with no missing dimers. These results indicate that occasional missing dimers on the B reconstruction may represent local seeds for the  $sp$  to  $sp^3$  transition observed experimentally.

#### IV. CONCLUSIONS

In conclusion, we have presented first principle molecular dynamics calculations on point and extended defects at the C-terminated stoichiometric SiC(001) surface. A detailed description of the local atomic rearrangement near the defect site and the electronic properties of the system show that the missing dimer is the most common point defect for this reconstruction, in agreement with experiment. The presence of missing dimers do not perturb at

all the C-terminated Bridge reconstruction. However, this point defect may be considered a seed for the  $sp$  to  $sp^3$  transition (extended defect) observed experimentally. The calculated STM images for both the clean and the defected surfaces compare well with recent experimental data.

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## FIGURES

FIG. 1. (a) Calculated STM images at constant current for the metastable reconstructions of C-SiC(001). The panels indicate: Top: filled states images, and Bottom: empty states images, at +0.5V bias voltage for the three reconstructions,  $p(1 \times 2)$ , Bridge, Staggered dimers respectively, from left to right. Because of strong differences in the electronic surface states, the images sampling filled states were obtained at -1V for  $p(1 \times 2)$  and -1.5V for the two  $c(2 \times 2)$  reconstructions. (b) Top view of the atomic structure for the three metastable reconstructions of C- $\beta$ -SiC(001): black (grey) spheres indicate C (Si) atoms.

FIG. 2. Missing dimer at the C-SiC(001) surface: (a) equilibrium geometry and (b) calculated STM image, for filled states; the STM image is at constant current, with -1V bias voltage.

FIG. 3. Calculated STM images for the defected  $sp \rightarrow sp^3$  C-SiC(001) surface, with a defect concentration of 1/2. (a) Filled states STM image, computed at constant current and at a bias voltage = -2V. The grey spheres indicate topmost C-dimers in the relaxed configuration. (b) Empty states STM image, computed at constant current and at a bias voltage = 1 V. The height profile along the XX' line is shown in the bottom panel.

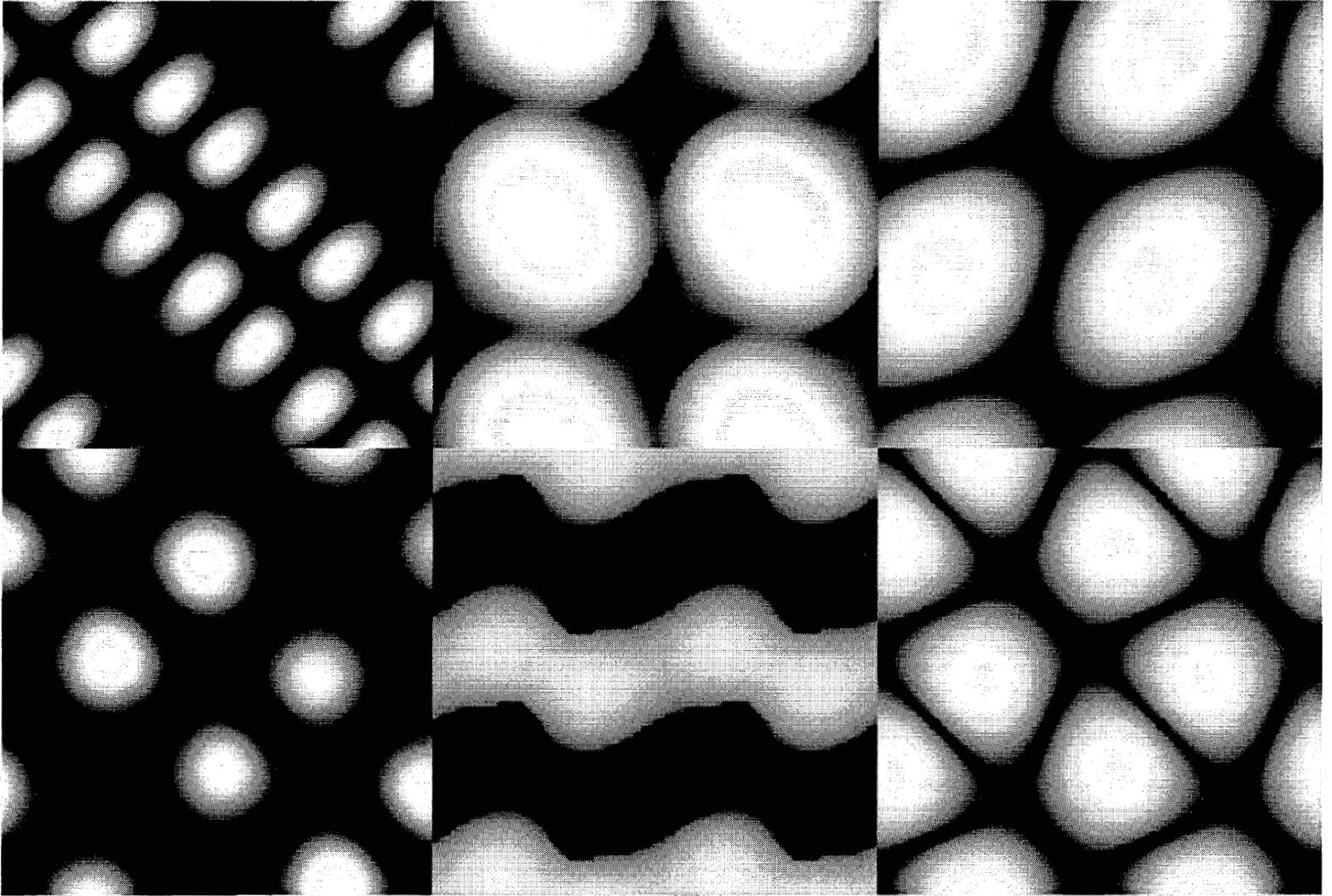
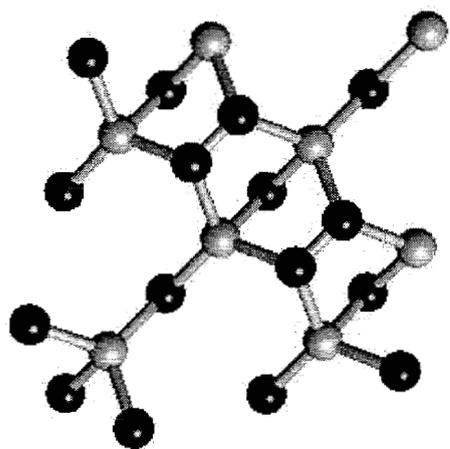
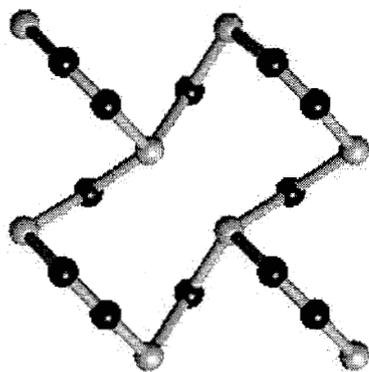


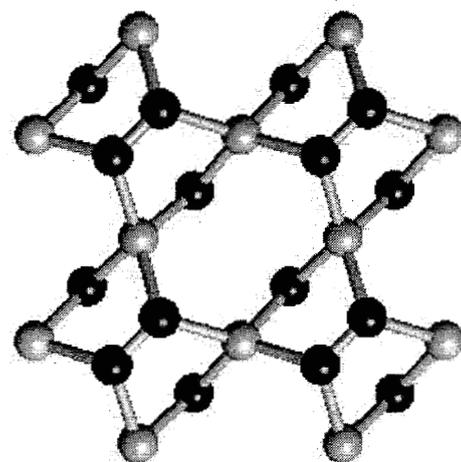
Fig. 1-a / Catellani, Galli



DR



B



SD

Fig. 1-b / Catellani, Galli

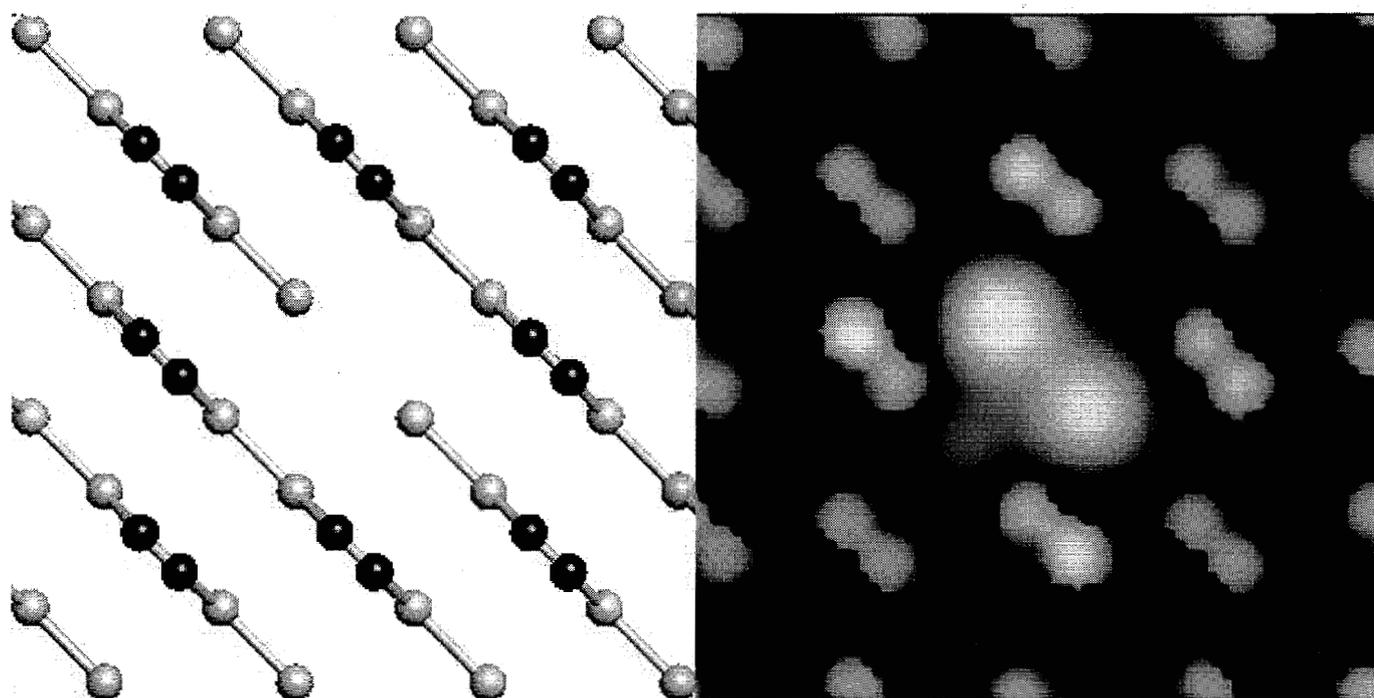


Fig. 2 / Catellani, Galli

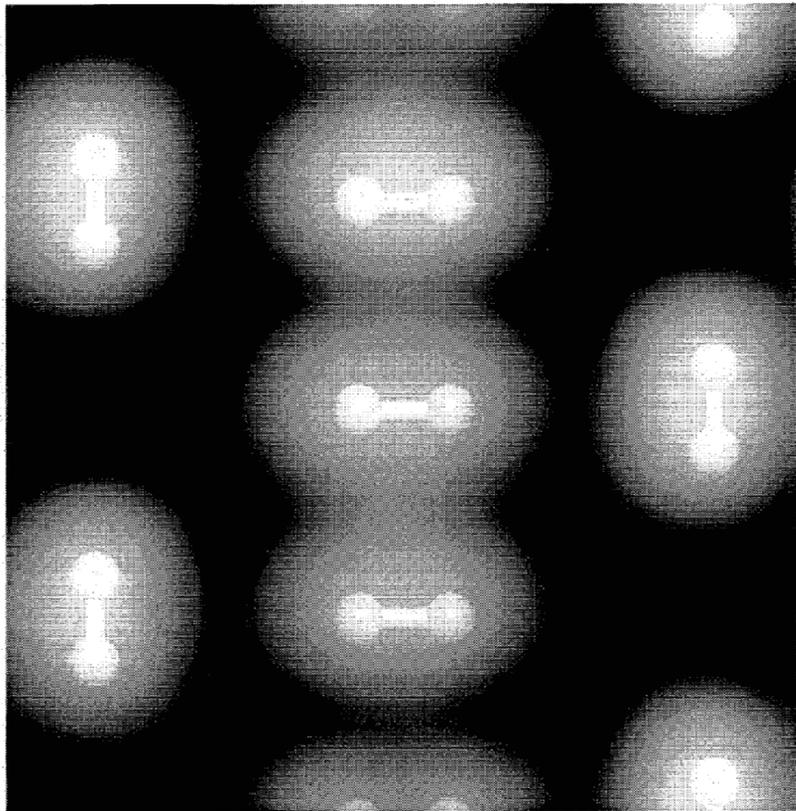


Fig. 3-a / Catellani, Galli

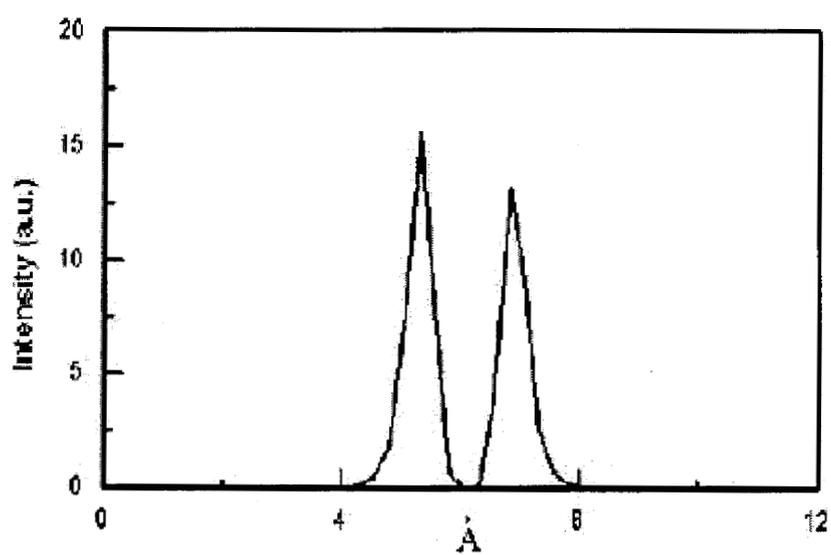
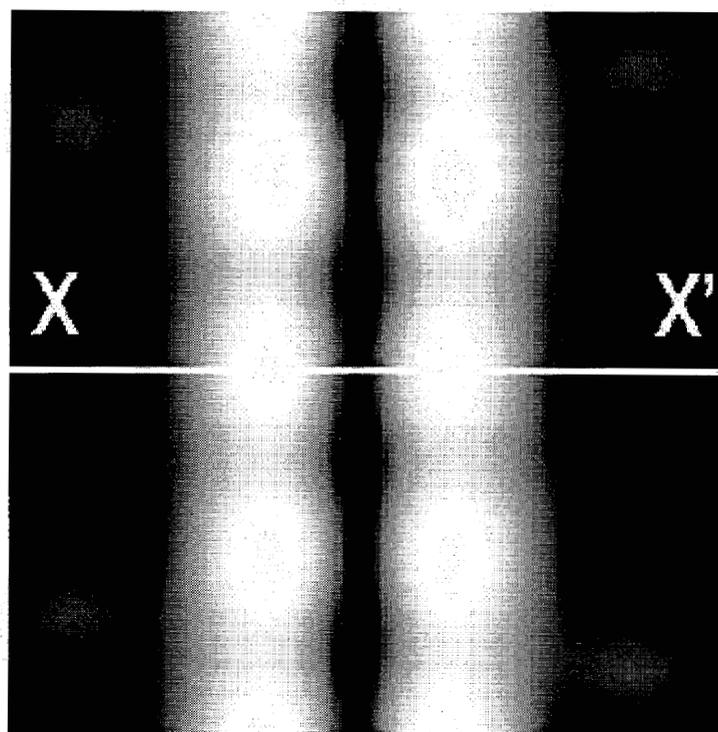


Fig. 3-b / Catellani, Galli