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Large Scale Hexagonal Domainlike Structures Superimposed on the Atomic Corrugation of a Graphite Surface Observed by Scanning Tunneling Microscopy

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Scanning tunneling microscopic images of large scale hexagonal domainlike waves superimposed on the normal atomic corrugation have been obtained on a highly oriented pyrolytic graphite surface. This hexagonal pattern had a spacing of 44 ± 2 Å, an amplitude of 3.8 ± 0.2 Å, and an orientation of about 30° with respect to the atomic corrugation. The appearance of this type of structure may be caused by a rotation of the topmost layer of graphite relative to its neighboring underlayers.

Introduction

We report here observations of hexagonal domainlike waves superimposed on the atomic corrugations in images of a highly oriented pyrolytic graphite (HOPG) surface observed by scanning tunneling microscopy (STM). This domainlike pattern with a spacing of about 44 ± 2 Å and top-to-bottom separation of about 3.8 ± 0.2 Å was stable, reproducible, and did not interfere with the observation of atomic corrugation. STM is a powerful technique for the study of the electronic topography of surfaces and adsorbed layers.[1] Since the tunneling current results from an overlap of wave functions of the tip with those of the sample, the STM images essentially represent the properties of the electronic structure of the surfaces, despite the fact that images in some cases closely resemble the geometric surface topography, that is, the atomic arrangement at the surface.[1] For example, atoms on a graphite surface are structurally identical; however, STM can distinguish atoms that have C atoms directly below them in the second layer from those that do not, in spite of the weak interaction between the layers.[2] Charge density waves observed by STM with some low dimensional materials, such as TaS_2,[3] $TaSe_2$,[4] and $NbSe_3$,[5] are interesting examples of the effect of a very slight displacement of atoms by only a few tenths of an angstrom (below the STM's resolution) which can give rise to a completely new pattern superimposed on the atomic corrugation in the STM images. Since the electronic features of a solid surface can dominate the STM images, it sometimes becomes very difficult to assign the STM image to any

kind of geometric structure of atoms on the surface. Several anomalous features of the STM images of graphite surfaces have already been reported. These include (1) a giant corrugation of up to 24 Å between the atomic sites and the center of the carbon rings,[3b–d,6–8] (2) large asymmetry between adjacent carbon sites on the (0001) surface of hexagonal graphite,[3b–d,6–8] (3) a superlattice with a size $\sqrt{3}$ times the basic graphite hexagon and rotated 30°,[9,10] and (4) a large scale hexagonal pattern with spacings of 4, 10, and 110 Å on a graphite surface covered by some metal species.[5b] Although some theoretical studies have been carried out and explanations proposed, the source of these anomalous images is not understood very well. In this paper, we show another anomalous pattern on a graphite surface observed by STM.

Experimental Section

The scanning tunneling microscope used in this study was a commercial instrument (Nanoscope II, Digital Instruments, Inc., Santa Barbara, CA). The STM tip was made by electrochemically etching a 250 μm diameter Pt–Ir (80:20) wire (Digital Instruments) in a solution of saturated $CaCl_2$:H_2O:HCl (60:36:4 by volume) following the procedures described elsewhere.[11] Highly oriented pyrolytic graphite was obtained from Dr. Arthur Moore of Union Carbide Corp., Parma, OH. The HOPG was cleaved by peeling back the surface with adhesive tape. All images were obtained at room temperature in air.

Results and Discussion

The large scale hexagonal pattern on an STM image of HOPG is shown in Figure 1a. The dark line crossing the picture is a double atomic step with the right side 6.8 ± 0.2 Å higher than the left one (the graphite planes are separated by about 3.4 Å). The large hexagonal pattern is clearly seen on the left side of the figure for the lower layer but is less apparent on the right upper layers. However essentially the same pattern can be seen on the right side after Fourier transform filtering. This is shown in the insert of Figure 1a, which represents a filtered image

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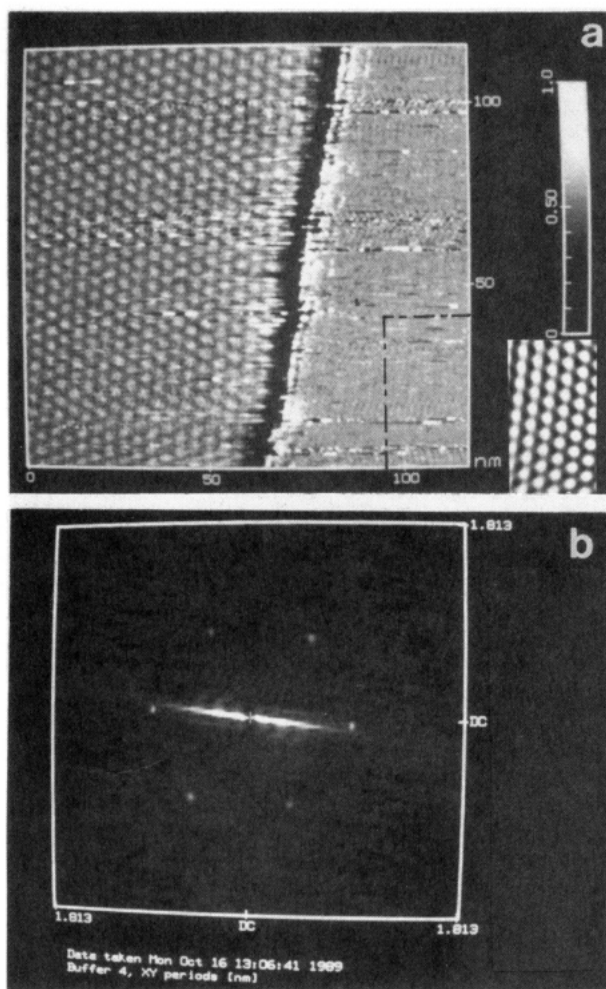
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Figure 1. (a) Unfiltered STM image of graphite which shows a double atomic step with the right side about 6.8 ± 0.2 Å higher than the left. The depression (deep black line) seen to the left of the boundary is an artifact that arises from feedback overshoot during the scan. The insert at the lower right corner shows a part of the Fourier transform filtered image of a portion of the right side as indicated by the dashed lines. Data were taken in a constant current mode with 2.4 nA tunneling current and tip-sample bias of 178 mV. (b) Two-dimensional Fourier transform spectrum of the raw data in part a. The six peaks (white spots) represent the hexagonal symmetry and the bright line reflects the double atomic step boundary seen in part a.

of the lower right corner of the figure. The amplitude of the hexagonal pattern on the right side is about 5 times smaller than that on the left. Fourier transforms of the images shown in Figure 1a give six dominant peaks which reflect the hexagonal symmetry (Figure 1b). Note that these six spots correspond to the hexagonal wave rather than the atomic corrugation. These two patterns are well separated and cannot be confused in Fourier transforms, and will be discussed in detail below. The pattern in Figure 1b indicates clearly that the hexagonal corrugations on both sides of Figure 1a have exactly the same orientation and spacing, otherwise, twin spots, that is, a total of 12 spots, should appear in the Fourier transform. This was further confirmed by comparing two different enlarged images from each side of Figure 1a; both top view and Fourier transforms showed the same orientation and spacing. Although similar images are obtained from both sides, those shown in Figures 2, 3, and 4 are all from the left side. Clearer hexagonal patterns in forms of a gray scale image and topographic plot are shown in parts a and b of Figure 2, respectively. The average peak-to-trough
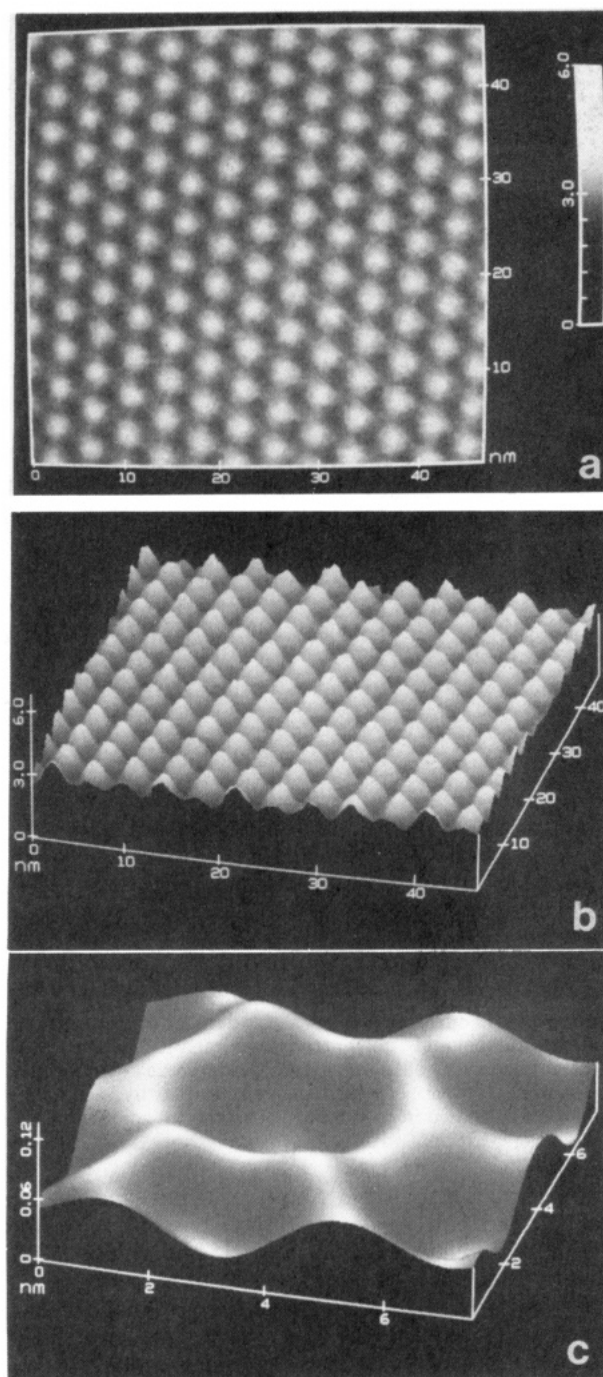
Figure 2. Unfiltered STM image of graphite taken on the left side of the step in Figure 1a with a tunneling current of 2.4 nA and bias voltage of 200 mV with tip positive. The peak-to-peak spacing is 44 ± 2 Å and peak-to-trough separation is 3.8 ± 0.2 Å. (a) Gray scale image. (b) Topographic plot. (c) Filtered STM image of graphite showing a single ring of the large hexagonal pattern. Tunneling current, 2 nA; bias voltage, 20.1 mV with tip negative.

height is 3.8 ± 0.2 Å and the peak to peak spacing is 44 ± 2 Å. A single ring of the hexagonal pattern is shown in Figure 2c.

Since the images shown here are anomalous, we performed several experiments to see if they arose from artifacts. Tip contamination, e.g., from picking up pieces of carbon from the HOPG surface, was a primary concern. From time to time the top was oscillated for a few seconds by setting the integral gain of the STM to about 500. This oscillation showed up on the display as a grainy pattern of light and dark. Other methods, such as withdrawing
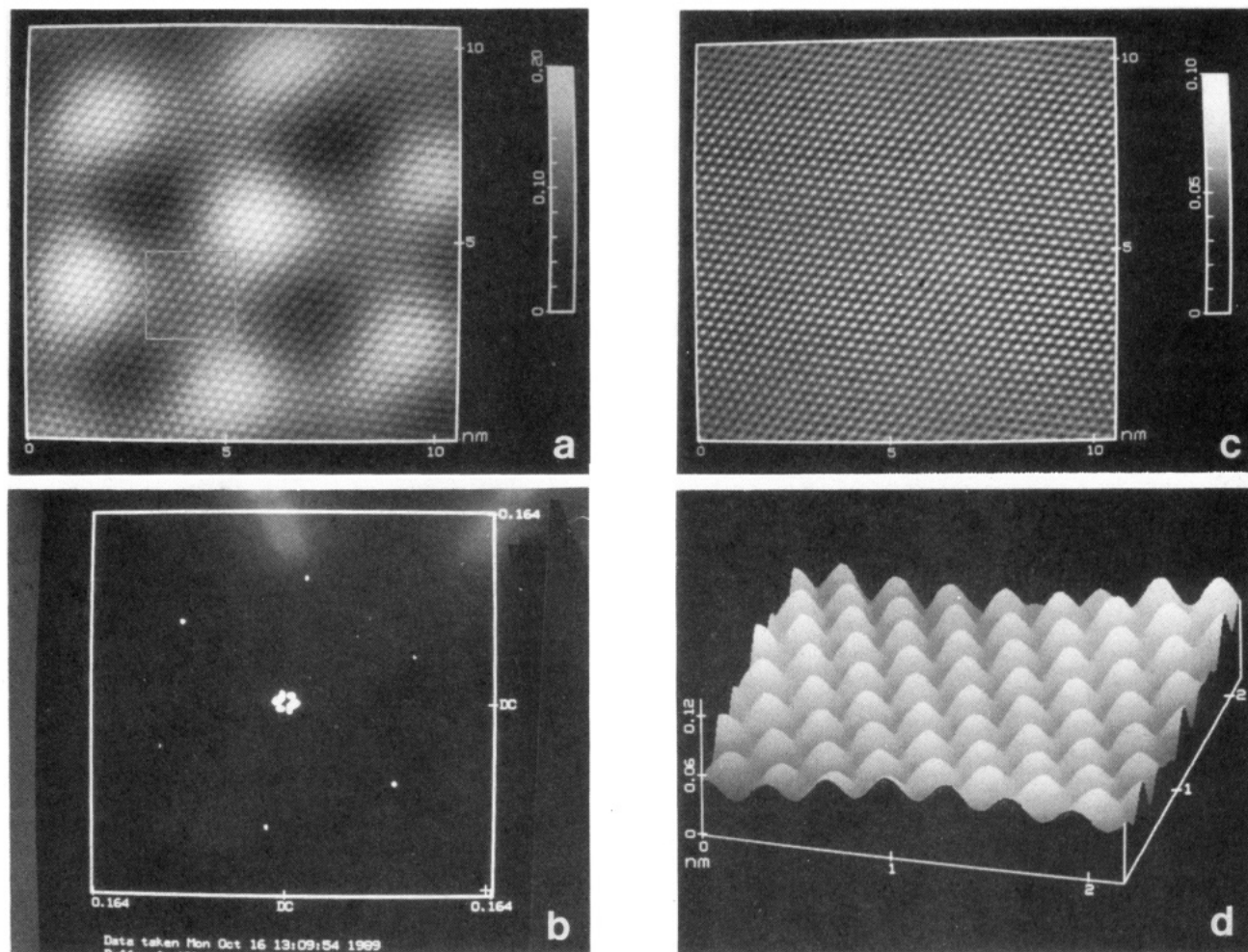
Figure 3. (a) Fourier transform filtered image of graphite which shows both individual atom structure and the large hexagonal pattern. (b) Two-dimensional Fourier transform spectrum of the raw data in part a. The outside six peaks correspond to the atomic corrugation and the inside six peaks arise from the large hexagonal pattern. The misorientation angle between these two patterns is about 30°. (c) Fourier transform filtered image obtained by selecting only the first-order lattice spots (the outside six peaks) in the Fourier transform as shown in part b. (d) Surface plot zoomed in from the image in part a indicated by a square. Tunneling current, 2.4 nA; bias voltage, 178 mV with tip negative.

and reengaging the tip a couple of times, and even reetching the tip, were also used to get rid of any contamination on the end of the tip. However, the large hexagonal pattern was not affected at all by these operations. Variation of the other parameters over certain ranges, such as bias voltage (−200 to 178 mV), set point current (2 to 2.4 nA), scan size (10 to 396 nm), scan rate (3.13 to 78.13 Hz), and image modes, had no influence on the real time images. The hexagonal domainlike patterns, with the same spacing, were always clearly shown. Clearly, this pattern is almost the same as the normal atomic corrugations, except for the size. However it does not arise from a calibration error. When a smaller area (10 by 10 nm) was scanned, actual atomic structure appeared. Figure 3a shows the hexagonal domainlike waves superimposed on the normal atomic corrugation. Interestingly, these two coexisting patterns do not interfere with each other. Two sets of peaks appear in the two-dimensional Fourier transforms (Figure 3b). In this figure the outside six peaks correspond to the actual atomic corrugation, while the inside six peaks arise from the large hexagonal pattern. This assignment could be tested by comparing the inverse transformed images in real space. For example, when only the outside six peaks were used, the Fourier transform filtered images showed pure atomic corrugation (Figure 3c). On the other hand, only a large hexagonal pattern like Figure 2 would appear if just the inside six peaks were

transformed. The orientation angle between these two patterns was about 30°. Figure 3d shows a surface plot of an enlarged small region, indicated by a square in Figure 3a. Note that this atomic corrugation is quite similar to the large hexagonal pattern shown in Figure 2b. Figure 4 shows another unfiltered image of graphite in which both corrugations could be directly identified. Interestingly, in the center, some adatoms or atomic-size particles, presumably formed during the cleavage,[12] appear and do not affect the pattern.

Because the sample was exposed to air, surface contamination could play a role in the observed image. However, there are several reasons why we feel that contamination is not responsible for our results. (1) The amplitude of the large hexagonal pattern on the right side of Figure 1 is about 5 times larger than that on the left side, with the two sides separated by a distinct step. It seems unlikely that impurities would be distributed in such a manner across the surface of the sample. (2) STM images and computer simulations of purposely deposited isolated molecules on the surface of graphite show periodic oscillations emanating from the molecules, with an amplitude that decays with distance.[9] Preferentially adsorbed species on adatoms on the graphite surface should have a similar effect on the STM images. This is not shown in

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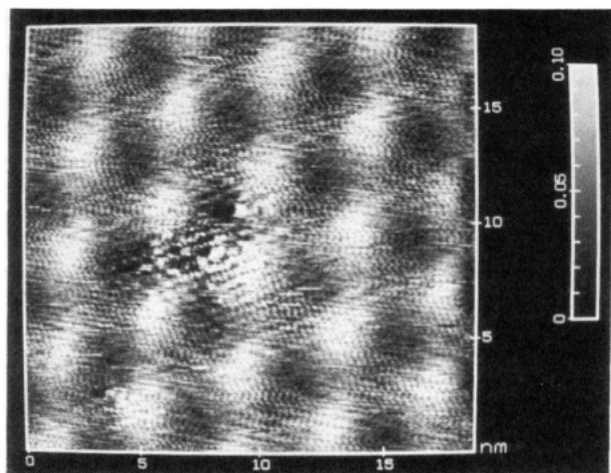
Figure 4. Raw STM image of graphite which shows that the adatoms have no influence on the large hexagonal pattern. Tunneling current, 2.4 nA; bias voltage, 178 mV with sample positive.

our results however, e.g., as in Figure 4. Adsorption of impurities on the flat HOPG surface should be less favorable compared to defects or adatoms. Thus adsorption on the flat surface should not give rise to detectable perturbations in the surface electronic charge density and produce large hexagonal patterns. (3) Surface contamination was believed to cause the giant atomic corrugations, i.e., with a peak-to-peak amplitude of up to 24 Å, observed in STM images of a graphite surface.[6c] The atomic corrugations reported here, however, are about 0.8 Å, which is in good agreement with the theoretical predictions,[13,14] again suggesting that surface contamination is not important in our results. Finally, no evidence of surface-contamination-induced superstructures on graphite has been reported previously.

Large hexagonal patterns with spacings of 10 and 110 Å have also previously been reported on graphite surfaces covered with some chemical species which were assumed to interact with the substrate and lead to new patterns.[5b] In our case, the spacing is about 44 ± 2 Å and no monolayers were purposely deposited on the graphite surface. Compared to these previous images of graphite, a fundamental difference is that here *the large hexagonal pattern was superimposed on the atomic corrugation.* Multiple tip effects on images of graphite have also been described.[15-17] It has been clearly shown that a new pattern could be generated only when double tips simultaneously image different surface regions with different orientations. This can arise when a scan takes place near a grain boundary, across which two tips are able to image different crystal faces at the same time. If both tips image a single crystal plane, the results would be indistinguishable from those obtained with a single tip.[15] A rotation of one crystal face of the graphite surface relative to its adjacent area is essential for the generation of a new pattern. In our case, both sides of the step (Figure 1a) have exactly the same orientation, and the same pattern is seen even for those

regions that are thousands of angstoms away from the step. Obviously, multiple tip effects cannot explain our results. A reviewer suggested that large tips, which are incommensurate with the substrate and may contain several domains, might produce similar superstructures. However, we doubt that atomically resolved images could be obtained with such tips, since usually "tunneling must involve a single or at most a couple of tip atoms, when atomic resolution is achieved."[1c] In our case, both atomic corrugation and large hexagonal patterns were clearly imaged by using the same tip at the same time.

Since the atoms below the topmost layer can influence the electronic structure of the atoms on the surface, and thus the STM images of the graphite,[3b-d,6-8] and the charge density on monolayer graphite, according to the computations,[13] is different from that at the surface of a sample consisting of several layers, we propose that a rotation between the first two layers might be responsible for the pattern observed here. Theoretical calculations show that a slipped top layer of graphite relative to subsurface layers, as could occur during cleavage, can create larger corrugation amplitudes and be responsible for the loss of the trigonal symmetry in the STM images of a graphite surface.[2c] The suggestion of interlayer rotation seems to be supported by the results shown in Figure 4. The adatoms or atomic size particles have no effect on the large hexagonal pattern. This implies that the effect that produces the new pattern arises from inside of graphite rather than from the surface itself. This also seems to be consistent with the observation that the amplitude of the hexagonal wave is about 5 times weaker on the right side than on the left side of the step shown in Figure 1a. If we assume the pattern arises from the upper layers imaged on the left, the weaker image seen on the right is the result of two additional atomic layers (6.8 ± 0.2 Å) above the rotated planes. Since the tunneling current is proportional to the local density of states at the surface,[14] this large hexagonal pattern is essentially generated by a perturbation in the surface density of states induced by an interlayer rotation. We should point out, however, that we could not purposely effect such an interlayer rotation of HOPG, although it could arise accidentally during the cleavage step. A very similar type of pattern was found independently in the STM image from a different HOPG specimen. The rotation pattern can easily be visualized by overlaying two identical hexagonal patterns on transparencies and rotating one with respect to the other. The spacing of the large hexagonal pattern that arises depends upon the angle between the two patterns and can clearly be very different from the spacing reported here. Intercalation, e.g., of alkali metals, can also produce hexagonal patterns with spacings larger than the usual atomic corrugations.[18] However, we feel this is unlikely for the results reported here, since previous results with intercalation show much smaller spacing and our sample never underwent any treatment that would lead to such intercalation.

We should also point out that the images shown here are very similar in appearance to the charge density waves (CDWs) observed by STM on other low dimensional materials, such as, TaS_2,[3] $TaSe_2$,[4] and $NbSe_3$.[5] Early studies have indicated that a very small displacement of atoms (0.05 Å) can generate a CDW.[19] Since this small displacement is below the resolution of STM, the CDWs are always seen as a new pattern with a large spacing

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superimposed on the normal atomic corrugation in STM images.[3] The concept of CDWs was first proposed for one-dimensional metals[20] and later was extended to two-dimensional materials.[21] Although a large amount of experimental data on CDWs have been obtained,[22] the detailed structure and dynamics of the CDWs was only established by STM.[3] To our knowledge, no CDW has been reported for graphite, although unexpected structures, such as a superlattice, have been observed on graphite surfaces.[9,10] It is not clear whether a CDW-type lattice distortion could occur on graphite.

Since HOPG is a popular substrate in STM for deposition of molecular or biological species,[23-36] it is important to realize that apparent modifications in the atomic corrugation in STM images of HOPG do not necessarily reflect the presence of foreign species on the graphite surface. Moreover, the results suggest that STM images are affected by structures and layers that are several layers below the surface and that such subsurface structures can affect surface electron distributions, even for layered materials like HOPG with rather weak electronic interactions perpendicular to the (0001) surface. After the original submission of our manuscript, we became aware of other reports of large corrugations on HOPG.[37,38] An hexagonal pattern with a spacing of about 77 Å was reported by Kuwabara et al.,[37] who propose the same explanation as we do for the pattern. Note, however, that these authors did not see the larger corrugation pattern resulting from a perturbation in deeper layers superimposed on more discernible atomic corrugations, as reported here.

Conclusions

(1) An anomalous hexagonal pattern with a spacing of 44 ± 0.2 Å and an amplitude of 3.8 ± 0.2 Å has been observed by STM on a cleaved graphite surface. Such a superstructure differs substantially from most of those observed previously in a number of ways. The pattern reported here is stable and appears over a large area (several thousand angstroms) without any decay in amplitude. Most importantly, this pattern is supermposed on the normal atomic corrugations of amplitude about 0.8 Å. (2) Tip or surface contamination, and multiple tip or tip geometry effects are unlikely to be the cause of the large scale hexagonal domainlike structure. Interlayer rotation is proposed. (3) We suggest that multilayer electronic interactions can be important in the observed STM images and that one must be cautious in interpreting observed large periodic structures with HOPG substrates in terms of surface layers of purposely adsorbed species.

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