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Theory and observation of highly asymmetric atomic structure in scanning-tunneling-microscopy images of graphite

David Tománek, Steven G. Louie, H. Jonathon Mamin, David W. Abraham, Ruth Ellen Thomson, Eric Ganz, and John Clarke

Department of Physics, University of California, Berkeley, California 94720 and Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Images of the (0001) surface of graphite observed in the scanning-tunneling microscope (STM) show a strong asymmetry in the tunneling current between neighboring carbon atoms in the hexagonal ring. The magnitude of this asymmetry is seen to be almost independent of the polarity and to decrease slightly with increasing amplitude of the bias voltage for voltages below 1 V. A theory is developed that explains this anomaly as a purely electronic effect, arising from the symmetry of the states scanned by the STM, which dominates over the topography of graphite. The predicted trends for the bias-voltage dependence of the asymmetry are confirmed experimentally.

Images of graphite[1-4] obtained in the scanning-tunneling microscope (STM) reveal two anomalous features: "giant corrugations" (enormous apparent heights of atoms above the centers of the carbon rings)[1-4] and a substantial asymmetry in the apparent heights of neighboring carbon sites.[3,4] Neither of these features can be understood within the simplistic picture that the STM images total charge densities at the surface. The first anomaly has been attributed to the unusual electronic structure of a single graphitic layer, in which the Fermi surface collapses to only one point in the surface Brillouin zone (BZ).[5] However, to explain the large apparent magnitude of the corrugations, one also has to consider large-scale surface deformations induced by elastic interactions between the STM tip and the surface,[6] especially in the case of contaminated surfaces.[4] The second anomaly, a large apparent asymmetry leading to the resolution of only every other atom in the STM images [Fig. 1(a)], is unexpected, since the weak interaction between layers should ensure that the total charge densities on these atoms are practically identical. A recent calculation[3,7] on a graphite slab revealed some asymmetry between these sites, but does not explain the main experimental findings present in this paper: The asymmetry is large at a low bias voltage, decreases with increasing voltage, and is independent of its polarity. All three experimental observations are well explained by the model outlined here, which demonstrates that the asymmetry is primarily a property of the bulk material. Using *ab initio* methods, we calculate STM current densities which lead to images closely resembling experimental observations (see Fig. 1).

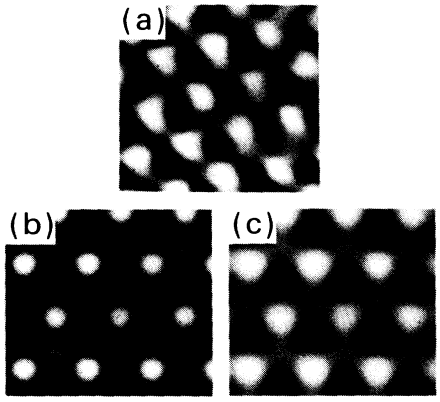

FIG. 1. (a) Observed and (b) and (c) calculated STM current densities $j(x,y,z=\text{const})$ for a bias voltage $V=0.1$ V. In (c), calculated results of (b) have been Fourier analyzed and filtered to mimic the experimental conditions. On the grey scale, white corresponds to large current densities.

The graphite samples were prepared by cleaving highly oriented pyrolythic graphite in air. The STM was operated in the current-imaging mode,[2] in which the tunneling tip is scanned across the surface at constant height and bias voltage, and the variations in the tunneling current j constitute the image. We emphasize that in this mode the deformation of the graphite surface remains constant and amplification of the atomic heights therefore does not occur. Thus, even for a surface exposed to air, we expect the observed variations of the tunneling current to be the same as those on a clean surface. By contrast, the asymmetry observed in images obtained in the topographic mode, in which the tip-to-surface separation varies, depends strongly on the surface deformation and hence on the level of contamination of the surface and the tunneling tip.[4]

Figure 1(a) shows a typical current image of a 12×12 Å^2 graphite sample obtained in air at a bias voltage $V=0.1$ V. As seen, the STM image does not reflect the expected honeycomb atomic arrangement, but rather shows only a sublattice with a hexagonal close-packed structure, which contains every second atom. The contrast between the neighboring sites in terms of the current asymmetry is very large. In hexagonal graphite (with *ABAB* stacking), the crystal is composed of an α sublattice consisting of atoms with neighbors directly above and below in adjacent layers and a β sublattice consisting of sites without such neighbors (Fig. 2). Our theory presented below predicts that the atoms visible in the STM image

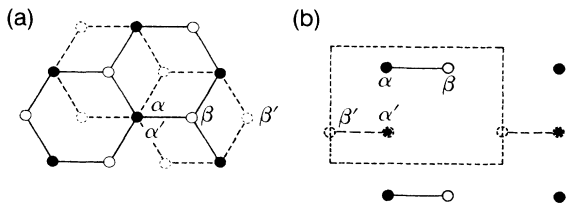

FIG. 2. Schematic drawing of two successive layers of hexagonal graphite in (a) the top view and (b) the side view. The unit cell is enclosed by a dashed line in (b).

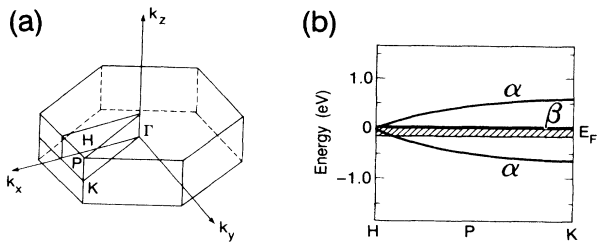

FIG. 3. (a) The Brillouin zone and (b) the schematic band structure of the π states of hexagonal graphite along the P line. States sampled by the STM at small voltages are crosshatched in (b).

are of the β type.

For a given small positive bias voltage V, the tunneling current density $j(\mathbf{r})$ can be obtained from a simple extension[7] of the expression derived by Tersoff and Hamann,[8]

$$j(\mathbf{r},V) \propto \int_{E_F-eV}^{E_F} dE \rho(\mathbf{r},E) \ , \tag{1a}$$

where

$$\rho(\mathbf{r},E) \equiv \sum_{n,\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \delta(E_{n\mathbf{k}}-E) \ . \tag{1b}$$

Here, $\rho(\mathbf{r},E)$ is the local density of states at the tip position $\mathbf{r}=(x,y,z)$, and the $\psi_{n\mathbf{k}}(\mathbf{r})$ are the eigenstates of the unperturbed surface with corresponding energy $E_{n\mathbf{k}}$. The implied assumptions[7,8] are a constant matrix element for tunneling and the description of the relevant tip states by s waves with a constant density of states for the tip in the narrow (but nonzero) energy region $(E_F-eV;E_F)$. The explanation of the observed asymmetry in the STM current is crucially dependent on the nature of the graphite eigenstates $\psi_{n\mathbf{k}}$, which contribute to the tunneling current. They are p_z in character and can be written as a linear combination of Bloch functions Φ_j localized on the α, α', β, and β' sites in the unit cell shown in Fig. 2(b),

$$\psi_{n\mathbf{k}}(\mathbf{r}) = c_{n\alpha}\Phi_\alpha(\mathbf{r},\mathbf{k}) + c_{n\alpha'}\Phi_{\alpha'}(\mathbf{r},\mathbf{k}) + c_{n\beta}\Phi_\beta(\mathbf{r},\mathbf{k}) + c_{n\beta'}\Phi_{\beta'}(\mathbf{r},\mathbf{k}) \ , \tag{2a}$$

where

$$\Phi_j(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}-\tau_j)} p_z(\mathbf{r}-\mathbf{R}+\tau_j) \ , \tag{2b}$$

$$j=\alpha,\alpha',\beta,\beta' \ .$$

The Fermi surface of graphite lies close to the P line in the Brillouin zone [Fig. 3(a)], defined by $\mathbf{k}=(\frac{1}{3},\frac{1}{3},\xi)$ (in units of the reciprocal lattice vectors). Along this line, the Hamilton matrix $H_{ij}(\mathbf{k})=\langle\Phi_i|H|\Phi_j\rangle$ is given in the nearest-neighbor approximation by

$$H(\tfrac{1}{3},\tfrac{1}{3},\xi) = \begin{array}{c} \\ \alpha \\ \alpha' \\ \beta \\ \beta' \end{array} \begin{array}{c} \begin{array}{cccc} \alpha & \alpha' & \beta & \beta' \end{array} \\ \begin{pmatrix} E_\alpha & t_\alpha(\xi) & 0 & 0 \\ t_\alpha^*(\xi) & E_\alpha & 0 & 0 \\ 0 & 0 & E_\beta & 0 \\ 0 & 0 & 0 & E_\beta \end{pmatrix} \end{array} . \tag{3}$$

Because of the crystal symmetry, the phase factors in Eq. (2b) add up in such a way that the states on the α atoms are decoupled from those on the β atoms in the whole crystal up to all orders of neighbor interactions. For the same reason, we obtain the *unexpected* result that the Bloch functions on β atoms do not interact with those on β atoms on neighboring planes, leading to a diagonal β submatrix. Since the atomic environment of the α and β sites is similar, we expect $E_\alpha \approx E_\beta$. Along the P line, this Hamiltonian then gives rise to a doubly degenerate band at $E=E_\beta$ near E_F, with wave functions localized on the β sites, and to a dispersive band with wave functions localized on the α sites [Fig. 2(b)]. The STM, which scans a narrow energy region below E_F corresponding to $\mathbf{k}$ states near the P line, detects all β states and only a very small fraction of the α states. It is this "density of states" effect, rather than a different spatial extension of wave functions on neighboring sites,[9] which causes the dramatic asymmetry in Fig. 1.

The extension of the physical picture from the bulk to the (0001) surface is straightforward. The P line in the bulk BZ collapses to the point $\bar{K}$ in the surface BZ. The α band folds to a continuum of states spread over approximately 1.2 eV around E_F and the β band is essentially a δ function at E_F. The physical origin of the asymmetry in the tunneling current j between the α and the β sites is unchanged. As the magnitude of the bias voltage is increased, the tunneling process samples states increasingly far from the P line (or $\bar{K}$ point), where α and β states are not completely decoupled. However, because of the large band dispersion near P or $\bar{K}$, the part of the BZ sampled by the STM is still very small, which causes a decrease, but not a disappearance, of the asymmetry for larger bias voltages V.

We have calculated the electronic structure of graphite quantitatively using the *ab initio* pseudopotential local-orbital method.[10] We used a Gaussian basis,[11] norm-conserving ionic pseudopotentials of Hamann-Schlüter-Chiang type,[12] and the Hedin-Lundqvist[13] form of the exchange-correlation potential in the local-density approximation. The calculations are performed fully self-consistently on graphite slabs with four layers. The irreducible part of the surface BZ is sampled by a fine mesh consisting of 61 $\mathbf{k}$ points. A $\mathbf{k}_\parallel$-resolved density of states is derived from the four-layer slab results by broadening energy levels using Gaussians with a half-width at half maximum of 0.2 eV. Calculations on bulk graphite yielded similar results, supporting our claim that the effect is a

bulk, rather than a surface property. Since the α and the β densities of states are nearly symmetric around E_F [Fig. 3(b)], the tunneling current is expected *not* to depend on the polarity of the bias voltage. Only at large voltages is the tunneling current expected to be different for the two polarities.

Figure 1(b) shows a predicted tunneling current density image, obtained from Eq. (1a) for $V=0.1$ V and a tip-to-surface separation of 1 Å. When comparing this image with the experimental image in Fig. 1(a), one should bear in mind that the relatively large size and irregular shape of the real STM tip limits the lateral resolution. We can mimic this effect by filtering out the high-frequency Fourier components from the calculated current density shown in Fig. 1(b) to produce Fig. 1(c), which shows a strong similarity to the experimental data.

To obtain a quantitative comparison between the experimental and calculated data, we define the asymmetry between the tunneling current j at the α and β sites by $A \equiv [j(\beta)-j(\alpha)]/[j(\beta)+j(\alpha)]$. In the experiment, $j(\alpha)$ and $j(\beta)$ were extracted from a whole image by averaging over sites with the low and high current density, respectively.[14] In general, we expect A to depend on the tunneling voltage V and the tip height h above the surface (or the tunneling resistance). Figure 4 summarizes our results for this asymmetry as a function of the bias voltage V. Calculated values of A (from the unfiltered densities) for $h=0.5$ and 1 Å are given by broken and solid lines, respectively. These results indicate that A decreases with increasing voltage and is almost independent of h in this height range.[15] The experimental data, taken at a fixed but unknown height, show very similar trends, with A decreasing from ≈ 0.2 at 0.05 V to ≈ 0.1 at 0.5 V bias. The complete data set has been obtained using the same tip and sample. The values of the asymmetry shown in Fig. 4 were among the largest obtained; in some runs A was substantially smaller, probably due to the finite resolution of the microscope. This finite resolution can be modeled by filtering out the high-frequency Fourier components of the current density with a Gaussian. The filtered theoretical values for A are shown as the dotted curve in Fig. 4. The same filter parameters have been used for all voltages in Fig. 4 and correspond to those used in Fig. 1(c). We further note that h was almost certainly greater than 1 Å in the experiment; if so, A would be further reduced below the computed values.

An important test of the theory is the dependence of A on the polarity of the bias voltage. Data in the inset of Fig. 4, obtained by reversing the bias polarity in the middle of one scan, indicate that A is insensitive to the polarity. These results agree with our prediction and mitigate against surface states as the origin of the asymmetry.

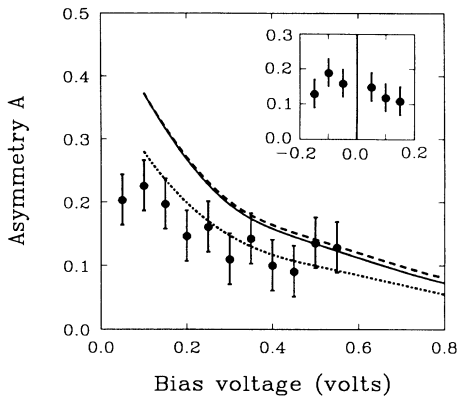

FIG. 4. Asymmetry $A \equiv [j(\beta)-j(\alpha)]/[j(\beta)+j(\alpha)]$ of the tunneling current j as a function of the bias voltage V. The solid and broken lines represent calculated results at a tip-surface separation $h=1$ and 0.5 Å, respectively. The dotted lines represents theoretical data at 1 Å, which have been filtered to mimic the finite experimental resolution. The experimental points are constant resistance data corresponding to an unknown value of h. The inset shows the observed polarity dependence of A.

In summary, we have investigated the graphite surface using scanning tunneling microscopy and *ab initio* band structure calculations. In the current imaging mode, we observe a strong asymmetry between the neighboring carbon sites. This is explained by the unique symmetry of the states near $\bar{K}$ in the surface Brillouin zone near the Fermi energy. Hence, the asymmetry has an electronic and not a topographic origin. Our calculation predicts significant asymmetry at low bias voltages, its decrease with increasing bias voltage, and its independence of polarity, in agreement with experiment.

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[1] R. V. Coleman, B. Drake, P. K. Hansma, and G. Slough, Phys. Rev. Lett. **55**, 394 (1985); Sang-Il Park and C. F. Quate, Appl. Phys. Lett. **48**, 112 (1986); P. K. Hansma, Bull. Am. Phys. Soc. **30**, 251 (1985).

[2] A. Bryant, D. P. E. Smith, and C. F. Quate, Appl. Phys. Lett. **48**, 832 (1986).

[3] G. Binnig, H. Fuchs, Ch. Gerber, H. Rohrer, E. Stoll, and E. Tosatti, Europhys. Lett. **1**, 31 (1986).

[4] H. J. Mamin, E. Ganz, D. W. Abraham, R. E. Thomson, and J. Clarke, Phys. Rev. B **34**, 9015 (1986).

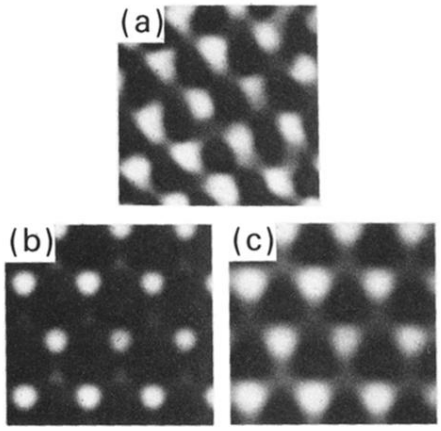
[5] J. Tersoff, Phys. Rev. Lett. **57**, 440 (1986).

[6] J. M. Soler, A. M. Baro, N. Garcia, and H. Rohrer, Phys. Rev. Lett. **57**, 444 (1986).

[7] A. Selloni, P. Carnevali, E. Tosatti, and C. D. Chen, Phys. Rev. B **31**, 2602 (1985).

[8] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998

(1983); Phys. Rev. B **31**, 805 (1985).
[9]C. F. Quate, Phys. Today **39** (No. 8), 26 (1986).
[10]C. T. Chan, D. Vanderbilt, and S. G. Louie, Phys. Rev. B **33**, 2455 (1986); C. T. Chan, D. Vanderbilt, S. G. Louie, and J. R. Chelikowsky *ibid.* **33**, 7941 (1986).
[11]S. Fahy, S. G. Louie, and M. L. Cohen, Phys. Rev. B **34**, 1191 (1986).
[12]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
[13]L. Hedin and B. J. Lundqvist, J. Phys. C **4**, 2064 (1971).
[14]The presence of a position-insensitive offset current could modify the magnitude of the observed asymmetry.
[15]At substantially larger height values, A is expected to decrease, as discussed in Ref. 8. The extremely low charge density values in a region many angstroms above the surface are not reproduced accurately enough within our method of calculation.



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