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Multiple-tip interpretation of anomalous scanning-tunneling-microscopy images of layered materials

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Graphite and other layered materials have been the substrates for numerous studies with the scanning tunneling microscope (STM) and, more recently, the atomic-force microscope. We argue in this paper that the experimental images for this class of materials are dominated by only three independent Fourier components. A nonideal tip can change the relative amplitudes and shift the relative phases of these components. This changes the shape and amplitude of the protrusions in the image which are interpreted as atoms. The effect of the STM tip on the images can be quantified with the assumption of multiple atomic tips. The multiple-tip model can explain many of the anomalous images that have been obtained, and can aid in their interpretation.

The scanning tunneling microscope (STM) and the atomic-force microscope (AFM) have produced images of the surfaces of both conductors and insulators on a scale as small as atomic dimensions.[1,2] From these images, the positions and identity of surface atoms can be determined.[3]

Layered materials, such as graphite and transition-metal dichalcogenides, are especially attractive as STM and AFM substrates for atomic-scale imaging. These surfaces have been extensively imaged because it is easy to prepare atomically flat regions over thousands of square angstroms. The surfaces remain uncontaminated and can be examined in air and in liquids.

The crystal structure of the surface of layered materials studied to date is either a triangular or a honeycomb lattice. In this paper we demonstrate that their images are dominated by only three independent Fourier coefficients. The threefold symmetry of the surface requires the coefficients to be equal in amplitude. If the threefold symmetry is broken for some reason, then the amplitude of these coefficients may no longer be equal, and the images can change significantly. We show that the symmetry may be broken by an asymmetric tip. This must be taken into account when interpreting the STM and AFM images.

The sample surface is probed by monitoring the tunneling current between the tip and the sample. The tunneling current depends on both the geometry and the electronic structure of the tip and sample surfaces. However, since pointed transition-metal tips are used as the probes, the STM images usually reflect only the properties of the sample.

Tersoff and Hamann[4] have shown explicitly how the STM images will depend on the sample properties alone by calculating the tunneling current using the transfer Hamiltonian method.[5] Using this method, one extends time-dependent perturbation theory to transitions between the two nonorthogonal basis sets of the electrodes. The spatial dependence of the tunneling current is contained in the tunneling matrix element. In the limit of low temperatures and low voltages, only electronic states at the Fermi energy can make tunneling transitions, and the tunneling current I_0 is proportional to the sum of the square of the matrix elements between these states. This is expressed as

$$I_0 \propto \left| \sum_{\mu,\nu} \langle \psi_\mu | H_T | \psi_\nu \rangle \right|^2 . \tag{1}$$

The indices μ and ν label the tip and sample wave functions, respectively, and H_T is the term in the Hamiltonian that allows transitions between the two states. The summation is restricted to states at the Fermi level.

Tersoff and Hamann modeled the tip potential by a spherical potential well. They assumed that ψ_μ, the tip wave function, approaches an s state asymptotically far from the tip, and in particular, at the sample surface. With this approximation, they could then evaluate (1) for arbitrary sample wave functions. They found that

$$I_0 \propto \sum_{\nu} |\psi_\nu(\mathbf{r}_0)|^2 = \rho(\mathbf{r}_0, E_F) , \tag{2}$$

where $\mathbf{r}_0$ is the origin of the tip s state and ρ is the local density of states (LDOS). The tunneling current is seen to be proportional to the LDOS for the sample at the Fermi energy, evaluated at the center of the tip.

We now evaluate the approximate charge density at the center of the tip for electrons at the Fermi energy. We consider only layered materials of which the top layer is in a triangular or honeycomb lattice. Since these surfaces are periodic, the charge density can be expanded in a Fourier series in the transverse direction. The amplitude of the Fourier coefficients fall off quickly with spatial frequency. The reason for this decrease is that high-frequency components decay into the vacuum (which we define to be in the z direction) more quickly than low-frequency components. This can be seen by considering the Schrödinger equation outside the surface, where the potential is constant. Each Fourier component of the wave function $\psi_{\mathbf{k}_\parallel} \propto e^{i\mathbf{k}\cdot\mathbf{r}} e^{-k_z z}$ must satisfy the equation

$$(k_z^2 - k_\parallel^2) = 2m\phi/\hbar^2 . \tag{3}$$

In Eq. (3), k_z is the magnitude of the imaginary wave vector perpendicular to the surface, $\mathbf{k}_\parallel$ is the wave vector parallel to the surface, and ϕ is the work function of the sample. The decay rate of the Fourier component into the vacuum, which is proportional to k_z, increases for larger

transverse wave numbers. The charge density at the Fermi energy $\rho(E_F,\mathbf{r}_0)$, which is the quantity that the STM monitors, is proportional to the sum of the modulus squared of the wave functions [Eq. (2)]. In Fourier space this is just a sum of the two-dimensional self-convolutions of the wave functions. Since the Fourier transform of each wave function is peaked at the origin, the transform of $\rho(E_F,\mathbf{r}_0)$ will also be peaked at the origin.

The suppression of high-spatial-frequency components is significant for real surfaces. We consider graphite as an example. The work function of graphite is about 5 eV, and the magnitudes of its two smallest transverse wave vectors are 1.70 and 3.41 Å^{-1}. If we assume that the amplitudes of the these two Fourier coefficients are equal in the atomic plane, then, using Eq. (3), we discover that at only 2 Å into the vacuum the second coefficient has fallen to less than 1% of the first.

The dominance of the lowest Fourier components is seen experimentally. In Fig. 1(a) we show an experimental STM image of the graphite surface. This image, along with all the others shown in this paper, was taken in constant-distance mode, where the feedback cannot respond to the atomic corrugations.[6,7] The bright areas correspond to regions of increased tunneling current, which should occur when the tip is positioned over an atom. An interpretation of the observed triangular lattice is that because of electronic structure effects from the atomic plane below the surface, only every other atom of the honeycomb lattice is imaged.[8,9]

Figure 1(b) is the Fourier transform of the image in Fig. 1(a). The transform is dominated by six Fourier coefficients. The smallest transverse wave numbers in the Fourier series for either a triangular lattice of a honeycomb lattice are six wave vectors of equal magnitude oriented towards the vertices of a regular hexagon. Since the configuration-space image is a real function of position, then the amplitude of the Fourier coefficients must be equal for equal and oppositely oriented wave vectors. The six corresponding plane waves therefore combine to make three sine waves separated by 120°. The dc component does not effect the image. The STM image is thus dominated by these three sine waves.

AFM images of layered materials probe not the charge density at the Fermi energy, but the total valence charge density. However, at each energy, the same argument applies and the higher transverse wave vectors again fall off more rapidly into the vacuum. AFM images will also be dominated by these three sine waves.

We now turn to the effect that nonideal tips will have on the STM and AFM images of layered materials. The reason we consider this effect is that anomalous images of these layered materials seem to be the norm rather than the exception. A variety of experimental STM images that have been seen for graphite are displayed in the left-hand column of Fig. 2. Because the surface of graphite has threefold symmetry, and also because different images have been seen over the same area of graphite, the variety of the images cannot be due to some surface property of graphite. Binnig *et al.*[10] and Schneir, Sonnenfeld, Hansma, and Tersoff[11] have suggested that this variety may be due to an asymmetric tip. We will pick a specific model for this tip and show that all the images of Fig. 2 can be accounted for.

Tersoff and Hamann assumed an s-state tip wave function in their theory of the STM. We now relax this approximation. Chen[12] has modeled the tip more accurately by including higher-order spherical harmonics in the expansion of the tip wave function. He has shown that the tunneling matrix element for the lth harmonic is proportional to the lth-order Taylor-expansion coefficient of the sample wave function evaluated at the center of the tip. We choose a more physical way of modeling a nonideal tip. Since a tip is composed of atoms, we approximate a nonideal tip with a linear combination of two or more s states, corresponding to the closest tip atoms to the sample. For specificity, we consider only two-tip atoms. In Eq. (1), we replace the bra $\langle\psi_\mu|$ by the sum $\langle\psi_{\mu 1}|+\langle\psi_{\mu 2}|$, corresponding to a linear combination of two s states. The matrix element in Eq. (1) becomes a sum of two matrix elements, both of which can be evalu-

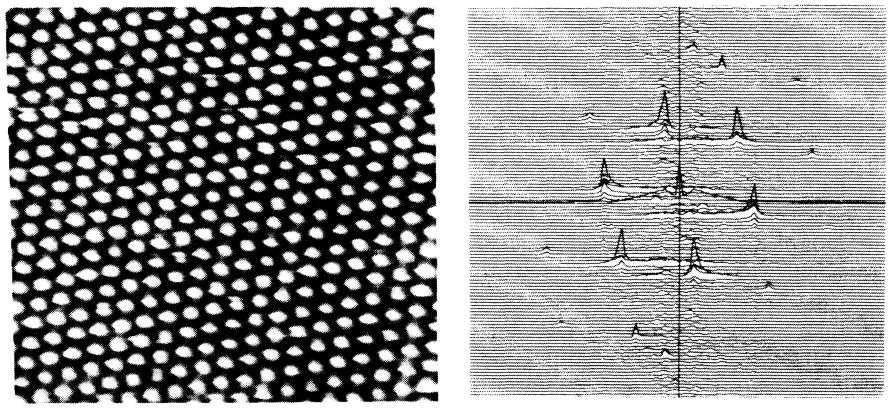

FIG. 1. (a) An experimental STM image of a graphite lattice. Every other atom in the honeycomb lattice is thought to be suppressed due to electronic structure effects, giving rise to an apparent triangular lattice. (b) The Fourier transform of the image. The lowest-order Fourier coefficient dominates the image.

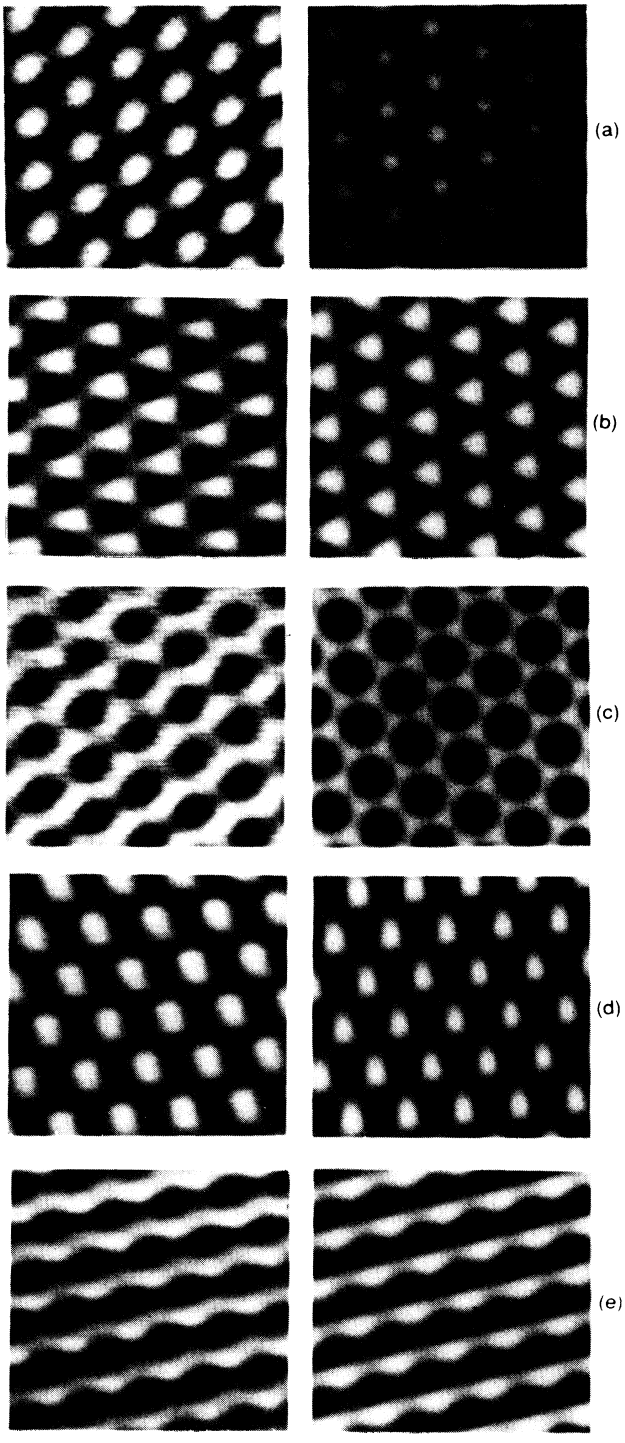

FIG. 2. Anomalous STM images of graphite. The experimental images are displayed in the left-hand column. They have been tilted in order to compensate for thermal drift and they have been filtered. The computer-generated images corresponding to the experimental data are displayed in the right-hand column. They are just a linear combination of three sine waves, as described in the text. The amplitudes and phases of the sine waves have been adjusted to match the data. We conjecture that a multiple tip is responsible for the modification of the Fourier coefficients.

ated independently using the approximation of Tersoff and Hamann. The tunneling current emanating from a two-atom tip is then written

$$I \propto \sum_{\nu} \left| \sum_{\mu} \psi_{\nu}(\mathbf{r}_1) e^{i\phi_{\mu 1}} + \psi_{\nu}(\mathbf{r}_2) e^{i\phi_{\mu 2}} \right|^2 . \quad (4)$$

ψ_{ν} is again the sample wave function, now evaluated at the centers $\mathbf{r}_1$ and $\mathbf{r}_2$ of the two-atom tip. $\phi_{\mu i}$ is the phase of the μth tip state wave function on atom i. The relative phase of the two s states depends on which of the many tip wave functions participates in the tunneling. Since we sum over tip wave functions with a wide variety of relative phases, the interference term in (4) will tend to sum to zero, and we can write

$$I \propto \sum_{\nu} |\psi_{\nu}(\mathbf{r}_1)|^2 + |\psi_{\nu}(\mathbf{r}_2)|^2 = \rho(\mathbf{r}_1, E_F) + \rho(\mathbf{r}_2, E_F) . \quad (5)$$

The STM image will be a superposition of two images, the second shifted by the relative separation of the two tip atoms. For surfaces with large unit cells, such as the 7×7 reconstruction of the Si(111) surface, we would see this superposition as a doubling of atoms. This has been observed experimentally.[13]

However, in layered materials that have images dominated by only three independent Fourier components, the superposition takes on a different character. When two sine waves of the same wave number are added, the result is a third sine wave of the same wave number but with a different amplitude and phase. Therefore, when two images of a layered material are superimposed, the resultant image is a superposition of three sine waves of differing phases and amplitudes. The experimental images in the left-hand column of Fig. 2 are, in fact, each dominated by three Fourier components of different amplitude and phase. We demonstrate this effect explicitly by displaying in the right-hand column computer-generated images. The artificial images are a sum of *only* three sine waves, with the amplitude and phase chosen to match the character of the experimental images.

We consider each pair in turn, assuming that the single-tip image is of a triangular lattice [Fig. 2(a)]. If one of the Fourier components suffers a relative phase shift of $\pi/2$, then a triangular array of triangles will be imaged [Fig. 2(b)]. A honeycomb array will be imaged if one of the components suffers a relative phase shift of π [Fig. 2(b)]. If the amplitude of two of the Fourier coefficients dominates the third, then the image will show a triangular array of ellipses [Fig. 2(d)]. If, on the other hand, the amplitude of one of the Fourier coefficients dominates the other two, then the image will be dominated by rows [Fig. 2(e)]. Although we cannot predict the configuration of the tip from the STM images, since many tip configurations can give rise to the same image, we can understand how these anomalous images arise and that they are not a property of the sample.

It is necessary to understand how the nature of the tips can affect the interpretation of the images. In the case of graphite, there are currently two quantitative predictions of the STM images.[8,9] The unit cell of a graphite monolayer consists of two inequivalent atoms. Selloni and co-

workers[8] predict that there will be only a slight difference in the LDOS centered on these two atoms, while Batra *et al.*[9] claim that only alternate atoms appear in STM topographs. One might hope to resolve the question experimentally. However, there are experimental STM images that seem to verify each calculation. The experimental image in Fig. 2(a) seems to verify the prediction of Batra *et al.*, while the image in Fig. 2(b) seems to agree with Selloni *et al.* The only difference between the two STM images is that there is a relative phase shift of $\pi/2$ between one of the Fourier coefficients and the other two. Experimentally there is no way to tell from these two images which image represents the charge density at the Fermi level and which is a superposition due to multiple atomic tips.

The nature of the tip has a subtle effect on the STM and AFM images of highly periodic surfaces and must be taken into account when interpreting them.

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[1]Paul K. Hansma and Jerry Tersoff, J. Appl. Phys. **61**, R1 (1987).

[2]G. Binnnig and H. Rohrer, IBM J. Res. Dev. **30**, 355 (1986).

[3]R. M. Feenstra, J. A. Stroscio, J. Tersoff, and A. P. Fein, Phys. Rev. Lett. **58**, 1192 (1987).

[4]J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).

[5]C. B. Duke, *Tunneling in Solids,* Solid State Physics, Vol. 10, edited by E. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), pp. 207–213.

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

[7]Sang-il Park and C. F. Quate, Rev. Sci. Instrum. (to be published).

[8]A. Selloni, P. Cornevali, E. Tosatti, and C. D. Chen, Phys. Rev. B **31**, 2602 (1985); **34**, 7406 (1986).

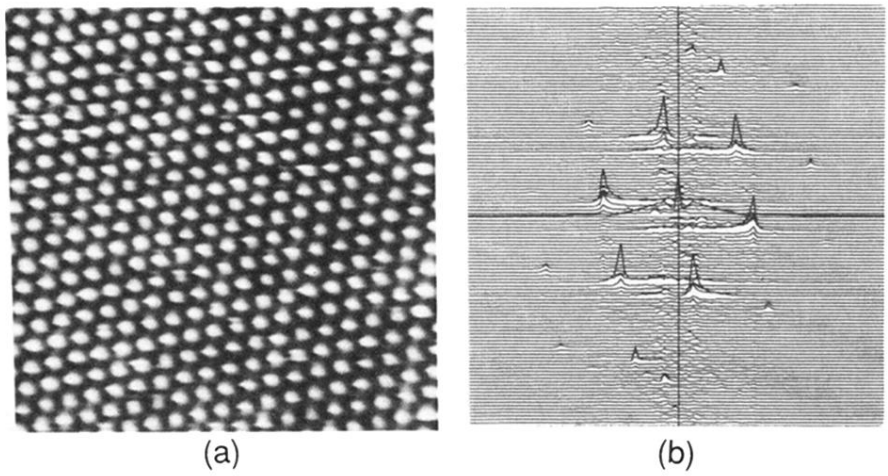
[9]I. P. Batra, N. García, H. Rohrer, H. Salemink, E. Stoll, and S. Ciraci, Surf. Sci. **181**, 126 (1987).

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

[11]J. Schneir, R. Sonnenfeld, P. K. Hansma, and J. Tersoff, Phys. Rev. B **34**, 4979 (1986).

[12]J. C. Chen, IBM Technical Report No. RC-12505, 1987 (unpublished).

[13]S. I. Park, J. Nogami, and C. F. Quate, Phys. Rev. B **36**, 2863 (1987).



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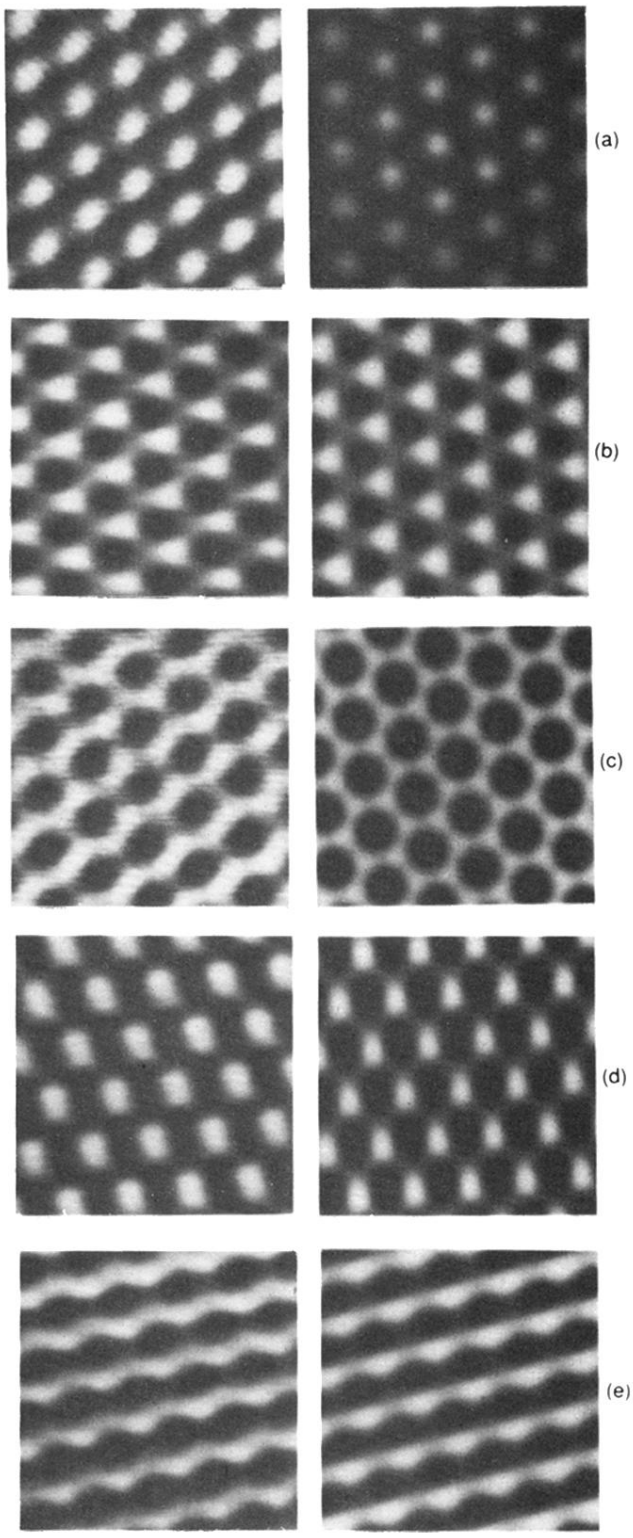

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