

to the classical length dependence of  $\langle \Phi_N \rangle$  can be probed experimentally. Such experiments will prove instrumental in establishing whether disorder, which is well-known to affect the transport properties<sup>19</sup> of wide classes of electronic systems, such as semiconductors, plays a crucial role in transport in MBEDs. If disorder does play a significant role, then this will certainly add

further complications in the design of MBEDs for practical use. Alternatively, if heavily doped liquid crystal systems can be easily designed, then such systems would possess optimal efficiencies and would be of extreme technological importance because of their inherent rigidity.

**Acknowledgment.** We thank R. Freisner and M. A. Fox for stimulating discussions at the outset of this work and the NSF for funding this work.

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## Scanning Tunneling Microscopy Investigations of the Electronic Structure of Potassium-Graphite Intercalation Compounds

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The scanning tunneling microscope (STM) has been used to probe the surface electronic structure of the stage-1 potassium-graphite intercalation compound ( $KC_8$ ) in real space with atomic resolution. Tunneling images of  $KC_8$  are found to exhibit new  $2a$  superlattice peaks as well as the peaks usually found for native graphite. Experiments that have probed the dependence of the  $KC_8$  images on sample-tip bias voltage and separation indicate that the new features observed in the STM images are determined by electronic effects and not elastic deformations of the graphite surface.

### Introduction

The scanning tunneling microscope (STM) is a uniquely powerful tool for probing the local electronic and structural properties of surfaces in vacuum, air, and liquids.<sup>1</sup> One material that has been the focus of many STM studies is highly oriented pyrolytic graphite (HOPG, Figure 1a),<sup>1-8</sup> in large part because it can be easily imaged with atomic resolution. At a more fundamental level, however, it is well-recognized that STM images of HOPG can exhibit two anomalous features including giant ( $>1$  Å) vertical corrugations and a large asymmetry in the observed heights of adjacent carbon sites (typically only alternate atoms are detected). Large vertical corrugations have been explained in terms of a model that considers elastic interactions, mediated by a contamination layer, between the tip and the graphite surface.<sup>3</sup> On the other hand, the asymmetry between adjacent carbon atoms in images of HOPG has been explained by a model based on the unique electronic structure of graphite.<sup>2</sup> Specifically, this "electronic" model suggests that the carbon site asymmetry is due

to large differences in the local density of states (LDOS) between the two structurally distinct surface sites in graphite (A and B, Figure 1a) near the Fermi level (i.e., the energy regime typically probed with the STM).

To further test this latter model, we have initiated studies of graphite intercalation complexes, and in this Letter we report atomically resolved STM images of the stage-1 potassium-graphite compound,  $KC_8$  (Figure 1b).<sup>9</sup> This material consists of ordered layers of potassium ions between every carbon layer. The spacing between carbon layers is increased 2 Å upon potassium intercalation, and therefore the interlayer (carbon-carbon) interaction is significantly reduced compared with graphite. In addition, the carbon sites in the surface and underlying layer are structurally equivalent in contrast to the two distinct sites in HOPG.<sup>2a</sup> We believe that images of  $KC_8$ , which characterize the effects of these changes caused by intercalation, should provide a critical test of the above models for STM imaging of graphite.

### Experimental Section

Gold-colored stage-1 potassium-graphite materials were prepared according to the standard two-zone technique.<sup>9</sup> In a typical procedure a two-bulb Pyrex tube containing HOPG and excess potassium metal (at opposite ends) was sealed under vacuum and differentially heated for 12 h. The temperature of the graphite end was maintained at 300 °C while the alkali-metal end was kept at 250 °C. The  $KC_8$  samples were removed from the sealed reaction tube inside an inert atmosphere glovebox that was equipped with a purification system that reduced the concentration of oxygen and water to  $<1$  ppm. Elemental analysis confirmed that the material was indeed bulk  $KC_8$ .

All of the STM experiments were carried out in an inert-atmosphere glovebox using a Nanoscope (Digital Instruments, Inc., Santa Barbara, CA) instrument as described previously.<sup>10</sup> The

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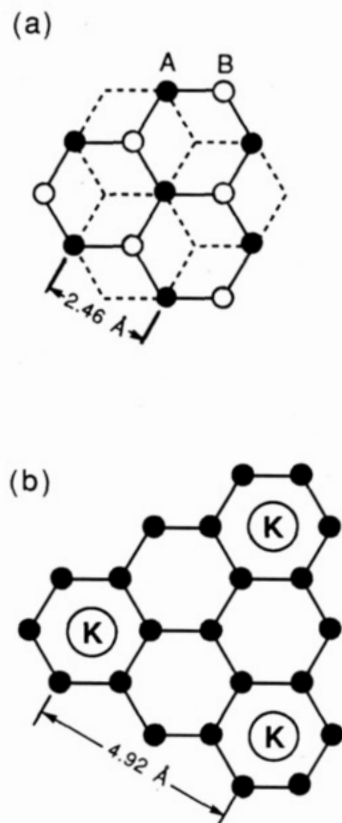
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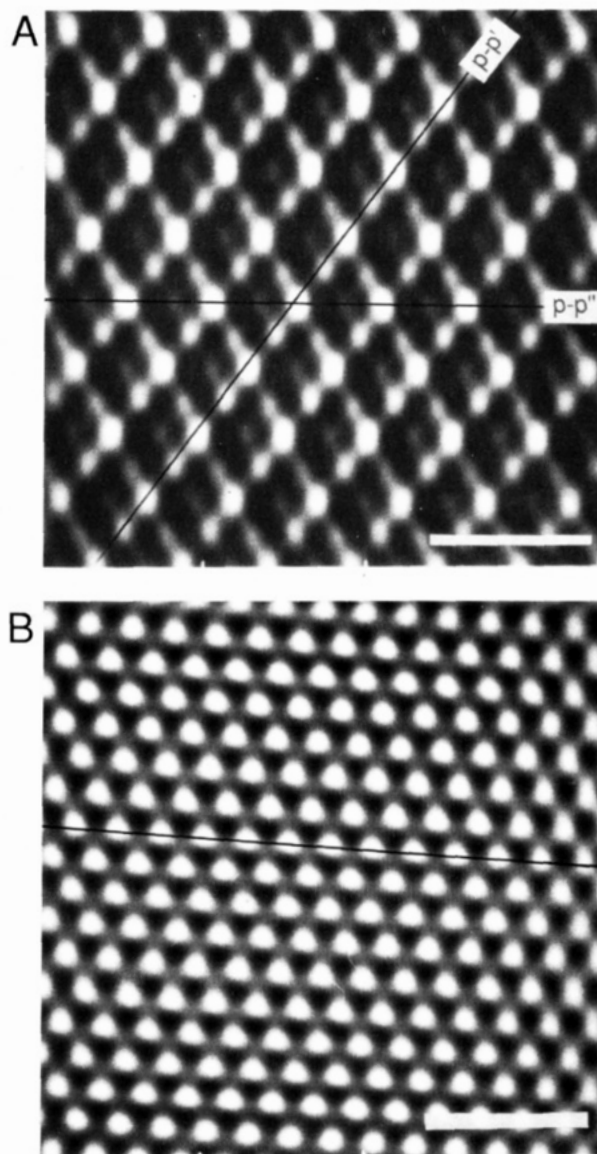


**Figure 1.** (a) Schematic top view of HOPG. The surface layer (solid lines connecting the carbon atoms) and underlying layer (dotted lines connecting the carbon atoms) are displaced such that the A surface sites are directly above a carbon atom in the underlying layer, but the B surface sites are not. (b) Schematic top view of  $\text{KC}_8$ . The surface sites all lie directly over a carbon atom in the underlying layer.

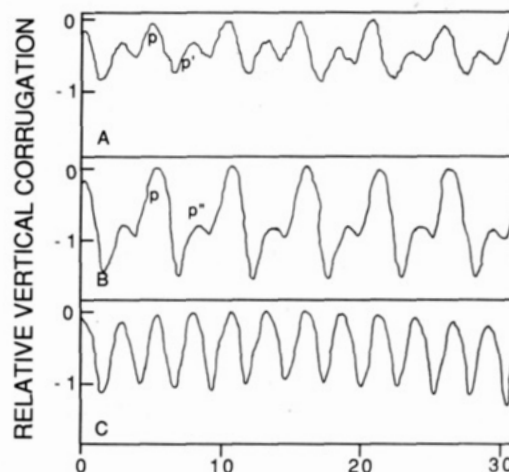
tunneling probes were platinum-iridium (80%–20%) wire that was mechanically cut to form the tip. The  $\text{KC}_8$  samples could be cleaved repeatedly after mounting on the STM stage to expose new surfaces.<sup>11</sup> Freshly cleaved surfaces were stable for at least 4 h in the glovebox.

### Results and Discussion

A typical<sup>12</sup> constant-current image of  $\text{KC}_8$  recorded with a tunneling current of 4 nA and a sample vs tip bias voltage ( $V_b$ ) of  $-15$  mV is shown in Figure 2 along with an image of HOPG. Lighter areas in these images correspond to apparent surface protrusions while darker areas indicate depressions. Under the bias conditions used to record the  $\text{KC}_8$  image tunneling occurs from filled states near the Fermi level ( $E_F$ ) in  $\text{KC}_8$  to empty tip states. It is obvious from a comparison of the  $\text{KC}_8$  and HOPG images that a larger periodic structure is present in the image of the potassium intercalation compound. Periodic structure larger than observed in images of HOPG has also been reported for the related material  $\text{LiC}_6$ .<sup>7b,c</sup> The new structure observed in our images of  $\text{KC}_8$  is two times larger than the peak spacing in HOPG (i.e.,  $4.9 \pm 0.2$  vs.  $2.46$  Å) and matches the periodicity of potassium in bulk  $\text{KC}_8$  ( $d(\text{K-K}) = 4.92$  Å) determined from diffraction measurements.<sup>9b</sup> In addition, the new  $2a$  ( $a = 2.46$  Å) structure is stable, reproducible, and appears to be ordered over areas at least as large as  $400 \times 400$  Å. Further analysis of this  $\text{KC}_8$  image reveals two other sites that lie between the dominant peaks (p). These sites,  $p'$  and  $p''$ , are clearly visible in profiles of the surface



**Figure 2.** Top-view images of (A)  $\text{KC}_8$  and (B) HOPG recorded with tunneling current of 4 nA and a sample vs tip bias voltage of  $-15$  mV. The raw image data was low-pass filtered prior to display. The white bar in each image corresponds to  $10$  Å.

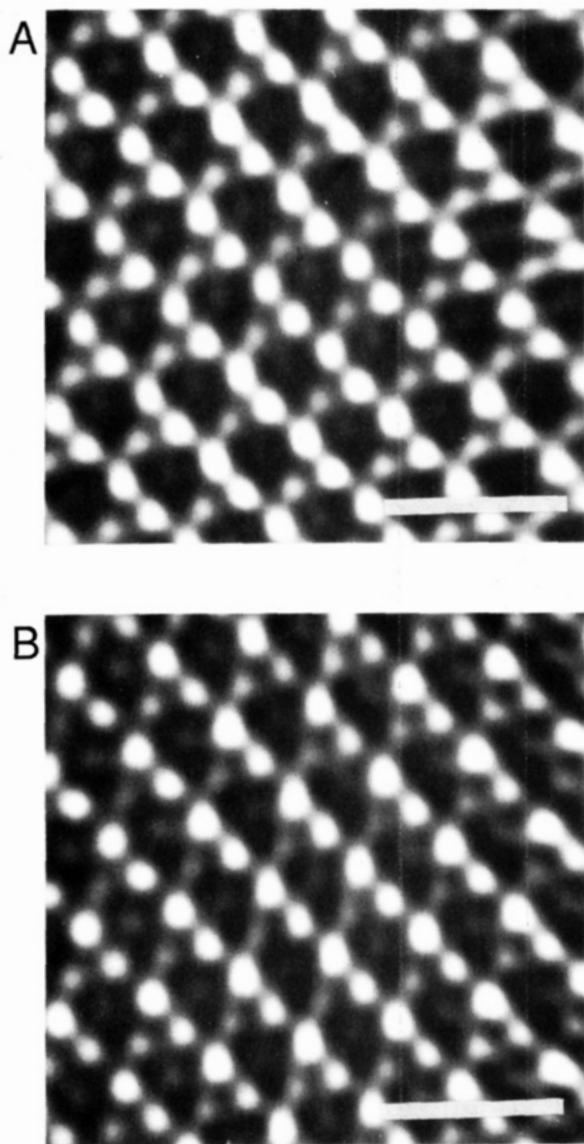


**Figure 3.** Profiles of the surface corrugation relative to the largest peaks in the  $\text{KC}_8$  and HOPG images. The profiles are taken along the lines  $p$ - $p'$  (A) and  $p$ - $p''$  (B) in Figure 2A for  $\text{KC}_8$  and along the single line (C) in Figure 2B for HOPG. The scales are in angstrom units.

corrugation (Figure 3) taken along the lines indicated in Figure 2. Notably, the  $2.5 \pm 0.2$  Å separation between the  $p$ - $p'$  and  $p$ - $p''$

(11) Although it is possible for K/Cs metal to be on the surface of HOPG, previous studies have demonstrated that at room temperature all of it is intercalated (Law, A. R.; et al. *Surf. Sci.* **1985**, *152*, 284).

(12) Images displayed herein are typical of those recorded for several samples using different tips. Reported lattice constants are averages of measurements taken from at least 20 different images. The error bar represents one standard deviation.



**Figure 4.** Top-view images of  $\text{KC}_8$  recorded simultaneously with a bias voltage of  $-75$  mV (A) and  $+75$  mV (B) on alternate forward x-scans. The white bar corresponds to  $10$  Å.

peaks is similar to the peak separation in HOPG (Figure 3C) suggesting that the  $p$ ,  $p'$ , and  $p''$  peaks may be located at alternate carbon sites as in graphite.<sup>2-8</sup>

These experimental results are unexpected in light of electronic band calculations that have successfully explained the asymmetric structure in images of HOPG.<sup>2</sup> Specifically, recent calculations suggest that all of the carbon sites of stage-1 intercalation compounds such as  $\text{KC}_8$  should be imaged without asymmetry because the carbon atoms in adjacent layers are equivalent (Figure 1).<sup>2a,13</sup> In an effort to understand the differences between our experimental results and this theoretical work, we have carried out a number of additional imaging experiments. Images of  $\text{KC}_8$  re-

corded with values of  $V_b$  between  $-750$  and  $750$  mV show the same features ( $p$ ,  $p'$ ,  $p''$  peaks) as Figure 2A ( $V_b = -15$  mV). Analysis of the relative corrugation between the  $p$ - $p'$  and  $p$ - $p''$  sites for these images did not yield a systematic trend for the corrugation vs  $V_b$ ; i.e., the corrugation differences were similar to those displayed in Figure 3. In addition, two images recorded simultaneously by switching  $V_b$  on alternate forward x-scans between  $-75$  and  $+75$  mV have an identical peak registry (Figure 4). These two images demonstrate that the spatial location of the filled and empty states near  $E_f$  are the same. Since the potassium is completely ionized in  $\text{KC}_8$  (the  $4s$  level lies  $1.8$  eV above  $E_f$ <sup>14</sup>), this pair of images also indicates that it is unlikely the new  $2a$  feature corresponds to a direct image of the ionized potassium sites.

It is also unlikely that the new features observed in images of  $\text{KC}_8$  are due to tip-sample forces that locally deform the surface,<sup>4</sup> a model which has been proposed to explain anomalous corrugations in HOPG.<sup>15</sup> For example, images of  $\text{KC}_8$  recorded in the constant-height mode,<sup>6c</sup> in which the tip-sample forces remain nearly the same while scanning the surface,<sup>3</sup> are the same as Figure 2A. In addition, similar images are obtained in the constant-current mode for tunneling currents from  $8$  to  $0.5$  nA ( $V_b = -15$  mV). Since this decrease in tunneling current corresponds to an increase in tip-sample separation (i.e., a decrease in tip-sample elastic interaction), these results show that the new features cannot be due to local sample deformations.

Hence, we suggest that the features observed in the STM images of  $\text{KC}_8$  are due to a new electronic state near  $E_f$ . Although current models used to interpret STM imaging of HOPG cannot explain our experimental observations for  $\text{KC}_8$ , recent electronic structure calculations on bulk  $\text{KC}_8$  and  $\text{CsC}_8$  predict that intercalation will give rise to a new interlayer band near  $E_f$ .<sup>16</sup> Furthermore, data from angle-resolved photoelectron spectroscopy (ARPES) studies of  $\text{KC}_8$  and  $\text{CsC}_8$  support the existence of this new state.<sup>17</sup> Interestingly, it has been suggested on the basis of the ARPES results that this state may be due to a surface charge density wave.<sup>17b</sup> The  $2a$  superlattice observed in the STM images of  $\text{KC}_8$  may correspond to the first real-space observation of such a charge modulation in this material. Alternatively, electrostatic interactions between the potassium sites and the carbon layers could lead to a  $2a$  modulation in the charge density. An electrostatic mechanism would, however, yield images having the trigonal symmetry of the lattice (Figure 1b) in contrast to our experimental results. A charge density wave phase does not have this symmetry constraint.<sup>18</sup> Additional studies designed to clearly identify the nature of these new and interesting electronic features in  $\text{KC}_8$  are in progress.

**Acknowledgment.** We thank A. W. Moore (Union Carbide) for the generous donation of HOPG. C.M.L. acknowledges partial support from Presidential Young Investigator and David and Lucile Packard Fellowship Awards, and Rohm and Haas.

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