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Potassium absorption into the graphite (0001) surface: Intercalation

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Evaporation of potassium onto the graphite (0001) surface results in intercalation when potassium is evaporated from a hot molecular-beam source onto a graphite sample with high surface step density. Low-energy electron-diffraction (LEED) and Auger-electron spectroscopy (AES) studies indicate that after initial absorption of potassium from a hot source, the graphite surface structure became $A/ABAB\cdots$ stacking (where "/" indicates potassium), with a disordered potassium layer intercalated between two graphite layers which have been shear shifted and expanded to a separation of 5.35 Å. Further adsorption of potassium onto the sample surface results in $A/A/ABAB\cdots$ stacking with 5.35 Å separation between each of the three top graphite layers, indicating the formation of a stage-1-like intercalate within the surface region although with disordered potassium. These structures indicate that potassium intercalates into the graphite (0001) surface in a layer-by-layer fashion.

I. INTRODUCTION

Recently, there has been widespread interest in the quasi-two-dimensional properties of graphite intercalation compounds with particular emphasis on their structure and phase transitions.[1–6] It is generally accepted that in the intercalation process the alkali-metal atoms diffuse from the periphery of the graphite layer planes into part or all of the interlayer spaces. However, there has been a series of macroscopic experiments that have indicated, for graphite exposed to bromine vapor, that bromine entered the sample principally through the ends of a c-axis—oriented graphite cylinder.[7] We have previously presented a microscopic study of potassium deposited onto graphite as determined by low-energy electron-diffraction (LEED) and Auger-electron spectroscopy (AES),[8] within which we outlined ordered structures formed by potassium adsorbed on a low-step-density graphite (0001) surface. Here we report the application of these techniques to the study of the intercalation process of potassium into graphite. The advantages of these surface-sensitive techniques are that they may give insight to the process of surface reconstruction and intercalate triggering in the surface region of the graphite sample. In addition, the investigation is necessary for the eventual understanding of the rich variety of intercalate stages and surface structures in the alkali-metal—graphite system.

II. EXPERIMENTAL AND THEORETICAL

A standard four-grid LEED-AES apparatus mounted in a ultrahigh-vacuum (UHV) chamber (base pressure 1×10^{-10} Torr) was used in these studies. Natural graphite crystal platelets, obtained from Ticonderoga Mines, were initially cleaved in air with subsequent installation onto a manipulator which had the possibilities of heating the sample to 1300 K and cooling to about 30 K. The graphite crystals were held on the manipulator by an O-ring molybdenum foil which covered the edge of the graphite slice so that the c face of the graphite was exposed. A potassium molecular-beam source shielded from the graphite by a shutter was also installed in the vacuum chamber. The distance between the potassium source and graphite surface was about 7 cm.

AES and LEED were used to select a clean and large grain (approximately 1 mm diam.) on the surface. After cleaving, the principal surface contaminant, as monitored by AES, was oxygen at a level of about 6% of a monolayer. It should be noted that under the "scotch-tape technique" used for cleaving the graphite in this study, cleavages resulting primarily in six-fold-symmetric LEED patterns were obtained (in comparison with the three-fold patterns previously obtained under nitrogen-gas cleaving[9].) The six-fold symmetry of the patterns indicates that a large number of monoatomic steps are present at the surface so that both of the two possible terminations of the hcp (0001) surface (A and B terminations) are observed.

After examining the surface structure of clean graphite as described previously,[9] pure potassium was evaporated from the molecular-beam source onto the graphite substrate. The degree and extent of adsorption and absorption of potassium was changed by controlling the temperatures of the potassium source and of the graphite substrate and the total time of evaporation. The temperatures were measured by chromel-alumel thermocouples. After each potassium deposition the composition of the surface was determined by AES with low-energy (600-eV) and high-energy (3-keV) primary-electron excitation. The potassium/graphite surfaces were then examined by LEED. The sample surfaces were aligned normal to the incident-electron beam under the criterion of equivalence (to within a few percent of absolute intensities) of degenerate beams. The first- and second-order diffracted-beam intensities were measured for each potassium/graphite surface structure with a spot photometer. The experimental intensity profiles were then normalized to the incident-beam current.

Details regarding the theoretical calculation method have been described previously.[10] Briefly, full dynamical LEED calculations similar to those recently used by Van Hove and Somorjai in studying hydrogenless benzene molecules[11] were performed for a variety of layer-stacking sequences in graphite. Reverse-scattering perturbation was used to define the multiple scattering for each layer (where there are two atoms per unit cell) and renormalized forward scattering was used to describe interlayer scattering.[10] Five phase shifts were used to describe the graphite substrate[12] and the potassium was treated as an incoherent scatterer. Since the diffraction process is primarily sensitive to the periodic nature of the surface structure, the lack of superstructure upon potassium adsorption indicated the possibility of disorder of the potassium on or in the graphite surface. The general effect of random disorder in LEED is mainly an overall reduction in the intensity of the diffracted beams with accompanying increase in background intensity (diffuse scattering).[10,13] As a result, no specific attempt was made to model possible potassium disorder other than to ignore the absolute intensities of the experimental and calculated spectra as is generally done for systems where random occupation of adsorption sites is believed to occur.[14,15]

III. RESULTS AND DISCUSSION

A. Clean graphite substrate: *ABAB* · · · stacking

Graphite is highly anisotropic and characterized by a layered structure with an hcp lattice (*ABAB* · · · stacking; see Fig. 1). The single layer has a honeycomb structure with two carbon atoms per unit cell. Previous LEED studies have indicated that the graphite (0001) surface is terminated in *ABAB* · · · stacking with a 0.05-Å contraction of the top carbon-layer spacing.[9] The present LEED results for clean graphite differ from the previous ones[16] only in that the sample shows a sixfold LEED pattern instead of the initially observed threefold pattern. This is a result of the presently used cleaving procedure which generates a surface with monoatomic steps, i.e., both *A* and *B* terminations of the hcp stacking occur on the surface. The domains of these terminations have a larger linear dimension than the coherence length of the incident electrons but smaller dimension than the beam size; therefore the normal incidence LEED pattern has sixfold symmetry as a result of averaging over the two different terminations. The diffracted-beam widths for the sixfold-symmetric pattern had an energy (scattering-vector) dependence consistent with monoatomic steps on the surface.[10,17] The $\vec{k}$-space widths of the diffracted beams, when deconvoluted from the instrumental broadening and assuming a Poisson distribution of terrance widths, yielded a most probable interstep separation of 85^{+21}_{-6} Å,[17,18] and hence a surface step density of approximately 1%. Consequently, for comparison to calculations, the calculated beam intensities must be averaged for both terminations.[18] This was done for the present clean graphite sample with results for first- and second-order beams at normal incidence shown in parts of Figs. 2 and 3. Best agreement between calculations and experiment is again obtained for *ABAB* · · · stacking with a top-surface-layer contraction of 0.05 Å. As the observation of a sixfold-symmetric diffraction pattern at normal incidence did not change upon the adsorption/absorption of potassium, similar averaging of calculated intensities over the possible *A*- or *B*-surface termination of graphite was also undertaken in the analysis of the observed potassium/graphite surface structures.

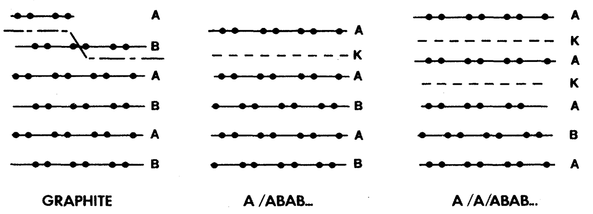

FIG. 1. Schematic structures of layer stacking for clean graphite with monoatomic steps, first-graphite-layer intercalated structure (*A* /*ABAB* · · ·), and first-two-layer intercalated structure (*A* /*A* /*ABAB* · · ·). Solid lines represent graphite layers with stacking noted and dashed lines represent potassium layers.

B. First-graphite-layer intercalation (FGLI): *A* /*ABAB* · · · stacking

Potassium atoms can be readily intercalated into a graphite (0001) surface with high surface-defect numbers (high step density) when the temperature of the potassium

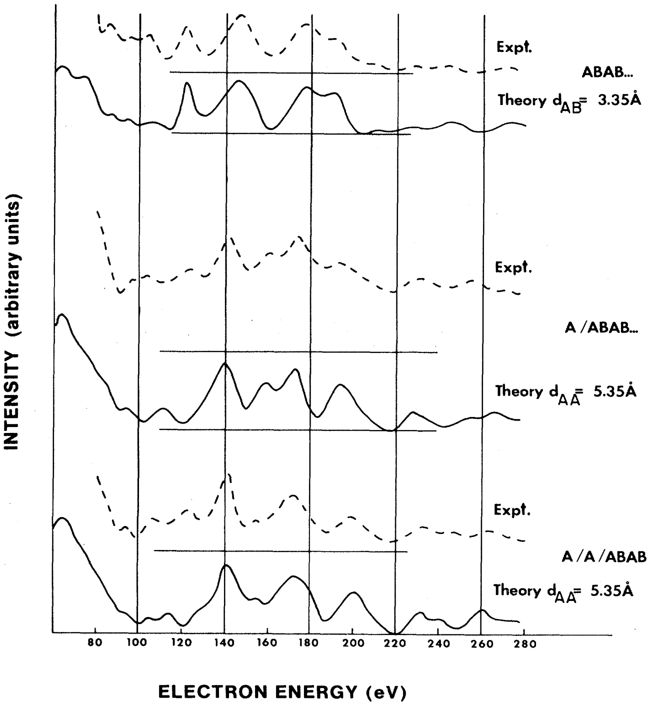

FIG. 2. Experimental and calculated intensity-energy spectra for the first-order beam at normal incidence for clean graphite (*ABAB* · · · stacking) with 3.35-Å interlayer spacings, for the FGLI case *A* /*ABAB* · · · stacking with 5.35-Å *A*-*A* graphite-layer spacing and 3.35-Å *A*-*B* graphite-layer spacing, and for the SGLI case (*A* /*A* /*ABAB* · · · stacking) with 5.35-Å *A*-*A* graphite-layer spacing and 3.35-Å *A*-*B* graphite-layer spacing.

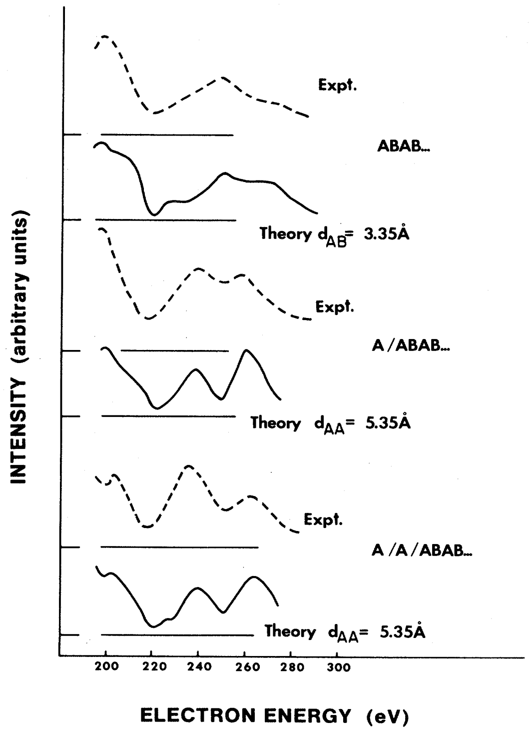

FIG. 3. Experimental and calculated intensity-energy spectra for the second-order beam at normal incidence. Structures as in Fig. 2.

source is from 200 to 350 °C, the temperature of the substrate is from −80 °C (the lowest temperature used during evaporation) to room temperature, and evaporation continues for several minutes at a rate of approximately 2×10^{14} potassium atoms per min. Typical experimental conditions where source and substrate temperatures at 320 and −60 °C, respectively, with evaporation lasting 8 min and the background pressure in the chamber at less than 3.5×10^{-10} Torr. AES measurements indicated that after such evaporation the ratio of the peak-to-peak signal in $dN(E)/dE$ for potassium to that for carbon (denoted as D) was about 0.5 under low-energy primary-electron excitation (600 eV), and was about 0.7 at high-energy primary-electron excitation (3 keV). As the mean free paths of the carbon (272-eV) and the potassium (251-eV) Auger electrons are essentially equivalent, the difference in the ratio D must be due to the increased sampling depth of the higher-energy primary-electron beam[19] resulting in a larger depth sensitivity of the emitted Auger electrons. This increase in the ratio D upon going to high primary-electron energy indicates, therefore, that the observed potassium is not localized to the top of the graphite surface, but is distributed within the surface region, e.g., intercalated.

For such a sample, however, no LEED superstructure is observed, even upon decreasing the temperature of the sample to −80 °C. Hence, the potassium at the surface may be in a 1×1 structure on the surface or it is possible that the potassium is disordered at and within the surface region. The latter point is consistent with high-stage potassium intercalates in graphite at or near room temperature. These possibilities will be addressed below.

LEED *I-V* spectra measured for the first- and second-order beams at normal incidence for this system are shown in Figs. 2 and 3. The spectra show clear differences with those of clean graphite.[20] As noted, however, they may be the result of a C(0001)-(1×1)K structure (although high background scattering was observed). A dynamical calculation assuming such a model (although the model is unphysical since it assumes a potassium nearest-neighbor distance of 2.46 Å, which is 40% smaller than in bulk potassium) is shown in Fig. 4. The agreement is the best obtained as a function of varying potassium-layer spacing and site symmetry for this model and is expectedly poor. Hence, the adsorbed potassium is not in an ordered 1×1 structure on the surface, but is disordered.

If the disordered potassium layer was restricted to the top surface of the graphite it would result in an overall reduction of the clean graphite diffracted-beam intensities and increased background scattering. This is not the case since the individual spectra change upon absorption (Fig. 4). If, as implied by the AES measurement, the potassium were *absorbed* into the graphite and disordered, e.g., between the first two carbon layers, one would expect, due to the large size (approximately 4 Å) of the potassium atom, that the absorption would result in dilation of the top carbon layer. A calculation assuming such a model and retaining the *ABAB* · · · stacking of graphite gave the results shown also in Fig. 4. Agreement with experiment is again very poor. It should be noted, however, that the experimental spectra for the potassium/graphite system of

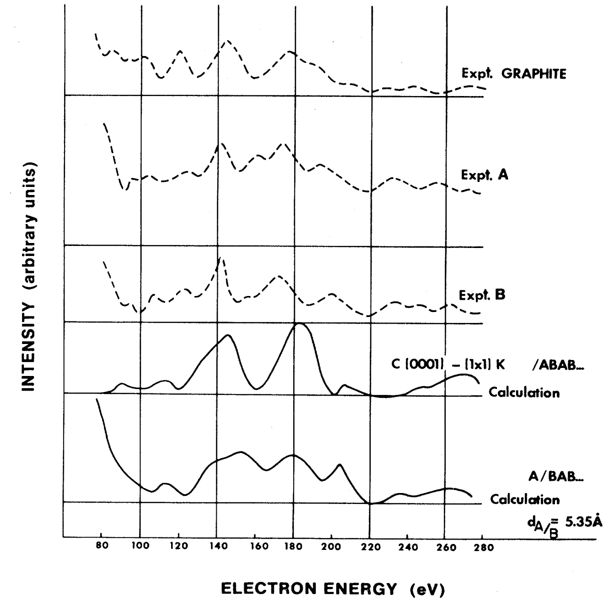

FIG. 4. First-order, normal-incidence intensity-energy spectra for clean graphite, graphite exposed to about 1.5-monolayer equivalents of potassium (Expt. *A*), graphite exposed to about 2.5-monolayer equivalents of potassium (Expt. *B*), calculations for C[0001]-(1×1)K, and calculations for *A*/*BAB* · · · stacked graphite with the first *A*-*B*—layer spacing at 5.35 Å and subsequent ones at 3.35 Å.

Fig. 4 show some resemblance [especially in the (130—210)-eV region] to previously calculated intensities[9] for a graphite surface with a shear shift of the top carbon layer to form *AABAB* ⋯ stacking. In fact, in all known cases of bulk graphite intercalates, intercalation changes the stacking sequence in graphite and dilates the structure along the *c* axis to accommodate the intercalant.[21,22] The weak Van der Waals bonding between layers of graphite make intercalation possible because the strain energy of dilation along the *c* axis is small. Conversely, the strong intralayer bonding insures that the structure of the hexagonal carbon layer will be not affected greatly by intercalation.

Thus, incorporating these points we used a model assuming disordered potassium between the first two carbon layers in graphite which have been stacked using *A*/*A* stacking and dilated. Dynamical LEED calculations were undertaken for this model with the first interlayer spacing d_{AA} between the two *A*-carbon layers varied from 3.35 to 5.65 Å, and the subsequent *BABA* ⋯ stacked layers kept at the bulk graphite 3.35-Å separation. As noted, the potassium intercalant was assumed to be disordered and its contribution to the structural model was limited to the simple expansion and shift of the top-layer spacing. No additional possible contributions to the elastic or inelastic parts of the scattering potential were included. The coherent elastic scattering contributions would be nil from a disordered potassium layer (except for overall decrease of scattered intensity). The inelastic contributions due to potassium are well described by simply retaining the inelastic scattering of graphite to be active between the dilated top graphite layers. This is appropriate, since the inelastic (imaginary) part of the scattering potential for most all materials lies in the range of -3 to -6 eV and has been shown to be a variable to which surface structure determination is not very sensitive. A -5-eV value has been used in this study for the inelastic part of the scattering potential for graphite (and thus also for potassium).

Figures 2 and 3 show the averaged (sixfold) LEED calculations for the first- and second-order beams for the *A*/*ABAB* ⋯ stacking (FGLI) model described above. Comparison to the experimental spectra for the FGLI calculation with a first-graphite-layer separation of 5.35 Å (60% change) indicates very good agreement in both first- and second-order beam spectra at normal incidence. This layer separation is consistent with x-ray measurements for intercalated-graphite-layer spacing in potassium intercalated graphite.[21,22] Because there may have been domains of graphite without intercalant in the top surface layer, the experimental curves may show the result of averaging over the two kinds of domains, clean graphite and FGLI. The variance with calculations in the (100—130)-eV energy region can be resolved by such averaging. It should be noted again that the potassium is *disordered* in this FGLI structure at room temperature which is in variance with both the bulk potassium intercalant studies[3–5,21,22] and the previous LEED studies which indicated 2×2 and $\sqrt{3}\times\sqrt{3}-R\,30°$ structures for potassium adsorbed on graphite (0001).[8]

The intercalation forming the *A*/*ABAB* ⋯ stacked graphite is unstable in vacuum. This FGLI system returns gradually at room temperature and at pressures of 2×10^{-10} Torr to the system of disordered potassium on a graphite substrate which is in the normal graphite termination of *ABAB* ⋯ stacking. This relaxation process is readily characterized by the change in the three-peak structure at 120—220 eV in the first-order beam of the FGLI system to a two-peak structure. Such a change is shown in Fig. 5 and indicates a change of the FGLI *A*/*ABAB* ⋯ stacking to normal graphite *ABAB* ⋯ stacking over the period of about 1 h at room temperature. This behavior indicates that at room temperature the intercalated potassium readily migrates to the surface of the graphite and desorbs. It is believed that potassium does not diffuse more deeply, into the graphite, as this would signal changes in the LEED spectra to be described in the next section and not observed in this case. AES spectra taken near the end of this relaxation effect show the same ratio *D* of the potassium-to-carbon signal for both low- and high-energy primary electron excitation. This is consistent with the potassium being localized to the top surface of the sample. The value of the ratio *D* in-

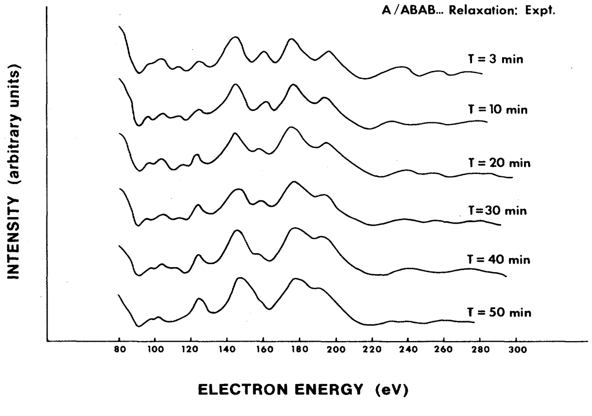

FIG. 5. Time variation for the first-order beam intensity of the FGLI structure for the sample at 2×10^{-10} Torr pressure.

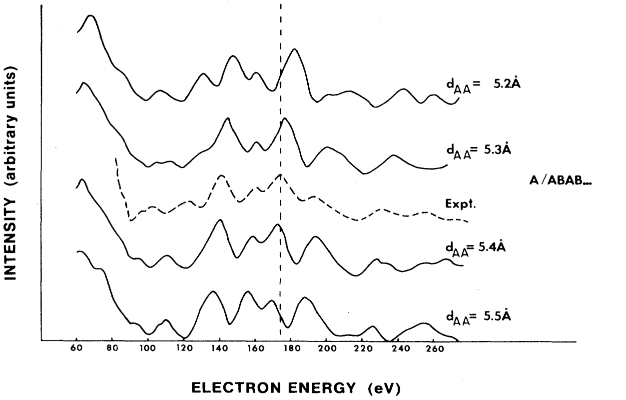

FIG. 6. Dependence of calculated first-order beam intensities on top *A*-*A* graphite-layer spacing in the FGLI structure. d_{AA} is top-layer spacing. Note that this variation cannot be used to explain the changes observed in Fig. 5.

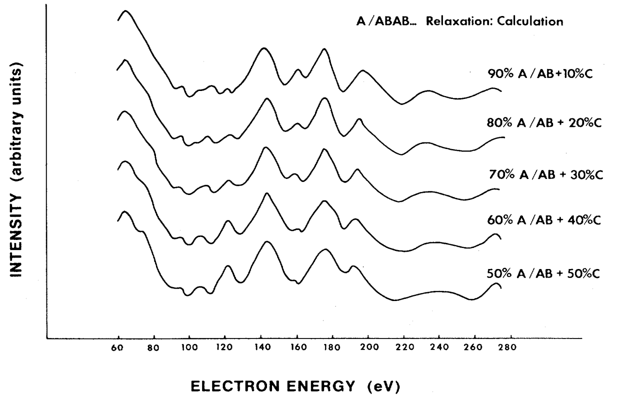

FIG. 7. Calculated first-order beam spectra for a model assuming two types of domains at the sample surface—clean graphite (*C*) and FGLI structure (*A/AB*), as a function of various proportions of the two types of domains at the surface. Note the good agreement between this succession of curves (with decreasing amount of FGLI surface) and the experimentally measured time dependence (with increasing time) of the first-order curves of Fig. 5.

dicates that the surface coverage of potassium at this point is $\Theta \approx 0.12-0.17$. It is well to note again that the potassium is disordered, and hence the LEED *I-V* spectra are demonstrative of clean graphite (with a fair amount of diffuse scattering present).

In attempting to understand this mode of relaxation, the time rate of change of the experimental first-order beam spectra (Fig. 5) were compared to theoretical *I-V* spectra calculated for various top-layer spacings d_{AA} (Fig. 6) in the FGLI model. It is clear from comparing these two figures [cf. (120—220)-eV regions] that the experimental behavior is not modeled well by a continuously decreasing top-interlayer spacing. An alternate model for the deintercalation is one in which the surface is composed of two kinds of domains, clean graphite and FGLI graphite, with an increasing fraction of clean graphite domains as a function of time. Comparison of Fig. 7 to Fig. 5 shows good agreement between the two-domain models and the experimentally determined time variation of the LEED spectra [cf. (120—220)-eV region]. This indicates that the migration of potassium to the top surface with time and subsequent evaporation does not result in a uniformly dispersed lower-concentration potassium intercalant layer. Instead, a complete small domain at the surface (probably defined by step edges on the surface, e.g., a step terrace) becomes devoid of potassium without affecting the potassium concentration in other small domains at the surface until all domains become devoid of intercalated potassium. Such proposed behavior clearly depends on the presence of steps at the surface and although it has been shown that a large number of steps are present on this graphite surface, a detailed study of intercalation relaxation versus step density is yet to be done.

C. Second-graphite layer intercalation (SGLI): *A/A/ABAB* · · · stacking

Further deposition of potassium on the FGLI surface (an additional 4-min exposure to the K beam) results in changed experimental LEED *I-V* spectra as shown in Figs. 2 and 3, but does not result in prominent superstructure. Since the FGLI structure has been described above as due to intercalation of the first graphite layer, further deposition of potassium may result in intercalation of subsequent layers. Therefore, to test this proposal, the theoretical calculations were undertaken with a structural model including two expanded graphite top-layer spacings and shear shifts to the *A* stacking for the top two layers. Since the absorbed potassium produced no ordered superstructure, its contribution to the scattering was treated identically to that in the FGLI model.

Of major interest in comparing the calculated data to experiment is the peak structure in the (160—220)-eV region of the first-order spectra. The experimental structure in that region cannot be reproduced by calculations using the *A/ABAB* · · · stacking FGLI model even under expansion of the top-layer spacing from 5.15 to 5.65 Å (Fig. 6). Use of the *A/A/ABAB* · · · stacking SGLI model, however, results in very good agreement (Figs. 2 and 3) for both the first- and second-order beams under the conditions of 5.35-Å first-graphite-layer spacing, 5.35-Å second-graphite-layer spacing, and 3.35-Å third- and subsequent-layer spacings.

The *A/A/ABAB* · · · stacked SGLI system is also unstable in a vacuum in that, as a function of time, the LEED spectra change. In comparing the spectra changes to the previously described structures, the sequence of structure changes are SGLI structure → FGLI structure → disordered potassium on graphite.

D. Additional structures

It should be noted here that further exposure of the *A/A/ABAB* · · · structured surface to the potassium beam (an additional 2—3 min) results in a weak but sharp 2×2 superlattice with high background intensity at room temperature. This superlattice may be the result of ordering in the surface-adsorbed potassium or ordering of potassium in the underlayers of the surface intercalated graphite. The high background scattering, however, implies much surface-localized disorder and preliminary LEED calculations of a 2×2 overlayer on graphite are not consistent with the diffracted intensities measured for this weak 2×2 structure. The implication of both of these points is that the potassium is ordering within the graphite at these higher exposures.

As noted earlier, 2×2 ordering is observed for bulk stage-1 potassium intercalates.[3–5,20,21] The disorder of the surface-localized potassium may, however, be a direct result of the high step density at the surface or it may be due to the enhanced vibrational properties of the graphite (and hence potassium) atoms at the surface.[23,24] Under this latter condition, as the graphite sample is exposed to more potassium it intercalates into deeper graphite layers. By the third graphite layer, the vibrational properties of the graphite atoms have approached those of bulk atoms; therefore, potassium atoms intercalating into the third and subsequent layer in a layer-by-layer fashion will see a bulk environment and form the bulk stage-1 2×2 ordering. The weak 2×2 superlattice presently observed under large potassium exposure is consistent with this picture. However, further analysis is required to understand more clearly the basis for the weak superstructure.

It is seen above that potassium deposited on a high-defect-level graphite surface readily intercalates. Since the major defects in the cleaved graphite are steps, it is proposed that diffusion of surface adsorbed potassium to step edges promotes intercalation at such sites. This is clearer in light of the fact that, for a low-step-density graphite surface (threefold-symmetric LEED pattern),[9] the above-noted diffraction-spectra changes indicating intercalation have not been observed.

It should also be noted here that x-ray measurements of ordering in bulk samples were made for potassium/graphite samples prepared under thermodynamic equilibrium with resultant full K-layer packing to the stage-1 C_8K structure. The present samples, which showed no long-range order upon intercalation, were not prepared under equilibrium conditions and, although the AES measurements indicate nearly full potassium-layer packing under first-layer intercalation, subsequent-layer intercalation (for which AES sensitivity is much reduced) may not result in fully packed potassium layers thereby affecting possible ordering of the potassium. The disordered-potassium behavior is also in contrast to the observation of 2×2 and $\sqrt{3}\times\sqrt{3}\text{-}R30°$ structures for potassium on a low-defect graphite (0001) surface.[8] The surface disorder present in the current case may, however, be the basis for disorder of the surface-localized potassium as we also did not observe ordering of adsorbed potassium on the high-defect surface.

IV. CONCLUSION

A high-step-density (1%) cleaved graphite surface exposed to a potassium-atom flux from a hot source becomes intercalated in a layer-by-layer manner inward from the surface. The point of intercalation is believed to be the step edges on the surface. LEED measurements indicate that intercalation of potassium dilates the graphite-layer spacing from 3.35 to 5.35 Å and induces a shear shift of the graphite layers to $A/A/A\cdots$ stacking (with potassium in between the graphite layers). The two latter points are in excellent agreement with x-ray measurements on stage-1 potassium intercalates; however, intercalation of the top two graphite layers does not result in an ordered structure for the potassium over the studied temperature range as is observed in x-ray measurements for stage-1 intercalates.

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