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# Electronic structure and phase transitions of submonolayer potassium on graphite

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We study the electronic structure of K adlayers on graphite using a simplified tight-binding model in the coverage ($\Theta$) range between 0.01 and 1.0 monolayers. We find that the coverage dependence of the K adsorption energy at low $\Theta$ arises mainly from the band-energy change reflecting the two-dimensional and semimetallic band structure of the substrate graphite rather than the dipole-dipole interaction. This former term is virtually absent for metallic substrates and thus may be the origin of the unusual structural properties observed recently in the K/graphite system.

## I. INTRODUCTION

Alkali-metal adsorption on solid surfaces has been studied for many years as a prototype chemisorption system showing various interesting properties.[1-3] Very recently, Li, Hock, and Palmer[4] reported an unusual structural phase transition in adsorbed submonolayer K on graphite based on their low-energy electron-diffraction and electron-energy-loss experiments conducted at a low temperature (90 K). At very low K coverages ($\Theta$), they observed a dispersed phase with a huge K-K spacing. The K-K spacing of this phase was gradually compressed up to a critical coverage ($\Theta_1$) which roughly corresponds to a $7\times7$ structure in units of the graphite lattice constant. For higher coverages, a close-packed $2\times2$ phase ($\Theta_2$) coexisting with the dispersed $\Theta_1$ phase starts to grow until the whole surface is covered by it.

A number of experiments have been performed to date to investigate the phase diagrams of adsorbed alkali-metal layers on transition metals.[5] Various commensurate and incommensurate phases were observed as functions of coverage and temperature. For metal substrates, the repulsive dipole-dipole interaction $p^2r^{-3}$ ($p$ is the magnitude of the adatom dipole moment and $r$ the interatomic distance between neighboring adatoms) plays a dominant role for phase transitions at lower coverages.[6] In addition, there is a contribution from the long-range indirect interaction mediated by substrate electrons which is oscillatory and anisotropic.[7] In most cases, the lattice constant varies fairly continuously as the coverage is increased from one phase to a neighboring phase with higher atomic density, and the large difference in density between successive phases reported for K/graphite ($\Theta_2/\Theta_1\sim12$) has never been observed for adsorption on metals.

The purpose of the present paper is to try to clarify the origin of the above-mentioned unusual structural properties of K/graphite. Since the first-principles calculation covering a wide $\Theta$ range is not yet feasible for K/graphite, we calculate the electronic structure of K/graphite using a simplified tight-binding model and discuss the coverage dependence of the adsorption energy. It will be shown within this model that the main component contributing to the decrease in the adsorption energy at low coverages with increasing $\Theta$ is the band-energy change rather than the electrostatic energy among adsorbate dipole moments. This term, which reflects the two-dimensional and semimetallic band structure of graphite, is virtually absent for metallic substrates, and may explain why such a phase transition has been observed so far only on graphite.

## II. MODEL

We model the K/graphite surface with a simplified tight-binding model, which explicitly takes into account the long-range Coulomb interaction. Similar models have been used previously for theoretical studies of alkali-metal intercalated graphite compounds[8,9] and their surfaces.[10] The substrate is represented by one graphite layer. This may be a reasonable approximation as the interlayer coupling is very small in graphite.[11] In addition, it has been shown for higher-stage graphite intercalation compounds (GIC) that the charge redistribution between alkali-metal and graphite layers is mostly confined to the nearest-neighbor (NN) graphite layers.[12]

We write the total energy of the system as

$$E_t=\langle H_0\rangle+U+\frac{N_aA}{r_0^p}\ . \tag{1}$$

The first term in Eq. (1) is the expectation value of the one-electron Hamiltonian $H_0$ (band energy). Instead of modeling the K layer by a classical charge sheet,[8-10] we include both the C and K orbitals in $H_0$. For the graphite layer, we consider the $\pi$ and $\pi^*$ bands originating from C $2p_z$. The deeper $\sigma$ band is expected to interact with K valence states only weakly. For the K layer, we consider the lowest K 4$s$ band. The one-electron Hamiltonian $H_0$ is written as

$$H_0=\sum_{i,\sigma}\epsilon_i c_{i\sigma}^{\dagger}c_{i\sigma}+\sum_{i,j,\sigma}V_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}\ , \tag{2}$$

where the site indices $i$ and $j$ denote either the $2p_z$ orbital in the graphite layer or the $4s$ orbital in the K adlayer with spin $\sigma$. $\epsilon_i$ is the site energy of these orbitals. As for the off-diagonal transfer energy $V_{ij}$, we take the matrix element between the NN C $2p_z$ orbitals [$\gamma_0$ as in standard notation, $\gamma_0 = -2.5$ eV (Ref. 13)], that between the NN K $4s$ orbitals ($T$), and that between the NN C $2p_z$ and K $4s$ orbitals ($V$). We assume that K atoms form an $M \times M$ hexagonal lattice ($M = \sqrt{3}, 2, \sqrt{7}, 3, \ldots$) in units of the graphite lattice constant, and adsorb on the sixfold-hollow site, so that each K atom has six NN C atoms with which to interact via $V$. It seems unlikely that K atoms sit on the top site of C atoms as the number of the NN C atoms is reduced. For $T$, we assume the exponential form, $T = T_0 \exp(-\lambda r_0)$, where $r_0$ is the NN K-K distance ($r_0 = M a_0$ a.u., where $a_0$ is the graphite lattice constant, $a_0 = 4.65$ a.u.).

$U$ in Eq. (1) is the electrostatic energy due to the charge redistribution. In order to discuss the layer charge distribution in higher-stage GIC's, Safran and Hamman[8] used

$$U = -\tfrac{1}{2} \sum_{i,j} \Delta n_i \Delta n_j |z_i - z_j|^2 , \tag{3}$$

where $\Delta n_i$ and $z_i$ denote the induced charge and the $z$ coordinate of layer $i$, respectively. Equation (3) is not applicable in the present case, since we need to consider variation in the induced charge in the plane in order to be able to reproduce the dipole-dipole interaction between the adatom-dipole moments. Accordingly, we utilize the expression

$$U = \tfrac{1}{2} \sum_{i,j} U_{ij} \Delta n_i \Delta n_j . \tag{4}$$

In Eq. (4), $\Delta n_i$ and $U_{ij}$ are the induced charge on site $i$ and the Coulomb potential, defined, respectively, by

$$\Delta n_i = \sum_{\sigma} \langle c_{i\sigma}^{\dagger} c_{i\sigma} \rangle - n_i^0 , \tag{5}$$

$$U_{ij} = \frac{1}{r_{ij}} [1 - \exp(-U_0 r_{ij})] , \tag{6}$$

where $r_{ij}$ denotes the interatomic distance between sites $i$ and $j$. The orbital occupation for the isolated layers, $n_i^0$, is unity for both C $2p_z$ and K $4s$. To account for the finite sizes of atomic orbitals, we utilize a simple model potential Eq. (6) which deviates from $1/r_{ij}$ at smaller $r_{ij}$ and takes an on-site repulsion energy $U_0$ at the origin. In the present work, we do not consider the site dependence of $U_0$ to reduce the number of parameters. We perform calculations for several values of $U_0$ and examine how the qualitative features of the results are influenced by this parameter. Equation (4) is based on the classical charge-transfer model[14] and ignores intra-atomic[15] and interatomic polarization effects.[16] Recent first-principles calculations[16-18] demonstrated that the latter is especially important. However, these effects are beyond the scope of the present model.

Finally, the third term in Eq. (1) represents the phenomenological short-range repulsion among K cores ($N_a$ is the total number of adatoms on the surface). Equation (1) without $U$ is used commonly as a basis of molecular-dynamics studies based on the tight-binding Hamiltonian. A derivation of Eq. (1) with $U$ is given in the Appendix.

Minimizing $E_t$ for a fixed $r_0$ yields the self-consistent equation for the one-electron state with energy $\epsilon_m$ ($m$ stands for both the **k** vector in the surface Brillouin zone and the band index),

$$\sum_j [(\epsilon_i + \Delta_i)\delta_{ij} + V_{ij}] \psi_{m\sigma}(j) = \epsilon_m \psi_{m\sigma}(i) , \tag{7}$$

where $\Delta_i$ is the Hartree potential at site $i$ given by

$$\Delta_i = \sum_j U_{ij} \Delta n_j . \tag{8}$$

The occupation number at site $i$ is calculated from

$$n_i = \sum_{\sigma} \langle c_{i\sigma}^{\dagger} c_{i\sigma} \rangle = \sum_{m,\sigma} |\psi_{m\sigma}(i)|^2 , \tag{9}$$

where the summation over $m$ is taken for the occupied states below the Fermi energy ($E_F$). As in standard band calculations, Eqs. (7)–(9) are solved iteratively until self-consistency is obtained for the charge density.

We define the band-energy change and the electrostatic energy per K atom as

$$h_0(\Theta) = \frac{\langle H_0 \rangle - \langle H_0 \rangle_g}{N_a}, \quad u(\Theta) = \frac{U}{N_a} , \tag{10}$$

where $\langle H_0 \rangle_g$ is the band energy of an isolated graphite layer. The adsorption energy per K atom, $\epsilon_{\rm ad}(\Theta)$ ($>0$), is then given by

$$\begin{aligned} \epsilon_{\rm ad}(\Theta) &= \frac{[N_a \epsilon_{4s}^0 + \langle H_0 \rangle_g] - E_t}{N_a} \\ &= \epsilon_{4s}^0 - \left[ h_0(\Theta) + u(\Theta) + \frac{A}{r_0^p} \right] , \end{aligned} \tag{11}$$

where $\epsilon_{4s}^0$ denotes the site energy of an isolated K atom, which may be different from that of K adatoms in Eq. (2). Strictly speaking, we should have included a term for the short-range repulsion energy between the K and C cores in Eq. (1). However, since this term is proportional to $N_a$, its effect can be included in Eq. (11) simply by shifting $\epsilon_{4s}^0$ by a constant. Thus, the coverage dependence of $\epsilon_{\rm ad}(\Theta)$ is governed by the three terms in the square brackets in Eq. (11).

## III. RESULTS AND DISCUSSION

### A. Case of complete charge transfer

Calculations are performed in the coverage range between $M = \sqrt{3}$ ($C_6K$) and 20 ($C_{800}K$). In order to have a rough idea of the physics of the present system, we first study the simplest case where K atoms are perfectly ionized; $\epsilon_{4s} - \epsilon_{2p_z} = \infty$. The matrix element between the NN K $4s$ orbitals ($T$) and that between the NN C $2p_z$ and K $4s$ ($V$) are also set equal to 0, so that the problem is reduced to the screening properties of a single graphite layer. We choose the distance between the K and C layers, $z_{\text{C-K}}$, as 4.9 a.u., assuming the K-C bond length to be the sum of the atomic radii of both elements. In this case, the only free parameter is the on-site Coulomb repulsion energy $U_0$.

Figure 1(a) shows the induced charge $\Delta n_i$ on C sites as a function of lateral distance from a K site for $C_{450}K$ (NN K-K distance $r_0 \sim 70$ a.u.) with $U_0=5$ eV. The induced charge $\Delta n_i$ is seen to consist of a fairly localized part which is extended up to ~tenth-neighbor C sites, and a delocalized part with a nearly constant density filling the rest of the surface. For large $M$, the profile of the localized charge remains essentially unchanged, whereas the density of the latter decreases as $M^{-2}$. The existence of the delocalized charge may imply that positive charges cannot be perfectly screened by graphite because of the semimetallic nature of the material. These qualitative features of the induced charge are insensitive to the choice of $U_0$, except that the induced charge becomes a little more localized for smaller $U_0$.

In order to make a comparison with the screening properties of a metallic system with a finite density of states at $E_F$, we calculated $\Delta n_i$ for an artificial graphite substrate where $E_F$ is shifted upwards such that 30% of the $\pi^*$ band is filled [$n_i^0$ in Eq. (5) is redefined as 1.3 for C $2p_z$]. The calculated $\Delta n_i$ in Fig. 1(b) is seen to be more localized near K sites than that in Fig. 1(a) and, more importantly, the nearly uniform charge in the tail region is replaced by an oscillatory one that may be interpreted as the Friedel oscillation characteristic of metallic screening. Thus, it is confirmed that the delocalized part of the induced charge in Fig. 1(a) originates from the semimetallic nature of graphite.

In Fig. 2(a) we plot the electrostatic energy $u(\Theta)$ as a function of $M^{-3}$ for three values of the on-site Coulomb parameter $U_0$. $u_0(\Theta)$ becomes a linear function of $M^{-3}$ if the K-K interaction is of the dipole-dipole type. The absolute value of $u(\Theta)$ depends significantly on $U_0$, while its variation with coverage, which is more relevant to the discussion of structural properties, is less sensitive to $U_0$. The calculated $u(\Theta)$ fits a linear curve except at very low coverages, which means that the electrostatic energy between K atoms can be described by the dipole-dipole interaction in a wide $\Theta$ range. The derivation at low coverages may result from the delocalized part of the induced charge that spreads throughout the whole surface.

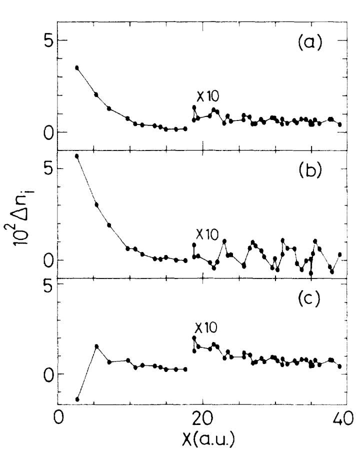

FIG. 1. The induced charge $\Delta n_i$ on C sites as a function of lateral distance $X$ from a K core for $C_{450}K$ ($M=15$). The lines between calculated points are merely guides for the eye. (a) and (b) show the limit of complete K ionization with semimetallic and artificial metallic $\pi^*$ bands, respectively. (c) shows a more realistic case with covalent K-C interaction and with partial charge transfer from K to C.

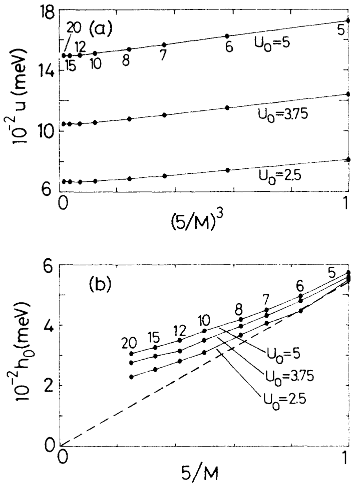

FIG. 2. (a) The electrostatic energy $u(\Theta)$ vs $M^{-3}$ and (b) band-energy change $h_0(\Theta)$ vs $M^{-1}$ for K/graphite in the limit of complete K ionization, i.e., $\epsilon_{4s}-\epsilon_{2p_z}=\infty$, $V=0$, and $T=0$ for three values of the on-site Coulomb energy; $U_0=2.5$, 3.75, and 5 eV. The NN K-K distance is given by $4.65\times M$ a.u. and small numbers near filled circles indicate $M$. $u_0(\Theta)$ becomes a linear function of $M^{-3}$ when the electrostatic K-K interaction is described by the dipole formula. $h_0(\Theta)$ becomes a linear function of $M^{-1}$ in the rigid-band model where the unperturbed $\pi^*$ band of graphite is filled by K 4s electrons.

The solid lines in Fig. 2(b) show the band-energy change $h_0(\Theta)$ as a function of $M^{-1}$. In contrast to the electrostatic energy $u(\Theta)$, it is rather insensitive to the on-site Coulomb parameter $U_0$. In the rigid-band model where K 4s electrons fill the unperturbed $\pi^*$ band, its coverage dependence arises from the upward shift of $E_F$. Near the K point in the surface Brillouin zone of graphite, the $\pi^*$ band has a well-known linear energy dispersion, $\epsilon_{\pi^*}(\mathbf{k})=\sqrt{3}\gamma_0|\mathbf{k}|a_0/2$. This dispersion leads to the linear density of states of the $\pi^*$ band. Using this, we obtain for the band-energy change

$$h_0(\Theta)=\frac{1.1\gamma_0}{M}(\text{eV}) . \qquad (12)$$

The calculated $h_0(\Theta)$ deviates from Eq. (12) [dashed line in Fig. 2(b)], especially at low coverages, because the Hartree potential $\Delta_i$ in Eq. (7) modifies the actual one-electron wave functions from those of the unperturbed $\pi^*$ band. In the case where the substrate is a two-dimensional metal with a constant density of states $2/W$ (where $W$ is the bandwidth), we have, within the rigid-band model, $h_0(\Theta)=W/(4M^2)$. Assuming $W \sim 5$ eV, the value obtained for the band-energy change is one order of magnitude smaller than that obtained from Eq. (12) in the dispersed phase with $M \geq 7$. For a three-dimensional metallic substrate, $h_0(\Theta)$ vanishes within the rigid-band model, since $E_F$ cannot be shifted by an adsorbate layer. Going beyond the rigid-band model, $h_0(\Theta)$ gives rise to an oscillatory and anisotropic interaction.[7] It may be concluded that the large coverage dependence of the band-energy change $h_0(\Theta)$ is peculiar to the semimetallic and two-dimensional band structure of graphite.

### B. Case of partial charge transfer

In the preceding subsection, we have shown that the band-energy change $h_0(\Theta)$ may make a significant contribution to the coverage dependence of the K adsorption energy. Since this term should be very sensitive to the electronic band structure near $E_F$ which is modified by the NN K-K ($T$) and C-K ($V$) orbital interactions assumed to be 0 in the preceding subsection, we need to consider a more realistic case where these interactions are finite. It will be shown in the following that the band-energy change $h_0(\Theta)$ dominates the coverage dependence of the K adsorption energy at low coverages even in such a case.

To determine $T_0$ and $\lambda$ for the NN K-K interaction $T = T_0 \exp(-\lambda_0 r_0)$, we have performed pseudopotential band-structure calculations for several isolated hexagonal K layers using local-density-functional theory.[19] The calculated bandwidths of the 4s band along the Γ-K line in the surface Brillouin zone are 3.34, 3.07, and 2.67 eV for $r_0 = 8.05$, 8.5, and 9.3 a.u., respectively. By comparing these values with the corresponding bandwidth, $9|T_0|\exp(-\lambda r_0)$, in the present model, we obtain $T_0 = -1.58$ eV and $\lambda = 0.18$ a.u. The total energy per K atom of the isolated K layer is given by

$$E_t = \epsilon_{4s} + \alpha_0 T_0 \exp(-\lambda_0 r_0) + \frac{A}{r_0^p} , \tag{13}$$

where $\alpha_0$ is a constant that depends on the occupation of the K 4s band. We obtain numerically $\alpha_0 = 2.0$ for the half-filled K 4s band. The parameter $A$ is related to the lattice constant $r_m$, which minimizes the total energy by

$$A = \frac{\alpha_0 |T_0| r_m^{p+1}}{p} \exp(-\lambda r_m) . \tag{14}$$

$A$ was determined using $p = 12$ (the repulsive part of Lennard-Jones potential) and $r_m = 8.542$ a.u., which was obtained from the above-mentioned band-structure calculations. We set $\epsilon_{4s} - \epsilon_{2p_z} = 0.7$ eV, and $U_0 = 2.5$ eV, $V = -1$ eV so that the positive charge on K sites in the dispersed phase reproduces the experimental value of $\sim 0.7$ estimated from plasmon frequency[20] and work-function measurements.[21] Of course, there are other sets of parameters that reproduce the same charge on K sites. Here, we show results for a parameter set with a fairly large $V$, in order to demonstrate that the conclusion regarding the coverage dependence of the band-energy change $h_0(\Theta)$ obtained in Sec. III A assuming $V = 0$ remains valid even when the K-C orbital interaction $V$ is substantial.

Figures 3(a)–3(c) show the calculated band-energy change $[h_0(\Theta)]$, electrostatic energy $[u(\Theta)]$, and the induced charge $(\Delta n_{4s})$ as a function of coverage $(M^{-2})$. The band-energy change $h_0(\Theta)$ in Fig. 3(a) has a large negative value at the lowest coverages because $h_0(\Theta)$ is lowered relative to the band energy of a clean graphite layer, $\langle H_0 \rangle_0$, via the covalent K-C interaction introduced by the K 4s-C $2p_z$ overlap ($V$). The calculated $h_0(\Theta)$ increases monotonically up to an intermediate coverage with $M = 3$. The magnitude of its variation at low coverages ($M \geq 5$) is a little larger than that in Fig. 2(b) calculated assuming the complete charge transfer from K since, in addition to the upward shift of $E_F$, a diagonal term in $H_0$, $\epsilon_{4s}[1 - |\Delta n_{4s}|]$, also makes a small contribution to the increase in the band-energy change $h_0(\Theta)$ because of the coverage dependence of $\Delta n_{4s}$. Around $M = 3$, the direct K-K interaction ($T$) begins to increase rapidly, leading to a large lowering of $h_0(\Theta)$ at the condensed phase with $M = 2$ (metallic K-K cohesion). To demonstrate this effect more clearly, we show the band-energy change $h_0(\Theta)$ calculated without the K-K orbital overlap ($T$) by the dashed line in Fig. 3(a).

The induced charge on a K site, $\Delta n_{4s}$, is seen to be fairly constant in the low coverage range with $M \geq 6$. Actually, the recent plasmon frequency and work-function measurements both suggested that the K charge is rather insensitive to the K coverage in the dispersed phase in spite of the large work-function decrease.[20,21] For $M \leq 6$, $\Delta n_{4s}$ starts to decrease rapidly because $E_F$ reaches the lower edge of the major part of the K 4s density of states. In contrast to Fig. 2(a), the electrostatic energy $u_0(\Theta)$ in Fig. 3(b) does not increase at low coverages, suggesting

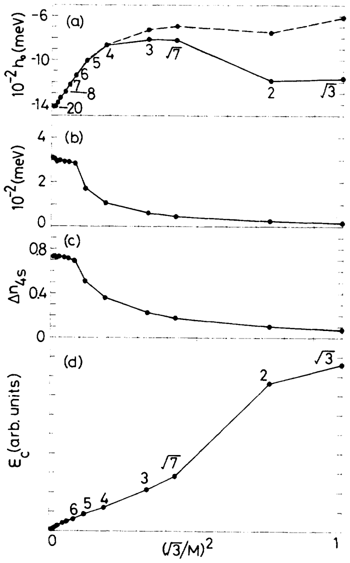

FIG. 3. (a) The band-energy change $h_0(\Theta)$, (b) electrostatic energy $u(\Theta)$, (c) induced charge $\Delta n_{4s}$, and (d) cohesive energy $\epsilon_c(\Theta)$ as a function of coverage $(M^{-2})$ for K/graphite in the case of partial K ionization with a parameter set, $\epsilon_{4s} - \epsilon_{2p_z} = 0.7$ eV, $V = -1.0$ eV, $U_0 = 2.5$ eV, and $T = -1.582 \exp(-0.837M)$ eV.

that the deviation from the localized dipole model is even larger for the present case. In Fig. 1(c), we plot the induced charge $\Delta n_i$ on C sites corresponding to the conditions of Fig. 3 with $M=15$. It is seen that $\Delta n_i$ is actually more delocalized than in Fig. 1(a). In particular, $\Delta n_i$ on the NN C site that interacts with the K 4$s$ orbital via $V$ takes a negative value. The origin of this behavior may be a strong correlation between the occupation numbers of these two sites introduced by $V$; namely, the increase in the orbital occupation of the NN C site necessarily leads to an increase in that of the K 4$s$ orbital, which is energetically unfavorable. However, at present we are not sure if this effect is realistic or simply manifests the limit of the charge-transfer model adopted here. For $M \leq 6$, the electrostatic energy $u(\Theta)$ decreases rapidly following the coverage dependence of the induced charge, $\Delta n_{4s}$.

Figure 3(d) shows the cohesive energy of the K layer defined by $\epsilon_c(\Theta)=\Theta\epsilon_{\text{ad}}(\Theta)$ as a function of coverage ($M^{-2}$). Here we choose $\epsilon_{4s}^0$ in Eq. (11) such that the K adsorption energy $\epsilon_{\text{ad}}(\Theta)$ for $C_{800}K$ ($M=20$) is equal to 1 eV. This value is smaller than the typical adsorption energy of K on transition-metal substrates ($\sim$2 eV). However, the interaction between K and graphite may be weaker than that between K and transition-metal substrates with a large density of states at $E_F$. The calculated $\epsilon_c(\Theta)$ curve has three features: (i) a convex curvature at low coverages due to the rapid rise in $h_0(\Theta)$ as shown in Fig. 3(a), (ii) a concave curvature in the intermediate region with $2 \leq M \leq 3$ originating from the K-K cohesion, and, finally, (iii) a concave curvature at the highest coverages due to the core-core repulsion. The first feature indicates that the K-K interaction can be repulsive at low coverages even without the dipole-dipole interaction.

At zero temperature, the first-order phase transition between two coverages takes place if a straight line that contacts the cohesive-energy curve $\epsilon_c(\Theta)$ tangentially at these two coverages can be drawn. Although our $\epsilon_c(\Theta)$ is computed only at discrete coverage values, its concave curvature in the intermediate coverage range implies the existence of a phase transition from dispersed phase to condensed phase. As discussed above, the large increase in the band-energy change $h_0(\Theta)$ at low coverages, which leads to a large convex curvature of the cohesive-energy curve, plays an essential role in this phase transition. For metallic substrates, the adsorption energy in the low-coverage regime decreases as a function of coverage mainly due to the dipole-dipole interaction. The localized dipole model gives the electrostatic energy,

$$u(\Theta)=0.23\mu_{\text{D}}^2/M^3 \text{ eV} ,$$

where $\mu_{\text{D}}$ denotes the adatom dipole moment in Debye units. Even with a large value for the dipole moment, say $\mu_{\text{D}}=10$ Debye, we have $u(\Theta)\sim 70$ meV at $M=7$, which is three times smaller than the change in the band energy $h_0(\Theta)$ shown in Fig. 3(a). This may explain why the large difference in density between dispersed and condensed phases has not been observed so far on metallic substrates.

## IV. SUMMARY

We have studied the electronic structure of K/graphite based on a simplified tight-binding model. We suggest that the structural properties of this system at lower coverages are mainly determined by the band-energy change rather than the dipole-dipole interaction. This band-energy term is virtually absent in metallic substrates and, hence, may be the origin of the observed unusual structural properties of K/graphite. Our model is certainly oversimplified in the treatment of the charge density, and the results should only be taken qualitatively. We hope that the present analysis may give impetus to more sophisticated theoretical studies of the present system.

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## APPENDIX

In this Appendix, we give a derivation of Eq. (1). It is assumed that each atomic site has only one atomic orbital and that these atomic orbitals form an orthonormal set. For simplicity, the spin index $\sigma$ is omitted in this Appendix. The atomic orbital on site $i$ located at $\mathbf{r}_i$ is denoted by $\phi_i(\mathbf{r}-\mathbf{r}_i)$. The electron density is given by

$$\begin{aligned}\rho(\mathbf{r})&=\sum_i \langle C_i^\dagger C_i\rangle \rho_i(\mathbf{r}) ,\\ \rho_i(\mathbf{r})&=|\phi_i(\mathbf{r}-\mathbf{r}_i)|^2 ,\end{aligned} \tag{A1}$$

where we have neglected the off-diagonal charge proportional to $\phi_i^*\phi_j$ with $i\neq j$, assuming that the overlap between $\phi_i$ and $\phi_j$ is small. We define the induced charge on site $i$ by $\Delta n_i=\langle C_i^\dagger C_i\rangle - n_i^0$, where $n_i^0$ is the ionic charge of atomic site $i$.

The electrostatic energy of the system is given by

$$\begin{aligned}E_{\text{el}}=\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{1}{2}\sum_{i,j}{}'\frac{n_i^0 n_j^0}{|\mathbf{r}_i-\mathbf{r}_j|}\\ -\sum_i \int d\mathbf{r}\frac{n_i^0\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_i|} ,\end{aligned} \tag{A2}$$

where pairs with $i=j$ are excluded from the summation in the second term. By inserting Eq. (A1) into Eq. (A2), we have

$$E_{\mathrm{el}}=\frac{1}{2}\sum_{i,j}\Delta n_i\Delta n_j\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\sum_{i,j}(n_i^0+\Delta n_i)\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})[\rho_j(\mathbf{r}')-\delta(\mathbf{r}'-\mathbf{r}_j)]n_j^0}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\frac{1}{2}\sum_{i,j}{}'\,n_i^0n_j^0\left[\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}-\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]-\frac{1}{2}\sum_i(n_i^0)^2\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{A3}$$

The last term of Eq. (A4) is constant, since the total number of atomic sites are conserved and thus can be omitted. By defining $U_{ij}$, $V_i$, and $V_s(i,j)$ by

$$U_{ij}=\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{A4}$$

$$V_i=\sum_j\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})[\rho_j(\mathbf{r}')-\delta(\mathbf{r}'-\mathbf{r}_j)]n_j^0}{|\mathbf{r}-\mathbf{r}'|}\ ,$$
$$V_s(i,j)=n_i^0n_j^0\left[\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}-\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\ , \tag{A5}$$

we have

$$E_{\mathrm{el}}=\sum_i V_i\langle C_i^\dagger C_i\rangle+\frac{1}{2}\sum_{i,j}U_{ij}\Delta n_i\Delta n_j+\frac{1}{2}\sum_{i,j}{}'\,V_s(i,j)\ . \tag{A6}$$

$V_i$ is the Hartree potential felt at site $i$ when there is no charge redistribution in the system. If the summation over $j$ in Eq. (A5) is dominated by the term with $j=i$, $V_i$ becomes independent of the atomic position $\mathbf{r}_i$. $V_s(i,j)$ vanishes as the overlap of $\phi_i$ and $\phi_j$ tends to zero if both $\rho_i$ and $\rho_j$ are spherical. If not, $V_s(i,j)$ decays as $1/|\mathbf{r}_i-\mathbf{r}_j|^3$ or faster.

We define the one-electron Hamiltonian by $H_0=\hat{T}+\sum_i V_iC_i^\dagger C_i$ with the kinetic-energy operator $\hat{T}$. The total energy of the system is then written as

$$E_t=\langle\hat{T}\rangle+E_{\mathrm{el}}$$
$$=\langle H_0\rangle+\frac{1}{2}\sum_{i,j}U_{ij}\Delta n_i\Delta n_j+\frac{1}{2}\sum_{i,j}{}'\,V_s(i,j)\ . \tag{A7}$$

Equation (A7) has the same form as Eq. (1). In general, $V_s(i,j)$ may be replaced by a phenomenological potential that incorporates the short-range repulsion due to the overlap of core orbitals. Part of the exchange and correlation energies may be included by adjusting matrix elements in $H_0$.

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