

## Calculated bond properties of K adsorbed on graphite

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The properties of the chemical bond of K adsorbed on a graphite(0001) surface have been studied for different coverages, by means of a full-potential slab method. Specific modifications of the Hamiltonian are performed in order to make it possible to study K on graphite in the disperse phase (dilute limit). It is found that K forms a metallic state when covering a graphite surface with a  $(2 \times 2)$  coverage. For a  $(3 \times 3)$  coverage as well as in the disperse phase K is found to form an ionic bond with graphite. It is shown that in the disperse phase, the hybridization between the K  $4s$  level and graphite is weak. Our findings are consistent with recent experiments. Furthermore the cohesive energies of K adsorption on graphite are found to be larger in the  $(2 \times 2)$  coverage compared to the  $(3 \times 3)$  coverage. [S0163-1829(98)03743-6]

### I. INTRODUCTION

The chemisorption of alkali metals at surfaces have been a source of controversy, mostly concerning the nature of the chemical bond, which has been extensively discussed in the literature.<sup>1-10</sup> It is known that K can grow on graphite in a few different phases. Li, Hock, and Palmer<sup>8</sup> show that K grows in a disperse phase at low K coverage. At a critical coverage, corresponding to a K-K distance of about 14 Å, a phase transition occurs and a  $(2 \times 2)$  structure starts to form. It is shown in Ref. 8 that the disperse and  $(2 \times 2)$  phases coexist until the  $(2 \times 2)$  phase forms a complete monolayer. At even higher K coverage a  $\sqrt{3} \times \sqrt{3} R30^\circ$  phase is suggested.<sup>11</sup> In Refs. 8 and 9 the plasmon frequency for the disperse and  $(2 \times 2)$  phase, was investigated by means of electron-energy-loss spectroscopy (EELS). In the disperse phase the plasmon frequency is shown to increase with increasing coverage. It is argued that this can be interpreted as an effect of charge transfer from the K atom to the graphite substrate, i.e., an ionic contribution to the chemical bond of K on graphite. Further, for the  $(2 \times 2)$  phase the intensity from the plasma mode dies away and three new loss peaks appear. According to Refs. 8 and 9 the new feature in the EELS spectrum can partly be interpreted as a sign of hybridization between the  $4s$  and  $4p$  states of K, which serves as an indication of a metallic state of the K layer. This finding of a metallic  $(2 \times 2)$  state is supported in a recent photoemission study of K on graphite<sup>12</sup> in which a clear presence of its  $4s$ -K levels close to (below) the Fermi level is found. These results are contradicted by XPS measurements by Johnson, Starnberg, and Huges<sup>13</sup> who concluded that the  $4s$  electrons,

for a  $(2 \times 2)$  coverage of K on graphite, are completely transferred to the substrate. It is, however, unclear how the authors reach this conclusion since they only show results from a K/graphite system where K partly was intercalated into the graphite substrate.

In a recent theoretical work the bonding of K on graphite in the  $(2 \times 2)$  and  $(4 \times 4)$  phase was studied by means of a first-principles total-energy pseudopotential method.<sup>14</sup> For the  $(4 \times 4)$  phase a substantial charge transfer from the K layer to the graphite layer was found whereas in the  $(2 \times 2)$  phase this charge transfer is small, but on the other hand a large redistribution of charge within the  $(2 \times 2)$  K layer was found. These findings give further support to the picture of an ionic disperse phase and a metallic  $(2 \times 2)$  phase. However, no information about the band structures are given in Ref. 14 and the calculations are only performed for one point in the Brillouin zone, namely, the  $\Gamma$  point.

It is often argued that the disperse phase of K on graphite is an effect of the dipole-dipole repulsion that occurs if the bond between K and graphite is ionic. This argument was questioned in a recent work by Ishida and Palmer,<sup>15</sup> who investigated the energetics of K adsorption on graphite by means of a qualitative tight-binding model. In this work it was illustrated that also the band energy favors a disperse phase and that this might dominate over the dipole-dipole energy. The large band energy effect at low coverage is explained to have its origin in the weak screening of the electrons induced in the graphite layer from the ionized K atoms. This effect would never occur for a metallic substrate since in that case good screening is expected.

In another recent work<sup>16</sup> the nature of the chemical bond

of disperse K on graphite was investigated by means of x-ray adsorption (XA) and autoionization spectroscopy as well as *ab initio* calculations. The measurements were actually performed on a graphite substrate covered with a monolayer of Ar and the so called  $Z+1$  approximation was adopted to interpret the results of a core ionized Ar atom as equivalent to a K atom. This study also confirms that disperse K forms an ionic bond with a graphite substrate.

The main issue of the present paper is to give additional evidence as regards the nature of the chemical bond for different coverages of K on graphite. While discussing ionicity it is quite common to describe it in terms of charge transfer, which always accompanies the formation of an ionic bond. Even if some charge redistribution takes place in a system it is hard to assign different fractions of charge as belonging to a specific atom. Any calculated or measured charge transfer depends on some arbitrary division of the solid into different regions ascribed to different atoms. Therefore charge transfer is not a well-defined quantity.<sup>17</sup> This is important to have in mind while discussing adsorption of K on graphite since the extension of an atomic K  $4s$  orbital is much larger than the bond distance between K and the graphite substrate. Another way of characterizing an ionic bond is to look at the occupation of atomiclike orbitals. In the present work an unoccupied and narrow  $4s$  derived peak originating from K will be adopted as a criterion of an ionic bond between K and the graphite substrate. On the other hand, a broad  $4s$  derived peak that is pinned at the Fermi level will be interpreted as a metallic state. To make any quantitative conclusion of the charge redistribution (charge transfer) is beyond the scope of the present work.

This work should be regarded as a continuation of part of the theoretical work presented in Ref. 16. In Sec. II a brief discussion about the calculational method is presented. The main results are shown in Sec. III, while an analysis of the results is presented in Sec. IV.

## II. DETAILS OF THE CALCULATIONS

The calculational method used<sup>18</sup> in the present work is based on linear muffin-tin orbitals.<sup>19</sup> We have adopted a base geometry consisting of muffin-tin spheres and an interstitial region as well as a vacuum region. Inside the muffin tins the density and potential are expanded by means of spherical harmonic functions times a radial component. In the interstitial region the expansion of the density and potential makes use of a Fourier series. The interstitial basis function is a Bloch sum of Neuman or Hankel functions. Each Neuman or Hankel function is then augmented (replaced) by a numerical basis function inside the muffin-tin spheres, in the standard means of the linear muffin-tin method. In the vacuum region the wave function is a function that is the solution to the planar averaged Schrödinger equation, and is composed of a plane wave traveling parallel to the surface times a function that depends on the  $z$  direction (perpendicular to the surface). In the present method no approximation is assumed concerning the shape of the density or potential, and this so-called full potential treatment is quite important when considering surface geometries. In the calculations presented below we have approximated the graphite (0001) surface with a free-standing monolayer of graphite. We believe that this is an

adequate approximation since the interaction between different graphite layers is known to be small. This approximation was used successfully in a previous work.<sup>20</sup> In the calculations of the  $(2 \times 2)$  coverage a supercell with eight C atoms and one K atom was used. Seven  $k$  points were sampled in the irreducible part, (1/12th) of the Brillouine zone. For the  $(3 \times 3)$  coverage each cell contains 18 C atoms and one K atom and four  $k$  points were sampled in the irreducible part, (1/12th) of the Brillouin zone (for the hollow site symmetry). Some tests with larger  $k$  point sets were performed without noticing any significant change of the calculated results. A larger number of  $k$  points were used in the last iteration in order to give a well-converged density of states (DOS). The so-called muffin-tin radius is chosen to be 2.0 Å for the K atoms and 0.7 Å for the C atoms. Furthermore, the maximal values of  $l$  used in the expansion of the muffin-tin potential and density was chosen to be 4. Moreover, 256 two-dimensional stars were used in the expansion of the vacuum density and potential and the vacuum region was calculated to extend 40 a.u. outside the boundary between the interstitial and vacuum region. From convergence tests of the number of  $k$  points, the number of Fourier components as well as the maximal value of  $l$ , the total energy was found to be converged within 0.03 eV.

To simulate the disperse phase (one single K atom on an empty graphite surface) the same supercell as for the  $(3 \times 3)$  coverage was used. To remove residual K-K bonding effects, we explicitly switched off the interaction between K atoms by writing the matrix elements of the  $4s$  states of the Hamiltonian as  $\langle 4s|H|4s \rangle = \epsilon_{4s} \langle 4s|4s \rangle$ , i.e., as the atomic  $4s$  level times the overlap matrix element. The matrix elements from K  $4p$ ,  $\langle 4p|H|4p \rangle$ , was treated in the same way and the hybridization terms  $\langle 4s|H|4p \rangle$  and  $\langle 4p|H|4s \rangle$  were set to be identically zero. The atomic levels,  $\epsilon_{4s}$  and  $\epsilon_{4p}$  were taken from an atomic calculation using the self-consistently calculated potential for K on graphite. These atomic levels were calculated in the same manner as for the core electrons. Inside the muffin-tin sphere the atomic potential is taken to be identical to the spherical average of the self-consistent muffin-tin potential. Outside the muffin-tin sphere the potential is extrapolated by the following equation:

$$V(r) = \frac{Zq^2}{r} e^{-r/B} + C, \quad (1)$$

where  $Z$  is the atomic number,  $q$  is the elementary charge, and  $B$  and  $C$  are parameters determined by a fit to the outermost points of the muffin-tin potential. Thus, the asymptotic behavior of the atomic potential is identical to a screened Coulomb potential. The calculation of  $\epsilon_{4s}$  and  $\epsilon_{4p}$  was then done for this potential extrapolated to a distance 2.5 times the K muffin-tin radius and atomic boundary conditions were imposed for the K  $4s$  and  $4p$  wave functions.

Since the addition of electrons to the system due to one single K atom on an empty graphite surface is negligible we will in the DOS plots define the Fermi level for disperse K on graphite to be identical to the Fermi level of the free graphite surface. We believe that this type of calculations will serve as a good model for a single atom on a substrate. This method has three minor artifacts that, however, do not

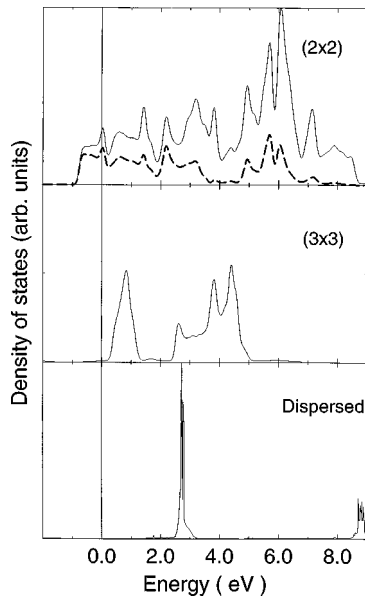


FIG. 1. Calculated K projected DOS for the (2×2) (upper panel), (3×3) (middle panel), and disperse phase (lower panel). The total DOS projected to K is plotted by solid lines. For the (2×2) also the 4s contribution to the DOS at the K site is shown (dashed line). The Fermi level is shown by a vertical solid line.

seriously affect our results presented below. First of all, since our disperse phase is modeled in a supercell with the (3×3) structure the system will have a numerical Fermi level (due to a charge neutrality condition) that differs from our definition above. This will cause a small error in the charge density as well as the potential, which also might have some small effect of the eigenvalues. Second, the translation symmetry of the supercell will give rise to an indirect *ad atom*—*ad atom* interaction via the substrate atoms, which might give some unphysical contribution to the dispersion of a given *ad atom* energy level. We find it likely that this is the origin of the small splitting of the K 4s peak, which is seen in some of our densities of states shown below (Figs. 1 and 2). Third, the electrostatic potential used to calculate the atomic energies  $\epsilon_{4s}$  and  $\epsilon_{4p}$  is affected by the presence of the neighboring K atoms in the (3×3) geometry. In order to estimate the error in  $\epsilon_{4s}$  and  $\epsilon_{4p}$  due to this artificial electrostatic potential these atomic quantities were also calculated for the (2×2) coverage and compared to the the (3×3) coverage a shift of  $\sim 0.3$  eV was found.

### III. RESULTS

In Secs. III A and B we have assumed that the K atoms are located at the hollow sites and that the distance between the K atoms and the graphite substrate is 2.6 Å. In a previous theoretical study<sup>14</sup> it was argued that the bond distance differs for different K coverage on the order of  $\sim 0.1$  Å. However, the discrepancy in bond distance between theory and experiment for the (2×2) phase is  $\sim 0.2$  Å (Ref. 14) and therefore we have simply chosen to adopt the experimental value from the (2×2) phase and use it for all coverages. The sensitivity of the bond distance will be discussed in Sec. III C. The main issue of Sec. III C is to compare our results with recent experimental results.<sup>16</sup>

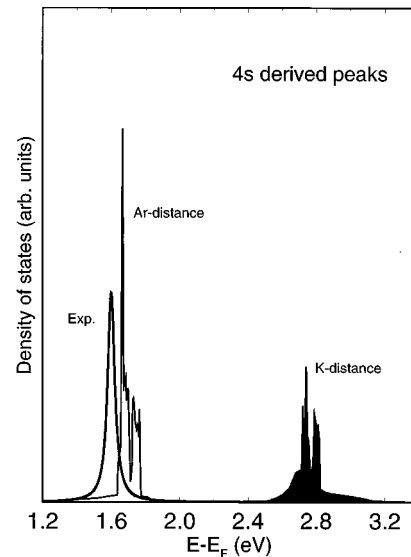


FIG. 2. Calculated DOS for K adsorbed on graphite for two different bond distances, with the Fermi level at zero energy. The experimental result is represented by a Lorentzian with FWHM 0.05 eV.

#### A. Coverage dependence in the electronic structure of the K adsorption on graphite

To begin with we discuss the results of the calculated (2×2) coverage of K on graphite. The atom projected density of states (DOS) from the K atom is shown in the upper panel of Fig. 1. The total DOS projected on the K atom as well as the 4s contribution are shown. The total DOS is mainly built up from the 4s and 4p contributions. Notice the strong hybridization between the 4s and 4p levels, which gives rise to a broad sp band. Since the density of states is large at the Fermi level and since a nonzero part of it is occupied it is clear that the K (2×2) overlayer is in a metallic state. Most of the contribution to the DOS at the Fermi level comes from the 4s states.

Our conclusion that the (2×2) monolayer of K on graphite is metallic is in line with the EELS measurements by Li and co-workers<sup>8,9</sup> and photoemission measurements by Benich *et al.*<sup>12</sup> as well as the theoretical study by Ancilotto and Toigo.<sup>14</sup> In Ref. 12 photoemission shows a  $\sim 1$  eV broad K 4s feature just below the Fermi level. This is in good agreement with our calculated occupied part of the density of states projected on the K atom, which has a width of  $\sim 0.9$  eV.

Next the (3×3) coverage of K on graphite is investigated. This coverage is somehow hypothetical since K is known to grow in either a disperse phase or in the (2×2) phase as mentioned in the Introduction. However, it is useful to study also this coverage to illustrate the transition from a metallic to an ionic state as the K atoms become more dilute. The atom projected density of states for the K atom for this system is shown in the middle panel of Fig. 1. The most striking feature is the occurrence of a 4s derived peak, which is unoccupied and has a width of only  $\sim 0.9$  eV. The center of the 4s derived peak is situated  $\sim 1.0$  eV above the Fermi level. It is interesting to notice the large difference between the densities of states for the (2×2) and (3×3) phases. In the (2×2) phase the overlap between the different K atoms

seems to be large enough to create an  $sp$  band whereas in the  $(3\times 3)$  phase the overlap is smaller and the DOS shows distinct and separated  $4s$  and  $4p$  peaks. Since the  $4s$  peak is unoccupied we conclude that K is ionic in the  $(3\times 3)$  coverage on graphite.

Another set of calculations concerns the disperse phase of K on graphite. The projected density of states from the region around the K atom for this system is shown in the lower panel of Fig. 1. Compared to the  $(3\times 3)$  phase the unoccupied  $4s$  derived peak is now much more narrow and shifted upwards to a position 2.7 eV above the Fermi level. The  $4s$  derived peak is now only 0.10–0.15 eV wide. As seen in Fig. 1 (and Fig. 2) the  $4s$  peak shows some signs of a double structure. We believe this is a small artifact of our model as discussed in Sec. II. This narrow and unoccupied  $4s$  derived level is a clear signature of an ionic bond between K and the graphite substrate. It is interesting to compare the middle and lower parts of Fig. 1, since the difference in the DOS between the two are due to the K-K  $4s$  interactions. Clearly our way to remove this interaction has a very dramatic influence on the electronic structure, resulting in an atomic like DOS. This is in agreement with expectations about the electronic structure of an impurity, where the only level broadening mechanism is the hybridization with other states.

### B. Cohesive energies of K adsorbed on graphite

In order to investigate the energetics of the different overlayer coverages we have calculated the cohesive energies of K adsorbed on graphite in the  $(2\times 2)$  and  $(3\times 3)$  structures. The cohesive energies are defined by

$$E_{coh}^{n\times n} = (E_K^{atom} + E_{graphite}^{n\times n}) - E_{K/graphite}^{n\times n}, \quad (2)$$

where the different energies are the total energies of a free K atom, a clean graphite surface and K adsorbed on graphite, respectively.  $E_{graphite}^{n\times n}$  and  $E_{K/graphite}^{n\times n}$  are both calculated in the same geometry with the only difference being that the K atom is present in the latter case. The cohesive energies for K adsorbed on graphite are found to be 3.88 eV for the  $(2\times 2)$  phase and 3.74 eV for the  $(3\times 3)$  phase.

We suggest that this difference in cohesive energy between the  $(2\times 2)$  and  $(3\times 3)$  systems can serve as an explanation of the  $(2\times 2)$  island growth. In the  $(3\times 3)$  case the overlap between the  $4s$  orbitals is smaller and, especially since the  $4s$  states are unoccupied, these states do not contribute much to the chemical bond, while in the  $(2\times 2)$  phase the overlap is larger, the states are occupied, and therefore contributes to the cohesive energy. This makes the latter energetically favorable. On the other hand as long as the K atoms are ionic they will repel each other due to the negative Coulomb interaction between the K ions. Also the band-energy effects, due to the polarization of the graphite substrate, discussed by Ishida and Palmer<sup>15</sup> might favor the disperse phase over the  $(3\times 3)$  phase. We have therefore three competing mechanisms, two of which favor isolated K ions (electrostatic and polarization of graphite) and another that favors island formation (overlap of the K  $4s$  orbitals).

To illustrate the influence of the overlap between the K  $4s$  orbitals also the cohesive energy of free standing K monolayers (i.e., no graphite are present) with the same structure and lattice parameters as in the case of  $(2\times 2)$  and  $(3\times 3)$

coverage, respectively, was calculated. Using the lattice parameter of the  $(2\times 2)$  coverage a cohesive energy of 0.78 eV was found whereas the cohesive energy of a free-standing monolayer with the same lattice parameter as the  $(3\times 3)$  coverage was found to be only 0.18 eV. This clearly shows that the cohesion between the K atoms favors the  $(2\times 2)$  coverage compared to the  $(3\times 3)$  coverage.

We speculate that the above mentioned arguments can serve as an explanation for why the  $(3\times 3)$  phase, as well as other coverages between  $(2\times 2)$  and the disperse phase, never are energetically favorable. However, to get a complete understanding of this issue one has to take lattice relaxations into account when calculating the cohesive energy, something that we have not done. It is also not completely clear to what extent the local density approximation, LDA, used in the present scheme is able to give the correct cohesive energies.

### C. Theory versus experiment: disperse phase

In a recent publication<sup>16</sup> the nature of the chemical bond for disperse K on graphite was investigated experimentally as well as theoretically. The experiment was actually performed for a monolayer of Ar on a graphite substrate. Because of the so-called  $Z+1$  approximation the final state of a core-excited Ar atom can be viewed as equivalent to a K atom. By means of x-ray adsorption spectroscopy (XAS) the position of the  $4s$  derived peak can be measured. Since the experimental broadening is quite large it is not possible to determine the width of the  $4s$  derived peak from the XAS measurements. However, the core-excited Ar turns out to have two different decay channels; these are the decay of the  $4s$  electron back to the  $2p_{3/2}$  core hole and the transfer of the  $4s$  electron into the graphite bands before the decay back to the core hole. Since these two decay processes have the same time scale a typical decay spectra will show two different features. This type of spectra was first observed for  $N_2$  on graphite.<sup>21</sup> From the relative intensity between the two different features a ratio between the two different characteristic times can be obtained. Thus, with knowledge of the core-hole lifetime (for core-excited Ar), a characteristic charge-transfer time can be derived that in turn corresponds to a hybridization width.<sup>21</sup> From the above-described experiment the position of the  $4s$  derived peak in ‘‘quasipotassium’’ was found to be 1.6 eV above the Fermi level with a hybridization width of 0.05 eV.

We will now discuss how well the experiment explained above can be described by our theoretical model. First of all the validity of the  $Z+1$  approximation is investigated by comparing calculations of K as well as core-excited Ar on a graphite substrate. In this test we did not find any significant (for our present purposes) difference in the density of states, orbital occupation, Fermi level, etc. Since the experiment was performed on a system with Ar on graphite one has to take into account the difference in bond distance for K and Ar, respectively. Therefore we have recalculated the electronic structure for disperse K on graphite using the bond distance of Ar on graphite, 3.2 Å.<sup>22</sup> In Fig. 2 the  $4s$  derived peaks for the two different bond distances are shown together with the experimental result. The  $4s$  derived peak

calculated with the new bond distance has a position 1.7 eV above the Fermi level and a width of 0.05–0.1 eV. Notice the good agreement between the experimental result and our calculations using the Ar bond distance, as regards both the peak position as well as the hybridization width. On the other hand, the calculations of K on graphite using the proper bond distance for K show that the  $4s$  peak is located at 2.7 eV, which is 1.1 eV above the experimental value obtained from core-excited Ar. Furthermore, the hybridization width is slightly broader in this case, 0.1–0.15 eV. In order to investigate the sensitivity to the uncertainty in the input bond distance we have also performed calculations for 3.1 and 3.3 Å. From this we observe that the peak position moves 0.03 eV if the bond distance is changed by 0.1 Å (starting from 3.2 Å) and no significant change of the hybridization width is found. Another issue which has to be raised to justify the comparison of our calculations of K with core-excited decay spectra from Ar is the position of the adsorbed atoms. K is known to adsorb on the so-called hollow site position at graphite while Ar is known to form an incommensurable structure.<sup>23</sup> To find out how sensitive the  $4s$  peak is to the adsorption site we also performed calculations of K at the so called on top site on graphite, assuming the bond distance to be 3.2 Å as before. It was found that the position of the  $4s$  derived peak shifts less than 0.01 eV compared to the results for the hollow site.

From the data described above we conclude that XAS and decay spectra from core-excited Ar on graphite can give valuable information about the electronic structure of disperse K on graphite, if the difference in bond length is taken into account. We believe that this kind of combination of experiment and first-principles calculations can be performed for any study of alkali metal adsorbed on some surface. We also conclude that the theoretical model used is successful in describing the electronic structure of the dispersed phase, without having to go to an extremely large supercell. This promising result opens the possibility that this approach may have a more general applicability.

In another recent experimental work by Hellsing *et al.*<sup>24</sup> the width and position of the K  $4s$  derived peak of disperse K on graphite was estimated to be 2.4 eV and 0.15 eV, respectively, in reasonable agreement with our calculated values (2.7 eV and 0.1 to 0.15 eV, respectively). The values in Ref. 24 was obtained by fitting photodesorption data to a parameter model describing the photodesorption cross section.

#### IV. DISCUSSION

In the above sections we learned that K adsorbed on graphite forms an ionic bond for the  $(3\times 3)$  and disperse phase whereas the  $(2\times 2)$  phase is found to be metallic. These conclusions are evident from the DOS projected to the muffin-tin sphere of K (Fig. 1). However, the unoccupied K  $4s$  derived peaks do not mean that one electron is transferred from the K muffin-tin sphere towards the graphite plane. First of all the K  $4s$  wave function has a large extension and most of its weight is situated outside the K muffin-tin sphere and therefore a large fraction of the K  $4s$ -like states is present in the graphite plane even for the metallic  $(2\times 2)$  phase. Secondly, because of the large volume of the K

muffin-tin sphere a lot of graphitelike states happen to be inside the K sphere. The number of graphitelike states inside the K sphere is found to be quite insensitive to the K coverage but does of course depend strongly on the bond length between K and graphite. From our calculations, taking 2.6 Å as the bond distance, we found  $\sim 0.80$  electrons inside the K muffin-tin sphere for the metallic  $(2\times 2)$  phase and  $\sim 0.65$  electrons for the ionic  $(3\times 3)$  and disperse phase. Most of this change has its origin in the change of the  $4s$  orbital occupation, which is decreased from  $\sim 0.20$  to  $\sim 0.09$  electrons.

One question of large interest is why the hybridization width of the  $4s$  derived peak is so small for disperse K on graphite. In Sec. III C we found that the hybridization width seems to be independent of the adsorption site. From this we conclude that it is difficult to use symmetry arguments based on the adsorption geometry as an explanation of the weak hybridization. Since the  $4s$  derived peak of K has its position in the energy range of the so called  $\pi^*$  band of graphite the overlap  $\langle 4s|\pi^* \rangle$  is of central importance for the understanding of the hybridization between K  $4s$  and graphite. One possibility is that the  $\langle 4s|\pi^* \rangle$  overlap is small since the extension of the  $4s$  orbitals is much larger than the distance between K and graphite. The  $\pi^*$  band is built up from the carbon  $p_z$  orbitals, which are directed normal to the graphite plane and have a positive and a negative side on opposite sides of the plane. If the  $4s$  wave function has a similar amplitude at both sides of the graphite layer a partial cancellation between different parts of the overlap integral will occur and  $\langle 4s|\pi^* \rangle$  will therefore be small. To investigate this possibility we have calculated the atomic K  $4s$  radial wave function, using an extrapolation of the self-consistent potential at the K site. The radial  $4s$  wave function has its outer maximum at  $\sim 2$  Å, which is less than the distance between the K atom and the graphite plane, 2.6 Å. The decay of the  $4s$  atomic wave function is, however, slow and half of the maximal amplitude is found at a distance as large as  $\sim 5$  to 6 Å. The  $p_z$  orbitals has its maximal value at  $\sim 0.3$  to 0.4 Å from its origin. Since the variation of the K  $4s$  wave-function amplitude is small in the range where the  $p_z$  orbital has its main weight it is clear that a fractional cancellation of different parts of the overlap integral actually might occur.

Another interesting question regarding the hybridization and the  $4s$  peak position is how these quantities are related to the atomic quantity  $\epsilon_{4s}$ . From the calculations of the disperse phase we found that  $\epsilon_{4s}$  is located  $\sim 1$  eV above the Fermi level, almost independent of the bond distance. The  $4s$  peak position on the other hand strongly depends on the bond distance, as shown in Fig. 2. From this it is evident that the difference in peak position for different bond distances is almost exclusively a hybridization effect. In the case of a  $(3\times 3)$  coverage  $\epsilon_{4s}$  turns out to be close to the Fermi level and also in this case the  $4s$  derived peak is pushed upwards due to the hybridization between graphite and K, which in this case serves as the driving mechanism for the creation of the ionic bond.

#### V. CONCLUSIONS

We have performed first-principles calculations in order to investigate the bonding properties of K on graphite. The

disperse phase as well as the  $(3 \times 3)$  phase are found to be ionic and have an unoccupied  $4s$  derived level above the Fermi level. In the disperse case the  $4s$  level is only 0.10–0.15 eV broad, which indicates that the hybridization between K  $4s$  and the graphite band is weak, something that can be understood by studies of the shape of atomic K  $4s$  and C  $2p_z$  orbitals. These findings are consistent with recent experiments on core-excited Ar, “quasipotassium,” on graphite, concerning the peak position as well as the peak width. The  $(2 \times 2)$  phase of K on graphite is found to form a metallic state, due to the large overlap between the different K  $4s$  and  $4p$  orbitals, which form a covalent bond. Furthermore, the cohesive energy of K adsorbed on graphite is found to be larger for the  $(2 \times 2)$  coverage compared to the

$(3 \times 3)$  coverage, in line with the experimental fact that a  $(3 \times 3)$  phase is never observed. Finally, we note that the theoretical method used here to simulate the dispersed phase seems promising and may be used to study similar problems.

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