Potassium intercalation in graphite: A van der Waals density-functional study

Eleni Ziambaras,1 Jesper Kleis,1 Elsebeth Schröder,1 and Per Hyldgaard1,2

1Department of Applied Physics, Chalmers University of Technology, SE–412 96 Göteborg, Sweden
2Microtechnology and Nanoscience, MC2, Chalmers University of Technology, SE–412 96 Göteborg, Sweden

(Dated: April 1, 2007)

Potassium intercalation in graphite is investigated by first-principles theory. The bonding in the potassium-graphite compound is reasonably well accounted for by traditional semilocal density functional theory (DFT) calculations. However, to investigate the intercalation formation energy from pure potassium atoms and graphite requires use of a description of the graphite interlayer binding and thus a consistent account of the nonlocal dispersive interactions. This is included seamlessly with ordinary DFT by a van der Waals density functional (vdW-DF) approach [Phys. Rev. Lett. 92, 246401 (2004)]. The use of the vdW-DF is found to stabilize the graphite crystal, with crystal parameters in fair agreement with experiments. For graphite and potassium-intercalated graphite structural parameters such as binding separation, layer binding energy, formation energy, and bulk modulus are reported. Also the adsorption and sub-surface potassium absorption energies are reported. The vdW-DF description, compared with the traditional semilocal approach, is found to weakly soften the elastic response.

I. INTRODUCTION

Graphite with its layered structure is easily intercalated by alkali metals (AM) already at room temperature. The intercalated compound has two-dimensional layers of AM between graphite layers giving rise to interesting properties, such as superconductivity. The formation of an AM-graphite intercalate proceeds with absorption of AM atoms on graphite and absorption of AM atoms below the top graphite layer, after which further exposure to AM atoms leads the AM intercalate compound.

Recent experiments on the structure and electronic properties of AM/graphite systems use samples of graphite that are prepared by heating SiC crystals to temperatures around 1400 C. This heat-induced graphitization is of great value for spectroscopic studies of graphite systems, since the resulting graphite overlayers are of excellent quality. The nature of the bonding between the SiC surfaces and graphite has been explored experimentally with photoemission spectroscopy and theoretically with a van der Waals density functional (vdW-DF) theory approach that accounts for the van der Waals (vdW) forces.

Here we investigate with density functional theory (DFT) the effects on the graphite structure and the energetics and the elastic response when potassium is intercalated. The final intercalate compound is C8K. The AM intercalate system is interesting in itself and has been the focus of numerous experimental investigations. Graphitic systems are also ideal test materials in ongoing theory development that aims at improving the description of the nonlocal interlayer bonds in sparse systems. Standard DFT approaches are based on local (local density approximation, LDA) and semilocal approximations (generalized gradient approximation, GGA) for the electron exchange and correlation. Such regular DFT tools do not treat correctly the weak vdW binding, e.g., the cohesion between (adjacent) graphite layers. The failure of traditional DFT for graphite makes it impossible to obtain a meaningful comparison of the energetics in on-surface AM adsorption and subsurface AM absorption. Conversely, investigations of graphitic systems like C8K permit us to test the accuracy of our vdW-DF development work.

We explore the nature of the bonding of graphite, the process leading to intercalation via adsorption and absorption of potassium, and the nature of potassium-intercalated graphite C8K using a recently developed vdW-DF density functional. This choice of functional is essential for a comparison of graphite and C8K properties because of the inability of traditional GGA-based DFT to describe graphite. We calculate the structure and elastic response (bulk modulus B0) of pristine graphite and potassium intercalated graphite and we present results for the formation energies of the C8K system.

The intercalation of potassium in graphite is preceded by the adsorption of potassium on top of a graphite surface and potassium absorption underneath the top graphite layer of the surface. In this work we study how potassium bonds to graphite in these two parts of the process towards intercalation. Our vdW-DF investigations of the bonding of potassium in or on graphite supplements corresponding vdW-DF studies of the binding of polycyclic aromatic hydrocarbon dimers, of the polyethylene crystal, of benzene dimers, and of polycyclic aromatic hydrocarbon and phenol molecules on graphite.

The outline of the paper is as follows. Section II contains a short description of the materials of interest here: graphite, C8K, and graphite with an adsorbed or absorbed K atom layer. The vdW-DF scheme is described in Sec. III. Section IV presents our results, Sec. V the discussion, and conclusions are drawn in Sec. VI.
II. MATERIAL STRUCTURE

Graphite is a semimetallic solid with strong intra-plane bonds and weakly coupled layers. The presence of these two types of bonding results in a material with different properties along the various crystallographic directions. For example, the thermal and electrical conductivity along the carbon sheets is two orders of magnitude higher than that perpendicular to the sheets. This specific property allows heat to move directionally, which makes it possible to control the heat transfer. The relatively weak vDW forces between the sheets contribute to another industrially important property: graphite is an ideal lubricant. In addition, the anisotropic properties of graphite make the material suitable as a substrate in electronic studies of ultrathin metal films.

The natural structure of graphite is an $AB$ stacking, with the graphite layers shifted relative to each other, as illustrated in Fig. 1. The figure also shows hexagonal graphite, consisting of $AA$-stacked graphite layers. The in-plane lattice constant $a$ and the layer separation $d_{C-C}$ is also illustrated. In natural graphite the primitive unit cell is hexagonal, includes four carbon atoms in two layers, and has unit cell side lengths $a$ and height $c = 2d_{C-C}$.

The physical properties of graphite have been studied in a variety of experimental and theoretical work. Some of the DFT work has been performed in LDA, which does not provide a physically meaningful account of binding in layered systems. At the same time, using GGA is not an option because it does not bind the graphite layers. For a good description of the graphite structure and nature the vDW interactions must be included.

Alkali metals (AM), except Na, easily penetrate the gallery of the graphite forming alkali metal graphite intercalation compounds. These intercalation compounds are formed through electron exchange between the intercalated layer and the host carbon layers, resulting in a different nature of the interlayer bonding type than that of pristine graphite. The intercalate also affects the conductive properties of graphite, which becomes superconductive in the direction parallel to the planes at critical temperatures below 1 K.

The structure of AM graphite intercalation compounds is characterized by its stage $n$, where $n$ is the number of graphite sheets located between the AM layers. In this work we consider only stage-1 intercalated graphite C$_8$K, in which the layers of graphite and potassium alternate throughout the crystal. The primitive unit cell of C$_8$K is orthorhombic and contains sixteen C atoms and two K atoms. In the C$_8$K crystal the K atoms are ordered in a ($2 \times 2$) registry with K-K separation $2a$, where $a$ is the in-plane lattice constant of graphite. This separation of the potassium atoms is about 8% larger than that in the natural K bcc crystal (based on experimental values). The carbon sheet stacking in C$_8$K is of $AA$ type, with the K atoms occupying the sites over the hollows of every fourth carbon hexagon, each position denoted by $\alpha$, $\beta$, $\gamma$, or $\delta$, and the stacking of the K atoms perpendicular to the planes being described by the $\alpha\beta\gamma\delta$-sequence as illustrated in Fig. 2.

III. COMPUTATIONAL METHODS

The first-principle total-energy and electronic structure calculations are performed within the framework...
of DFT. The semilocal Perdew-Burke-Ernzerhof (PBE) flavor\(^{29}\) of GGA is chosen for the exchange-correlation functional for the traditional self-consistent calculations underlying the vdW-DF calculations. For all GGA calculations we use the open source DFT code DACAP\(^{24}\) which employs Vanderbilt ultrasoft pseudopotentials\(^{26}\), periodic boundary conditions, and a plane-wave basis set. An energy cut-off of 500 eV is used for the expansion of the wave functions and the Brillouin zone (BZ) of the unit cells is sampled according to the Monkhorst-Pack scheme.\(^{27}\) The self-consistently determined GGA valence electron density \(n(r)\) as well as components of the energy from these calculations are passed on to the subsequent vdW-DF calculation of the total energy.

For the adsorption and absorption studies a graphite surface slab consisting of 4 layers is used, with a surface unit cell of side lengths twice those in the graphite bulk unit cell (i.e., side lengths \(2a\)). The surface calculations are performed with a \(4 \times 4 \times 1\) \(k\)-point sampling of the BZ.

The (pure) graphite bulk GGA calculations are performed with a \(8 \times 8 \times 4\) \(k\)-point sampling of the BZ, whereas for the CsK bulk structure, in a unit cell at least double the size in any direction, \(4 \times 4 \times 2\) \(k\)-points are used, consistent also with the choice of \(k\)-point sampling of the surface slabs.

We choose to describe CsK by using a hexagonal unit cell with four formula units, lateral side lengths approximately twice those of graphite and with four graphite and four K-layers in the direction perpendicular to the layers. CsK can also be described by the previously mentioned primitive orthorhombic unit cell containing two formula units of atoms but we retain the orthorhombic cell for ease of description and for simple implementation of numerically robust vdW-DF calculations.

In all our studies, except test cases, the Fast Fourier Transform (FFT) grids are chosen such that the separation of neighboring points is maximum \(\sim 0.13\) \(\text{Å}\) in any direction in any calculation.

### A. vdW density function calculations

In graphite, the carbon layers bind by vdW interactions only. In the intercalated compound a major part of the attraction is ionic, but also here the vdW interactions cannot be ignored. In order to include the vdW interactions systematically in all of our calculations we use the vdW-DF of Ref.\(^{16}\). There, the correlation energy functional is divided into a local and a nonlocal part,

\[
E_c = E_c^{\text{LDA}} + E_c^{\text{nl}},
\]

where the local part is approximated in the LDA and the nonlocal part \(E_c^{\text{nl}}\) is consistently constructed to vanish for a homogeneous system. The nonlocal correlation \(E_c^{\text{nl}}\) is calculated from the GGA-based \(n(r)\) and its gradients by using information about the many-body response of the weakly inhomogeneous electron gas:

\[
E_c^{\text{nl}} = \frac{1}{2} \int_{V_0} \int_{V} dr \int dr' n(r) \phi(r, r') n(r').
\]

The nonlocal kernel \(\phi(r, r')\) can be tabulated in terms of the separation \(|r - r'|\) between the two fragments at positions \(r\) and \(r'\) through the parameters \(D = (q_0 + q_0')|r - r'|/2\) and \(\delta = (q_0 - q_0')/(q_0 + q_0')\). Here \(q_0\) is a local parameter that depends on the electron density and its gradient at position \(r\). The analytic expression for the kernel \(\phi\) in terms of \(D\) and \(\delta\) can be found in Ref.\(^{16}\).

For periodic systems, such as bulk graphite, CsK, and the graphite surface (with adsorbed or absorbed K-atoms), the nonlocal correlation per unit cell is simply evaluated from the interaction of the points in the unit cell \(V_0\) with points everywhere in space \((V)\) in the three (for bulk graphite and CsK) or two (for the graphite surface) dimensions of periodicity. Thus, the \(V\)-integral in Eq. (2) in principle requires a representation of the electron density infinitely repeated in space. In practice, the nonlocal correlation rapidly converges and it suffices with repetitions of the unit cell a few times in each spatial direction. For graphite bulk the \(V\)-integral is converged when we use a \(V\) that extends \(9(7)\) times the original unit cell in directions parallel (perpendicular) to the sheets. For the potassium investigation a significantly larger original unit cell is adopted (see Fig. 2); here a fully converged \(V\) corresponds to a cell extending five (three) times the original cell in the direction parallel (perpendicular) to the sheets for CsK bulk. To describe the nonlocal correlations (2) for the graphite surface a sufficient \(V\) extends five times the original unit cell along the carbon sheets.

For the exchange energy \(E_x\) we follow the choice of Ref.\(^{16}\) of using revPBE\(^{22}\) exchange. Among the functionals that we have easy access to, the revPBE has proved to be the best candidate for minimizing the tendency of artificial exchange binding in graphite.\(^{15}\)

Using the scheme described above to evaluate \(E_c^{\text{nl}}\), the total energy finally reads:

\[
E^{\text{vdW-DF}} = E^{\text{GGA}} - E^{\text{GGA}}_c + E^{\text{LDA}}_c + E^{\text{nl}}_c,
\]

where \(E^{\text{GGA}}\) is the GGA total energy with the revPBE choice for the exchange description and \(E^{\text{GGA}}_c\) \((E^{\text{LDA}}_c)\) the GGA (LDA) correlation energy. As our GGA calculations in this specific application of vdW-DF are carried out in PBE, not revPBE, we further need to explicitly replace the PBE exchange in \(E^{\text{GGA}}\) by that of revPBE for the same electron charge density distribution.

### B. Convergence of the local and nonlocal energy variation

DFT calculations provide physically meaningful results for energy differences between total energies.\(^{3}\) To understand materials and processes we must compare total
energy differences between a system with all constituents at relatively close distance and a system of two or more fragments at “infinite” separation (the reference system). Since the total energy \( E_{\text{tot}} \) consists both of a long-range term and shorter-ranged GGA and LDA terms it is natural to choose different ways to represent the separated fragments for these different long- or short-range energy terms.

For the shorter-range energy parts (LDA and GGA terms) the reference system is a full system with vacuum between the fragments. For LDA and GGA calculations it normally suffices to make sure that the charge density tails of the fragments do not overlap, but here we find that the surface dipoles cause a slower convergence with layer separation. We use a system with the layer separation between the potassium layer and the nearest graphite layer(s) \( d_{C,K} = 12 \text{ Å} (8 \text{ Å}) \) as reference for the adsorption (absorption) study.

The evaluation of the nonlocal correlations \( E_{\text{nl}} \) requires additional care. This is due to technical reasons pertaining to numerically stability in basing the \( E_{\text{nl}} \) evaluation on the FFT grid used to converge the underlying traditional-DFT calculations. The evaluation of the nonlocal correlation energy, Eq. (2), involves a weighted double integral of a kernel with a significant short-range sensitivity. The problem of FFT sensitivity of the evaluation/absorption cases and one or more for fragments in the doubled unit-cell and doubled gridding reference. We have explicitly tested that using a FFT grid spacing of \(< 0.13 \text{ Å} \) (but not larger) for such reference calculations is sufficient to ensure full convergence in the reported \( E_{\text{nl}} \) (and \( E_{\text{vdW}}-\text{DF} \) total) energy variation for graphitic systems.

C. Material formation and sorption energies

The cohesive energy of graphite (G) is the energy gain, per carbon atom, of creating graphite at in-plane lattice constant \( a \) and layer separation \( d_{C,C} \) from isolated (spin-polarized) carbon atoms.

\[
E_{G,\text{coh}}(a, d_{C,C}) = E_{G,\text{tot}}(a, d_{C,C}) - E_{C,\text{atom,tot}} \tag{4}
\]

where \( E_{G,\text{tot}} \) and \( E_{C,\text{atom,tot}} \) are total energies per carbon atom. The graphite structure is stable at the minimum of the cohesive energy, at lattice constants \( a = a_G \) and \( 2d_{C,C} = c_G \).

The adsorption (absorption) energy for a \((2 \times 2)\) K-layer over (under) the top layer of a graphite surface is the difference in total energy [from Eq. (3)] for the system at hand minus the total energy of the initial system, i.e., a clean graphite surface and isolated gas-phase potassium atoms. However, due to the above mentioned technical issues in using the vdW-DF we calculate the adsorption and absorption energy as a sum of (artificial) stages leading to the desired system: First the initially isolated, spin-polarized potassium atoms are gathered into a free floating potassium layer with the structure corresponding to a full cover of potassium atoms. By this the total system gains the energy \( \Delta E_{K,\text{layer}}(a_G) \), with

\[
\Delta E_{K,\text{layer}}(a) = E_{K,\text{tot}}(a) - E_{K,\text{atom,tot}}. \tag{5}
\]

In adsorption the potassium layer is then simply placed on top of the four-layer \((2 \times 2)\) graphite surface (with the K atoms above graphite hollows) at distance \( d_{C,K} \). The system thereby gains a further energy contribution \( \Delta E_{K,G}(d_{C,K}) \). This leads to an adsorption energy per K-atom

\[
E_{\text{ads}}(d_{C,K}) = \Delta E_{K,\text{layer}}(a_G) + \Delta E_{K,G}(d_{C,K}). \tag{6}
\]

In absorption the top graphite layer is peeled off the \((2 \times 2)\) graphite surface and moved to a distance far from the remains of the graphite surface. This process costs the system an (“exfoliation”) energy \( -\Delta E_{C,G} = -[E_{\text{tot,C,G}}(d_{C,C} = c_G/2) - E_{\text{tot,C,G}}(d_{C,C} \to \infty)] \). At the far distance the isolated graphite layer is moved into AA stacking with the surface, at no extra energy cost. Then,
the potassium layer is placed midway between the far-
away graphite layer and the remains of the graphite sur-
face. Finally the two layers are gradually moved towards
the surface. At distance 2d_{C,K} between the two topmost
graphite layers (sandwiching the K-layer) the system has
further gained an energy \( \Delta E_{C,K,G}(d_{C,K}) \). The absorp-
tion energy per K-atom is thus

\[ E_{\text{abs}}(d_{C,K}) = -\Delta E_{C,G} + \Delta E_{K,\text{layer}}(a_G) + \Delta E_{C,K,G}(d_{C,K}). \]  

Similarly, the \( C_8K \) intercalate compound is formed
from graphite by first moving the graphite layers far
apart accordion-like (and there shift the graphite stack-
ing from \( ABA \cdots \) to \( AAA \cdots \) at no energy cost), then
changing the in-plane lattice constant of the isolated
graphene layers from \( a_G \) to \( a \), then intercalating K-layers
(in stacking \( \alpha \beta \gamma \delta \) between the graphite layers, and fi-
nally moving all the K- and graphite layers back like an
accordion, with in-plane lattice constant \( a \) (which has the
value \( a_{C,K} \) at equilibrium).

In practice, a unit cell of four periodically repeated
graphite layers is used in order to accommodate the
potassium \( \alpha \beta \gamma \delta \)-stacking. The energy gain of creating
a \((2 \times 2)\) graphene sheet from 8 isolated carbon atoms is
defined similarly to that of the K-layer:

\[ \Delta E_{C,\text{layer}}(a) = E_{C,\text{layer,tot}}(a) - 8E_{C,\text{atom,tot}}. \]  

The formation energy for the \( C_8K \) intercalate com-
 pound per K atom or formula unit, \( E_{\text{form}} \), is thus found
from the energy cost of moving four graphite layers
apart by expanding the \( (2 \times 2) \) unit cell to large height,
\( -\Delta E_{G,\text{acc}} \), the cost of changing the in-plane lattice con-
stant from \( a_G \) to \( a \) in each of the four isolated graphene
layers, \( 4(\Delta E_{\text{C,layer}}(a) - \Delta E_{\text{C,layer}}(a_G)) \), the gain of creat-
ing four K-layers from isolated K-atoms, \( 4\Delta E_{\text{K,layer}}(a) \),
plus the gain of bringing four K-layers and four graphite
layers together in the \( C_8K \) structure, \( \Delta E_{C_8K,\text{acc}}(a, d_{C,K}) \),
yielding

\[ E_{\text{form}}(a, d_{C,K}) = \frac{1}{4} \left[ -\Delta E_{G,\text{acc}} + 4\Delta E_{\text{C,layer}}(a) - 4\Delta E_{\text{C,layer}}(a_G) \right. \]
\[ + \left. 4\Delta E_{\text{K,layer}}(a) + \Delta E_{C_8K,\text{acc}}(a, d_{C,K}) \right]. \]  

The relevant energies to use for comparing the three
different mechanisms of including potassium (adsorp-
tion, absorption and intercalation) are thus \( E_{\text{ads}}(d_{C,K}) \),
\( E_{\text{abs}}(d_{C,K}) \) and \( E_{\text{form}}(a, d_{C,K}) \) at their respective mini-
mum values.

\[ \text{IV. RESULTS} \]

Experimental observations indicate that the intercala-
tion of potassium into graphite starts with the absorption
of evaporated potassium into an initially clean graphite
surface. This subsurface absorption is preceded by ini-
tial, sparse potassium adsorption onto the surface, and
proceeds with further absorption into deeper graphite
voids. The general view is that the K atoms enter graph-
te at the graphite step edges. The amount and position of intercalated K atoms is controlled by the tem-
perature and time of evaporation.

Below, we first describe the initial clean graphite sys-
tem, and the energy gain in (artificially) creating free-
floating K-layers from isolated K-atoms. Then we present
and discuss our results on potassium adsorption and sub-
surface absorption, followed by a characterization of bulk
\( C_8K \).

For the adsorption (absorption) system we calculate the
adsorption (absorption) energy curve, including the equi-
librium structure. As a demonstration of the need for
a relatively fine FFT griding in the vdW-DF calcula-
tions we also calculate and compare the absorption
curve for a more sparse FFT grid. For the bulk sys-
tems (graphite and \( C_8K \)) we determine the lattice pa-
rameters and the bulk modulus. We also calculate the
formation energy of \( C_8K \) and the energy needed to peel
off one graphite layer from the graphite surface and com-
pare with experiment.

A. Graphite bulk structure

The present calculations on pure graphite are for the
natural, \( AB \)-stacked graphite (lower panel of Fig[1]). The
cohesive energy is calculated at a total of 232 structure
values \((a, d_{C,C})\) and the equilibrium structure and bulk
modulus \( B_0 \) are then evaluated using the method de-
scribed in Ref. [52].

Figure [8] shows a contour plot of the graphite cohesive
energy variation \( E_{G,\text{coh}} \) as a function of the layer sep-
deration \( d_{C,C} \) and the in-plane lattice constant \( a \), calcu-
lated within the vdW-DF scheme. The contour spacing
is 5 meV per carbon atom, shown relative to the energy
minimum located at \((a, d_{C,C}) = (a_G, c_G/2) = (2.476 \text{ A},
3.59 \text{ Å})\). These values are summarized in Table [1]together
with the results obtained from a semilocal PBE calcu-
lation. As expected, and discussed in Ref. [14], the
semilocal PBE calculation yields unrealistic results for
the layer separation. The table also presents the cor-
responding experimental values. Our calculated lattice
values obtained using vdW-DFT are in good agreement
with experiment [40] and close to those found from the
older vdW-DF of Refs. [14] and [15], (in which we for \( E^0_c \)
assume translational invariance of \( n(r) \) along the graphite
planes,) at \((2.47 \text{ Å}, 3.76 \text{ Å})\).

Consistent with experimental reports [56] and our previ-
ous calculations [14,15,45] we find graphite to be rather soft,
indicated by the bulk modulus \( B_0 \) value. Since in-plane
compression is very hard in graphite most of the softness
suggested by (the isotropic) \( B_0 \) comes from compression
perpendicular to the graphite layers, and the value of
\( B_0 \) is expected to be almost identical to the \( C_{33} \) elastic
We find the energy cost of peeling off a graphite layer from the graphite surface (the exfoliation energy) to be ∆E_{C,G} = −435 meV per (2 × 2) unit cell, i.e., −55 meV per surface carbon atom (Table I). A recent experiment measured the desorption energy of polycyclic aromatic hydrocarbons (basically flakes of graphite sheets) off a graphite surface. From this experiment the energy cost of peeling off a graphite layer from the graphite surface was deduced to −52 ± 5 meV/atom.

Our value −55 meV/C-atom is also consistent with a separate vdW-DF determination of the binding (−47 meV per in-plane atom) between two (otherwise) isolated graphene sheets.

For the energies of the absorbate system and of the C$_8$K intercalate a few other graphite-related energy contributions are needed. The energy of collecting C atoms to form a graphene sheet at lattice constant $a$ from isolated (spin-polarized) atoms is given by $\Delta E_{C,layer}(a)$; we find that changing the lattice constant $a$ from $a_0$ to the equilibrium value $a_{0,K}$ of C$_8$K causes this energy to change a mere 30 meV per (2 × 2) sheet. The contribution $\Delta E_{G,acc}$ is the energy of moving bulk graphite layers (in this case four periodically repeated layers) far away from each other, by expanding the unit cell along the direction perpendicular to the layers. Thus, $\Delta E_{G,acc} = 32\Delta E_{G,coh}(a_G, c_G/2) − 4\Delta E_{C,layer}(a_G)$ taking the number of atoms and layers per unit cell into account. We find the value $\Delta E_{G,acc} = −1600$ meV per (2 × 2) four-layer unit cell. This corresponds to −50 meV per C atom, again consistent with our result for the exfoliation energy, $\Delta E_{C,G}/8 = −55$ meV.

**B. Creating a layer of K-atoms**

The (artificial) step of creating a layer of potassium atoms from isolated atoms releases a significant energy $\Delta E_{K,layer}$. This energy contains the energy variation with in-plane lattice constant and the energy cost of changing from a spin-polarized to a spin-balanced electron configuration for the isolated atom.

The creation of the K-layer provides an energy gain which is about half an eV per potassium atom, depending on the final lattice constant. With the graphite lattice constant $a_G$ the energy change, including the spin-change cost, is $\Delta E_{K,layer}(a_G) = −476$ meV per K atom in vdW-DF (−624 meV when calculated within PBE), whereas $\Delta E_{K,layer}(a_{0,K}) = −473$ meV in vdW-DF.

**C. Graphite-on-surface adsorption of potassium**

The potassium atoms are adsorbed on a usual ABA…stacked graphite surface. We consider here full (one monolayer) coverage, which is one potassium atom per (2 × 2) graphite surface unit cell. This orders the potassium atoms in a honeycomb structure with lattice constant $2a_G$, and a nearest-neighbor distance within the K-layer of $a_G$.

The unit cell used in the standard DFT calculations for adsorption and absorption has a height of 40 Å and includes a vacuum region sufficiently big that no interactions (within GGA) can occur between the top graphene sheet and the slab bottom in the periodically repeated image of the slab. The vacuum region is also large in order to guarantee that the separation from any atom to the dipole layer always remains larger than 4 Å.

In the top panel of Fig. 4 we show the adsorption energy per potassium atom. The adsorption energy at equilibrium is −937 meV per K atom at distance $d_{C,K} = 3.02$ Å from the graphite surface.

For comparison we also show the adsorption curve calculated in a PBE-only traditional DFT calculation. Since

![Graphite cohesive energy](image)

**FIG. 3:** Graphite cohesive energy $E_{G,coh}$ (AB-stacked), based on vdW-DF, as a function of the carbon layer separation $d_{C,C}$ and the in-plane lattice constant $a$. The energy contours are spaced by 5 meV per carbon atom.

**TABLE I: Optimized structure parameters and elastic properties for natural hexagonal graphite (AB-stacking) and the potassium-intercalated graphite structure C$_8$K in A0A3A3A; A6Aα… stacking.** The table shows the calculated values of the in-plane lattice constant $a$, the (graphite-)layer-layer separation $d_{C,C}$, and the bulk modulus $B_0$. In C$_8$K the value if $d_{C,C}$ is twice the graphite-potassium distance $d_{C,K}$.

|          | Graphite | C$_8$K |
|----------|----------|--------|
|          | PBE      | vdW-DF | Exp. | PBE      | vdW-DF | Exp. |
| $a$ (Å)  | 2.473    | 2.476  | 2.459$^a$ | 2.494 | 2.494 | 2.480$^b$ |
| $d_{C,C}$ (Å) | 4      | 3.59   | 3.336$^a$ | 5.39  | 5.53  | 5.35$^c$ |
| $B_0$ (GPa) | 27     | 37$^{de}$ | 37  | 26  | 47$^{de}$ |

$^a$Ref. 46, $^b$Ref. 53, $^c$Ref. 4, $^d$Ref. 18.

*Value presented is for $C_{33}$; for laterally rigid materials, like graphite and C$_8$K, $C_{33}$ is a good approximation of $B_0$. 

Coefficient of expansion.
FIG. 4: Potassium adsorption and absorption energy at the graphite surface as a function of the separation $d_{C-K}$ of the K-atom layer and the nearest graphite layer(s) (at in-plane lattice constant corresponding to that of the surface, $a_G$). Top panel: Adsorption curve based on vdW-DF calculations (solid line with black circles) and PBE GGA calculations (dashed line). The horizontal lines to the left show the energy gain in creating the isolated K layer from isolated atoms, $\Delta E_{K-layer}(a_G)$, the asymptote of $E_{ads}(d_{C-K})$ in this plot. Bottom panel: Absorption curve based on vdW-DF calculations. The asymptote is here the sum $\Delta E_{K-layer}(a_G) - \Delta E_{C-G}$. Inset: Binding energy of the K-layer and the top graphite layer (“C-layer”) on top of the graphite slab, $\Delta E_{C-K-G}$. The dashed curve shows our results when in $E_{C}^{\text{nl}}$ ignoring every second FFT grid point (in each direction) of the charge density from the underlying GGA calculations, the solid curve with black circles shows the result of using every available FFT grid point.

the interaction between the K-layer and the graphite surface has a short-range component to it, even GGA calculations, such as the PBE curve, show significant binding ($-900$ meV/K-atom at $d_{C-K} = 2.96$ Å). This is in contrast to the pure vdW binding between the layers in clean graphite. Note that the asymptote of the PBE curve is different from that of the vdW-DF curve, this is due to the different energy gains ($\Delta E_{K-layer}$) in collecting a potassium layer from isolated atoms when calculated in PBE or in vdW-DF.

For K-adsorption the vdW-DF and PBE curves agree reasonably well, and the use of vdW-DF for this specific calculation is not urgently necessary. However, in order to compare the adsorption results consistently to absorption, intercalation and clean graphite, it is necessary to include the long-range interactions through vdW-DF. As shown for the graphite bulk results above, PBE yields quantitatively and qualitatively wrong results for the layer separation.

D. Graphite-subsurface absorption of potassium

The first subsurface adsorption of K takes place in the void under the top-most graphite layer. The surface adsorption of the first K-layer causes a lateral shift of the top graphite sheet, resulting in a $A/K/ABA\ldots$ stacking of the graphite. We have studied the bonding nature of this adsorption process by considering a full $p(2 \times 2)$-intercalated potassium layer in the subsurface of a four-layer thick graphite slab.

Following the receipt of Section III for the absorption energy (7) the energies $\Delta E_{C-K-G}$ are approximated by those from a four-layer intercalated graphite slab with the stacking $A/K/ABA$, and the values are shown in the inset of Fig. 4. The absorption energy $E_{abs}$ is given by the curve in the bottom panel of Fig. 4 and its minimum is $-952$ meV per K atom at $d_{C-K} = 2.90$ Å.

To investigate what grid spacing is sufficiently dense to obtain converged total-energy values in vdW-DF we do additional calculations in the binding distance region with a more sparse grid. Specifically, the inset of Fig. 4 compares the vdW-DF calculated at full gridding with one that uses only every other FFT grid point in each direction, implying a grid spacing for $E_{C}^{\text{nl}}$ (but not for the local terms) which is maximum 0.26 Å. We note that using the full grid yields smaller absolute values of the absorption energy. We also notice that the effect is more pronounced for small separations than for larger distances. Thus given resources, the dense FFT grid calculations are preferred, but even the less dense FFT grid calculations yield reasonably well-converged results. In all calculations (except tests of our graphitic systems) we use a spacing with maximum 0.13 Å between grid points. This is a grid spacing for which we have explicitly tested convergence of the vdW-DF for graphitic systems given the computational strategy described and discussed in Sec. III.

E. Potassium-intercalated graphite

When potassium atoms penetrate the gallery of the graphite, they form planes that are ordered in a $p(2 \times 2)$ fashion along the planes. The K intercalation causes a shift of every second carbon layer resulting into an $AA$ stacking of the graphite sheets. The K atoms then simply occupy the sites over the hollows of every fourth carbon hexagon. The order of the K atoms perpendicular to the planes is described by the $a_\parallel b_\parallel \gamma_\parallel \delta_\parallel$ stacking, illustrated in Fig. 2.

For the potassium intercalated compound $C_8K$ we calculate in standard DFT using PBE the total energy at 132 different combinations of the structural parameters $a$
TABLE II: Comparison of the graphite exfoliation energy per surface atom, $E_{C,G}/8$, graphite layer binding energy per carbon atom, $\Delta E_{C,acc}/32$, the energy gain per K atom of collecting K- and graphite-layers at equilibrium to form $C_8K$, $\Delta E_{C,acc}/4$, and the equilibrium formation energy of $C_8K$, $E_{form}$.

| Method    | $\Delta E_{C,G}/8$ [meV/atom] | $\Delta E_{C,acc}/32$ [meV/atom] | $\Delta E_{C,K,acc}/4$ [meV/C$_8$K] | $E_{form}$ [meV/C$_8$K] |
|-----------|-------------------------------|---------------------------------|-----------------------------------|----------------------|
| vdW-DF    | $-55$                         | $-50$                           | $-818$                           | $-861$               |
| PBE       | $-$                           | $-$                             | $-511$                           | $-$                  |
| Exp.      | $-52 \pm 5^a$                | $-$                             | $-$                              | $-1236^b$           |

*aRef. 51*  
*bRef. 1*

FIG. 5: Formation energy of $C_8K$, $E_{form}$, as a function of the carbon-to-carbon layer separation $d_{C,C}$ and half the in-plane lattice constant, $a$. The energy contours are spaced by 20 meV per formula unit.

and $d_{C,C}$. The charge densities and energy terms of these calculations are then used as input to vdW-DF. The equilibrium structure and elastic properties ($B_0$) both for the vdW-DF results and for the PBE results are then evaluated with the same method as in the graphite case.

Figure 5 shows a contour plot of the $C_8K$ formation energy, calculated in vdW-DF, as a function of the C-C layer separation ($d_{C,C}$) and the in-plane periodicity ($a$) of the graphite-layer structure. The contour spacing is 20 meV per formula unit and are shown relative to the energy minimum at ($a$, $d_{C,C}$) = (2.494 Å, 5.53 Å).

V. DISCUSSION

Table I presents an overview of our structural results obtained with the vdW-DF for graphite and $C_8K$. The table also contrasts the results with the corresponding values calculated with PBE where available. The vdW-DF value $d_{C,C} = 5.53$ Å for the $C_8K$ $C-C$ layer separation is 3% larger than the experimentally observed value whereas the PBE value corresponds to less than a 1% expansion. Our vdW-DF result for the $C_8K$ bulk modulus (26 GPa) is also softer than the PBE result (37 GPa) and further away from the experimental estimates (47 GPa) based on measurements of the $C_{33}$ elastic response. A small overestimation of atomic separation is consistent with the vdW-DF behavior that has been documented in a wide range of both finite and extended systems. This overestimation results, at least in part, from our choice of parametrization of the exchange behavior—an aspect that lies beyond the present vdW-DF implementation which focuses on improving the account of the nonlocal correlations, per se. It is likely that systematic investigations of the exchange effects can further refine the accuracy of vdW-DF implementations. In any case, vdW-DF theory calculations represent, in contrast to PBE, the only approach to obtain a full ab initio characterization of the AM intercalation process.

The $C_8K$ system is more compact than graphite and this explains why PBE alone can here provide a good description of the materials structure and at least some materials properties, whereas it fails completely for graphite. The distance between the graphene sheets upon intercalation of potassium atoms is stretched compared to that of pure graphite, but the (K)-layer to (graphite)-layer separation, $d_{C,K} = d_{C,C}/2 = 2.77$ Å, is significantly less than the layer-layer separation in pure graphite. This indicates that $C_8K$ is likely held together, at least in part, by shorter-ranged interactions.

Table II documents that the vdW binding nevertheless plays an important role in the binding and formation of $C_8K$. The table summarizes and contrasts our vdW-DF and PBE results for graphite exfoliation and layer binding energies as well as $C_8K$ interlayer binding and formation energies. The vdW-DF result for the $C_8K$ formation energy is smaller than experimental measurements by 31% but it nevertheless represent a physically motivated ab initio calculation. In contrast, the $C_8K$ formation energy is simply unavailable in PBE because PBE, as indicated, fails to describe the layer binding in graphite. Moreover, for the vdW-DF/PBE comparisons that we can make—for example, of the $C_8K$ layer interaction $\Delta E_{C,K,acc}$—the vdW-DF is found to significantly strengthen the bonding compared with PBE.

It is also interesting to note that the combination of shorter-ranged and vdW bonding components in $C_8K$ yields a layer binding energy that is close to that of the graphite case. In spite of the difference in nature of interactions, we find almost identical binding energies per layer for the case of the exfoliation and accordion in graphite and for the accordion in $C_8K$. This observation testifies to a perhaps surprising strength of the so-called soft matter vdW interactions.

In a wider perspective our vdW-DF permits a first comparison of the range of AM-graphite systems from adsorption over absorption to full intercalation and thus
insight on the intercalation progress. Assuming a dense 2 × 2 configuration, we find that the energy for potassium adsorption and absorption is nearly degenerate with an indication that absorption is slightly preferred, consistent with experimental behavior. We also find that the potassium absorption may eventually proceed towards full intercalation thanks to a significant release of formation energy.

VI. CONCLUSIONS

The potassium intercalation process in graphite has been investigated by means of the vdW-DF density functional method. This method includes the dispersive interactions needed for a consistent investigation of the intercalation process. For clean graphite the vdW-DF predicts — contrary to standard semilocal DFT implementations — a stabilized bulk system with equilibrium crystal parameters in close agreement with experiments. Two limits of the absorption process have been investigated by the vdW-DF, namely single layer subsurface absorption and the fully potassium intercalated stage-1 crystal C₃K. Here the vdW-DF is shown to enhance the (semi-)local type of bonding described by traditional approaches. The significant impact on the materials behavior indicates that the vdW-DF is needed not only for a consistent description of sparse matter systems that are solely stabilized by dispersion forces, but also for their intercalates.

We thank D.C. Langreth and B.I. Lundqvist for stimulating discussions. Partial support from the Swedish Research Council (VR), the Swedish National Graduate School in Materials Science (NFSM), and the Swedish Foundation for Strategic Research (SSF) through the consortium ATOMICS is gratefully acknowledged, as well as allocation of computer time at UNICC/C3SE (Chalmers) and SNIC (Swedish National Infrastructure for Computing).

* Electronic address: hyldgaard@chalmers.se

1. S. Aronson, F.J. Salzano, and D. Ballafiore, J. Chem. Phys. 49, 434 (1968).
2. D.E. Nixon and G.S. Parry, J. Phys. D 1, 291 (1968).
3. R. Clarke, N. Wada, and S.A. Solin, Phys. Rev. Lett. 44, 1616 (1980).
4. M.S. Dresselhaus and G. Dresselhaus, Adv. Phys. 30, 139 (1981).
5. D.P. DiVincenzo and E.J. Mele, Phys. Rev. B 32, 2538 (1985).
6. N.B. Hannay, T.H. Geballe, B.T. Matthias, K. Andreas, P. Schmidt, and D. MacNair, Phys. Rev. Lett. 14, 225 (1965).
7. R.A. Jishi and M.S. Dresselhaus, Phys. Rev. B 45, 12465 (1992).
8. T. Kihlgren, T. Balasubramanian, L. Walldén, and R. Yakimova, Surf. Sci. 600, 1160 (2006).
9. M. Breitholtz, T. Kihlgren, S.-Å. Lindgren, and L. Walldén, Phys. Rev. B 66, 153401 (2002).
10. I. Forbeaux, J.-M. Themlin, and J.-M. Debever, Phys. Rev. B 58, 16396 (1998).
11. T. Kihlgren, T. Balasubramanian, L. Walldén, and R. Yakimova, Phys. Rev. B 66, 235422 (2002).
12. I. Forbeaux, J.-M. Themlin, A. Charrier, F. Thibaudau, and J.-M. Debever, Appl. Surf. Sci. 162–163, 406 (2000).
13. E. Ziambaras, Ph.D. thesis, Chalmers (2006).
14. H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S.I. Simak, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. 91, 126402 (2003).
15. D.C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B.I. Lundqvist, Int. J. Quantum Chem. 101, 599 (2005).
16. M. Dion, H. Rydberg, E. Schröder, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004); 95, 109902(E) (2005).
17. T. Thonhauser, V.R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D.C. Langreth, Van der Waals density functional: Self-consistent potential and the nature of the van der Waals bond, http://arxiv.org/abs/cond-mat/0703442
18. N. Wada, R. Clarke, and S.A. Solin, Solid State Comm. 35, 675 (1980).
19. H. Zabel and A. Magerl, Phys. Rev. B 25, 2463 (1982).
20. J.C. Barnard, K.M. Hock and R.E. Palmer, Surf. Science 287–288, 178 (1993).
21. K. M. Hock and R. E. Palmer, Surf. Science 284, 349 (1993).
22. Z.Y. Li, K.M. Hoch, and R.E. Palmer, Phys. Rev. Lett. 67, 1562 (1991).
23. S.D. Chakarova and E. Schröder, Materials Science and Engineering C 25, 787 (2005).
24. L.A. Girifalco and M. Hodak, Phys. Rev. B 65, 125404 (2002).
25. J.P. Perdev, J.A. Chevary, S.H. Vesko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B 48, 6671 (1992).
26. J.P. Perdev, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
27. Y. Zhang and W. Yang, Phys. Rev. Lett. 80, 890 (1998).
28. B. Hammer, L.B. Hansen, and J.K. Nørskov, Phys. Rev. B 59, 7413 (1999).
29. S.D. Chakarova-Käck, J. Kleis, and E. Schröder, Appl. Phys. Rep. 2005-16 (2005).
30. J. Kleis, B.I. Lundqvist, D.C. Langreth, and E. Schröder, Towards a working density-functional theory for polymers: First-principles determination of the polyethylene crystal structure, http://arxiv.org/abs/cond-mat/0611498
31. S.D. Chakarova-Käck, E. Schröder, B.I. Lundqvist, and D.C. Langreth, Phys. Rev. Lett. 96, 146107 (2006).
32. S.D. Chakarova-Käck, O. Börck, E. Schröder, and B.I. Lundqvist, Phys. Rev. B 74, 155402 (2006).
33. A. Puzder, M. Dion, and D.C. Langreth, J. Chem. Phys. 124, 164105 (2006).
34. T. Thonhauser, A. Puzder, and D.C. Langreth, J. Chem. Phys. 124, 164106 (2006).
35. D.D.L. Chung, J. Mat. Sci. 37, 1475 (2002).
36. M. Breitholtz, T. Kihlgren, S.-Å. Lindgren, H. Olin, E.
Wahlström, and L. Walldén, Phys. Rev. B 64, 073301 (2001).
37 Z.P. Hu, N.J. Wu, and A. Ignatiev, Phys. Rev. B 33, 7683 (1986).
38 J. Cui, J.D. White, R.D. Diehl, J.F. Annett, and M.W. Cole, Surf. Sci. 279, 149 (1992).
39 L. Österlund, D.V. Chakarov, and B. Kasemo, Surf. Sci. 420, L437 (1991).
40 Y. Baskin and L. Meyer, Phys. Rev. 100, 544 (1955).
41 W. Eberhardt, I.T. McGovern, E.W. Plummer, and J.E. Fisher, Phys. Rev. Lett. 44, 200 (1980).
42 A.R. Law, J.J. Barry, and H.P. Hughes, Phys. Rev. B 28, 5332 (1983).
43 R. Ahuja, S. Auluck, J. Trygg, J.M. Wills, O. Eriksson, and B. Johansson, Phys. Rev. B 51, 4813 (1995).
44 N.A.W. Holzwarth, S.G. Louie, and S. Rabii, Phys. Rev. B 26, 5382 (1982).
45 H. Rydberg, N. Jacobson, P. Hyldgaard, S.I. Simak, B.I. Lundqvist, and D.C. Langreth, Surf. Sci. 532-535, 606 (2003).
46 Open-source plane-wave DFT computer code DACapo, http://www.fysik.dtu.dk/CAMPOS/]
47 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
48 H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13, 5188 (1976).
49 D.C. Langreth, private communication; J. Kleis and P. Hyldgaard, unpublished.
50 The transition from on-surface adsorption to subsurface absorption is identified in experiment by a work function change, Refs. [20 and [21].
51 R. Zacharia, H. Ulbricht, and T. Hertel, Phys. Rev. B 69, 155406 (2004).
52 E. Ziambaras and E. Schröder, Phys. Rev. B 68, 064112 (2003).
53 D.E. Nixon and G.S. Parry, J. Phys. C 2, 1732 (1969).
54 O. Gunnarsson, B.I. Lundqvist, and J.W. Wilkins, Phys. Rev. B 10, 1319 (1974). Since no spin-polarized version of vdW-DF exists at present, we calculate the the energy cost for changing the spin of isolated potassium atoms in PBE. The spin-change cost is thus determined to be 26 meV/K-atom.
55 L. Bengtsson, Phys. Rev. B 59, 12301 (1999), and references therein.
56 The choice of exchange flavor in vdW-DF was set in Ref. [15] to avoid artificial bonding in noble-gas systems and to better mimic exact exchange calculations for those systems. However, it is far from certain and even unlikely that the conclusions drawn for noble-gas systems carry over to bonding separations smaller than 3 Å.