Structural Energies in Stage-One Graphite Intercalation Compounds

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A Thomas-Fermi density-functional theory is developed for structural energies in stage-one alkali-graphite intercalation compounds. Correct trends for lattice constants and elastic moduli are obtained. We compute corrugation energies ΔE and alkali-alkali spring constants k, which determine in-plane intercalant diffusion and domain-wall structure. k is determined by electrostatic effects, and is mainly independent of intercalant. ΔE depends strongly on intercalant size; thus Li differs substantially from K, Rb, and Cs.

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We have developed a Thomas-Fermi–type density-functional theory for structural energies in first-stage alkali-metal–graphite compounds. A variety of phenomena have been studied in these compounds which are of general interest in two-dimensional physics, including the dynamics of domain growth,[1] two-dimensional liquid-state diffusion,[2] and domain-wall structure in incommensurate systems.[3] We will briefly explain our formalism and demonstrate its utility by computing the lattice constants and elastic moduli for the stage-one alkali-graphite intercalation compounds; we find that experimental trends are reproduced correctly by our theory. We then identify and compute several key structural parameters which are relevant for the phenomena mentioned above.

We use density-functional theory because of its proven reliability for the ground-state properties of a wide class of solids.[4] We are interested in computing small variations in the energy of a substantial number of atomic configurations in a variety of compounds having low symmetry and large unit cells, and we judge that a self-consistent density-functional approach involving the solution of a wave equation would be far too costly for our purposes. Instead a simplified formulation employing the Thomas-Fermi approximation has been used; we have already described this approach as applied to pure graphite.[5] Its main advantage is that the total energy is written as a functional of the charge density *only*:

$$E_T[\rho] = T_{\mathrm{TF}}[\rho_v] + T^{(1)}[\nabla\rho_v] + V_{\mathrm{C}}[\rho_v] + V_{xc}[\rho_c + \rho_v], \qquad (1)$$

i.e., kinetic energies T plus potential energies V. ρ_v denotes the valence and ρ_c the core charge densities of the solid. T_{TF} represents a Thomas-Fermi kinetic energy ($\sim\rho^{5/3}$), and $T^{(1)}$ is a gradient correction to T_{TF} of the von Weizsäcker form,[6] $\gamma|\nabla\rho|^2/\rho$. This form of the kinetic energy is only valid in the limit of slowly varying densities; therefore we evaluate T as a function of the valence charge ρ_v only. The core contributions to the kinetic energy are incorporated in a pseudopotential[7] which is used in the evaluation of the Coulomb energy $V_{\mathrm{C}}[\rho]$. V_{C} thus contains both the classical electrostatic energy of the system and the core part of the kinetic energy. The final term, V_{xc}, represents the electronic exchange and correlation energies evaluated in the standard local-density approximation. V_{xc} has a nonlinear dependence on ρ, so that it is important[8] to use the full charge density $\rho = \rho_v + \rho_c$ in its evaluation.

The crucial simplification in the present implementation of density-functional theory comes in the choice of ρ_v, the input to Eq. (1). To obtain ρ_v we first use a fully self-consistent, wave-mechanical density-functional formulation to compute the wave functions ψ_g of a single plane of graphite in isolation from the rest of the system. The charge density of each graphite plane in the intercalation compound is then taken to be $\rho_g(r) = \int^{k_{\mathrm{F}}^+} |\psi_g(r,k)|^2 \times d^3k$. The Fermi level k_{F}^+ is fixed so that both the carbon and intercalant electrons are accommodated in the graphite bands; full charge transfer is assumed. We then assemble these planes into a three-dimensional crystal and construct ρ_v by linear superposition[9]: $\rho_v(\vec{r}) = \sum_{\vec{R}} \rho_g(\vec{r} - \vec{R})$. ($\vec{R}$ specifies the positions of the graphite planes in the crystal). The alkali atoms enter Eq. (1) in V_{C} through their ionic pseudopotential and in V_{xc} through ρ_c. By this scheme ρ_v contains the real physics of the covalent C bond charge, which would be poorly described by a variational minimization of the approximate functional E_T of Eq. (1). E_T is only required to describe small *changes* involving alkali-alkali and alkali-graphite interactions.

With this construction of ρ_v we obtain the total energy E_T from Eq. (1). V_C is obtained by an Ewald summation, while the other terms require three-dimensional integrals over the unit cell which are performed by Fourier techniques. We achieve an overall numerical accuracy of 0.03 eV per intercalant atom.[10] In Fig. 1 we give several examples of our calculated energies versus out-of-plane spacing c_0. Li and K results are shown, with in-plane densities fixed at ambient values: $\mathrm{LiC_6}$ and $\mathrm{KC_8}$. $\mathrm{RbC_8}$ and $\mathrm{CsC_8}$ are quite similar to $\mathrm{KC_8}$. A number of features are common to both the Li and the heavy alkali compounds. In both, Coulomb and exchange-correlation contributions dominate the total energy. The start of an increase in V_C at large lattice constant in $\mathrm{LiC_6}$ (and its rise slightly beyond the edge of the plot for $\mathrm{KC_8}$) is a direct manifestation of the strong attractive electrostatic force between the positively charged alkali planes and the negatively charged C planes. At shorter distance the effective Coulomb energy becomes repulsive; this is a reflection of the pseudopotential approximation which, as mentioned above, folds some of the core energies into an effective ionic interaction. This repulsion becomes important at much shorter layer spacing in $\mathrm{LiC_6}$ than in $\mathrm{KC_8}$. The smaller lattice constant of $\mathrm{LiC_6}$ is due to the greater binding energy of its shallowest core electron (~ -60 eV) as compared with the heavier alkali metals (~ -20 eV)—the Li core is much more compact than the others.

From Fig. 1 we have computed the out-of-plane lattice constant c_0 and the elastic moduli C_{33} (the out-of-plane compressional modulus) and C_{44} (the shear modulus) for all of the stage-one alkali-graphite compounds; our results are shown in Fig. 2. As the top panel shows, our ionic model is capable of accurately predicting the out-of-plane lattice constants (to within 2%) for all the alkali compounds except Li. For Li we obtain a lattice constant which is about 20% too large. We speculate that this is evidence for a degree of covalency in the Li-C interaction which induces an additional contraction in the layer spacing.[11] Still, our calculation correctly reproduces the trend in the alkali-graphite lattice constant.

C_{33} in Fig. 2 is obtained from the curvature of E_T in Fig. 1 around equilibrium. This calculation is more demanding than that for c_0 and is not as quantitatively accurate as the one for the equilibrium lattice constant itself. Still, it correctly reproduces the observed[12] trends in C_{33}: high for $\mathrm{LiC_6}$, low for $\mathrm{KC_8}$ and $\mathrm{RbC_8}$, and slightly higher again for $\mathrm{CsC^8}$. The computations used to obtain the shear modulus C_{44} are similar to those displayed in Fig. 1 (Ref. 10); we simply apply a small shear strain to the crystal and monitor the change in E_T. As for C_{33} we reproduce trends down the alkali column for

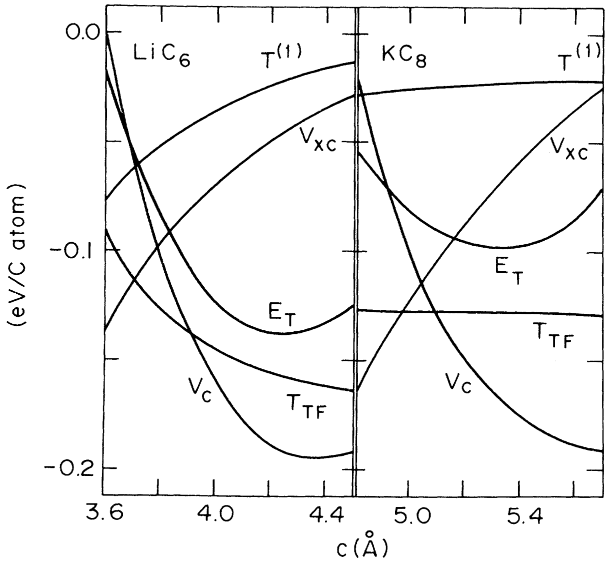

FIG. 1. The total energy and its components as a function of plane-plane separation for the compounds $\mathrm{LiC_6}$ and $\mathrm{KC_8}$.

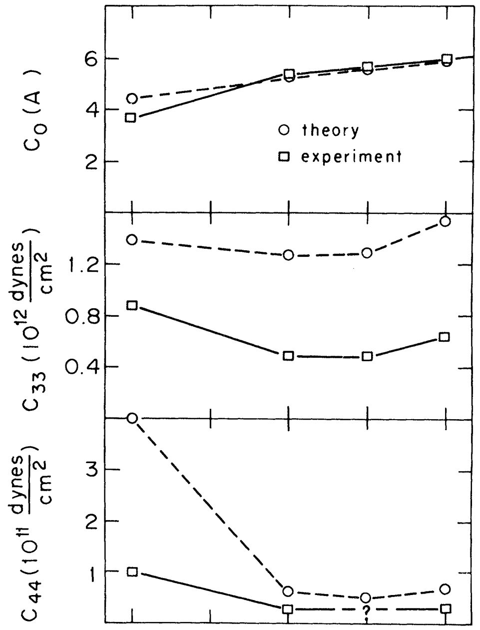

FIG. 2. Out-of-plane lattice constant c_o, compressional modulus C_{33}, and shear modulus C_{44} for the first-stage alkali-metal–graphite intercalation compounds. Theory is shown by circles, experiment (from Ref. 12) by squares.

C_{44}. This is notable since C_{44} is generally a factor of 10 smaller than C_{33}; this shows that we can accurately predict phenomena occurring on widely different energy scales.

Having established the applicability of our Thomas-Fermi scheme to alkali-graphite energetics, we now show the results of further calculations which apply this method to study the two-dimensional structural phenomena mentioned at the outset.

By studying large amplitude strains of the intercalant planes relative to the C planes, we have computed the activation energy (sometimes called the corrugation energy) for intercalant-atom motion parallel to the host planes. The kinetics of domain growth[1] and steady-state diffusion in the two-dimensional liquid state[2] are both determined by this corrugation. We find the minimum-energy alkali position to be over the center of a C hexagon. As expected, the saddle point for motion to the neighboring preferred site passes over the center of a C-C bond. The energy per intercalant at the saddle point relative to the minimum, ΔE, is given in Table I. While these calculations have been performed for stage-one compounds for specific in-plane densities, they have more general applicability.[13] Therefore we have used the ΔE's of Table I to estimate the in-plane alkali in-plane diffusion constants D which are relevant for the stage-two alkali compounds, for which measurements have been performed.[2] We estimate D using[10] $D \approx a^2 \nu_0 \times \exp(-\Delta E/kT)$, where ν_0 is an in-plane alkali vibrational frequency and a is the in-plane graphite lattice constant, $a = 2.46$ Å. For the Rb and Cs compounds the agreement is quite satisfactory.

From a theoretical point of view the most striking trend in the corrugation energy ΔE is the much greater activation barrier for Li than for the other alkali compounds. Recent neutron measurements confirm[14] that ΔE is indeed quite large for LiC_6 ($\Delta E \approx 0.7$ eV). The D for Li in Table I is much too low, however; the mechanism for Li diffusion may well be different from the hopping model used above, and it may involve both C-plane and Li motions.[10] Our theory shows that this difference between the ΔE's of Li and the other alkalis has a very simple origin. Since the Li atoms lie much closer to the C planes than does K, Rb, or Cs, they move through a host charge density with a much greater in-plane corrugation amplitude. Thus the energy of the Li's varies more strongly with in-plane position.

TABLE I. Barrier heights, theoretical and experimental diffusion constants, and intrinsic alkali-alkali spring constants for the stage-one compounds. We take $T = 523$ K.

X	ΔE (eV)	D (cm^2/sec)	D_{expt} (cm^2/sec)	k (eV/Å^2)
Li	1.30	1.0×10^{-5}	. . .	0.25
K	0.18	1.0×10^{-5}	. . .	0.26
Rb	0.14	2.0×10^{-5}	5.7×10^{-5} [a]	0.28
Cs	0.18	0.7×10^{-5}	7.6×10^{-5} [a]	0.28

[a] Ref. 2.

Under some conditions the in-plane alkali lattice contains locally registered domains[3] separated periodically by domain walls[15] (i.e., "discommensurations" or "solitons"). The structure of these walls is determined by a competition between the intercalant-host interaction characterized by the corrugation energy ΔE and the intercalant-intercalant interaction. In order to estimate the compliance of the intercalant layer exclusive of corrugation effects, we perform a new set of Thomas-Fermi calculations in which the graphite charge density is averaged parallel to the host planes. This frees the calculation from the constraint of periodicity and permits the intercalant energy to be studied as a continuous function of the in-plane alkali-alkali lattice constant. The curvature of the resulting total energy around the LiC_6 or MC_8 (M = K, Rb, Cs) concentration provides an estimate of the effective "spring constant" k for nearest-neighbor alkali-alkali interactions—see Table I. k is reasonably independent of alkali species; the alkali-alkali interaction is dominated by the classical electrostatic energies V_C. The overall behavior of the in-plane V_C is a general feature of the lamellar charge distribution in the intercalation compound[16] and is hence relatively insensitive to the details of the alkali species.

According to Bak,[15] ΔE and k determine domain-wall widths w according to[15] $w \sim 2a^2(2k/\Delta E)^{1/2}$. The predicted domain-wall widths for the K, Rb, and Cs compounds are fairly large, about five alkali lattice constants ($w \sim 15$ Å). However, for Li the corrugation ΔE dominates k and w is very small, les than one lattice spacing. The resulting prediction[15] is that domain-wall lattices should be well organized in the heavy alkalis but rather "chaotic" in Li-graphite. Domain-wall lattices have been seen in stage-two K and Rb compounds,[3] although domain-wall widths have not been estimated. Domain walls have not been studied in the Li compound.

In summary, we have developed a Thomas-Fermi–type density-functional theory which provides an economical means of calculating structural energies in graphite intercalation compounds. We verify that this theory correctly reproduces trends in the lattice constants and elastic moduli of these compounds. We identify and compute two key parameters, the corrugation energy ΔE and the alkali-layer compliance k. ΔE and k determines the physics of alkali diffusion and of domain-wall structure. k is almost invariant from compound to compound because it is determined by simple electrostatic forces which are general to lamellar structures. On the other hand, ΔE depends strongly on the lattice constant c_0 and is thus much greater for Li-graphite. Thus Li-graphite has a higher activation energy for diffusion and should exhibit narrower and more disordered domain walls.

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