

# Charge density and charge transfer in stage-1 alkali-graphite intercalation compounds

C. Hartwigsen, W. Witschel, and E. Spohr

Department of Theoretical Chemistry, University of Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

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First-principles electronic structure calculations are carried out for the stage-1 alkali graphite intercalation compounds  $\text{LiC}_6$  and  $\text{XC}_8$  ( $X=\text{Li, Na, K, Rb, and Cs}$ ). We analyze the charge densities and the differences to the reference charge densities of graphite host and intercalant sublattice. For the alkali metals Na, K, Rb, and Cs the computed charge transfer is nearly constant at a value of 0.7 elementary charges ( $e$ ); values of  $0.5e$  and  $0.4e$  are found for the Li compounds  $\text{LiC}_6$  and  $\text{LiC}_8$ , respectively. It is shown that the main fraction, about  $0.4e$ , of the charge transfer is a geometrical consequence of the simple overlap of the charge densities of the graphite and intercalant sublattices. [S0163-1829(97)05508-2]

## I. INTRODUCTION

Graphite intercalation compounds (GIC's) have been the subject of many experimental and theoretical investigations (Dresselhaus and Dresselhaus<sup>1</sup> and references therein<sup>2</sup>). The anisotropy of these materials results in unusual electronic and chemical properties. Especially the Li compounds have received experimental attention due to their possible applications in electrochemical cells.<sup>3</sup> GIC's are commonly classified into donor and acceptor types, depending on whether the graphite layers in the GIC acquire a negative or a positive charge. In alkali GIC's the metal atoms always act as donors. Nevertheless the exact magnitude of charge transfer in GIC's has been highly controversial in spite of the progress made in both experimental and theoretical methods.

During the past ten years the local density approximation within the density-functional theory has been developed to a commonly accepted model for calculating electronic and structural properties of solids. Once the electronic ground state of a system is determined partial charges of each atom and therefore the charge transfer occurring in the system can be assigned. Unfortunately "charge transfer" is not observable in a quantum-mechanical sense, i.e., there is no unambiguous way to calculate its value from the electronic ground-state wave function. Several different methods have been proposed to distribute the total charge between the atoms constituting the system. Most theoretical treatments of charge transfer are based on the projection of the electronic wave functions<sup>4-6</sup> or charge densities<sup>7</sup> onto selected atomic reference states. But even the same method can lead to different results due to the use of different orbital representations.<sup>8</sup> Other methods assign point charges to the atomic positions in order to fit the computed electrostatic potential at a number of points on or near the van der Waals surface.<sup>9</sup> Because of this lack of a unique definition of the term "charge transfer" the use of different methods has led to the controversy over the experimental and theoretical results for the alkali GIC's. We present here the results of a parameter-free *ab initio* study of a series of stage-1 alkali GIC's. All calculations have been performed by exactly the same theoretical model and analysis, so that trends within the series can become obvious. Previous theoretical studies of

the charge transfer considered only a subset of the alkali GIC's that we take into account in the present study.

## II. METHOD

### A. Computational details

In our *ab initio* study the charge density is calculated within the framework of the local-density approximation to the density-functional theory (LDA/DFT). The electron-ion interactions are described by separable norm-conserving pseudopotentials in the Kleinman-Bylander form.<sup>10</sup> Exchange and correlation energy is calculated with the parametrization given by Perdew and Zunger<sup>11</sup> according to the quantum Monte Carlo results of Ceperley and Alder.<sup>12</sup> The single-particle orbitals are expanded in a plane-wave basis set with a cutoff energy of 60 Rydberg (Ry) at 9 or 18 special  $\mathbf{k}$  points in the Brillouin zone. The Kohn-Sham equations are solved by direct minimization of the total-energy functional with a preconditioned conjugated gradient scheme.<sup>13,14</sup> Periodic boundary conditions are applied throughout all calculations.

For carbon and the alkali metals smooth pseudopotentials have been generated using the scheme of Troullier and Martins.<sup>15</sup> Pseudopotential parameters are summarized in Table I. The pseudopotential parameters for carbon are taken from Ref. 16. For lithium and sodium one-electron pseudopotentials have been generated for  $l=0$  and  $l=1$  where

TABLE I. Pseudopotential parameters for the alkali metals.  $r_l$  ( $l=0,1,2$ ) are cutoff radii.  $l_{\text{loc}}$  stands for the angular momentum of the local part of the pseudopotential.  $Z$  is the number of valence electrons. For potassium an excited configuration, given in the second line, is used for the generation of the  $l=2$  part of the potential (see Ref. 50).

|    | $Z$ | Configuration         | $r_{l=0}$ | $r_{l=1}$ | $r_{l=2}$ | $l_{\text{loc}}$ |
|----|-----|-----------------------|-----------|-----------|-----------|------------------|
| Li | 1   | $2s^1 2p^0$           | 2.37      | 2.37      |           | 1                |
| Na | 1   | $3s^1 3p^0$           | 2.94      | 2.94      |           | 1                |
| K  | 7   | $3p^6 3d^0 4s^1$      | 3.51      | 1.06      | 3.69      | 0                |
|    |     | $3p^6 3d^{0.25} 4s^0$ |           |           |           |                  |
| Rb | 7   | $4p^6 4d^0 5s^1$      | 3.49      | 1.38      | 3.70      | 0                |
| Cs | 7   | $5p^6 5d^0 6s^1$      | 3.98      | 2.00      | 2.98      | 0                |

$l=1$  has been chosen as the local part. For the heavier alkali metals simple one-electron pseudopotentials are known to give only poor results. The frozen core assumption fails as the inner  $p$  electrons show significant relaxation depending on the chemical environment.<sup>17</sup> Within the pseudopotential approach this effect can be taken into account by either introducing a nonlinear core-exchange correction<sup>18</sup> or explicitly treating the inner  $p$  electrons as valence states.<sup>19,20</sup> The second possibility is more straightforward and we treat the inner  $p$  electrons explicitly. Due to the localized nature of the  $p$  electrons their description by a plane-wave basis set requires large cutoff energies of 50 to 60 Ry to yield sufficiently converged results. Nevertheless this requirement does not increase the computational effort substantially, as for an appropriate treatment of the weak interplanar interactions in GIC's a cutoff energy of approximately 60 Ry is required. For K, Rb, and Cs the  $l=0$  component is chosen to be the local part of the pseudopotential; nonlocal parts are incorporated for  $l=1,2$ . In the case of Rb and Cs semirelativistic pseudopotentials have been generated by averaging over all scalar terms of the fully relativistic potentials.<sup>21</sup> All pseudopotentials have been carefully tested by calculating the lattice constants of diamond and the bcc alkali-metal crystals. All our results are close to the experimental values with errors typical for DFT-pseudopotential studies of these materials.<sup>19,22</sup>

Several equivalent intercalation sites in GIC's, denoted by Greek letters, exist for the intercalants within a single plane. The arrangement of the intercalants in adjacent planes is called the stacking sequence. A stacking sequence  $\alpha\alpha$  means that all intercalants in different planes have the same positions when looking along the  $c$  axis. For computational reasons calculations are performed for a single unit cell with intercalant stacking sequence  $\alpha\alpha$  which, except in the case of  $\text{LiC}_6$ , differs from the experimentally observed stacking sequence. As a test, we also calculated the properties of  $\text{KC}_8$  with stacking sequence  $\alpha\beta$ . Almost the same value for the charge transfer is obtained, indicating that the stacking sequence is only of minor importance. All calculations are performed with the experimentally determined lattice constants<sup>23</sup> except for the hypothetical compounds  $\text{LiC}_8$  and  $\text{NaC}_8$ . Lattice constants of the hexagonal unit cell of  $\text{LiC}_8$  ( $a=4.64$  Å,  $c=3.58$  Å) and  $\text{NaC}_8$  ( $a=4.94$  Å,  $c=4.78$  Å) are determined by minimizing the total energy with respect to the lattice constants.

### B. Calculation of the charge transfer

The electronic charge of an atom  $i$  can be obtained by integrating the total charge density within the volume  $V_i$  belonging to this particular atom. The atoms-in-molecules construction by Bader<sup>24</sup> is used to define each volume  $V_i$ . The Bader construction is a physically motivated distribution of the total volume between atoms that is based on the topology of the total electronic charge distribution. The boundary surface of  $V_i$  is defined by the condition that the gradient of the electronic density,  $n(\mathbf{r})$ , is zero on this surface, i.e.,

$$\nabla n(\mathbf{r}) = 0. \quad (1)$$

Therefore, the total charge  $Q_i$  of an atom  $i$  in a chemical compound is defined as

$$Q_i \equiv Z_i - \frac{1}{\Omega} \int_{V_i} d\mathbf{r} n(\mathbf{r}), \quad (2)$$

where  $Z_i$  is the atomic number of atom  $i$ , and  $\Omega$  the volume of the elementary cell. As a consequence of this definition the charge transfer occurring in a system can be divided into two components:<sup>25</sup> the first component corresponds to the change of charge due to the change of the volume  $V_i$  of atom  $i$  when another atomic species is introduced into the system. This so-called geometrical charge transfer occurs in every system, even if there are no physical interactions between the primary system and the added atoms. The second component of the charge transfer is caused by the donor or acceptor character of the added atomic species, resulting in a transfer of charge density into or out of the volume  $V_i$ .

In order to distinguish between the purely geometrical effect and the charge transfer due to physical interactions, the actual charge density  $n(\mathbf{r})$  in Eq. (2) has to be replaced by the difference charge density

$$\delta n(\mathbf{r}) = n(\mathbf{r}) - n_{\text{ref}}(\mathbf{r}). \quad (3)$$

$n_{\text{ref}}(\mathbf{r})$  is the superposition of the charge densities of the graphite host and the intercalant sublattice, calculated separately in the geometry of the compound system. The charge transfer calculated from  $\delta n(\mathbf{r})$  will be called physical charge transfer as it takes into account only the changes of  $n(\mathbf{r})$  caused by physical interactions between the graphite host and the intercalant. The total charge transfer is the sum of the geometrical and the physical components.

In the case of the layered GIC's, the analysis of the charge densities can be greatly simplified if plane-averaged densities

$$n(z) = \frac{1}{A_{xy}} \int \int_{\Omega} dx dy n(\mathbf{r}) \quad (4)$$

are considered rather than the complete three-dimensional density  $n(\mathbf{r})$  ( $A_{xy}$  is the area of the plane in the unit cell). In this case the boundary between the graphitic sheets and the intercalant planes [Eq. (1)] is replaced by a single point  $z_{\text{bdy}}$  where the condition

$$\left. \frac{dn(z)}{dz} \right|_{z_{\text{bdy}}} = 0 \quad (5)$$

is fulfilled. The charge on the intercalant is given by

$$Q_I = Z_I - \frac{2A_{xy}}{\Omega N_I} \int_0^{z_{\text{bdy}}} dz n(z), \quad (6)$$

and the physical charge transfer is

$$q_I = \frac{2A_{xy}}{\Omega N_I} \int_0^{z_{\text{bdy}}} dz \delta n(z). \quad (7)$$

The intercalant plane is located at  $z=0$ . The factor 2 reflects the symmetry of the system;  $N_I$  is the number of intercalated atoms.

Up to this point our analysis of the plane-averaged charge density appears to be identical to the method already described by Benedek *et al.*<sup>25</sup> Two differences exist, however: in our study the reference density  $n_{\text{ref}}(\mathbf{r})$  is the superposition

of the densities of nonintercalated graphite and the alkali sublattice, whereas Benedek *et al.* used the electronic ground-state density of the graphite lattice and isolated alkali atoms to calculate  $n_{\text{ref}}(\mathbf{r})$ . We decided to use the charge density of the complete alkali sublattice of the GIC for  $n_{\text{ref}}(\mathbf{r})$  because we are mainly interested in the charge transfer between the graphitic and intercalant planes without considering possible contributions resulting from the alkali-alkali interactions. Nevertheless, the difference is probably of minor importance, since, as Benedek *et al.* stated, at least in the case of Rb the charge density of the Rb sublattice is very similar to that of the superimposed atomic densities. The second difference is that we use the total electronic charge density  $n(z)$  in Eq. (6) and Eq. (7) and not just the valence charge density, as in the work of Benedek *et al.* This is necessary since Bader's boundary condition [Eq. (1)] is valid for total densities rather than valence densities. The full charge density was computed by simply adding the core densities from the inner electrons to the computed valence charge densities. Especially in the calculations of the GIC's with lithium and sodium, where  $1e$  pseudopotentials have been applied, the inclusion of the core densities is crucial. A charge transfer between  $0.4$  and  $0.7e$  is observed in this case, whereas the use of the valence density always results in a complete charge transfer of  $1e$  (see Sec. III A).

### III. RESULTS

#### A. Charge densities

The valence charge densities  $n(\mathbf{r})$  of some of the alkali GIC's have been computed and published by several other groups<sup>26–28</sup> using different computational methods. The interactions between the graphite host and the intercalated metals are rather weak and not much insight can be gained from  $n(\mathbf{r})$  since the valence charge densities are almost identical to a superposition of the valence charge densities of the two sublattices. The nature of the alkali-graphite interactions is more clearly reflected by the difference density  $\delta n(\mathbf{r})$ . Figures 1 and 2 show  $\delta n(\mathbf{r})$  for  $\text{LiC}_6$ ,  $\text{LiC}_8$ , and  $\text{KC}_8$  within and perpendicular to the graphitic plane. The difference charge densities of  $\text{RbC}_8$  and  $\text{CsC}_8$  are similar to that of  $\text{KC}_8$  and are therefore not shown here.

##### 1. $\text{LiC}_6$ , $\text{LiC}_8$

Figure 1 shows  $\delta n(\mathbf{r})$  of  $\text{LiC}_6$  in the graphitic plane and within a perpendicular plane containing the lithium atoms in contour representation (left) and as three-dimensional plots (right). From Fig. 1(a) it is obvious that intercalation of lithium in graphite leads to two different types of  $\text{C}_6$  hexagons in the graphite host.  $\delta n(\mathbf{r})$  in the middle of the  $\text{C}_6$  hexagons lying above and below the lithium atoms is higher than in the middle of the adjacent ones.  $\delta n(\mathbf{r})$  is negative everywhere in the graphitic plane, except in the centers of the  $\text{C}_6$  hexagons directly above the Li atoms, indicating that there is a net charge transfer from the graphitic plane towards the intercalant plane. The character of the charge transfer can be seen from Fig. 1(b). Figure 1(b) shows a significant increase of charge density along the Li-C directions, where the maximum lies closer to the carbon atoms. At both the carbon and the lithium sites the charge density is reduced relative to

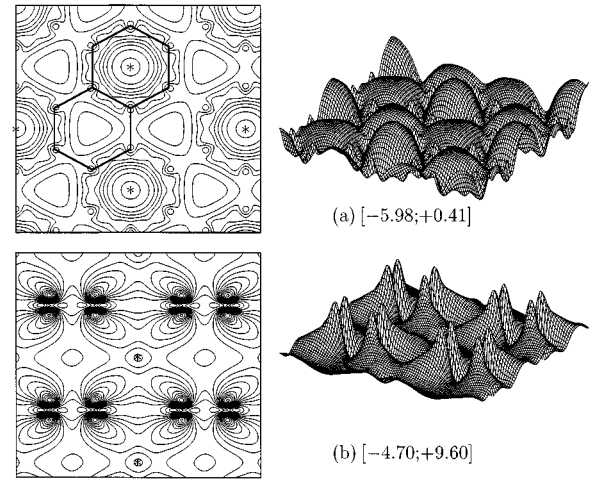


FIG. 1. Difference charge density  $\delta n(\mathbf{r})$  of  $\text{LiC}_6$  in the graphitic plane (a) and perpendicular (b). Positions of the lithium atoms are denoted by stars. Positions of the carbon atoms are denoted by the two hexagons. Contour values on the left side are chosen for a clear representation of the underlying structure. Small asymmetries are a consequence of numerical inaccuracies in the generation of contours. The numbers in brackets shown below the three-dimensional representations on the right side denote the range of  $\delta n(\mathbf{r})$  (in units of  $0.01$  elementary charges per  $\text{\AA}^3$ ).

the reference state. This behavior is characteristic for a covalent bond. From the shape of  $\delta n(\mathbf{r})$  in Fig. 1(b) one recognizes the  $\pi^*$  character of the Li-C bonds with respect to the graphitic plane. Our results agree with the findings by Kohanoff *et al.*<sup>26</sup> who computed the additional charge distribution  $n_{\text{add}}(\mathbf{r})$  for  $\text{LiC}_6$ , i.e.,  $n_{\text{add}}(\mathbf{r}) = n_{\text{LiC}_6}(\mathbf{r}) - n_{\text{C}_6}(\mathbf{r})$ . For

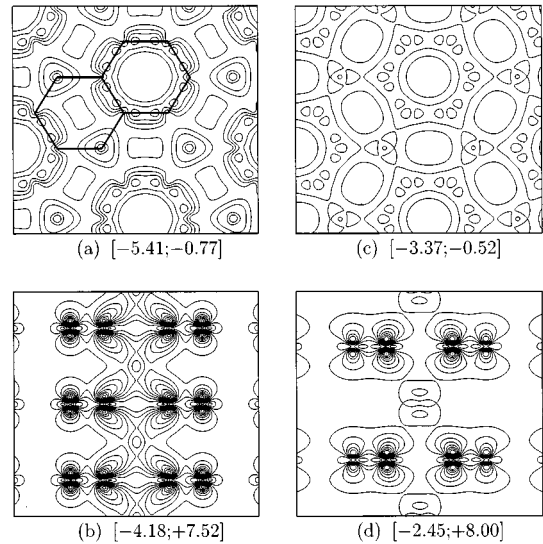


FIG. 2. Difference charge density  $\delta n(\mathbf{r})$  in contour representation for  $\text{LiC}_8$  (a,b) of  $\text{KC}_8$  (c,d) in the graphitic plane (a,c) and in a perpendicular plane containing the intercalant (b,d). Contour values are chosen for a clear representation of the underlying structure. Small asymmetries are consequences of numerical inaccuracies in the generation of contours. See also Fig. 1.

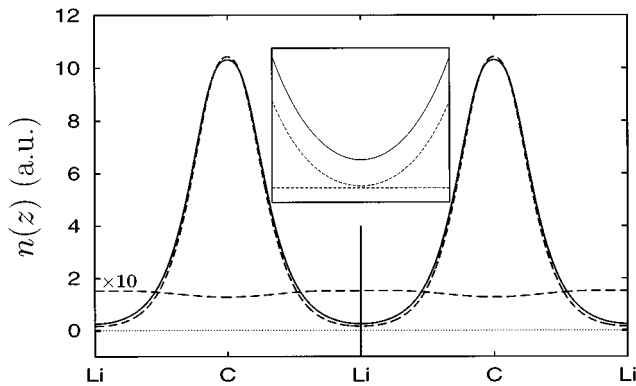


FIG. 3.  $n(z)$  of  $\text{LiC}_6$  (continuous line) computed from the valence charge only. Broken lines give  $n(z)$  of the isolated sublattices where the density contribution from the lithium atoms is multiplied by 10 for better legibility. The marks along the  $x$  axis give the position of the graphite and lithium planes. The magnified inset demonstrates, that the minimum of  $n(z)$  coincides exactly with the lithium planes.

direct comparison we also computed  $n_{\text{add}}(\mathbf{r})$  and obtained the same values as Kohanoff *et al.* The main difference between  $\delta n(\mathbf{r})$  and  $n_{\text{add}}(\mathbf{r})$  is a relative shift of approximate  $0.017e/\text{\AA}^3$  of the  $n_{\text{add}}(\mathbf{r})$  values relative to  $\delta n(\mathbf{r})$ , which is a consequence of the fact that the integrals of  $n_{\text{add}}(\mathbf{r})$  and  $\delta n(\mathbf{r})$  over the complete unit cell yield  $1e$  and  $0e$ , respectively.

## 2. $\text{XC}_8$ , $X=\text{Na, K, Rb, and Cs}$

Figure 2 shows the difference charge densities for  $\text{LiC}_8$  and  $\text{KC}_8$ . The comparison of Figs. 2(a) and 2(b) with Fig. 1 reveals that, except for the different symmetry, which is a consequence of the different stoichiometry, only small quantitative differences exist between  $\text{LiC}_6$  and  $\text{LiC}_8$ . The electronic structure is very similar and the partial occupation of an almost graphitic  $\pi^*$  band originating from carbon  $p_z$  states is evident. These states are polarized by the alkali atoms. In Fig. 2(b) the carbon  $p_z$  states show a strong orientation towards the Li atoms, whereas in the case of  $\text{KC}_8$  [Fig. 2(d)] this orientation is still visible but much less pronounced, indicating that the alkali-carbon interactions have a more covalent character in the case of Li. For the same reason the range of  $\delta n(z)$  is smaller for  $\text{KC}_8$  than for  $\text{LiC}_8$ .

### B. Charge transfer

Charge transfer in stage-1 alkali GIC's has been calculated by analyzing planar averaged charge densities  $n(z)$  (see Sec. II B). In Fig. 3 the valence charge density  $n(z)$  of  $\text{LiC}_6$  together with the valence charge densities of the graphite host and the intercalant sublattice is given. Contrary to the density contribution of the graphite host, which is centered around the graphitic planes, the charge introduced by the lithium atoms is almost homogeneously distributed over the whole unit cell. The complete valence density of  $\text{LiC}_6$  is very similar to the superimposed valence densities of the two sublattices; its minimum is located exactly in the middle between two adjacent graphitic planes. Therefore, on the basis of the valence charge densities,  $z_{\text{bdy}}$  in Eq. (5) would coin-

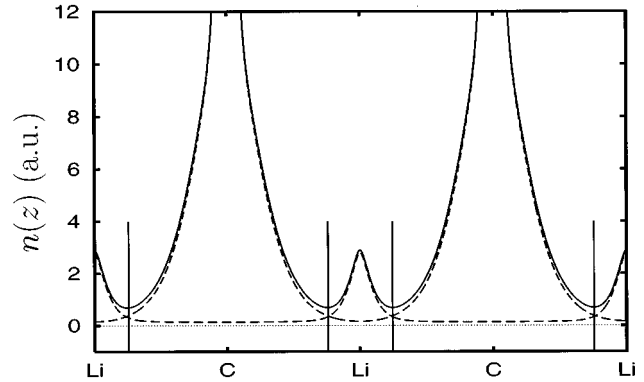


FIG. 4.  $n(z)$  of  $\text{LiC}_6$  (continuous line) computed from the total charge. Broken lines correspond to  $n(z)$  of the carbon and lithium sublattices. See also Fig. 3.

cide with the intercalant planes, and calculation of the charge transfer using Eq. (6) would yield a complete charge transfer of the  $2s$  lithium electrons to the graphite host.

Bader's boundary criterion, however, refers to the total charge densities, and core contributions must be included. Figure 4 shows the total electronic density when the  $1s$  electrons of both carbon and lithium atoms are considered. Minima between the graphitic and the intercalant plane are clearly visible. The minimum of  $n(z)$ , i.e.,  $z_{\text{bdy}}$ , is no longer identical to the position of the intercalant planes. Integration of  $n(z)$  from 0 to  $z_{\text{bdy}}$  yields  $0.5e$  remaining on the Li atom. This result is contrary to the picture of a fully ionized lithium in  $\text{LiC}_6$  obtained by an experimental study.<sup>29</sup> To further clarify the character of the graphite-lithium interactions the planar difference density  $\delta n(z)$  is given for  $\text{LiC}_6$  in Fig. 5. It shows the existence of a region with increased charge density (*b*) lying between the graphitic (*c*) and the intercalant regions (*a*). The difference charge density inside region *b* ( $0.24e$ ) stems from both the lithium atom ( $0.07e/\text{atom}$ ; region *a*) and the carbon atoms ( $0.03e/\text{atom}$ ; region *c*) which clearly illustrates the covalent character of the bonding.

For all other alkali GIC's the charge density was analyzed in an analogous manner. The charge transfer data are collected in Table II. One notices that there is a total charge transfer of  $0.5e$  ( $0.4e$ ) in the case of  $\text{LiC}_6$  ( $\text{LiC}_8$ ) and an almost constant value of about  $0.7e$  for the remaining alkali GIC's. The smaller value for the lithium compounds is a

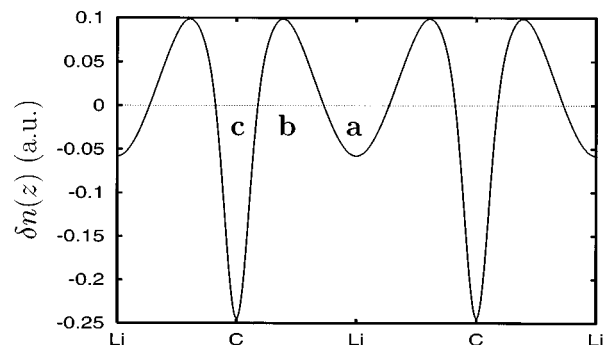


FIG. 5. Planar difference density  $\delta n(z)$  for  $\text{LiC}_6$ .

TABLE II. Charge transfer in units of the elementary charge in stage-1 alkali GIC's. For an explanation of the regions *a*, *b*, and *c*, see text.

|                              | Charge transfer |          |           | Region   |          |          |
|------------------------------|-----------------|----------|-----------|----------|----------|----------|
|                              | total           | physical | geometric | <i>a</i> | <i>b</i> | <i>c</i> |
| LiC <sub>6</sub>             | -0.515          | -0.070   | -0.445    | -0.071   | +0.243   | -0.029   |
| LiC <sub>8</sub>             | -0.404          | -0.023   | -0.381    | -0.024   | +0.230   | -0.025   |
| NaC <sub>8</sub>             | -0.703          | -0.252   | -0.451    | -0.147   | +0.267   | -0.015   |
| KC <sub>8</sub>              | -0.692          | -0.250   | -0.442    | -0.254   | +0.364   | -0.014   |
| KC <sub>8</sub> <sup>a</sup> | -0.663          | -0.231   | -0.432    | -0.237   | +0.333   | -0.012   |
| RbC <sub>8</sub>             | -0.671          | -0.234   | -0.437    | -0.236   | +0.336   | -0.012   |
| CsC <sub>8</sub>             | -0.657          | -0.219   | -0.438    | -0.219   | +0.310   | -0.011   |

<sup>a</sup>Calculated with the experimental lattice constant of RbC<sub>8</sub>.

consequence of the more covalent character of the lithium-carbon interactions relative to the other alkali GIC's (see Fig. 2), which is also true for alkali organometallic compounds.<sup>30</sup> The reason for the difference of the calculated charge transfer between LiC<sub>6</sub> and LiC<sub>8</sub> is at present not clear. The values in Table II include three significant figures; the systematic error due to the choice of methods is, however, larger than 0.001*e*. Nevertheless, as all calculations were done on the same level of theory, one can assume that systematic errors (for instance, due to the definition of charge transfer) cancel when comparing data for the whole series. Our calculations will thus give the correct trends, even if the differences are small compared to the systematic error of the method.

From the values in Table II one can see that the charge transfer has its smallest value for the lithium compounds, reaches a maximum for sodium, and then decreases slowly in the series of the heavier alkali atoms potassium, rubidium, and cesium. This is somewhat surprising since, parallel to the decreasing ionization energies in the sequence sodium, potassium, rubidium, and cesium, one would expect at least a small increase of the total charge transfer. Therefore, in addition to the ionization energy another parameter must exist which determines the magnitude of the charge transfer. One such parameter is the interlayer distance. It is easy to understand that the distance between graphitic and intercalated planes also affects the charge transfer, since the total charge transfer is zero in the limit of infinitely separated planes. When the interlayer distance increases parallel to the increasing atomic radii from NaC<sub>8</sub> to CsC<sub>8</sub> there is a trend in the total charge transfer opposite to the one related to the ionization energy.

In order to test this idea, we computed the charge transfer of KC<sub>8</sub> using the experimental lattice constants of RbC<sub>8</sub>. The charge transfer calculated in this way is indeed smaller than in RbC<sub>8</sub> and also smaller than in KC<sub>8</sub> when using the correct lattice constants (see Table II). We thus conclude that there are two different trends determining the total charge transfer in alkali GIC's: (i) increasing charge transfer with decreasing ionization energy of the alkali metal and (ii) decreasing charge transfer with increasing interlayer distance.

In all stage-1 alkali GIC's the geometrical part of the charge transfer gives the dominant contribution to the total charge transfer. The geometrical charge transfer has a nearly constant value of 0.43–0.45*e*/alkali-atom, the only exception

being the hypothetical system LiC<sub>8</sub>, where we find a somewhat smaller value of 0.38*e*/atom. As a consequence of the more covalent bonding the physical charge transfer is very small for the lithium compounds (0.07*e* and 0.02*e* for LiC<sub>6</sub> and LiC<sub>8</sub>, respectively). The more ionic bonding of the remaining alkali GIC's results in values of 0.22–0.25*e*/alkali-atom for all other compounds.

#### IV. DISCUSSION AND CONCLUSION

The calculated charge densities and difference charge densities show a common behavior for all stage-1 alkali GIC's. The intercalated planes are made up from partially ionized alkali atoms. The bonding interactions between graphite and the intercalants result in a region of increased charge density located between the graphitic and the intercalated planes. This region refers to the so-called interlayer state already observed in other theoretical<sup>31,32</sup> and experimental<sup>33–35</sup> studies. The lithium GIC's differ from the other alkali GIC's in that the bonding character is more covalent.

The amount of charge transfer in alkali GIC's has been discussed controversially for a long time. Pietronero and Strässler<sup>36</sup> correlated the charge transfer with the changes of the intralayer carbon bond lengths upon intercalation and found an almost constant value of 0.4*e* for all stage-1 compounds. Most theoretical calculations of the charge transfer are based on first-principles band-structure calculations. The first calculations were done for KC<sub>8</sub><sup>37,38</sup> where the authors found a charge transfer of  $\approx 0.7e/K$  atom. In a more recent Korringa-Kohn-Rostoker (KKR) *ab initio* calculation of KC<sub>8</sub> DiVincenzo and Rabii<sup>39</sup> concluded that the charge transfer is complete. Theoretical work by Holzwarth *et al.*<sup>40</sup> also shows complete charge transfer in LiC<sub>6</sub>. In a DFT/pseudopotential study of potassium adsorbed on graphite Ancilotto and Toigo<sup>41</sup> found a charge transfer of 0.18*e* from each K atom to the graphite substrate in the case of a (2 × 2)K overlayer. This is interesting insofar as this system is very similar to KC<sub>8</sub>, and that earlier experimental results<sup>42</sup> also suggested an almost complete charge transfer for the K atoms. The charge transfer of 0.18*e* calculated by Ancilotto and Toigo rather corresponds to the charge transferred from the K atoms into the interlayer region (region *b* in Fig. 5, i.e., 0.36*e* for KC<sub>8</sub>) than to what is defined as the total charge transfer in our study. In a recent DFT/pseudopotential study of Rb-intercalated graphites Benedek *et al.*<sup>25</sup> found a charge transfer of 0.75*e* for the stage-1 compound, which is very

similar to ours ( $0.67e$ ). This finding is not surprising as they also used plane-averaged densities and the Bader criterium (see Sec. II B) to determine the charge transfer. The small difference in their calculation and ours are mainly a consequence of the choice of different unit cells and  $\mathbf{k}$ -point sets in the calculations and the fact that Benedek and Smith analyzed only the valence charge density rather than the total charge density, which results in slightly different values of  $z_{\text{bdy}}$ .

On the experimental side there is no clear picture of the charge transfer in stage-1 alkali GIC's. X-ray photoemission (XPS),<sup>43,44</sup> electron energy loss spectroscopy<sup>44</sup> (EELS) and de Haas-van Alphen<sup>45</sup> measurements on  $\text{KC}_8$  were interpreted as an indication for total charge transfer. Further detailed high-resolution EELS measurements on K, Rb, and Cs stage-1 GIC's have demonstrated<sup>46</sup> that the states above the Fermi level, which are relevant for the charge transfer, are identically perturbed by the different intercalants. This result suggests that the charge transfer is complete for the heavy alkali metal stage-1 GIC's. On the other hand, in an x-ray-absorption near-edge photoabsorption spectroscopy<sup>47</sup> (XANEPS) and<sup>48</sup> EELS study of  $\text{KC}_8$  a charge transfer of  $0.85e$  and  $0.5e$  is found, respectively. An Auger spectroscopy study<sup>49</sup> of  $\text{CsC}_8$  is also in disagreement with full ionization of the Cs atom; instead a charge transfer of only  $0.7e$  is observed.

The differences in the experimental results obtained by different methods are a consequence of the approximations being made and the reference states being used in the data analysis (see also Ref. 48). A unique experimental definition of charge transfer does not exist, consistent with the fact that

charge transfer is not a quantum-mechanical observable.

## V. SUMMARY

We have performed first-principles total-energy calculations to study the charge-density distribution of all stage-1 alkali graphite intercalation compounds including also the hypothetical compounds  $\text{LiC}_8$  and  $\text{NaC}_8$ . The amount of charge transfer from the alkali atoms to the graphite host was determined from an analysis of plane-averaged densities. For the stage-1 alkali GIC's we find a nearly constant charge transfer of  $0.7e$ /alkali atom with the exception of the Li compounds where we find  $0.5e$  for  $\text{LiC}_6$  and  $0.4e$  for  $\text{LiC}_8$ . In all cases, the major part ( $0.4e$ ) of the charge transfer results from a simple overlap of the charge densities of the sublattices. Our comparison with other theoretical and experimental results makes it clear that the use of a unique definition is crucial for the discussion of charge transfer, especially when comparing different compounds. In the present study we systematically compared the various compounds using a common definition of charge transfer. This study is thus an important step towards a consistent description of charge transfer in alkali GIC's.

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