Inorg. Chem. **2006**, *45*, 9387–9393

Inorganic Chemistry

Article

Electronic Structure and Charge Transfer in the Ternary Intercalated Graphite β-$KS_{0.25}C_3$

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Received July 5, 2006

The electronic structure of the ternary intercalated graphite β-$KS_{0.25}C_3$ is studied by means of a first-principles density functional theory approach. The nature of the partially filled bands is analyzed, and the K sublayers of the intercalate are shown to have an important contribution to the Fermi surface. This K-based contribution confers a sizable three-dimensional character to the conductivity even if considerably less than that for the related binary KC_8. The electronic structure of β-$KS_{0.25}C_3$ differs noticeably from that of the related ternary compound, KH_xC_4. The charge transfer is analyzed, and a way to evaluate it, which can be used in general for intercalated graphites, is proposed. The charge transfer per C atom in this ternary material is shown to be smaller than that in the KC_8 binary compound despite a more favorable stoichiometry ratio between K and C.

Introduction

The literature on graphite intercalation compounds[1–3] has vastly grown since the report by Fredenhagen and Cadenbach[4] concerning KC_8, RbC_8, and CsC_8 back in 1926. These materials are low-dimensional systems that exhibit a wealth of interesting properties, and their study still remains a lively and challenging field. For instance, although not superconducting itself, graphite becomes superconducting after partial filling of the π^*-type bands as a result of the charge transfer. Very recently, the reports of superconductivity in CaC_6 at 11.6 K[5] have launched a large interest on this particular aspect of their physics because this T_c doubles the highest reported values for these compounds.[6] Interestingly, this discovery has reopened the discussion about the origin of superconductivity in these materials.[7] Superconductivity is, however, just one of the many facets making intercalated graphites attractive.[1–3]

One of the most interesting synthetic developments in the field has been the preparation of *ternary* intercalated graphites. Numerous compounds of this type are presently known.[8] Among the several reasons why these ternaries are interesting is that, in principle, this is a way to change the degree of

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10.1021/ic0612395 CCC: $33.50

charge transfer, which is known to exert strong control on the physical behavior. For instance, the study of the graphite−K system has shown the existence of several well-defined phases, KC_8, KC_{24}, KC_{36}, KC_{48}, KC_{60}, etc.[9] Thus, formally assuming a complete electron transfer from K to the graphene layers, the largest charge transfer attained in this series is 0.125 electrons per C atom in KC_8. However, when the intercalation of K is carried out in the presence of a more electronegative third element such as S, for instance, compounds such as α-$KS_{0.15}C_3$[10] and β-$KS_{0.25}C_3$[11] are obtained, in which the formal charge transfers are 0.233 and 0.166, respectively. However, it can be objected that the transfer must not be complete. This is, in fact, an important warning because a rough but realistic evaluation of the charge transfer is one of the important keys in trying to rationalize the physical and chemical behavior of intercalated graphites.[1−3] For this purpose, the Pietronero−Strässler formula[12] has been invaluable because of its simplicity and the apparently realistic results. The charge transfer per C atom values evaluated from this formula are 0.068 for α-$KS_{0.15}C_3$, 0.066 for β-$KS_{0.25}C_3$, and 0.056 for KC_8, clearly showing that, although the very qualitative trend is confirmed, to assume a complete transfer (i.e., a purely ionic description of the intercalate and intercalate−graphene interactions) is an oversimplification. Both the direct bonding interactions between the graphene and intercalate layers and those within the intercalate subnetwork may influence the electronic structure of these materials and, thus, the charge transfer.

The variety of possible bonding situations in ternary intercalated graphites is illustrated, for instance, by systems such as β-$KS_{0.25}C_3$[11] and α-$Li_{0.5}Ca_3C_6$.[13] The first contains triple-layered K−S−K sheets, which can be described as related to fragments of the K_2S structure, between the graphene planes.[14] The second contains five-layered Li−Ca−Li−Ca−Li sheets, which can be described as fragments of the $CaLi_2$ structure, a $ThMn_2$ Laves type phase.[15] As highlighted by these two systems, the balance between the covalent and ionic components of the bonding in the intercalate may be very different and thus may influence in a very different way the intercalate−graphene interaction, the charge transfer, and the electronic structure. In situations like these, where different types of bonding coexist in a material, only first-principles quantum mechanical approaches can lead to a realistic description of the electronic structure. We report here a first-principles density functional theory (DFT) study of one of the structurally best characterized of these materials, β-$KS_{0.25}C_3$.[11] This will also lead us to reconsider the evaluation of the charge transfer in intercalated graphites.

Computational Details

The first-principles calculations were carried out using a numerical atomic orbitals DFT approach,[16] which has been recently developed and designed for efficient calculations in large systems and implemented in the *SIESTA* code.[17−19] The use of atomic orbitals instead of plane waves greatly facilitates a chemical analysis of the results. We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew et al.[20] Norm-conserving scalar relativistic pseudopotentials[21] factorized in the Kleinman−Bylander form were used.[22] We have used a split-valence double-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 100 meV.[23] The 5s and 5p electrons of Ba, the 1s electrons of Li, and the 3s and 3p electrons of Ca and K were treated as valence electrons. The energy cutoff of the real-space integration mesh was 150 Ry. The Brillouin zone (BZ) was sampled using a grid of $7 \times 10 \times 5$ k points for K_4SC_{12}, $4 \times 10 \times 5$ for $K_8S_2C_{24}$, $2 \times 10 \times 5$ for $K_{16}S_4C_{48}$, $10 \times 6 \times 4$ for KC_8, $7 \times 7 \times 3$ for CaC_6, $7 \times 7 \times 4$ for BaC_6, and $7 \times 7 \times 8$ for LiC_6.[24] We have checked that the results are well converged with respect to the real-space grid, the BZ sampling, and the range of atomic orbitals.

Results and Discussion

A. Crystal Structure. The crystal structure of β-$KS_{0.25}C_3$ is built from exactly superimposed graphene planes alternating with triple-layered K−S−K slabs along the c direction (see Figure 1a).[11] A projection of the crystal structure along the interlayer direction is shown in Figure 1b, where the hexagonal symmetry is clearly seen. The intercalate is a triple-layered sheet in which the two K outer layers and the S inner layer form hexagonal lattices. The S atoms reside in the octahedral holes between the K layers (see Figure 1a). In fact, this triple layer is strongly related to the triple-layered K−S−K slabs that can be found perpendicular to the [111] direction in the K_2S antifluorite structure.[14] However, the S positions (empty circles) in the intercalate triple layer have an occupation factor of 50%. Within the graphene planes, the C−C distance is found to be 1.433 Å. This is 0.9% larger than the distance in graphite (1.42 Å) and, according to the Pietronero−Strässler formula,[12] implies a charge transfer of 0.066 electrons per C atom.

The partial occupation of the S sites forces us to model the structure with appropriate supercells. Before considering

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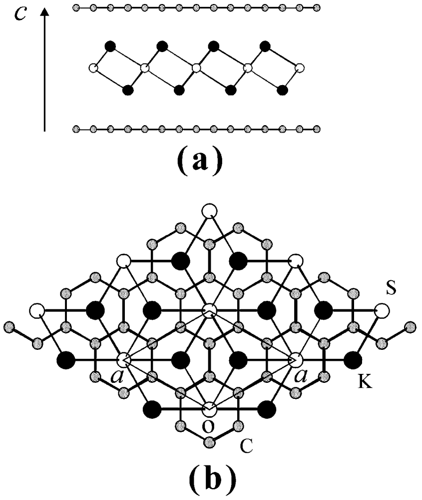

Figure 1. Crystal structure of β-KS$_{0.25}$C$_3$: (a) view perpendicular to the *c* direction; (b) view along the *c* direction. The gray, black, and white circles are C, K, and S sites, respectively. The occupation factor of the S positions is 50%.

this aspect, let us remark that the occupation of these sites has been shown to be perfectly statistical. Only in some cases is observed a doubling of the *c* parameter associated with an ordering of the occupation of the S sites, while all other structural details remain unaffected.[11] Thus, appropriate models can be built on the basis of just one graphene layer and one intercalate layer. The simplest model is that shown in Figure 2a with a K$_4$SC$_{12}$ repeat unit (model 1). More complex models are those shown in parts b and c of Figure 2 with K$_8$S$_2$C$_{24}$ (model 2) and K$_{16}$S$_4$C$_{48}$ (model 3) repeat units, respectively. Whereas in model 1 all K atoms are bonded to S atoms, in models 2 and 3, there are $^3/_8$ and $^7/_{16}$ K atoms nonbonded to S atoms, respectively. We have carried out calculations for the three models. However, we found that, as far as the nature of the band structure near the Fermi level and the charge transfer are concerned, no major differences are observed in the results (see below). Model 1 is found to be the lowest energy one; models 2 and 3 are found to be higher in energy by 0.073 and 0.327 eV per K$_4$SC$_{12}$ unit, respectively. Clearly, the system prefers to avoid having too many K atoms nonbonded to S atoms. The structural optimization of model 1 leads to very small changes, with the energy being only 67 meV per unit cell lower. Thus, for simplicity, except when otherwise stated, all results reported here will be for model 1 based on the crystal structure.

B. Electronic Structure, Partially Filled Bands, and the Fermi Surface. The calculated band structure for K$_4$SC$_{12}$ (model 1) in a region 4 eV above and below the Fermi level is shown in Figure 3a. The associated density of states (DOS) for a broader energy range as well as the K, C, and S contributions are shown in Figure 4. Both the band structures and DOS provide complementary insight concerning the nature of the bonding in this phase. Essentially, the results of Figure 4 show that the DOS of the system can be seen as the superposition of a graphene contribution, with the minimum separating the π-type bonding and antibonding states below the Fermi level because the graphene layer acts as the electron acceptor (note that, as is well-known, the σ bands considerably overlap with the π-type bands in the region below -4 eV), a relatively narrow peak around -2 eV, mostly associated with the S$-$K bonding levels of the intercalate (note a quite strong S$-$K mixing, clearly showing that the S$-$K bonds have an important covalent contribution), and a mostly K contribution starting just after the S$-$K bonding states up to high energies. The counterpart of the S$-$K peak (i.e., the states containing the antibonding S$-$K contributions) appears as a very broad contribution to the bunch of K states above the Fermi level. The K contribution below the S$-$K peak is not nil but quite small, showing that the K$-$graphene bonding has only a minor covalent contribution. What is very clear is that there is a quite large participation of K into the states below the Fermi level, and, thus, a formally ionic approach to the material would not be realistic. An important observation is that the mostly K contribution already starts below the Fermi level. In fact, at the Fermi level, the contributions of the graphene layers, K, and S are 67.4%, 26%, and 6.6%, respectively. Thus, it is clear that the intercalate contributes as much as one-third of the states that dominate the transport properties of the material.

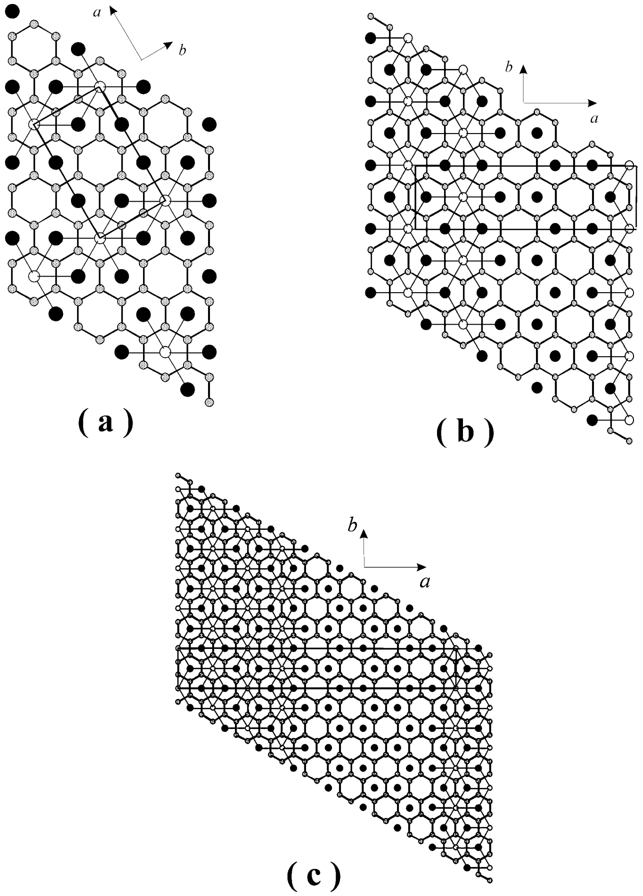

Figure 2. Different models used in the study of the electronic structure of β-KS$_{0.25}$C$_3$: (a) model 1 (K$_4$SC$_{12}$ repeat unit); (b) model 2 (K$_8$S$_2$C$_{24}$ repeat unit); (c) model 3 (K$_{16}$S$_4$C$_{48}$ repeat unit). The gray, black, and white circles are C, K, and S atoms, respectively.

Let us now turn to the band structure, which provides more detailed insight. The band structure of Figure 3a may be understood in a transparent way when it is compared with those of the graphene and intercalate layers calculated

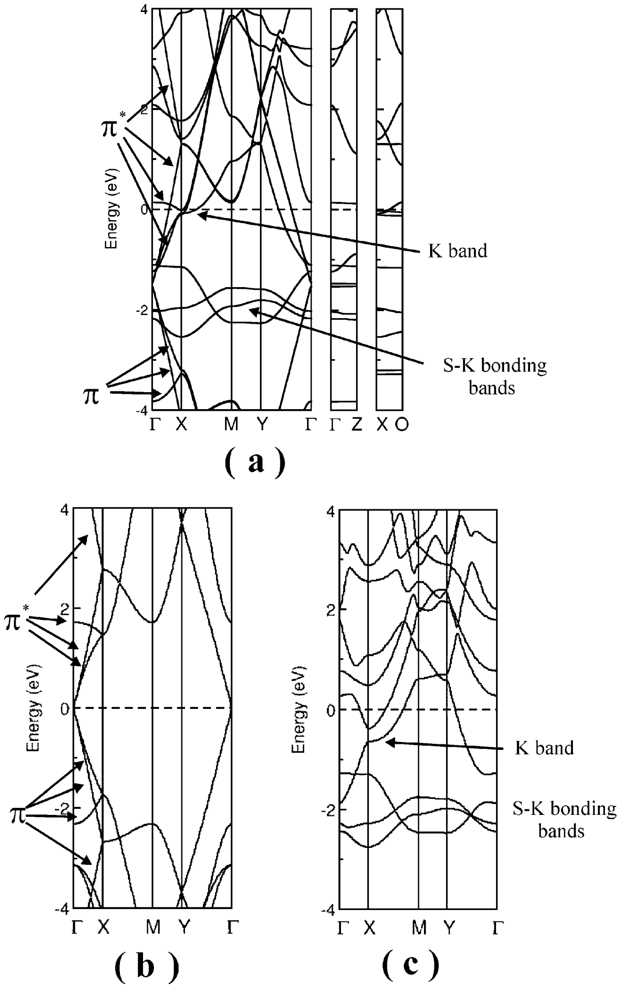

Figure 3. Calculated band structures for (a) β-$KS_{0.25}C_3$, (b) the graphene layers in β-$KS_{0.25}C_3$, and (c) the intercalate layers in β-$KS_{0.25}C_3$. The band structures in parts b and c have been calculated using exactly the same geometry as in the ternary system. The dashed line refers to the Fermi level and $\Gamma = (0, 0, 0)$, $X = (^1/_2, 0, 0)$, $Y = (0, ^1/_2, 0)$, $M = (^1/_2, ^1/_2, 0)$, $Z = (0, 0, ^1/_2)$, and $O = (^1/_2, ^1/_2, ^1/_2)$ in units of the orthorhombic reciprocal cell vectors.

separately with exactly the same geometry as that in the complete structure (see parts b and c of Figure 3, respectively). Because the repeat unit of the graphene layer here contains 12 C atoms, the π and π* bands are folded, leading to six subbands each. Eight of these bands, those lying near the Fermi level, are shown in Figure 3b. The band structure for the intercalate layers is shown in Figure 3c. The repeat unit of these layers contains one S atom and four K atoms. The three lower bands are dominated by the S p character (approximately two-thirds) mixed with a very sizable contribution of K orbitals; i.e., they are S−K bonding levels. At energies lower than those shown in Figure 3c, a mainly S s band is found. Thus, there are two electrons left to fill the next K-based bands, which are quite dispersive and even interpenetrate the S−K bonding ones.

With these results in mind, it is a very simple task to understand the band structure of Figure 3a. This band structure is simply the superposition of the graphene bands with the three S−K bonding bands and the lower of the mostly K bands. Because of the electron transfer, there is a downward shift of the graphene bands of approximately 1 eV and an upward shift of approximately 0.5 eV of the three S−K bonding bands as well as the lower mostly K band. The other K bands, including a second one, which was also partially filled in the isolated intercalate layer, experience larger upward shifts and become irrelevant for the physics of the system. As a matter of fact, the mostly K band is the only one among those crossing the Fermi level, which exhibits some dispersion along the interlayer direction (approximately 0.35 eV; see Γ → Z and X → O in Figure 3a) and, thus, which can confer some three-dimensional character to the conductivity. To see what is the nature of this band, we have shown in the inset of Figure 4 the contribution of the different K orbitals to the DOS. It is clear that this band is mostly based on the p_x, p_y, and s orbitals of K so that it may be described as a band concentrated in the two outer K layer planes of the intercalate. Analysis of the wave vectors shows that the coupling between the different K layers along the *c* direction is provided by a small participation of S orbitals and the π system of graphene.

The analysis of the band structure and DOS clearly shows that both the graphene and K layers provide partially filled bands and thus contribute to the metallic conductivity of the material. The calculated Fermi surface is reported in Figure 5, which, for clarity, shows a view along a direction slightly tilted with respect to the interlayer *c* direction. This Fermi surface contains two components very different in origin. The first component, disregarding the small avoided crossings, may be described as arising from the superposition of two triangular prisms. This portion has an almost perfect hexagonal-like shape (note that we have only represented the Fermi surface in the first BZ even if two of the arms of the star go out of this zone along the *a* direction and slightly overlap around the X point). This portion, exhibiting an almost nil warping along the interlayer direction, originates from the graphene bands. The second contribution, which superposes with the outer part of the first one, can be described as originating from the superposition of a series of considerably warped cylinders stacked along *a** in such a way that they slightly hybridize in the region around X, leading to a formally open (but almost closed) contribution along *a**. This is the contribution originating from the two K layers and that confers a nonnegligible three-dimensionality to the conductivity. As mentioned before, the nature of the partially filled bands and Fermi surface does not qualitatively change with the structural model used for the computations once the corresponding foldings are taken into account. Thus, Figure 5 is really a good representation of the Fermi surface of β-$KS_{0.25}C_3$. In fact, this is not surprising given the nature of the partially filled K band, which can only be slightly shifted by the different occupations of the S sites. This Fermi surface nicely agrees with the conductivity studies on this phase,[10] which show that the resistivity anisotropy stands practically halfway between that of a perfectly two-dimensional metallic intercalated graphite like AsF_5C_6[25] and that of an almost three-dimensional one like LiC_6.[26]

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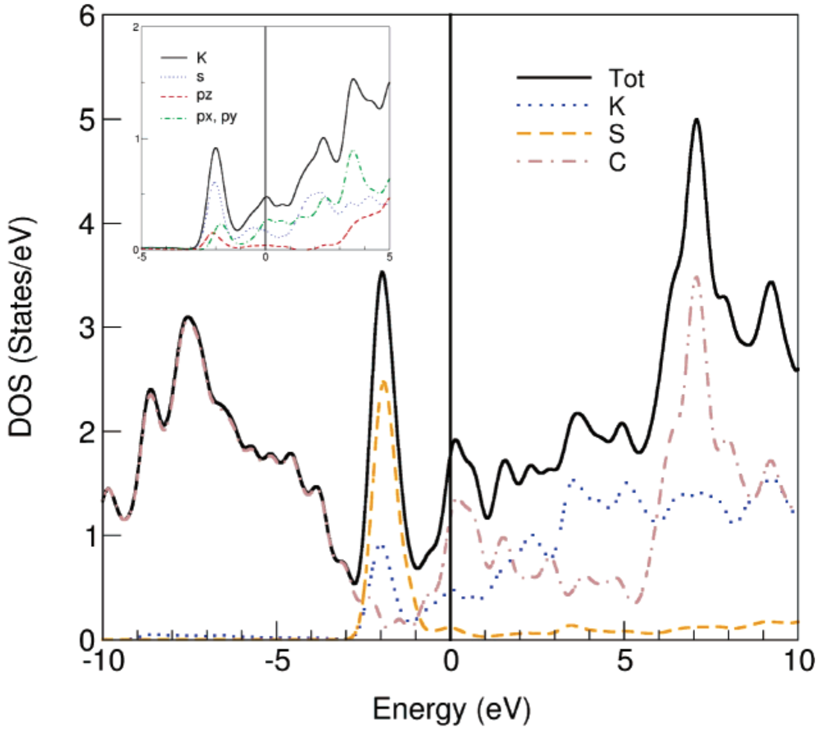

Figure 4. (a) Calculated DOS for β-$KS_{0.25}C_3$ as well as local contributions of the K and S atoms. The inset shows the contribution of the s, p_x, p_y, and p_z orbitals of K to the DOS.

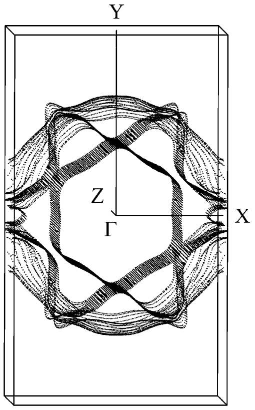

Figure 5. Calculated Fermi surface for β-$KS_{0.25}C_3$.

At this point, it is useful to compare our results with those for the related KH_xC_4 and KC_8 intercalated graphites, which have also been the subject of DFT calculations using local basis sets.[27,28] The first is a ternary system in which triple-layered K−H−K slabs are found between the graphene planes. In that case, the Fermi surface contains a contribution of the graphene layers and a contribution of the H inner layer of the intercalate, which originates from a weakly dispersive H-based band.[27] This feature contrasts with the present results because the intercalate contribution originates from a quite dispersive band originating from the outer layers of the intercalate. The present Fermi surface is also remarkably different from that of the binary KC_8 intercalated graphite. The Fermi surface in that case contains cylindrical components at the corners of the BZ and three-dimensional components at the center.[28] The existence of genuine three-dimensional components in contrast with the warped two-dimensional one in β-$KS_{0.25}C_3$ is also in nice agreement with the respective resistivity anisotropies.[10] Thus, the present results seem to be in excellent agreement with the available conductivity data and thus provide a simple conceptual basis for future work on this phase. Given the shape of Figure 5, more detailed characterization of the Fermi surface of β-$KS_{0.25}C_3$, especially through magnetoresistance measurements, would be very interesting. We note that quite large zones of the Fermi surface associated with the graphene component are very well nested by a 0.39*b** vector (or five equivalent ones due to the approximate 6-fold symmetry of this component) so that electronic instabilities could develop in this material at low temperature if pure enough samples can be prepared. Interesting physics could still be uncovered in this material.

C. Charge Transfer. The analysis of the DOS clearly shows that the K levels have an important participation in the filled bands, and thus an ionic type approach is not realistic for this material. According to a Mulliken population analysis, the average charges for the K, S, and C atoms are +0.222, −0.393, and −0.041, respectively. The K charge is notably smaller than that calculated by adopting exactly the same computational details for typical ionic salts of K (for instance, +0.575 for KF). Bearing in mind the possible shortcomings of the Mulliken analysis, we also evaluated these charges using the Voronoi deformation density (VDD)[29]

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and Hirshfeld[30] approaches. The average charges for the K, S, and C atoms are +0.164, −0.522, and −0.011, respectively, according to the VDD approach and +0.158, −0.370, and −0.022, respectively, according to the Hirshfeld approach. The charge for the K atom in KF is +0.354 according to the VDD approach and +0.387 according to the Hirshfeld approach. These figures, together with the calculated DOS (Figure 4), are quite clear in showing an important participation of the K orbitals in the covalent bonding of the intercalate.

However, the important point here concerns the charge of the C atoms, i.e., the transfer to the graphene layers. According to the three schemes, the transfer per C atom (−0.041 [Mulliken], −0.011 [VDD], and −0.022 [Hirschfeld]) is smaller than that predicted by the Pietronero−Strässler formula[12] for β-$KS_{0.25}C_3$ (−0.066) as well as the K−graphite binary KC_8 (−0.056). Thus, the trend in the charge transfer may be reversed with respect to that of the commonly accepted Pietronero−Strässler approach. Because the present results are based on first-principles calculations, which, in principle, should be more precise than those coming from the Pietronero−Strässler formula,[12] we decided to look in more detail at this aspect. We carried out calculations for KC_8 as well as the series of binaries AC_6 (A = Li, Ca, Ba), which have different structures although the same stoichiometry.[32] The calculated charges per C atom in KC_8 according to the Mulliken, VDD, and Hirschfeld analyses are −0.054, −0.035, and −0.043, respectively. When these values are compared with those for the ternary β-$KS_{0.25}C_3$, it is clear than the charge transfer is larger for the binary whatever approach is used for estimating the charge.

Of course, any scheme used to infer the charge from the wave function has some arbitrariness. Our study for the five above-mentioned compounds suggests that the trends in the calculated charges according to the Mulliken, VDD, and Hirschfeld schemes follow qualitatively similar behaviors. However, we have also found that none of the three schemes is free from occasional deviations from the general trend for some variation in technical details of the computation (extension of the basis set orbitals, types of inner electrons treated explicitly in the calculations, etc.). Although these are really exceptions on fairly regular trends, we decided to see if there is a simple yet robust way to estimate such a transfer. We have found that a really robust series of values of the charge transfers to the graphene layers may be obtained by integration of the electron density from the graphene plane up to the parallel planes between the intercalate and graphene corresponding to the minimum in the electron density along the interlayer direction. Thus, the electron density is partitioned into the graphene and intercalate layers with a simple and structurally meaningful criteria and in a way that can be easily implemented in any DFT code. In fact, this scheme can be considered as a simplified version of the Bader approach[31] because of the simplicity of the geometry of the intercalated graphites. The calculated charges according to this approach as well as those calculated from the Pietronero−Strässler formula[12] are reported in Table 1. The reversal of the charge transfer for the β-$KS_{0.25}C_3$ and KC_8 systems is thus confirmed by this scheme. The CaC_6 system is found to have a clearly larger charge transfer than LiC_6, as predicted by the Pietronero−Strässler formula. However, BaC_6 is found to exhibit a comparable charge transfer, whereas this is not the case according to the Pietronero−Strässler formula. We have checked that the result for BaC_6 is stable with respect to the computational details. The three AC_6 (A = Li, Ca, Ba) compounds have not only different intercalate atoms but also different stacking and symmetry.[32] All of these features are taken into account automatically in the DFT calculations, whereas only the (average) C−C bond length in graphite enters explicitly in the Pietronero−Strässler formula. This feature, which is really what makes this formula so easy to use (even in the absence of a detailed structure for the intercalate, it can be applied), is also its weak point. Because the strength of the interaction between the graphene and intercalate layers is not explicitly considered, the subtle differences in the interaction, and thus the relative weight of the ionic/covalent interactions, which influence the charge transfer, may not be well taken into account. This may be particularly the case when intercalates of quite different size (and stacking) such as in LiC_6 and BaC_6 are compared.

Table 1. Calculated Charge Transfer per Carbon Atom According to the Present Work and the Pietronero−Strässler Formula[12] for Several Graphite Intercalation Compounds

compound	this work	Pietronero−Strässler formula
KC_8	0.092	0.056
β-$KS_{0.25}C_3$	0.082	0.066
CaC_6	0.132	0.103
LiC_6	0.093	0.072
BaC_6	0.138	0.067

In our opinion, the charge-transfer values evaluated on the basis of a quantum-mechanical-based approach not only are more realistic (at least on a comparative basis) but also offer the advantage of being able to provide simple yet sound arguments in order to understand the differences. For instance, in the present case, it is clear from the Mulliken, Hirschfeld, or VDD approaches that at least half of the positive charge of K originates from transfer to S within the intercalate layer. This simply means that K can use a smaller part of its electrons for transfer to the graphene layers. In other words, the K atoms must be better potential donors in the binary compound than in the ternary compound, something that is very clear from the present calculations. The charge of a K atom in KC_8 (+0.432 [Mulliken], +0.344 [Hirschfeld], and +0.280 [VDD]) not only is larger than it is in β-$KS_{0.25}C_3$ (+0.222 [Mulliken], +0.158 [Hirschfeld], and +0.164 [VDD]) but also is very similar to the charge in a typically ionic compound such as KF (+0.575 [Mulliken], +0.387 [Hirschfeld], and +0.354 [VDD]). Thus, K is a considerably better donor in the KC_8 binary. This does not mean that the total transfer per C atom, which is the only meaningful measure of transfer, cannot be larger in a ternary

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compound. The stoichiometry forced by the inner structure of the intercalate in the ternaries may be such that the decrease in the transferring potentiality is more than compensated for by the stoichiometric ratio. However, a second effect may go against the transfer to the graphene layers in some ternaries. The bonding within the intercalate may lead to relatively low-lying partially bonding levels, which thus keep part of the electrons that otherwise would be transferred. For instance, the overlap of the in-plane K orbitals in β-$KS_{0.25}C_3$, made possible by the structure of the intercalate itself, renders the K atom less of an electron donor because it keeps some electrons in the mainly K partially filled band. The decrease in the stoichiometric ratio between C and K (β-$KS_{0.25}C_3$ vs KC_8) cannot overcome the effective decrease in the electron-transfer ability of K because of the combined effect of the S−K bonding and the direct in-plane K−K interactions. Let us note that Mizuno et al.,[28] in their study of the electronic structure of KC_8, nicely showed that the Fermi surface contains two different components: a two-dimensional one originating from graphene and a three-dimensional one, which has some K character but mostly originates from the graphene layers again. Thus, in agreement with our charge analysis, KC_8 behaves as a more typical ionic compound than β-$KS_{0.25}C_3$.

In conclusion, it is clear that in ternary intercalate graphites the bonding within the intercalate may exert strong control of both the states at the Fermi level and the charge transfer, which can be very different from those in the related binary compounds. Understanding the delicate interplay between the different bonding ingredients in these materials is something that requires an unbiased first-principles approach. The β-$KS_{0.25}C_3$ ternary intercalated graphite may exhibit an interesting physical behavior, and further physical characterization of this material would be worth doing.

Acknowledgment. This work was supported by DGES-Spain (Projects BFM2003-03372-C03 and FIS2005-00655) and Generalitat de Catalunya (Projects 2005 SGR 683 and 2005 SGR 00036). Part of the computations described in this work were carried out using the resources of CESCA.

IC0612395