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Electronic structure and properties of light atoms intercalated in graphite

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Abstract. Using the extra-orbital model, we calculate the electronic structure of one or two atoms of Li, Be, B, C or N, represented by $2s-2p$ orbitals, intercalated between graphite layers. To do so, (i) we have regenerated the π -band structure of $2p_z$ states in pure graphite within a Slater–Koster scheme; (ii) we have calculated the corresponding intersite Green functions within the corresponding D_{3h} symmetry point group; and (iii) we have computed the transfer integrals between the intercalated atom and a neighbouring carbon atom by using the basic two-centre atomic integrals. Within our simple model we discuss the natures of the various electronic situations in terms of the various types of impurities considered. Finally we calculate the electronic binding energies of the corresponding diatomic intercalated molecules (Li_2 , Be_2 , C_2 , N_2) with respect to the differing geometrical configurations.

1. Introduction

The defects formed in initially pure and perfect graphite irradiated or bombarded by a flux of particles give rise to a significant change in the physical properties of the considered system (Kelly 1981). More generally the intercalation of isolated impurities or pairs of atoms in graphite is a technologically important problem. However, owing to its difficulty, a proper treatment of such interstitial particles remains a challenge, especially for heavy defects (K, Rb, Cs, . . . ; Br, . . .), which introduce strong lattice relaxation: see for example the intercalate sandwich thicknesses in the corresponding intercalation compounds compared to the pure graphite interlayer spacing, as well as more details on the deformation of the graphite host (Dresselhaus and Dresselhaus 1981, Dresselhaus 1984). Also, a few papers only have been devoted to the detailed understanding of the electronic structure of one atom (or one diatomic molecule) intercalated in otherwise pure graphite. In the particular case of a self-interstitial in graphite, we defer to Heggie (1991) and references therein. As we essentially focus on light atoms (Li, Be, B, C and N) in graphite, we neglect in the present paper the relaxation of the host as a first-step calculation of the electronic structure of (isolated or interacting) interstitials between graphite layers. More precisely we use an extra-orbital tight-binding model, which we require to satisfy the Friedel sum rule, so that, although quite crude, our self-consistent treatment in the sense of Friedel is able to obtain reasonable physical tendencies along the series. The complexity of the considered system, especially in the case of two

intercalants, and the purpose of pointing out general trends with respect to various chemical species, are the main reasons why we choose here a simplified tight-binding model instead of *ab initio* band-structure calculations.

Within the extra-orbital tight-binding approximation, Priester *et al* (1982) calculated the electronic structure of an isolated carbon atom located above a single graphitic layer; see also Crowell (1985) and references therein for a phenomenological expression of the repulsive interaction between such a carbon atom and the adjacent graphite plane. Recently a semiclassical interatomic potential was used for carbon (Heggie 1991) and applied to a self-interstitial in graphite—supercell and cluster approaches—in particular to calculate the formation energy. Also first-principles calculations have been performed on the formation energy and migration barrier of an in-plane self-interstitial in graphite (Kaxiras and Pandey 1988); however, in the present paper we will essentially focus on various interplane intercalants. Except for the case of a self-interstitial in graphite, there have been only a few papers that have considered the electronic structure of other types of interstitial atoms in graphite. For example, Volpilhac and Achard (1989) treated the case of a single Li atom intercalated in graphite within a similar extra-orbital tight-binding method, but their study is essentially analytical without detailed numerical results.

The present work is an extension of Parlebas *et al* (1983). As in that earlier reference, we take into account here the three-dimensional π -band structure and the corresponding intersite Green functions of the host graphite within D_{3h} symmetry, but in the present calculation we take more points in the Brillouin zone as well as a smaller energy mesh. This increase of precision is required by the further calculation of narrow impurity virtual bound states especially near the Fermi energy where the pure density of states is very small. Our pure graphite electronic structure has already been reported elsewhere within a simplified tight-binding scheme (Rakotomahevitra *et al* 1991). The outline of the paper is as follows. In section 2 we give the general formulation for s and p impurity orbitals as well as the expression of the formation energy. Next we apply our formalism to the simple case of Li, and to the more difficult cases of Na, K, Rb, respectively, described by one *ns* orbital with $n = 2, \dots, 5$ (section 3), and to the series Be, B, C, N described by the 2s and 2p orbitals (section 4). Finally we present some preliminary results on the electronic binding energies between two interstitial atoms (section 5).

2. Formulation of the interstitial electronic structure

Postponing the problem of two interacting interstitial atoms to section 5, we first consider the intercalation of one impurity at site 0 (figure 1); for a detailed discussion of the interstitial position, see Taji *et al* (1986). Let us label $\{|0l\rangle\}$ the extra electronic orbitals brought by the impurity and corresponding to the renormalized impurity levels $\{E_0^l\}$. The Hamiltonian of the dilute intercalated graphite is written for a given spin direction as

$$H = H_0 + \sum_l |0l\rangle E_0^l \langle 0l| + \sum_{R,l} (|Rz\rangle \beta_{R0}^z \langle 0l| + \text{HC}) + \sum_R |Rz\rangle V_R^z \langle Rz| \quad (2.1)$$

where H_0 is the pure graphite Hamiltonian (Parlebas *et al* 1983, Rakotomahevitra *et al* 1991), β_{R0}^z is the hopping integral between the interstitial orbital $|0l\rangle$ (with $l = s, x, y$ and z) and a $2p_z$ neighbour carbon orbital $|Rz\rangle$ at site R . Within an energy region centred at the Fermi energy E_F , the graphite π -bands are uniquely built from the $2p_z$ orbitals and,

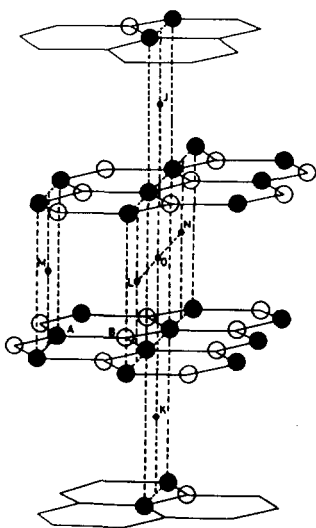


Figure 1. The A (●) and B (○) carbon atoms of (unrelaxed) graphite containing impurities at various intercalated positions (O, L, N, J, M, K).

in a range of about 10 eV around E_F , only the π -bands need to be considered in a first-step approximation. For a detailed discussion on that point with respect to the effects of the σ states, we refer to Safran and Hamann (1981) as well as to Holzwarth *et al* (1983). Finally in equation (2.1), V_R^z is the induced potential on the graphitic carbon orbital at a neighbouring site R and due to the intercalation of the impurity atom at 0.

The local density of states (LDOS) per spin at the impurity site 0 is expressed by

$$n_0(E) = -\pi^{-1} \text{Im} \sum_l G_{00}^l(E) \quad G_{00}^l(E) = [E - E_0^l - \Delta_{00}^l(E) - \Gamma_{00}^l(E)]^{-1} \quad (2.2)$$

with

$$\Delta_{00}^l(E) = \sum_{R', R''} \beta_{0R'}^{lz} G_{R'R''}^{0zz}(E) \beta_{R''0}^{zl} \quad (2.3)$$

and

$$\Gamma_{00}^l(E) = \sum_{R'} V_{R'}^z \left(\sum_{R''} \beta_{0R''}^{lz} G_{R''R'}^{0zz}(E) \right)^2 \quad (2.4)$$

In equations (2.3) and (2.4) $G_{R'R''}^{0zz}(E)$ is the pure graphite intrasite ($R' = R''$) or intersite ($R' \neq R''$) Green function $\langle R'z | (E - H_0 + i0)^{-1} | R''z \rangle$. The latter is obtained through a summation in the (1/24th) Brillouin zone, using time reversal symmetry and introducing 12 proper rotations of the D_{3h} group (Parlebas *et al* 1983). Similarly, at a neighbouring site R of the interstitial position 0, the variation of the LDOS up to lowest order in V_R^z is (Khalifeh and Demangeat 1983)

$$\begin{aligned} \delta n_R(E) = & -\pi^{-1} \text{Im} \left(\sum_{l, R', R''} G_{RR'}^{0zz}(E) \beta_{R'0}^{zl} G_{00}^l(E) \beta_{0R''}^{lz} G_{R''R}^{0zz}(E) \right. \\ & + \sum_{R'} G_{RR}^{0zz}(E) V_{R'}^z G_{R'R}^{0zz}(E) \\ & \left. + 2 \sum_{l, R', R'', R'''} G_{RR'}^{0zz}(E) V_{R'}^z G_{R'R''}^{0zz}(E) \beta_{R''0}^{zl} G_{00}^l(E) \beta_{0R'''}^{lz} G_{R'''R}^{0zz}(E) \right). \quad (2.5) \end{aligned}$$

Also within the same approximation the number of states brought by the intercalated atom below energy E and per spin direction is given by

$$Z(E) = -\pi^{-1} \sum_l \{ \text{Arg}[G_{00}^l(E)]^{-1} - \pi \} - \sum_R V_R^z n_R^0(E) \quad (2.6)$$

with

$$n_R^0(E) = -\pi^{-1} \text{Im} G_{RR}^{0zz}(E). \quad (2.7)$$

Finally let us recall here the expression of the electron contribution to the formation energy of one interstitial atom (e.g. Priester et al 1982):

$$\Delta E = 2E_F Z(E_F) - 2 \int_{-\infty}^{E_F} Z(E) dE - \sum_l N^l E_l^{\text{at}}. \quad (2.8)$$

In equation (2.8) the absolute position of E_F is adjusted in order to reproduce the work function of pure graphite (Michaelson 1977) and E_l^{at} is the atomic energy of the l orbital for the considered atom to be inserted in graphite; N^l is the corresponding electron number of symmetry l brought by the impurity. Let us now turn to our numerical applications (sections 3 and 4): actually for simplicity we present all our results with the first-step assumption $V_R^z = 0$, consistent with the other basic approximations of the present model. More precisely, from equation (2.6) and owing to the fact that the LDOS on a carbon site at the Fermi level, $n_R^0(E_F)$, is negligibly small, it can be seen that the effect of V_R^z on the generalized phase shift at E_F , $Z(E_F)$, is finally very small too. Also, relaxation of carbon atoms around an isolated impurity will modify the value of V_R^z ; this would have to be taken into account in a consistent way, but is beyond the scope of the present calculation.

3. Case of an alkaline impurity

In this simple case the index l of equation (2.1) is reduced to s only. Disregarding the p levels in the alkaline impurities is actually also a first-step approximation leading only to preliminary results that ought to be refined in a more complete model (Volpilhac and Achard 1989). The hopping integrals β_{R0}^{zs} between the interstitial $2s$ state (case of Li) and its first (1) and second (2) carbon neighbour $2p_z$ orbital are calculated from two-centre atomic orbitals (Clementi and Roetti 1974). For a Li impurity, β_{R0}^{zs} is simply expressed in terms of $\text{sp}\sigma(1)$ or $\text{sp}\sigma(2)$ (see table 1 and the insert of figure 2(a) where $\text{sp}\sigma(D)$ has been plotted for a variable distance D between the lithium atom and its carbon neighbour). The Slater exchange potential coefficient α has been fixed at 0.8. We assume the Friedel (1958) sum rule, which expresses that there is one external $2s$ electron brought by the Li impurity intercalation:

$$2Z(E_F) = 1 \quad E_0^s = E_F - \text{Re} \Delta_{00}^{ss}(E_F) \quad (3.1)$$

where $Z(E)$ and $\Delta_{00}^{ss}(E)$ are given by equations (2.6) and (2.3), the factor 2 standing for the two spin directions. As a result of requiring the Friedel sum rule to be fulfilled, we obtain the renormalized impurity level $E_0^s(\text{Li}) = 3.910$ eV. From our results on the LDOS at the Li site (figure 2(a)) and on the total number of displaced states $Z(E)$ below a given energy E (figure 2(b)), we find a large induced DOS, i.e. a virtual bound state, denoted

Table 1. Basic two-centre integrals between the interstitial 2s or 2p states and its first (1) or second (2) carbon neighbour 2p_z orbital estimated from atomic orbitals (Clementi and Roetti 1974). For Be, $pp\sigma(i)$ and $pp\pi(i)$ cannot be calculated from the p orbital atomic data since the latter are not available for Be in Clementi and Roetti (1974): the corresponding values are obtained from the case of B. The first and second nearest distances are $D_1 = 1.83 \text{ \AA}$ and $D_2 = 2.09 \text{ \AA}$. In the last column of the table we have listed the interstitial energy level E_0 deduced from the Friedel rule (Fermi energy $E_F = -0.040 \text{ eV}$). All values in eV.

	$sp\sigma(1)$	$pp\sigma(1)$	$pp\pi(1)$	$sp\sigma(2)$	$pp\sigma(2)$	$pp\pi(2)$	E_0
Li	2.091	—	—	1.838	—	—	3.910
Be	3.975	—	—	3.216	—	—	6.450
B	4.246	5.419	-2.734	3.016	4.310	-1.785	1.740
C	3.777	5.218	-2.169	2.428	3.840	-1.334	-3.630
N	3.130	4.689	-1.682	1.860	3.236	-0.981	-4.960

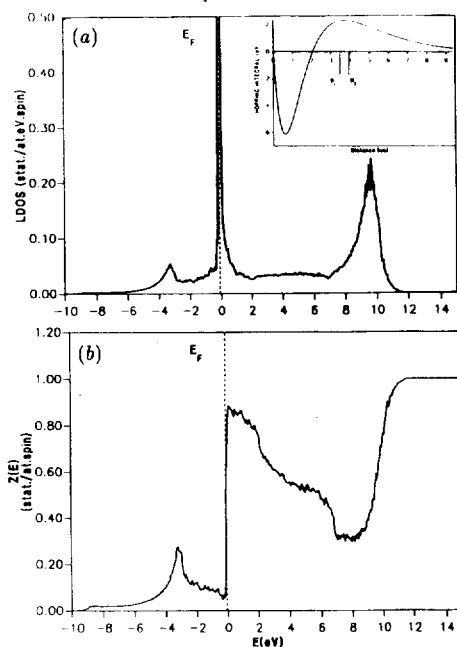


Figure 2. (a) The LDOS per spin direction on the intercalation site of Li. The insert shows the hopping integral $sp\sigma(D)$ versus the interatomic distance D between the impurity atom and the carbon neighbour atomic units (D_1 and D_2 being the first and second nearest-neighbouring distances). (b) Total number of states $Z(E)$ below E per spin with respect to E .

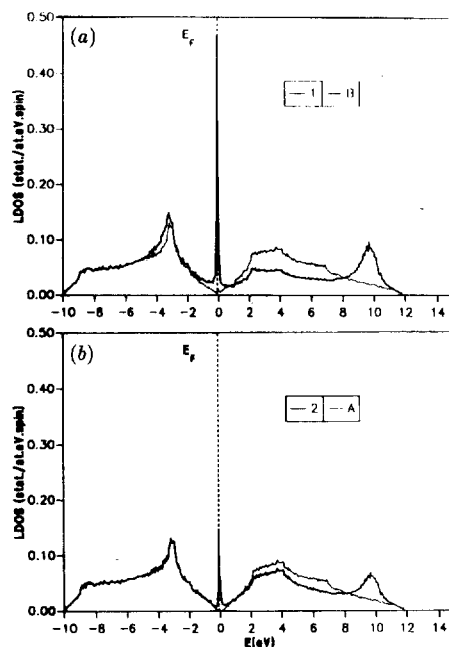


Figure 3. The LDOS per spin on (a) the first and (b) the second nearest carbon neighbours. The thin curves report the LDOS before intercalation, i.e. pure graphite A and B LDOS: note that there is a slight difference, especially at the Fermi level ($E_F = -0.04 \text{ eV}$), between the two distinct carbon sites (in standard graphite). The number of k -points in the reduced Brillouin zone is 70 000 and the energy mesh 0.01 eV .

vbs, at the Fermi energy $E_F = -0.040 \text{ eV}$, where the pure graphite DOS is very small (see the LDOS for pure carbon atoms A and B in figure 3). However, the vbs is also present at E_F on the six neighbours of the Li atom (figure 3), i.e. two first and four second

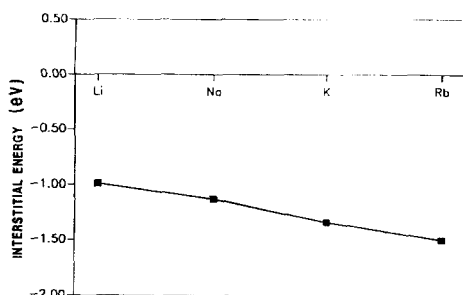


Figure 4. Electronic part of the interstitial energy down the alkali column.

neighbours. On the central Li, we find a remaining charge of $0.483 e^-$ while a charge of $0.454 e^-$ is transferred from the Li to its six neighbours. Thus a total charge of $0.937 e^-$ is spread on the seven-atom cluster built from the Li atom and its neighbouring carbon atoms. Within our simple model, when going deeper into the alkali column, the hopping integrals decrease as well as the E_0^s interstitial energy position with respect to the Fermi energy, yielding a reduction of the charge transfer from the corresponding impurity to the graphite. This result might be compared with recent experimental data (Estrade-Swarckopf and Rousseau 1992) on higher-stage Cs-graphite intercalation compounds where incomplete charge transfer was found from alkali to carbon. Also we obtain a slow variation of the formation energy from -0.989 eV for Li to -1.490 eV for Rb (figure 4). In this latter case, we get $E_0^s(\text{Rb}) = -0.112$ eV, i.e. a value very close to E_F . Apart from the case of the heavy alkaline interstitials (K, Rb), the other light elements of the column, especially Li and Na, induce quite a large charge transfer from the impurity (donor level) to the neighbouring carbon levels, in agreement with the situations in the corresponding intercalation compounds, at least those involving Li, since Na does not intercalate into graphite, from an experimental point of view. Finally let us point out the following. The formation energy is actually given by a summation of an electronic contribution, as considered here, and a contribution resulting from the local distortion, as discussed by Kaxiras and Pandey (1988) in the case of in-plane carbon. This latter contribution is probably small in the case of Li but probably not for K and Rb. Moreover, the large charge transfer from the impurity to the neighbouring carbon atoms does modify the electronic structure of those atoms around the impurity; this leads to additional contribution to V_R^z . Therefore, before performing a detailed comparison with experimental data, such effects would have to be included.

4. Case of Be, B, C and N

In order to study this series, the index l of equation (2.1) runs over $l = s, x, y$ and z . The basic two-centre integrals $pp\pi(i)$ and $pp\sigma(i)$ between the interstitial ($2p_x, 2p_y, 2p_z$) state and its first ($i = 1$) or second ($i = 2$) carbon neighbour ($2p_z$) orbital as well as the previously considered $sp\sigma(i)$ are calculated from atomic orbitals (Clementi and Roetti 1974) and listed in table 1. Then β_{R0}^z of equation (2.1) for $l = p_x, p_y, p_z$ and for a given i is a linear combination of $pp\pi(i)$ and $pp\sigma(i)$ given by Nussbaum (1966). The Slater exchange potential coefficient α is again fixed at 0.8. Also from atomic considerations, according to Clementi and Roetti (1974), we take an average difference

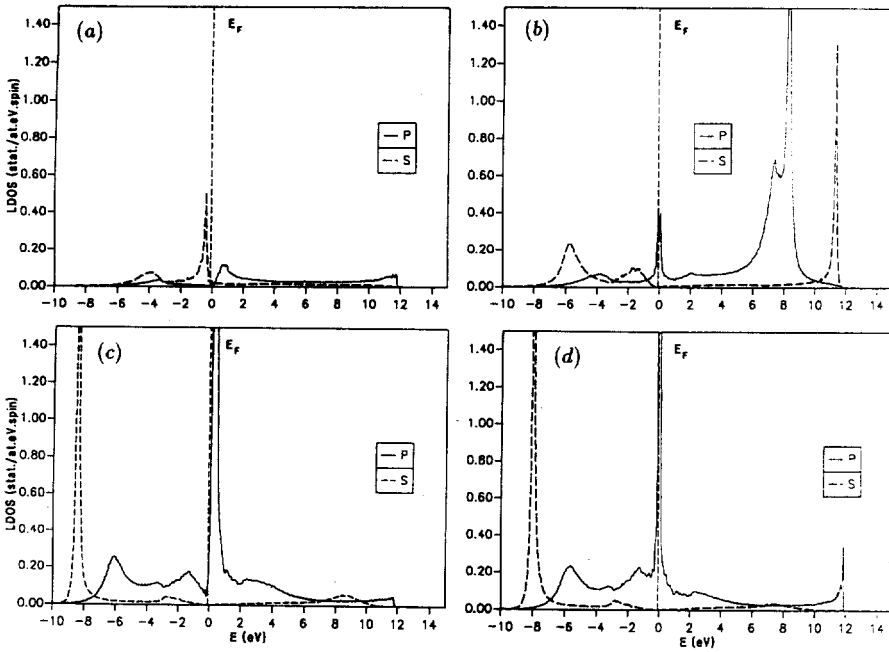


Figure 5. The s (---) and p (—) contributions to the LDOS per spin on the interstitial sites for (a) Be, (b) B, (c) C and (d) N.

$E_0^p - E_0^s = 5$ eV along the whole considered series. As a consequence E_0^s is the only remaining parameter and is deduced from the Friedel rule:

$$2Z(E_F) = N_{sp} \quad (4.1)$$

where $N_{sp} = 2, 3, 4$ and 5 , respectively, for Be, B, C and N, i.e. the $2s$ and $2p$ electron numbers brought by the corresponding impurities. When going from Be to N we find that E_0^s goes deeper and deeper in energy from 6.450 eV above E_F for Be to -4.960 eV (below E_F) for N (table 1). Similarly E_0^p goes from 11.450 eV for Be to 0.040 eV (very close to E_F) for N. This last result is quite natural since N corresponds to the half-filled p spin orbitals, i.e. about three p electrons. Let us give the following comment on our calculation. In the case of an alkaline impurity (section 3), we considered E_0^s as the only renormalized impurity level. When only E_0^s is present and V_R^Z is neglected on the nearest carbon neighbours, then E_0^s is obtained through the Friedel screening rule; the renormalization of the atomic level E_s^{at} (occurring when the impurity is brought into the graphite) is taken into account through this screening rule. In the present case, both E_s^{at} and E_p^{at} would need to be renormalized, so that the Friedel rule is no longer enough to determine them. A realistic way would be to compute them self-consistently by taking into account the carbon environment in the unrelaxed configuration as well as the relaxation contribution that modifies the V_R^Z term. This leads to very heavy computations, which are under present investigation but only for a simpler case consisting of a single adatom on a single graphitic layer.

Our present results are summarized in figures 5 and 6, respectively, for the LDOS on the impurity site and for $Z(E)$. They essentially reflect the fulfilment of the Friedel sum rule. For Be there is a filled s VBS just below E_F , which goes then deeper in energy along

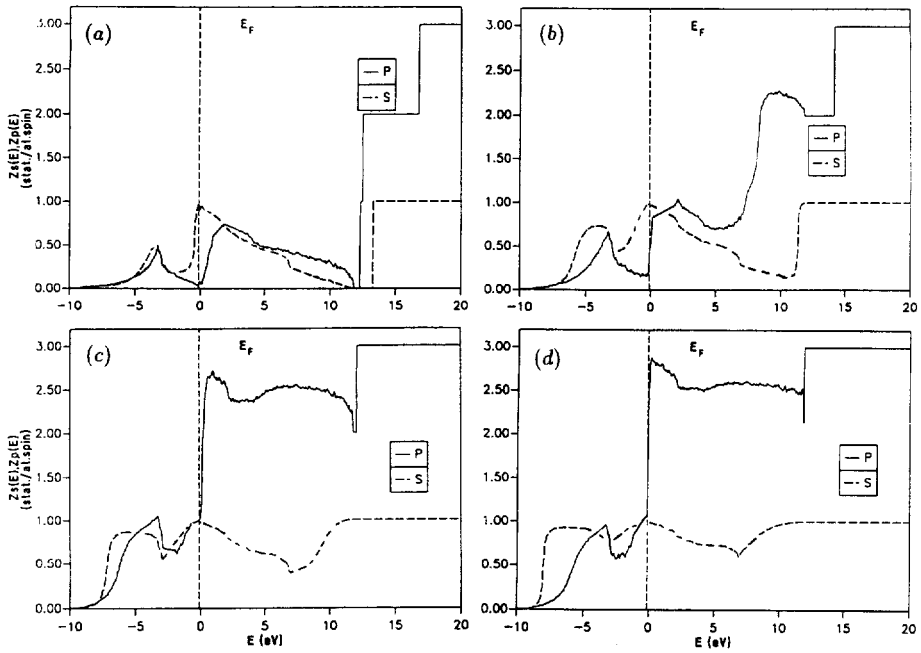


Figure 6. The s (---) and p (—) contributions to the total number of states below E per spin for (a) Be, (b) B, (c) C and (d) N.

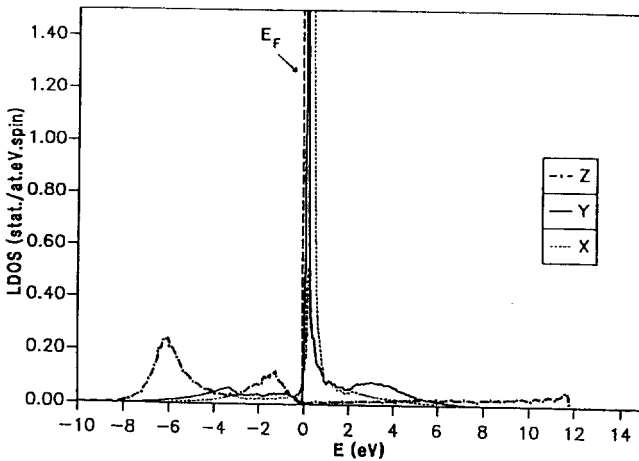


Figure 7. The p_x (·····), p_y (—) and p_z (---) contributions to the LDOS per spin on a self-interstitial of C.

the series $\text{Be} \rightarrow \text{N}$. Also for Be there is only a small p (p_z) contribution below E_F , whereas for B, C and N there is always a p vbs at E_F . In the case of a self-interstitial of carbon (figures 5(c), 6(c) and 7) a filled vbs appears below E_F , which is mainly of p_z symmetry, while vbs of non-degenerate x and y symmetries lie just above E_F . This result fully agrees with Priester *et al* (1982), although in their case owing to their intercalation

symmetry—interstitial just above a hexagon—the x and y contributions are equal. For a boron impurity the p_z VBS is half-filled at E_F (figures 5(b) and 6(b)), whereas for a nitrogen impurity the p_z VBS is filled and the p_y VBS is half-filled (figures 5(d) and 6(d)). To save space we do not show the corresponding partial p_x , p_y , p_z contributions to $Z(E)$ for B and N. Also it should be noted that, owing to our simplified ($2p_z$) band structure, we find bound states for the whole series falling at higher energies above the pure graphite π conduction band DOS (figure 6). In figure 5 we omit to indicate the positions of these various bound states. Also we find a remaining charge of $1.101 e^-$ on the Be site (0.723 s and 0.378 p contributions), where two electrons were brought originally, with a total charge transfer of $1.345 e^-$ (0.828 s and 0.517 p contributions) onto the six neighbours. If we require strict charge neutrality on the impurity and its first and second neighbours, usually we have to put a repulsive potential on the neighbours (Rakotomahevitra *et al* 1991), unless the case of N is considered. In that case and in our present model, we obtain $4.490 e^-$ on the impurity site (1.681 s and 2.879 p contributions), $0.490 e^-$ on the neighbours (0.160 s and 0.330 p contributions), which gives about $5 e^-$ on the considered cluster, just about the N_{sp} number of electrons brought by one N interstitial.

Finally let us just mention that for Be we find again a negative formation energy of $-2.1 eV$ (similarly to the alkaline impurities), whereas for B, C, N we always obtain positive results, i.e. the intercalation does not occur spontaneously (Charlier *et al* 1989) although our method is too crude to give but semiquantitative insights. For example, for a C impurity we get a formation energy of about $12.0 eV$ instead of $7 eV$ (Heggie 1991).

5. Binding energy for intercalated diatomic molecules

We now focus attention on the band contribution $\Delta E_{\lambda\mu}$ to the interaction energy of a pair of interstitial atoms located at sites λ and μ —for a discussion of other contributions see Gautier *et al* (1976) and Moraitis and Demangeat (1981). In fact $\Delta E_{\lambda\mu}$, also called binding energy, is directly deduced from the preceding one-impurity electronic structure as follows:

$$\Delta E_{\lambda\mu} = - \int_{-\infty}^{E_F} [Z_{\lambda\mu}(E) - Z_\lambda(E) - Z_\mu(E)] dE \quad (5.1)$$

where Z_λ or Z_μ is defined by equation (2.6) and $Z_{\lambda\mu}$ is the corresponding quantity for the two impurities (for a discussion on that point, see Moraitis and Demangeat (1981)). In the simple case when the summation over l of equation (2.1) is limited to s and when $V_R^z = 0$, then $\Delta E_{\lambda\mu}$ can simply be written as

$$\Delta E_{\lambda\mu} = \frac{2}{\pi} \text{Arg} \int_{-\infty}^{E_F} dE \left(1 - \frac{|\Delta_{\lambda\mu}^{ss}(E)|^2}{(E - E_\lambda^s - \Delta_{\lambda\lambda}^{ss})(E - E_\mu^s - \Delta_{\mu\mu}^{ss})} \right) \quad (5.2)$$

with

$$\Delta_{\lambda\mu}^{ss}(E) = \sum_{R,R'} \beta_{\lambda R}^{sz} G_{RR'}^{0zz} \beta_{R'\mu}^{zs}$$

In equation (5.2) $\Delta_{\lambda\lambda}^{ss}$ and $\Delta_{\mu\mu}^{ss}$ are given by equation (2.3) and the factor 2 is due to spin degeneracy. Let us mention that in $\Delta E_{\lambda\mu}$ the direct term proportional to $\beta_{\lambda\mu}$ has

Table 2. Band-structure contribution to the binding energies $\Delta E_{\lambda\mu}$ (eV) between two identical intercalated atoms (Li_2 , Be_2 , B_2 , C_2 , N_2) located at sites λ and μ , i.e. O, L, M, J, N, K (see figure 1). The last line gives the length of the various diatomic molecules.

$\Delta E_{\lambda\mu}$ (eV)	OL	OM	OJ	LN	KJ
Li_2	-0.855	0.141	-0.986	0.007	0.036
Be_2	-0.317	1.078	-0.773	0.005	0.008
B_2	-1.318	-0.328	0.227	0.003	-0.015
C_2	0.488	1.913	1.510	0.195	0.009
N_2	0.675	1.641	1.139	0.143	-0.007
Distance (Å)	2.46	2.46	3.34	4.92	6.68

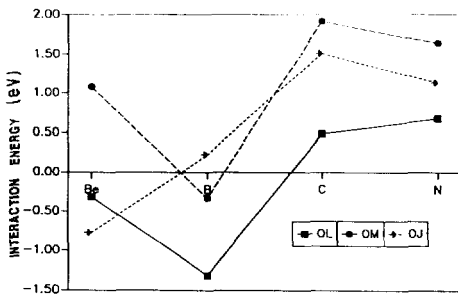


Figure 8. Band-structure contribution to the binding energies of pairs OL (—), OM (---) and OJ (····) along the series Be, B, C, N, the lengths OL and OM being equal.

been disregarded, an approximation that is reasonable when the distance between the impurities is larger than the distance between each impurity and its surrounding neighbours. Our numerical results are summarized in table 2 and figure 8 for Li_2 , Be_2 , B_2 , C_2 , N_2 molecules and for various positions of these molecules within graphite. Let us stress the following points.

(i) Within the same interlayer plane there is a strong anisotropy effect: $\Delta E_{\text{OL}} \neq \Delta E_{\text{OM}}$, although the distance $\text{OL} = \text{OM}$. Actually we can observe that the OL pair has two common neighbouring carbon atoms contributing to the binding energy ('through-bond coupling') whereas the OM has none (figure 1).

(ii) The binding energy ΔE_{OJ} between two interstitials (O, J) located on each side of a graphitic plane is rather large: two Li or Be atoms attract each other quite strongly while two B, C or N atoms repel each other (figure 8). It is interesting to note that the result for two Li intercalants turns out to be consistent with the stacking of Li atoms in C_6Li (Robinson and Salamon 1982).

(iii) Quite generally the strong variation of $\Delta E_{\lambda\mu}$ along the 2p series (figure 8) recalls to mind a similar binding energy variation for substitutional impurities along the 3d series due to the corresponding change of the impurity phase shift (Parlebas 1974, Daniel and Koenig 1989).

(iv) Also within the same interlayer plane the long-range binding energy ΔE_{LN} is negligible for Li, Be and B, but not for C and N.

(v) The binding energy ΔE_{KJ} of the interstitials (K, J) with two graphitic planes (i.e. a sandwich) between them is quite small for all the considered impurities. However, this type of interaction might change the stacking of the empty graphitic sandwich from AB

to AA like in the stage 2 compound $C_{12}Li$. Finally let us remark that it would be interesting to resume the above calculations in a pseudo-graphite host, where atoms A and B are strictly equivalent, in order to make contact with actual intercalation compound structure.

6. Conclusions

In this paper we have essentially presented a semiquantitative study of electronic properties of light impurities (Li, Be, B, C, N) intercalated between graphitic layers. Although our extra-orbital tight-binding approach is quite crude (only $2p_z$ orbitals for the frozen bulk and $2s, 2p_x, 2p_y, 2p_z$ orbitals for the impurity), we were sure to satisfy the total charge neutrality condition (Friedel rule) in order to determine the renormalized impurity levels along the series. As a consequence we were able to show some physical electronic tendencies within the series. The present calculation has to be completed by several extensions of the present model: (i) in addition to the p_z graphitic orbitals, the rest of the valence and conduction states should be included for the host; (ii) for the alkali dopant the p levels should be incorporated as well as the previously considered s orbitals, especially for the heavier alkalis (K, Rb, Cs); (iii) also, in particular for these latter dopants, the strong induced lattice relaxation of the host ought to be taken into account and its effect on the transfer integrals; and (iv) finally, the induced potential on the carbon atoms around the dopant should be treated in a consistent way. Nevertheless, the present results represent the first physical trends in the simplest reasonable model before performing more sophisticated calculations.

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References

- Charlier A, Charlier M F and Fristot D 1989 *J. Phys. Chem. Solids* **50** 987
Clementi E and Roetti C 1974 *Atomic Data and Nuclear Data Tables* ed K Way, vol 14, Nos 3-4 (New York: Academic)
Crowell A D 1985 *Surf. Sci.* **161** L597
Daniel E and Koenig C 1989 *J. Physique* **50** 2637
Dresselhaus M S 1984 *Phys. Today* **37** 60
Dresselhaus M S and Dresselhaus G 1981 *Adv. Phys.* **20** 129
Estrade-Szwarckopf H and Rousseau B 1992 *J. Phys. Chem. Solids* **53** 419
Friedel J 1958 *Suppl. Nuovo Cimento* **7** 287
Gautier F, Moraitis G and Parlebas J C 1976 *J. Phys. F: Met. Phys.* **6** 381
Heggie M I 1991 *J. Phys.: Condens. Matter* **3** 3065
Holzwarth N A W, Louie S G and Rabii S 1983 *Phys. Rev. B* **28** 1013
Kaxiras E and Pandey K C 1988 *Phys. Rev. Lett.* **61** 2693
Kelly B T 1981 *Physics of Graphite* (New York: Academic Science)
Khalifeh J and Demangeat C 1983 *Phil. Mag.* **B 47** 191
Michaelson H B 1977 *J. Appl. Phys.* **48** 4729
Moraitis G and Demangeat C 1981 *Phys. Lett.* **83A** 460
Nussbaum A 1966 *Solid State Phys.* **18** 165
Parlebas J C 1974 *J. Phys. F: Met. Phys.* **4** 1392

- Parlebas J C, Dreyssé H, Moraitis G and Gautier F 1983 *Synth. Met.* **8** 205
- Priester C, Allan G and Conard J 1982 *Phys. Rev. B* **26** 4680
- Rakotomahevitra A, Demangeat C, Parlebas J C, Moraitis G and Razafindrakoto E 1991 *6th Int. Symp. on Intercal. Comp. Proc.* (Switzerland: Trans Tech Publications)
- Robinson D S and Salamon M B 1982 *Phys. Rev. Lett.* **48** 156
- Safran S A and Hamann D R 1981 *Phys. Rev. B* **23** 565
- Taji Y, Yokota T and Iwata T 1986 *J. Phys. Soc. Japan* **55** 2676
- Volpilhac G and Achard F 1989 *J. Phys. Chem. Solids* **50** 1163