Density-functional theory calculations of the electron energy-loss near-edge structure of Li-intercalated graphite

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ABSTRACT

We have studied the structural and electronic properties of lithium-intercalated graphite (LIG) for various Li content. Atomic relaxation shows that Li above the center of the carbon hexagon in a AAAA stacked graphite is the only stable Li configuration in stage 1 intercalated graphite. Lithium and Carbon 1\(s\) energy-loss near-edge structure (ELNES) calculations are performed on the Li-intercalated graphite using the core-excited density-functional theory formulation. Several features of the Li 1\(s\) ELNES are correlated with reported experimental features. The ELNES spectra of Li is found to be electron beam orientation sensitive and this property is used to assign the origin of the various Li 1\(s\) ELNES features. Information about core-hole screening by the valence electrons and charge transfer in the LIG systems is obtained from the C 1\(s\) ELNES and valence charge density difference calculations, respectively.

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1. Introduction

From the search for alternative and clean energy sources to the technology-driven surge in the mass of portable electronic devices, the need for energy storage devices keeps increasing. This dramatic increase and the growing lobby from environmental pressure groups encourage renewed interest in battery technology for energy storage. Carbon materials have been suggested and are now widely used as anode materials for lithium-ion batteries [1–4]. For this, graphite is one of the most promising anode materials owing to its cheapness, inertness (health and safety) and its high theoretical lithium intercalation capacity of 372 mAh/g. Alkali-doped pillared carbon materials have also been suggested as possible vehicle for hydrogen storage [5]. A high pressure, high Li capacity LiC\(_2\) compound has been found to have several similar physical properties with ambient pressure LiC\(_6\) [6]. Numerous theoretical studies have been conducted in order to elucidate the electronic, structural and energetic properties of adsorbed metal atoms on graphene or their intercalation into graphite [7–17] and carbon nanotubes [18–20]. A study of the diffusion of Li atoms inside carbon nanotubes has also been undertaken [21].

Despite the extensive theoretical and experimental [6,22–28] studies conducted on Li-intercalated graphite (LIG) a unanimous understanding of the nature of charge transfer in these materials is far fetched [21]. While some workers find complete transfer [9,12,24,29,30] of the alkali metal’s s electrons into graphite, others suggest a partial charge transfer [11,13–15,25]. X-ray spectroscopy [9,25,31–33] and electron energy-loss spectroscopy (EELS) [24,34] have been used to probe the nature of the charge transfer in LIG materials. It is still not clear from these measurements what the status of the Li charges is.

In this work, we perform density-functional theory (DFT) calculations on LIG materials (Li\(_x\)C\(_6\)) for Li content \(x\) ranging from 0.167 to 1. Two possible Li arrangements were considered: (1) one in which all the interstitial spaces between the
graphene layers contained Li atoms and (2) the case where only one of every two interstitial spaces contained Li atoms. In Table 1, the various systems investigated and the type of Li arrangements (1 or 2) considered are listed. Detailed charge transfer and energy-loss near-edge structure (ELNES) calculations are performed. We find that when Li atoms are arranged such that one-dimensional Li chains running across the center of the C hexagons of AAAA stacked graphite are formed (type 1), lesser Li charge is given to the sea of interstitial conducting charges than in systems whereby only alternating layers do contain Li atoms. The sea of electrons run parallel to and are somewhat closer to the graphene sheets than to the Li planes. Orientation resolved ELNES calculations are used to identify and assign the various ELNES features that are often reported in the X-ray absorption near-edge structure (XANES) and ELNES spectra of LIG materials. An important fraction of the Li 1s ELNES spectrum is found to originate from the dipole-forbidden 1s → 2s transition. A feature in this spectrum whose presence or absence can signal the absence or presence of the linear Li chains in LIG systems is found at an energy of about 13 eV above the Fermi level.

### 2. Computational details

The systems under study here consist of graphite supercells made of two graphene layers containing 36 C atoms and 1 to 6 Li atoms. The Li atoms are inserted midpoint between the two graphene sheets and directly above the center of the C hexagons. For each Li content the out-of-plane supercell size is fixed at 7.1 Å while the in-plane size is fixed at 7.43 Å. DFT calculations are performed using the ab initio Full-Potential-Linearized-Augmented-Plane-Wave (FLAPW) package WIEN2k [35,36]. The exchange and correlation energy is treated using the local density approximation [37] which is a fit to the Green’s-function Monte Carlo calculations of Ceperley and Alder [38].

For the LiC₆ system the out-of-plane supercell size was systematically optimized and we found an equilibrium supercell size of 7.1 Å. This value is smaller than the reported experimental value of 7.4 Å [7], which is in line with the tendency of LDA to underestimate lattice parameters. It is however, higher than that of pure graphite. Throughout the rest of this work and as already pointed out earlier, for all Li contents, the out-of-plane supercell size was fixed at 7.1 Å. It is well known that, depending on the Li concentration, graphite adopts a range of stacking orders when Li is intercalated into it. We ignore the effect of this Li concentration dependent stacking sequence and consider only AAAA stacked graphite for all the systems investigated. Hartwigsen et al. [13] found that the graphite stacking sequence in LIG systems is of minor importance especially for charge distribution.

For both carbon and lithium the 1s states are treated as core states while the 2s and 2p states are the valence states. Muffin-tin radii (RMT) are fixed at 1.3 (2.0) atomic units (a.u.) for C (Li), while a RMT × Kmax value of 5.5 is used (RMT = 1.3 a.u.); Kmax being the plane wave cut-off. Up to 100 k-points are used to sample the full Brillouin zone (32 in the irreducible Brillouin zone (IBZ)). For the ELNES calculations, the core-hole effect is introduced via the so-called excited-core method. In this method the occupancy of the core state is reduced by 1 while a neutralizing charge of 1e (e is the charge of an electron) is inserted as a background charge. This method has been found to correctly model the ELNES spectra of graphite [39], carbon nanotubes [40], diamond and amorphous carbon [41]. The decomposition of the ELNES spectrum into its various components is done using the formulation of Nelhiebel et al. [42] which has been implemented in the WIEN2k code [35] and applied to hexagonal boron nitride [43], carbon nanotubes [40] and graphite [39]. ELNES is a measure of the double differential scattering cross-section for the excitation of an atom by fast electrons and is given by the expression

\[
\frac{d^2\sigma}{dE dQ} = 4\alpha^2 \frac{k}{a_0^2 K_0^2} \frac{1}{Q^2} S(Q, E),
\]

(1)

where \(a_0\) is the Bohr radius, \(\gamma = (1 - \beta)^{-1/2}\) is the relativistic factor, \(K_0\) and \(k\) the fast electron wave vectors before and after interaction, respectively, and \(Q = K_0 - k\) is the momentum transfer. The dynamic form factor \(S(Q, E)\) is defined as

\[
S(Q, E) = \sum_i \langle i | e^{iQr} | f_i \rangle^2 \delta(E + E_i - E_f)
\]

(2)

for excitations from states \(i\) with eigenvalue \(E_i\) to state \(f\) with eigenvalue \(E_f\). For small Q the exponential can be expanded as \(e^{iQr} \approx 1 + iQr + \ldots\). The first term does not contribute to the scattering cross-section because the initial \(i\) and final \(f\) states are orthogonal. Only retaining the linear term leads to the so-called dipole-approximation which is often used in the analysis of ELNES and which implies that the initial and final states are related through \(\Delta l = \pm 1\), where \(l\) is the orbital angular momentum quantum number of the excited atom. For K-edges this means transition from \(s \rightarrow p\). However, since we retain the full exponential in Eq. (2) our results also contain the non-dipole contributions. We shall show that the latter are important for the Li K-edge.

Valence electron densities are calculated using the LAPW5 package of the WIEN2k code. The charge transfer in LIG is studied by considering the charge density difference which is defined by:

\[
\Delta n_{V}(r) = n_{V}(r) - n_{C}(r) - n_{Li}(r).
\]

(3)

where \(n_{V}(r)\) is the valence electron density of the LIG system and \(n_{C}(r)\) and \(n_{Li}(r)\) those of graphite and lithium occupying the same supercell, respectively.

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**Table 1** - The different LiₓC₆ systems studied and the type of Li arrangements considered: (1) one in which all interlayer spaces between graphene sheets contain Li atoms and (2) one in which only one of the two interlayer spaces contain Li atoms.

<table>
<thead>
<tr>
<th>System</th>
<th>x</th>
<th>Type</th>
</tr>
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<tbody>
<tr>
<td>LiC₁₈</td>
<td>1/6</td>
<td>2</td>
</tr>
<tr>
<td>LiC₁₂</td>
<td>1/3</td>
<td>2</td>
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<tr>
<td>LiC₆</td>
<td>1/3</td>
<td>1</td>
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<tr>
<td>LiC₁₂</td>
<td>1/2</td>
<td>2</td>
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<tr>
<td>LiC₆</td>
<td>2/3</td>
<td>1</td>
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<tr>
<td>LiC₆</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
3. Results

3.1. Relaxation of internal coordinates in LiC₆

Six Li atoms were inserted randomly in between the graphene sheets of a 36 atom supercell ABAB stacked graphite and all the atomic positions were relaxed using the MINI package of the WIEN2k code. In order to understand the changes that take place during the relaxation of the LIG systems, we have also considered the relaxation of another system. This system consists of 3 Li atoms adsorbed on a 18 atom graphene sheet (to maintain the LiC₆ stoichiometry) in a supercell of sides $7.43 \times 7.43 \times 10 \, \text{Å}^3$. The changes in total energy per Li atom during the course of the relaxation of the two systems are shown in Fig. 1, respectively. For the Li-on-graphene system (Li on isolated graphene sheet), the Li atoms attained their most stable positions (above and at the center of the C hexagons) within the first few relaxation moves. For the case of LIG, two plateaus can be seen in the energy profile. The first, occurring within roughly the first 50 DFT steps, results when all the Li atoms are directly above the center of the carbon hexagons of one graphene layer and directly below the C atoms (atop position) of the other layer. This point in which graphite maintains its ABAB stacking, is followed by a process accompanied by a steep energy decline whereby the graphite layer whose C atoms are directly above the Li atoms undergo a glide along the $(-110)$ direction until its C hexagons are directly centered above the Li atoms. It is at this point that graphite undergoes the transformation from ABAB to AAAA stacking which is well known for Li intercalation into graphite to form LiC₆.

The final structure of LiC₆ is shown in Fig. 2. The structure clearly shows the AAAA stacked graphite with Li atoms forming linear chains that run across the center of the C hexagons. During the relaxation of the Li-adsorption on graphene and intercalation into graphite no Li atom crossed from one interlayer to the next. This can be understood by noting that studies of Li adsorption on graphene [17] and carbon nanotubes [19] both show a high energy barrier of more than 7 eV to cross the C hexagon.

3.2. Density of states

The electronic density of states (DOS) has been calculated for all Li concentrations and it is found that for all the Li contents investigated in this work the LIG systems are metallic. The metallic character arises from the filling of the graphite states that are unoccupied in pure graphite thereby shifting the Fermi level to higher energies. Typical DOS plots are shown in Fig. 3 for graphite, LiC₃₆, LiC₁₂ and LiC₆. An important aspect of the DOS is the presence of Li 2s states around the Fermi level as the inset in Fig. 3 shows. This means that not all the Li 2s electrons have been transferred to graphite, thereby sup-
porting a partial charge transfer of the Li electrons. However, the weak nature of this DOS is consistent with a net charge of less than 0.05e.

3.3. Energy-loss near-edge structure

Within the excited-core approximation, C and Li 1s ELNES spectra have been calculated. For both edges we adopted a microscope convergence angle $\alpha$ and collection angle $\beta$ of 1.9 and 3.0 mrad, respectively. The C 1s ELNES spectra are shown in Fig. 4 for LiC$_{18}$ and LiC$_6$. The LiC$_{18}$ system is constructed by inserting a Li atom in each interstitial region between the two graphene layers of a 36 atom bilayer AAAA stacked graphite. For this stoichiometry and with respect to each Li atom, three inequivalent carbon positions are possible: C atoms of the C hexagons above and below the Li atom ($\sim 2.3$ Å from the Li atoms), next neighbors located at $\sim 3.4$ Å and $\sim 4.2$ Å away from the Li atoms, respectively. In order to check the range of Li perturbation on the electronic structure of graphite for this system we have calculated the ELNES spectra of C atoms in these three positions. For LiC$_6$ all C atoms are equidistant ($\sim 2.3$ Å) from the Li atom. The spectra of C in LiC$_6$ and the 3 carbon positions of LiC$_{18}$ are shown in Fig. 4. Two major changes are seen in the C 1s ELNES spectra of all LIG systems with respect to that of graphite. The $\pi^*$ feature (appearing at the Fermi level) is greatly suppressed upon Li insertion and the $\sigma^*$ onset (showing up more than 5 eV beyond the Fermi level) is shifted to lower energies. A visible difference between the ELNES of the various carbon positions in LiC$_{18}$ is the size of the shift of the $\sigma^*$ onset which is seen to decrease with increasing distance from the Li atom as the oblique line in the right panel of Fig. 4 shows.

Several groups have measured the C 1s ELNES spectra [24,34], hard X-ray scattering spectra [25], inelastic X-ray scattering spectra (IXSS) [29] and soft X-ray emission spectra [9] of LIG systems. While Hightower et al. [24] found that the $\pi^*$ peak of graphite was greatly suppressed in LiC$_6$, they did not find a shift in the $\sigma^*$ onset with respect to that of graphite. Schulke et al. [29] also did not find this shift. However, a careful look at their IXSS measurement reveals that the slope of the $\sigma^*$ onset is stronger for graphite than LiC$_6$. This is indicative of a degree of shift of the $\sigma^*$ feature to lower energies. A more recent measurement by Balasubramanian et al. [25] found a shift of 0.6 eV. They attributed this shift to lengthened C-C bonds in LiC$_6$. The C-C bond lengths in our LiC$_6$ were barely 0.01 Å longer than that of graphite, yet the shift of the $\sigma^*$ onset was found to be 0.9 eV. Shifts of this magnitude cannot be explained by such bond length changes [44] only. We will show that the shift is a consequence of the screening of the coulomb potential by the accumulation of Li 2s conduction electrons around the carbon atoms. Such a screening should decrease as the distance from the Li atom increases. This trend is supported by the weakened shift in the $\sigma^*$ onset as the distance from the Li atom increases. Charge transfer analysis supports this trend. For example, in Figs. 5 and 6, we show the charge transfer landscape near the graphene layer and in the interstitial region between the C and Li layer of the LiC$_{18}$ system, respectively. Within the interlayer region between the C and Li layers and directly above the carbon hexagons surrounding the Li atom there are more charges than above carbon rings further away. Another finding that supports the idea that screening is the cause of the shift of the $\sigma^*$ onset is the C core-level shift. We have calculated the core-level energies (following the procedure of ref. [45]) of the carbon atoms located at 2.3 and 4.2 Å away from the Li atom and we find that the core-level energy of the nearest C atom is larger than that of the farthest atom by 0.5 eV.

![Fig. 4](image1.png)  
**Fig. 4** – Carbon 1s ELNES spectra of LiC$_{18}$ and LiC$_6$ compared with that of graphite. For LiC$_6$ all C positions are equivalent. The distances $d = 2.3$, 3.4 and 4.2 Å in the right panel denote the distances of the three inequivalent C positions from the Li atom.

![Fig. 5](image2.png)  
**Fig. 5** – Charge transfer landscape at about 0.1 Å above the graphene layer on a plane parallel to the graphene layer of LiC$_{18}$. The scales show the charge transfer (in e/Å$^3$) as obtained using Eq. (3). Negative (positive) numbers indicate charge depletion (accumulation).
A decomposition of the C 1s spectra into \( \pi^* \) (out-of-plane) and \( \sigma^* \) (in-plane) components reveals that a non-negligible amount of \( \sigma^* \) features appear at energies that are conventionally attributed to \( \pi^* \) scattering (0–5 eV above Fermi level). There is therefore, a Li-mediated modification of the hybridization of the carbon atoms of graphite.

The lithium 1s spectra of the LIG systems are shown in Fig. 7. That of LiC\(_6\) is reproduced in Fig. 8 for momentum transfer perpendicular and parallel to the c-axis. We have shifted these spectra by 56 eV for easy comparison with measurements. Within the first 15 eV above the Fermi level (about 15 eV above edge onset) we have identified seven features: feature A at \( \sim 57 \) eV, B at \( \sim 59 \) eV, C at \( \sim 62 \) eV, D at \( \sim 65 \) eV, E at \( \sim 67 \) eV, F at \( \sim 69 \) eV and G at \( \sim 71 \) eV. As Fig. 7 shows, feature C is very sensitive to the orientation of the electron beam; it vanishes as the momentum transfer becomes perpendicular to the c-axis. Features A, B, C and D have been commonly reported for LIG systems [25,28,29,34]. In addition to these features Schulke et al. [29] and Hightower et al. [24] measured features at \( \sim 70 \) and \( \sim 71 \) eV, respectively. Both features correspond to the G feature in this work. Due to energy resolution limitations, feature E may only show up as a weak feature in the measurements. Feature F has been consistently absent in all available measurements apart from the measurement of Hightower et al. [24] which revealed a weak feature at about 69 eV (\( \sim 13 \) eV above the edge-onset). In our calculations this feature is only present in LiC\(_{36}\) and LiC\(_{12}\). The common characteristic of these two systems is that while an interstitial layer contains Li atoms, the next does not (type 2 arrangement). All the layers of the other systems contain Li atoms (type 1 arrangement). In order to understand the origin of this feature we have plotted in the inset of Fig. 7 the 2s, 2pz and 2pxy components around this feature. It results from in-plane bonding of the Li atom. This feature demonstrate that more pxy charge is depleted. The presence of this feature in the spectrum of Ref. [24] and the lack of a shift in the \( \sigma^* \) edge-onset of the C 1s spectrum reported therein may suggest that the Li concentration in that sample was lower than that in LiC\(_6\). The presence of Li in all the layers of LIG systems imply the formation of linear chains of Li running across the C hexagons of graphite. Therefore, the presence of feature F in

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**Fig. 6** – Charge transfer landscape on a plane running through the center of the interlayer region between a graphene layer and a Li layer and parallel to the graphene plane of LiC\(_{18}\). The scales show the charge transfer (in e/Å\(^2\)) as obtained using Eq. (3). Negative (positive) numbers indicate charge depletion (accumulation).

**Fig. 7** – Lithium 1s ELNES spectra of LIG systems for momentum transfer perpendicular and parallel to the c-axis. The inset shows the decomposition of the spectrum of LiC\(_{36}\) into the 2s, p\(_z\) and p\(_{xy}\) components around F feature at \( \sim 69 \) eV for q\(/\)c.

**Fig. 8** – Lithium 1s ELNES spectra of LiC\(_6\) for momentum transfer perpendicular and parallel to the c-axis.
any Li 1s spectrum of a LIG system may signal the absence of these linear Li chains. The staging of LIG systems is characterized by the presence (stage 1) and absence (stages 2 and 3) of these chains. Feature F can thus be used to characterize the various stages of LIG systems.

Recently, Balasubramanian et al. [25] performed multiple scattering calculations of the near-edge X-ray absorption fine structure (NEXAFS) of LiC6. Their calculations reproduced features B, C, D and G. However, for momentum transfer parallel to the c-axis, only feature D showed up in their calculations, even though their measurement for that orientation revealed more than one feature.

The assignment of features A, B, C and D is still lacking or not accurate. In order to resolve this we decomposed the spectra of Li in Fig. 9. Our analysis shows that the dipole-forbidden 1s → 2s transition is very important for energy losses lower than 75 eV. Most assignments overlook this component which can become dominant, depending on the microscope setting. For almost parallel illumination (small collection angle) this component may dominate, depending on the microscope setting. For almost parallel illumination (small collection angle) this component may dominate, depending on the microscope setting. For almost parallel illumination (small collection angle) this component may dominate, depending on the microscope setting.

As it was pointed out in the introduction, there are two viewpoints regarding the nature of the charge transfer in LIG systems. One holds that Li atom gives away only a fraction of its 2s electron [13–15,25] and the other argues that the entire 2s electrons are transferred to graphite [9,12,24,29,30]. Both arguments presuppose that the Li charges can only be transferred to the C atoms of graphite. It is well known that interlayer states exist in graphite [10]. When Li is intercalated into graphite what becomes of these interlayer states? In order words, to which atoms should they be assigned? How much Li charge goes into these states? We will not answer these questions, rather we will begin by limiting the charge transfer analysis to the charge given up by Li and we will not go into the specifics of how much charge carbon has received. Based on this we will find that Li in all the LIG systems gives away almost its entire 2s electron.

The electron density of states has been used to perform charge transfer quantification [15]. We follow the same procedure for our LIG systems. The total DOS was integrated over an energy interval ΔEF up to the Fermi level, where ΔEF is the difference between the Fermi energy and the Dirac point (defined as the point where the density of states vanish). We find that ΔEF varies from 0.75 eV for Li1/6C6 (LiC36) to 1.75 eV for LiC6. For all the LIG systems a charge transfer of (1.0 ± 0.08)e/LiC6 was found. This value should be compared with the value of 0.90e obtained in Ref. [15] using similar method for Li on graphene. Note that we have used the total DOS for this calculation, implying that the interlayer state DOS was included. Since the shift in the Dirac point is a consequence of the filling of the previously unoccupied states by Li valence electrons, this charge of (1.0 ± 0.08)e is thought to be the charge transfer from Li. Thus this methods demonstrates an almost total charge transfer from Li.

### 3.4. Charge transfer

As it was pointed out in the introduction, there are two viewpoints regarding the nature of the charge transfer in LIG systems. One holds that Li atom gives away only a fraction of its 2s electron [13–15,25] and the other argues that the entire 2s electrons are transferred to graphite [9,12,24,29,30]. Both arguments presuppose that the Li charges can only be transferred to the C atoms of graphite. It is well known that interlayer states exist in graphite [10]. When Li is intercalated into graphite what becomes of these interlayer states? In order words, to which atoms should they be assigned? How much Li charge goes into these states? We will not answer these questions, rather we will begin by limiting the charge transfer analysis to the charge given up by Li and we will not go into the specifics of how much charge carbon has received. Based on this we will find that Li in all the LIG systems gives away almost its entire 2s electron.

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*Fig. 9 – The 2s, pxy and pz components of the Li 1s ELNES spectrum of LiC6 for momentum transfer q parallel and perpendicular to the c-axis. Note that the dipole-forbidden 1s → 2s transition is not weak.*

*Fig. 10 – The effect of microscope collection angle β on the Li 1s ELNES spectrum. The convergence angle θ is set at 1.87 mrad. The inset shows how the 1s → 2s transition becomes dominant for small β.*
Spectroscopic methods have been suggested and used for charge transfer quantification of these materials, yet the results are conflicting [24,25,28,46]. An early Auger electron spectroscopy study on LiC$_6$ and CsC$_8$ [46] has been conducted in order to study charge transfer in these materials. The finding of that measurement was that the screening of the core-electron renders inadequate the use of such methods for charge transfer analysis as the intensity of the $\pi^*$ peak was consistent with a transfer of four electrons from each Li atom into the $p_z$ orbitals of carbon. Core-hole screening was suggested to be responsible for this discrepancy. This can easily be checked by performing ELNES calculations with and without core-hole effect taken into account. We know that if charges are transferred into the $p_z$ orbitals of graphite we expect a decrease in the scattering cross-section corresponding to the transition into this orbital. The C 1s ELNES spectra on Fig. 4 show a dramatic decrease in the $\pi^*$ ELNES feature of both LiC$_6$ and LiC$_{18}$. By assuming that the $p_z$ orbital of pure graphite is empty and denoting the ratio of the integrated $\pi^*$ differential cross-section of pure graphite to the total integrated differential cross-section by $R_0(\Delta E)$ and the corresponding ratio for LIG system as $R(\Delta E)$, we evaluate the charge transfer (in e) into the $p_z$ orbital by the expression

$$
\Delta Q_{pz}(\Delta E) = \frac{R_0(\Delta E) - R(\Delta E)}{R_0(\Delta E)(1 - R(\Delta E))}.
$$

Each integration is over the same energy window $\Delta E$ which is measured from the Fermi level. Fig. 11 shows the dependence of $\Delta Q_{pz}(\Delta E)$ on $\Delta E$ for LiC$_6$ and LiC$_{18}$. For LiC$_6$, both core-hole and non-core-hole calculations are considered. We see almost no dependence on $\Delta E$ for this quantity especially when core-hole effects are not accounted for. For LiC$_{18}$ core-hole calculations are performed and the three inequivalent carbon positions are reported showing that charge transfer to graphite occurs within the first two carbon shells.

Fig. 11 – Charge transfer from ELNES quantitative analysis of LiC$_6$ and LiC$_{18}$. Non-core-hole and core-hole ELNES spectra are considered for LiC$_6$. For LiC$_{18}$ core-hole calculations are performed and the three inequivalent carbon positions are reported showing that charge transfer to graphite occurs within the first two carbon shells.
to be 0.03 e/Li. Therefore, 97% of Li 2s electrons are delocalized throughout the crystal as conduction charges. We suggest that the notion of charge transfer in LIG systems should only be limited to the part of Li 2s electrons that are still bound to the Li nucleus and a subsequent charge redistribution as a result of a change in effective atomic volumes on bringing together Li and graphite to form a LIG system: the so-called geometrical charge transfer [11]. In what follows we will not distinguish between these two aspects of charge transfer.

Valence charge density differences were evaluated using Eq. (3) and are presented in Fig. 13. The entire density profile is fitted as a linear combination of Gaussian functions each of which is assigned to one of three layers: (1) graphitic, (2) interstitial and (3) lithium layers. This partitioning permits us to quantify the charges within each of the three regions. These regions correspond to those defined in Ref. [13]. Fig. 14 shows the charge transfer per C atom for the graphitic and the interstitial regions between the graphene and Li layers and that per Li atom for the Li layers. Charges deplete from the graphitic and lithium layers and accumulate in the interstitial region. The amount of charge extracted from Li and the graphite layers increases as the Li content increases and the extraction from Li atoms is about five times higher when the Li layers are distant apart (type 2 arrangement). We find that 0.036 e/C and 0.057 e/Li are extracted from C and Li, respectively, and deposited into the interstitial region for LiC6. These values compare well with the values of 0.03 e/C and 0.07 e/Li as obtained by Hartwigsen et al. [13] for this system.

The latter method of charge transfer analysis is not able to capture any changes that may occur within each plane parallel to the graphene sheets. In fact, on inspection of Figs. 5 and 6 we notice that at about 0.1 A˚ away from a graphene sheet of LiC18, a complex charge transfer takes place. The C–C bonds of the C6 rings located above and below the Li atoms experience a charge depletion of about −0.03 e/Å3 while about +0.02 e/Å3 accumulates on these C atoms. A better insight
into the charge transfer on the carbon atoms of these C₆ rings can be obtained by inspecting the charge density difference along a line parallel to the c-axis and passing through one of the carbon atoms of these rings. This charge density as a function of distance from the atom and for various Li contents is shown in Fig. 15 and clearly shows that charges accumulate on these C atoms. For type 1 intercalation, these charges extend to distances of about 1 Å above and below the carbon atoms and pass through a maximum at a distance of about 0.3 Å, meanwhile for type 2 intercalation the charge distribution passes through two maxima: one at ~0.20 Å and a second broader one at ~0.9 Å.

4. Summary

Within the core-hole implementation, we have shown that the main changes in the C and Li 1s ELNES spectra can be accurately described. A feature showing up in the Li 1s spectrum at about 13 eV above threshold is found which can be used to characterize the stagings in LIG systems. We have found that, depending on the microscope settings, the dipole-forbidden 1s → 2s ELNES transitions in Li can be very important compared to the dipole allowed 1s → 2p transitions. Charge transfer quantification based on C 1s ELNES spectroscopy is seen to be inaccurate if core-screening cannot be explicitly quantified. Based on the density of states, we have found that Li gives up its entire 2s electron when it is intercalated into graphite.

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