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THEORETICAL STUDY OF LiC_6

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Abstract: We have studied the relative stability of the $\text{A}\alpha\text{A}\alpha\text{A}\alpha$ and $\text{A}\alpha\text{A}\beta\text{A}\gamma$ stackings of stage 1 lithium in graphite at zero temperature, focusing on the Li-C chemical bond in each case. We have determined the equilibrium atomic structure of LiC_6 with a first-principles molecular dynamics technique, in particular for the Li atoms equilibrium positions, and the effect of Li-intercalation on the graphite planes. We found that the $\text{A}\alpha\text{A}\alpha\text{A}\alpha$ stacking is favorable, although the energy difference turns out to be quite small. A very slight distortion of the graphite lattice gives rise to two different classes of hexagonal rings, depending on whether they are occupied by lithium atoms.

1. Introduction

Intercalation of graphite provides a means for controlled variation of its physical properties over a wide range, which makes graphite intercalation compounds (GICs) interesting from a technological point of view. For this reason, research in the synthesis and physical properties of GICs has been very active over the past decades. Nevertheless, many physical and chemical properties of these materials are still poorly understood. Pristine graphite is a semimetal with a very low, and highly anisotropic electrical conductivity. Conduction takes place mainly within the graphite layers and it is therefore regarded as a primarily two-dimensional phenomenon. When intercalated with alkali metals such as Li, K, Rb or Cs the system becomes metallic, and the conductivity can reach values typical of Cu. In a very simplified way this feature is explained in terms of a rigid band model, where the lowest unoccupied π -bands of pristine graphite are partially filled with the electrons supplied by the donor alkali intercalants [1,2].

We shall be concerned here with the crystal structure of LiC_6 , the least anisotropic and with the highest in-plane density of Li atoms of the alkali doped GICs. This is a stage 1 compound where the intercalant layers form an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ superlattice. The graphite layers are arranged in an AA stacking, i.e. consecutive sheets are not displaced relative to one another, unlike in pristine graphite which has an AB stacking [3]. The stacking of Li layers at very low

temperatures is still a matter of some experimental controversy [3-7]. In Fig. 1 we show the two proposed arrangements $A\alpha A\alpha A\alpha$ and $A\alpha A\beta A\gamma$.

Figure 1: The two proposed stackings for LiC_6 : (a) $A\alpha A\alpha A\alpha$, and (b) $A\alpha A\beta A\gamma$

While electron diffraction studies [4] indicate that the zero temperature structure is $A\alpha A\beta A\gamma$ for $T < 220$ K, neutron scattering measurements [5-7] imply an $A\alpha A\alpha A\alpha$ arrangement for $T < 715$ K. Both kinds of experiments, as well as X-ray diffraction [3], agree instead in an $A\alpha A\alpha A\alpha$ structure at room temperature. At $T = 715$ K Robinson and Salamon [5] report a phase transition identified with the dimensional melting of the Li sublattices. The critical exponents extracted there are consistent with the three-dimensional, three-state Potts model's universality class. Such a model is coherent with the $A\alpha A\alpha A\alpha$ stacking for the ground state [8].

The next question we want to address here concerns the effects of alkali intercalation on the graphite host, with the exception of the modification of the stacking of the graphite planes from AB to AA. This latter issue is beyond the scope of the present calculation. X-ray powder-diffraction measurements [3] indicate a c-axis expansion of 10%, and a 1% increase of the in-plane lattice constant. The resolution of the diffraction peaks is not enough to show whether a distortion of the carbon rings exists. In an earlier theoretical calculation [9], Holzwarth et al. argued that the charge redistribution might result in a small lattice relaxation, but no quantitative calculations were reported.

2. Theoretical Method

We have performed our calculations with a first-principles molecular dynamics technique (CP) [10]. We have used a supercell containing 72 carbon and 12 lithium atoms (300 valence electrons),

with hexagonal periodic boundary conditions. The C atoms were arranged in three layers of 24 atoms each, separated by layers of four Li atoms. In such a structure both the $A\alpha A\alpha A\alpha$ and $A\alpha A\beta A\gamma$ stackings can be fitted. Thus, it is expected that the two calculations are of comparable accuracy. This will lead to large cancellation of errors and thus to a meaningful comparison. The ions and electrons have been described in the local-density approximation (LDA) to density functional theory (DFT), within the framework of non-local norm-conserving pseudopotentials, to represent the core electrons [11]. The effective single particle wave functions at the Γ -point of the supercell's Brillouin zone have been expanded in plane waves with the upper cutoff at 35 Ry, corresponding to 17000 basis functions. The accuracy of the pseudopotentials and the adequacy of the cutoff have already been tested extensively [12,13]. We have taken the experimental values for the lattice constants [3], i.e. $c=3.705 \text{ \AA}$ and $a=2.485 \text{ \AA}$, corresponding to a nearest-neighbor distance $d_{C-C}=1.4345 \text{ \AA}$, with the Li atoms placed in a plane equidistant $c'=1.8525 \text{ \AA}$ from the graphitic planes. The dimensions of our supercell are given by $a_S=8.607 \text{ \AA}$ and $c_S=11.115 \text{ \AA}$.

Minimization of the system's total energy has proved difficult because steepest descent, conjugated gradients [14] and preconditioned conjugated gradients [15] techniques lead to a very poor convergence. In order to circumvent these problems it was necessary to use instead a dynamical simulated annealing technique as in the original CP paper [10], followed by a steepest descent minimization when convergence was in sight.

3. Results and Discussion

We have performed the above described calculation for the two different stackings $A\alpha A\alpha A\alpha$ and $A\alpha A\beta A\gamma$ at fixed ionic positions. Our results indicate a difference in total energy of $\Delta E \simeq 0.014 \text{ eV}$ per unit cell (i.e. per Li atom) between the two stackings, favorable to $A\alpha A\alpha A\alpha$. This energy difference is very small, but there is experimental evidence indicating that the energy barrier between them could be rather high (of the order of 1 eV) [16]. Therefore metastability of the $A\alpha A\beta A\gamma$ phase is likely. This energy difference results from a delicate interplay of kinetic, exchange and correlation, and electrostatic energy, resulting in a slightly more convenient combination for the $A\alpha A\alpha A\alpha$ stacking. In Fig. 2 we show the charge density relative to AA graphite with the same lattice constants in three mutually orthogonal planes. Figures 2(a) and 2(b) present the graphitic plane, 2(c) and 2(d) a plane oriented along the c-axis passing for a Li and a C-C bond, and 2(e) and 2(f) a plane which contains the Li and cuts the C-C bond. Figures 2(a) and 2(b) show that a small fraction of the charge associated with the C-C bonds (σ -bonds) in the graphitic plane is removed from the plane towards the π -orbitals in both stackings. These orbitals, identified with the lowest unoccupied states in graphite, are partially filled with the electrons transferred from the Li atoms, as can also be seen in plots (c) to (f). The reduction of the in-plane C-C bond charge originates in the polarization of the valence states. Then, the bands are modified and the rigid band picture breaks down. What also becomes apparent in these figures is that the charge transfer, although high, is not complete. Some charge remains localized close to the Li atoms, and this could explain a bond length slightly shorter than what is expected from theoretical models [17,18].

Figure 2: Charge density difference with AA graphite. Left panel for $A\alpha A\alpha A\alpha$, and right for $A\alpha A\beta A\gamma$ stacking. Contour lines expressed in $e/(a.u.)^3$. Distances expressed in Bohrs. Dashed lines indicate the graphitic planes. Crosses mark the projected location of the Li atoms. Slight asymmetries in the pictures are due to numerical noise.

The other feature appearing clearly in Fig. 2(a) is the existence of two kinds of C-C bonds. Even if all C sites are equivalent, and Li atoms lie above and below a 6-fold ring, the associated bonds are weakened. Figure 2(e) cuts the graphitic planes through the bonds, and it shows a greater reduction of charge close to the Li. Therefore, in stacking $A\alpha A\alpha A\alpha$ each C atom is two-fold coordinated with a weak bond, and one-fold with a strong bond. We now contrast the behavior of $A\alpha A\alpha A\alpha$ and $A\alpha A\beta A\gamma$. In the $A\alpha A\beta A\gamma$ stacking the number of sites occupied by a Li is twice that in $A\alpha A\alpha A\alpha$ because of the displacement of successive Li layers. This leads to a reversed situation as in $A\alpha A\alpha A\alpha$, in which two bonds are strong and one weak. Bearing these observations in mind, we have relaxed the ions towards the equilibrium using a combined steepest descent technique for both ions and electrons. The result is that the weakened bonds tend to increase the bond length, as would be expected, and as was conjectured by Holzwarth et al. [9]. In Fig. 3(a) we show the resulting in-plane structure, where the distortion was exaggerated for the sake of clarity. The lengthened bonds turn out to increase by $\Delta l_{\text{long}} \sim 0.003$ Bohr and, since our calculation is at constant volume, the remaining bonds decrease their length by $\Delta l_{\text{short}} \sim -0.006$ Bohr.

Figure 3: Optimized in-plane structure of LiC_6 for stackings $A\alpha A\alpha A\alpha$ (a) and $A\alpha A\beta A\gamma$ (b). Open circles represent C atoms and filled big circles Li atoms (out of the plane). In (a) there are Li above and below the plane. In (b) the shaded circles are above and the empty below the plane.

The numbers presented here for the bond length are merely indicative of the order of magnitude of the distortion. In order to obtain better numbers, it is necessary to sample the Brillouin zone more accurately by including K-points other than Γ . The same procedure applied to stacking $A\alpha A\beta A\gamma$ gives just the opposite distortion; i.e. two short bonds and one long bond per C atom, with $\Delta l_{\text{long}} \sim 0.003$ Bohr and $\Delta l_{\text{short}} \sim -0.0015$ Bohr. This is shown schematically in Fig. 3(b). The energy decrease due to ionic relaxation is very small, i.e. one order of magnitude smaller than the energy difference between the two stackings. Note that these numbers are within the experimental accuracy reported by Guerard and Herold [3], but in principle it should be possible to detect a splitting of the diffraction peak at very low temperatures. Let us remark also that since all C atoms are still equivalent, no splitting is expected in the ^{13}C NMR spectrum, although it is possible to have a shifting of the resonance.

Work is currently in progress to confirm these results with more accurate all-electron calculations.

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