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Polymeric forms of carbon in dense lithium carbide

Xing-Qiu Chen1,2,4, C L Fu1 and C Franchini3

1 Oak Ridge National Laboratory, Materials Science and Technology Division, Oak Ridge, TN 37831, USA
2 Shenyang National Laboratory for Materials Sciences, Institute for Metal Research, Chinese Academy of Sciences, Shenyang, 110016, People’s Republic of China
3 Faculty of Physics, University of Vienna and Center for Computational Materials Science, A-1090 Vienna, Austria

E-mail: xingqiu.chen@imr.ac.cn

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Abstract

The immense interest in carbon nanomaterials continues to stimulate intense research activities aimed at realizing carbon nanowires, since linear chains of carbon atoms are expected to display novel and technologically relevant optical, electrical and mechanical properties. Although various allotropes of carbon (e.g., diamond, nanotubes, graphene, etc) are among the best-known materials, it remains challenging to stabilize carbon in the one-dimensional form because of the difficulty of suitably saturating the dangling bonds of carbon. Here, we show through first-principles calculations that ordered polymeric carbon chains can be stabilized in solid Li$_2$C$_2$ under moderate pressure. This pressure-induced phase (above 5 GPa) consists of parallel arrays of twofold zigzag carbon chains embedded in lithium cages, which display a metallic character due to the formation of partially occupied carbon lone-pair states in sp$_2$-like hybrids. It is found that this phase remains the most favorable one in a wide range of pressures. At extreme pressure (larger than 215 GPa) a structural and electronic phase transition towards an insulating single-bonded threefold-coordinated carbon network is predicted.

(Some figures in this article are in colour only in the electronic version)
double bonds [8]. The alternation of bonds and the resulting insulating groundstate is induced by a Peierls-like instability. Massive doping, however, lifts the Peierls instability and leads to a highly conducting metallic regime [9, 10].

Like hydrogen, lithium forms several binary compounds with carbon [11], but none of them reveal 1D features similar to $(C_2H_2)_n$. On the carbon-rich side the best-known materials are lithium–graphite intercalation compounds such as LiC$_6$ [12], whereas on the Li-rich side the only compound which can be produced directly from the elements is Li$_3$C$_2$, characterized by triple bonded C≡C dimers [13, 14]. Considering that charge is donated from Li to C in Li$_2$C$_2$, one might expect that Li$_2$C$_2$ under pressure could be transformed to a polycarbonate-like structure with 1D characteristics. This expectation is based on two reasons: (1) the pressure decreases the lattice spacing and, therefore, increases the interaction between C≡C dimers, and (2) the role of the C–H bond in C$_2$H$_2$ could be replaced by that of the lone-pair orbital in Li$_2$C$_2$ in the stabilization of a chain-like structure.

In this study, we applied density functional theory (DFT) to perform an extensive search for possible structural candidates for Li$_2$C$_2$ under pressure. Over 200 crystal structures were explored with different local environments of carbon atoms. We find that by application of low pressure (5 GPa) triple bonded C≡C dimers in Li$_2$C$_2$ can be transformed into metallic carbon linear chains encapsulated in lithium cages. The pressure-dependent evolution of this structure shows that the carbon chains are stable over a wide range of compressions, and are eventually converted into insulating single-bonded C–C cubic networks above 215 GPa. Thus, our computational experiment reveals that it is possible to construct conductive linear chains of carbon by simply compressing solid Li$_2$C$_2$ at pressures accessible to modern high pressure technology. Considering that Li$_2$C$_2$ can be easily produced and that, unlike polycarbonate, the conductivity arises naturally upon pressure without the need of any doping treatment, we believe that our study will stimulate prompt experimental investigations in the foreseeable future.

First-principles calculations were mainly performed using the Vienna ab initio simulation package (VASP) [23, 24] with the ion–electron interaction described by the projector augmented wave potential (PAW) [25]. We used the generalized gradient approximation within the Perdew–Burke–Ernzerhof (PBE) parameterization scheme [26] for the exchange–correlation functional. Brillouin zone integrations were performed for special $k$ points according to Monkhorst and Pack technique. The energy cutoff for the plane-wave expansion of eigenfunctions was set to 500 eV. Optimization of structural parameters was achieved by the minimization of forces and stress tensors. Highly converged results were obtained adopting a very high energy cutoff of 500 eV for the basis sets, and utilizing a dense $12 \times 12 \times 12$ $k$-point grid for the Brillouin zone integration. For the proposed Bm nb phase, phonon spectra under pressure were performed using density functional perturbation theory as implemented in the Quantum-ESPRESSO code [27], using norm-conserving pseudopotentials.

Structural properties: the prediction of crystal structure by means of first-principles methods remains a complex task and a good choice of initial configurations is crucial to perform an accurate structural search. Recent studies have demonstrated that a large pool of randomly selected initial configurations is a necessary ingredient for an accurate structural search [28–30]. In our study, to form random unit cells we have chosen Bravais matrix with random lattice parameters and random cell angles (including all seven crystal classes). For each initial configuration the internal degrees of freedom (atomic positions) were selected by a random modification of several structural possibilities found in literature. Finally, the unit cell volume was properly scaled in order to reproduce the desired pressure. At this point we have performed a full structural optimization (cell shape, lattice parameters and internal positions) for each starting configuration according to a quasi-Newton algorithm where forces and the stress tensor are used to determine the search directions for finding the equilibrium configuration. This computational procedure reduces substantially the risk of being trapped in metastable solution (local minima of the potential energy surface) and permits the exploration of a large number of different structures. We have tested local carbon environments including triple bonded dimers, carbon linear chains (polyene- and polycarbonate-like structures) and three-connected nets [31] (planar (graphite like), puckered ($\alpha$-arsenic structure) or more complex conformations such as those observed in ThSi$_2$ [32], SrSi$_2$ [33] and DyGe$_3$ [34]).

The energy/pressure relations derived from our DFT structural search are depicted in figure 1. The low pressure insulating orthorhombic Immm phase (figure 2(a)) is correctly predicted to be the lowest energy phase at zero pressure, with structural parameters in excellent agreement with experiment (see table 1). At 5 GPa this phase is transformed into a metallic phase with Bm nb symmetry characterized by zigzag chains of carbon atoms which are embedded in hexagonal Li cages (figure 2(b)). The Bm nb phase remains the most favorable solution until 215 GPa, at which pressure an insulating phase of cubic $I\bar{2}3$ symmetry with the threefold carbon polymeric network (figure 2(c)) is stabilized. The pressure-induced structural evolution is accompanied by a peculiar modulation of the carbon bonds from C≡C triply bonded dimers (Immm) to sp$^3$-like twofold-coordinated carbon chains (Bm nb), and finally to a sp$^3$-like threefold-coordinated carbon network, which is very similar to that in the high pressure cubic gauche structure of solid nitrogen (cg-N) [15].

At 5 GPa, we find a sudden volume collapse of 25%, as shown in figure 1(c), related to the Immm $\rightarrow$ Bm nb phase transformation. The Bm nb phase is found to be energetically stable against a phase separation into bcc Li and LiC$_6$, as well as against a decomposition into bcc Li and graphite. Here, we should mention that the ab initio treatment of graphite within a conventional GGA approach suffers from the well-known limitations related to the fact that van der Waals interactions between graphic layers are poorly described. In order to minimize the effects of vdW errors we have followed the procedure tested by Mounet and Marzari [16] which consists in the calculation of the equation of state (EOS) in the variable $c/a_0$ with the in-plane lattice parameter $a_0$ kept fixed to the experimental value. The so
Figure 1. DFT calculated energy/pressure relations for Li$_2$C$_2$. (a) Energy difference ($\Delta E$) versus volume ($V$), (b) enthalpy difference ($\Delta H$) versus pressure, and (c) volume ($V$) versus pressure. In panels (a) and (b), the energy zero refers to the energy of the Immm phase at 0 GPa. The thin curves in panel (a) represent the relationship between $\Delta E$ and $V$ for other structures considered here. The thick and thin curves in panel (c) denote the stable and unstable pressure regions for corresponding phases, respectively.

Table 1. DFT optimized structural parameters for the Immm (No. 71), Bmmb (No. 63) and I2$_3$ (No. 199) structures of Li$_2$C$_2$. Lattice parameters ($a$, $b$, and $c$) and bond length of carbon ($L_{C-C}$) are given in angstrom.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Expt [14]</th>
<th>DFT (0 GPa)</th>
<th>DFT (5 GPa)</th>
<th>DFT (215 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>3.652</td>
<td>3.635</td>
<td>3.134</td>
<td>4.172</td>
</tr>
<tr>
<td>$b$</td>
<td>4.831</td>
<td>4.849</td>
<td>2.503</td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>5.434</td>
<td>5.389</td>
<td>7.237</td>
<td></td>
</tr>
<tr>
<td>$L_{C-C}$</td>
<td>1.226</td>
<td>1.221</td>
<td>1.431</td>
<td>1.597</td>
</tr>
<tr>
<td>Li</td>
<td>4j:(0, 0.5, 0.236)</td>
<td>4j:(0, 0.5, 0.239)</td>
<td>4c:(0, 0.25, 0.153)</td>
<td>8a:(0.306, 0.306, 0.306)</td>
</tr>
<tr>
<td>C</td>
<td>4g:(0, 0.127, 0)</td>
<td>4g:(0, 0.126, 0)</td>
<td>4c:(0, 0.25, 0.452)</td>
<td>8a:(0.073, 0.073, 0.073)</td>
</tr>
</tbody>
</table>

obtained EOS and bulk modulus are in fair agreement with the experimental values [17, 18] and the expected error associated with the GGA binding energy, $\sim 0.05$ eV C$^{-1}$, does not affect the alloy stability reported here. Additional support for the stability of the proposed Bmmb structure is provided by the absence of any imaginary frequency in the calculated pressure-dependent phonon spectrum reported in figure 3.

The predicted pressure-induced structural evolution from the Immm phase to the Bmmb structure can be ascribed to the modification of the lattice parameters (elongation of
Figure 2. Schematic illustration of the pressure-induced structural sequence (a) Immm → (b) Bmmb → (d) I213 with smaller balls for C and larger balls for Li. Curved arrows in panel (a) indicate the rotation of C≡C pairs which leads to the zigzag C–C arrangement sketched in panel (b). Panel (d) illustrates the threefold carbon polymeric network. Panel (c) shows the change in energy (ΔE) when rotating the C≡C pairs as shown in panel (a) for three different volumes of the Immm structure. Note that the lattice parameters are allowed to relax (but with the constraint of constant volume) in obtaining each of the curves in (c).

Figure 3. Pressure-dependent phonon dispersions for the proposed Bmmb phase at the pressures of 0, 10, 20, 30, 50, and 70 GPa.

Figure 4. Panel (a): DFT band structures of the Bmmb phases; band labeling, see text. Charge-density contours of (b) C–C σ bonded states of bands b1, b2 and (c) lone-pair states of bands b3, b5.

c and compression of the ab plane of the Immm phase) and concomitant rotations of the carbon dimers, according to figures 2(a) and (b). Energetically, the crucial mechanism governing the Immm to Bmmb transition is the rotation of the carbon dimers, as illustrated in figure 2(c). At zero pressure (corresponding to a volume of V = 11.875 Å³) the rotation of dimers is highly unfavorable, but with increasing pressure the energy barrier is reduced and disappears at a volume of V = 9.0 Å³, corresponding to 5 GPa. Upon this structural transformation, the C≡C dimers are converted into zigzag carbon chains with a C–C bond length of 1.43 Å and a large inter-chain distance of 3.13 Å. The carbon chains in the Bmmb phase are parallel arrays of polymeric chains along the b axis direction (figure 2(b)). Although the Bmmb phase is calculated to be the most stable in a very wide pressure range of 5–215 GPa, at pressures above 150 GPa it becomes very close in energy to a tetragonal phase of I41/amd symmetry. In this I41/amd phase the carbon atoms also form zigzag chains, but with blocks of chains oriented 90° with respect to each other, similar to the Ge-network of BaGe2 [19]. At 215 GPa we predict a second structural transition towards an insulating cubic I213 phase (see figure 2(d)), accompanied by a volume collapse of 8%. This phase has a σ-character single-bonded C–C bond length of 1.60 Å at 215 GPa, which resembles that of diamond at 0 GPa (1.55 Å). This phase is similar to the high pressure cubic gauche structure of solid nitrogen (cg-N [20]) as experimentally synthesized by Eremets et al [21] and as theoretically studied by us [15].

Electronic properties: at zero pressure the Immm phase exhibits a wide gap of 3.9 eV which slightly decreases upon pressure, reaching the value of 3.7 eV at the critical pressure of 5 GPa, at which the transition towards the metallic Bmmb structure occurs. Upon further compression, the metallic regime is finally destroyed at 215 GPa, at which pressure the most stable I213 phase shows a gap of 2.7 eV. The calculated DFT gaps of insulators are generally too small. By performing a screened exchange hybrid density functional calculation for Li2C2 within the Heyd–Scuseria–Ernzerhof scheme we obtain a significantly larger gap (5.8 eV) for the Immm phase at 0 GPa.

The bonding property of the metallic Bmmb structure is dominated by sp²-like hybrids. Two of the carbon electrons form covalent σ-type bonds (bands b1 and b2 in figure 4(a)) connecting neighboring carbons along the zigzag backbone with a bond angle of 123°. These σ-character states (figure 4(b)) display quasi-1D features as reflected by square root singularities [10] in the density of states profile (figure 5). Our analysis also revealed lone-pair orbitals localized at the carbon sites, as depicted in figure 4(c). The bands formed
by the lone-pair orbitals, however, are overlapped in energy with the bands formed by the \( \pi \)-type bonding and antibonding orbitals of carbon. In order to accommodate ten electrons per \( \text{Li}_2\text{C}_2 \) formula unit (with the charge donated from Li to C) in the energy bands of \( \text{Li}_2\text{C}_2 \), the Fermi level has to intersect both the lone-pair and \( \pi \)-state bands. In other words, there are holes in the lone-pair state and electrons in the antibonding \( \pi \)-state. The electron-deficient lone-pairs are distributed into the fully occupied band b3 and partially filled band b5. Formally, a lone-pair state should trap two electrons but we find that about 1.7e are trapped in band 5. The remaining electrons occupy the \( \pi \)-states, which are characterized by the charge-density lobes aligned perpendicular to the plane defined by the zigzag chains. These orbitals form bands with \( \pi \)-type bonding and antibonding character, as indicated by the respective bands b4 and b6 in figure 4(a). The bonding b4 band is fully occupied whereas the antibonding b6 band is partially filled with occupancy of 0.3e.

As mentioned already, conjugate polymers represent the only known producible form of carbon-chain based structures. In order to highlight the structural similarities between archetypal linear carbon chains of polycetylene and C–C chains of the \( \text{Bmmb} \) structure, we compare their corresponding local structure in figure 6. In spite of some visual similarity, significant differences can be realized, which explain the distinctly different electronic character: the covalent nature of the C–H bond in polycetylene is replaced by the ionic C–Li bond in \( \text{Li}_2\text{C}_2 \), which is stabilized by the formation of the lone-pair in \( \text{sp}^2 \)-like hybrids. In polycetylene a Peierls distortion is observed [8] which induces alternating single and double bonds with an angle of 120° and a gap opens up, and substantial doping is required in order to lift the system towards a conducting regime. A different stabilization mechanism is found for the \( \text{Bmmb} \) phase of \( \text{Li}_2\text{C}_2 \): holes are created in the lone-pair band b5 which prevent the Peierls-like splitting of states, and thereby the system is metallic.

To ascertain the distinct structural and electronic properties of the predicted \( \text{Bmmb} \) phase, we carried out additional calculations with four different supercells containing a larger number of atoms (\( \text{Li}_{16}\text{C}_{16}—2a \times 2b \times c \), \( \text{Li}_{24}\text{C}_{24}—2a \times 3b \times c \), \( \text{Li}_{32}\text{C}_{32}—2a \times 2b \times 2c \), and \( \text{Li}_{64}\text{C}_{64}—2a \times 4b \times 2c \)) and performing the full structural relaxation without any symmetry constraints. Indeed, all derived optimized structures converge to the same \( \text{Bmmb} \) phase and display identical structural (carbon linear chains) and electronic (metallic \( \text{sp}^2 \)-like hybrids) characteristics. This computational experiment unambiguously proves that the linear C–C chains in the \( \text{Bmmb} \) phase are conducting and do not undergo any Peierls-like dimerization. Also, it is interesting to note that there is a resemblance between our proposed \( \text{Li}_2\text{C}_2 \) \( \text{Bmmb} \) structure and \( \text{Li}_x\text{B} \) (\( x = 0.90 \) and 0.95) [22]. In the latter, each B–B chain is encaged in a subnetwork of sixfold \( \text{Li}_6 \) octahedra. However, in \( \text{Li}_x\text{B} \) the bonding picture is very similar to that calculated for the hypothetical carbon chains (\( \alpha \)-carbyne or \( \beta \)-carbyne), which is still intrinsically different from the current case of \( \text{Li}_2\text{C}_2 \).

The metallic character of compressed \( \text{Bmmb} \)-type \( \text{Li}_2\text{C}_2 \) is maintained until the occurrence of the second pressure-induced transition at 215 GPa, when the cubic \( I2_3 \) phase is stabilized. This new phase is insulating with a gap of 2.7 eV (figure 2(c)). Although the carbon atoms in this structure are threefold-coordinated, the structure is stabilized by the presence of near tetrahedral \( \text{sp}^3 \)-hybridized electronic states. For the \( \text{sp}^3 \)-like hybrids in this case, there are three covalent \( \sigma \)-character bonds connecting each carbon atom to its three nearest neighbors; the remaining two electrons form a lone-pair orbital, which does not participate in the direct bonding with other atoms. The occupied states consist of two distinct groups very similar to those of \( \text{cg-N} \) [15]. The lowest energy states (more than \( -6 \) eV below the top of the valence band) correspond to the \( \sigma \) C–C bonding states. The second lowest group, ranging from \( -6 \) eV to the top of valence band, consists of nonbonding states, which relate to the lone-pair orbital. Although the C–C bond angle (110°) is very close to that in diamond (109°) the bonding scheme is very different, as discussed in [15].

In summary, our extensive computational study demonstrates that metallic linear chains of carbon can be formed by compressing lithium carbide at relatively low pressure.
The conducting properties of these polyyne-like structures embedded in lithium cages originate from the formation of partially filled lone-pair orbitals which favor ionic C–Li bonds and suppress the tendency towards a Peierls-like insulating behavior. One important observation of the present study is that the chain-like structure is stable in a wide pressure range, i.e., from 5 GPa to 215 GPa, which is accessible to standardly used high pressure equipment, therefore we believe that our findings will encourage immediate experimental investigations.

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