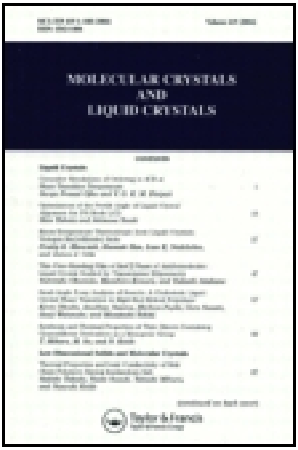

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: R. Setton & J. Conard (1994): Madelung Energy and Stability of the Compound Li_7C_{24} Prepared Under Pressure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 307-312

To link to this article: http://dx.doi.org/10.1080/10587259408050122

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 307–312
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Printed in the United States of America

MADELUNG ENERGY AND STABILITY OF THE COMPOUND Li_7C_{24} PREPARED UNDER PRESSURE

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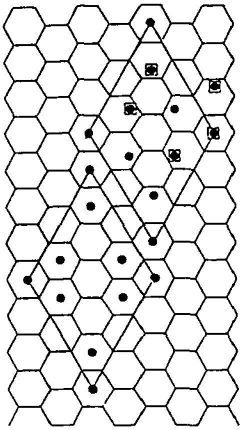
Abstract Li-graphite compounds were recently obtained under pressure with a Li/C ratio as high as 1/2. At ambient temperature and pressure, the system relaxes to a composition close to Li_7C_{24}, and the IR frequencies, the positions of the X-ray diffraction lines and ^{7}Li NMR point to a lattice composed of two-dimensional clusters of 7 Li atoms on a substrate of 24 C atoms, but neither the calculated structure factor nor ^{7}Li NMR give evidence of local axial symmetry, as found for instance in LiC_6.

The Madelung energy of structures obtained by modifying the positions of the Li atoms in the clusters was calculated. A significant gain in stabilization was found for a radial shift of the peripheral Li atoms placing them about 3.2 Å from each other within each cluster, in a configuration reminiscent of a Penrose lattice, with 5 or 6 nearest neighbors for each Li. A rough modelization of Li-Li covalency was also included by localizing some negative charge between first-neighbor Li^+ ions, with a consequent further gain in stability. The Madelung energy is comparable to that of other LiC_n structures ($2 \leq n \leq 6$). In all cases, energetically favorable structures are characterized by 'smooth' local potentials of electrostatically equivalent species.

INTRODUCTION

It was recently found that first-stage lithium graphite intercalation compounds (GICs) with a particularly high value of the Li/C ratio can be obtained under pressure[1]. As deduced from the volume variations in the course of the preparation, Li/C tends towards 1/2, the maximum value for single-layered monoatomic species but, at ambiant temperature and pressure, Li/C ≈ 1/3.7 and a possible corresponding lattice is shown in Figure 1, in which a cluster of 7 Li atoms is seen to lie in epitaxy on a substrate of 24 C atoms, with about 3.7_+ Å between the midplanes of the graphene layers on either side of



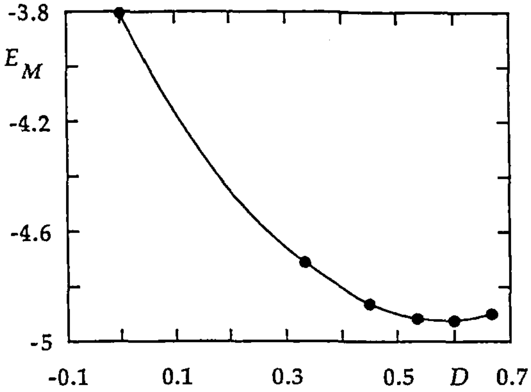


FIGURE 1 (left) Lower left: lattice of Li_7C_{24}; the projection of the position of the Li atoms on the graphene layer corresponds to D = 0 (epitaxy). Upper right: lattice of Li_7C_{24} with 6 out of 7 Li atoms shifted to D = 0.583. The five Li atoms singled out by a square are the nearest neighbors to the Li atom at the center of the circle on which they lie.

FIGURE 2 (right) Normalized Madelung energy M_E vs. radial displacement of the peripheral Li atoms.

the intercalated layer[2]. This structure has been used in connexion with the determination of some properties of the 'relaxed' system, such as X-ray diffraction and ^{7}Li NMR, but neither structure factor calculations nor NMR yield complete confirmation, and further data are required for a full knowledge of the structure. However, the value 11.1 Å = 3x(3.7) Å for the lattice parameter *c* now seems certain.

We have tried to determine if Madelung energy calculations could throw light on the problem by indicating the most probable among a number of cognate structures directly derived from the one shown in Figure 1, the criterion being of course that the stablest system would be the one with the greatest loss of electrostatic energy (maximum value of $-M_E$), even though a negative value of M_E does not guarantee the existence of a structure.

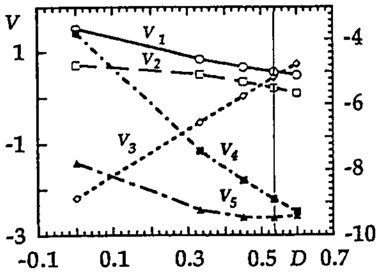
RESULTS AND DISCUSSION

Madelung energies were calculated by the Ewald method with standard procedures[3]. The three-tiered lattice was obtained by successively translating the intercalate layer in Figure 1 by the vectors (1/3, 2/3) and (2/3, 1/3). Since the seven-atoms cluster of epitaxic Li atoms only occupies seven out of the twelve available centers of hexagons, we first examined the effect of shifting the six peripheral Li atoms radially, thus increasing the area under each cluster and hence the distance between the atoms in all first-neighbor pairs. As seen in Figure 2, in which the *normalized Madelung energy* (eV per single Li atom) is plotted as a function of the displacement D ($D = 0$ for peripheral atoms at the center of a carbon hexagon, $D = 1$ for atoms shifted outwardly till the C-C bond), the energy of stabilization increases, reaches a maximum value, then decreases when the shift is too large. By quadratic interpolation, the maximum energy of stabilization is found to be at the Li-Li distance 3.18 Å, with $D = 0.583$; it is then $-M_E = 4.923$ eV/Li atom, an increase of 29% with respect to the value 3.805 eV/Li atom at $D = 0$, with the Li-Li distance then equal to 2.47 Å.

It is interesting, at this point, to discuss the local potentials V_j at the j energetically different sites of the lattice. Ewald-type calculations of the Madelung energy give direct access to V_j values. For the epitaxic lattice ($D = 0$), the potentials can be divided into 5 groups:

V_1: 12 C atoms, mean potential = +1.526 V ($q = -0.2917$);
V_2: 6 C " " " +0.720 V ($q = -0.2917$);
V_3: 6 C " " " -2.187 V ($q = -0.2917$);
V_4: 6 Li " " " -7.926 V ($q = +1.0$);
V_5: 1 Li " " " -3.805 V ($q = +1.0$).

Since the contribution of the atoms at each site to the final energy is q_jV_j, it is clear that the potential V_3 is highly disruptive since the energy contributed is positive, hence repulsive. Figure 3 shows the variation of the potentials at the three carbon sites as D varies from 0 to 0.6. The reversal of sign of V_3 is at the root of the increase in stability since $V_3 > 0$ for $D > 0.44$, and the range $0.44 \leq D \leq 0.65$ constitutes a *zone of stability* since none of the potentials are then disruptive. The value $D = 0.583$ is close to $D = 0.536$, at which all the distances between first-



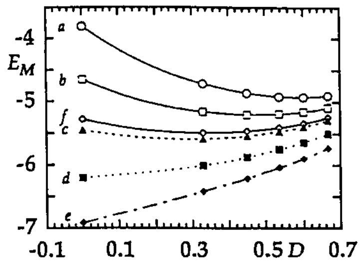


FIGURE 3 (left) Variation of the local potentials (V) in the lattice of Li_7C_{24} vs. D; V_1, V_2, V_3, left-hand scale; V_4, V_5, right-hand scale. The vertical line at $D \approx 0.536$ indicates the value at which all the distances between nearest-neighbors are equal, close to the D value for maximum energy of stabilization.

FIGURE 4 (right) Energy of stabilization M_E vs. D in the presence of a model covalent charge q_c between nearest-neighbor Li atoms; *a)* $q_c = 0$; *b)* $q_c = -0.05$; *c)* $q_c = -0.10$; *d)* $q_c = -0.15$; *e)* $q_c = -0.20$; *f)* $q_c = -0.09$ (see text).

neighbor Li atoms are identical and equal to 3.12 Å; at that point, the Li-Li distance is 0.15 Å larger than the distance 3.03 Å found in the free metal. This configuration is reminiscent of a Penrose lattice (see Fig. 1): the Li atoms at the center of the clusters still have 6 symmetrically placed peripheral nearest-neighbors (NN) at 60° from each other, whereas each peripheral atom has only 5 NN, also placed on a circle but at 60°, 90°, 60°, 90° and 60° instead of 72° for each interval if the placing had been completely symmetrical. The local potentials of the C sites are now $V_1 \approx +0.57$ V, $V_2 \approx +0.21$ V, $V_3 \approx +0.44$ V, while those of the Li sites are $V_4 \approx -8.8$ V and $V_5 \approx -9.4$ V (Figure 3). Spreading the clusters therefore results in a considerable decrease of the differences in local potentials among both the C and the Li atoms.

Since the Li atoms in Li_7C_{24} are certainly closer to each other than they are in the stable GIC LiC_6, we have tried to modelize the possible presence of a weak 'covalent bond' by placing a small negative charge between the Li atoms of each of the 12 NN pairs. This could, for instance, be due to an overlap of pure *s* orbitals, or to a mixing of p_x and p_y orbitals, or to any other hybridization not involving the graphitic π electrons. As seen in Figure 4, the presence of this negative charge midway between the Li^+ ions immediately affects the zone of stability and improves the cohesion of the structure, but a number of conflicting consequences are simultaneously present: for instance, if each charge is larger than -0.15, the zone of stability is practically reduced to a point. When *D* is too large, the interaction between the Li^+ ions and the covalent charges is too small, i.e. there is no Li-Li bond. When *D* is small, the presence of even a small amount of charge between the Li^+ ions compensates their reciprocal repulsion but decreases somewhat the attraction between the graphene layers and the intercalate.

Previous work[4] resulted in the elaboration of two empirical expressions relating the optimal concentration n_{max} of intercalate to the interlayer distance d_I in the GIC MC_n, namely

$$n_{max} = 0.11082\ (d_I)^{2.74} \qquad (1)$$

and the absolute value of the optimal charge q_{opt} to d_I:

$$|q_{opt}| = 9/(d_I)^{2.74}. \qquad (2)$$

Equation (1) yields $n_{max} = 4.0$ for $d_I = 3.71$, a value fairly close to $n = 3.43$ for Li_7C_{24}, suggesting that this compound should probably be fairly stable, even at normal pressure. From equation (2) and with the same value of d_I, $|q_{opt}| = 0.247$ and the total charge on the graphene layer would then be about -5.95. If the remaining charge available from the 7 Li atoms is localized between the two Li^+ ions in each pair of NN, q_C should be about $-(7 - 5.95)/12 = -0.09$. Curve *f* in Figure 4 shows the variation of M_E with *D* for this value of q_C. Maximum stability corresponds to $D = 0.33$, and the Li-Li distance between NN is now 2.87 Å. This is substantially smaller than the distance 3.12 Å mentioned above, but more in line with the value deduced from NMR spectroscopy which would favor even shorter distances[5].

It is quite obvious that we seem to have reached the limit of information obtainable from simple Madelung energy calculations: because the method is not self-consistent, and owing to the lack of precise data concerning the actual position of the Li atoms in the lattice, it is at best only possible to compare a range of values of the Madelung energy with values calculated for similar existing or hypothetical compounds. All but one of the values of $-M_E$ in Table I refer to epitaxic lattices, with no covalent charges between the Li atoms of NN pairs, and one can see that the Madelung energy of epitaxic Li_7C_{24}, though lower, is quite comparable to the values calculated for other lattices with d_1 = 3.714 Å.

TABLE I Madelung energy of epitaxic LiC_n compounds

Compound	$-M_E$ (eV per Li atom)
$(LiC_2)_1$	4.586
$(Li_3C_8)_1$	4.442
$(Li_3C_8)_2$	4.475
$(Li_2C_6)_1$	4.543
$(Li_2C_6)_2$	4.570
$(Li_7C_{24})_3$	3.805
$(Li_7C_{24})_3$	4.923*
$(LiC_6)_1$	4.500

*Non-epitaxic, maximum value, with D = 0.583

From the values in the Table, it seems however highly likely that $D > 0$, and that D probably lies within the range 0.3 to 0.6 given above. The calculation of other parameters, such as the Born-Mayer potentials, etc. will be undertaken when supplementary experimental data will be available.

REFERENCES

1. V. V. Avdeev, V. A. Nalimova and K. N. Semenenko, High Pressure Research, 6, 11 (1991)
2. D. Guérard and V.A. Nalimova, these Proceedings
3. R. Setton, Synthetic Metals, 34, 279 (1989)
4. R. Setton, Materials Science Forum, 91-93, edited by D. Tchoubar and J. Conard, (Trans Tech Publications, Switzerland, 1992), p. 763.
5. J. Conard, V. A. Nalimova, D. Guérard, these Proceedings.