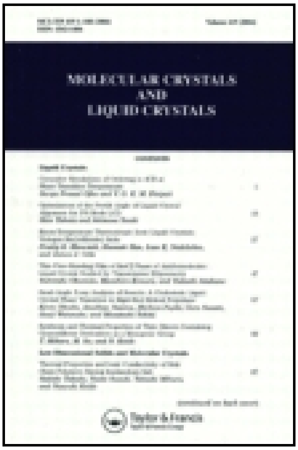

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Oct 2006.

To cite this article: J. Conard , V. A. Nalimova & D. Guerard (1994): NMR Study of LIC$_X$ Graphite Intercalation Compounds Prepared Under High Pressure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 25-30

To link to this article: http://dx.doi.org/10.1080/10587259408051661

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 25–30
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Printed in the United States of America

NMR STUDY OF LIC$_X$ GRAPHITE INTERCALATION COMPOUNDS PREPARED UNDER HIGH PRESSURE

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ABSTRACT A highly saturated Li graphite intercalation compound synthesized under high pressure , was investigated after pressure relaxation by ^{7}Li NMR spectroscopy. At low temperature the sample exhibits a doublet at 256 ppm downfield from Li$^+$. The lineshape agrees with the simulation of an island of 7 Li atoms with nearest neighbours at 2.46 Å distances, in good agreement with a local LiC$_2$ structure. This confirms short metal-metal bondlengths and possible Li-Li covalent bonds which were shown by IR Spectroscopy.

INTRODUCTION

First stage alkali metal graphite intercalation compounds (GICs) LiC$_6$ and MC$_8$ are well documented for their crystalline and electronic structure. It was shown that charge transfer in these compounds is very high (>90%)[1, 2, 10]. The nearest M-M in-plane distances are large enough (4.26 and 4.92 Å, respectively) and direct interaction between metal atoms in such ordered layers seems to be not very significant and mainly electrostatic. The investigations of the high pressure synthesis of alkali metal GICs[3, 4] have shown the possibility of obtaining much more saturated stage 1 compounds than by traditional methods. For Lithium, the most highly saturated compound obtained under high pressure was LiC$_2$, which contains 3 times more Lithium than normal LiC$_6$. The most evident structure, when all the positions over the graphite hexagons are occupied by Lithium atoms, is presented in Fig 1a. It contains very short (2.46 Å) Li-Li distances in the intercalated layer. Nearly the same Li-Li distances were observed in tetrahedral Li$_4$ clusters with some organic molecules and in Li triangles in Ni phenyl-Li complexes[5]. It is thought that covalent Li-Li bonds are present, involving Li 2p orbitals. Taking into account very short Li-Li distances and a very low probability for the existence of Li$^+$ ions at these distances, we propose this unusual covalent type of bonding in the metal layer. It should be accompanied by a decrease in the charge transfer per Li atom, from metal to graphite. Using IR-spectroscopy, we have shown[6] in the metal layer in LiC$_X$, the presence of covalent Li-Li bonds in equilateral lithium triangles with the length 2.46 Å (Fig1b).

In this paper we report the use of ^{7}Li Nuclear Magnetic Resonance, after pressure release, to characterize the metallic state in LiC$_X$ by the observation of a Knight shift.

SYNTHESIS AND CARACTERIZATION

LiC_2 samples were synthesized from Highly Oriented Pyrolytic Graphite (HOPG) with a misorientation angle along the c-axis less than 1° and Lithium of 99.7% purity. Synthesis was carried out under a pressure of 50-60 kbar and a temperature up to 280°C in the anvil crater-toroid apparatus. The composition was monitored by measuring the volume of the sample under pressure using the technique described elsewhere[4]. After the synthesis, the sample was kept in liquid nitrogen to prevent its decomposition. The stability of the compound obtained was checked by the constancy of the volume when it was kept in a closed ampoule, at ambient pressure and temperature, since decomposition should be essentially accompanied by a volume increase (a loss of one intercalated lithium atom among the 24 carbon atoms of the unit cell involves an increase of the total volume close to 10%). But IR spectrocopy investigations have shown that heating the sample quickly decomposes it to LiC_6 and Li.

This is the reason why, samples studied by ^7Li NMR were checked by X Rays before and after the NMR investigations. In fact, there were no noticeable changes due to the NMR investigations. Observed hkl reflections are shown in Fig. 1. Comparison of their positions with those calculated for different structural models has shown that the experimental data correspond to a hexagonal unit cell with a=8.63 Å. There are several possible compositions for the unit cell with this a parameter. Calculation of the intensities of hkl reflections shows that the most probable one is the unit cell Li_7C_{24} (or $LiC_{3.4}$), shown in Fig 1b. This unit cell does not exclude the presence of LiC_2 in the sample since the LiC_2 unit cell is included in that of Li_7C_{24} as well as that of LiC_6. It seems that $LiC_{3.4}$ is a stable step in the process of the decomposition of LiC_2 compound:

$$12\ LiC_2 \dashrightarrow Li_7C_{24} + 5\ Li_{met} \dashrightarrow 4\ LiC_6 + 8\ Li_{met}$$

but there are different compositions which correspond to this unit cell and which contain Li_x clusters, from $Li_{11}C_{24}$ (or $LiC_{2.2}$) to LiC_6C_{24} (or LiC_4).

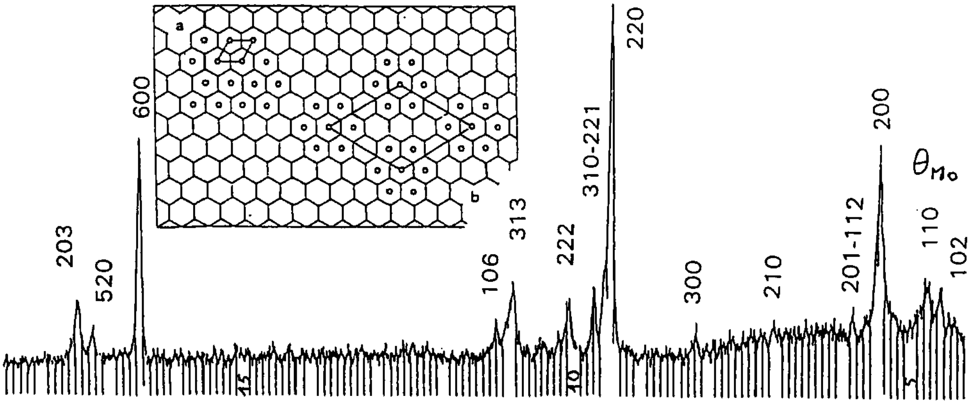
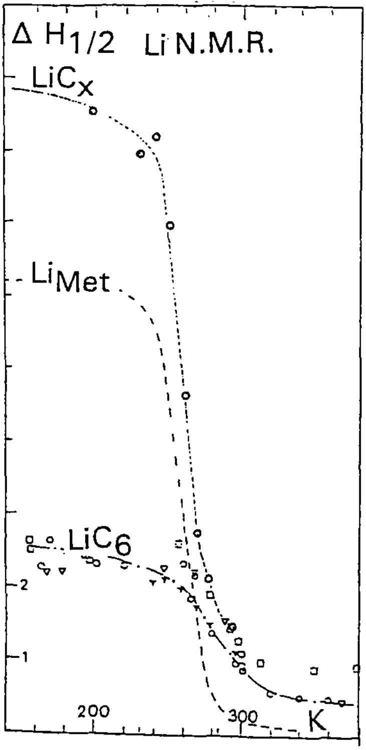


Fig. 1 X rays diffraction diagram and lattices showing LiC_2 and Li_7C_{24} stoichiometries.

LINESHIFT, LINEWIDTH and DYNAMICS of ^{7}Li

In Li-GICs the ^{7}Li Knight shift is concentration-dependent and gives the projection of the density of states at E_F on the 2*s* component of the alkali atom. It also gives the residual alkali *s*-character or the difference to complete ionization[7].

In LiC_x samples at room temperature an intense Lorentzian line is observed at 260 ppm from the Li^+ position, very close to the position for metallic lithium (Fig.2). On decreasing the temperature, there is an overall line widening of up to 9 G, to be compared to the 6 G linewidth of the pure metallic Li line. The flat top of the line for H_0//c is resolved into a doublet when H_0//a,b which does not exist in the metallic Lithium line, which is always Lorentzian. The well-known LiC_6 line at 42 ppm is also observed and is very small in freshly prepared samples (Fig.3). The change of the overall linewidth with temperature is given in Fig.2 and is compared to metallic Li and LiC_6. Clearly, a higher local field attributed to nearer Li nuclei is responsible for the low temperature linewidth. But narrowing occurs in the same temperature range, showing that the diffusion process needs approximately the same activation energy corresponding to the potential saddle point between two carbon atoms.



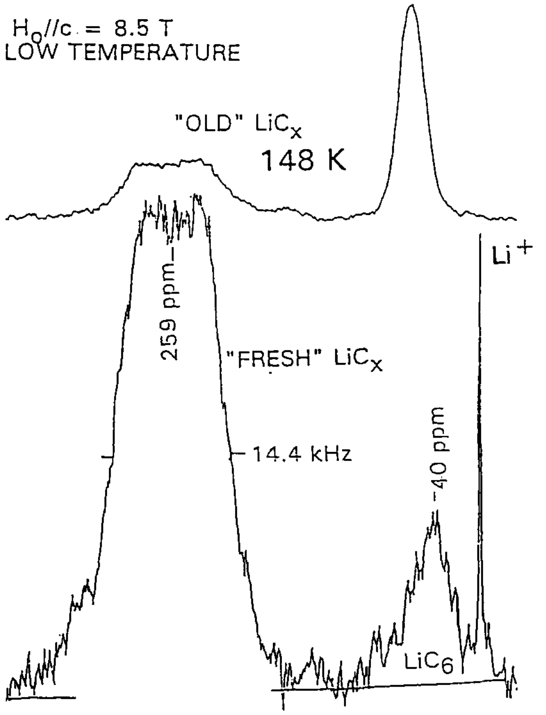


Fig.2: Linewidth vs T. Fig.3: Low temperature spectra for fresh and old samples.

^{7}Li NMR LINESHAPE AND SIMULATION

It is seen in Fig.3 that, at low temperature, the lineshape is resolved into a Gaussian doublet with a small Lorentzian line due to excess metal or resulting from the slow decomposition of LiC_2. The doublet doubles its separation value when the sample orientation, relative to the magnetic field, rotates from H_0//c to Ho//a,b, in agreement with a dipolar structure .The doublet is characteristic of a cluster of Li atoms, where each has an odd number of nearby first neighbours. We therefore simulated the spectral structure from the Li_7 island model and we obtained a doublet with small shoulders (Fig.4) quite comparable to the experimental one but suggesting a slightly shorter Li-Li distance.

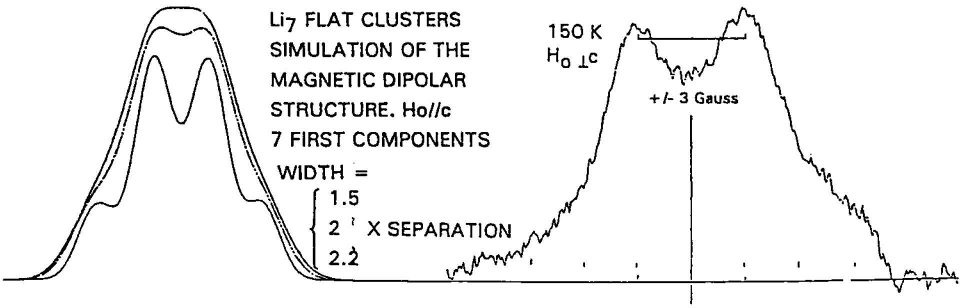


Fig. 4. Lineshape simulation compared to observed ones.

^{7}Li NMR RELAXATION

It was shown in LiC_6[10-12] that the RT relaxation mechanism has three main components:

- scalar interaction with conduction electrons, with a Korringa law K^2T_1T=ctt (with K: lineshift to the ionic position and T_{1S}: relaxation time),

- quadrupolar mechanism (T_{1Q}), due to coupling between the ^{7}Li electrical quadrupole moment and the electrical field gradient (EFG) fluctuations due to the lattice point charge modulation by the phonons and to free carrier motion,

- dipolar mechanism (T_{1D}), when the atomic diffusion starts, near room temperature, involving a high Li-vacancy ratio.

EFG did not give any observable structure in LiC_x, probably because of too a high dipolar field and too high an asymmetry for the external lithium sites. But it was demonstrated in other alkali GICs that the screening was essentially localized to the neighbouring π orbitals and the EFG was almost constant (Vzz = 10^6 $V.cm^{-2}$). Then the two last mechanisms would not vary very much at constant temperature. Therefore it is interesting to predict and compare the Korringa $T_1{}^x$ of LiC_x to the $T_1{}^6$ of the LiC_6:

$T_1{}^s = T_1{}^6 .(K^6/K^x)^2 = 2.(40/260)^2$ = 47ms, in agreement with the experimental value 40 ms and different from the Li metal value, namely 150 ms. For about the same Knight shift, the difference between the LiC_x and the metal relaxation T_1 values results from differences in the local symmetry and the orbital Li contribution to the density of states at the Fermi level. We are then confident that the coincidence between the metal and $LiC_{3.4}$ Knight shifts does not impair the NMR check of the proposed model.

^{13}C NMR STUDIES

A stack of LiC_x particles approximately oriented with H_0//a,b were studied by ^{13}C NMR. A line or group of lines is found with the top at -93ppm/C_6H_6 the overall values being distributed between -84 and -98 ppm Fig. 5. This position is in agreement with the known ordered values for MC_6, MC_8 and MC_{24}. But the observed shift is less than the proportionality to the composition 1/x, which probably means that we observe at the π orbital carbon level, the consequence of a limited ionization of Li atoms. But we also expect bandshape and curvature changes, effects which also contribute to the deviation of the shift from the proportionality to the metal content.

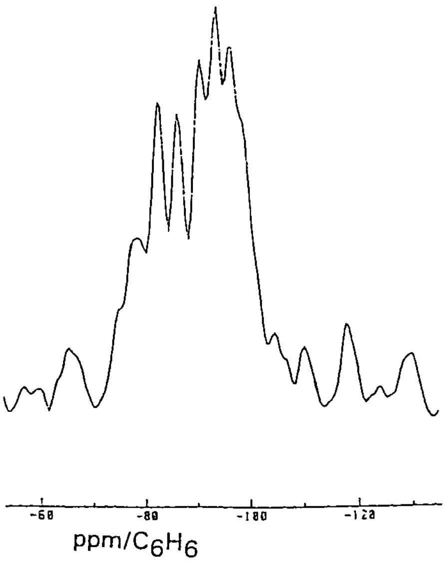


Fig.5: ^{13}C NMR at 8.5 T.

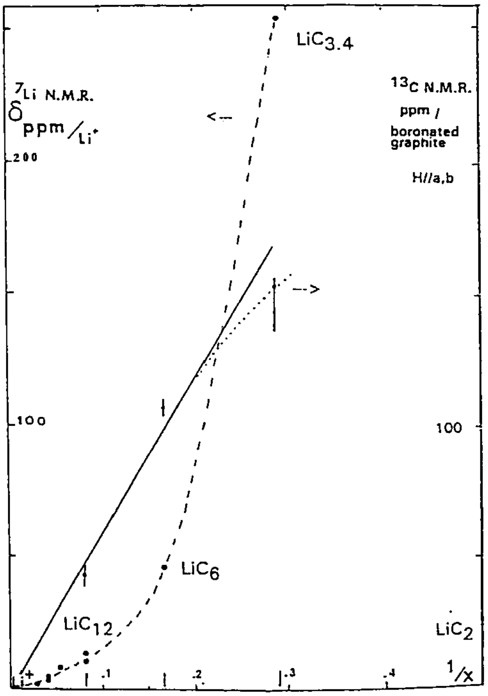


Fig.6: ^7Li and ^{13}C lineshifts vs Li content 1/x

DISCUSSION

The Li clusters have been studied by various experimental and theoretical methods[9,13], and, among them, Li_7 is known to be stable. In free space or in an adsorbed phase, it takes a pentagonal bipyramid shape, but other equilibrium shapes are not very far in stability, provided they are not too highly symmetrical (Jahn-Teller effect). We deduce that the flat symmetrical islands result from the graphite constraints in agreement with a Li-C covalencypreviously found in LiC_6.

The bondlengths are also very short in Li_2 (2.67 Å), Li_2^+ (2.85 Å) and Li_7 (3.14 Å), with a very high p-orbital character (60%)[9]. Thus, it seems acceptable to consider Li_7 as a flat cluster with the graphite lattice and in self equilibrium, since Li diffusion occurs at a time scale of 4.10^{-5} sec. at R.T. The pronounced Li p-orbital character is specific to lithium and results from the very small size of the 2*s*-orbital. From ESR[13], we know that in Li-clusters, it has the same value as in the bulk metal. Then, part of the electron density may be localized on the *2p* orbital of lithium, giving covalent Li-Li bonds in the layer.

The ionization energy of a cluster of seven Li atoms is divided by a factor of about 2, relative to the atomic value (5.39 eV for Li)[15]. This explains why lithium compact islands ($E_i \approx 2.7$ eV) are e-donors relatively to graphite ($E_i = 3.9$ eV). The $LiC_{3.4}$ phase seems to be metastable at ambient conditions but even after one year of keeping the sample under these conditions, it still contains more than 20% of the highly saturated phase. The presence of Li diffusion at room temperature, as seen by NMR, which would permit the clusters to change their shape and size, proves that the Li_7 islands are stable atomic groups. The covalency between Li atoms could be responsible for this attraction, in agreement with a strong overlap of 2*p* orbitals. But it seems that it is impossible to keep the LiC_2 phase stable without high pressures, because of the small distances among the Li atoms in the whole metallic layers.

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