

Clustering and polymerisation of $\text{Li}_{15}\text{C}_{60}$

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The structural and electronic properties of lithium intercalated fullerenes (of which $\text{Li}_{15}\text{C}_{60}$ is the most representative) are still puzzling and unclear. Above 520 K, X-ray/neutron diffraction show an *fcc* phase in which the 15 Li atoms clusterize in the octahedral interstices. However, at lower temperatures a change in crystalline symmetry and also in the electronic properties takes place as observed from ^{13}C , $^7\text{Li}/^6\text{Li}$ NMR and X-ray diffraction measurements. X-ray diffraction data suggest the presence of two different stable structures: a tetragonal monomeric and an orthorhombic polymerised phase. Detailed ^{13}C magic angle spinning NMR experiments in the latter phase, evidence sp^3 bondings among the carbon atoms, whereas the relative (sp^2/sp^3) intensities, together with X-ray data, suggest a C_{60} polymerisation as [2 + 2] cycloaddition. Multiple Quantum NMR experiments on ^7Li confirm the presence of lithium clusters, as observed by X-ray diffraction in the high temperature phase, also at lower temperatures. However, the inferred cluster size is significantly smaller than that suggested by stoichiometry. The distortion in the low-*T* structure of $\text{Li}_{15}\text{C}_{60}$, is supposed to induce the migration of Li atoms from octahedral to tetrahedral voids, thus accounting for the lower number of Li atoms in the clusters. Further evidence about this scenario is obtained also from preliminary measurements of line shapes and T_1 relaxation times, which exhibit a multi-exponential recovery with very different constants, hardly compatible with a single family of Li atom sites.

Unlike other alkali doped fullerenes, Li_xC_{60} has been somewhat overloaded in recent works on fullerene doped systems. Probably this could be due to difficulties in its preparation and perhaps to its lack of superconducting properties. However, the small radius of the intercalant gives Li_xC_{60} some peculiar properties, rather different from the better known A_xC_{60} (where $A = \text{K}, \text{Rb}, \text{Cs}$ and $1 \leq x \leq 6$). Namely, fullerenes show a considerable degree for Li atom acceptance, yielding systems with x as high as ~ 30 . Being the less studied of the alkali doped fullerenes very little is known about its properties, especially in the low-*T* lattice distorted phase, which occurs for temperatures below 520 K. Apart from some basic structural features evidenced by X-ray and quasielastic and inelastic neutron scattering [1], there exist many questions regarding both the behaviour of Li atoms but also that of the fullerene host lattice.

These include the existence in the low-*T* phase of Li clustering, the C_{60} packing and polymerisation, the possible charge transfer and interaction between Li and C_{60} , etc., which are decisive in the construction of a model that would explain the electronic properties of the Li_xC_{60} systems.

In this work we report on investigations performed on $\text{Li}_{15}\text{C}_{60}$, a typical representative of the whole class of compounds, both by using local techniques such as NMR, as well as X-ray diffraction to elucidate its structural characteristics.

1. Experimental

The samples were prepared by thermal decomposition under dynamic vacuum of high purity, isotopically enriched $^7\text{LiN}_3$ mixed with stoichiometric amounts of C_{60} . Heating the mixture at ~ 450 K yielded $\text{Li}_{15}\text{C}_{60}$ with a 5% accuracy

in lithium content. Annealing for several hours at 520 K gave powder pellets of improved crystallinity and homogeneity. Depending on preparation conditions some of the samples turned out to be a mixture of polymerised with non-polymerised phases, whereas most of them resulted in a single non-polymerised phase. Here we are concerned only with the former type of samples.

X-ray measurements were performed with a GADDS (Bruker AXS) diffractometer. For the NMR lineshape measurements we used a Spinmaster (Stelar) spectrometer, whereas for those involving more complex multi-quantum NMR a home-built instrument was employed.

2. Fullerene polymerisation in $\text{Li}_{15}\text{C}_{60}$

The presence of a polymerised structure in a crystalline lattice is reflected not only in the modified electron density distribution but can also alter the lattice symmetry group and/or the lattice parameters. Therefore the joint use of experimental techniques such as NMR and X-ray diffraction capable of detecting these changes, could provide useful information on polymerisation.

We measure the $\text{Cu } K_\alpha$ X-ray diffraction intensity as a function of sample temperature from 300 up to ~ 550 K. From comparison with well know powder diffraction patterns for $\text{Li}_{12}\text{C}_{60}$ [1] and pristine C_{60} [2] we deduce the presence of two distinct phases at room temperature. Successive indexing procedures identify one tetragonal and one orthorhombic phase; the respective lattice parameters and symmetries are shown in Table 1. Preliminary results from structure refinement performed on the orthorhombic phase suggest a 1D carbon polymerisation of C_{60} .

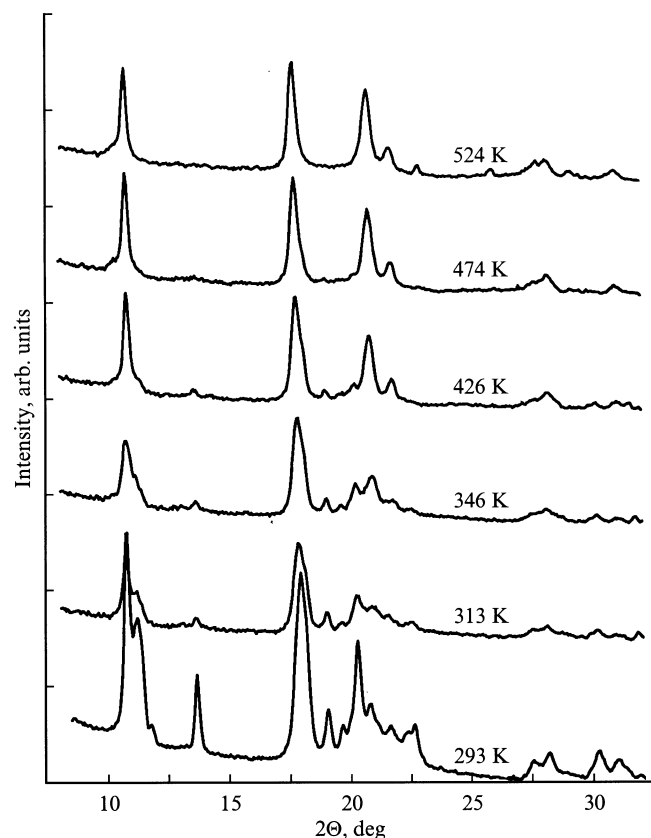


Figure 1. X-ray diffraction patterns for a $\text{Li}_{15}\text{C}_{60}$ sample as a function of temperature. The room temperature spectrum shows the coexistence of an orthorhombic and a tetragonal phase, which upon heating transform into a single cubic phase. The spectra were recorded using a laboratory $\text{Cu K}\alpha$ radiation.

As the temperature is increased (Fig. 1) the intensities relative to the two distinct phases begin to merge, so that for $T > 550 \text{ K}$ only one pattern, compatible with a single cubic phase, is present. The occurrence of an orthorhombic-to-cubic transition (besides the already known tetragonal-to-cubic transition [1]) implies therefore the disappearance of C_{60} polymerisation upon sample heating.

Lattice symmetries and parameters for the orthorhombic and tetragonal phase of $\text{Li}_{15}\text{C}_{60}$ as obtained from X-ray diffraction measurements

Symmetry	Angles	Lattice parameters, Å
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a = 9.06, b = 9.32, c = 15.10$
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$	$a = b = 9.87, c = 14.30$

Further evidence about fullerene polymerisation in $\text{Li}_{15}\text{C}_{60}$ was obtained by static and magic angle spinning (MAS) ^{13}C NMR. At room temperature, the static lineshapes display an inhomogeneously broadened shift-anisotropy powder pattern, typical of static sp^2 fullerene carbons. Moreover, two additional sharp peaks are found at 155 and at 59 ppm, which could be respectively attributed

to a motionally averaged $\text{C}_{60}^{n-} sp^2$ line and to sp^3 hybridised carbons. These findings suggest both a blocked rotation for a considerable amount of C_{60} molecules due to covalent bonding in a polymer configuration and also the presence of a phase inhomogeneity as found from X-ray diffraction.

Additional evidence about these result comes from MAS experiments which allow more precise quantitative assignments for the individual peaks. From an accurate fit of the lineshapes one can evaluate the intensity ratio $f = I_{sp^3}/I_{sp^2}$ from which (once the C_{60}^{n-} contribution is subtracted) an average number of four sp^3 atoms per C_{60} molecule can be inferred.

This result is compatible with several bonding configurations among C_{60} molecules which may include two $[2+2]$ cycloadditions, regular 2D single bond polymerisation or even random 2D polymerisation. However, the symmetry requirements from the X-ray diffraction data restrict the possible structures to those where C_{60} polymerisation takes place in rows of $[2+2]$ cycloadditions, giving rise to an 1D polymerised structure (Fig. 2). This is supposed to induce a local structure disorder which, apart from X-ray measurements, is supported also by the presence of two slightly shifted sp^3 lines in NMR spectra [3].

Finally, one should note that, although there is an important C_{60} - C_{60} interaction which brings to fullerene polymerisation, the Li - C_{60} interaction is only secondary. Several NMR measurements support this conclusion: a) the absence of a J couplings among ^7Li and ^{13}C , b) the

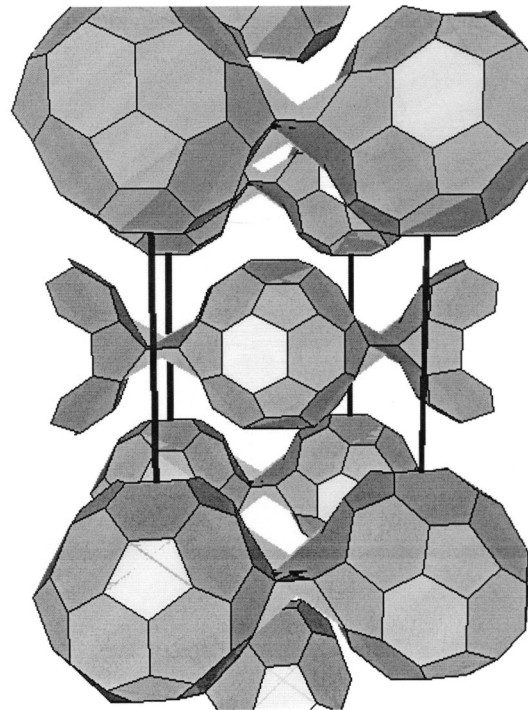


Figure 2. Pictorial view of the polymerised $\text{Li}_{15}\text{C}_{60}$ structure as obtained from X-ray diffraction data. The horizontal planes contain fullerenes with a 1D polymeric structure, $[2+2]$ cycloaddition along the a direction. The sp^2/sp^3 intensity ratio is consistent with the NMR results.

absence of cross-polarisation transfer between these atoms (for contact times as long as 20 ms at room temperature), c) the presence of a considerable ^7Li motional narrowing due to lithium diffusion processes.

3. Lithium clustering studied by single and multiple-quantum NMR

Both conventional and the more advanced multiple-quantum (MQ) NMR provide a wealth of information on lithium behaviour in $\text{Li}_{15}\text{C}_{60}$, including its dynamics, diffusion, clustering, etc. We use standard NMR to measure the temperature dependence of ^7Li line width and shape as well as the spin-lattice relaxation time; MQ NMR instead is a more suitable method to investigate potential cluster formation. Indeed, the monitoring of time evolution of MQ coherences in coupled spin systems provides an excellent tool to study their clustering properties.

The ^7Li (spin 3/2) line shapes, measured by a magic echo sequence, display symmetric features at all temperatures. At 50 K the line consists of two distinct peaks: a narrow peak — attributed to the $(1/2, -1/2)$ transition, and a broad peak — ascribed to the satellite transitions $(\pm 1/2, \pm 3/2)$. As the temperature increases both of them merge into a single central peak, 1.8(1) kHz. The rather narrow single line observed at room temperature as compared to that measured at 50 K (4.3(2) kHz FWHM) suggests motional narrowing due to rotational lithium diffusion inside the clusters (cfr. infra). The diffusion, however, is believed to stop at temperatures below 50 K, since no significant change in line shape and width are observed for $T < 50$ K.

The absence of any distinguishable quadrupole powder pattern in the whole temperature range could be due to an averaging of the anisotropic part of the quadrupole and dipole interactions. Since no indication for a ^7Li Knight shift was found, we believe the clusters not to show metallic properties.

A simple rough estimate for the aggregation of lithium atoms in clusters can be made from dipolar line width calculations, where we consider the interactions among N equal 3/2 spins.

They yield a theoretical line width of 4.6 kHz FWHM, slightly in excess with respect to the measured value at 50 K, suggesting either an underestimated internuclear distance or a reduced average number of lithium nuclei per cluster.

A more direct evidence on Li clustering is obtained by multiple quantum NMR experiments. In case of N spin-3/2 nuclei the set of possible quantum coherences ΔM goes from 0 to $3N$. They can be detected by a radio frequency coil only after exciting and successively converting them into single quantum coherences (which correspond to the familiar transverse magnetisation).

With the use of an appropriate multiple quantum excitation-detection sequence, essentially based on the magic-echo scheme [4], one can obtain a dipolar and a quadrupolar echo provided the condition $\tau_2 = \tau_1/2$ is

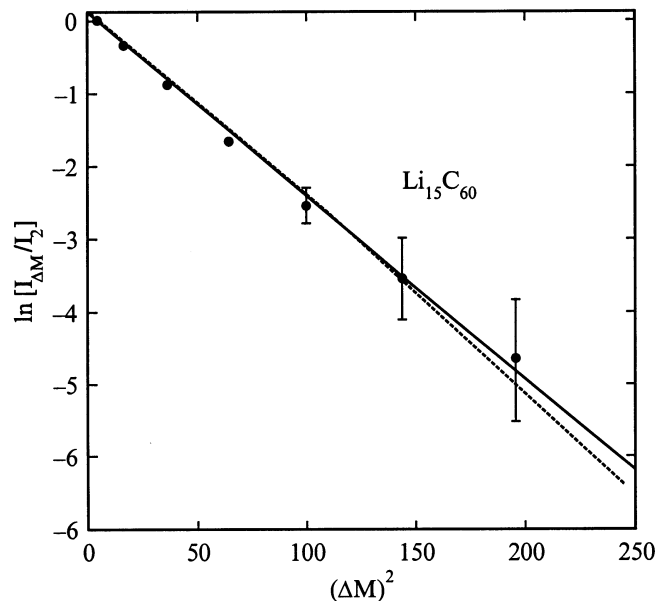


Figure 3. Logarithm of the intensity profile $I_{\Delta M}/I_2$ as a function of $(\Delta M)^2$ for $\text{Li}_{15}\text{C}_{60}$. The solid and the dotted lines are fits according to slightly different models, both yielding $N = 9(1)$ for the number of lithium atoms in a cluster.

satisfied (here τ_1 is the rotating-frame defocusing time and τ_2 — the laboratory-frame refocussing time). A systematic increment of the dynamical evolution time τ_1 leads to an ever increasing signal intensity for all orders of coherence. This confirms the presence of strongly dipolar-coupled ^7Li spins whose network grows wider the longer τ_1 . However, beyond a certain threshold time ($\tau_1 = 2.5$ ms in our case), the intensity will not rise anymore, indicating that the limit of a finite size cluster has been reached.

In the presence of the saturation regime the intensities of various MQ transitions follow an approximate Gaussian distribution function. In the particular case of nuclei with spin 3/2, the intensity profile $I_{\Delta M}$ as a function of $(\Delta M)^2$ follows the curve $I_{\Delta M} \propto \exp[-(\Delta M)^2/5N]$ [5].

Therefore, from a logarithmic plot of the ratio $I_{\Delta M}/I_2$ as a function of $(\Delta M)^2$, where I_2 is the intensity of double-quantum-coherence (i.e. $I_{\Delta M}$ when $\Delta M = 2$), one can easily evaluate the number of interacting spins which make up a cluster. Such a plot and the relative fit for the case of $\text{Li}_{15}\text{C}_{60}$ are shown in Fig. 3. The fitted value $N = 9(1)$ is significantly lower than the expected stoichiometric value 15. Apart from a very improbable underestimate from the statistical analysis (whose correctness was tested also by simulations), we believe that a more realistic reason for the inferred cluster size could be found in the presence of structural disorder. Indeed, one can assume that the previously empty tetrahedral sites, under lattice deformation will be partially filled, therefore accounting for the lower number of atoms in the octahedral clusters.

4. Summary

The intercalation compound $\text{Li}_{15}\text{C}_{60}$ has been studied with ^{13}C , ^7Li NMR and *X*-ray diffraction in its low-temperature phase ($T < 530\text{ K}$).

^{13}C MAS experiments showed evidence for sp^3 bonding among carbon atoms, whereas the relative intensities sp^2/sp^3 suggest C_{60} polymerisation.

MQ NMR experiments on ^7Li confirm the presence of lithium clusters, previously shown by *X*-ray diffraction in the high temperature phase, also at lower temperatures. The inferred cluster size, significantly smaller than that suggested by stoichiometry, can be explained as a consequence of C_{60} lattice distortion. In this case the overall number of atoms in octahedral sites would be reduced by a partial occupation of tetrahedral sites too.

References

- [1] L. Cristofolini, M. Riccò, R. De Renzi. *Phys. Rev.* **B59**, 8 343 (1999).
- [2] M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, M. Perroux. *Phys. Rev. Lett.* **74**, 278 (1995).
- [3] M. Tomaselli, B.-H. Meier, M. Riccò, T. Shiroka, A. Sartori. *Phys. Rev.* **B63**, 113 405 (2001).
- [4] W.K. Rhim, A. Pines, J.S. Waugh. *Phys. Rev. Lett.* **25**, 218 (1970).
- [5] M. Tomaselli, B.H. Meier, M. Riccò, T. Shiroka, A. Sartori, submitted to *J. Chem. Phys.*