

# Charge transfer in fullerene polymer $\text{Li}_4\text{C}_{60}$ studied by Compton Spectroscopy

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## Introduction

Solid fullerene polymerization is a well-established and deeply investigated phenomenon vby now [1].  $\text{C}_{60}$  can polymerize undergoing high temperature and high pressure treatments, after ion irradiation or by exposure to light [2]. In all these cases, fullerene units invariably connect together by four-membered carbon rings, via [2+2] cyclo-addition reactions [3]. The intercalation of light electron donors (i.e. alkali atoms Li or Na) in the voids of the host fullerene lattice can sometimes induce the formation of polymerized structures. In this case, the charge transfer from the metal to the highly electronegative  $\text{C}_{60}$  provides the necessary chemical pressure to put adjacent buckyballs close enough to establish intermolecular bonds. A large variety of 1D [4,5] and 2D [6] fulleride polymer structures was found when intercalated with small-alkali atoms. In addition to the aforementioned cycloaddition mechanism, fullerenes can connect also through single C-C bonds. In the latter category, lithium intercalated fullerides  $\text{Li}_x\text{C}_{60}$  ( $x \leq 6$ ), are remarkable because their structure consists of 2D polymeric fullerenes interconnected by a sequence of single C-C bonds and four-membered carbon rings, propagating along two orthogonal directions on the polymer plane [7].  $\text{Li}_4\text{C}_{60}$  belongs to this class of compounds, together with the isostructural alkali-earth intercalated  $\text{Mg}_2\text{C}_{60}$  polymer, suggesting that the on-ball charge transfer is the key factor driving the polymerization arrangement in these systems [8]. The coexistence of the two bonding schemes was also observed in the fullerenium salt  $\text{C}_{60}(\text{AsF}_6)_2$ . In this solid, the fullerene units are oxidized to the state  $\text{C}_{60}^{2+}$ , a rather unstable condition, which results in an unusual 1D zigzag polymerization [9]. In addition to its original structure,  $\text{Li}_4\text{C}_{60}$  shows a very large ionic conductivity already at low temperature, which stands as an exceptional properties for a solid material. The ionic conductivity reaches the value of  $\sigma \sim 10^{-2}$  S/cm at room temperature, which is comparable to that observed in liquid electrolytes, indicating that this material could possibly find applications in the field of energy storage as an solid alternative material to be used fuel cells in devices [10]. This physical property originates from the presence of intrinsic unoccupied sites interconnected by 3D pathways in the crystalline structure, allowing the diffusion of the  $\text{Li}^+$  ions. The large amplitude movements of the  $\text{C}_{60}$  cages e.g. their rotations or radial deformations, can provide the necessary impulsion to the  $\text{Li}^+$  ions to jump from one site to another. Such dynamical disorder is intrinsically involved into the atomic mechanisms leading to oxygen diffusion in certain oxides, like the onset of  $\text{MoO}_x$  free rotations in  $\text{Bi}_2\text{6Mo}_{10}\text{O}_{69}$  [11]. In general the superionic character of a material follows an order-disorder transition which unlocks some of these large amplitude movements. In  $\text{Li}_4\text{C}_{60}$ , no such transition is observed and the superionic nature of the material appears progressively in an apparently very ordered fullerene host structure.

It is possible to break the intermolecular bonds and to recover the monomer phase through a moderate thermal annealing. This phase shows an unexpected metallic behaviour [12].

This result appears in contrast with the common accepted theories which indicate the  $A_4C_{60}$  compounds (A = alkali metal) as Mott-Jahn Teller insulators [13,14].

#### Experimental plan

According to the above discussion we propose to investigate the origin of the conductivity properties of the  $Li_4C_{60}$  compound with Compton Spectroscopy (CS). CS is indeed a direct probe of the momentum distribution of the electrons present in the system, and therefore a probe of the electronic wave functions delocalisation. The major advantage of CS is its enhanced sensibility to the electron states having a spatially broad distribution, an advantage which can be exploited in the case of  $Li_4C_{60}$  where the number of electrons belonging to Li is rather small. Using polymerised C<sub>60</sub> as reference sample, we should be able to distinguish the momentum distribution of  $Li^+$  ions. We may then be able to identify the charge transfer between  $Li^+$  and C<sub>60</sub>. Although charge transfer is very difficult to directly characterize, this system actually represents an ideal case as all atoms have a low atomic number, and the signal will not be drawn by the core-electrons contribution. As a function of temperature, we will follow the transition from insulator to metallic phase.

Samples will be prepared under inert atmosphere as described elsewhere, and sealed in containers with Be windows with high to X-rays transmission. In order to get high statistics data, we plan to perform measurements lasting at least 24h per temperature and sample. We aim therefore at having all necessary data within 4 weeks of measurements.

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