Structure and dynamics of the fullerene polymer Li$_4$C$_{60}$ studied with neutron scattering

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Abstract

The two-dimensional polymer structure and lattice dynamics of the superionic conductor Li$_4$C$_{60}$ are investigated by neutron diffraction and spectroscopy. The peculiar bonding architecture of this compound is definitely confirmed through the precise localisation of the carbon atoms involved in the intermolecular bonds. The spectral features of this phase are revealed through ab-initio lattice dynamics calculations and inelastic neutron scattering experiments. The neutron observables are found to be in very good agreement with the simulations which predict a partial charge transfer from the Li atoms to the C$_{60}$ cage. The absence of a well defined band associated to one category of the Li atoms in the experimental spectrum suggests that this species is not ordered even at the lowest temperatures. The calculations predict an unstable Li sublattice at a temperature of $\sim$ 200 K, that we relate to the large ionic diffusivity of this system. This specificity is discussed in terms of coupling between the low frequency optic modes of the Li ions to the soft structure of the polymer.

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Solid fullerene polymerization is a well-established and deeply investigated phenomenon by now. C₆₀ can polymerize undergoing high temperature and high pressure treatments, after ion irradiation or by exposure to light. In all these cases, fullerene units invariably connect together by four-membered carbon rings, via [2+2] cyclo–addition reactions.

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 C₆₀ provides the necessary chemical pressure to put adjacent buckyballs close enough to establish intermolecular bonds. A large variety of 1D and 2D 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 Li₄C₆₀ (x ≤ 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. Li₄C₆₀ belongs to this class of compounds, together with the isostructural alkali-earth intercalated Mg₂C₆₀ polymer, suggesting that the on-ball charge transfer is the key factor driving the polymerization arrangement in these systems. The coexistence of the two bonding schemes was also observed in the fullerenum salt C₆₀(AsF₆)₂. In this solid, the fullerene units are oxidized to the state C₆₀⁺, a rather unstable condition, which results in an unusual 1D zigzag polymerization.

In addition to its original structure, Li₄C₆₀ 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. This physical property originates from the presence of intrinsic unoccupied sites interconnected by 3D pathways in the crystalline structure, allowing the diffusion of the Li⁺ ions. The large amplitude movements of the C₆₀ cages e.g. their rotations or radial deformations, can provide the necessary impulsion to the Li⁺ ions to jump from one site to another. Such dynamical disorder is intrinsically involved into the atomic mecha-
nisms leading to oxygen diffusion in certain oxides, like the onset of MoO$_x$ free rotations in Bi$_{26}$Mo$_{10}$O$_{69}$. In general the superionic character of a material follows an order-disorder transition which unlocks some of these large amplitude movements. In Li$_4$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. This result appears in contrast with the common accepted theories which indicate the A$_4$C$_{60}$ compounds (A = alkali metal) as Mott-Jahn Teller insulators.

In the present work we report on the use of neutron scattering to study Li$_4$C$_{60}$: in a first part, the structure is investigated by neutron powder diffraction performed at low temperature, i.e. in a regime where the Li diffusion is hindered. Rietveld refinements are used to precisely localise the carbon atoms of the distorted fullerene cage—especially those involved in the intermolecular bonds—and to reveal the Li positions in the host lattice. In a second part, these structural informations are used to calculate the lattice dynamics of the polymeric system in the harmonic approximation. The phonon dispersion curves, the vibrational density of states and the thermodynamics properties of this molecular system are discussed. The validity of the model is illustrated by the excellent comparison between the neutron scattering observables calculated from simulations and observed in our inelastic neutron scattering investigations (INS).

In the last part, we present briefly the INS results obtained on this system in the monomeric phase at high temperature. The experimental data are interpreted based on DFT Molecular Dynamics simulations (MD-DFT).

II. EXPERIMENTAL METHODS

Li$_4$C$_{60}$ samples were prepared by thermal decomposition of 99% isotopically pure $^7$Li azide. Details in the procedure are described elsewhere. Isotopical enrichment was required to avoid neutron absorption problems arising from the natural fraction of $^6$Li. Samples
 handling was always performed in controlled atmosphere (high vacuum or Ar glove box with oxygen and moisture values below 1 ppm).

The neutron powder diffraction measurements were performed at the Institut Laue Langevin (ILL), Grenoble using the Super D2B two-axis diffractometer, operating in Debye-Scherrer geometry and in high resolution mode (neutron wavelength $\lambda = 1.59432\text{Å}$). A 1.5 gr sample was sealed into a cylindrical vanadium can with indium o-ring. Measurements were performed using a Closed Cycle Refrigerator allowing data to be collected at 3.5 K, with an accumulation time of 10 hours.

Inelastic neutron scattering experiments were performed at the ILL, on the thermal time of flight spectrometer IN4C, and on the Filter Analyser Spectrometer IN1BeF. Additional measurements were performed at the Laboratoire Léon Brillouin (CEA Saclay) on the cold TOF spectrometer Mibemol, to follow the evolution of the dynamics during the depolymerisation process at high temperature. On IN4C, several incident wavelengths were used (1.1, 1.4, 1.5 and 2.4 Å), allowing the dynamics to be measured either in Stokes or in anti-Stokes: using short wavelengths, the dynamics can be measured at low temperatures in an extended energy range, while using a relatively large wavelength, the dynamics can be measured in an extended energy range in anti-Stokes, albeit at temperatures relatively high. On IN1BeF, the measurements were conducted at low T (10 K). In both experiments, the 1.5 g sample was sealed inside an Al flat container with an Indium ring. On Mibemol the 1.5 gr sample was sealed inside a cylindrical niobium can and heated up to 800 K during 12 hours using a high temperature furnace. The incident neutron wavelength was set to 5 Å to have the maximum neutron flux at the sample position. The spectra were recorded as a function of time in order to follow the de–polymerisation process.

III. SIMULATIONS

Geometry relaxations, total energy calculations and molecular dynamics simulations were performed using the projector–augmented wave (PAW) formalism of the Kohn-Sham density functional theory, within the generalized gradient approximation (GGA), implemented in the Vienna ab initio simulation package (VASP). The GGA was formulated by the Perdew–Burke–Ernzerhof (PBE) density functional. For the total energy calculations, the electronic functions were calculated at gamma point (k=0) and energy cut–offs of
400 eV and 499 eV were used for C and Li atoms respectively. For the geometry relaxations, the energy cut–off were increased by 30% and a 2x2x1 Monkhorst-Pack\textsuperscript{23} $\mathbf{k}$ grid scheme was used to attain an increased precision. The break conditions for the self-consistent field (SCF) and for the ionic relaxation loops were set to $10^{-5}$ eV and $10^{-6}$ eV Å\textsuperscript{-1}, respectively. The latter break condition means that the obtained Hellmann– Feynman forces are less than $10^{-6}$ eV Å\textsuperscript{-1} for the final geometries (further details about the way such calculations are performed can be found in\textsuperscript{24}). Both full (lattice constants and atomic positions) and partial (only atomic positions) geometry relaxations were carried out. Total energies were calculated for the 108 generated structures resulting from the individual displacements (atomic displacement = 0.03 Å) of the 18 symmetry inequivalent atoms in the monoclinic (I2/m) phase, along the six inequivalent Cartesian directions ($\pm x$, $\pm y$ and $\pm z$). Phonons are extracted from these calculations using the direct method as implemented in the Phonon software\textsuperscript{25,26}. The phonon spectra obtained using the fully and partially relaxed structures differ only slightly, so that only the results reported in this paper concern the fully relaxed structure, which details are given in section \textsuperscript{III}.

The charge distribution was calculated from the VASP relaxed geometries using the Bader scheme analysis\textsuperscript{27}. To this aim we have used the code \textit{bader} developed by Henkelmann’s group\textsuperscript{28} which allowed us deriving the partial charges on each atom.

The results of the lattice dynamics calculations will be discussed based on the usual properties: phonon dispersion curves, total and partial phonon density of states. In particular, a weighted phonon dispersion curve image is also discussed: for each phonon $|j\mathbf{q}\rangle$ characterised by energy $\hbar\omega_j(\mathbf{q})$ and momentum $\hbar\mathbf{q}$, an intensity is calculated by:

$$I_{\{\mu\}}(j, \mathbf{q}) = \sum_{\{\mu\}} || \mathbf{e}_j(\mathbf{q} | \mu) ||^2$$

with $\mathbf{e}_j(\mathbf{q} | \mu)$ being the polarisation vector of the phonon $|j\mathbf{q}\rangle$ for atom $\mu$ in the unit cell. This allows spotting the atoms which are involved in each mode, and we will call this quantity $I_{\{\mu\}}(j, \mathbf{q})$ the \textit{participation factor} of the ensemble of atoms $\{\mu\}$ to the phonon mode $|j\mathbf{q}\rangle$ in the rest of this paper.

Several thermodynamics functions (Heat capacity, Entropy, Free energy, mean square atomic displacement) obtained in the framework of the harmonics approximations\textsuperscript{29} are also presented and discussed. These quantities are extracted from the calculations using the
The neutron observable $S(Q, \omega)$ and $G(\omega)$ are calculated for a powder according to the PALD method. The PALD approach is based on a set of modes $|j\vec{q}\rangle$ for which the coherent dynamical structure factor in the "one–phonon" approximation is computed for a large number of $\vec{Q} = \vec{q} + \vec{G}_{hkl}$, with random orientation on a dense equidistant $||\vec{Q}||$ grid. $\vec{G}_{hkl}$ represents the vectors of the reciprocal lattice of the crystal. In phonon creation (Stokes):

$$S_{coh}(\vec{Q}, \omega) = \frac{n(\omega, T) + 1}{2\omega} \sum_j F_j(\vec{Q}) \delta(\omega - \omega_j(\vec{Q}))$$

with the one phonon form factor:

$$F_j(\vec{Q}) = \left\| \sum_{d=1}^{N_d} \frac{b_d^{coh} e^{-W_d(\vec{Q})}}{\sqrt{M_d}} \vec{Q} \cdot \vec{e}_j(\vec{Q} | d) \right\|^2$$

and the bose thermal population factor $n(\omega, T) = (\exp(\hbar \omega/k_B T) - 1)^{-1}$. Index $d$ refers to the $d$th atom among the $N_d$ atoms in the unit cell, with mass $M_d$ and coherent scattering length $b_d^{coh}$. $W_d(\vec{Q})$ is the Debye-Waller factor of atom $d$. At a final stage, $S_{coh}(\vec{Q}, \omega)$ is regrouped according to an adjustable $\Delta||\vec{Q}||$ and $\Delta\omega$ and orientationally averaged to obtain the isotropic function $S_{coh}(Q, \omega)$.

If the incoherent scattering length of carbon is negligible, that of lithium possesses a non negligible value, and one has to account for this scattering in the calculations. The Li total scattering cross section is therefore expressed as $S(Q, \omega) = S_{coh}(Q, \omega) + S_{inc}(Q, \omega)$ with the powdered averaged one phonon incoherent cross section approximated to:

$$S_{inc}(Q, \omega) = \frac{N_d Q^2}{2} \sum_{d=1}^{N_d} \frac{b_d^{inc} e^{-2W_d(Q)}}{M_d} g_d(\omega)$$

with $g_d(\omega)$ being the partial phonon density of state of atom $d$:

$$g_d(\omega) = \frac{1}{3N} \sum_{j\vec{q}} \|\vec{e}_j(\vec{q} | d)\|^2 \delta(\omega - \omega_j(\vec{q}))$$

The calculated $S(Q, \omega)$ spectra were subsequently adapted to the experimental conditions (temperature, instrument dependent scattering $(Q, \omega)$ range, resolution function) to allow for a direct comparison with the data. In particular, the INS-weighted spectra were convoluted with a Gaussian whose energy-dependent width follows the resolution of the instruments used in this study. The calculated and experimental $S(Q, \omega)$ spectra were therefore treated the same way. In particular, the grouping and treatment performed in
order to derive the generalised density of states (GDOS) is identical for both sets of data.

The structure of the high temperature monomeric phase of Li$_4$C$_{60}$ was taken from[12]. As this structure is orientationally disordered, lattice dynamics simulations cannot be performed as described above, and had to be performed differently from the polymeric (ordered) phase. We used DFT Molecular simulations to grasp the global picture of the dynamics. The molecular dynamics simulations were performed at 800 K using a Nose-Hoover thermostat[33] as implemented in the vasp simulation package. The MD increment time was set to 1 fs and a total simulation time of 3 ps was probed. The neutron weighted density of states were derived from the trajectories according to the Fast Fourier Transform of the atomic velocity auto–correlation function. These operations were performed using the nMoldyn package[34]. The simulation box used is restricted to the I$_{4}$/mmm unit cell, i.e. containing only 2 molecular units. As periodic boundary conditions were applied, artificial correlations between the rotating C$_{60}$ units can be introduced. However these increased correlations mostly affect the quasielastic scattering region of the neutron spectra, which we do not discuss in the present paper.

IV. RESULTS AND DISCUSSION

A. Neutron diffraction

Diffraction data were collected within the angular range 2$\theta$ = 10° - 145° with a step of 0.05° (high resolution mode). Rietveld analysis was performed using the GSAS+EXPGUI software. The starting peak profile was determined by a preliminary Le Bail pattern decomposition and the background contribution was modelled with a polynomial curve containing 21 coefficients. The structural analysis was started irrespectively of the Li ions, in virtue of the low (negative) scattering length of $^7$Li with respect to C. At the beginning, the fullerene arrangement was obtained by considering the carbon positions of the polymeric chains in KC$_{60}$ (where C$_{60}$ are connected by [2+2]-cycloaddition bonds), as described elsewhere[35]. Then, the fullerene chains were correctly rotated around their axis and the necessary transformations were applied to the atomic coordinates, in order to match the correct symmetry and the cell dimensions of Li$_4$C$_{60}$ ($a = 9.329(1)$ Å, $b = 9.054(1)$ Å, $c = 14.984(1)$Å, $\beta =$
90.91(1)°, space group I2/m), with the [2+2] polymerisation running along the b-axis. At this stage, we found that the minimum in the $R_{wp}$ agreement factor was reached by rotating the fullerene chains by 102° with respect to their arrangement in KC$_{60}$. As expected, the diffraction profile was not well described during the Rietveld refinement ($R_{wp} = 7.68\%$) at this step. However, a dramatic improvement was reached when the position of the carbons C(15), which is involved in the single C-C bonds, and of its first neighbours (C(5) and C(16)) were refined. Although the refinement process was always rather stable, thanks to the high number of observables available (1401), soft constraints were applied to carbon positions of the whole asymmetric unit and the convergence was reached by slowly decreasing the F-factor (penalty factor) at each cycle.

Further enhancement of the quality of the fit (to $R_{wp} = 5\%$) was gained with the refinement of the carbon C(1) forming the four-membered carbon ring and its neighbours (C(2) and C(3)). Finally, the fractional coordinates of all the remaining ten C atoms of the asymmetric unit were stepwise refined. The best agreement between the observed and calculated data was obtained for an interfullerene C(15)-C(15) bond of 1.61(2) Å. The latter distance is significantly smaller than that previously derived from synchrotron data ($d_{C(15)-C(15)} = 1.75(2)\AA$), falling into a more reasonable range if one compares it with typical C-C bond length. Moreover, no anomalous distances were detected over the whole fullerene molecule, the bond lengths distance being all close to the standard values of 1.54 Å and 1.42 Å, for sp$^3$ and sp$^2$ C-C bonds respectively.

Solid State NMR and DC and AC conductivity clearly indicates that the Li ions are pinned at special positions in the lattice at the temperature at which the diffraction data were collected. This means that no ionic diffusion is expected at 3.5 K. The structural analysis performed at room temperature using the synchrotron data distinguished two types of symmetry inequivalent Li ions, located respectively inside the pseudo-tetrahedral (Li$_T$) and pseudo-octahedral (Li$_O$) voids of the parent cubic lattice. In the present low temperature neutron investigation, the study of the small alkali ion position was tempted by means of Fourier maps analysis, i.e. exploiting the large contrast arising from the negative neutron scattering length of $^7$Li. We found that a significant fraction of intercalated alkali ions occupy the position (0.44(1) 0 0.76(1)), which corresponds to the small pseudo-tetrahedral voids, in agreement with the previous analysis. The insertion of Li$_T$ atoms with full occupancy improved significantly the quality of the fit ($R_{wp} = 3.99\%$).
FIG. 1. Powder diffraction pattern of $^7$Li$_4$C$_{60}$ at 3.5 K. The data are indicated by black crosses, the Rietveld fit by the solid red line and the difference by the solid blue line. Ticks marks indicate the reflection positions ($R_{wp} = 3.83\%$, $R_{F2} = 1.16\%$). The fulleride structure is displayed in the inset, with the carbon nomenclature.

By contrast, the Fourier maps did not provide clear evidences of the occupation of the larger pseudo-octahedral sites, showing at these positions an unexpectedly poor contrast. The reason for this observation was first ascribed to the combined effect of the small absolute value of $^7$Li scattering length, as compared to C, in addition to the low amount of the alkali ions in the compound. In fact, if both effects are taken into account, the contribution of Li to the scattered intensity turns out to be two orders of magnitude smaller than that of carbon. Another hypothesis is that the LiO ions present a certain degree of disorder, e.g. populating different octahedral sites in the lattice with similar energy and experiencing slightly different local potentials. This hypothesis is supported by DFT calculations. The spread of LiO ions onto different positions in the different octahedral voids in the lattice is expected to strongly reduce the contrast of the Fourier maps.

However, a careful analysis of the scattering reveals the existence of negative intensity close
to the position (0.28, 0, 0.32), which is significantly shifted with respect to the center of the octahedral void. The insertion of the LiO alkali ion at this position with a full occupancy allowed to further reduce the agreement factor ($R_{wp} = 3.83\%$), suggesting that LiO ions tend to move out from the center of the octahedral interstices with decreasing temperature. A similar behaviour was recently observed for highly-doped Li fullerene compounds, where Li ions were found to form clusters around the center of the tetrahedral positions of the parent cubic lattice$^{38}$ in the ground-state, leaving the octahedral sites unoccupied.

In the final configuration, the closest Li-Li distance found is of 2.9(1) Å, similar to the atomic distance found in Li metal (3.04 Å), while the Li$^+-$C$_{60}$ contacts reveal a short distance of the order of $\sim 2.4$ Å, which is equal to the sum of the ionic radius of Li$^+$ (0.7 Å) and the Van der Waals radius of C (1.7 Å). The result of the Rietveld refinement performed on the neutron data is displayed in Fig. 1.

B. Lattice Dynamics Calculations

1. Geometry optimization and electronic properties

The geometry relaxation was performed in two steps: the first one consisted in optimizing the atomic positions while keeping the lattice parameters at the values obtained by neutron diffraction. The initial experimental structure described above was therefore used as initial guess. The optimized geometry obtained this way was further relaxed letting all lattice parameters varied. The optimized structure was then considered for phonon calculations. We have checked that both relaxed geometries gave comparable results in term of phonon dispersion curves and phonon density of states. We however observed that the full relaxation allowed one to have a slightly better result with no negative phonon frequency in any part of the Brillouin zone, and a slightly better agreement with the neutron derived phonon DOS. The resulting structure has lattice parameters $a = 9.38$ Å, $b = 9.12$ Å, $c = 15.59$ Å, with angles $\alpha = \gamma = 90^\circ$ and monoclinic angle $\beta = 91.18^\circ$. This gives a $\Delta V/V = 5\%$ expansion of the lattice with regards to the experimental structure. Relaxed interatomic distances are, $a_{cc}(66) \sim 1.44$ Å (sp$^2$ bonds between two hexagons); $a_{cc}(65) \sim 1.42$ Å (sp$^2$ bonds between one hexagon and one pentagon); $a_{cc}(sb) \sim 1.56$ Å (sp$^3$ single bond between adjacent molecules), $a_{cc}([2+2]) \sim 1.64$ Å (sp$^3$ bond in the [2+2] cycloaddition). In agreement with the diffraction
FIG. 2. a) Structure of Li$_4$C$_{60}$ as obtained from geometry optimisation, in the space group I2/m. Grey sticks are carbon bonds, magenta and brown spheres are carbon atoms involved in the covalent intermolecular bonds: [2+2] bridges and single bonds respectively. Red and orange spheres represent Li$_T$ and Li$_O$ respectively. b) View along the $c$ axis of one polymeric plane (the Li ions have been omitted for clarity).

investigations, the Li atoms are substantially displaced with regards to the centers of the parent tetrahedral and octahedral voids in cubic C$_{60}$. They form atomic planes of atoms in the space between two successive polymer sheets (see Fig. 2).

2. Raman and IR modes

The crystal symmetry point group of the system is $C_{2v}$, which comprises the inversion symmetry element. The irreducible representation of the point group is therefore composed of the non-degenerate $A_g(R)$, $B_g(R)$, $A_u(IR)$ and $B_u(IR)$ representations. By consequence, the phonon modes at point $\Gamma$ are either Raman ($R$) or Infrared ($IR$) active. Two of these Raman active modes are represented in figure 3.

Fig. 3(a) represents the pattern of a Raman active mode characteristic of the [2+2] bonding. It is calculated at $\sim$840 cm$^{-1}$ and shows a pattern representing the breathing
of the planar square-like bridge. Our calculation predicts a Ag Raman active mode at a frequency of 1441 cm$^{-1}$. This pure cage deformation mode is represented in Fig. 3(b). A mode in the Raman spectra of the polymeric fullerides is observed in this frequency range. The latter feature is often used as an experimental probe of the polymerisation scheme (i.e. giving the number and type of covalent intermolecular bonds) and/or charge transfer between the alkali ion and the fullerene molecule. This mode is derived from the Ag(2) "pinch mode" of the pristine $C_{60}$, the latter being observed at 1469 cm$^{-1}$. Its frequency is observed to downshift according to both the intermolecular bonding scheme and the excess charge of the cage, according to the empirical rule: -6/7 cm$^{-1}$ per excess electron, -2.5 cm$^{-1}$ per single covalent bond and -5.5 cm$^{-1}$ per [2+2] covalent bond (7 and reference therein). Following this law, we anticipate a charge transfer of about 2e per cage[7,10], while Macovez et al. derived a value close to 2.7e from the analysis of the photoemission spectrum of a Li$_4$C$_{60}$ film[31]. While a direct measure of the on-ball charge transfer is made difficult by the polymeric nature of the compound, the lithium tendency to provide a partial charge transfer in intercalated fullerene systems is known[32]. The analysis of our simulations, using the Bader approach, indicates a total charge of 726.1 electrons per C$_{60}$ which means a charge of $\sim$-3e per cage and a partial charge transfer from the Li atoms to the C$_{60}$ cage, which amounts $\sim$0.75e per alkali ion. Even though the difference between the charge transfer estimated experimentally and derived from the simulations is rather large, the partial nature
FIG. 4. Left: Dispersion curves along high symmetry directions. Right: Partial dispersion curves along high symmetry directions. From left to right, contributions from Li$_T$, Li$_O$ and carbon atoms. The color scheme represents the value of the participation factor of the atom in the modes: the darker the color, the larger the participation (normalized to unity, i.e. a value of one represents maximum participation factor).

is perfectly reproduced.

3. Phonon dispersion curves and Phonon DOS

Figure 4 shows the dispersion curves of the phonon branches calculated along several high symmetry directions in the first Brillouin zone. The high symmetry points coordinates are given in table 1 in the system of reciprocal vectors (\(\vec{A}, \vec{B}, \vec{C}\)) of the crystallographic unit cell (I2/m). Due to the weak monoclinic character of the unit cell, propagation vectors of the form [0, 0, \(\xi\)] will have major out-of-plane components, and will refer to phonon modes propagating out of the polymer plane. By contrast, propagation vectors of the form [\(\xi\), \(\eta\), 0], will refer to phonon modes propagating inside the polymer plane.

The dispersion curve pattern is typical of an anisotropic molecular crystal, its molecular nature being revealed by flat "molecular" modes in the high frequency range (\(E \geq \sim 30\) meV) separated from "lattice" modes by a small 2 meV gap between 28 and 30 meV. The
strong anisotropy between the in plane covalent bonds and the out-of-plane van der Waals interactions is observed by the rather flat dependence of the molecular modes along the \(e.g.\) \(\Gamma\)-\(Z\) line, while a substantially larger dispersion is calculated for \(e.g.\) the modes in the \([110, 120 \text{ meV}]\) range along the \(\Gamma\)-\(X_1\) direction. These high frequency molecular modes essentially involve carbon motions, keeping the Li ions at rest, as seen from the lack of intensity in this energy range for Li participations factors (see Fig.4 Li\(_O\) and Li\(_T\)) and Li partial density of states (pDOS) (see Fig.5). As already discussed for other polymeric forms of C\(_{60}\), these phonon modes share strong similarities with those of bulk C\(_{60}\), but their DOS spectrum also significantly differ at some places, which can be ascribed to the reduced symmetry of the polymeric cage and to the different nature of the hybridization of some C-C bonds at the cage surface\(^{43–45}\). In particular, the sharp contribution in the total DOS at \(\sim 103-105 \text{ meV}\) originates from the deformation of the \([2+2]\) cyclic bond, which appears as a very local mode featuring a sharp peak in the pDOS of the C atoms involved in this bond (see brown line in Fig.5). By contrast, the single bond deformations (bending and stretch) seem to be distributed over a much larger energy range, giving only a significant contribution to the DOS in the 130–135 meV energy range (see magenta line in Fig.5).

The anisotropy and reduced symmetry of the system is clearly seen in the lattice mode region (\(E \lesssim 30 \text{ meV}\)) of the phonon density of states (DOS) represented in Fig.5. The flat contribution of the out-of-plane transverse acoustic mode along the \((X_2VMA)\) directions, give the first van Hove singularity at 5.5 meV. The anisotropy of the polymeric system is further reflected by the pseudo gap (4 meV) separating this contribution to the second van Hove singularity in the DOS observed at \(\sim 9 \text{ meV}\), which results from the flat dependence of the in-plane acoustic modes in the same region of the Brillouin zone.
FIG. 5. Total (black line) and partial density of state of the different atomic species: all C (grey line), Li\textsubscript{T} (red line and area), Li\textsubscript{O} (orange line and area), C(1) –involved in the [2+2] bonds – (brown line and area), C(15) –involved in the single intermolecular bonds– (magenta line and area).

At larger frequencies, a series of flat optical branches is observed in the ∼ 10–20 meV range, followed by a pseudo gap range ∼ 22 meV and an intense flat band at ∼ 25 meV. Then follows the 2 meV real gap region between 26.5 meV and 28.5 meV featuring no intensity in the DOS spectrum. It is well known that the polymeric forms of C\textsubscript{60} have typical modes that appear in the so-called "Gap" region of bulk C\textsubscript{60} ([8-33 meV], see e.g.\textsuperscript{44–46} and references therein). In particular, cage librations modes, with the C\textsubscript{60} cages rotating around their principal axis of symmetry, i.e. implying inter-molecular bonds to be slightly deformed, are usually found in this range. These modes located at ∼ 3.5 meV in bulk monomeric C\textsubscript{60} are shifted to the 10–30 meV range for polymeric forms of C\textsubscript{60}, depending on the precise bonding scheme. These librations are calculated at ∼ 25.7 meV, 32.3 meV and 32.6 meV for Li\textsubscript{4}C\textsubscript{60}. The rotation axis main components of the latter rotations are lying along the \(\vec{c}\), \(\vec{a}\) and \(\vec{b}\) unit cell vectors respectively, as represented on Fig. 6. In monomeric C\textsubscript{60}, the first intramolecular vibration is a Raman active five fold degenerate H\textsubscript{g} mode at ∼ 33 meV. Polymerisation lifts its degeneracy and we observe ghosts of this mode at ∼ 17 meV, 18 meV, 19 meV, 24.4 and 35 meV. (See e.g. Fig\textsuperscript{7(a)}). All these optical branches have rather flat
dispersion, and they give sharp contributions to the DOS. In particular, the flat dispersions of the cage deformation mode in the 17 meV region (see Fig.4, right panel) gives a rather intense and sharp feature in the total DOS and C pDOS spectra.

(a) Libration around the \( \vec{c} \) axis at 25.7 meV
(b) Libration around the \( \vec{a} \) axis at 32.3 meV
(c) Libration around the \( \vec{b} \) axis at 32.6 meV

FIG. 6. The three rotation–like modes.

The Li phonon modes extend up to a maximum energy of \( \sim 45 \) meV. Fig.4 and Fig.5 show that they are grouped into three energy bands for each Li ion type: centred around \( \sim 12, 19 \) and 36 meV for \( \text{Li}_T \) ions, and around \( \sim 15, 25 \) and 40 meV for \( \text{Li}_O \) ions. These groups imply either ferro (in–phase displacement of the two symmetry related ions) or anti-ferro translation modes (out–of–phase displacement of the two symmetry related ions) along the \( a, b \) and \( c \) axis respectively (see Fig. 8). In the lowest frequency group, the modes concern both \( \text{Li}_T \) and \( \text{Li}_O \) ions, with concomitant orthogonal displacements along the \( a \) and \( c \) axis, as shown on Fig. [8(a)].

The sharp contributions of these modes to the DOS, and the fact that the Li ions do not have a significant participation factor in the acoustic bands suggest a quite weak interaction between the Li and the C atoms, \( i.e. \) in good agreement with the partial charge transfer between the alkali atoms and the fullerene cages. The large mass difference between the Li and the fullerene explains the very weak coupling of the Li ions movements to the polymer vibrations in the acoustic range, with a vanishing participation factor of the alkali atoms.
FIG. 7. Selected Hybrid modes.

(a) $H_g$ ghost (1) at 16.9 meV
(b) Hybrid mode at 18 meV
(c) Hybrid mode at 30.2 meV

FIG. 8. Selected pure Li modes.

(a) Pure Li$_T$ at 11.1 meV
(b) Pure ferro Li$_T$ mode (translations along $b$) at 19 meV
(c) Pure anti-ferro Li$_O$ mode (translations along $b$) at 24.4 meV

for non zero propagation vectors (i.e. except at $\Gamma$ point). A careful analysis of the dis-
persion curves and polarization vectors reveals a certain degree of hybridisation between the fullerene modes and the LiO and LiT modes. In particular it is found that the Li ions follow adiabatically the fullerene movements for the libration modes (see Fig. 6). A coupling between the $H_g$ derived modes and the Li translations, either in–plane or out–of–plane is also observed (see e.g. the modes shown in Fig. 8). These hybrid modes imply deformations of the fullerene cage, and are of particular interest as they bring the Li ions far away from their equilibrium positions. The latter original dynamics might contribute to the large ionic diffusivity proper to this system.

A very sharp feature is observed in the LiT partial phonon DOS (pDOS) at a frequency of 19.2 meV. The latter feature originates from the flat bands observed in this energy range in Fig. 4. No fullerene modes are calculated in this region over the entire Brillouin zone. By contrast the LiO related modes in the 25 meV range show a more pronounced dependence with the propagation vectors, resulting in a larger dispersion and a broader feature in the corresponding pDOS. This latter observation originates from the presence of fullerene modes in this region, e.g. libration around the $a$ axis.

4. Thermodynamic functions

As seen in Fig. 9, the additive combination of small mass and small frequency for typical Li vibrations is responsible for their very large mean square displacement (MSD) $\langle u^2 \rangle$, even at relatively low temperature. In particular, it is calculated to be much larger than their carbon equivalent in the temperature range from 0–800 K. As an example, $\langle u^2_{LiT} \rangle$ (0 K) = $\langle u^2_C \rangle$ (800 K). The alkali sub–lattices appear therefore as soft lattices with large amplitude harmonic vibrations, embedded inside a stable stiff carbon matrix, albeit showing a certain degree of flexibility thanks to the presence of soft cage deformation modes. The difference in stiffness and stability of the carbon and lithium sublattices is further reflected in the molar heat capacity and entropy represented in Fig. 9, although the fraction of Li atoms in the system is weak, the specific heat at $\sim$ 100 K originates to a significant extent (close to a third) from Li vibrations, while the classical atomic limit of $3k_B$ is almost attained at 300 K. By contrast, it is still half $k_B$ for carbon at 400 K. Of course, the large amplitude vibrations of Li imply also a large value of their corresponding vibrational entropy at relatively low temperatures, ($\sim 6$ cal/mol.K at $\sim 200$ K, i.e. six times larger than that of carbon).
The most interesting consequence of the latter consideration is the Li derived free energy which becomes negative at a temperature of $\sim 250$ K. This suggests that the Li sub-lattices becomes unstable above these temperatures, even in the harmonic approximation, while the sustaining fullerene framework keeps its stability. If one accounts for anharmonic terms, the Li atoms frameworks is likely to have melted at such temperatures. As no important change is expected for the global structure, the transition from an ordered Li sub-lattice to a liquid-like structure is certainly of second order character.

C. Inelastic neutron scattering

1. $S(Q,\omega)$ maps of the polymer phase

In Fig. [10] the measured $S(Q,\omega)$ of Li$_4$C$_{60}$ collected at 330 K on IN4 and using an incident wavelength of 2.41 Å is shown on the top left panel. It is compared to that obtained using a 1.4 Å incident wavelength at 10 K (right panel). The bottom panel of Fig. [10] corresponds to the PALD simulated $S(Q,\omega)$ in the same conditions ($E = \hbar\omega$). The PALD spectra were convoluted to an energy resolution of 0.1 meV, with a Q resolution of 0.1 Å$^{-1}$, e.g. to what corresponds at the elastic conditions using a 2.4 Å incident neutron on IN4. The main characteristic features of the data are perfectly reproduced by the simulations, over a wide $(Q, \omega)$ range, both in term of $E$ and $Q$ dependence of the spectra. In particular, one observes a strongly $Q$-modulated signal, typical of coherent scattering, with maxima of intensity located around 3.4 and 5.7 Å$^{-1}$. These features are commonly observed in fullerene systems (see e.g. [31] and reference therein) and reflect the coherent nature of carbon, large symmetry of the fullerene cages and are typical of modes implying rotations of the cages. At low $Q$ and $\omega$, one observes an intense signal emerging form the elastic scattering at $\sim 0.75, 1$ and 2.2 Å$^{-1}$ in the experimental spectra. These features correspond to acoustic branches which extend up to $\sim 6$ meV according to our simulations. It is interesting to observe that a $Q$ cut of the intensity at an energy of 6 meV shows a rotation-like $Q$ dependence with maxima at 3.4 and 5.7 Å$^{-1}$. This suggests a strong hybridization between modes of translational and rotational nature at the Brillouin zone edges, e.g. strong rotation-translation coupling of the cages. This is also observed for modes in the higher energy range ($\hbar\omega \lesssim 19$ meV) where both maxima are also observed, by contrast to the high frequency modes ($\hbar\omega \geq 30$ meV)
FIG. 9. Thermodynamic functions (per mole) of the total (black), carbon (grey), Li$_T$ (red) and Li$_O$ (orange) atoms, as a function of temperature. From top to bottom: Mean squared displacement, Free energy, Entropy and Heat Capacity.
FIG. 10. $S(Q, \omega)$ ($E = \hbar \omega$) maps of Li$_4$C$_{60}$ measured at 330 K and 2.4Å (top left panel, with negative energy transfer), and at 10 K and 1.4Å (top right panel, with positive energy transfer). The corresponding simulated PALD maps are shown in the bottom panel for comparison. The spectra were normalized to the integrated intensity in the [16, 19 meV] regions.

meV) whose Q dependencies have a completely different scheme.

2. GDOS $G(\omega)$ in the polymer state

The Generalised Density of States (GDOS) of Li$_4$C$_{60}$ was extracted from $S(Q, \omega)$ following the standard data treatment described elsewhere$^{159}$ in the framework of the “incoherent approximation” and it is shown in Fig. 12.

Two datasets are shown: one measured at 320 K using a relatively large incident wave-
FIG. 11. Energy cuts \(E = \hbar \omega\) along selected lines in the \(S(Q, \omega)\) map according to Fig. 10: a) \(E = -5\) meV, \(dE = 2\) meV; b) \(E = -9.5\) meV, \(dE = 4\) meV; c) \(E = 9.5\) meV, \(dE = 4\) meV; d) \(E = -17\) meV, \(dE = 4\) meV; e) \(E = 17\) meV, \(dE = 4\) meV; f) \(E = -25\) meV, \(dE = 6\) meV; g) \(E = 25\) meV, \(dE = 6\) meV; h) \(E = -32\) meV, \(dE = 8\) meV; i) \(E = 32\) meV, \(dE = 8\) meV

length of 2.4 Å in anti-Stoke mode, and one measured at 10 K in Stoke mode. The latter spectrum is composed of several datasets, measured either on the IN4C or the IN1BeF spectrometers, in order to cover the large range of incident wavelength necessary to probe the complete spectrum of this compound. Each dataset was normalized to a common energy range to allow for a reliable match between the data measured at different conditions. The 320 K and 10 K spectra show the same characteristics: a first feature at 7 meV, followed by a range dominated by a double peak structure at 17 and 19 meV. In the pseudo-gap
FIG. 12. Generalised density of states derived from inelastic neutron data collected at 320 K (incident neutron wavelength 2.4 Å - circles top curve) and 10 K (IN4C for energy lower than 60 meV: incident neutrons 2.2 Å, 1.4 Å and 1.1 Å. IN1BeF for energy larger than 60 meV - squares). Data are compared to calculations (solid lines from top to bottom): GDOS of carbon and Li$_T$ (black line) and total GDOS (blue line). Partial GDOS for C (grey line), Li$_T$ (red line and area) and Li$_O$ (orange line and area) are also shown. For clarity, the GDOS were shifted by ∼ 0.005 units, except for the partial GDOS. For the same reason, the calculated spectra are not shown for frequency larger than 45 meV, the corresponding spectra in that range being totally dominated by the C partial GDOS.

A feature is observed at 24 meV which seems better defined at low temperature, while significantly softened and split at 320 K. This mode was observed in the HREELS spectrum of a thin film of Li$_4$C$_{60}$[III]. At larger frequencies, the GDOS features the typical fulleride molecular modes.

The data are compared to the GDOS calculated for the model developed in the previous section. Two spectra are shown (blue and black lines respectively): the first represents the total GDOS, i.e. comprises the sum of the C (grey line), Li$_T$ (red line and area) and Li$_O$ (orange line and area) partial GDOS contributions. The second one represents the sole sum of the C and Li$_T$ contributions only. The latter spectrum would correspond to the case where the Li$_O$ atoms vibrations were absent or distributed over a large spectrum range, i.e.
reflecting a structural disorder, giving a featureless contribution to the total GDOS difficult to measure.

The calculated spectra are in very good agreement with the data, in the complete frequency range. In particular, the principal low frequency features of the experimental data are reproduced. The first peak of the doublet (at 17 meV) can be attributed to C\textsubscript{60} vibrations, while the second peak of the doublet matches a significant feature of the Li\textsubscript{T} partial GDOS. The feature at 24 meV can be attributed to an hybrid mode, with carbon and Li\textsubscript{O} contribution. However, the corresponding contribution in the total GDOS is significantly more intense than what is observed in the data. Actually the double peak feature is also much less defined in this spectrum. By contrast, a much better agreement with the experimental GDOS is obtained for the black spectrum: the 24 meV peak is less intense (with regards e.g. to the intensity at 33 meV) and comparable to what is observed, and the double peak feature much better defined. This suggests that the Li\textsubscript{O} contribution to the GDOS is no really observed in the data. This could reflect the disordered nature of the Li\textsubscript{O} sub-lattice, in good agreement with the diffraction data. In that case its corresponding GDOS would certainly be smoothed all over the [10,50] meV range, resulting in a featureless contribution, difficult to measure in these conditions. To achieve such measurements, polarized neutrons investigations would be useful as they would allow separating the coherent (mostly C) from the incoherent (essentially Li) contributions to the GDOS and therefore isolate the Li modes.

3. Transformation to the monomer phase

After the Li4C\textsubscript{60} sample was heated at 700 K for 12h, the polymer phase was transformed into a monomeric phase. Figure 13 shows the evolution of the GDOS with time obtained on the Mibemol spectrometer using a 5 Å incident wavelength. It is compared to the total and partial GDOS derived from MD simulations. The spectral weight is observed to be progressively transferred to low frequency in the monomer phase compared to the polymer phase, in agreement with a change in the intermolecular force constant. In particular, the modes in the [10, 30] meV disappear. The simulations show a very good agreement with the experimental spectra, in particular concerning the position and shape of the first intramolecular peak at 33 meV. The GDOS in the gap region (i.e. in the [10, 30] meV
FIG. 13. Generalised density of states derived from inelastic neutron data collected at 700 K for 12h (incident neutron wavelength 5 Å - circles top curve). Data are compared to calculations (solid lines from top to bottom): GDOS of carbon and \( \text{Li}_T \) and total GDOS. Partial GDOS for C (blue area), \( \text{Li}_T \) (magenta area) and \( \text{Li}_O \) (red area) are also shown. For clarity, the GDOS were shifted by \( \sim 0.005 \) units, except for the partial GDOS.

range) is however not nul. According to the simulation, it contains contributions from the Li atoms, albeit more structured in the data rather than in the simulations. A phase segregation, constituted of Li clusters and \( \text{C}_{60} \) monomer can probably be responsible of this excess structured features in the gap.

V. CONCLUSIONS

In this paper we have reported an extended neutron scattering investigation of the \( \text{Li}_4\text{C}_{60} \) compound. Diffraction allowed to propose a structure which presents a certain degree of disorder associated with one of the Li atoms in the structure, referred to as \( \text{Li}_O \).

The lattice dynamics simulations allowed to calculate the phonon dispersion curves and phonon DOS and identify Raman and IR active modes. The use of the PALD method allowed calculating the \( S(Q,\omega) \) maps of the system together with the Generalysed Density of States (GDOS), both being neutron observables. The DFT simulations are coherent with a 3e charge transfer from the Li to the \( \text{C}_{60} \) molecule, and the peculiar polymeric bonding scheme proposed initially from diffraction and Raman investigations are confirmed by the
very good match between the experimental and simulated $S(Q, \omega)$ maps and GDOS. The inelastic features from the Li$_{O}$ atoms are not observed in the experimental data, suggesting a disordered Li$_{O}$ sublattice. The presence of hybrid Li–C modes at relatively low frequencies, associating Li translations and either C$_{60}$ rotations or cage deformations, are highlighted. These modes have to be considered to grasp the full atomic description of the ionic diffusivity in this solid. In particular, a peak in the GDOS localized at 24 meV, and attributed to an hybrid C and Li$_{O}$ feature is found to be temperature dependent. This experimental feature should be followed thoroughly with temperature in further investigations as it could shed light on the influence of the Li disorder and large amplitude C$_{60}$ modes on the ionic conduction in this system and could reveal the microscopic origin of the Li mobility of this crystal.

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