

Structure and Dynamics of Carbon Buckyballs Encapsulated to Single-Walled Carbon Nanotubes

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Abstract The structural and dynamical attributes of C60 chains inserted inside Single Walled carbon Nanotubes (SWNT) have been investigated by x-ray and neutron refraction, and inelastic neutron scattering (INS). The mensuration have been performed on a large mass of a very high quality carbon peapods sample. We showed that powder refraction could hardly give definitive response on the way the C60s are bonded inside SWNT. However, the comparison of the neutron-derived generalized compression of states (GDOS) of the inserted C60 peas with the GDOS of the same objects derived from lattice dynamics computations led to unambiguous results. The witnessing of excitations in the 8-15 meV span is a clear evidence for the presence strong bonds among C60s in the sample. In the same time, the witnessing of a very weak quasi-elastic signal may be relevant to rotational motions of C60 monomers inside the SWNT. These results suggest that peapods are built of a mixed phase of C60 monomers and C60 n-mers.

Keywords: structural, Carbon Nanotubes, Buckyball, X-Ray, refraction, energy

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1. Introduction

Since their first witnessing in 1991, single-wall carbon nanotubes (SWNT) have inspired remarkable advances in science and engineering at the nanometer scale during the past decade. Due to their size and geometry, SWNT provide a unique chance for nanoscale engineering of novel one-dimensional materials created by self-assembly of atoms or molecules inside the SWNT's hollow core. Lately, SWNT encapsulating fullerenes -the so-called peapods- have been successfully synthesized [1]. Peapods are interesting materials as new solid phase of pure carbon constructed by zero (fullerene) and one-dimensional (nanotube) sp² network. In addition, peapods are predicted to exhibit superconductivity attributes upon alkaline doping [2]. Both structural and vibrational research have been devoted to peapods. Transmission electron microscopy (TEM) images [1] have first shown the quasi 1D chains organized by C60 inside SWNT. Then, Raman studies have been carried out [3], and no definitive clear results were reported about the structural organization of the C60s inside SWNT. The photo polymerization of C60s under a 488 nm laser excitation has been evidenced, suggesting that the C60s are freely spinning inside SWNT at room temperature. Besides, a Raman experience has been per organized at Helium temperature to get rid of C60 photo polymerization, and then the spectra were indeed found to be stable. However,

the witnessing of a mode at 90 cm⁻¹, close to the frequency of the so-called Einstein dumbbells mode (96 cm⁻¹), could be relevant to the presence of dimers of C60 in the hollow core of SWNT. X-Ray [3,4] (XRD) and electron [3,5] (ED) refraction studies indicate that the inter-C60 distances in the inserted chains were included in the [9.5-9.8 Å] span, in rather good agreement with the results of compression-functional theory based computations [6], involving van der Waals bonding among C60s. Nevertheless, the thermal expansion of C60 chains, estimated from the XRD mensuration, is found to be much smaller than that of 3D plastic phase of C60, and even comparable to the in-plane dilatation for graphite. This last result suggest that the C60 are linked together by covalent bonds. Here we face the ambiguity of the results obtained so far: on one hand, structural data affirm to a van der Waals bonding among C60s, and on the other hand, methods involving dynamical attributes (thermal expansion, vibrations) are consistent with a polymer-like structure for the C60 chain inserted inside SWNT. In this research, we show that powder refraction is not the best suited method to investigate the bonding among C60s in peapods, and we present the results of an inelastic neutron scattering (INS) research. On the basis of our previous INS investigations on pure SWNT [7] and polymeric C60 [8,9] on one hand, and using the results of our lattice dynamics computations of the GDOS of the inserted C60 chains on the other hand, we discuss the stacking of C60s inside SWNT (as monomers, dimers or polymeric chain).

2. Experiential Section

The peapod sample was prepared on the basis of a sample of raw SWNT of very well-controlled diameter. The synthesis of the raw sample, as well as the C60 intercalation has been described elsewhere [10]. A large mass of 900 mg has been prepared for the INS experience, and a characterization of this sample was performed by x-ray and neutron refraction on a small part and the whole mass of the sample, respectively. No differences among the patterns were found which indicates a good homogeneity of the sample. The XRD characterization of this sample is reported in details in a previous research [4]. The XRD patterns were obtained using a powder diffractometer equipped with a curved position sensitive detector INEL CPS120 allowing one to measure simultaneously 2θ angles ranging from 2 to 120° . A wavelength of 1.542 \AA was used. We calculated the refraction pattern of a powder of peapod bundles, and we adjusted the structural parameters in order to get the best agreement with the experimental refraction pattern. The conclusions on the structure of this powder is that it is built of large bundles of about 30 tubes, with a very narrow diameter distribution centered around 13.6 \AA . The filling rate of these peapods is found to be high circa 80% and a C60-C60 distance of 9.8 \AA is determined. A 300 mg sample of raw SWNT was used as a reference for the INS research. It was synthesized by the arc-discharge method and XRD characterization revealed that it was of very similar structure that that of peapod, e.g. the bundles parameters (tube diameter, number of tubes in the bundles) can be considered as equivalent for both samples.

3. Results and Discussion

In order to determine the bonding scheme of C60 inside SWNT, we calculated the refraction patterns of peapods with different types of C60 stacking –as monomers, dimers or trimers and we compared the calculated refraction profiles with the experimental refraction pattern. The results are shown in Figure 1. We observe that the calculated refraction patterns of peapods built of C60s stacked as monomers, dimers or trimers can be very similar, depending of the distances among the C60s. At first sight, these distances are unknown when C60s are in the hollow core of a SWNT. If the inter C60 distances are set in so a way that the dimer (or trimer) chain periodicity is commensurable with the monomer chain periodicity, it has been established that only very small differences become in the refraction patterns [4] of dimer (or trimer) peapods and monomer peapods. This witnessing brings us to the conclusion that a powder refraction based determination of the C60 bonding scheme in peapods is very difficult due to the precision required in the experimental refraction patterns. Nevertheless, it must be pointed out that the intensity of the peak relevant to the C60 periodicity can be dramatically enhanced by considering an oriented peapods sample [11]. In that case, the distinctive features among n-mer chains could possibly be apperceived. Another way to determine the C60 bonding scheme is to consider the inter C60 vibrations. From previous studies on pure and alkaline-doped C60 [8,12], it has been shown that INS was perfectly suited to investigate the energy span where inter C60 interactions dominate the spectrum, namely the [0-50meV] energy span. In specific, it was found that the-inter molecular modes region (below 8meV) of the 3D-crystalline state of C60 GDOS is clearly separated from the intra molecular modes region (above 30meV) by a $\sim 22\text{meV}$ gap.

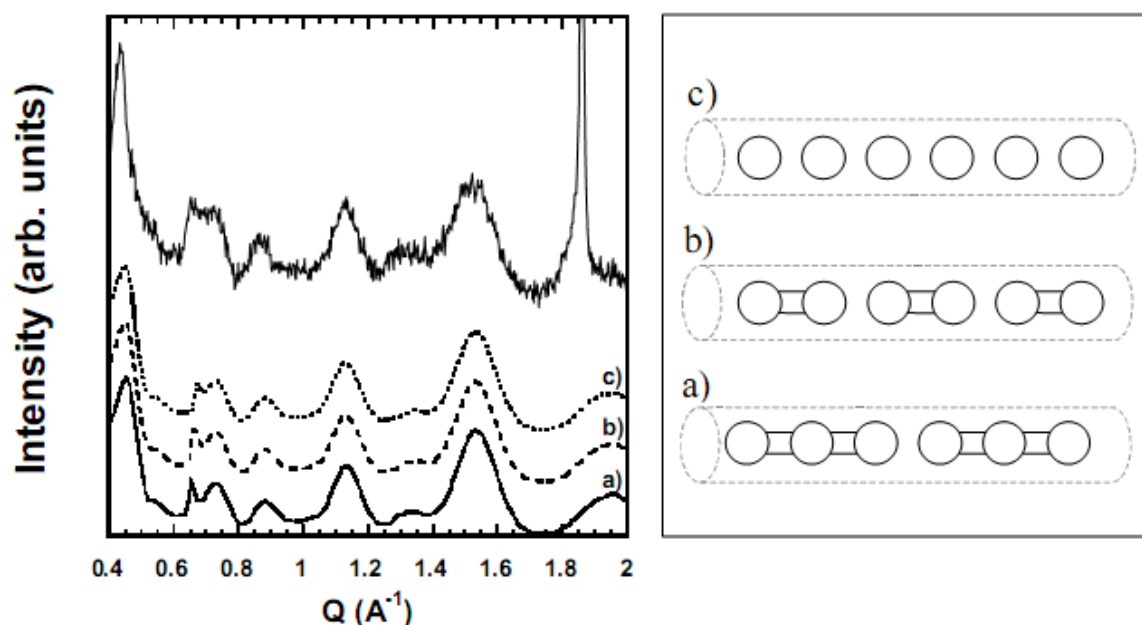


Figure 1. Left part: upper line: Experimental powder refraction pattern of the peapods sample. Bottom lines: computed powder diffraction patterns of peapods with different types of stacking for the C60s: a) monomer chain, b) dimer chain, c) trimer chain. Right part: Schematic representations of the C60 packings

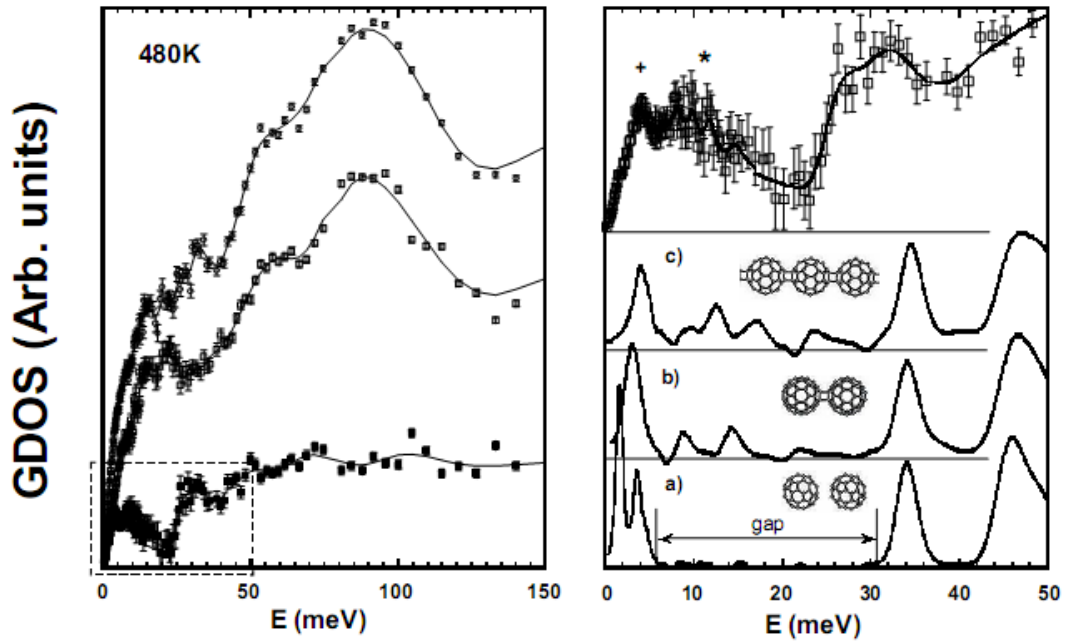


Figure 2. Left part: GDOS of the peapod sample (top curve), of the reference SWNT sample (middle curve) and of inserted C60 chains (bottom curve), at 480K. Right part: Low energy span of the GDOS of inserted C60 (top curve). Lattice dynamical computations of the GDOS of chains of a. monomers (M model), b. dimers (*D* model) and c. polymers (*P* model). The cross points the mode related to C60 translations/librations and the star indicates the position of the mode observed by Raman spectroscopy at 90cm^{-1}

When doped C60 phases are considered, a filling of the low energy side of this span is apperceived, and these new modes are associated to inter C60 vibrations involving covalent bonding among C60s. The IN6 Time of Flight (TOF) spectrometer at the Institute Laue Langevin (Grenoble) is well-suited to derive the GDOS of the peapod sample and the reference nanotube sample in the [0-50meV] span due to its high flux and its good resolution. A neutron wave length of 4.12\AA was used and the mensuration were performed at 300K and 480K to get a convenient intensity in the neutron energy gain side. TOF data were treated using a standard procedure to obtain the $S(Q, \omega)$ scattering law. From this quantity, both the imaginary part of the generalized susceptibility $\omega - 1\chi''(\omega)$ and the GDOS $G(\omega)$ can be derived, which are convenient functions todiscuss dynamical induced disorder and vibrations, respectively. The results concerning the dependence of $\omega - 1\chi''(\omega)$ with the temperature are described elsewhere [13]. They have pointed out a very weak quasi elastic signal in the peapod sample, probably coming from rotational disorder of C60 monomers more or less freely rotating inside the tubes. As a consequence, we can conclude that a part of the C60s in SWNT stand as monomers in the [300-400K] temperature span. Unfortunately, the research of this signal at lower temperatures proved very difficult due to the weak intensity in the neutron energy gain side for such temperatures, so the complete research of the quasi-elastic contribution (as Q , and T dependence) has not been possible. The left part of Figure 2a shows the GDOS of the peapod sample and of the raw nanotube sample at a temperature of 480K. By subtracting the GDOS of SWNT from that of peapods after a proper normalization, the GDOS of the C60 chains inserted into SWNT is obtained (one can observe that this GDOS does not go below 0 at any point, which confirms the hypothesis of a weak coupling among the C60s and the tube). Attention is given

to the [0 – 50 meV] span of this GDOS (right part of Figure 2). The general shape of the GDOS of the C60 fetter displays two regions separated by a gap around 20 meV. The GDOS in the inter-molecular region features a peak at 4 meV (cross mark in Figure 2), a shoulder at 1.8 meV and a large unresolved band at $\sim 12\text{meV}$. Above the gap, a peak is clearly apperceived around 33 meV, which is characteristic of the Hg (1) intra-molecular mode of C60.

The witnessing of this peak is a reliable confirmation of the procedure used for the data treatment. Lattice dynamical computations have been performed in order to assign the modes apperceived in the low frequency span. The model we used involves force constants for both intra tube [14] and intra-C60 [15] interactions. The van der Waals interactions among the tube and the C60s on one hand, and among the C60s on the other hand were taken into account using a Lennard-Jones potential found to describe correctly the interaction among C60 and grapheme [16]. Three different types of stacking were considered for C60 in the hollow core of SWNT, namely a monomer chain (M model), a dimer chain (*D* model) and a polymeric chain (*P* model). All computations were performed at 0 K, therefore no thermal induced dynamical disorder is considered. Each calculated GDOS was folded to a resolution function suited to the IN6 spectrometer, and the same data treatment was applied (subtraction of the GDOS of the raw nanotubes from the GDOS of peapods after proper normalization) in order to get the GDOS of the inserted C60 chains. The resulting GDOS are displayed in the right part of Figure 2. If consideration is first given to the results of the *M* model (line *a* in Figure 2), one observes a large gap from 6 meV to 30 meV, which separates the inter C60 modes below 6 meV from the intra C60 modes above 30 meV. The Hg (1) mode of C60 clearly becomes in the computation. In the inter-molecular energy span, two

features become at 1.7 meV and 3.5 meV, relevant to C60 librations and C60 translational vibrations, respectively. Then comparison with the experimental GDOS, the mismatch concerning the low frequency peaks positions on one hand, and the broadness of the gap on the other hand leads us to consider other structures than the *M* model. The *D* model (line b in Figure 2) displays slightly different features than the *M* model. The two sharp peaks in the inter C60 span are indeed replaced by a broader peak around 3 meV, which is organized by the unresolved contributions of librational and translational modes of the C120 dimers. In the region among 8 and 30 meV, e.g. the gap region in the *M* model, two additional modes become at 9 meV and 14 meV. These modes are found to be relevant to the Einstein dumbbell mode of the C120 dimer and to the libration-like modes where the balls undergo small magnitude rotations perpendicular to the dimer axis, respectively. In the GDOS inside the *P* model (line c in Figure 2), one observes a gain of the intensities of the modes among 8 and 20 meV relatively to the intensity of the first peak. This can be explained by the fact that the dumbbell like mode becomes a translational mode having a strong dispersion along the tube axis, giving rise to a broad contribution in the gap region of the GDOS. Moreover, the upshift of the first mode to 4 meV is coherent with a hardening of the libration-like and translational modes when the number of covalent bonds gains. As a result, even if none of these three models perfectly fits the experimental GDOS (which is quite unlikely given the simplicity of the model and the experimental effects of the high temperature used for the mensuration), we find a rather good agreement among the positions of the features in the *D* model and the *P* model, and the positions of the features in the experimental data. On the contrary, the hypothesis of peapods containing only monomers is rejected because this assumption necessary leads to a lack of vibrations in the [6 – 15 meV] span of the GDOS, which is at variance with the experience. This suggests that at least a part of the C60 balls are linked together by strong bonds. These oligomers are responsible for the wide contribution apperceived in the experimental GDOS in the [6 – 15 meV] span. In particular, this wide band involves the Raman active stretching bond mode that is calculated at 9.5 meV in our model and which have been apperceived at ~11 meV [4] (see the star in right section of Figure 2). The case of a long C60 polymer encapsulated in the SWNT is unlikely according the too large inter C60 distance given by refraction ($9.8 \text{ \AA} > 9.2 \text{ \AA}$) and the witnessing of a quasi-elastic signal. However, a mixed phase of C60 monomers and C60 oligomers would be compatible with the 9.6 Å determined by electron refraction to be the averaged inter C60 distance. Since no radiation-induced polymerization can occur using neutrons, these results suggest that n-mer like structures are organized inside the nanotubes during the synthesis.

4. Conclusions

In summary, we studied C60 chains inserted into SWNT by X-ray and neutron refraction, and by INS. Powder refraction was found to be very difficult to use in order to determine the bonding scheme of the C60 balls inside the nanotube. However, INS proved very useful to investigate the C60 bonding scheme. We derived the GDOS of the chains of C60 inside the SWNT from the measurement of the GDOS of a peapod sample and an empty nanotube sample. The experimental GDOS is discussed in the light of lattice dynamical computations performed with three different models for the C60 stacking inside the tubes. In particular, a broad unresolved band is apperceived in the low energy side of the gap separating inter-C60 modes from intra-C60 modes. This feature is found to be relevant to strong bonds among C60 monomers, such as valence interactions. The latter witnessing, together with the presence of a dynamical disorder induced quasi elastic signal, leads us to experience that peapods are filled with a mixed phase of free monomers and n-mers structures, the proportions of which remaining uncharted.

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