Communications: Nanomagnetic shielding: High-resolution NMR in carbon allotropes

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The understanding and control of the magnetic properties of carbon-based materials is of fundamental relevance in applications in nano- and biosciences. Ring currents do play a basic role in those systems. In particular the inner cavities of nanotubes offer an ideal environment to investigate the magnetism of synthetic materials at the nanoscale. Here, by means of ^{13}C high resolution NMR of encapsulated molecules in peapod hybrid materials, we report the largest diamagnetic shifts (down to -68.3 ppm) ever observed in carbon allotropes, which is connected to the enhancement of the aromaticity of the nanotube envelope upon doping. This diamagnetic shift can be externally controlled by *in situ* modifications such as doping or electrostatic charging. Moreover, defects such as C-vacancies, pentagons, and chemical functionalization of the outer nanotube quench this diamagnetic effect and restore NMR signatures to slightly paramagnetic shifts compared to nonencapsulated molecules. The magnetic interactions reported here are robust phenomena independent of temperature and proportional to the applied magnetic field. The magnitude, tunability, and stability of the magnetic effects make the peapod nanomaterials potentially valuable for nanomagnetic shielding in nanoelectronics and nanobiomedical engineering. © *2010 American Institute of Physics*. [doi:10.1063/1.3284740]

Carbon nanotubes are intriguing new forms of carbon, offering molecular-scale cylinders expected to provide important solutions for challenges of 21st century materials engineering. Since 1991,[1] they have been extensively studied due to their unique properties presaging potential applications in electronic devices, composites, chemical, and biochemical sensors. They have diameters in the range of nanometers and lengths of several centimeters. Filling the interior of molecular cylinders such as multiwall nanotubes with Pb metal[2] or single wall nanotubes (SWNTs) with fullerene C_{60} (Ref. 3) has been demonstrated. The discovery of these new hybrid materials, which have been given the vernacular name "peapods," has generated a considerable amount of fundamental and experimental studies on their structural and electronic properties. However, little is known regarding their magnetic properties since experiments are quite difficult to elucidate due to the difficult-to-avoid presence of residual ferromagnetic catalyst in the samples. In this letter, highly magnetically purified samples[4] and specific isotopic enrichment have been used to circumvent this crucial problem. Hence, ^{13}C nuclear magnetic resonance (NMR) turns out to be suited to measure accurately the intrinsic local magnetic properties of hybrid materials such as peapods.

NMR studies of nanotubes, as with fullerenes 10 years ago,[5–7] are expected to further our understanding of the magnetism of individual molecules and its relationship with their aromatic character. In the case of peapod materials, the control and manipulation of the magnetism at the nanoscale inside the nanotubule can be considered through the possibility to tune the flow of currents around the ring system of the outer nanotube.

In the experiments discussed here, the magnetic properties of five different types of hybrid materials characteristic of the peapods with different preparation routes have been investigated. Separate batches of electric arc SWNTs with 1.1% ^{13}C natural abundance were produced at the University of Montpellier and purchased from Carbon Solutions Inc.

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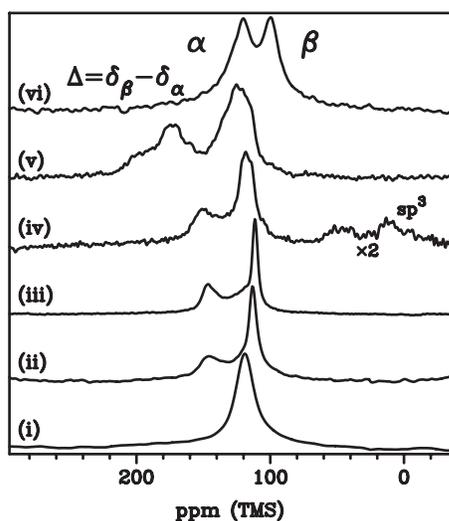
FIG. 1. ^{13}C NMR isotropic lines from high resolution MAS experiments (50.3 MHz) at a spinning rate of 10 kHz of magnetically purified single wall carbon nanotubes of 1.4 nm diameter and hybrid peapod materials with encapsulated molecules (i), C_{60} fullerene produced at Penn and Berkeley, respectively [(ii) and (iii)], hydrogenated $C_{60}H_x$ with $x<18$ (iv), Rb-intercalated C_{60} (v), and carbon nanotubes with 0.7 nm diameter (double-walled carbon nanotubes with the inner tube produced through the heating-induced coalescence of encapsulated C_{60} molecules) (vi). All the spectra from (ii) to (vi) present two contributions labeled α and β (line shifts and splittings are reported in Table I). Note that in spectrum (iv), the same Δ splitting is observed on C–C sp^2 and C–H sp^3 lines located at 45 ppm, clearly confirming the magnetic shieldings.

They were purified using a novel magnetic filtration method[4] at the University of Pennsylvania. The encapsulation of 25% ^{13}C enriched fullerenes (purchased from MER Corporation) within the SWNTs was conducted at the University of Pennsylvania and at the University of California Berkeley by using vapor phase filling.[8] The experimental procedures for the hydrogenation of C_{60} (University of Umeå) and the Rb intercalation (University of Pennsylvania) can be found in Refs. 9–12, respectively. The filling factor of C_{60} inside SWNTs was estimated to be 70% from high resolution transmission electron microscope measurements and the average diameter of the SWNTs was estimated to be about 1.4 nm.[4] High-resolution ^{13}C NMR experiments were carried out at the University of Montpellier on spectrometers Bruker and Tecmag Apollo at magnetic fields of 9.4, 4.7, and 3.3 T corresponding to Larmor frequencies of 100.6, 50.3, and 35.8 MHz, respectively. In all the experiments, the spin-
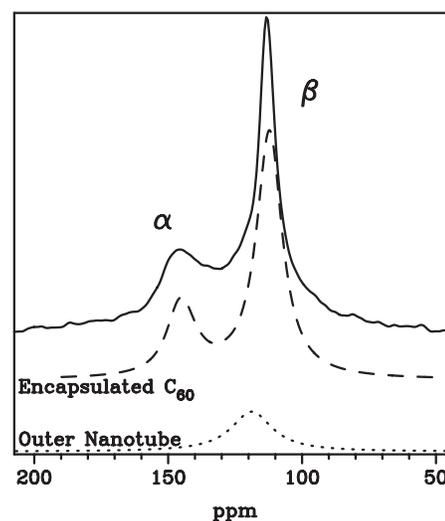
FIG. 2. ^{13}C NMR isotropic lines from high resolution MAS experiments (50.3 MHz) at a spinning rate of 10 kHz of 25% ^{13}C enriched C_{60} encapsulated inside natural abundance carbon SWNTs sample (ii) (solid line). 16% outer SWNTs contribution (dotted line), paramagnetic α, and diamagnetic β shifted lines from encapsulated C_{60} molecules.

lattice relaxation times were considered in order to measure NMR spectra under qualitative and quantitative conditions.

Figure 1 presents the high resolution ^{13}C NMR spectra recorded for magnetically purified empty SWNTs compared to the five peapod samples. A summary of line positions and line splittings can be found in Table I. According to the natural abundance of 1.1% of ^{13}C in the outer nanotube, the 25% abundance of ^{13}C in the enriched and encapsulated C_{60} fullerene and a filling factor of $\approx70\%$ of the inner cylindrical space of the SWNTs, the contribution to the total NMR signal intensity from the outer nanotube in the spectra of all the peapods from (ii) to (vi) is estimated to be $\approx16\%$. Consequently, these NMR spectra are dominated by the signal from the encapsulated molecules. A tutorial fit of the ^{13}C NMR spectrum of the C_{60} peapod sample (ii) is given in Fig. 2. The line shape of the outer SWNT is fixed according to the spectrum presented in Fig. 1(i) and its intensity following the previous remark. Two more contributions are needed to accurately fit the experimental data. The first line α at the position δ_α shows a paramagnetic shift of about 5 ppm from the line positions in fcc-C_{60} crystal[6] or in polymeric-C_{60} phases.[13] The second line β at the position δ_β presents a

TABLE I. ^{13}C NMR isotropic lines parameters for different encapsulated molecules inside carbon nanotubes. Paramagnetic α and diamagnetic β lines are observed in all the hybrid peapod materials in agreement with localized ring currents at the surface of the outer nanotube. We used $I_\alpha+I_\beta=100\%$, which gives directly the percentage between α and β encapsulated molecules. The 16% contribution of the outer nanotube is calculated from the integral of the spectra.

Encapsulated molecules	δ_α (ppm)	δ_β (ppm)	I_β (%)	$\Delta=\delta_\beta-\delta_\alpha$ (ppm)	$\delta_{outer-NT}$ (ppm)
C_{60} (ii)	148.2	111.3	68.2	−36.9	118.8
C_{60} (iii)	147.2	112.2	75.0	−35.0	118.8
Hydrogenated C_{60} (iv)	152.1	117.8	68.6	−34.3	118.8
Rb-intercalated C_{60} (v)	186.0	117.4	55.2	−68.3	128.0
Inner nanotubes ≈0.7 nm (vi)	125.8	99.2	59.6	−26.6	118.8
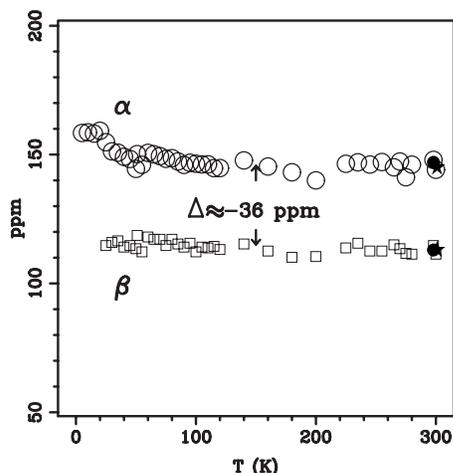
FIG. 3. Temperature dependence of the ^{13}C NMR line positions at 4.7 T (50.3 MHz) of the 25% ^{13}C enriched C_{60} peapods sample (ii). Open circles are for δ_α and open squares for δ_β. Solid circles and stars correspond to experiments performed at 9.4 T (100.6 MHz) and 3.3 T (35.0 MHz), respectively. Δ is proportional to the applied magnetic field and shows no dependence on temperature down to 20 K. At lower temperature, the broadening of the β line prevents an accurate determination of Δ.

larger diamagnetic shift in the range of $\Delta = \delta_\beta - \delta_\alpha \approx -36$ ppm. Approximately 75% of the signal is of β type and diamagnetically shifted with respect to normal fcc-C_{60}. As presented in Fig. 3, no dependence on temperature down to 20 K was observed in the spectra and Δ was clearly found to be proportional to the applied magnetic field. For all the investigated hybrid peapod materials, these two contributions α and β were observed with similar features as presented in Fig. 1 and Table I. This phenomenon is universal and even enhanced ($\Delta \approx -68.3$ ppm) in the case of the sample (v) corresponding to Rb-intercalated C_{60} peapods for which the outer SWNTs are charged with electrons transferred from the alkali.[14]

We show that peapods with several encapsulated molecules in the presence of an external magnetic field present robust diamagnetic and paramagnetic effects (Fig. 1) which are independent of temperature and proportional to the magnetic field strength (Fig. 3). Our results can be interpreted in terms of the magnetism of the carbon honeycomb structure with the retention and the destruction of delocalized π ring currents circulating around the outer nanotube. Our experimental findings definitively support important theoretical works on the diamagnetism of carbon materials which have been published in the past[6,7,5] and more recently.[15–18] Such magnetic properties are of great interest and, in particular, the case of charged C_{60} peapods which presents the largest diamagnetic shielding ever encountered in carbon allotropes. These experimental results provide new insight into the magnetic properties of carbon allotropes and ring current computations[6,5] as they clearly show that the largest obtainable diamagnetic shielding is not inside a doped C_{60} ball[7] but inside a doped carbon nanotube.

Concerning the slightly paramagnetic shifted line α, we suggest that defects such as vacancies, or holes in the outer shell will enhance the local paramagnetic ring currents.[19–21] π electrons are not free to process in the magnetic field but

are constrained to move along the bonds and the defects of the outer nanotube. This phenomenon is well known to quench diamagnetism in carbon allotropes via Van Vleck paramagnetism.[6]

To summarize our observations, we thus propose the following explanation for the observed α and β line positions; a major part of C_{60} molecules is β-type and experiences a diamagnetic shielding by the encapsulation in the SWNTs. A minor part is α-type and is located in the vicinity of defects or holes in the SWNTs. As discussed above, these molecules therefore do not exhibit any magnetic screening; on the contrary they feel a slightly paramagnetic effect from the defect. These features lead to a splitting $\Delta = \delta_\beta - \delta_\alpha$. The relatively broad distribution, as seen in Fig. 1 between the δ_β and δ_α lines, reflects C_{60} molecules in intermediate situations. In our analysis we have evaluated different *scenarios* that could potentially explain the two different lines in the NMR spectra. The most obvious option would be that the α-type molecules are positioned outside the SWNTs and therefore do not exhibit any diamagnetic screening. However this possibility is ruled out by their dynamical behavior showing that these molecules are not freely rotating as they would be if placed outside the SWNTs.[22] Also other possibilities, such as that the two lines would represent molecules in SWNTs with different diameters or chiralities, have been ruled out by our NMR experiments and computations.[15–18] We note however that there is currently only few theoretical calculations describing the effect of ring currents and their influence from the presence of different types of nanotube defects[6] and we look forward to such studies. We turn now to the case of Rb-intercalated C_{60} peapods (v) which needs a more extensive explanation. In this case, we observe to our extent the largest diamagnetic screening so far observed in carbon allotropes. The β-type molecules experience this large diamagnetic screening as compared to the α-type located at defects due to the extra number of electrons on the SWNTs, which increase the aromaticity of the nanotube envelope upon doping.[6,7,5] The NMR line position of the α-type molecules is broaden and reflects that the charge transfer to the C_{60} molecules is not homogeneous but lies in the range from 3 to 6 transferred electrons per C_{60} molecule.[23,24]

In the light of our study, it is now possible to tune and control the magnetic properties of peapods at the nanoscale by tailoring the molecular and electronic structures of the encapsulating SWNT. One potential and important application of this phenomenon in magnetic resonance imaging or spectroscopy would be to interface nanotubes with living cells[25] and to track them at the nanoscale through diamagnetic or paramagnetic magnetic fields, which affect NMR conditions.[26] Our current investigations presage that peapod hybrid materials and nanotubes, in general, are suitable for nanomagnetic shielding in nanoelectronics and nanobiomedical engineering and will presumably enhance in the near future experimental resolution to unprecedented levels.

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