Properties Of N@C_{60}-Derived Peapods

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Abstract. Using pulsed EPR techniques, the basic spin relaxation properties of N@C_{60}-based peapods were determined. In contrast to narrow line spectra typical for N@C_{60} in solid solution or in a C_{60} matrix, substantial line broadening is observed for the SWCNT-encapsulated N@C_{60} molecules, which might be indicative for uniaxial cage distortion by interaction with the nanotube.

INTRODUCTION

Recent progress in peapod preparation using a "solvent-based" procedure allows for the first time to consider the insertion of N@C_{60} into single wall carbon nanotubes (SWCNT) [1,2]. Because it was recently shown that N@C_{60} could be prepared as pure substance [3], it is now possible to use this exceptional spin probe to explore the electronic properties of nanotubes. In contrast to "seeding" with metallo-endofullerenes (MEF), N@C_{60} can be expected to be an "inert" spin probe, not subject to charge transfer when inserted in the SWCNT. In the future it also seems possible for the first time to prepare a densely packed one-dimensional electronic spin system with negligible exchange interaction. Properties of the so formed one-dimensional super-paramagnet could be explored easily because the electronic Zeeman interaction can be readily adjusted to be larger than the thermal energy even at standard liquid helium temperatures. In the current contribution we report on the first results of a pulsed EPR study by which the basic spin relaxation properties of N@C_{60} peapods were determined.

EXPERIMENTAL

Sample Preparation

N@C_{60} was prepared using an ion implantation apparatus developed at the Hahn-Meitner-Institute in the group of Weidinger [4]. The already optimized relatively low yield of 50 ppm relative to "empty" C_{60} obtained by this method necessitates the use of High-Performance Liquid Chromatography (HPLC) to obtain sufficiently high spin concentrations for a detailed EPR investigation. For this first study material enriched

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to the 200 ppm level was utilized. At this concentration level spatially isolated spin probes are inserted into the CNT, thus preventing line broadening by dipole-dipole interaction from the spin labels.

N@C_{60}-doped SWCNT were prepared using the procedure recently described by Simon et al. [2]. In brief, a saturated solution of N@C_{60}/C_{60} in hexane is used to suspend opened SWCNT. After approximately 2 h, the solvent is removed and toluene is used to extract C_{60} and N@C_{60}, not encapsulated by the SWCNT.

Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectra were measured either using a continuous wave (c. w.) (BRUKER ESP 300E) or pulsed (BRUKER ELEXSYS 680) spectrometer equipped with a variable temperature cryostat. C. w. spectra are used to check for any remaining non-inserted material, which can easily be discriminated from the peapod signal by their extremely narrow EPR lines. With a 2-pulse echo sequence echo-detected EPR spectra were recorded additionally, which instead of a field-modulated EPR signal allows to detect an undistorted EPR absorption spectrum if the spin dephasing time of the individual spin packets is larger than the time resolution of the spectrometer of approximately 100 ns. Under these conditions, narrow and broad signal components can be observed simultaneously. The echo signal decay as function of pulse separation was taken as measure of electron spin dephasing time.

RESULTS AND DISCUSSION

The c. w. EPR signal of the peapod preparation shows the characteristic 3-line spectrum of N@C_{60} superimposed on a broad unstructured signal of unknown origin in agreement with the previous observation [2]. Using electron spin echo detection, an additional broad resonance is detected at lower fields, as shown in Fig. 1. Such broad absorptions can be easily missed using c. w. techniques because of the reduced response with respect to field modulation. From the spectral characteristics we conclude that copper-based radicals of unknown origin contribute considerably to the total spin number in the sample. At higher spectral resolution the signal of N@C_{60} is clearly identified by its characteristic hyperfine coupling constant (hfcc) of a(N) = 0.57 mT (see Fig. 2). Final decomposition after numerically removing the broad signal results in a spectrum showing exclusively the EPR signal of N@C_{60}, is shown in Fig. 3. The lines can be fitted by using Gaussian line shape functions of width 3.1 ($m_I = 0$ hyperfine component (hfc)) and 4.8 MHz width ($m_I = \pm 1$ hfc) (FWHM). Although it is tempting to interpret this difference in width by assuming a distribution of nitrogen hfcc as major source of inhomogeneous line broadening, numerical artifacts originating from spectral decomposition, which could contribute to this apparent difference, cannot be completely excluded at present. The width of the underlying individual spin packets was estimated from the echo signal decay. A bi-exponential echo decay with characteristic time constants of 600 and 8000 ns was observed (B_0 = 346 mT). These values can be translated to Lorentzians of width 500 and 40 kHz, thus indicating substantial inhomogeneous broadening of the observed N@C_{60} signals.

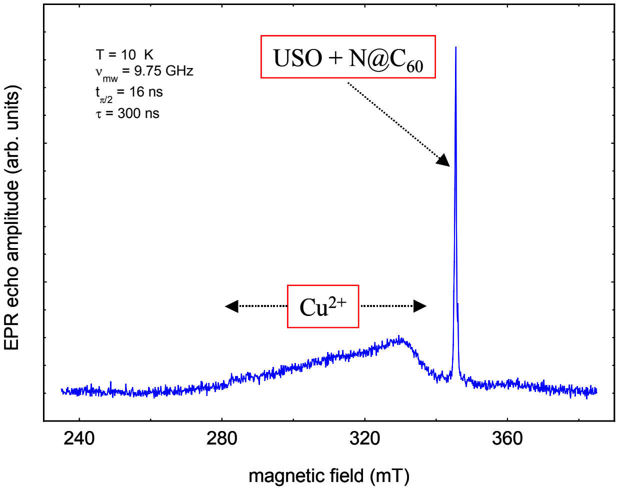

FIGURE 1. Echo-detected EPR of N@C_{60} peapods. EPR absorption originates from a Cu^{2+} radical and superimposed three lines from N@C_{60} (not resolved on this scale) with another strong signal from an "unidentified spin object".

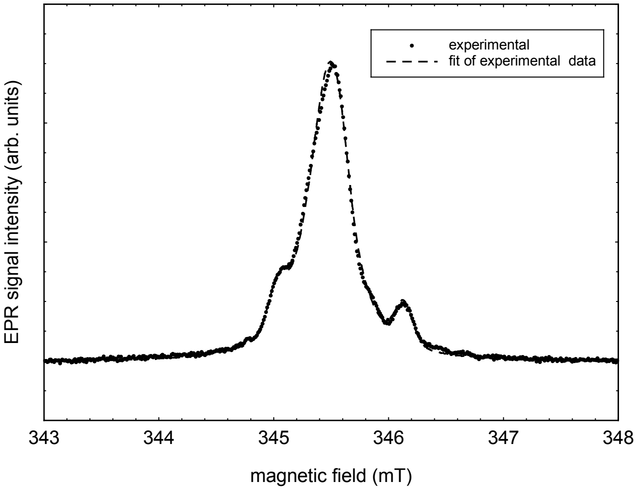

FIGURE 2. Part of the spectrum shown in Fig. 1 under higher spectral resolution. The experimental data were fitted by a superposition of an equidistant three-line spectrum of a(N) = 0.57 mT and a broader signal which is slightly down field shifted.

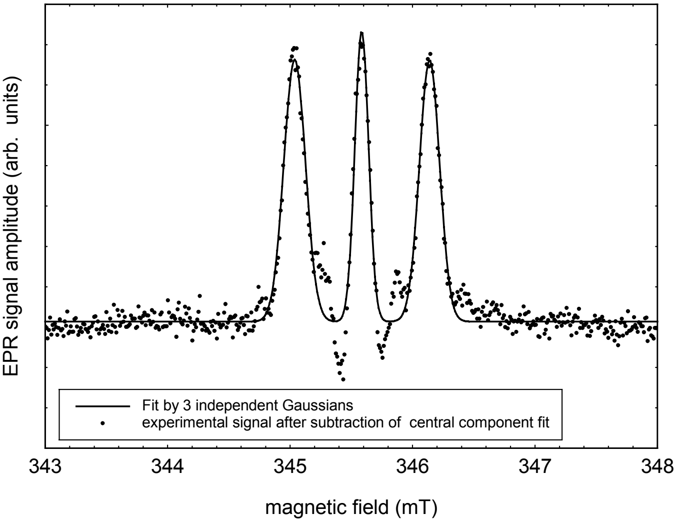

FIGURE 3. Echo-detected EPR absorption of N@C_{60} peapods (T = 10 K).

Obviously the use of highly enriched N@C_{60} material is mandatory for a detailed study aiming for the elucidation of the anticipated influence of itinerant spins in metallic CNT on the relaxation properties of the nitrogen spin probe. However, even the results presented in this preliminary study indicate that subtle effects of encapsulation might be detectable either via a variation of nitrogen hfc because of a change in effective volume seen by the atom or by Zero-Field-Splitting because of cage deformation.

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