¹³C NMR spectroscopy of carbon nanohorns

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We report the results of a carbon-13 nuclear magnetic resonance spectroscopic investigation of the structure of carbon nanohorn aggregates (CNHs). The results show that CNHs consist of two components, characterized by different chemical shifts and spin lattice relaxation (T_1) behavior. The first component has a chemical shift of 124 ppm and displays rapid spin-lattice relaxation behavior and is assigned to the nanotubelike horns on the particles' surfaces. The second component has a chemical shift of 116 ppm and much slower spin-lattice relaxation behavior and is assigned to the graphitelike part of the CNH aggregrate. The results of integrated peak area measurements indicate a 1:2 ratio of nanohorns to the graphitelike substrate. The absence of a clear Korringa behavior for the temperature dependence of T_1 and the lack of a Knight shift ruled out any metallic behavior and indicated instead behavior characteristic of semiconductor materials with paramagnetic centers due to structural defects providing an effective relaxation mechanism in the nanohorn domains. We also observed an anomalous change in T_1 near 17 K in the nanohorn domains suggesting the development of an antiferromagnetic correlation between localized electron spins.

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I. INTRODUCTION

Nanocarbon materials, such as carbon nanohorn aggregates¹ (CNHs), have recently attracted considerable attention since they are promising nano-scale materials with potential applications in a broad variety of fields, such as catalyst supports in fuel cell electrodes,² in gas storage devices,^{3–5} and as well as in drug delivery systems.⁶ Each nanohorn is composed of a horn-shaped, cap-closed carbon nanotube (CNT) formed out of a single-walled graphene sheet (average diameter and $2 \sim 3$ nm, Fig. 1)¹ and several of them together form a flowerlike aggregate with a rather uniform diameter of about 100 nm. CNHs, have very large surface areas due to the presence of these structures which enable them to support very fine catalyst particles as well as entrap drug molecules and even gases.

While there has been a considerable amount of work carried out in order to develop industrial uses for these novel materials,^{2–6} even some of the more fundamental properties of CNHs, such as their interior structures and, electronic and magnetic properties, are not well understood since the nanohorn aggregates have inhomogeneous, disordered structures. Such information is, nevertheless, of considerable fundamental interest, plus, it could also lead to designing structural modifications which would improve the material's properties for industrial or medical applications. In addition, since CNHs can be considered to be the precursors for CNTs, since they are synthesized under more moderate conditions (at room temperature without any metal catalysts) than those used¹ for CNTs, a detailed structural analysis of CNHs might lead to a better understanding of how CNTs are formed.

One of the basic questions regarding CNHs is whether or not there are any interior structures. To date, two models have been proposed, based on transmission electron microscopy (TEM) observations,¹ electron diffraction,¹ x-ray diffraction,⁷ and electron spin resonance (ESR) studies.^{8,9} The first model states that each aggregate consists of only tubular nanohorns. In the second model, the CNHs are thought to consist of a core formed from highly disordered "nanographite" (nanometer sized graphite particles) whose surfaces are covered with tubular nanohorns. In other work, *ab initio* electronic structure calculations have predicted that both metallic as well as semiconducting structures could occur, based on the horn morphologies, i.e., the presence of defect structures.¹⁰ However, direct experimental results on



FIG. 1. (Color online) TEM images of carbon nanohorns. The inset shows a schematic diagram of a typical hornlike outer part of CNHs.



FIG. 2. (a) Static ¹³C NMR spectrum for 97% ¹³C enriched CNHs taken at RT in a magnetic field of 8.4 T. The inset shows a static NMR spectrum for CNHs with natural abundance obtained at 80 K in the same magnetic field. These spectra were obtained by spin echo mapping method. (b) Magic angle spinning NMR spectrum for 97% ¹³C enriched CNHs spun at 15.000 kHz taken at 300 K in a magnetic field of 14.1 T. The asterisks stand for spinning sidebands. The system frequency was 150.870 MHz.

these systems concerning such properties are very limited. A Curie-Weiss-like paramagnetic behavior was observed in the temperature dependence of the magnetic susceptibility⁹ and ESR linewidth^{8,9} in the nanohorn part, indicating that localized electron spins, which originate from the edge states or structural defect sites, exist. Moreover, an indication of the development of an antiferromagnetic correlation between these spins has been observed in the interior nanographite part of the structure.⁸ These reports, however, lack consistency with each other in the structure assignments, spin density estimates, etc., and warrant further experimental investigations on these properties.

In this study, therefore, we have investigated the structural, electronic, and magnetic properties of CNHs by using ¹³C nuclear magnetic resonance (NMR) spectroscopy, which is an excellent probe of nanoscale structured materials. Our NMR results show a clear two-component behavior with the development of magnetic correlations at low temperatures, unambiguously establishing the existence of magnetic interactions in CNHs, and form the basis for future studies of chemically modified CNHs having industrial applications.

II. EXPERIMENT

The 97% ¹³C enriched CNHs were synthesized by CO₂ laser ablation at room temperature from a 97% ¹³C enriched graphite target using the same method as descirbed for CNHs at natural abundance ¹³C levels.¹¹ It should be noted that throughout the synthesis process, no metal catalyst (which could significantly increase the NMR spectral linewidth, as seen in carbon nanotube experiments^{12,13}) was used. The yield of CNHs, as estimated from thermogravimetric analysis (TGA) and TEM observation, was almost 90 at. %, with about 10 at. % amorphous carbon and large (1 μ m) graphite particles being obtained as by-products,¹⁴ similar to the results obtained with natural abundance ¹³C graphite. The surface structural features observed by TEM were the same as those for CNHs at natural abundance. About 200 mg of

CNHs were used for static NMR measurements. To avoid adsorption of paramagnetic oxygen molecules, the CNHs were sealed in a glass ampoule after heating to 350 °C in a vacuum of 1×10^{-5} Torr for two hours. For magic angle spinning (MAS) NMR experiments, 30 mg of sample was used and this measurement was done using air to drive the NMR rotor.

Static NMR measurements were performed by using a "home-built" NMR spectrometer using a Tecmag console in the temperature range 8–300 K and at a magnetic field strength of 8.4 T.¹⁵ NMR spectra were obtained by using a spin-echo pulse sequence $(\pi/2 - \tau - \pi - \tau - \text{acquisition})$ with 16-step phase cycling. The 90° pulse widths were 5 μ sec at 300 K and 8 μ sec at 8 K. The spin-lattice relaxation time, T_1 , was measured by using a progressive saturation method. Magic-angle sample-spinning NMR measurements were made with a modified Bruker AMS600 FT-NMR spectrometer at room temperature in a magnetic field of 14.1 T (corresponding to a 150 MHz ¹³C NMR Larmor frequency). T_1 on this instrument (under MAS) was determined by using an inversion recovery method. The typical 90° pulse here was 22 μ sec.

III. RESULTS AND DISCUSSION

A typical TEM of ¹³C enriched CNHs is shown in Fig. 1. The structural features are identical to that observed for ¹³C-natural abundance CNHs. The inset shows a schematic diagram of the nanohorn part. We show in Fig. 2(a), the ¹³C NMR spectrum of [¹³C-97%]-labeled CNHs at 8.4 T and at room temperature and, inset, a natural abundance spectrum obtained at 80 K. Due to the large chemical shift anisotropy observed in graphitic structures, both spectra are very broad spreading from –100 ppm to more than 300 ppm downfield from tetramethylsilane [(TMS) the chemical shift reference]. The natural abundance spectrum shows axial symmetry and it can be simulated using σ_{11} =195 ppm, σ_{22} =165 ppm, σ_{33} =10 ppm, close to values which are typical for aromatic and graphite-related materials having sp^2 hybridization, includ-



FIG. 3. (a) Inversion recovery spin-lattice relaxation time measurement. The spectra recovered asymmetrically. (b) Two-Lorenzian deconvolution of the central peak in the MAS spectrum. The peak positions for the fast and slow relaxation components are 124 ppm and 116 ppm, respectively.

ing carbon nanotubes.^{12,13} The spectrum for the ¹³C-enriched CNHs has a somewhat different line shape, due to an additional dipole-dipole interaction between ¹³C nuclei in this highly enriched sample. Figure 2(b) shows the MAS NMR spectrum of this ¹³C-enriched sample (measured at a spinning speed of 15 kHz). There is apparently only a single peak with an isotropic chemical shift value of 117.9 ppm. The asterisks represent the spinning sidebands which, as expected, encompass the entire 300 to -100 ppm chemical shift range. These results are somewhat surprising in that we find no clear evidence for multiple types of carbon-nanohorn and graphitic materials. However, this situation changes when we investigate the spin-lattice relaxation behavior of these materials.

We show in Fig. 3(a), the evolution of the nuclear magnetization measured for the central or isotropic peak shown in Fig. 2(b), using an inversion recovery $(180^\circ - \tau - 90^\circ)$ pulse sequence. From these partially relaxed spectra, it is clear that multicomponent behavior can be observed. That is, the spectra recover asymmetrically. The more deshielded resonance feature centered near 125 ppm recovers much more rapidly than does the more shielded feature centered near 115 ppm. Rather more accurate isotropic chemical shift values for each component can be estimated via a two-Lorentzian deconvolution of the central line, as shown in Fig. 3(b), in which we obtain chemical shift values for the fast and slow relaxation components of 124 ppm and 116 ppm, respectively, and a ratio of integrated intensity for the fast and slow relaxation components of 1:2. Although our sample includes 10% graphite, this ratio nevertheless strongly indicates that there are two very different nanographite structures in CNHs, consistent with the ESR results reported by Garaj et al.8 However, the assignment of these two sets of resonances is not clear from these results alone.

Table I shows the measured chemical shifts for different carbon materials.^{12,13,16–20} Comparing these chemical shifts with the present results, we can see that the 124.3 ppm chemical shift of the rapidly relaxing component is essentially the same as the 124–126 ppm seen¹² in CNTs while the

116.4 ppm shift of the more slowly relaxing component is consistent with an assignment to a graphitic core since this shift is in the range 108–119 ppm observed in graphites.¹⁷ On increasing the recycle time from 30 to 400 s, we also find a small (10%) increase in intensity of the spinning sideband indicating that the component having the longest T_1 also has the largest chemical shift anisotropy, consistent again with its graphitelike character.

A similar two-component behavior is observed in the static spin-lattice relaxation measurements, Fig. 4(a). Here, we show the magnetization recovery curve of enriched CNHs (intensities taken at the peak position of 122 ppm) at 280 K. The magnetization recovery curve cannot be fit by a single or stretched exponential curve (commonly used when there is a T_1 distribution), but can be fit quite well by a double exponential:^{12,13,21}

TABLE I. Chemical shifts of certain carbon materials.

Carbon Materials	Chemical Shift (ppm)	
Diamond ^a	35	
Graphite ^b	$108 \sim 119$	
Solid Benzene ^c	120	
KC ₈ (metallic GIC) ^d	81, 87	
C_{60}^{e}	143	
K ₃ C ₆₀ ^e	187, 195	
C_{70}^{e}	130, 144, 147, 150	
$\mathrm{CNTs}^{\mathrm{f}}$	124, 126	
CNHs (97% ¹³ C enriched)	116, 124	

^aFrom Ref. 16.

^bFrom Refs. 17 and 18.

^cFrom Ref. 18.

^dFrom Ref. 19.

^eFrom Ref. 20.

^fFrom Refs. 12 and 13.



confirming that these carbon nanohorn aggregates consist of two components having different spin-lattice relaxation rates. The fitting parameters are $\alpha = 0.32$, T_1 for the fast component $T_{1f}=2.0$ s, and T_1 for the slow component $T_{1s}=10.0$ s, at 300 K. Since the pre-exponential factor α represents the relative fraction of the two components, we deduce that the atomic ratio of the surface nanohorn part to the interior graphitelike part is 1:2. This ratio is the same as that obtained from the double-Lorentzian deconvolution of the central line in the MAS spectrum, Fig. 3(b). While there can, of course, be other species present and there can also be small distributions in properties within a species, these results give us some confidence that there are, nevertheless, two basic components in CNH aggregates. This two-component behavior was observed over the whole temperature range investigated, down to 8 K. As shown in Fig. 4(b), all magnetization recovery data could be fitted quite well by using the double exponential method. Below 40 K, the center of gravity of the FIG. 4. (a) Magnetization recovery curve (closed squares) in a progressive saturation T_1 measurement taken at the peak maximum (122 ppm) at 280 K. The solid and dashed lines represent the double exponential and single exponential fitting curves, respectively. (b) Temperature dependence of the magnetization recovery profile (symbols) and the two exponential fits (solid lines).

spectrum shifted downfield slightly and the spectra were somewhat broadened implying that the local magnetic environment of the ¹³C nuclei is modified at temperatures below 40 K [Fig. 5(a)]. Due to this shift and broadening, as shown in the inset of Fig. 5(b), the pre-exponential factor α , gradually decreases, i.e., the fraction of fast relaxation component decreases, indicating that this downfield shift and broadening mainly occur in the fast relaxation component. We return to this topic again, below.

Multicomponent behavior in ¹³C spin-lattice relaxation has been observed in NMR studies of CNTs. Tang *et al.*¹² reported a two-component T_1 behavior in CNTs with both components following a Korringa behavior (T_1T =constant) at temperatures above 200 K. However, ¹³C T_1 measurements on CNTs by Goze Bac *et al.*¹³ have shown that the relaxation behavior is dominated by thermally activated small amplitude motions of the nanotubes. No well-defined temperature dependence for the spin-lattice relaxation rate was seen in the NMR experiments of ¹³C-enriched CNTs synthesized via catalytic decomposition of methane.²² In metallic systems like graphite intercalation compounds¹⁹ (GICs) and alkali-doped fullerenes,²⁰ ¹³C NMR spectra show a clear Knight shift, in addition the chemical shift and relaxation



(1)

FIG. 5. (a) Temperature variation of static ¹³C NMR spectra. Below 40 K, the center of gravity of the spectrum shifted downfield slightly and the spectra were somewhat broadened. (b) Temperature variation of the spin-lattice relaxation rate (T_1^{-1}) for the fast (closed circles) and slow (open squares) components of relaxation. The peak near 17 K is an indication of strong antiferromagnetic correlations that develop between the localized spin states belonging to the nanohorn part. Inset shows the temperature variation of the pre-exponential factor.

times follow Korringa behavior. The temperature dependence of the relaxation rates, obtained from the static NMR experiments of CNHs, for both components, is shown in Fig. 5(b). For the fast relaxing component, the low temperature region ($T \le 40$ K) is much more complex than the slow relaxation component, which appears to follow a linear Korringa-like behavior below 100 K. A linear fit to the relaxation data below 100 K for the slow relaxation component gives $T_1T=2032$ s K. If this behavior is indeed due to a metallic nature of the graphitelike core of CNHs, then the Korringa constant and the density of states (DOS) at the Fermi energy (E_F) are related by²³

$$\frac{1}{T_1 T} = \frac{2\pi k_B}{\hbar} A_{dip}^2 \rho(E_F), \qquad (2)$$

where A_{dip} is the hyperfine coupling constant for the anisotropic part of Knight shift (the isotropic part vanishes for perfect sp^2 hybridization and the curvature induced effect on the DOS is very small¹²) and $\rho(E_F)$ is the DOS at the Fermi energy. From ESR splittings of carbon radicals,²⁴ we have $A_{dip}=4.7 \times 10^{-7}$ eV and with a T_1T value of 2032 s K, we get $\rho(E_F)=0.052$ states/eV atom. Components of the anisotropic Knight shift arising from the electron-nuclear dipolar interaction are related to the Fermi level DOS by²⁰

$$K_{\parallel} = \left(\frac{\gamma_e}{\gamma_n}\right) A_{dip} \rho(E_F), \quad K_{\perp} = -\frac{1}{2} \left(\frac{\gamma_e}{\gamma_n}\right) A_{dip} \rho(E_F), \quad (3)$$

where γ_{e} and γ_{n} are the gyromagnetic ratios of the electron and the nucleus, respectively. Using the DOS value estimated from the relaxation rate, the complete Knight shift tensor can be obtained in ppm as (64, 64, -32). Since graphene is considered to be a model compound for a wide variety of carbon materials, the chemical shift of a single graphene plane with zero DOS at E_F can be considered as the chemical shift of CNHs. For a single graphene plane with zero DOS at E_F the chemical shift is (183, 183, 20).¹⁷ Therefore, the total NMR shift for this part of CNHs will be (247, 247, -12) which should give the isotropic shift as 161 ppm. The double-Lorentzian deconvolution of the NMR spectra gives only a shift of 116 ppm for this part of the CNHs. This analysis, therefore, shows that though T_1 appears to follow a linear temperature dependence below 100 K, it does not represent true metallic behavior.

For highly ¹³C-enriched materials, spin diffusion to localized electron spins can provide a very effective relaxation pathway, if there are indeed such localized electron spins. In these carbon nanohorn aggregates, localized electron spins are expected to exist at defect sites, at tube tips, at bends in the tubular part, at pentagonal sites²⁵ in the surface nanohorn part, and at edges of graphene sheets in the interior graphitelike part. Indeed, ESR and magnetic property measurements suggested the existence of localized electron spins at edges of graphite sheets and the tip^{8,9} of CNHs. Large fluctuating magnetic fields caused by localized electron spins enhance spin-lattice relaxation rates of neighboring ¹³C nuclei via the direct dipolar interaction, and this accelerates the spin-lattice relaxation of neighboring ¹³C sites via spin diffusion mediated by dipole-dipole interactions between ¹³C nuclei. In which case, essentially all nuclei in a particle are effectively coupled to a relaxation center. In this case, the inverse of T_1 is given by

$$\frac{1}{T_1} = \frac{8.5NC}{d^3},$$
(4)

where, N, C, and d stand for the concentration of electron spins, the relaxation time at the unit distance from the paramagnetic center, and a diffusion barrier radius, respectively.^{26,27} Assume now that C and d are of the same order as those estimated for enriched diamond, i.e., $C \approx 1$ $\times 10^{-42}$ cm⁶ s⁻¹ (after correcting for differences in external magnetic field strength) and $d \approx 1.3 \times 10^{-7}$ cm.²⁷ We can then estimate our spin density to be on the order of 10¹⁹ $\sim 10^{20}$ spins cm⁻³ ($\sim 10^{19}$ spins g⁻¹, using a specific density value of 1.36 g cm^{-3} for CNHs) for the surface nanohorn part and $10^{18} \sim 10^{19}$ spins cm⁻³ (~10¹⁸ spins g⁻¹) for the interior, graphitelike part. These values are similar to those observed for activated carbon fibers having high surface area, but are larger than those obtained in the ESR studies.^{8,9} The origins of the differences are not known; however, they may be attributable to differences in sample preparation and heat-treatment methods, but more work will need to be done to clarify this question. Since there are so many structural defects in CNHs, simple Raman processes involving lattice vibrations that lead to a T^2 dependence for the high temperature region of T_1 , are also not seen for either of these components.

As can be seen in Fig. 5(b), below 40 K, the T_1 of the fast relaxation component begins to decrease with decreasing temperature, then, at 17 K, it increases again, indicating that some type of transition is occurring in the fast relaxation (nanohorn) component. One possible origin for this anomaly could be the development of magnetic order correlations between the localized electron spins via a small amount of conductive carriers, which might lead to a spin-glass like or spin freezing phase transition, instead of a "complete" longrange magnetic order phase transition, as observed in activated carbon fibers.²⁸ In such materials, the localized electron spins originating from nonbonding edge states of π electrons (with a concentration of $\sim 10^{19}$ spins g⁻¹) show antiferromagnetic interactions, mediated by itinerant π electrons in the graphite network. A similar antiferromagnetic interaction could appear in CNHs, with the relatively high concentration of localized electron spins in the surface nanohorn domain being responsible for this "phase transition." A similar effect was observed in Garaj's ESR study,⁸ although they conclude that the magnetic anomaly was due to localized spins in the interior graphite-like part, instead of the nanohorn part. However, no magnetic phase transition was reported in the Bandow ESR study.⁹ These discrepancies all certainly point toward subtle effects of sample preparation causing differences in spin density in such nanostructures. The relationships between spin density and magnetism for different carbon-based materials are listed in Table II. Regardless of the structure of these nanocarbons, the appearance of magnetic correlations depend primarily on the density of the localized electron spins. The threshold for

	Structure of Nanocarbons	Spin Density (spins g ⁻¹)	Magnetism
Garaj <i>et al</i> .ª	nanohorn	1.3×10^{16}	CW paramagnetism
	nanographite	6×10^{18}	antiferromagnetism
Bandow et al. ^b	nanohorn	2×10^{18}	CW paramagnetism
This work	nanohorn	$\sim 10^{19}$	antiferromagnetism
	nanographite	$\sim \! 10^{18}$	CW paramagnetism
Shibayama et al. ^c	activated carbon fibers	1.8×10^{19}	antiferromagnetism

TABLE II. The list of spin density and magnetism for components of carbon nanohorn aggregates and activated carbon nanofibers.

^aFrom Ref. 8. ^bFrom Ref. 9.

^cFrom Ref. 28.

development of antiferromagnetic correlations is $\sim 5 \times 10^{18}$ spins g⁻¹, and if the spin density exceeds this threshold, then antiferromagnetic correlations develop. This indicates the possibility that the magnetic properties of these and other nanocarbon materials may be controllable by engineering structural defects.

IV. CONCLUSION

The results we have presented above are of interest since they clearly show that CNHs consist of two components, characterized by different chemical shifts and spin-lattice relaxation behavior. The faster relaxation component (which has the chemical shift of 124 ppm) can be assigned to surface nanohorns, while the slow relaxation component (with the chemical shift of 116 ppm) corresponds to the graphitelike core structure. The atomic ratio of the surface nanohorn part to the interior graphitelike part is 1:2. The electronic properties of both components indicate that they are nonmetallic. The main spin-lattice relaxation mechanism appears to be rapid spin diffusion to localized paramagnetic centers (electron spins) that arise from structural defects. The faster spin-lattice relaxation rates observed in the surface nanohorn part suggest that the density of the localized electron spins—coming from structural defects—is much higher in these surface structures than in the graphitelike interior. The temperature dependence of the spin lattice relaxation rates in the nanohorn parts shows an anomaly below 40 K, indicating that magnetic correlations develop at these low temperatures, due to the large spin density in the nanohorn domain.

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