Electronic properties of carbon nanohorns studied by ESR

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The magnetic properties of carbon nanohorns were investigated by electron spin resonance. Two decoupled electronic systems were found. The first one, which has a spin susceptibility linearly varying with temperature, was tentatively attributed to two-dimensional graphenelike sheets. The second contribution, showing a Curie-like behavior with a non-negligible Pauli part, was ascribed to the interior of the structures of coagulated nanohorns. Surprisingly, this second line shows a strong suppression of susceptibility at 17 K. Due to a concomitant line broadening and *g* shift below 17 K, this transition was assigned to antiferromagnetic pairing of localized spins. The low spin concentration is implying that a kind of magnetism, mediated by the free spin carriers, has to be invoked to explain the phenomenon.

I. INTRODUCTION

Series of nanostructured carbon material were synthesized recently and these materials are getting a lot of attention due to a variety of unexpected physical properties. These structures are fullerenes,[1] multiwall carbon nanotubes (MWNT),[2] single-wall carbon nanotubes (SWNT),[3,4] onions,[5] cones.[6] The latest member of this series are the nanohorns.[7] Many fascinating electronic properties have been discovered in these nanostructures. For example, SWNT are expected to show nonconventional electronic behavior due to their one-dimensional character,[8,9] and fullerenes are showing a wide range of different ground states such as superconductivity, ferromagnetism, antiferromagnetism, spin-density waves, etc.[10] Little is known about the electronic properties of the youngest member of the carbon nanostructures family, the nanohorns, and this is the motivation for the present study.

The nanohorn system, discovered recently by Iijima *et al.*,[7] is showing unique structural features. From the production technique and morphology, nanohorns can be regarded as structural precursors of SWNT. Nanohorns appear at the surface dahlia flowerlike structures that have nearly uniform diameter distribution around 80 nm [Fig. 1(b)]. The highly disordered surface of dahlia particles consists not only of single-wall cone-shaped tubular structures sticking out (''nanohorns'') but also of disordered free-standing graphene sheets [Fig. 1(c)]. The radius of the nanohorns is around 2 -3 nm, bigger than that of SWNT, and the average cap angle is 20°. A recent theoretical study has shown that both structures, planar graphene sheets and cone-shaped nanohorns, are stable with very similar structural energies.[11] The inside of the dahlia particle consists of crushed and irregular nanohorns and graphene sheets, compacted and partially amorphous. This picture of the system is supported by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman observations.[7] X-ray diffraction measurements are suggesting that single-wall graphite sheets (graphene) are dominant structures in the system.[7] Dahlia particles are further coagulating in bigger structures [Fig. 1(a)], forming a very light, porous black powder. Let us now clarify the nomenclature. The whole material itself was named ''nanohorns'' by its discoverers. The same name was also used for conical graphitic shapes (horns), which coagulate further into hedgehoglike particles, named ''dahlias.'' To be more distinctive, we used the word ''dahlias'' when discussing overall properties arising from nanohorn coagulation, and the word ''nanohorns'' was used for discussing properties arising from isolated cones.

Here we report the investigation of the electronic and magnetic properties of the nanohorn/dahlia particles by electron spin resonance (ESR). Our study reveals an unusual two-dimensional (2D) graphenelike electronic system, presumably at the surface of the dahlia particles. In the interior of the dahlia particles, where the disordered and smashed nanotubes and graphene sheets are present with some amorphous carbon, the electronic properties are governed by graphitic domains and localized spins, and the transport is by hopping. In this part of the sample, electron correlation effects are present at low temperatures. We also see a strong oxygen effect on spin relaxation, as was reported before by Bandow *et al.*[12]

II. EXPERIMENT

Nanohorns were prepared by high-power CO_2 laser evaporation of graphitic rods in argon gas flow, as reported in Ref. 7. The soot was sonicated afterwards in ethanol, and filtered to remove fibrous materials that might have been included during collection of the sample. With repeated centrifugation and sedimentation, larger graphitic particles were removed. Finally, nanohorn material of very high structural purity was obtained. Sample characterization by TEM, SEM, x-ray diffraction, electron energy-loss spectroscopy, and Raman spectroscopy revealed no presence of graphitic impurities of any kind, nor of noncarbon materials. It is worth emphasizing that no metal catalyst was used during the production process.

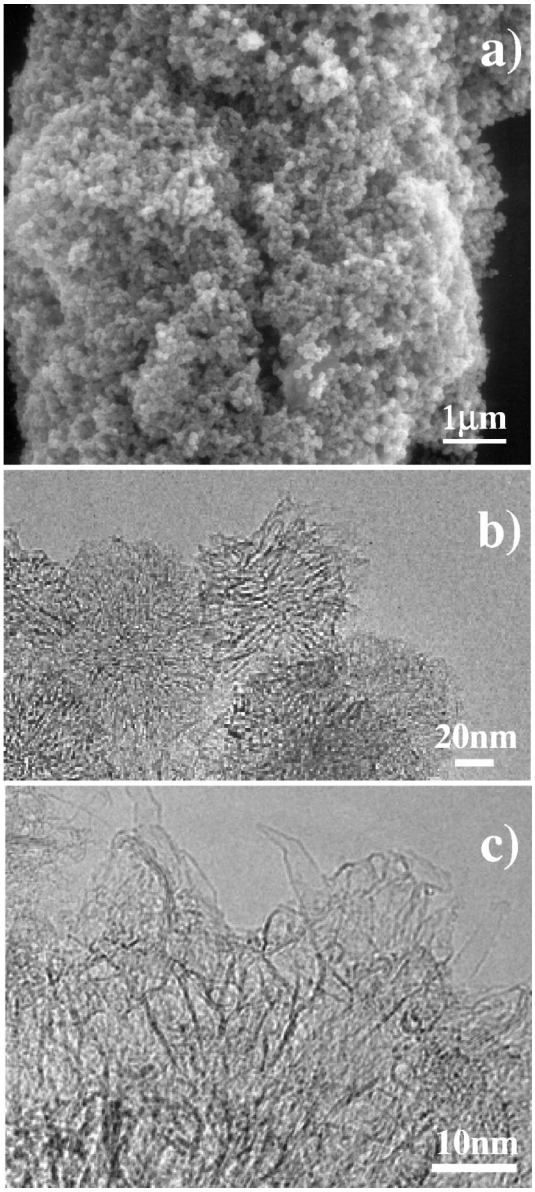

FIG. 1. Carbon nanohorns: (a) SEM image of coagulated dahlia flowerlike particles; (b) TEM micrograph of individual dahlia particles; (c) details of disordered edge states of dahlia particles, conelike tubular structures (nanohorns) and disordered graphene sheet are visible (high resolution TEM).

ESR spectra were measured with a Bruker ESP 300E X-band spectrometer in the temperature range $5-300$ K on a standard amount of 1 mg of nanohorn powder. Magnetic field and microwave frequency were calibrated using a NMR gaussmeter and a frequency counter. ESR intensities were calibrated using a diphenylpicrylhydrazyl sample as a reference. All the measurements were performed several times with many different nanohorn samples and were reversible in temperature. Although all the samples were coming from the same batch, this way we excluded artifacts due to sample preparation and ensured reproducibility of the measurements.

III. RESULTS AND DISCUSSION

The electron spin resonance spectrum reveals two distinct lines: a broad one of 4.5 G linewide (peak-to-peak), and a narrow one of 2.5 G at room temperature (Fig. 2). The broad line is very sensitive to oxygen concentration. This line is strongly broadened up to 80 G at only 200 mbar of air pressure, and could hardly be recognized at ambient air pressure due to the broadening. As the two lines have very similar g factor and the narrow line has much lower intensity, it is hidden by the broad one once the oxygen is removed. We shall see below that this narrow line is a unique feature of the nanohorns. In the measured range of oxygen pressures, the broadening of the 4.5-G (broad) line varies linearly with oxygen concentration. This effect, the influence of oxygen on spin relaxation, was recognized before for conducting (conjugated) polymers[13] and activated carbon fibers (ACF).[14] By analogy with polymers, the strong broadening of the line in the presence of oxygen can be attributed to strong exchange interaction between molecular oxygen (triplet ground state, $S=1$) and the host spin carriers. In order to have strong exchange coupling, oxygen molecules should come very close to mobile electrons. To have exchange interaction effective enough, oxygen should be immobile,[13] and it is probably fixed at defect (''active'') places in the carbon matrix inside the porous structure of dahlia particles. Otherwise, the broadening can also be attributed to the dipolar field of the paramagnetic oxygen molecules, affecting dangling bonds.[14] In contrast to conjugated polymers and ACF, the effect of broadening is an order of magnitude stronger, which suggests the higher mobility (hopping frequency) of spin carriers or, alternatively, the much higher oxygen absorbance of the sample at a given oxygen pressure. The latter is supported by the highly porous structure of the nanohorn sample and by the fact that the high vacuum is not good enough to remove all the oxygen from the structure; we had to apply the moderate heating during the pumping. By removing air and introducing different pressures of argon, no broadening was observed, which proves that the effect is due to oxygen. A preliminary ESR study of nanohorns in a limited-temperature range by Bandow *et al.*[12] has already shown this extreme sensitivity of spin relaxation to oxygen.

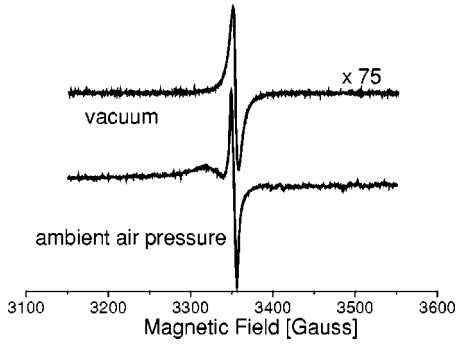

FIG. 2. Characteristic ESR spectrum of a carbon nanohorn powder. Under vacuum only one strong line is detectable (upper panel). Upon introducing oxygen, the line broadens in continuous fashion and reveals at $g=2.0023$ a smaller intensity line, which is unaffected by oxygen. Lower panel: Under ambient oxygen pressure, the smaller intensity narrow line is nicely visible, while the large intensity line is strongly broadened. The spin susceptibility of the narrow line is 100 times lower than that of the broad one. We attribute the narrow line to a graphenelike system and the broad line to disordered graphiticlike structures inside the dahlialike particles (see Fig. 1).

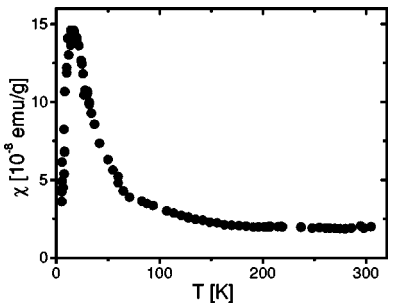

FIG. 3. Paramagnetic spin susceptibility versus temperature of the broad line. The Curie-like behavior with significant Pauli (conducting electron) part above 17 K is attributed to the graphitic and disordered interior of the dahlialike particles. Below 17 K, the strong decrease of the signal intensity is suggestive of singlet spin pairing.

For the investigation of the intrinsic behavior of the broad line, the sample was placed in a quartz tube and carefully pumped under the vacuum of 10^{-7} mbar for 5 h while heated at 300 °C, and then sealed in an ESR quartz tube. The temperature dependence of the ESR line was investigated in the range of 4–300 K. Two different kinds of samples were investigated: a pristine nanohorn sample, and a sample compacted by filtration of nanohorn suspension in propanol. Qualitatively, the ESR response of both samples was the same.

For both samples, the susceptibility of the line is strongly increasing with the decreasing temperature in a Curie-like fashion until 17 K. Below 17 K, a strong suppression of the susceptibility was observed (Fig. 3). Careful investigation of experimental conditions excludes instrumental artifacts (such as microwave power saturation or microwave heating). In the high-temperature region, together with the Curie-like component, a non-negligible Pauli component is present. The linewidth is decreasing monotonously with decreasing temperature. For the compacted sample, the linewidth at room temperature is broadened, compared to the pristine sample, but it drops to approximately the same value at the transition temperature of 17 K (Fig. 4). Below the transition temperature, the linewidth sharply increases for both samples. Above 17 K, the g factor stays constant at the value of $g=2.0019 \pm 0.0001$, and shows an increase below the transition temperature (not shown in the figures).

We believe that the broad line is coming from the denser, inner part of the dahlia particle. The strong temperature dependence of the linewidth is showing that the system is similar to a disordered metal. This effect, together with the relatively high paramagnetic susceptibility at room temperature, is supporting the notion that the interior is not amorphous, but upholds some of the structure of crushed nanotubes and touching graphene sheets. The touching sheets, with a distance of ~ 0.3 nm, resemble nanographitic particles. They are surrounded by amorphous carbon particles that can efficiently absorb oxygen giving the strong line broadening. In this picture, it is natural to assume that the transport mechanism is governed by hopping conduction that is confirmed by dc resistivity measurements.[15] It is well known that in a metallic system, there is a relation between ΔH_{pp} (ESR peak-to-peak linewidth) and ρ (resistivity), that is, between spin and moment relaxation of the electron (Elliott mechanism).

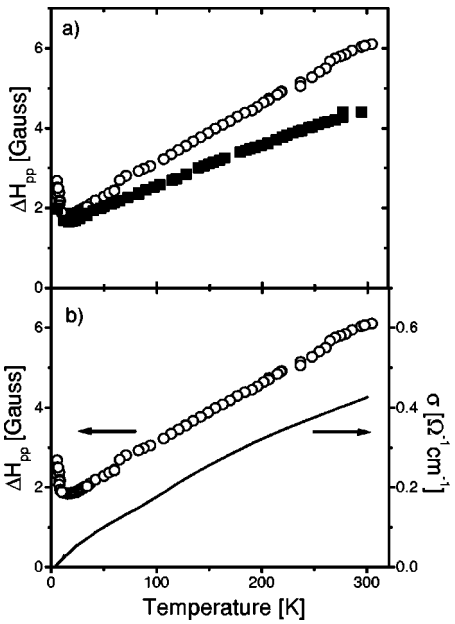

FIG. 4. (a) Temperature dependence of the ESR linewidth for a loose powder (squares) and compacted (open circles) nanohorn sample. Below the transition temperature at 17 K (see Fig. 3) a steep increase of the linewidth is detected. (b) Similar temperature dependencies of the electrical conductivity performed on a thick film of nanohorns (solid line) (Ref. 15) and the ESR linewidth (open circles) above 17 K, underlines the hopping mechanism of conduction and spin relaxation.

Moreover, a modified mechanism was applied for materials with hopping conduction.[16] The basic idea behind this model is that the rate of spin relaxation by the spin-orbit coupling is proportional not to the moment-relaxation rate, but to the hopping frequency, that is, to the conductivity (σ):

$$\Delta H_{pp}(T)=\Delta H_{pp}(0)+C\sigma(T). \tag{1}$$

In our case, as seen from Fig. 4(b), ΔH_{pp} and σ are closely following each other in a wide temperature range, justifying this approach. Furthermore, this model also explains the larger value of ΔH_{pp} in the compacted sample. There are two scales at which hopping is playing a role in the system: intradahlia and interdahlia hopping. In the case of the compacted sample, better contact between dahlia particles is reducing the interdahlia-hopping barrier, improving conductivity, and hence, enlarging the linewidth, as well. For both samples, the temperature-independent linewidth is the same $[\Delta H_{pp}(0)=1.2$ G] as expected, because it does not depend on hopping parameters.

The susceptibility above 17 K can be decomposed into Curie (localized spins) and Pauli (conduction electrons, temperature independent) parts. The exchange interaction between localized and conducting electrons is effectively mixing the systems, giving only one ESR line, which is a characteristic property of sp^2 carbon systems. The Curie-like part of the susceptibility is due to 1.2×10^{-4} localized spins per C atom (6×10^{18} spins/g). The Pauli susceptibility is relatively large, 0.63×10^{-8} emu/g, which accounts for as much as 1/3 of susceptibility at room temperature. This value is close to the Pauli susceptibility measured for multiwall carbon nanotubes (MWNT).[17] The density of states at the

Fermi energy $N(E_F)$ is related to the spin susceptibility by $\chi=\mu_B^2 N(E_F)$, where μ_B is Bohr magneton. In our case, it gives $N(E_F)=2.3\times10^{-3}$ states/eV atom, which is comparable both to MWNT and pristine graphite,[17,18] suggesting that the dahlia structure is partially metallic/semimetallic in nature. The significant Pauli susceptibility of the nanohorns is suggesting that the dahlia-particle interior consists of conductive percolative networks, as a residue from the crushed nanotubelike structures. In contrast to conduction electrons, the number of localized spins in the nanohorn system is one order of magnitude larger than in the case of MWNT, which originates from the much higher degree of disorder. A similar comparison between the ESR signals from nanohorns and SWNT's cannot be made, as it is still not clear what the nature of the ESR signals from SWNT's really is. The lack of the signal from SWNT's could be due to the 1D nature of the system, but it can very well be due also to the influence of rapidly spin-relaxing ferromagnetic impurities. Hence, the intrinsic signal from SWNT will remain unresolved until better purification processes are found, and at this point, we cannot make any comparison with the nanohorn system.

The large suppression of the paramagnetic susceptibility below 17 K and the sudden line broadening is suggesting antiferromagnetic (AFM) correlation between localized spins. In the view of the very small concentration of the localized spins (1.2×10^{-4} per C), their pairing into AFM singlet pairs is rather surprising and has to be resolved. Recently, Shibiyama *et al.*[19] reported disordered antiferromagnetic correlation in nanographite-based activated carbon fibers and they suggested that coupling is mediated by conducting electrons. It is likely that a similar situation is found in the nanohorn system.

The nature of the narrow line is even more intriguing. In contrast to the broad line, the narrow line does not broaden in oxygen atmosphere. To investigate the temperature evolution of the narrow line, the sample was sealed in a tube with ambient pressure of oxygen. In this way, the strong broadening of the broad line opens a window, enabling the study of the otherwise hidden narrow line (Fig. 2).

The susceptibility of the narrow line shows a nonmonotonous temperature behavior [Fig. 5(a)]: with decreasing temperature, the susceptibility first drops quite rapidly down to the point of inflection at $\sim$120 K, then it rises strongly in a Curie-like fashion. If we offset the Curie-like component, a quasilinear temperature dependence is observed [see inset of Fig. 5(a)]. Intriguingly, the g factor remains constant with a free-electron value of $g=2.002\,32\pm0.000\,04$ [Fig. 5(b)]. The linewidth does not change much in the temperature range of investigation [Fig. 5(b)].

Since the TEM micrographs give the impression of having crumpled graphene sheets on the surface of nanohorn dahlias, we tentatively attribute the narrow line to these graphene sheets. The peculiar temperature evolution of the ESR intensity of the narrow line is well fitted with a model of thermally activated susceptibility of a noncoupled graphene sheet. In graphene, the density of states is zero at the Fermi energy, and rises linearly and symmetrically above and below the Fermi energy. In the model, we take graphene sheet density of states, and we are taking into account the appearance of a small gap, attributed to the hybridization of the crossing bands at the Fermi level due to the curvature of the

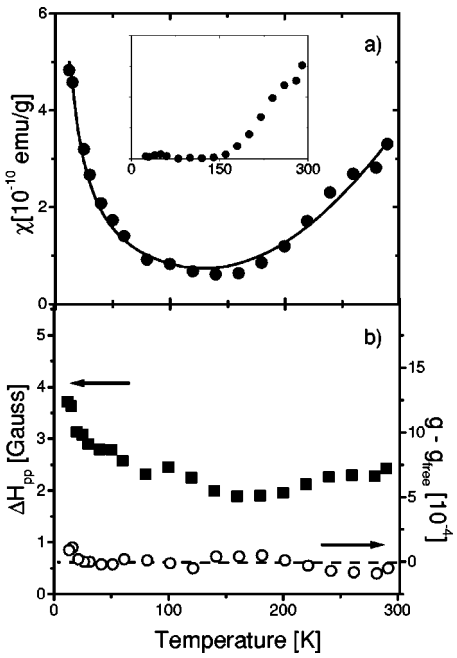

FIG. 5. (a) Paramagnetic susceptibility of graphenelike system. The expression for the spin susceptibility of graphene [see Eq. (2)] nicely follows the measured points. The inset shows a temperature-activated susceptibility after offsetting the Curie-like contribution. (b) The temperature dependence of the linewidth (circles) and the g factor (squares) of the narrow line.

sheets. Disorder and finite size of the system could give the same effect. Calculation of the paramagnetic susceptibility in this model gives the following relation:

$$\chi(T)=A\left[k_BT\ln\left(\exp\frac{\Delta}{k_BT}+1\right)-\Delta\right]+\frac{C}{T}, \qquad (2)$$

where the first part of the expression is attributed to Fermi-tail activation of Pauli susceptibility over the gap of $2\Delta=0.1$ eV into the linear density of states. The second factor is the Curie-like contribution that comes from narrow-peak (localized) density of states near the Fermi energy, which is likely to be an intrinsic property of the system. The nature of it will be discussed below. The fitting procedure is giving very good correspondence between the theoretical model and the data. The Curie contribution corresponds to 1.3×10^{16} spins/g. The small overall susceptibility is partly due to the fact that the signal was normalized with the whole mass of the sample and not only by the mass of the graphene sheets.

The next point, which supports our notion of the graphenelike nature of the system, is the g factor. In our system, the g factor is completely temperature independent and it has a free electron value. If the system were made of small, coupled graphitic crystals, the electron motion would average the highly anisotropic g factor of the graphite and the overall g factor would be given by $g(T)=g_\perp+1/3\Delta g(T)$, where $g_\perp$ (perpendicular to the graphene plane) should essentially be close to the free electron value,[20] and the anisotropy factor is given by $\Delta g=g_\parallel-g_\perp$. For disordered turbostratic carbon materials, the g-factor anisotropy (Δg) has been calculated by McCure (see Ref. 21). It is strongly temperature dependent and it is directly proportional to the frac-

tion of 3D states admixture in the π band. In the case of completely decoupled graphene sheets, Δg should disappear completely. Indeed, $\Delta g = 0.047$ at room temperature in graphite, and it varies as $1/T$ (Ref. 20). As our system does not show any temperature-dependent Δg contribution, we can claim that no measurable contribution of the 3D states is present and we are dealing with a 2D graphenelike structure. As the cones of the nanohorns have an unusual large radius and irregular structure, this subsystem could show a 2D nature as well.

The Curie-like contribution to the narrow line can be explained in the following way. Normally, highly reactive dangling bonds of the edges are easily saturated at the ambient conditions. Recently, theoretical investigations showed the appearance of nonbonding paramagnetic π-electron states at the zigzag graphene edge.[22,23] This phenomenon is responsible for introducing localized states near the Fermi level. Similar effects could arise from pentagon defects on tips of nanotubes or cones.[11] Coming over from the activated to the Curie-dominated temperature region, there is no change in g factor, suggesting that the same spin system is responsible for both temperature-activated and Curie-like behavior. One would expect a change in g factor if two different strongly coupled spin systems with different intrinsic g factors were responsible for each contribution.

Final support for the surface, graphene nature of the narrow line comes from the lack of oxygen-induced broadening. As oxygen is not absorbed on graphite surface, and has no effect on the spin relaxation in graphite, we believe that this should be the case for a single graphite sheet, that is for the graphene, on the surface of the dahlialike particle.

IV. CONCLUSION

In conclusion, we have investigated the electronic and magnetic properties of a carbon nanostructure, the nanohorns. ESR is revealing two electronic systems that are decoupled: (1) high surface disordered graphene sheets and large diameter cones giving a unique temperature-activated paramagnetic susceptibility and (2) a fairly conducting disordered structure at the interior of dahlia particles. For the dahlia-particle interior, the spin relaxation is governed mainly by hopping mechanism. Below 17 K, strong suppression of the susceptibility was observed, which is suggestive of an antiferromagnetic correlation between the localized electrons. However, the localized electron system is very dilute, so the nature of the exchange coupling remains unknown. Singlet coupling of localized spins, mediated by conduction electrons, was recently suggested.[19] This kind of magnetism in carbon materials could possibly explain our results. To clarify this phenomenon, further work is needed.

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