Modification of multiwall carbon nanotubes by electron irradiation: An ESR study

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Multiwall carbon nanotubes were irradiated by 2.5-MeV electrons with different fluences. Nanotubes appear to be very resistant to radiation, without radiolysis effects. The radiation-induced defects, which were nearly exclusively point defects, were found to significantly modify the electronic properties of the tubes near the Fermi level, as assessed by electron spin resonance. Pristine nanotubes appeared nearly free of paramagnetic defects, the density of which increased with the fluence. Furthermore, the position of the Fermi level as monitored by the *g* factor was very sensitive to the presence of defects in the rolled graphene plane.
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I. INTRODUCTION

Carbon nanotubes are a new mesoscopic form of graphite. Their small diameter is expected to induce interesting deviations from the two-dimensional band structure of graphite. Depending on the warping geometry, a nanotube can be either a metal, or a small or large gap semiconductor.[1–3] Every phenomenon that involves electrons of the Fermi surface should thus be sensitive to the geometrical properties of these nanostructures. For example, the density of states at the Fermi level, as well as the magnetic susceptibility,[4,5] are predicted to differ from those of graphite. Although the most spectacular effects are expected in singlewall nanotubes, nested multiwall nanotubes (MWNT) should also exhibit mesoscopic phenomena, since each layer is weakly coupled to its neighbors, and hence, conserves its quasi one-dimensional character.[6,7] One method to study these effects is electron spin resonance (ESR), which has proven to be very useful in macroscopic graphite compounds since it probes the conduction electrons. In doped polymers, and other kind of mesoscopic conjugated carbons, spin dynamics reveals the specificity of charge transport.[8,9] The study of carbon nanotubes by ESR should thus give useful indications of the behavior of conduction electrons.

Previous ESR measurements on MWNT are not entirely consistent with each other.[10–14] It appears that the results strongly depend both on the degree of purity of the samples and on the method of preparation. An interesting study by Kosaka *et al.* suggests that the as-grown nanotubes are rich in defects that can be annealed at high temperature to obtain an ESR behavior very different from graphite.[10] In this paper, we address the inverse problem, i.e., we studied the influence of irradiation-induced defects on the ESR properties of pristine purified MWNT. These defects are expected to modify the local Fermi surface and vary the density of states at the Fermi level, as well as the *g* factor and the spin dynamics.

II. EXPERIMENTAL

Multiwall carbon nanotubes were produced by the arc-discharge method using pure graphite electrodes. A liquid-phase separation method was used to purify the raw powder.[15] The mean outer diameter of MWNT as determined from TEM images is 12 nm with a mean inner diameter of 2 nm (the average number of shells is approximately 15). For irradiation experiments typically 1 mg of nanotube powder was wrapped in a 10-μm-thick copper foil. This copper bag was used as a sample holder transparent to the electron beam. The irradiations were performed with a Van de Graaff electron accelerator operating at 2.5 MeV, with a typical flux of 30 μ A/cm^2. For heat exchange reasons irradiations were performed in liquid hydrogen (21 K), and the samples were rewarmed to room temperature just after the irradiation. Four electron fluences were applied: 0.51, 1.07, 2.79, and 5.01 C/cm^2. A fifth sample was irradiated at room temperature by the γ-ray flux, originating from the interaction of the electron beam with a copper target. The purpose of this last irradiation was to assess the sensitivity of MWNT to radiolysis.

After irradiation the samples were wrapped with Teflon tape on a quartz rod and introduced into the continuous-flow helium cryostat of a Bruker ER 200D electron paramagnetic resonance (EPR) spectrometer operating in the *X* band, where *g* factors were measured using an NMR gaussmeter. The measurements were performed in the 4.2–300-K range.

III. RESULTS AND ANALYSIS

A. Irradiation effects

The energy losses of charged particles in matter are divided in two contributions: excitations and ionizations of the electrons on one side and direct knock-on collisions with nuclei on the other.[16] In metals electronic excitations are diluted by conduction electrons and no damage results from this process, i.e., only atomic displacements can create defects. In organic compounds, which are usually insulators, the excitations are localized and free radicals can be created in large quantities. As a result, stable paramagnetic defects can be present for a long time after irradiation, usually trapped on aromatic structures.[17,18] In graphitic materials, which have a low-carrier density, irradiation-effects may be

slightly different as compared to normal metals with a large carrier density. In the case of nanotubes electronic energy losses may have an influence on the creation of defects since part of the ensemble of nanotubes are large gap semiconductors.

It is possible to give a theoretical estimate of the maximum number of point defects created by 2.5-MeV electrons in a carbon target by collisions. We use the procedure described by Oen[19] to estimate the cross section for point defect creation. Taking 20 eV as a rough estimate for the displacement threshold energy, such a calculation gives a cross section of 40 barns; for a fluence of 1 C/cm^2, one achieves a maximum concentration of 2.5×10^{-4} dpa (displacement per carbon atom). For the sample irradiated at a fluence of 2.79 C/cm^2, we obtain 6.9×10^{-4}, that is, 1 defect for 1450 carbon atoms. In graphite most of the irradiation defects are paramagnetic and their density can therefore be measured by ESR.

Different kinds of metastable defects can be created by irradiation. Interstitial-vacancy pairs are well-known paramagnetic defects of neutron-irradiated graphite. Trapping of electrons by vacancies can create extrinsic holes in the π band. Coalescence of vacancies can also occur and form extended defects. Neutral bond rotation defects may also be present.[20] In this case, two carbon atoms are rotated with an angle of $\pi/2$, which produces two pairs of pentagons and heptagons in the hexagonal network. Such defects are not paramagnetic, but they are expected to modify the local density of states.[21]

Nanotube samples were examined before and after irradiation with a high-resolution transmission electron microscope (TEM). We did not detect any kind of damage to the tube walls, extended defects or collapsed tubes. Lattice fringes remained unchanged even for the most irradiated sample. On the other hand, the contrast under identical focalization conditions was not affected by the irradiation, which indicates that the density of irradiation defects was not large enough to affect visibly the crystalline structure. This is in contrast with the work of Crespi *et al.*,[22] where nanotubes were found to be irreversibly damaged after already 100 s of irradiation with 800-keV electrons in a TEM. This was due to the high electron flux in a TEM, which leads in the case of Ref. 22 to fluences at least two orders of magnitude higher than in the present study. Actually, the displacement cross-section drops very rapidly below electron energies of about 100 keV. This explains, for example, why the 20 keV electron beam of a scanning electron microscope can be used to ''solder'' nanotubes to gold electrodes without causing damage at low fluences.[23]

B. ESR analysis

We found that the γ-irradiated sample gave the same ESR signal as pristine nanotubes on the whole temperature range. No radiolysis occurs, in good agreement with the semimetallic character of the MWNT,[11] i.e., low-energy excitations are not efficient in producing damage in these conjugated carbon structures.

In contrast, the ESR signal of the four-electron-irradiated samples was strongly modified: a narrower and more intense line was detected, with a quasilorentzian shape. The spin susceptibility, deduced from the double integration of a Lorentzian fit of the signal, was found to vary linearly with the inverse of the temperature, as exemplified in Fig. 1(a). Hence it can be written as

$$\chi=\chi_1+\chi_2=c/T+\chi_2, \tag{1}$$

where two contributions are pointed out: a Curie-type term χ_1 varying as the inverse of the temperature, and a Pauli-like term χ_2 independent of T. The mass of all samples being comparable, it follows that the Pauli term depends only slightly on the irradiation fluence, whereas the Curie term strongly increases. In order to get a more quantitative insight into this point, we plot the variation of the parameter c/χ_2, which describes the ratio of the Curie contribution to the Pauli term versus T [Fig. 1(b)]. The fact that this coefficient is nearly proportional to the electron fluence indicates that irradiation created mainly localized defects, but only slightly modified, if at all, the metallic density of states. For pristine nanotubes $c/\chi_2\approx2$ K with $\chi_2=7\times10^{-9}$ emu/g. Note that the density of localized unpaired defects is very low in pristine nanotubes (about 2×10^{16}/g). From the EPR intensity data for the 2.79 C/cm^2 sample, we determined the number of Curie spins to be 1.14×10^{-4} spins/carbon. This repre-

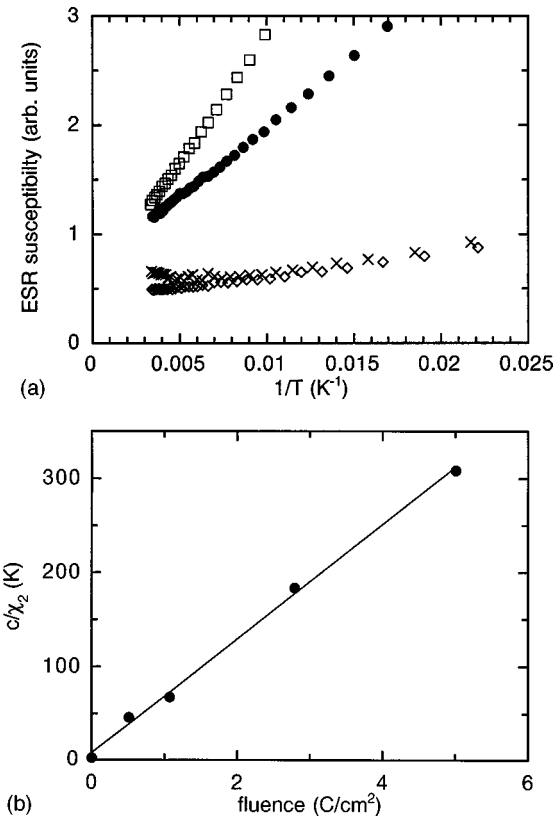

FIG. 1. (a) Paramagnetic susceptibility of the four irradiated samples versus the inverse temperature. Diamonds, 0.51 C/cm^2; crosses, 1.07 C/cm^2; full dots, 2.79 C/cm^2; squares, 5.01 C/cm^2. (b) Variation with electron fluence of the coefficient c/χ_2, which describes the ratio of the Curie to Pauli contributions in the data of (a). The main effect of electron irradiation is to introduce localized paramagnetic defects in the graphitic network of MWNT's. Note that pristine nanotubes are nearly free of such defects ($c/\chi_2=2$ K).

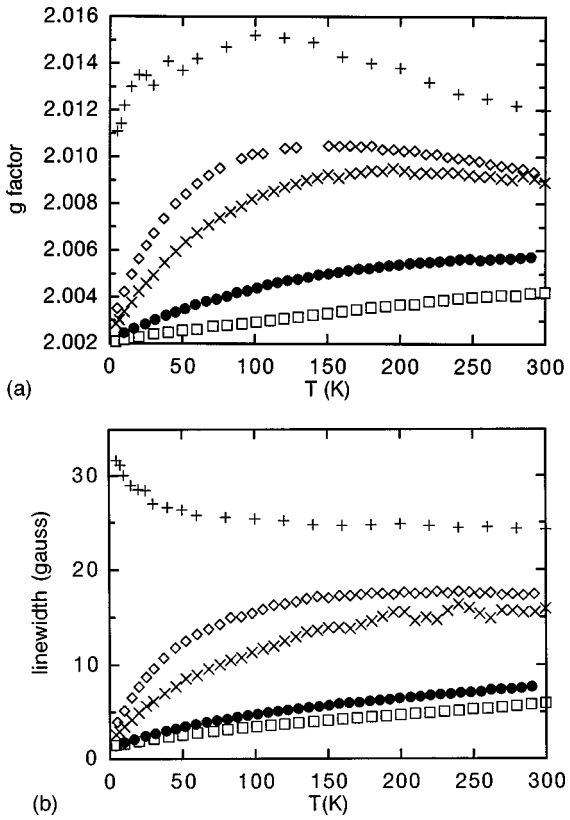

FIG. 2. The g factor (a) and the ESR linewidth—half-width of the absorption spectrum—(b) are strongly modified by electron irradiation over the entire temperature range. At low temperatures localized defects dominate the overall ESR behavior due to a bottleneck effect with conduction electrons. (A single ESR line is detected since the two spin systems are strongly exchange coupled.) The symbols are the same as in Fig. 1. The g factor and linewidth of pristine nanotubes are also plotted (+). Note the absence of a drop of the linewidth at low temperatures, in contrast to irradiated samples.

sents 17% of the theoretical estimate of irradiation-induced displacements given above. Electron irradiation of graphite gave comparable defect density for the same electron fluence as in carbon nanotubes.[24] It is probable that defect recombinations arise at room temperature. Moreover, some defects may be spinless.

Electron irradiation also strongly modifies the g factor and the linewidth of MWNT as shown in Fig. 2. With increasing fluence, both parameters decrease at high temperatures but are nearly fluence-independent at low temperatures. In fact, to compare the conduction electron paramagnetism of irradiated MWNT's with those of pristine samples over the entire temperature scale, the paramagnetic contribution of localized defects must be separated from that of the conduction carriers. Since the two spin systems are supposed to undergo a strong exchange interaction, via π orbitals, we used the celebrated exchange coupling model.[25–28] This model supposes that the bottleneck regime is achieved, i.e., one of the two spin systems dominates the overall behavior when its contribution to the susceptibility is dominant. In this way, conduction electron spins dominate at high temperatures when localized spins dominate at low temperatures. In such circumstances, the g factor is given by

$$g=\frac{g_1\chi_1+g_2\chi_2}{\chi_1+\chi_2}=\frac{g_1c/\chi_2+g_2T}{c/\chi_2+T}, \tag{2}$$

where g_1 and g_2 are the g value for localized spins and conduction electrons, respectively. The linewidth is given by

$$\Delta H=\frac{\Delta H_1\chi_1+\Delta H_2\chi_2}{\chi_1+\chi_2}=\frac{\Delta H_1c/\chi_2+\Delta H_2T}{c/\chi_2+T}, \tag{3}$$

where ΔH_1 and ΔH_2 are the linewidths for localized spins and conduction electrons, respectively. According to this model the low temperature limit of g and ΔH (respectively, g_1 and ΔH_1) are the localized defect values. It is worth mentioning here that g_1 is close to the 2.0029 value predicted by Ishii *et al.* for dangling bonds in amorphous carbon.[29] Our results are also in agreement with those of Müller,[30] who reports $g\approx 2.0023$ and a linewidth of 1.3 gauss for neutron irradiated graphite at high fluences (ΔH_1 varies here from 1.3 to 2.6 G).

Using the bottleneck approximation, it is thus possible to extract g_1 and ΔH_1 from the low temperature part of Fig. 2 and to calculate separately g_2 and ΔH_2 for the conduction electrons. Supposing that the temperature dependence of g_1 and ΔH_1 is low, as is often the case for sp^2 defects in conjugated carbons, we extract the temperature dependence of g_2 and ΔH_2 for the conduction carriers (Fig. 3). It is clear that the presence of irradiation defects influences strongly the conduction electron ESR behavior, which is rather surprising considering the low quantity of these defects per atom (about 1 per 1000).

To understand what happens in nanotubes, it is worth recalling the magnetic properties of planar graphite. In graphite both the g shift (g factor minus the free electron value) and the linewidth are strongly anisotropic. When the magnetic field is parallel to the graphene planes the g-factor has a minimum value and is slightly higher (2.0026) than the free-electron value due to the small spin-orbit coupling with carbon atoms. A strong g shift is measured when the field is perpendicular to the planes ($g_\perp=2.05$ at room temperature), and it increases at low temperature.[31] Due to motional averaging, one measures a g value of 2.018 at room temperature in polycrystalline graphite.[32] This is a special property of graphite due to the position of the Fermi level near the π bands crossing at K points of the hexagonal Brillouin zone, although no theory describes what happens in detail.[33] When a magnetic field is applied perpendicular to the plane, electrons condense on the $N=0$ Landau level, which induces this unusual anisotropic behavior.[34] When the field is parallel to the planes, no closed orbits are accessible and the effect disappears. The same argument applies also to the diamagnetic susceptibility and the magnetoresistance, which are at a minimum when the field is parallel to the planes. For a graphitic nanotube the cylindrical warping modifies this picture especially when the tube radius is small compared to the cyclotron radius (r_c) since closed orbits cannot form. In case of MWNT's of ≈ 10 nm diameter and at moderate fields, as used in X-band EPR (0.33 T), r_c is larger than the tube radius and some difference should be observed compared to macroscopic graphite. Indeed the average g value of nanotubes is different from graphite (2.0012 instead of 2.0018). We can

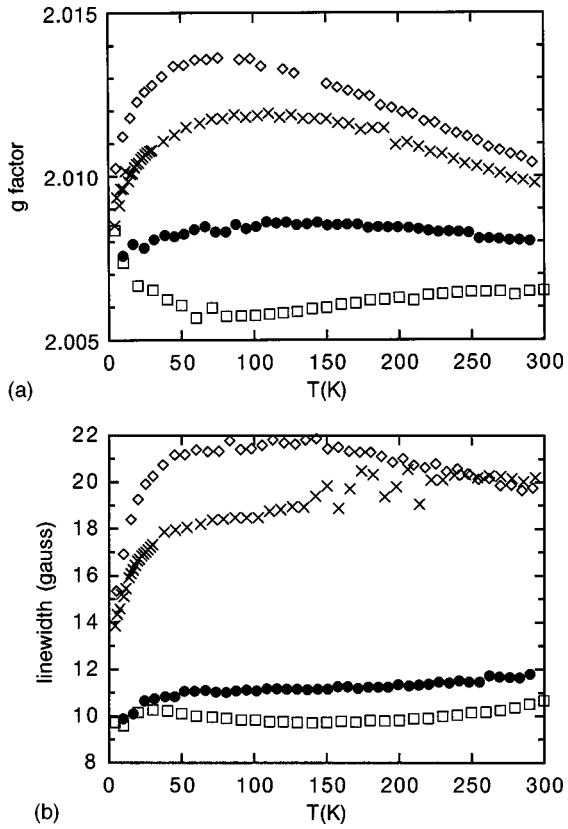

FIG. 3. After correction of the bottleneck effect, the ESR characteristics of the conduction electrons can be extracted from the data represented in Fig. 2. The decrease of the *g* factor with irradiation (a) reflects the Fermi-level displacement into the valence band (hole doping). The decrease of the linewidth (b) is due to the decrease of the *g* factor anisotropy and to an increase of motional averaging on the Fermi surface by defect-induced scattering. This explains why the linewidth is nearly temperature independent for the most irradiated samples.

expect that the *g* shift decreases with the tube diameter since it becomes more and more difficult to form Landau levels.

When the Fermi level is shifted from its original position (at the *K* points) into a band, the *g* shift perpendicular to the planes decreases toward the free-electron value. For this reason one observes an average *g* value higher than 2.010 only in well-graphitized carbons. In glassy graphite, the *g* value is isotropic and about 2.0027 due to the high density of localized states at the Fermi level. Anisotropy is also suppressed when extrinsic carriers are introduced for example by boron doping,[35] or by intercalation.[36] The modification of the *g* factor in graphitic materials is then particularly significant since it is sensitive to the band structure details at the Fermi level. The *g* factor is not sensitive to the spin dynamics, in contrast to the linewidth. In graphite electron irradiation creates vacancies, which trap electrons and shift the Fermi level in the valence band (as evidenced by Hall-effect measurements).[24] Consequently a *g* factor lowering is detected by ESR. We expect the same effect happens in MWNT.

In normal metals the ESR linewidth is determined by spin-lattice relaxation through lattice scattering and spin-orbit coupling.[37] However, Elliott's mechanism does not seem to apply directly to graphite due to its anisotropic nature.[32] In fact, the graphite linewidth is governed by a subtle motional narrowing of the *g*-value distribution over the Fermi surface, and thus depends on the spin diffusion rate. In most cases, it decreases with the *g*-value anisotropy, for example, when extrinsic carriers are introduced in the system.[38] As for the *g* factor, a complete theoretical description of the linewidth is still lacking for graphite.

We can now propose a consistent explanation to what happens in irradiated MWNT's. Due to the low vacancy concentration introduced by irradiation, the Fermi-level displacement in the valence band is small, and the resulting variation of the density of states cannot be directly evaluated by the spin susceptibility with the precision of ESR. However, the decrease of the *g* factor (Fig. 3) proves that the presence of a few extra carriers (in this case holes) modified the electronic properties by shifting the Fermi level away from the *K* points inside a band. The decrease of the linewidth with irradiation is due to the decrease of the *g* value anisotropy and to an increase of motional averaging by defect-induced scattering. This explains why the linewidth is nearly temperature independent in the most irradiated sample [Fig. 3(b)]. Note that a direct impurity relaxation mechanism cannot explain our results, since it is expected to broaden the line when there is an increase in the defect concentration.

All these results suggest that pristine nanotubes are true semimetals and nearly free of defects. If their electronic properties were determined by defects, the few added by irradiation would have no significant effects. It appears that the results of Kosaka *et al.*[10] are not compatible with the present study. In fact, we also performed high temperature annealing (at 2800 °C) of purified nanotubes and no significant difference was observed in the EPR behavior with respect to pristine tubes, contrary to the conclusions of Ref. 10.

IV. CONCLUSION

We have shown that electron irradiation creates paramagnetic point defects in multiwalled carbon nanotubes, but that their resistance to radiation is at least as good as bulk graphite. No radiolysis was observed in agreement with the semimetallic character of the nanotubes. Despite the low defect concentration introduced by irradiation, a significant modification of the electronic properties was measured by EPR. It appears that the Fermi level position is very sensitive to the presence of defects in the rolled graphene plane. Electron irradiation is hence a powerful tool to modify the electronic structure of carbon nanotubes.

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