

Electron spin resonance spectroscopy investigations of carbon nanotubes – epoxy composites

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Electron spin resonance investigations on carbon nanotubes-epoxy composites containing 1%, 2%, and 3% multiwalled nanotubes with a length of 10 μm are reported. The observed resonance spectrum is dominated by a strong line with a peak to peak width of about 14 Gauss, located at $g=2.023$, and characterized by a negligible asymmetry. It was found that the resonance line position (g factor), resonance line width, and double integral of the resonance line are essentially temperature independent in the range 150 K – 250 K. This resonance line was assigned to uncoupled electronic spins delocalized over carbon nanotubes.

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1. Introduction

Typically, graphite is a quasi semimetal characterized by a low number of charge carriers and a low density of states at the Fermi level [1,2]. Experimental data revealed that the quasi one-dimensional structure of nanotubes shows a significant departure from the physical properties of the graphene sheet. The outstanding features of nanotubes such as huge Young modulus (of the order of 1 TPa), electric conducting or semiconducting capabilities (depending on the chirality of the tube), high thermal conductivity, and excellent emission capabilities triggered a lot of theoretical and experimental studies [1-23].

Electron spin resonance (ESR) consists in the resonant absorption of energy from an incident electromagnetic radiation of frequency ν by an ensemble of electronic spins placed in an external magnetic field. The double integral of the ESR spectrum, S , is proportional to the static spin susceptibility of the sample. For symmetric Lorentzian or Gaussian lines, there is a simple relationship between S and the resonance line parameters [24];

$$S = KIH_{pp}^2 / mA \quad (1)$$

Where K is the line shape factor (constant for Lorentzian or Gaussian line), I is the resonance line intensity (or amplitude), H_{pp} is the peak-to-peak resonance line width, m is the mass of the sample and A is the spectrometer's gain. Non-interacting electronic spins are responsible for Gaussian like resonance shapes. The exchange interactions between electronic spins or the motional effects distort the resonance line towards a Lorentzian one [24]. A particular situation appears in

conducting materials (such as carbon nanotubes) due to the skin effect. If the length of the sample along the propagation direction of microwaves is larger than the skin depth, then the microwave field is damped within the sample. Hence, the resonance line shape becomes asymmetric. The distortion of the resonance line due to the skin effect is characterized by the asymmetry factor, defined as the ratio between the amplitude of the positive and of the negative lobe (I_1/I_2) [24]. For Dysonian lines this ratio is larger than 2.5 (see Fig. 1) [24].

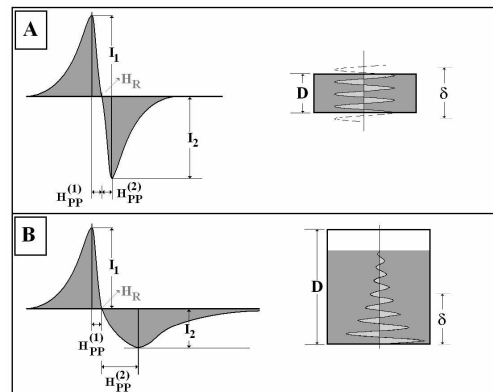


Fig. 1. A. Typical symmetrical resonance line (Lorentzian). B. Typical Dysonian line. D is the length of the conducting domain and d the skin depth.

ESR spectroscopy is a powerful technique in the investigation of carbon-based materials. Resonance spectra located close to the free electron g -value ($g_0=2.0023$) were

reported in graphite, amorphous carbon films, diamond nanoparticles, carbon onions, fullerenes, and carbon nanotubes [3-22]. Some of these materials exhibit conducting features.

Carbon nanotubes are either metallic or semimetallic [1,2,6]. There is a debate regarding the shape of the ESR lines of nanotubes. Some authors reported [9,13-15,17-20] symmetric line shapes (mostly Lorentzian) while others reported [6-8,10-12] asymmetric Dysonian line shapes. Some authors reported [4] that the resonance line shape is almost Lorentzian above 40 K and becomes asymmetric if the sample temperature is lowered below 40 K. The shape of the ESR spectra of carbon nanotubes is explained by the small diameter of nanotubes [1-2]. For a random distribution of nanotubes, the number of nanotubes lying along a given direction (actually along the external magnetic field direction) is significantly smaller than the number of nanotubes lying in a plane normal to this direction. Hence the ESR spectrum will be governed by the perpendicular component. As the diameter of single wall or multiwalled nanotubes is of the order of nanometers the resonance spectrum of isolated nanotubes will present a symmetrical Lorentzian or Gaussian shape. Carbon nanotubes ropes and agglomerated nanotubes are characterized by interconnected conducting domains of the order of 1 to 100 microns [1-2]. Such structures are characterized by resonance spectra presenting a Dysonian like shape. In composite materials, if the dispersion of nanotubes is good, the resonance line will present a symmetrical shape below the percolation threshold. Above the percolation threshold the composite becomes conducting and a Dysonian-like resonance shape is expected.

The ESR spectra of purified but not annealed nanotubes at room temperature consist of up to three overlapping lines (Fig. 2) [2-19]:

1. A wide symmetric resonance line with a width ranging from 10^2 to 10^3 Gauss (10,000 Gauss = 1 T). The line was assigned to catalyst residues [17-19]. The line is located at lower resonance fields because the uncoupled electronic spin is subjected to the combined action of the external magnetic field (H_R) and of the local (molecular) field, H_M [25];

$$h\nu = g\beta(H_R + H_M) \quad (2)$$

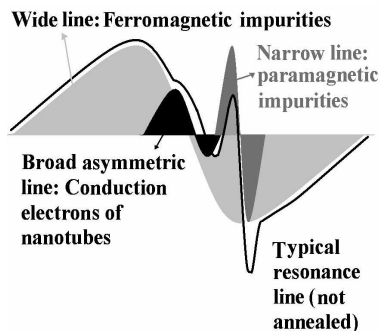


Fig. 2. The typical ESR spectrum of not annealed nanotubes. The wide line disappears by annealing.

2. A broad line, frequently reported to be asymmetric (Dysonian). This line is not located exactly at the theoretical g factor value ($g_{th} = 2.0023$) as the angular momentum is not completely quenched. The deviation of the resonance line position is controlled by the spin orbit coupling, λ , and by the energy difference, ΔE , between the corresponding electronic levels belonging to the same wave vector [24];

$$g = g_{th} + \frac{\lambda}{\Delta E} \quad (3)$$

The calculated value of the spin orbit splitting for carbon nanotubes is ranging from 0.05 eV [19] to 0.2 eV [23]. Most authors [6-18] reported that the double integral of this resonance line, S , is almost temperature independent in the temperature range 100 K to 300 K. This confirms that this line is originating from the conducting electrons residing on nanotubes (the temperature dependence of the susceptibility for metallic conductors is essentially temperature independent [12,25]).

3. A narrow line, located at higher resonance fields or lower g values than the broad line, assigned to paramagnetic impurities or defects. Frequently this line was associated with the presence of amorphous graphite. Typically, the intensity of this line decreases as the sample temperature is decreased [3,24]. The simultaneous presence of the broad and narrow resonances is considered as an indication of the heterogeneous nature of nanotubes [4].

In most cases there is a strong interaction between itinerant (conducting) and localized electrons. This corresponds to the bottleneck regime; in this case the temperature dependence of the g -factor of electrons delocalized over nanotubes is [4, 5];

$$g = \frac{g_l C + g_i \chi_i T}{C + \chi_i T} \quad (4)$$

Where the subscripts l and i identifies the localized and itinerant electrons, χ is the corresponding susceptibility and C is the Curie constant. The temperature independence of the g factor was considered [8,9] as a proof of the weak interaction between graphene sheets [17].

The temperature dependence of the resonance line width, H_{pp} , is described by [25]:

$$H_{pp}(T) = H_{pp}^0 + \alpha_H T^m \quad (5)$$

where H_{pp}^0 and α_H are constants and $m = -1/2$ (conduction electrons scattered by an interaction through the spin-orbit coupling of impurity atoms [9]), 0 (non-interacting graphene sheets [9]), or $3/2$ (conduction electrons scattered by the lattice vibrations below the Debye temperature [9]).

At fairly low temperatures (below 40 K), the double integral starts to increase as the temperature is lowered, as the Curie like pp becomes dominant (over the Pauli

one). Refined calculations show the possibility of a weak temperature dependence of the spin susceptibility [8];

$$\chi = a \left[K_B T \ln \left(1 + \exp \frac{\Delta}{K_B T} \right) - \Delta \right] + \frac{C}{T} \quad (6)$$

The square term reflects a Pauli like susceptibility where Δ is the gap into the linear density of states (equal to 0.05 eV), and the last term collects the Curie like contribution to the spin susceptibility.

This paper concentrates on the ESR study of carbon nanotubes dispersed within a polymeric matrix. The effect of nanotubes agglomeration on the ESR lines is analyzed in connection to the possibility of electronic jumps from one nanotube to the neighboring one.

2. Experimental

Electron spin resonance measurements on multiwalled nanotubes with a length of 10 μm dispersed in epoxy resins are reported. Composites containing 1%, 2%, and 3% nanotubes were investigated. The ESR spectra were recorded by using a Bruker ESP 300 spectrometer, operating in X band (~ 9 GHz) equipped with a variable temperature accessory. The external magnetic field was measured and controlled with an accuracy better than 0.1 Gauss by a NMR based magnetometer. In order to prevent resonance line saturation or distortion the microwave power was kept 1 mW and the modulation amplitude at 4 Gauss. The samples were prepared by dispersing multiwalled carbon nanotubes in epoxy resin. Details on sample preparation and characterization (mechanical and electrical) are available in [21,22]. The temperature dependence (in the range 150 K to 250 K) of the resonance line position (g factor), line width, and double integral was studied.

3. Results and discussion

The pristine epoxy resin showed no ESR line. In Fig. 3 it is shown a typical line of carbon nanotubes dispersed in epoxy resin at room temperature. A narrow, symmetrical, and intense line is observed. A detailed analysis revealed the possibility of a very weak and broad line in the wings of the main resonance. As the parameters of the broad line cannot be accurately estimated, the subsequent analysis will concentrate on the analysis of the narrow and intense line. All resonance spectra have the same shape (for all concentrations of nanotubes and temperatures). The percolation threshold for these composites is reached for a loading of the polymer matrix with about 4% wt nanotubes [21-22]. Hence, the measured samples were not loaded with a sufficient amount of nanotubes to observe Dysonian like resonance line shapes. The electron spin resonance spectra of carbon nanotubes dispersed in epoxy resin were fitted with an acceptable accuracy by a Lorentzian line shape [24]:

$$I = 16I_0 \frac{\left(\frac{H - H_R}{H_{PP}/2} \right)}{\left(3 + \left(\frac{H - H_R}{H_{PP}/2} \right)^2 \right)^2} \quad (7)$$

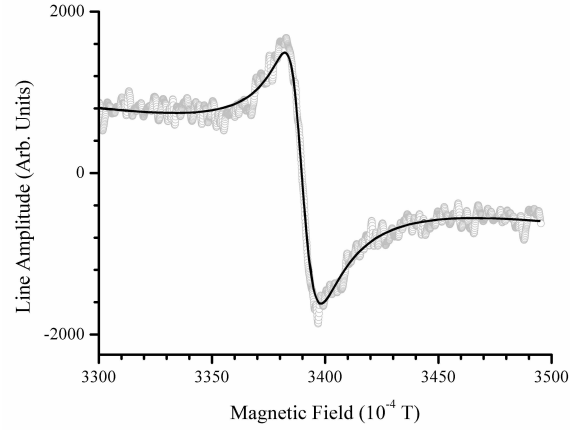


Fig. 3. The ESR spectrum of 1% (wt) multiwalled nanotubes with a length of 10 mm, dispersed in epoxy resin, at room temperature.

where I_0 is the amplitude of the resonance line and H_R is the resonance field. In Fig. 3 the black line represents the best fit obtained by using equation (7). It is observed that the agreement between the recorded spectrum and the theoretical shape is good. The same temperature dependence was observed for all samples (containing 1%, 2%, and 3% nanotubes).

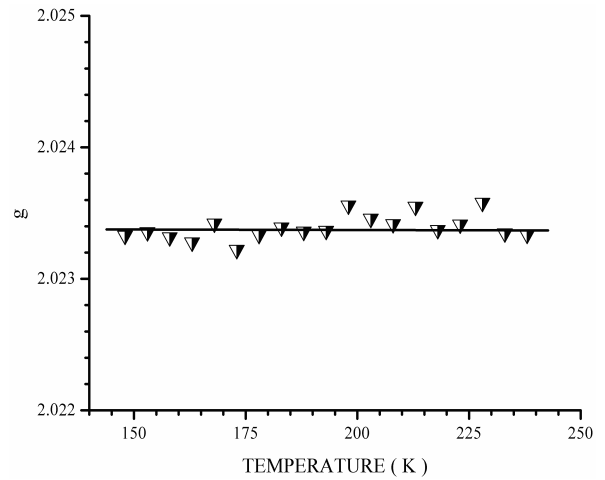


Fig. 4. The temperature dependence of the g factor in composites obtained by dispersing nanotubes within epoxy resin. The symbol size indicates the experimental errors.

The Lorentzian shape of the resonance spectra proved the good dispersion of nanotubes within the epoxy matrix.

The resonance line of carbon nanotubes dispersed in epoxy resin is located near the theoretical value of the g-factor ($g=2.0023$ [24]). The small shift in the g-factor at room temperature (of about 0.02-see Fig. 4) leads to $\Delta E \approx 10$ eV (assuming $\lambda = 0.2$ eV [23]). The expected value of ΔE for nanotubes should be of the order of eVs [1, 2, 23]. This discrepancy reflects that the recorded resonance spectrum is an average over all individual lines, corresponding to all nanotube orientation weighted by the nanotube population for the considered orientation. It is important to mention that the theoretical estimate of the spin-orbit coupling of nanotubes has large errors [23]. The temperature dependence of the g factor is shown in Fig. 4. It is observed that in the temperature range 150 K to 250 K, the g factor is essentially temperature independent. The same temperature dependence was observed for all samples (containing 1%, 2%, and 3% nanotubes).

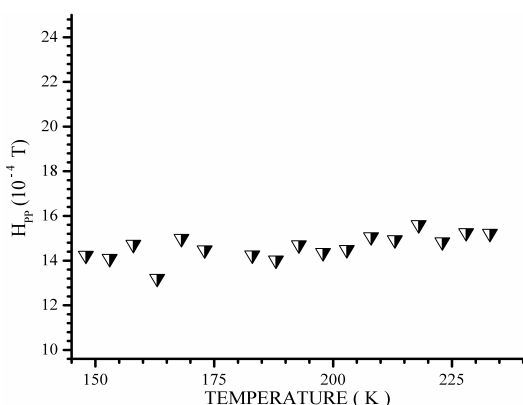


Fig. 5. The temperature dependence of the resonance line width in composites obtained by dispersing nanotubes within epoxy resin. The symbol size indicates the experimental errors.

This result rules out the effect of paramagnetic or magnetic impurities [24,25]. In the case electronic spins delocalized over paramagnetic impurities, the bottleneck would impose a temperature dependence of the g factor, as defined by eq. 4. For magnetic impurities, the decrease of the temperature is associated with an increase of the magnetization at saturation and hence of the local molecular field, H_M . Because the frequency of the exciting microwave field, ν , is constant, a decrease of the external magnetic field at which the resonance line is observed [25] (see eq. 2) is expected. In conclusion, this line originates from uncoupled electronic spins delocalized over carbon nanotubes. The temperature dependence of the resonance line width is extremely weak (Fig. 5). The same temperature dependence was observed for all samples (containing 1%, 2%, and 3% nanotubes). The experimental data are well described by the expression (5) for $m=0$.

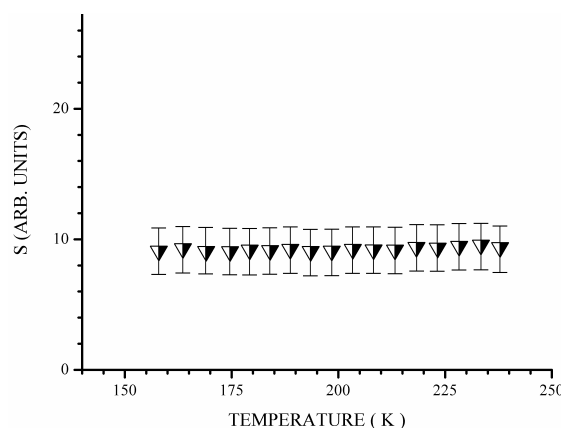


Fig. 6. The temperature dependence of the double integral of the resonance line, S , in composites obtained by dispersing nanotubes within epoxy resin.

This indicates that the concentration of paramagnetic and magnetic impurities is negligible. As it is observed in Fig. 6, the double integral of the resonance spectrum is almost temperature independent. The same temperature dependence was observed for all samples (containing 1%, 2%, and 3% nanotubes). This indicates a Pauli like spin susceptibility and confirms the assignment of the resonance line to conduction electrons [24,25].

3. Conclusions

ESR data on multiwalled nanotubes dispersed into epoxy resin were reported. The resonance line shape of multiwalled nanotubes-epoxy resin composites is well fitted by a symmetric Lorentzian line for all composites investigated (all were below the percolation threshold for conductivity). It was observed that below the percolation threshold for conductivity the g-factor, the resonance linewidth, and the double integral of the resonance line are temperature independent in the temperature range 150 K to 250 K. These features indicate that the resonance spectrum originates from the uncoupled electronic spins delocalized over carbon nanotubes.

Acknowledgements

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