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ESR study of potassium-doped aligned carbon nanotubes

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Opened, potassium-doped, and aligned carbon nanotubes were studied by electron spin resonance (ESR) measurements. Moderate K doping lowers the g factor of the pristine sample to 2.0028, and erases all the angular dependence. The Pauli susceptibility increases a factor of 3 upon doping, but the considerable Curie component shows that the tubes have suffered serious damage during the doping/depletion procedure. The temperature dependence of the ESR linewidth and g factor testifies that the K-doped tubes are still good conductors. [S0163-1829(96)05021-7]

Intercalation of alkali metals in graphite strongly changes the physical properties of the material. Semimetallic graphite becomes metallic and even superconducting upon suitable intercalation. Similarly, the pristine semiconducting C_{60} crystals exhibit a wide range of electronic properties (superconductors, paramagnetic insulator, anisotropic conductor, etc.) upon intercalation. Besides the fullerene family the carbon nanotubes belong to the newly discovered form of carbon. The temptation to use intercalation to modify their electronic properties is obvious. Successful intercalation of potassium and rubidium in a mixture of carbon nanotubes and carbon nanoparticles has already been reported and studied by x-ray diffraction and electron microscopy.[1]

Our production method of aligned nanotube thin films where the tubes are oriented perpendicular to the substrate, i.e., a Teflon sheet, has been described previously.[2] The aligned nanotube films are reasonably free of carbon nanoparticles other than nanotubes. The nanotubes investigated here are 10–20 nm in diameter with a length of the order of 1 μm. Their electronic properties have been characterized by ellipsometry, dc resistivity,[2] static magnetic susceptibility, and electron spin resonance (ESR) (Ref. 3) measurements. They reveal that the pristine nanotubes are semimetallic with a carrier density in the range 10^{18}–10^{19} cm^{-3} between 50–300 K.[3] The optical characteristics are in agreement with a metallic behavior while the dc resistivity is dominated by intertube transfer. Magnetic anisotropies of the static susceptibility and g factor of the carriers have been reported, and reveal axial symmetry.

Potassium doping of the nanotubes is performed as follows. We start from a purified powder of nanotubes and a minority of nanoparticles. An oxydation treatment at 620 °C is used to open the nanotubes.[4] It is followed by annealing at 2000 °C under vacuum. This treatment has been shown to anneal the defects caused by the opening procedure. After washing, the powder is mixed with *excess* potassium and enclosed in a copper tube. The doping is achieved under an applied pressure of 10 kbar at 100 °C.[5] After one day of heat treatment the copper tube was opened to air; the KOH was washed off with water/HCl solution in several steps. A thin film of these nanotubes has been obtained according to Ref. 2. The film deposition method aids in separating nanotubes from the remaining carbon nanoparticles. (It is important to eliminate the majority of the nanoparticles, since they can mask the intrinsic properties of the nanotubes.[6]) Here, we will compare the ESR properties of a pristine material (deposited nanotube film of the purified powder) and of a potassium-doped sample (K sample).

Effective incorporation of 1–2 % of potassium in the tubes is attested by x-ray microanalysis. This content is much lower than the reported KC_8 composition (first stage intercalation) of Ref. 1. This is the reason why we use ‘‘doping’’ instead of ‘‘intercalation,’’ although we believe that the potassium is in between the graphitic layers of the nanotubes. With respect to the low resolution of this method (beam size ~200 nm), K is distributed homogeneously in the film. A smaller amount of oxygen (~0.5%) is also found. Oxygen may be responsible for a partial dedoping and oxydation of potassium. Before the doping procedure, the films are almost oxygen free. Total oxydation of potassium is excluded: the oxygen content is significantly lower than the potassium content and in 30% of the regions investigated with the microprobe only potassium and no oxygen has been detected.

We have performed high resolution electron microscopy (HREM) on our samples. We did not find any evidence of a staging phenomena. Electron microscopy gives no evidence of potassium in the interior of the tube. Furthermore, microprobe analysis shows that the potassium is more or less uniformly distributed along the entire length of the tube and not concentrated at the ends as would be expected if the metal had entered from the opened ends. Most likely, as in Zhou's case, the potassium is intercalated. Note that potassium on the tube surfaces would have reacted with oxygen, and not given rise to an ESR signal. A strong evidence that the potassium is deep between the graphitic layers and the observed changes in the electronic properties are due to K doping comes from the fact that at high temperatures the signal changes as a function of time on the order of months, shifting back to the pristine values (i.e., both the g factor and the linewidth, however, not the Curie tail).

A disordered layer of carbon covering some nanotubes is sometimes detected by HREM. In these tubes, the external carbon shells resemble turbostratic carbon. Such a disordered layer may be due to destruction following the dedoping of potassium upon air exposure.[1] However, the majority of the nanotubes are intact with long continuous and parallel carbon shells.

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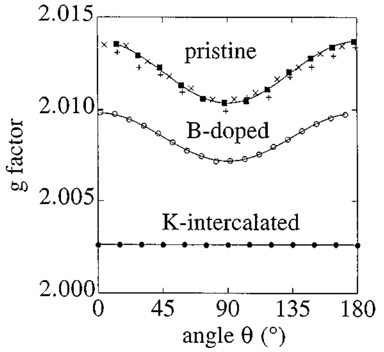

FIG. 1. Angular dependence of the g factor at room temperature. (■) pristine sample; (●) K-intercalated sample. For the sake of comparison, the dependence after the opening procedure (×), opening and annealing (+), and for a B-doped film (Ref. 11) (○) are given. $\theta=0°$ corresponds to the magnetic field parallel to the tube axis.

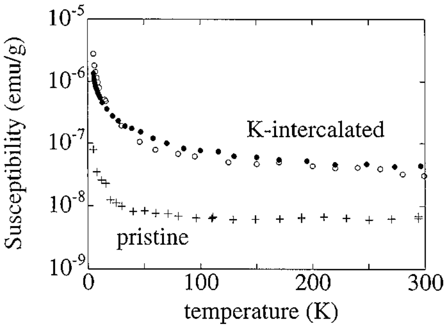

FIG. 2. Susceptibility of the pristine sample (+) and of the K sample (●). The (○) points correspond to the susceptibility of the K-intercalated powder before the film deposition procedure.

As mentioned above, the g factor of the ESR line is very sensitive to the orientation of the tube axis with respect to the magnetic field (measured by the angle θ). Figure 1 shows the room temperature dependence of the g factors with θ after each step of the interacalation procedure (i.e., for the pristine, opened, opened plus annealed, and K-intercalated samples). Before doping, the g factor varies between $g=2.014$ (tube axis parallel to the field) to $g=2.010$ (tube axis perpendicular to the field) while it is almost isotropic with $g=2.0028\pm0.0002$ after K doping. This behavior (reduction of the anisotropy, decrease of the angular average g factor) is characteristic of a successful doping.[7]

In graphite, the principal g factors and their variation with temperature are intimately related to the semimetallic behavior. The Fermi level is located in the band mixing region insuring coexistence of electrons and holes having different g factors. The measured g factor is the average of the individual values. When rotating the sample in the magnetic field, the weight on the individual values is modified because electrons and holes are located in different parts of the Brillouin zone. This leads to the anisotropic behavior.[8] The temperature dependence arises from the redistribution of electrons and holes. When the Fermi level is pushed away from the band mixing region, the previous arguments hold no longer. Intercalation induced charge transfer shifts the Fermi level away from the band mixing region and the temperature dependence is strongly depressed. Another way of suppressing the anisotropies and T dependence of the g factor is by pinning the Fermi level by defects.[7,9,10]

Qualitatively, we expect the same behavior in the nanotubes. We have already reported strong anisotropy and temperature dependence of the g factor in pristine material.[3] It was recently argued[11] that this behavior is not intrinsic but related to the defected structure of the nanotubes and that 2800 °C heat treatment anneals these defects and leads to an isotropic and temperature independent g factor. Our experiment contradicts the results of Ref. 11. For example, it can be seen in Fig. 1 that neither the opening procedure nor the subsequent annealing affect the g factor anisotropy (nor the temperature dependence as well).[12] Very low levels of boron doping ($\leqslant 1\%$) already reduces the g factor, and potassium doping leads to an almost isotropic and temperature independent g factor. Following the previous discussion, this suggests that charge transfer is at the origin of these changes. (Pinning of the Fermi level by defects can be ruled out since the spin susceptibility is still Pauli-like.)

The comparison of spin susceptibilities χ_S of the pristine and K-intercalated nanotubes is given in Fig. 2. A significant increase of the susceptibility is associated with the doping process. In order to emphasize the Pauli contribution of the susceptibility, we have plotted the product χT versus T in Fig. 3. In this representation, the slope of the straight lines gives the magnitude of the temperature independent (Pauli) component of the susceptibility. 1–2 % K doping leads to an increase of a factor 3 of the Pauli susceptibility: 7.5×10^{-8} emu/mole for pristine to 2.8×10^{-7} emu/mole for the K sample.[12,13] We attribute this increase entirely to the charge transfer from the potassium to the nanotubes. [Note that neither the g factor nor the linewidth are in agreement with conduction-electron spin resonance (CESR) of metallic potassium particles.]

More dramatic changes are observed in the Curie tails of the susceptibilities (given by the intercept of the straight line at 0 K). It is less than 10^{18} cm^3 in pristine materials; 1.7×10^{19} cm^3 is found in the K sample ($\sim$1–2 spins per 100 potassium atoms). These characteristics closely resemble those observed in high stage graphite doping compounds (GIC): the distorsion of the graphite lattice due to the incorporation of intercalants causes the formation of localized

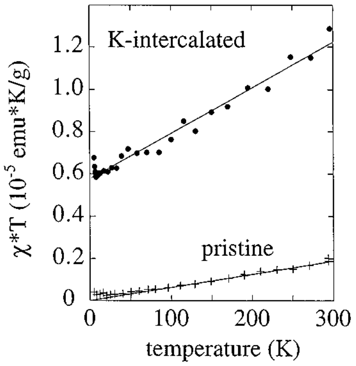

FIG. 3. Product χT of the susceptibility χ with the temperature T versus temperature for the pristine and K-intercalated films. The solid lines identify the Pauli component of the susceptibility. See Ref. 12.

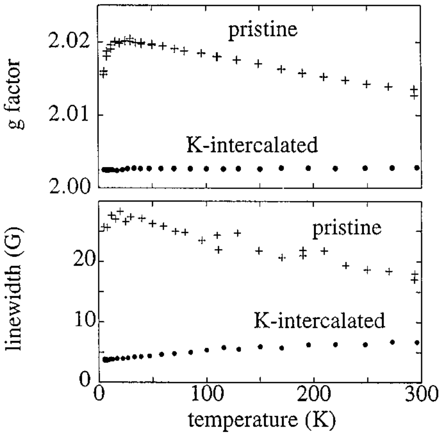

FIG. 4. Variations of the g factor and linewidth of the pristine and K-intercalated films with temperature (θ=0°).

spins. The localized spins may also come from the outer disordered shells of the tubes observed by HREM.

In absence of Coulomb enhancement, the density of states at the Fermi level $N(E_F)$ is 8.4×10^{-3} states/eV/atom for the K sample. In high stage GIC where the dilute limit model based on the Slonczewski-Weiss-McClure (SWC) (Refs. 14–16) band structure of graphite gives satisfactory results, $N(E_F)=8.4\times10^{-3}$ states/eV/atom corresponds to a Fermi energy $E_F\sim0.15$ eV and a carrier (electron) density $N_e\sim10\pm1\times10^{19}$ cm^3. It is essential to note that $E_F\sim0.15$ eV is above the region of band intermixing: in this regime the two-dimensional density of states holds and the relations between $N(E_F)$ and E_F or N_e are quite insensitive to the interplane organization. Because of this argument and despite the differences[17] in the interlayer organization between graphite and nanotubes, we believe that the previous estimates still give the correct order of magnitude of N_e in the K-doped nanotubes. Magnetotransport measurements are in progress to clarify this point. Indeed, this model cannot be used for the pristine sample.

An electron density of 10^{19} cm^3 corresponds to a charge transfer rate $f=0.1$ for 1% intercalated potassium. We have already seen that a fraction of the potassium might be oxydized: $f=0.1$ is thus a lower limit. f is close to 1 in high stage alkali GIC,[18,19] while it is $\sim$0.1 in acceptors intercalated GIC.[16]

The temperature dependence of the susceptibility is due to the localized spins. As can be deduced from Fig. 3, the fraction of the total susceptibility due to conduction electrons decreases strongly with temperature from its room temperature value $\sim$50% (this fraction reduces to 35% at 150 K, 15% at 50 K). The temperature dependence of the g factor and of the ESR linewidth shown in Fig. 4 probes this decreasing fraction and cannot be used, as such, as a signature of the conduction electrons in the whole temperature range. In graphitic materials, localized and itinerant spins are usually strongly coupled and the so-called bottleneck regime is achieved.[10] In this regime, the effective g factor and linewidth are obtained from the individual values by[20]

$$g=\frac{g_l\chi_l+g_c\chi_c}{\chi_l+\chi_c}, \tag{1}$$

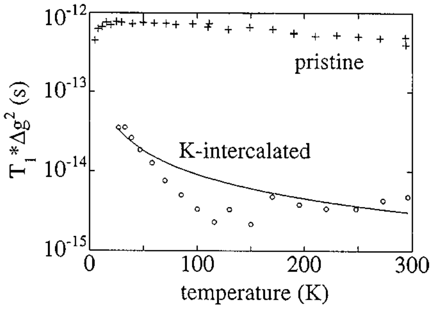

FIG. 5. Product $T_1(\Delta g)^2$ of the spin-lattice relaxation time T_1 with the square of the g shift Δg for the pristine and K-intercalated films (θ=0°). The solid line corresponds to an arbitrarily scaled $1/T$ law.

$$\Delta H\equiv\frac{1}{T_{\rm eff}}=\frac{\chi_l/T_l+\chi_c/T_c}{\chi_l+\chi_c}, \tag{2}$$

where the subscripts l and c refer to localized and conduction electron spin contributions, respectively, χ_l and χ_c being their respective susceptibilities. Using for g_l the experimental value at 30 K ($g_l=2.0024$), where the line is almost entirely due to localized spins, we find g_c by inverting formula (1): g_c increases from 2.003 to 2.004 with decreasing temperature from 300 to 30 K. These values are close to those reported for KC$_{24}$, KC$_{36}$ or RbC$_{36}$ GIC.[7] Using the same method for the linewidth with $\Delta H_l=4$ G, the CESR linewidth is found to decrease from 9 to 6 G when the temperature is decreased from 300 to 30 K.[21]

In metallic systems, the ESR linewidth is usually determined by spin relaxation due to lattice scattering according to the Elliott mechanism:[8,22] the momentum scattering by the phonons which determines the resistivity scattering time τ_R contributes to the spin relaxation with an efficiency measured by $(\Delta g)^2$ (Δg is the shift of the g factor with respect to the free electron value). The spin-lattice relaxation time T_1 ($\Delta H\equiv1/T_1$) is related to τ_R by the phenomenological relation

$$T_1=\alpha\tau_R/(\Delta g)^2. \tag{3}$$

α is a constant in the range 0.1–1.[22,23] We have suggested[3] that this mechanism is valid for the pristine sample for $T>50$ K. It is also responsible for the linewidth variation of GIC.[10,24] The product $T_1(\Delta g)^2$ is plotted versus temperature for both the pristine and K sample in Fig. 5. The decreasing product upon heating is in agreement with the thermal variation of τ_R (τ_R is expected to vary as $1/T$ at high temperature: a $1/T$ law is drawn as a solid line in Fig. 5). These observations indicate that the Elliott mechanism is responsible of the spin relaxation in K-intercalated nanotubes.

Relation (3) may be used to determine the resistivity relaxation time τ_R if one knows the value of α. Compiling available ESR and transport data at room temperature[10,18] on K-intercalated GIC, it can be shown that $\alpha\sim1$ in stage IX GIC (i.e., similar g as our pristine nanotubes) while $\alpha\sim0.1$ in stages II, III, and IV GIC (hence the same g as our K sample). Using these values at room temperature, the difference in the product $T_1(\Delta g)^2$ is reduced to one order of magnitude with $\tau_R \sim 4 \times 10^{-13}$ s for the pristine sample and $\tau_R \sim 4 \times 10^{-14}$ s for the K sample. These values are comparable to the graphite and high stage K-intercalated GIC, respectively.

In conclusion, the electronic and magnetic properties of the carbon nanotubes are very sensitive to potassium doping. The spin susceptibility increases considerably, while the ESR linewidth and g factor decrease, similarly to the effects observed for GIC. However, all these properties of the intercalated nanotubes move towards those of the pristine sample with time as oxygen diffuses into the sample and oxidizes the potassium (e.g., ΔH has changed from 6 G of the fresh sample to 9 G in two months).

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[1] O. Zhou, R. M. Fleming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Glarum, Science **263**, 1744 (1994).

[2] W. A. de Heer, W. S. Bacsa, A. Chatelain, T. Gerfin, R. Humphrey-Baker, L. Forro, and D. Ugarte, Science **268**, 845 (1995).

[3] O. Chauvet, L. Forro, W. Bacsa, D. Ugarte, B. Doudin, and W. A. de Heer, Phys. Rev. B **52**, R6963 (1995).

[4] P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Ijima, K. Tangaki, and H. Hiura, Nature **362**, 522 (1993).

[5] The initial idea for applying high pressure was to push potassium into the nanotube cores. However, HREM does not give any evidence for ''potassium wire'' inside the tubes.

[6] M. Kosaka, T. W. Ebbesen, H. Hiura, and K. Tanigaki, Chem. Phys. Lett. **225**, 161 (1994).

[7] P. Lauginie, H. Estrade, J. Conard, D. Guerard, P. Lagrange, and M. El Makrini, Physica B **99**, 514 (1980).

[8] Y. Yafet, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 1.

[9] K. A. Muller, Phys. Rev. **123**, 1550 (1961).

[10] A. S. Kotosonov, Carbon **26**, 735 (1988).

[11] M-Kosaka, T. W. Ebbesen, H. Hiura, and K. Tanigaki, Chem. Phys. Lett. **233**, 47 (1995).

[12] For the sake of comparison, the g factor of a boron doped sample has been added (white dots). For this sample which is not discussed here, the susceptibility at room temperature suggests a very low charge transfer.

[13] In pristine material, the deviation of χT versus T from a linear behavior at low temperature has been tentatively ascribed to localization in Ref. 3. Note that this effect is not observed above 10 K in the K-intercalated sample.

[14] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

[15] J. W. McClure, Phys. Rev. **108**, 612 (1957).

[16] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[17] D. Reznik, C. H. Olk, D. A. Neumann, and J. R. D. Copley, Phys. Rev. B **52**, 116 (1995) suggest that these differences might be not so important.

[18] D. G. Onn, G. M. T. Foley, and J. E. Fischer, Phys. Rev. B **19**, 6474 (1979); H. Suematsu, K. Higuchi, and S. Tanuma, J. Phys. Soc. Jpn. **48**, 1541 (1980); H. Suematsu, S. Tanuma, and K. Higuchi, Physica B **99**, 420 (1980).

[19] J. Conard, H. Estrade, P. Lauginie, H. Fuzellier, G. Furdin, and R. Vasse, Physica B **99**, 521 (1980).

[20] S. Schultz, M. R. Shanabarger, and P. M. Platzman, Phys. Rev. Lett. **19**, 749 (1967); S. E. Barnes, Adv. Phys. **30**, 801 (1981).

[21] Both the g factor and the linewidth of the localized spins are assumed to be temperature independent. This reasonable assumption for the g factor is questionable for the linewidth since motional narrowing can occur. However, one does not expect large variation of ΔH_l above 30 K where our reference point is taken.

[22] R. J. Elliott, Phys. Rev. **96**, 266 (1954).

[23] F. Beuneu and P. Monod, Phys. Rev. B **18**, 2422 (1978).

[24] T. Enoki, H. Inokuchi, and M. Sano, Phys. Rev. B **37**, 9163 (1988).