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ESR and conductivity of carbon nanotubes

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RÉSUMÉ

Les nanotubes de carbone obtenus par ablation laser s'auto-organisent en fibres cristallines de quelques dizaines de microns de long. Ces fibres contiennent des centaines de nanotubes formant un réseau triangulaire bidimensionnel. Dans cette communication, nous présentons nos résultats de RPE et de mesures de conductivité. Ils confirment les théories prédisant un comportement métallique des nanotubes non-chiraux.

mots-clés : nanotubes non-chiraux, comportement métallique, raie dysonienne, effet de peau

ABSTRACT

Carbon nanotubes obtained by laser ablation self-organise in crystalline ropes which are some tens micrometers long. These ropes contain hundreds of closed packed nanotubes on a two-dimensional triangular lattice. In this paper, we present our ESR and conductivity measurements on the bulk unoriented material. The results confirm the theoretical previsions about a metallic behaviour of achiral nanotubes.

key words : achiral nanotubes, metallic behaviour, dysonian lineshape, skin depth.

I. DESCRIPTION OF OUR MATERIAL

Our material is single wall carbon nanotubes (SWNT). The synthesis of this material which does not contain concentric shells is described in [1]. The material is produced by a double laser ablation of cobalt and nickel doped graphite targets [2].

The sample looks like black soot, very light and porous aggregates of a few millimetres thickness. Nanotubes are packed in a two dimensional triangular lattice and self-organise into ropes of hundreds angstroms in diameter. The diameter of the tubes is 13.8 Å, several nanometres for the fibres. This type of SWNT is predicted to be metallic [3,4,5], confirmed here both by ESR and resistivity measurements on bulk material.

II. RESISTIVITY MEASUREMENTS

Resistivity vs temperature measurements were carried out on an Oxford CF935P cryostat. Results are shown on figure 1 (ρ_{RT} is the room temperature resistivity). The behaviour of the resistivity ρ is typical of what we have observed in all our samples containing at least 70% of SWNT. ρ always varies around 10 or 50 mΩ.cm and confirms the metallic previsions. As we are only working on bulky materials, this is an averaged resistivity which is observed. From high temperatures down to T*, resistivity has a linear comportment. T* is a crossover temperature which is included between 150K and 250K for all samples. Below T*, the slope of ρ becomes negative; above T*, $d\rho/dT$ is equal to 2.10^{-4} /K.

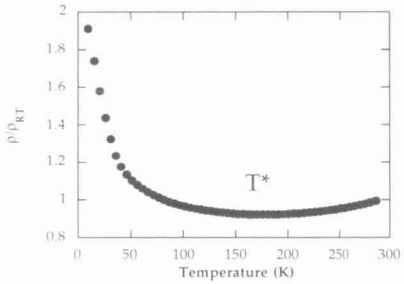

figure 1: ρ vs. T for pristine material

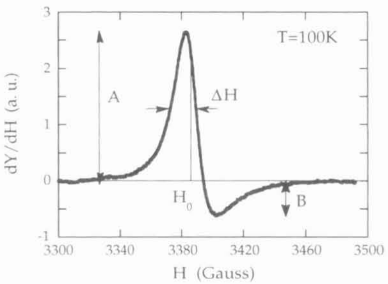

figure 2 : Dyson's ESR spectrum

III. ESR MEASUREMENTS

The ESR lineshape is dysonian (figure 2) i.e. it shows an asymmetry in the derivative absorption line, a g shift and a constant peak-to-peak width. Because our samples are aggregates of ropes containing nanotubes, they can be considered as isotropic 3D-conductors. There hence, Dyson's theory about ESR absorption in metals and the following works by Feher and Kip can be used [6,7]. We can also estimate the skin depth of our material in order to place oneself in Feher&Kip's appropriate numerical treatment. The classical skin depth is given by:

$$\delta = \frac{c}{\sqrt{4\pi^2 \sigma v}} \qquad (1)$$

c is the light celerity, σ the conductivity of the metal and υ is the frequency of the excitation field equal to 10 GHz; σ(10GHz) was estimated [8] and it has been found $\delta \approx 50\mu m$. For samples whose thickness averages 1mm, Feher and Kip's abacus can be used. Having A/B and ΔH as a function of the temperature (figure 3), we can obtain T_D, the time it takes for an electron to diffuse through the skin depth and T_1 the spin relaxation time (figure 4). The observed and pronounced peak around 150K has not been explained yet.

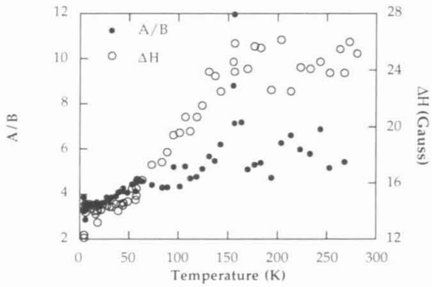

figure 3 : ΔH and A/B vs. temperature

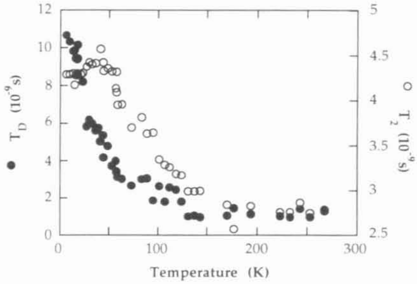

figure 4 : TD and T1vs. temperature

For sufficiently thin crushed samples (dimensions<d), a lorentzian line is observed. In this case, the ESR intensity shows a constant Pauli susceptibility down to 90K (figure 5). The susceptibility cannot be calculated explicitly because of the presence of other types of nanotubes such as chiral and hence insulating ones.

IV. DISCUSSION AND CONCLUSION

Starting by a classical diffusion equation, the diffusion time T_D is found to be

$$T_D = \frac{3\delta^2}{2v\Lambda} \qquad (2)$$

where v is the electron velocity and Λ the mean free path. We have also, τ being the mean collision time, e the electronic charge:

$$\tau = \frac{\Lambda}{v} \qquad \text{and} \qquad \rho = \frac{m^*}{ne^2\tau} \qquad (3)\ \text{and}\ (4)$$

From equations (1),(2),(3),(4), we obtain:

$$T_D = \frac{3ne^2c^2\rho^2}{8\pi^2 \upsilon m^* v^2} \propto \rho^2 \qquad (5)$$

Figure 6 shows the comparison between T_D and ρ^2.

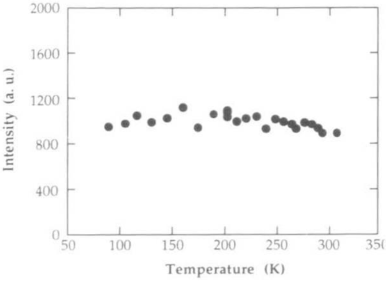

figure 5: ESR intensity vs. temperature

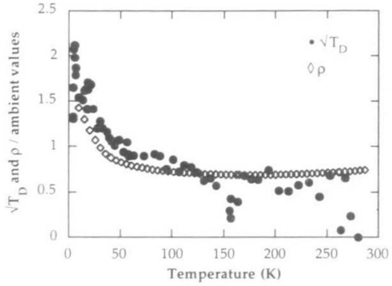

figure 6: comparison between $\sqrt{TD}$ and ρ vs.T

The presence of a dysonian lineshape even at low temperatures concludes to a metallic intrinsic character of our achiral nanotubes. Above T*, proportionality between ρ and T was tried to be explained by a Bloch-Gruneisen law [5] implying a electron-twiston interaction where twistons are tortionnal phonons which propagate along the tubes. The presence of a dysonian lineshape rejects other theories as a one dimensional metal-insulator transition below T* and indicates that T* only separates two different metallic regimes.

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