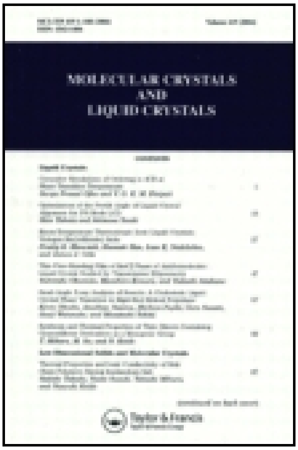


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Doping of Carbon Nanotubes by Heavy Alkali Metals

L. Duclaux [a] , K. Metenier [a] , J. P. Salvetat [a] , P. Lauginie [a] , S. Bonnamy [a] & F. Beguin [a]

[a] CRMD, CNRS-University, 1B rue de la Férollerie, 45071, Orléans, France

To cite this article: L. Duclaux, K. Metenier, J. P. Salvetat, P. Lauginie, S. Bonnamy & F. Beguin (2000): Doping of Carbon Nanotubes by Heavy Alkali Metals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 769-774

To link to this article: http://dx.doi.org/10.1080/10587250008025561

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 769-774
Reprints available directly from the publisher
Photocopying permitted by license only

Doping of Carbon Nanotubes by Heavy Alkali Metals

L. DUCLAUX, K METENIER, J. P. SALVETAT, P. LAUGINIE,
S. BONNAMY and F. BEGUIN

CRMD, CNRS-University, 1B rue de la Férollerie, 45071 Orléans, France

(Received May 30, 1999; In final form July 8, 1999)

Multiwall (MWNT) and single wall (SWNT) carbon nanotubes were intercalated with heavy alkali metals. From the point of view of their composition, alkali 2D superlattice, EPR and ^{13}C NMR characteristics, the intercalation compounds of MWNT (1st and 2nd stage) are close to their parent GIC. An expansion of the 2D triangular lattice of SWNT bundles was clearly detected, showing that the alkali atoms are intercalated in the free space between the tubes.

Keywords: Carbon nanotubes; intercalation; alkali metals; single wall nanotubes; multiwall nanotubes

INTRODUCTION

It has been shown that single wall nanotubes (SWNT) and multiwall nanotubes (MWNT) can be doped by alkali metals [1-5]. Intercalation is suspected to take place in the open channels of SWNT bundles [1-3], however due to structural disorder there is not any signature of the triangular 2D lattice [2]. Alkali atoms can also be inserted in the van der Waals galleries between the layers of electric arc MWNT, but a large amount of structural defects is introduced by this process [4]. Catalytic MWNT, that are less graphitized [6] than arc-grown MWNT may be suitable for reversible intercalation reactions. In this paper, we report on vapor phase reaction of heavy alkali metals with SWNT ropes and catalytic MWNT. Modifications of the electronic properties were investigated by ^{13}C NMR and EPR.

EXPERIMENTAL

MWNT were produced by catalytic decomposition of acetylene at 900°C on supported cobalt [6]. They showed a "fishbone" arrangement of the aromatic layers along the tube axis. Support and catalyst were eliminated by 72 % HF and 3 mol.l^{-1} HNO_3. Residual cobalt was eliminated by heat-treatment under argon flow above 2000°C, and MWNT were annealed: their aromatic layers became straight and continuous with defects located at "grain boundaries".

SWNT bundles from raw collarets were produced by electric arc discharge process [7]. In order to eliminate the metallic particles, they were heat treated at 1600°C during 48 hours under N_2 flow. After this treatment, the raw collarets contained SWNT bundles but also graphite particles and turbostratic cokes which initially encapsulated metallic particles. X ray diffraction showed that the 2D lattice of the SWNT is preserved after heat treatment without expansion.

The nanotubes host materials (SWNT or MWNT) were out-gassed at 400°C until pressure reached 10^{-4} mbar and reacted with excess of alkali metal vapor using the classical two bulb method with a small temperature gradient. The weight uptake after reaction was measured inside the glove box. In order to obtain 2nd stage MC_{24}-MWNT, stoichiometric amounts of MC_8–MWNT saturated compound and pristine MWNT were mixed and annealed under vacuum at 250°C for two weeks.

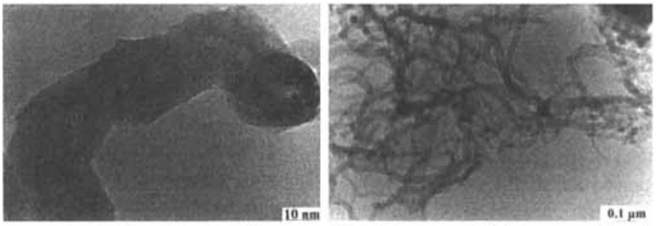
X ray diffraction was realized on the compounds in sealed capillaries (diameter 1 mm) using a curve position sensitive detector (INEL CPS 120). EPR spectra were recorded on samples in sealed quartz tube using a Bruker spectrometer at a frequency of 9.47 GHz. ^{13}C NMR was performed using a Bruker DSX 360 spectrometer (H_o=8.5 T).

RESULTS-DISCUSSION

Intercalation compounds of MWNT

In the conditions of saturation by alkali metal vapor, brown MC_8–MWNT (M=K and Cs) saturated first stage intercalation compounds were obtained. Their identity periods of 0.537 nm and 0.593 nm for M=K and Cs, respectively, are similar to those of parent GIC (0.535 nm and 0.593 nm). Asymmetric *hk* bands characterize a 2×2 R 0° 2D superlattice typical of a KC_8 derivative.

A TEM observation on a CsC_8–MWNT sample de-intercalated by air exposure and washing in water, showed that the tubular arrangement is globally preserved (Figure 1). However, crumple-sheet forms of carbon were observed in TEM images, interpreted by the destruction of some tubes induced by intercalation/de-intercalation processes.



(a) **(b)**

Figure 1 : TEM images of de-intercalated CsC_8-MWNT: (a) single nanotube, (b) global view.

The temperature dependence of EPR spectra of pristine and KC_8-MWNT were compared (Figure 2). MWNT revealed a small Curie component attributed to defects, associated to a Pauli term related to a greater amount of free carriers. The EPR line of the 1st stage KC_8-MWNT is dysonian, typical of a good conductor. The effective number of spins is multiplied by 40, illustrating an important charge transfer just as in alkali GIC. Only a Pauli term was detected. The g factor, previously T-dependent in pristine materials became T-independent due to the charge transfer shift of the Fermi level away from the quasi degeneracy region of the π bands.

Assuming a charge transfer comparable to KC_8 GIC, i.e. 0.9 electron per K atom, the ratio of this value to the effective number of spins (2.10^{-3} per C atom) should be of the same order as the ratio of Fermi temperature with room temperature. A Fermi temperature of 15000 K was roughly estimated for KC_8-MWNT in agreement with the value obtained for KC_8-GIC.

In the 1st stage CsC_8-MWNT, the EPR signal was undetectable probably because of a too large width, due to strong spin orbite interaction on this heavy alkali metal and to non-complete charge transfer [8].

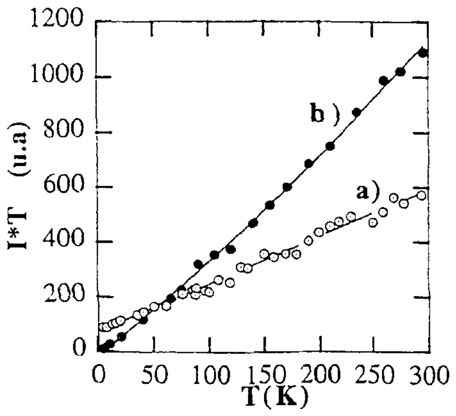


Figure 2 : Temperature dependence of the intensity (I) of the EPR signal expressed by I×T *vs* T: a) undoped MWNT; b) KC_8-MWNT. For the undoped sample, the ordinate scale has been strongly amplified.

^{13}C NMR on pristine MWNT showed a main peak (or a doublet) centered at the δ_{ab} position of graphene and a broad distribution tail over 500 ppm, as previously reported [9]. δ_{ab} and δ_c shifts of the 1st stage MC_8-MWNT (KC_8 or CsC_8) signal are practically of the same order as in GIC with an inversion of anisotropy attributed to the dipolar interaction of the ^{13}C nucleus with the π electrons. The observation of a peak instead of a plateau at δ_c could be due to powder orientation effects.

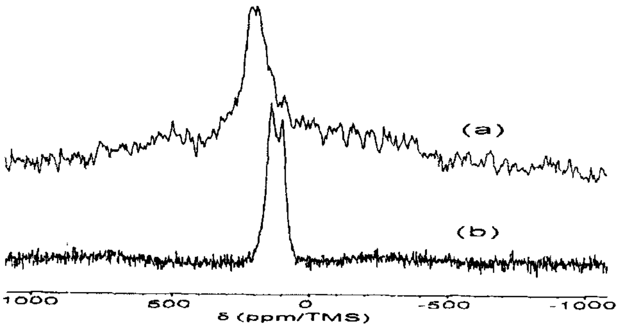


Figure 3 : ^{13}C NMR of : (a) MWNT; (b) 1st stage KC_8-MWNT

The X ray diffraction pattern of KC_{24}-MWNT is typical of a 2nd stage derivative with an identity period of 0.876 nm (Figure 4). However, the 002 and 003 lines are quite broad, showing that stage is not so well-defined, and domains are rather interstratified. Assymetric *hk.* bands demonstrate that the turbostratic arrangement of nanotubes layers still exists after intercalation. Since defined *hk.* lines belonging to the alkali superstructure were not found, the potassium atoms are probably arranged as a 2D liquid.

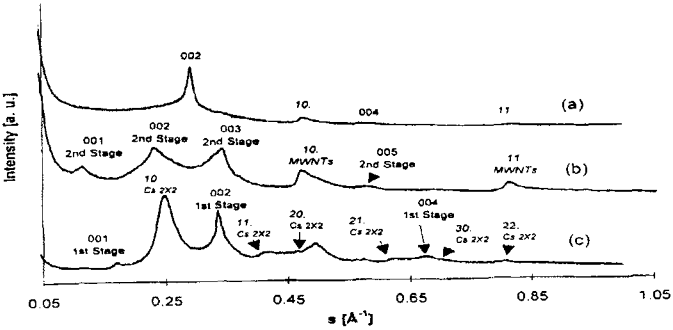


Figure 4 : X ray diffractograms: (a) MWNT; (b) 2nd stage KC_{24}-MWNT; (c) 1st stage CsC_8-MWNT (the lines of 2D 2×2 alkali lattice are indexed)

The dysonian EPR signal of 2nd stage KC_{24}-MWNT, is narrowed compared to that of KC_8-MWNT. The charge transfer is expected to be almost complete in the 2nd stage derivative, and the broadening due to spin-orbit interaction of the conduction electrons on alkali atoms is limited.

Intercalation compounds of SWNT

SWNT bundles from a collaret were exposed to K or Rb vapor, and weight uptake indicated $KC_{7\pm1}$ composition. Since graphite and coke saturation composition is KC_8, and the proportion of bundles in the collaret beeing of the order of 50 %, the composition of intercalated SWNT would be approximately $KC_{6\pm1}$.

Taking into account a van der Waals distance of 0.32 nm between the tubes, and the measured value of 2D lattice parameter of pristine nanotubes, 1.67 nm, the diameter of one tube is estimated to be 1.35 nm. Pristine tubes could be either (17,0) zigzag, (10,10) armchair or chiral intermediates. An expansion of the triangular lattice, proved by the shift of the *100* line, indicates that SWNT bundles were intercalated by the alkali atoms (Figure 5). The a parameter increased from 1.67 nm for pristine SWNT to 1.85 nm and 1.87 nm for tubes intercalated by potassium and rubidium, respectively. The stoichiometry and the lattice expansion are consistent with an occupation of each 3-fold symmetric interstitial "cavity" by more than one alkali atom. Our results are in agreement with electron diffraction studies showing that alkali intercalation occurs between SWNT [3]. However Zhou et al. did not detect any TEM contrast nor clear electron diffraction due to structural disorder induced by intercalation [2].

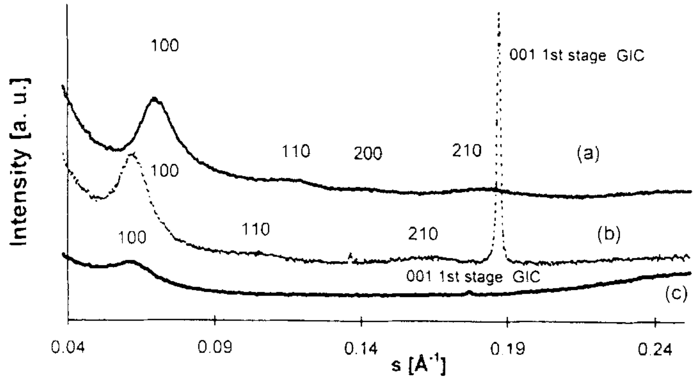


Figure 5 : XRD of (a) collaret containing SWNT; (b) collaret doped by K; (c) collaret doped by Rb

Three EPR lines were observed on pristine and $KC_{7\pm1}$ collarets: very broad (800 Gauss peak to peak), very narrow (1 Gauss) and dysonian shape attributed to SWNT (35 G).

CONCLUSION

Potassium and cesium have been intercalated in catalytic MWNT, yielding 1st stage compounds similar to their GIC equivalents from many respects : stoichiometry, interlayer spacing, 2D structure, metallic character. A narrowing of the EPR line of the 2nd stage derivatives confirmed a more complete charge transfer.

Rubidium or potassium intercalated in SWNT bundles are probably distributed all around the tubes. This kind of derivatives may be considered as intermediate between "graphite-like" (including MWNT) and fullerene materials.

Acknowledgements
The authors thank C. Journet and P. Bernier (GDPC, Montpellier, France) for supplying SWNT collarets. This work was partly supported by the E.C. TMR program NAMITECH, ERBFMRX-CT96-0067.

References

[1] R.S. Lee, H.J. Kim, J.E. Fischer, A. Thess and R.E. Smalley, *Nature* **388,** 255 (1997).

[2] S. Suzuki, C. Bower and O. Zhou, *Chem. Phys. Letters* **285,** 230 (1998).

[3] T. Pichler, M. Sing, M Knupfer, M. S. Golden and J. Fink, *Sol. State Com.* **109,** 721 (1999).

[4] 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).

[5] K. Metenier, L. Duclaux, H. Gaucher, J.P Salvetat, P. Lauginie, S. Bonnamy and F. Beguin, in *Progress in Molecular Nanostructures-Proceedings XII IWEPNM,* (ed. H. Kuzmany et al, 1998.), p. 51.

[6] A. Hamwi, H. Alvergnat, S. Bonnamy and F. Béguin, *Carbon* **35,** 723 (1997).

[7] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee and J.E. Fischer, *Nature* **388,** 756 (1997).

[8] P. Lauginie, A. Messaoudi and J. Conard, *Synth. Metals* **56,** 3002 (1993).

[9] Y. Maniwa, M. Sato, K. Kume, M.E Kozlov and M. Tokumoto, *Carbon* **34,** 1287 (1997).