



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Microstructural analysis of carbon nanotube fibers	Experiment number: ME-656
Beamline: ID13	Date of experiment: from: 02/02/04 to: 07/02/04	Date of report: February 20, 2004
Shifts: 12	Local contact(s): Manfred Burghammer, Christian Riekel	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Pichot Vincent*, Launois Pascale*

Laboratoire de Physique des Solides (UMR CNRS 8502), bât. 510, Université Paris Sud, 91405 Orsay Cedex, France

Zakri Cécile*, Poulin Philippe*

Centre de Recherche Paul Pascal, CNRS, Université Bordeaux I, Avenue Schweitzer, 33600 Pessac, France

Report:

Carbon nanotubes generate intense research activity, because of their exceptional electronic and mechanical properties. A spinning process was developed 3 years ago to assemble single wall carbon nanotubes (SWNTs) into macroscopic fibers, with diameters of 20 to 50 μm and lengths up to several tens of cm [1]. Industrial applications may be expected [2]. Previous X-ray scattering experiments showed that the nanotubes are preferentially aligned along the fiber axis [3]. Moreover, mechanical properties of the fibers are strongly dependent of nanotube alignment [4]. But the distribution of nanotube orientations around the fiber axis deduced from X-ray and Raman scattering [5] differs by a factor of two. Only the surface of the fiber was probed by Raman scattering while the whole fiber was probed by X-ray scattering. It was thus crucial to study how the SWNTs alignment varies from the core of the fiber to its skin by using a microscopic X-ray beam. This was the subject of the proposal of our experiment ME-656 (the interest of in situ measurements on stretched fibers was also noticed in the proposal; however, it was not possible to carry out such measurements during the allocated beam time due to important counting durations necessary to study the skin of the fibers. This point will be the subject of a new proposal).

Two kinds of fibers have been studied during the experiment:

- Fibers made with SWNTs produced by the electric arc technique using a mixture of Y and Ni as catalysts. This technique produces SWNTs assembled into bundles of several tens of nanotubes along with carbon impurities and catalysts. **5 fibers studied.**

- Fibers made with SWNTs synthesized by the HiPco (high pressure CO disproportionation) process: the nanotubes have a wider distribution in diameter. The dominant impurity in HiPco nanotubes is the metal catalyst (Fe). **6 fibers studied.**

Fibers were placed vertically, perpendicular to a microscopic X-ray beam of $1\mu\text{m} \times 2\mu\text{m}$ (width*height). By translating the fibers horizontally, we probed them from their skin to their core with a $1\mu\text{m}$ step. The

beamline settings allowed one to measure the weak diffuse scattering of carbon nanotubes (at $Q \sim 0.4 \text{ \AA}^{-1}$ for electric arc SWNTs, for instance), as well as the catalyst elements (Ni or Fe) around $Q \sim 3 \text{ \AA}^{-1}$. The signal coming from the skin of a fiber was much weaker than the one coming from the core of a fiber because of the difference of thickness between the core and the skin, then we had to scan the skin of the fiber several times to get enough statistic.

The experiment was performed only three weeks ago and we have only analysed yet the nanotube orientation at the skin and in the core of one of the fibers studied. These first results are presented below to show that the aim of the experiment has been reached: we have obtained data of sufficient quality to analyze the nanotube alignment and the catalyst concentration along the fiber diameter.

The analysis of the signal coming from the skin of a fiber made of nanotubes produced by electric arc is shown in figure 1.

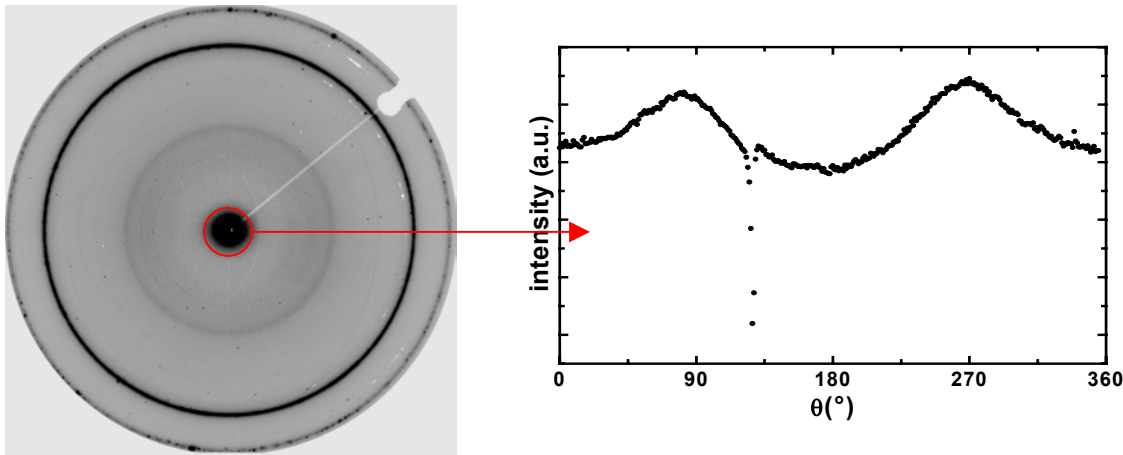


Figure 1: left: diffraction plane obtained on the skin of the fiber with MARCCD detector (image summation and background subtraction were performed to obtain a good statistic), right: azimuthal scan of the nanotube peak at 0.4 \AA^{-1} (red circle in the picture).

This result shows that the nanotubes are preferentially aligned along the fiber axis. The Half Width at Half Maximum (HWHM) of the two peaks (fig. 1 right) gives the distribution of nanotubes orientations. The curve is well fitted with gaussian distributions with a $\text{HWHM} = 30^{\circ}$ ($\pm 3^{\circ}$). For this fiber, the distribution of nanotube orientations measured in the core is similar: nanotubes have the same orientations in the core and in the skin of this fiber. If this result is confirmed for the other fibers studied, the hypothesis of a uniaxial Raman polarizability tensor for nanotubes [5] will have to be re-investigated.

The knowledge of the homogeneity (or non-homogeneity) of the fibers along their diameter is also important for the analysis of the fiber formation process or of their mechanical, electrical and electromechanical properties.

In conclusion, the experiments were successful and allowed new knowledge of the structural features of carbon nanotube fibers. Another very important scientific conclusion from these experiments is the raise of new questions about the fundamental optical properties of carbon nanotubes themselves. It seems that commonly accepted optical properties to model Raman spectroscopy results are questionable. In situ coupled Raman and X-ray analysis could be particularly useful to clarify the situation.

[1] B. Vigolo, A. Pénicaud, C. Coulon, C. Sauder, R. Paillet, C. Journet, P. Bernier and P. Poulin, *Science* 290, 1331 (2000)

[2] P. Poulin, B. Vigolo, P. Launois, P. Bernier: International patent number WO 03/ 014431 A1, about improvements of carbon nanotube fibers

[3] P. Launois, A. Marucci, B. Vigolo, P. Bernier, A. Derré and P. Poulin, *Journal of Nanoscience and Nanotechnology* 1, 125 (2001)

[4] B. Vigolo, P. Poulin, M. Lucas, P. Launois and P. Bernier, *Applied Physics Letters* 81, 1210-1212 (2002)

[5] E. Anglaret, A. Righi, J.L. Sauvajol, P. Bernier, B. Vigolo and P. Poulin, *Phys. Rev. B* 65, 165426 (2002)