



	Experiment title: <b>Determination of the PDF of anisotropic pyrocarbons, Si-B-C amorphous phases and Si-O-C fibers.</b>	<b>Experiment number:</b> HD-487
<b>Beamline:</b> ID15B	<b>Date of experiment:</b> from: 14 February to: 15 February 2011	<b>Date of report:</b> 01 July 2011
<b>Shifts:</b> 3	<b>Local contact(s):</b> Veijo Honkimaki	<i>Received at ESRF:</i>
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## Report:

The aim of the experiment on ID15B was to determine the Pair Distribution Function (PDF) of carbons obtained by pyrolysis of a gaseous precursor, the so called Pyrocarbons (pyCs). The allocated beam time was sufficient to also perform a preliminary study of the local structure of some amorphous Si-B-C phases and few Si-O-C fibers. The PDFs obtained for these materials are reported in what follows and are compared to those obtained by Neutron diffraction (D4 diffractometer at ILL) on the same materials.

### Experimental procedure

Samples were placed in a thin walled 2.5mm diameter silica capillary and the scattered intensity was measured using a large area detector (Pixium4700 Flat panel detector) which allows reaching up to  $30\text{\AA}^{-1}$  using Xrays of  $\sim 87\text{keV}$ . The diffraction measurements of the empty capillaries were also carried out.

The PDFs were then obtained after data reduction and Fourier transform.

Up to nine samples were placed on a sample holder. Before each acquisition, an absorption scan was performed (by scanning through the nine samples sequentially using the x-axis motor of the diffractometer) in order to locate precisely the middle of the capillary. The opening of the beam aperture was set to  $400\mu\text{m}$  in order to have a sufficient amount of powder in the beam and to avoid interactions between the beam and the edges of the capillaries.

Although the available capillaries were not homogenous in diameter and thickness (along the length) we selected an as homogeneous as possible set to perform the experiments. This procedure allowed to improve the reproducibility of the experiments.

Finally, the wavelength was determined to be of  $0.1424\text{\AA}$  using an iron standard.

## 1. PDF determination of anisotropic Pyrocarbons

The arrangement of carbon atoms in a Pyrocarbon is principally based on the stacking of graphene layers, as in graphite, but faulted to some extent: e.g. with a turbostratic arrangement, non-sp<sup>2</sup> carbon atoms, 5- or 7-membered rings, local curvature, etc. The aim of this work was to determine the local atomic structure of these pyCs.

Two different pyC types were characterized on ID15B: Smooth Laminar (SL) and Rough Laminar (RL). The 2D pattern, in figure 1a, shows that graphitic domains tend to orientate preferentially along the capillary axis during filling. However this artifact is cancelled when the pattern is integrated on 360° to obtain the raw pattern used to get the PDF.

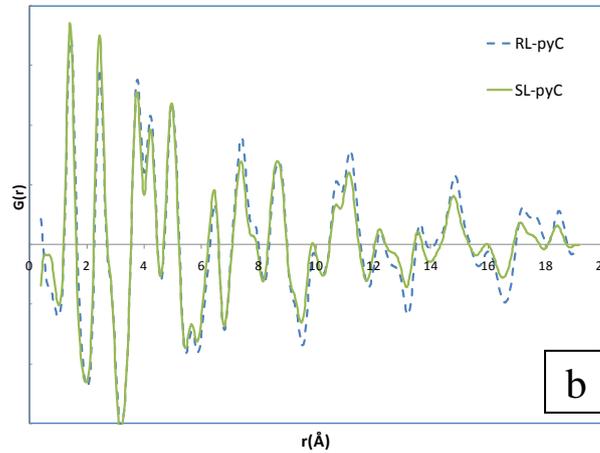
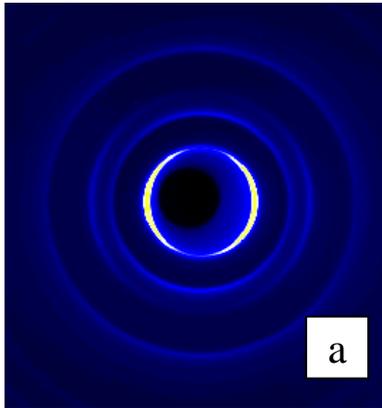


Figure1: 2D diffraction pattern for RL pyC (a) and PDFs for RL and SL pyCs obtained on ID15B (b).

As expected, both PDFs show short range structures very similar to the one of graphite: The first three peaks are positioned at real space distances of 1.40, 2.45 and 2.82Å, in agreement with the in-plane C-C bond distances in the aromatic-type ring of graphite.

The difference between the two materials lies essentially in the steeper decrease of  $G(r)$  with interatomic distance  $r$ , for SL pyC, than for RL pyC. This is related to the shorter range of structural coherence in both stacking and lateral extension of the graphene sheets in the Smooth Laminar sample.

The results are consistent with PDFs obtained by neutron diffraction. However, due to the sudden decrease of the atomic form factor with  $Q$  in the X-rays experiment, the PDFs obtained by X-ray exhibit broader peaks at low  $r$  and expand on a shorter  $r$ -range. Moreover, our samples were found to have a lower amount of hydrogen (around 1 at. %) than expected, the main differences observed between X-ray and Neutron PDFs are due to experimental peculiarities.

## 2. PDF determination of Si-B-C amorphous phases and Si-O-C fibers

The highly disordered structure of Si-O-C fibres and Si-B-C matrices leads to particular thermal properties (reactivity, crystallization, viscosity). Their behavior depends on the amounts of nanocrystalline (SiC, B<sub>4</sub>C, sp<sup>2</sup>-C) and amorphous phases (SiO<sub>x</sub>C<sub>y</sub>, B<sub>x</sub>C), in a way we have not elucidated yet. This project aims at the characterization of the local order in the various phases and particularly at their boundaries

### i. PDF determination of Si-B-C amorphous phases.

Several samples have been characterized on ID15B: two raw materials whose atomic compositions were respectively Si<sub>0.8</sub>B<sub>0.6</sub>C and Si<sub>0.4</sub>B<sub>0.7</sub>C. The latter was heat-treated at 1300°C in order to observe the crystallization of SiC. Figure 2 shows the PDFs of the Si<sub>0.4</sub>B<sub>0.7</sub>C sample obtained on ID15B and D4 (ILL-Neutrons). The main differences are located in the low  $r$  range of the diagram: two peaks located at 1.62Å and 2.81Å can be discerned only in the PDF obtained by neutron diffraction. The peaks are in the shoulder of the peaks located at 1.9 Å and 3.1Å, which are characteristic of the interatomic distances in the diamond-like structure of β-SiC. Thus, we may conclude that most peaks observed on the PDFs can be attributed to SiC nanoparticles, while two supplementary peaks observed in the neutron PDFs, may correspond to the first interatomic distances in the B<sub>x</sub>C amorphous phase surrounding the SiC nanoparticles (this phase, mainly composed of boron atoms, is a weak scatterer of X-rays).

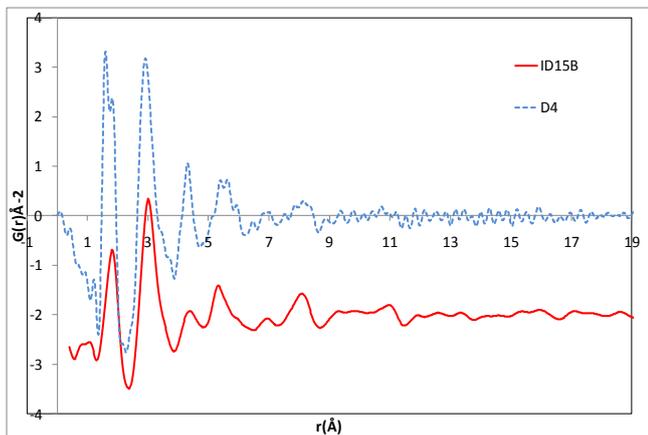


Figure 2: PDFs for  $\text{Si}_{0.4}\text{B}_{0.7}\text{C}$  sample obtained on ID15B-RX(red) and D4-Neutrons (blue).

## ii. PDF determination of Si-O-C fibers

The PDFs obtained on ID15B from the five Si-O-C fibres are reported on figure 3. The first three peaks are positioned at real space distances of around 1.8, 3.0 and 3.6 Å, which roughly match the Si-C, Si-Si/C-C and Si-C bond distances in  $\beta$ -SiC (1.89, 3.08 and 3.61 Å).

However, large differences can be seen between the fibres: ZMI and TyrannoS respectively being the most crystallized and amorphous ones. Indeed, while the PDF of ZMI fibre shows peaks on the whole distance range reported here, indicating crystalline order extending on a few nanometers, the PDF of TyrannoS is already vanishing at 1 nm (see also the disappearance of the 3.6 peak on this fibre). Moreover, for TyrannoS, the first peak is broader and shifted toward lower  $r$  values as compared to other, more crystalline, fibres.

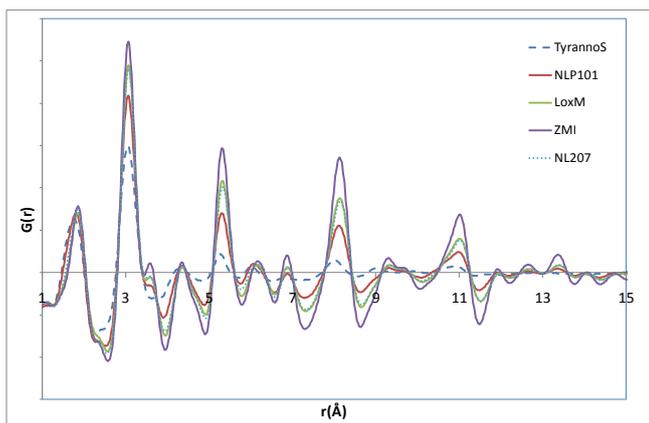


Figure 3: PDFs of the Si-O-C fibres characterized on ID15B.

An attempt to fit the experimental PDFs using only the  $\beta$ -SiC structure (figure 4) is not fully satisfactory. This is consistent with the presence of a  $\text{SiO}_x\text{C}_y$  amorphous phase, surrounding the SiC nanoparticles, which not taken into account. Further work is in progress to include this phase in the refinement.

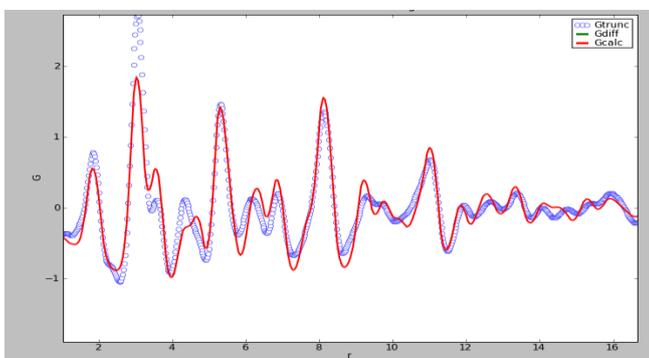


Figure 4: Fit of the TyrannoS PDF with a simulated PDF of  $\text{SiC}_\beta$  nanoparticles using PDFGUI software [1].

1. C. L. Farrow, P. Juhás, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, Th. Proffen and S. J. L. Billinge, [PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals](#), J. Phys.: Condens. Matter, **19**, 335219 (2007)